A study of reactive magnetron sputtering of alloy transparent conducting oxides from elemental targets

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A STUDY OF REACTIVE MAGNETRON SPUTTERING OF ALLOY TRANSPARENT CONDUCTING OXIDES FROM ELEMENTAL TARGETS

by

Iyad Safi

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of

Doctor of Philosophy of the Loughborough University

May 1997

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To my parents for their tremendous support

and

to my wife and children for their patience
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Methods of reactive magnetron sputtering using the sequential oxidisation of a sputtered metal film from two magnetron sources, in a rotating substrate system, have been developed. A rotation rate of around one revolution per second enhanced atomic level mixing of the film constituents on the substrate. Depending on the materials involved, two very fast feedback methods were employed to automatically control the admission rate of oxygen into the sputtering system. These methods were plasma emission monitoring (PEM), which was used to control the reactive sputter-deposition of In, Zn, W, V, Mo and Ti oxide, and voltage control, which was used to control the reactive sputter-deposition of Zn, Cu, Pb and Al oxide. The stoichiometry of the film was controlled by PEM or voltage control on one magnetron, and dopants were added by sputtering from the other magnetron. In other words, the former magnetron served two purposes; the first was to sputter metal and oxidise it, and the second purpose was to oxidise the metal sputtered from the other magnetron.

Both DC and 40 kHz-AC power have been used and combined together in a novel way using a filter to protect the DC power supply from the AC one. In addition to allowing the reactive sputtering process to be arc-free and hence eliminating the undesired effects of arcing in reactive sputtering (e.g., driving the process to become unstable, reducing the target lifetime and creating defects in the films), development of this technology permitted high rate sputter-deposition of a large range of films of alloy oxides where both the metallic composition and stoichiometry could be controlled. This was very valuable in identifying optimum electrically conducting and visually transparent films, and also valuable in producing transparent insulating oxide films of any composition and of a wide variety of refractive indices (between about 1.6 for Al₂O₃ and about 2.6 for TiO₂) for optical applications. Furthermore, this technique may also be capable of investigating other types of thin films (e.g., hard coatings, semiconducting films, superconducting films, ... etc.).

Electrical and optical properties of the produced films were determined by measuring the sheet resistance, using a four-point probe, and the transmittance and reflectance spectra of the visibly transparent films, using a spectrophotometer. In addition, the
refractive indices and thicknesses of the films were calculated from their reflectance spectra, so that the resistivity of the films could be determined. Finally, compositional measurements were carried out using Auger electron spectroscopy.

Well-known transparent conducting films such as indium tin oxide (ITO), zinc aluminium oxide (ZAO) and zinc indium oxide (ZIO) were deposited at wide windows of appropriate stoichiometries (about 4-6.5% of the control signal in PEM control or of the metallic cathode voltage in voltage control). The resistivity, optical transmittance at 550 nm, refractive index and deposition rate of the best films were $4.9 \cdot 10^{-6}$ $\Omega$.m, 79.5%, 2.04 and 0.91 nm/s for ITO, $17 \cdot 10^{-6}$ $\Omega$.m, 79.1%, 1.85 and 1.03 nm/s for ZAO and $11.7 \cdot 10^{-6}$ $\Omega$.m, 86.4%, 2.07 and 0.77 nm/s for ZIO, respectively. In addition, new types of oxide films, which have great promise, have been identified including indium titanium oxide (ITiO), indium aluminium oxide (IAO), indium zinc oxide (IZO), zinc titanium oxide (ZTiO), zinc tin oxide (ZTO), tin titanium oxide (TTiO) and vanadium molybdenum oxide (VMO). The resistivity, optical transmittance at 550 nm, refractive index and deposition rate of the best films were $4.6 \cdot 10^{-6}$ $\Omega$.m, 82.1%, 2.07 and 0.78 nm/s for ITiO, $5.7 \cdot 10^{-6}$ $\Omega$.m, 84.5%, 2.04 and 0.75 nm/s for IAO, $8.2 \cdot 10^{-6}$ $\Omega$.m, 86.5%, 1.96 and 1.47 nm/s for IZO, $76.8 \cdot 10^{-6}$ $\Omega$.m, 83.5%, 1.92 and 1.78 nm/s for ZTiO, $5 \cdot 10^{-3}$ $\Omega$.m, 74.2%, 1.95 and 1.76 nm/s for ZTO, $107.1 \cdot 10^{-6}$ $\Omega$.m, 84.5%, 2.01 and 0.39 nm/s for TTiO and $509 \cdot 10^{-6}$ $\Omega$.m, 76.8%, 1.77 and 0.70 nm/s for VMO, respectively. In general, the windows of appropriate stoichiometries were also wide (about 3.5-9% of the control signal). No intentional heating or external biasing were applied to substrate and no post-deposition annealing of any kind was carried out on any of the deposited films.
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<thead>
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<th>Symbol</th>
<th>Description</th>
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<tr>
<td>A</td>
<td>Area</td>
</tr>
<tr>
<td>a&lt;sub&gt;i&lt;/sub&gt;</td>
<td>Acceleration of an ion in the direction of an electric field</td>
</tr>
<tr>
<td>Al&lt;sub&gt;v&lt;sub&gt;c&lt;/sub&gt;&lt;/sub&gt;%</td>
<td>Percentage of aluminium magnetron voltage set-point</td>
</tr>
<tr>
<td>A&lt;sub&gt;m&lt;/sub&gt;</td>
<td>Atomic mass</td>
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<tr>
<td>Ar&lt;sub&gt;p&lt;sub&gt;er&lt;sub&gt;m&lt;/sub&gt;&lt;/sub&gt;%</td>
<td>Percentage of argon lines set-point</td>
</tr>
<tr>
<td>B</td>
<td>Magnetic field strength</td>
</tr>
<tr>
<td>C&lt;sub&gt;c&lt;/sub&gt;</td>
<td>Capacitance</td>
</tr>
<tr>
<td>c&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Average speed of particles</td>
</tr>
<tr>
<td>c&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Mean-square speed of particles</td>
</tr>
<tr>
<td>C&lt;sub&gt;b&lt;/sub&gt;</td>
<td>Bulk concentration of a component in a multicomponent cathode</td>
</tr>
<tr>
<td>c&lt;sub&gt;e&lt;/sub&gt;</td>
<td>Average electrons speed</td>
</tr>
<tr>
<td>c&lt;sub&gt;e&lt;/sub&gt;&lt;sup&gt;2&lt;/sup&gt;</td>
<td>Mean-square speed of electrons</td>
</tr>
<tr>
<td>c&lt;sub&gt;i&lt;/sub&gt;</td>
<td>Average ions speed</td>
</tr>
<tr>
<td>cos&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Power factor</td>
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<td>C&lt;sub&gt;s&lt;/sub&gt;</td>
<td>Surface concentration of a component in a multicomponent cathode</td>
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<td>Cu&lt;sub&gt;v&lt;sub&gt;c&lt;/sub&gt;&lt;/sub&gt;%</td>
<td>Percentage of copper magnetron voltage set-point</td>
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<td>c&lt;sub&gt;water&lt;/sub&gt;</td>
<td>Specific heat capacity of water. c&lt;sub&gt;water&lt;/sub&gt; = 4190 J/kg·K</td>
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<tr>
<td>d</td>
<td>Spacing between electrodes</td>
</tr>
<tr>
<td>d</td>
<td>Thickness</td>
</tr>
<tr>
<td>d&lt;sub&gt;film&lt;/sub&gt;</td>
<td>Film thickness</td>
</tr>
<tr>
<td>dN&lt;sub&gt;c&lt;/sub&gt;</td>
<td>Number of particles whose speeds lie between c and c + dc</td>
</tr>
<tr>
<td>d&lt;sub&gt;pit&lt;/sub&gt;</td>
<td>Pitch</td>
</tr>
<tr>
<td>d&lt;sub&gt;react&lt;/sub&gt;</td>
<td>Degree of reaction</td>
</tr>
<tr>
<td>E</td>
<td>Electric field strength</td>
</tr>
<tr>
<td>e</td>
<td>Electronic charge. e = 1.6·10&lt;sup&gt;-19&lt;/sup&gt;C</td>
</tr>
<tr>
<td>E&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Amplitude of an alternating electric field</td>
</tr>
<tr>
<td>E&lt;sub&gt;a&lt;/sub&gt;</td>
<td>Average ejection energy per sputtered atom</td>
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<th>Description</th>
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<tr>
<td>$E_{\text{Auger}}$</td>
<td>Measured energy of an Auger electron</td>
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<tr>
<td>$E_{\text{av}}^x$</td>
<td>Average kinetic energy of particles associated with motion in the $x$ direction according to Maxwell-Boltzmann distribution</td>
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<tr>
<td>$E_d$</td>
<td>Dielectric strength of an insulating layer</td>
</tr>
<tr>
<td>$E_e$</td>
<td>Electron kinetic energy</td>
</tr>
<tr>
<td>$E_i$</td>
<td>Ion energy</td>
</tr>
<tr>
<td>$E_{\text{photon}}$</td>
<td>Photon energy</td>
</tr>
<tr>
<td>$F$</td>
<td>Force</td>
</tr>
<tr>
<td>$f_{O_2}$</td>
<td>Oxygen flow rate</td>
</tr>
<tr>
<td>$f_r$</td>
<td>Reactive gas flow rate</td>
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<tr>
<td>$f_{r\text{m}}$</td>
<td>Flow rate of the reactive gas gettered by the sputtered material</td>
</tr>
<tr>
<td>$f(u)$</td>
<td>Number of particles per m$^3$ (density) with velocity between $u$ and $u + du$</td>
</tr>
<tr>
<td>$g(\lambda)$</td>
<td>Fraction of emitted photons corresponding to a transition that are detected</td>
</tr>
<tr>
<td>$I$</td>
<td>Current</td>
</tr>
<tr>
<td>$I_p$</td>
<td>Primary electron current generated at the cathode by an auxiliary source</td>
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<tr>
<td>$I_{\text{em}}(x)$</td>
<td>Emission intensity at any position $x$ in the discharge corresponding to the transition $i \rightarrow j$</td>
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<tr>
<td>$I_{\text{In}}^%$</td>
<td>Percentage of In line set-point</td>
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<td>$I_{\text{rms}}$</td>
<td>Root-mean-square current (or effective current)</td>
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<tr>
<td>$J$</td>
<td>Current density</td>
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<tr>
<td>$J_0$</td>
<td>Current density of atoms ejected perpendicular to the cathode surface</td>
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<tr>
<td>$J_{\text{de}}$</td>
<td>Electron current density to the anode</td>
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<tr>
<td>$J_i, J_{\text{di}}$</td>
<td>Ion current density to the cathode</td>
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<tr>
<td>$J_{\text{ds}}$</td>
<td>Ion current density to the substrate</td>
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<tr>
<td>$J_r$</td>
<td>Random thermal current density of a gas</td>
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<td>$J_{re}$</td>
<td>Random thermal current density of electrons</td>
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<tr>
<td>$J_{ri}$</td>
<td>Random thermal current density of ions</td>
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<tr>
<td>$j_\delta$</td>
<td>Current density of sputtered atoms ejected at an angle $\delta$ with respect to the normal of the cathode surface</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann's constant. $k = 1.38 \cdot 10^{-23} \text{ J / K} = 8.62 \cdot 10^{-5} \text{ eV / K}$</td>
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<tr>
<td>$k_{\text{film}}$</td>
<td>Film extinction factor</td>
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<tr>
<td>$k_{\text{subs}}$</td>
<td>Substrate extinction factor</td>
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<td>$K_{th}$</td>
<td>Thermal conductivity of a gas</td>
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<td>$L$</td>
<td>Thickness of the positive dark space</td>
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<td>Inductance</td>
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<td>Sheath thickness formed by electrons</td>
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<td>$L_i$</td>
<td>Sheath thickness formed by ions</td>
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<td>$M, m$</td>
<td>Mass</td>
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<td>Electron mass</td>
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<td>$m_i$</td>
<td>Ion mass</td>
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<td>$m_t$</td>
<td>Mass of the bombarded surface atoms</td>
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<td>$M_w$</td>
<td>Molecular mass of film material</td>
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<td>$m_w$</td>
<td>Mass of water</td>
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<tr>
<td>$N$</td>
<td>Total number of gas particles</td>
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<tr>
<td>$n$</td>
<td>Number of molecules in the unit volume of a gas</td>
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<tr>
<td>$n_o$</td>
<td>Plasma density</td>
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<tr>
<td>$n_{amb}$</td>
<td>Refractive index of the ambient medium</td>
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<tr>
<td>$N_\text{Av}$</td>
<td>Avogadro number. $N_\text{Av} = 6.022 \cdot 10^{23}$ atoms/mol</td>
</tr>
<tr>
<td>$n_{coll}$</td>
<td>Number of collisions in a time $\Delta t$</td>
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<tr>
<td>$n_D$</td>
<td>Plasma parameter</td>
</tr>
<tr>
<td>$n_e$</td>
<td>Electron density</td>
</tr>
<tr>
<td>$n_{film}$</td>
<td>Film refractive index</td>
</tr>
<tr>
<td>$n_H$</td>
<td>Gas density in the region of a magnetron cathode</td>
</tr>
<tr>
<td>$N_i$</td>
<td>Number of ions bombarding a unit area of the cathode per second</td>
</tr>
<tr>
<td>$n_i$</td>
<td>Ion density</td>
</tr>
<tr>
<td>$N_i^1$</td>
<td>Number of ions bombarding 1 cm$^2$ of the substrate per second</td>
</tr>
<tr>
<td>$N_{a}$</td>
<td>Number of sputtered cathode atoms from a unit area of the cathode per second</td>
</tr>
<tr>
<td>$N_{molec}$</td>
<td>Number of deposited compound molecules on 1 cm$^2$ of the substrate per second</td>
</tr>
<tr>
<td>$N_{m}$</td>
<td>Number of deposited metal atoms on 1 cm$^2$ of the substrate per second</td>
</tr>
<tr>
<td>$n_{subs}$</td>
<td>Substrate refractive index</td>
</tr>
<tr>
<td>$O_{\text{perm}}$</td>
<td>Percentage of oxygen lines set-point</td>
</tr>
<tr>
<td>$P$</td>
<td>Discharge power</td>
</tr>
<tr>
<td>$\bar{P}$</td>
<td>Average power</td>
</tr>
<tr>
<td>$p$</td>
<td>Pressure</td>
</tr>
<tr>
<td>$P_a$</td>
<td>Non-reactive gas pressure</td>
</tr>
<tr>
<td>$P_{\text{AC}}^{\text{Al} \leftrightarrow \text{Al}}$</td>
<td>Floating AC power between two aluminium magnetrons</td>
</tr>
<tr>
<td>$P_{\text{DC}}^{\text{Al}}$</td>
<td>DC power applied to an aluminium cathode/magnetron</td>
</tr>
<tr>
<td>$P_{\text{b}}^{\text{perm}}$</td>
<td>Percentage of lead magnetron voltage set-point</td>
</tr>
<tr>
<td>$P_{\text{AC}}^{\text{In} \leftrightarrow \text{Al}}$</td>
<td>Floating AC power between an indium and aluminium magnetrons</td>
</tr>
<tr>
<td>$P_{\text{DC}}^{\text{In}}$</td>
<td>DC power applied to an indium cathode/magnetron</td>
</tr>
<tr>
<td>$P_{\text{AC}}^{\text{In} \leftrightarrow \text{In}}$</td>
<td>Floating AC power between two indium magnetrons</td>
</tr>
<tr>
<td>$P_{\text{AC}}^{\text{In} \leftrightarrow \text{Sn}}$</td>
<td>Floating AC power between an indium and tin magnetrons</td>
</tr>
<tr>
<td>$P_{\text{AC}}^{\text{In} \leftrightarrow \text{Ti}}$</td>
<td>Floating AC power between an indium and titanium magnetrons</td>
</tr>
<tr>
<td>$P_{\text{AC}}^{\text{In} \leftrightarrow \text{Zn}}$</td>
<td>Floating AC power between an indium and zinc magnetrons</td>
</tr>
<tr>
<td>$P_i(x)$</td>
<td>Probability of exciting an atom to state $i$</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$P_M$</td>
<td>Power received by the main magnetron</td>
</tr>
<tr>
<td>$P_{\text{max}}$</td>
<td>Maximum power</td>
</tr>
<tr>
<td>$P_{\text{DC}}$</td>
<td>DC power applied to a molybdenum cathode/magnetron</td>
</tr>
<tr>
<td>$P_{\text{AC}}$</td>
<td>Floating AC power between the main and the secondary magnetrons</td>
</tr>
<tr>
<td>$P_{\text{O}_{2}}$</td>
<td>Oxygen partial pressure</td>
</tr>
<tr>
<td>$P_{\text{DC}}$</td>
<td>DC power applied to a lead cathode/magnetron</td>
</tr>
<tr>
<td>$P_t$</td>
<td>Reactive gas partial pressure</td>
</tr>
<tr>
<td>$P_S$</td>
<td>Power received by the secondary magnetron</td>
</tr>
<tr>
<td>$P_{\text{DC}}$</td>
<td>DC power applied to a tin cathode/magnetron</td>
</tr>
<tr>
<td>$P_{\text{Ti}}$</td>
<td>DC power applied to a titanium cathode/magnetron</td>
</tr>
<tr>
<td>$P_{\text{AC}}$</td>
<td>Floating AC power between a titanium and indium magnetrons</td>
</tr>
<tr>
<td>$P_{\text{AC}}$</td>
<td>Floating AC power between a titanium and tin magnetrons</td>
</tr>
<tr>
<td>$P_{\text{DC}}$</td>
<td>DC power applied to a vanadium cathode/magnetron</td>
</tr>
<tr>
<td>$P_{\text{AC}}$</td>
<td>Floating AC power between a vanadium and molybdenum magnetrons</td>
</tr>
<tr>
<td>$P_{\text{DC}}$</td>
<td>DC power applied to a tungsten cathode/magnetron</td>
</tr>
<tr>
<td>$P_{\text{AC}}$</td>
<td>Floating AC power between a zinc and aluminium magnetrons</td>
</tr>
<tr>
<td>$P_{\text{DC}}$</td>
<td>DC power applied to a zinc cathode/magnetron</td>
</tr>
<tr>
<td>$P_{\text{AC}}$</td>
<td>Floating AC power between a zinc and indium magnetrons</td>
</tr>
<tr>
<td>$P_{\text{AC}}$</td>
<td>Floating AC power between a zinc and tin magnetrons</td>
</tr>
<tr>
<td>$P_{\text{AC}}$</td>
<td>Floating AC power between a zinc and titanium magnetrons</td>
</tr>
<tr>
<td>$q$</td>
<td>Electric charge</td>
</tr>
<tr>
<td>$Q_{\text{w}}$</td>
<td>Amount of heat removed from the magnetron by the cooling water</td>
</tr>
<tr>
<td>$r$</td>
<td>Radius of a gas-molecule or a circle</td>
</tr>
<tr>
<td>$R$</td>
<td>Actual reflectance (after correcting the measured value)</td>
</tr>
<tr>
<td>$R$</td>
<td>Resistance</td>
</tr>
<tr>
<td>$R_{\text{dep}}$</td>
<td>Deposition rate</td>
</tr>
<tr>
<td>$R_{\text{dep}}$</td>
<td>Actual deposition rate</td>
</tr>
<tr>
<td>$R_{\text{dep}}$</td>
<td>Measured deposition rate</td>
</tr>
<tr>
<td>$R_{\text{meas}}$</td>
<td>Measured reflectance</td>
</tr>
<tr>
<td>$R_{\text{max}}$</td>
<td>Actual value of a reflectance maximum</td>
</tr>
<tr>
<td>$R_{\text{max}}$</td>
<td>Measured value of a reflectance maximum</td>
</tr>
<tr>
<td>$R_{\text{min}}$</td>
<td>Actual value of a reflectance minimum</td>
</tr>
<tr>
<td>$R_{\text{ox}}$</td>
<td>Oxidation rate</td>
</tr>
<tr>
<td>$R_s$</td>
<td>Sheet resistance</td>
</tr>
<tr>
<td>$R_{\text{sput}}$</td>
<td>Sputtering rate</td>
</tr>
<tr>
<td>$R_y$</td>
<td>Resistivity</td>
</tr>
<tr>
<td>$S_c$</td>
<td>Critical pumping speed</td>
</tr>
<tr>
<td>$S(E)$</td>
<td>Nuclear stopping power</td>
</tr>
</tbody>
</table>
Table of Principal Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_p$</td>
<td>Pumping speed of the pumping system for the reactive gas</td>
</tr>
<tr>
<td>$S_w$</td>
<td>Density of film material</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$T_0$</td>
<td>Period</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$T_{550}$</td>
<td>Transmittance at 550 nm</td>
</tr>
<tr>
<td>$t_B$</td>
<td>Required time for a dielectric to breakdown</td>
</tr>
<tr>
<td>$T_e$</td>
<td>Electron temperature</td>
</tr>
<tr>
<td>$T_i$</td>
<td>Ion temperature</td>
</tr>
<tr>
<td>$T_{ij}$</td>
<td>Probability that an electron will decay back from state $i$ to state $j$ through a radiative transition</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting point</td>
</tr>
<tr>
<td>$T_s$</td>
<td>Substrate temperature</td>
</tr>
<tr>
<td>$U_0$</td>
<td>Binding energy of the bombarded surface</td>
</tr>
<tr>
<td>$\bar{u}^2$</td>
<td>Mean-square velocity of particles in the $x$ direction</td>
</tr>
<tr>
<td>$V$</td>
<td>Voltage</td>
</tr>
<tr>
<td>$v$</td>
<td>Velocity</td>
</tr>
<tr>
<td>$V_B$</td>
<td>Breakdown voltage</td>
</tr>
<tr>
<td>$V_{Bias}$</td>
<td>Applied bias to a substrate</td>
</tr>
<tr>
<td>$V_{B_{min}}$</td>
<td>Minimum breakdown voltage</td>
</tr>
<tr>
<td>$V_c$</td>
<td>Potential at the cathode surface</td>
</tr>
<tr>
<td>$v_d$</td>
<td>Drift velocity</td>
</tr>
<tr>
<td>$V_f$</td>
<td>Floating potential</td>
</tr>
<tr>
<td>$V_{film}$</td>
<td>Volume of the film deposited on 1 cm$^2$ of the substrate in unit time</td>
</tr>
<tr>
<td>$V_{ins}$</td>
<td>Voltage across an insulating layer</td>
</tr>
<tr>
<td>$V_M$</td>
<td>Voltage of the main magnetron</td>
</tr>
<tr>
<td>$V_{max}$</td>
<td>Potential at $y_{max}$</td>
</tr>
<tr>
<td>$V_p$</td>
<td>Plasma potential</td>
</tr>
<tr>
<td>$V_{prob}$</td>
<td>Probe potential</td>
</tr>
<tr>
<td>$V_{r.m.s.}$</td>
<td>Root-mean-square voltage (or effective voltage)</td>
</tr>
<tr>
<td>$V_S$</td>
<td>Voltage of the secondary magnetron</td>
</tr>
<tr>
<td>$W$</td>
<td>Width</td>
</tr>
<tr>
<td>$W_1$</td>
<td>Amount of sputtered material that reaches a unit area of the substrate</td>
</tr>
<tr>
<td>$W_{film}$</td>
<td>Mass of the film deposited on 1 cm$^2$ of the substrate in unit time</td>
</tr>
<tr>
<td>$X_C$</td>
<td>Capacitive reactance</td>
</tr>
<tr>
<td>$X_L$</td>
<td>Inductive reactance</td>
</tr>
<tr>
<td>$Y$</td>
<td>Sputtering yield</td>
</tr>
<tr>
<td>$y_{max}$</td>
<td>The occurrence of maximum excursion from the cathode</td>
</tr>
<tr>
<td>$Z_{eqv}$</td>
<td>Equivalent impedance of the filter</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>$Z_i$</td>
<td>Atomic number of the bombarding ions</td>
</tr>
<tr>
<td>$Zn_{ve}$</td>
<td>Percentage of zinc magnetron voltage set-point</td>
</tr>
<tr>
<td>$Z_a$</td>
<td>Atomic number of bombarded surface atoms</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Angle</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Ionising power of electrons</td>
</tr>
<tr>
<td>$\gamma_e$</td>
<td>Secondary electron emission coefficient due to electron-bombardment</td>
</tr>
<tr>
<td>$\gamma_i$</td>
<td>Secondary electron emission coefficient due to ion-bombardment</td>
</tr>
<tr>
<td>$\Delta H_f$</td>
<td>Standard molar enthalpies of formation</td>
</tr>
<tr>
<td>$\Delta W$</td>
<td>The decrease of cathode mass per unit area, in kg/m$^2$, after being sputtered for $t$ seconds</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Ejection angle of sputtered atoms</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Phase difference</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Permittivity of free space. $\varepsilon_0 = 8.85 \cdot 10^{-12}$ F/m</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>Dielectric constant of an insulating layer</td>
</tr>
<tr>
<td>$\Theta_{ox}$</td>
<td>Degree of oxide coverage on the target surface</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Angle of incidence</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Mean free path of a molecule</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
</tr>
<tr>
<td>$\lambda_D$</td>
<td>Debye length</td>
</tr>
<tr>
<td>$\lambda_e$</td>
<td>Electronic mean free path</td>
</tr>
<tr>
<td>$\lambda_{em}$</td>
<td>Wavelength of an emission line</td>
</tr>
<tr>
<td>$\lambda_i$</td>
<td>Ionic mean free path</td>
</tr>
<tr>
<td>$\lambda_{max}$</td>
<td>Wavelength at which a reflectance maximum occurs</td>
</tr>
<tr>
<td>$\lambda_{min}$</td>
<td>Wavelength at which a reflectance minimum occurs</td>
</tr>
<tr>
<td>$\lambda_{\text{photon}}$</td>
<td>Photon wavelength</td>
</tr>
<tr>
<td>$\lambda_{\text{visible}}$</td>
<td>Photon wavelength in the range of visible light</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Mobility of charged particles</td>
</tr>
<tr>
<td>$\mu_e$</td>
<td>Mobility of electrons</td>
</tr>
<tr>
<td>$\mu_i$</td>
<td>Mobility of ions</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Frequency</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Molecule diameter</td>
</tr>
<tr>
<td>$\sigma_{\text{exc}}$</td>
<td>Excitation cross-section</td>
</tr>
<tr>
<td>$\sigma_{\text{mtr}}$</td>
<td>Cross-section for momentum transfer of the sputtered atom</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Potential</td>
</tr>
<tr>
<td>$\phi_A$</td>
<td>Work function of the analyser material in AES</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Angle of collision</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular frequency</td>
</tr>
<tr>
<td>$\omega_c$</td>
<td>Angular velocity or cyclotron frequency</td>
</tr>
</tbody>
</table>
## ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>Alternating current</td>
</tr>
<tr>
<td>AES</td>
<td>Auger electron spectroscopy</td>
</tr>
<tr>
<td>DC</td>
<td>Direct current</td>
</tr>
<tr>
<td>FCC</td>
<td>Federal communications commission</td>
</tr>
<tr>
<td>IAO</td>
<td>Indium oxide doped with aluminium</td>
</tr>
<tr>
<td>ITiO</td>
<td>Indium oxide doped with titanium</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium oxide doped with tin</td>
</tr>
<tr>
<td>IZO</td>
<td>Indium zinc oxide</td>
</tr>
<tr>
<td>PEM</td>
<td>Plasma emission monitoring</td>
</tr>
<tr>
<td>RF</td>
<td>Radio frequency</td>
</tr>
<tr>
<td>SPA</td>
<td>Successive plasma anodisation</td>
</tr>
<tr>
<td>SPPA</td>
<td>Successive pulsed plasma anodisation</td>
</tr>
<tr>
<td>SZD</td>
<td>Structure zone diagram</td>
</tr>
<tr>
<td>TTiO</td>
<td>Tin oxide doped with titanium</td>
</tr>
<tr>
<td>VMO</td>
<td>Vanadium molybdenum oxide</td>
</tr>
<tr>
<td>ZAO</td>
<td>Zinc oxide doped with aluminium</td>
</tr>
<tr>
<td>ZIO</td>
<td>Zinc indium oxide</td>
</tr>
<tr>
<td>ZTiO</td>
<td>Zinc oxide doped with titanium</td>
</tr>
<tr>
<td>ZTO</td>
<td>Zinc oxide doped with tin</td>
</tr>
</tbody>
</table>
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CHAPTER ONE

INTRODUCTION

The unique optical, electrical and mechanical properties of thin solid films, which are quite different from the relevant bulk material, have led them to play an irreplaceable and increasing role in many areas of today's very demanding and rapidly developing technology, especially in the electronic and optical industries. Good quality, high deposition rate, reproducibility, environmental stability as well as competitive cost are among the requirements a thin film must fulfil before being considered in any potential application.

The deposition of electrically conducting and visibly transparent semiconducting oxide films with a high quality at high rates may be considered as one of the most challenging domains in thin film technology. Thermal oxidation, spray pyrolysis, reactive evaporation and sputtering are among the techniques which have been used to deposit these films. The latter includes, diode, triode, magnetron and ion beam sputtering.

Magnetron sputtering has gained an increasing popularity in the last two decades. This is essentially because it permits large scale deposition of high quality films (e.g., homogeneous thicknesses, high density and superior adhesion to substrate) at relatively high rates and a controllable substrate temperature. Conventionally, films of transparent conducting alloy oxide have been magnetron-sputtered, in an oxygen atmosphere, from oxide or multi-element single targets using RF or DC power. However, high cost, complexity and lower deposition rates make RF sputtering less favourable compared with DC sputtering.

The main problem of DC reactive magnetron sputtering lies in the presence of the reactive gas (e.g., oxygen in the case of transparent conducting oxides) at both the target surface and the substrate which results in strong interactions of the reactive gas.
Chapter One

not only with the condensing material at the substrate but also with the target surface. This affects the stability of the sputtering process, lowers the deposition rate and leads sometimes to severe arcing. On the other hand, the composition of a sputter-deposited film is the same as that of the target from which it was sputtered. This makes the composition control of films which are DC-sputtered from a single target a very difficult task. Moreover, sputtering from a single target limits the possibility of obtaining a film of an alloy or multi-element compound if its constituents are either difficult or impossible to be formed in a single target.

The aims of this work were to study the reactive magnetron sputtering of alloy transparent conducting oxides films from two elemental targets. An airlocked spinning disc multiple station system was used; substrate rotation ensured mixing of the film constituents on an atomic level. The metallic composition of the film was easily manipulated by varying the magnitude of power applied to each magnetron. In practice, three different methods of power application were utilised; independently DC powered magnetrons and mid-frequency AC powered magnetrons in floating mode with and without a DC bias. The use of mid-frequency allowed the reactive sputtering process to be arc-free. On the other hand, film stoichiometry was manipulated by controlling the admission rate of oxygen into the sputtering chamber, using plasma emission monitoring or voltage control on one of the magnetrons, and dopants were added by sputtering from the second magnetron. These techniques permitted the sputter-deposition of a large range of alloy-oxide films, at high rates, where both the composition and stoichiometry could be controlled.

The thesis consists of ten different chapters and two appendices. The objective has been to build up the thesis in the best possible sequence of material accumulation. Excluding chapters one and ten, the thesis may be divided into three principal parts: (i) Chapters two to four are concerned with the theoretical aspects of the work; (ii) Chapters five and six are concerned with the details of the sputtering system, sputtering process and methods of control used in this work as well as with the techniques used for film characterisation; (iii) Chapters seven to nine are material-oriented and concentrate on the preparation conditions and the properties of the best transparent conducting films (except the case of aluminium oxide which is an insulator) produced in this work.

Chapter two introduces the concepts of glow discharge physical sputtering processes, including sputtering yield, threshold and rate. A comparison between the properties of sputtering and that of its main rival, vacuum evaporation, is made. In addition, processes at the substrate, including film nucleation and growth and factors influencing them, are also summarised. In chapter three, several configurations of sputter-deposition systems are described. This includes, DC and RF diode, triode, getter, ion beam and magnetron
sputtering. The latter is discussed in a more detailed approach. Chapter four highlights the problems associated with reactive magnetron sputtering, and the various methods of overcoming them. These include methods of process stabilisation and methods of control within the instability. In addition, the reasons behind arc initiation, time required for arcs to occur and methods of avoiding them are also discussed.

The practical side of the work is outlined in chapter five. A detailed description of the deposition system used in the course of this work is given. This includes the deposition chamber, the pumping and airlock systems, gas flow and pressure measurements, magnetron design, methods of power application and methods of reactive gas control. Furthermore, the deposition procedure followed throughout this work and the details of the deposition process are also discussed. Chapter six describes the techniques and instrumentation used for the characterisation of the thin films deposited in this work. Such a characterisation comprises the measurement of sheet resistance, transmittance and reflectance spectra as well as the composition of the films. Also, the methods used to calculate the refractive indices and thicknesses of the deposited films are also outlined.

In addition to giving a brief review concerning the physical concepts of semiconducting transparent conducting oxides and their practical applications, chapter seven concentrates on the preparation conditions and properties of indium oxide-based films, whereas chapters eight and nine concentrate on preparation conditions and properties of zinc oxide-based films and some other oxides, respectively. Finally, chapter ten presents concluding remarks and suggestions for future work.
CHAPTER TWO

INTRODUCTION TO GLOW DISCHARGE, PHYSICAL SPUTTERING PROCESSES AND FILM GROWTH

2.1. Introduction

Sputtering can be defined as the erosion of a solid surface, commonly termed "the target", due to the ejection of material as a result of energetic particle bombardment. The ejected material can be deposited onto another surface intercepting its trajectory.

Contrary to some opinion, cathode sputtering (i.e., where the target is held at a negative potential) is not a new technology. It was first reported in the literature in 1852, when Grove observed metal deposits, sputtered from the cathode of a glow discharge tube (thus called because it emits visible light), condensing onto the glass walls of his vacuum vessel. He was studying what is known now as "neon light". During the years immediately following its discovery, sputtering was widely used as a method for the deposition of thin films, for example coating astronomical mirrors and later decorating various articles with noble metal films. Around 1930 the technique was used for applying electrically conducting films of gold onto the wax masters of Edison phonographs. Being a slow process for the next 30 years, it became of lesser importance than the rapidly developing deposition of thin films by evaporation and condensation in high vacuum.

In this chapter, a summary of the concepts of plasmas and glow discharges will be introduced. The concepts of the sputtering process as a method of thin film deposition, and its associated parameters of sputtering yield, threshold and rate will be briefly
reviewed. Finally, processes at the substrate, such as thin film nucleation, growth and their influencing factors will also be summarised.

2.2. Concept of the glow discharge

The definition of sputtering from section (2.1) implies that, for sputtering to occur, there is a need for a means to both generate and accelerate the bombarding charged particles towards an oppositely biased target material. For an efficient process, massive ions are usually necessary to bombard a negatively biased target. The creation of such ions can be achieved either in the vicinity of the target material (e.g., glow discharge sputtering), or in a separate chamber (e.g., ion beam sputtering). In brief, sputtering consists of four processes: (i) Ion generation and acceleration towards the cathode; (ii) Ejection of cathode material; (iii) Transportation of ejected material to the substrate; (iv) Condensation of ejected material as a thin film. In physical sputtering, where no immediate chemical reaction with the cathode material is needed, an inert gas with sufficient atomic mass is usually used as a sputtering material as will be explained later. The most popular sputtering gas is argon due to its reasonably high atomic mass, availability and relatively low cost.

Glow discharge (or plasma) sputtering is the most common method of sputtering due to its practical simplicity. Essentially, a high negative potential is applied between two parallel electrodes in an inert gas atmosphere with a partial pressure ranging from 1 to 1000 mTorr. Positive ions are generated as a result of electron-gas atom collisions, and due to the electric field, the ions drift toward the cathode, and electrons toward the anode. A schematic diagram of such an arrangement is shown in figure (2.1).

Although the above explanation is correct, the actual situation is not as simplistic. For example, the electric field in a glow discharge chamber is not uniform. The behaviour of electrons and ions is not symmetrical due to the substantial difference in their masses, and hence in their mobilities and kinetic energies (Appendix one). Other factors such as inert gas pressure, applied voltage and the physical configuration of the electrodes, also influence processes within the vacuum chamber.

It is more convenient to introduce the concept of plasmas and related terminology, prior to describing the characteristics and regions of a glow discharge.
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Evacuated Chamber

![Diagram of a diode plasma system](image)

\[ \text{Electric Field} = \frac{V}{d} \]

Power Supply  Load Resistors

**Figure (2.1): A simplified diode plasma system.**

### 2.2.1. Summary of plasma properties

A plasma is a quasineutral gas of charged and neutral particles which exhibits collective behaviours. The quasineutrality means that the plasma is sufficiently neutral that one can assume \( n_i \approx n_e \approx n \) where \( n_i, n_e \) and \( n \) are ion, electron and plasma density respectively, but not so neutral that all electromagnetic forces disappear. On the other hand, as the charged particles of the plasma move around, they can produce regional densities of positive or negative charge which originate electric fields. Motion of charges also generates currents, and hence magnetic fields. These fields influence the motion of other more remote charged particles. Hence, the collective behaviour means motions that depend not only on local conditions but also on the state of the plasma in remote regions. In other words, the plasma body, on average, is approximately electrically neutral. Any perturbation from this neutrality (a charge imbalance), would result in electric fields that would tend to move the charges in such a way as to eliminate the imbalance.

Forming and sustaining plasmas requires some external energy source for ion production. In a steady state, the rate of ionisation must balance the rate of ion and electron losses from the plasma due to recombination and diffusion to the boundary. Although there is not a distinct phase change from a neutral gas to a plasma, plasma is called "the fourth state of matter" because it is formed by adding energy to a gas.

Plasmas are conductive and can be classified according to their "degree of ionisation"; the fraction of the original neutral species (atoms and/or molecules) which have become...
ionised. They are either partially ionised, with a degree of ionisation less than unity, or fully ionised with a degree of ionisation approaching unity. Plasmas generally encountered in thin film processing techniques and systems are typically formed by partially ionised gas at a pressure well below atmospheric. They are very weakly ionised where the degree of ionisation ranges from $10^{-5}$ to $10^{-1}$.

Finally, the terms "plasma" and "glow discharge" are used in journals concerning thin film technology almost interchangeably. In reality, there is a slight difference between these terms due to the fact that there are regions in the discharge such as the cathode sheath (will be described later) which do not really satisfy the definition of a plasma. In practice, this difference is not usually significant since the plasma of interest here is always a part of a glow discharge.

### 2.2.2. Debye shielding

An important and unique property of a plasma is its ability to eliminate or "shield" a potential-perturbing charge. Due to the tendency of a plasma towards electrical neutrality, charges in the plasma tend to redistribute themselves so as to shield the plasma from the electric field generated by the perturbing charge.

Consider two charged spheres of opposite sign immersed in a plasma, creating an electric field within the plasma, as shown in figure (2.2).

![Figure (2.2): Debye shielding. Reproduced from reference 5.](image)

The spheres would attract particles of opposite charge to themselves, and a cloud of these particles would surround or shield the relevant sphere. The distance over which a small potential can perturb a plasma (the cloud radius) is known as the self shielding or Debye length $\lambda_D$. It is a measure of the shielding distance or sheath thickness. To
calculate this length, it is assumed, as for many calculations in plasmas, that ions are immobile due to the fact that \( m_i \gg m_e \) where \( m_i \) and \( m_e \) are ion and electron mass respectively, and hence all electrical activities in a plasma are carried out by electrons moving in a uniform background of positive charge formed by ions. Solving Poisson's equation in one dimension (see section A1.5) gives:

\[
\lambda_D = \left( \frac{\varepsilon_0 k T_e}{n e^2} \right)^{1/2} \tag{2.1}
\]

where \( \varepsilon_0 \) is the permittivity of free space, \( k \) is Boltzmann's constant, \( T_e \) is the electron temperature (see section A1.1), \( n \) is the plasma density, and \( e \) is the electronic charge. The above equation can be written as:

\[
\lambda_D (\text{cm}) = 743 \left[ \frac{T_e (\text{eV})}{n (\text{cm}^{-3})} \right]^{1/2} \tag{2.2}
\]

Clearly \( \lambda_D \) has to be much smaller than the dimensions of the system for an ionised gas to be a plasma. On the other hand, Debye shielding is only statistically valid if the number of particles in a Debye sphere, \( N_D = n^3 \pi \lambda_D^3 \), is large enough (collective behaviour). \( N_D \) is commonly called "the plasma parameter"\(^{10} \).

### 2.2.3. Plasma potential \( V_p \)

Due to the much higher mobility of electrons in a plasma compared with ions (see section A1.3), they tend to reach the edges of the plasma faster than the latter\(^7 \). In a plasma generated in a metal chamber, therefore, electrons diffuse towards the walls of the chamber giving rise to a gradual increase in the net positive charge of the plasma. As the net positive charge of the plasma increases, it becomes more energetically difficult for electrons to leave the plasma, because the walls become more negative than the plasma. Eventually, a steady state condition will be reached in which the plasma potential is high enough for the loss rate of electrons to be reduced to the same level as the loss rate of ions. This allows the plasma to maintain its neutrality. The plasma potential can then be defined as the average potential of the body of the plasma relative to the chamber potential. It is a few volts more positive than the chamber potential, which means that, on average, the plasma potential is at least several volts more positive than the most positive surface in contact with the plasma.

### 2.2.4. Floating potential \( V_f \)

When an isolated object (e.g., glass substrate) is immersed in a plasma, it will be charged negatively, and hence acquires a negative potential with respect to the plasma\(^{11} \). This is
due to the much higher random thermal current density of electrons compared with that of ions (see section A1.1). As it charges negatively, the object attracts ions and repels electrons. Thus the current density of electrons to the object (electron flux) decreases, whereas the ion flux increases, but the object continues to gain negative charges until ion and electron current densities are equal. The potential acquired by the object at this equilibrium point is called the floating potential, and the corresponding measured current density is zero. It is obvious that the floating potential should be more negative than the plasma potential in order to repel electrons. Only those electrons with a kinetic energy higher than \(-e(V_f - V_p)\) can reach the substrate, whereas all ions will impinge. The floating potential is given by the following equation\(^10\):

\[
V_f = -\frac{kT_e}{2e} \ln \left( \frac{2\pi m_e}{m_i} \right) \left[ \left( 1 + \frac{T_i}{T_e} \right) \right] \tag{2.3}
\]

where \(T_i\) is the ion temperature. Since \(T_e >> T_i\) (section A1.1), the last term in the logarithm can be neglected. The above equation becomes:

\[
V_f = -\frac{kT_e}{2e} \ln \left( \frac{2\pi m_e}{m_i} \right) \tag{2.4}
\]

and indicates that the floating potential is linearly proportional to the electron temperature.

### 2.2.5. Current-voltage characteristic of plasma

The current-voltage characteristic (or I-V curve) of a probe immersed in a plasma can be obtained by inserting a small wire or plane surface\(^12\). Langmuir and Mott-Smith\(^13\) were the pioneers to use such an I-V curve as a plasma diagnostic. An ideal curve is shown in figure (2.3). This curve can be divided into three distinct regions\(^14\).

At a high enough negative bias (region I), the probe collects all positive ions which diffuse towards it from the plasma and repels electrons. Hence the potential of the probe is more negative than the plasma potential. In other words, the current density measured is, \(J_i\), the random thermal current density of the ions. These ions form a positive space charge or a sheath of thickness \(L_i\)
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Electron current density saturated. All electrons collected. Ions repelled.

Random current.

Ion current density saturated. All ions collected. Electrons repelled.

Figure (2.3): Schematic of current-voltage characteristic of a Langmuir probe.
Reproduced from reference 12.

The sheath is "dark" because it is almost free of electrons so that few of the atoms available in it can be excited, and few of the ions can recombine. If the voltage drop across the sheath is $V = |V_{\text{prob}} - V_p|$, where $V_{\text{prob}}$ and $V_p$ are the probe and plasma potential respectively, $J_n$ is given by space charge limited current or Child-Langmuir Law:

$$J_n = \left(\frac{4\varepsilon_0}{9}\right)\left(\frac{2e}{m_i}\right)^{1/2} \frac{V^{3/2}}{L_i^2}$$  \[2.5\]

As the potential of the probe is made relatively more positive (moving towards region II), the probability that plasma electrons with sufficient kinetic energy to overcome the applied bias and reach the probe surface increases up to a certain potential, at which the electron current density to the probe is equal to that of ions. This potential is the floating potential (see section 2.2.4) and the corresponding measured current density is then zero.

As the probe potential is made more positive than the floating potential (region II), the ion current density decreases, whereas that of the electrons increases (so does the
measured current density) to a point where the probe collects the full random thermal current density of both ions and electrons. This means that at this point, the probe exerts no force on either ions or electrons; the probe is at the same potential as the plasma. The corresponding measured current density is then the difference in magnitude between the random thermal current density of electrons and ions, and approximately equals the random thermal current density of electrons, since $J_i << J_e$. Thus the plasma potential is the potential at which the measured current to the probe approaches its upper saturation value.

At high positive bias (region III), the probe collects all electrons which diffuse towards it from the plasma, repelling ions. In other words, the current density measured is $J_e$, the electron random thermal current density. These electrons form a dark negative space charge, a sheath of thickness $L_e$. If the voltage across the sheath is $V$, $J_e$ is then given by equation (2.5), replacing $m_i$ with $m_e$. For a given magnitude of $V$, taking $m_i = 6.6 \cdot 10^{-23} \text{g}$, $m_e = 9.1 \cdot 10^{-28} \text{g}$, and $J_{re}/J_{ri} \approx 1835$ as in (section A1.1), it is found that $L_e/L_i \approx 6.3$. It can be concluded, then, that for a given magnitude of the potential difference between the probe and the plasma, an electron sheath will be several times thicker than an ion sheath.

As will be discussed in chapter five, the use of a Langmuir probe was unnecessary for the aims of this work, and was replaced by a probe termed the "substrate condition probe".

2.2.6. Characteristics of the glow discharge

The glow discharge is the simplest and most common technology for creating and accelerating positive ions for bombardment of a target held at negative potential, in order to sputter its material. As the title indicates, it is very important when carrying out a sputtering experiment to first understand the processes that take place in a glow discharge vacuum chamber.

Figure (2.4) shows the current-voltage characteristics of a DC glow discharge of neon at 1 mTorr.

If a DC voltage is applied between two parallel plates in a chamber filled with a gas at a low pressure, no appreciable current can be detected so long as the voltage is below a certain value called the breakdown voltage. If, however, the cathode is irradiated using an auxiliary source such as ultraviolet radiation, cosmic rays, x-rays, photons or
Figure (2.4): Characteristics of a DC glow discharge of neon at a pressure of one Torr.
Reproduced from reference 17.
such like, a small current will flow between the electrodes due to the emission of electrons from the cathode, and extinguish when the irradiating source is cut-off. If the spacing between the electrodes, \( d \), is increased during irradiation, and the applied voltage is higher than the ionisation potential of the working gas, the current increases. This increase can be attributed to two reasons:

1. The ionising power of electrons, \( \alpha \), can be defined as the average number of ions produced by one electron per unit length\(^{14} \). It is a function of the applied voltage and pressure (\( \propto V/p \)) at a fixed temperature. The ionising power increases first abruptly with applied voltage (electron energy) to a maximum, decreasing at higher values of electron energy. Since each ionising collision between an electron and a neutral gas atom produces two electrons and an ion (see section A1.4) that contribute to the current, it is then apparent from the definition that the number of ions (and electrons) produced by an electron is proportional to the spacing between the electrodes at fixed applied voltage and pressure.

2. The secondary electron emission coefficient, \( \gamma_1 \), can be defined as the average number of secondary electrons emitted from the cathode surface per incident ion. Like \( \alpha \), it is a function of the applied voltage and pressure (\( \propto V/p \)) at a fixed temperature. The accelerated ions, upon striking the cathode, give rise to the emission of electrons, called "secondaries", from the cathode surface. These electrons also contribute to the current.

Townsend has described the current, \( I \), in such a system (part AB in figure 2.4) in terms of \( \alpha \), \( \gamma_1 \), \( d \), and \( I_0 \) which is the primary electron current generated at the cathode by the auxiliary source, by the following equation:

\[
I = \frac{I_0 \cdot \exp(\alpha d)}{1 - \gamma_1 \left[ \exp(\alpha d) - 1 \right]} \tag{2.6}
\]

If the applied voltage is increased (region BC in figure 2.4), both \( \alpha \) and \( \gamma_1 \) increase (the increase in \( \alpha \) is much sharper), the denominator of equation (2.6) then approaches zero, and the current becomes infinite, limited only by the external circuit resistance. This is the so called gas breakdown and the corresponding voltage is called the breakdown voltage, \( V_B \).

Once breakdown has occurred, the gas begins to glow. This glow, which is due to the relaxation of the excited atoms as mentioned in section (A1.4), is said to be self-sustained in that the discharge is not dependant any more on the external irradiating source. For a discharge to be self-sustained, a secondary electron created in the cathode sheath (dark space as it will be described shortly) must produce, during its journey from
the cathode to the anode, a sufficient number of ions that can reach the cathode and release, upon striking it, a new secondary electron. For example, if $\gamma_i$ for a combination of cathode material and bombarding ions is 0.1, each secondary electron released from the cathode should produce 10 ions that can reach the cathode and have enough energy to release a new secondary electron.

The values of breakdown voltages that equation (2.6) predicts are higher than experimental results, largely due to this equation assuming a uniform field between the electrodes which is not the real case. As they have much lower mobility, ions tend to accumulate in front of the cathode giving rise to a positive space charge or sheath in the vicinity of the cathode that sharply increase the electric field there, and hence increasing $\alpha$ and $\gamma_i$ with applied voltages much faster than equation (2.6) predicts.

Breakdown voltage depends mainly on the mean free path of secondary electrons and hence on the pressure $p$ (see section A1.2), as well as on the spacing between the electrodes $d$. If the product $pd$ is too low, the number of ions produced by a secondary electron will be small. If this product is too high, the resultant ions will be involved in inelastic collisions and strike the cathode with insufficient energy to release secondary electrons. This is a qualitative statement of Paschen's law:

$$V_B = \frac{A(pd)}{C + \ln(pd)}$$  \[2.7\]

where $A$ and $C$ are gas dependent constants. Figure (2.5.a) shows a plot of Paschen's law which has a minimum denoted $V_{B_{\text{min}}}$.

Returning to figure (2.4) and in particular to the transition region CD, it is found that any further increase in current (e.g., by reducing the external circuit resistance) results in a decrease in voltage. This is a quite unusual behaviour and needs to be clarified. As mentioned earlier, the linear distribution of voltage between the two electrodes in the Townsend region is not valid when the gas breaks down. The dominant region of the discharge then becomes the positive space charge formed near the cathode, due to the substantial difference in the mobility of electrons and ions in an electric field. Almost all the applied voltage appears across this positive space charge and hence the anode of the system acts as if it was pushed towards the cathode, to an imaginary position $A_1$ on the knee of the non-linear voltage distribution, where $d$ becomes smaller (see figure 2.5.b). The glow discharge becomes a current-controlled device. In most electrode systems the product $pd$ is greater than that corresponding to $V_{B_{\text{min}}}$. As the discharge
Figure (2.5): (a) A plot of Paschen's law for argon. (b) Positions of the imaginary anode and the associated potential distribution. Replotted from references 14 and 18.
current increases in the CD region of figure (2.4), more ions are produced. The density of the space charge increases leading to a steeper voltage distribution across the dark space (narrower dark space; the imaginary anode is at $A_2$ in figure 2.5.b) and hence smaller $d$. This makes the product $pd$ smaller, which corresponds to a lower operating voltage (figure 2.5.a) and continues, with current, until a point (D in figure 2.4) roughly corresponds to $V_{\text{B_{mn}}}$ where the discharge is said to be in normal glow.

In the normal glow at point D, where the current in the system is still relatively low, the cross-sectional area of the glow is less than the actual area of the cathode. This glowing area of the cathode is just sufficient for the available current to fulfil the requirement of minimum current density to produce sufficient secondary electrons to keep the discharge self-sustained. If the current is allowed to increase in the normal glow region (towards E in figure 2.4), the system responds by increasing the glowing area of the cathode and maintaining a constant current density. Whilst the current density is constant, so too is the voltage across the dark space. The position of the imaginary anode is then unchanged and the operating voltage still roughly equals $V_{\text{B_{mn}}}$ until point E is reached, where the whole area of the cathode is covered with glow.

If the current to the system is increased beyond the point E, the current density, $J$, and hence the density of the space charge both increase. This leads to a decrease in the thickness, $L$, of the positive dark space. Aston derived the empirical relation:

$$L = \frac{A}{p} + \frac{B}{\sqrt{J}}$$  \[2.8\]

where $p$ is the pressure of the system, and both $A$ and $B$ are constants for a given electrode-gas combination. The position of the imaginary anode moves closer to the cathode (position $A_3$ in figure 2.5.b) resulting in an even lower value of the product $pd$, which corresponds to an operating voltage higher than $V_{\text{B_{mn}}}$ as in figure (2.5.a). This is the abnormal glow, where an increase in the current density is accompanied by an increase in the operating voltage, $V$, (or more precisely the voltage drop across the dark space, the so called "cathode fall"). Aston also developed the following empirical equation for the cathode fall:

$$V = C_1 + \frac{C_2 \sqrt{J}}{p}$$  \[2.9\]

where both $C_1$ and $C_2$ are constants for a given electrode-gas combination.

The abnormal glow is the only mode of interest in glow discharge sputtering since it allows the bombardment of the entire cathode area with energetic ions and hence
increases the amount of sputtered material, ensures high cathode utilisation and produces more uniform coatings.

As glow discharge sputtering is usually performed in the abnormal mode of a glow discharge where \( p_d \) and corresponding \( V_B \) are well to the left of \( V_{B_{\text{sta}}} \) in figure (2.5.a), either a relatively high voltage or a short-lived increase in pressure are often required to start the discharge\(^\text{17}\).

If the current is increased further beyond the point \( F \) in figure (2.4), the potential drops drastically and the discharge becomes an arc.

2.2.7. Regions of glow discharge

As mentioned earlier, the DC glow discharge commonly used for sputtering is operated in the abnormal mode. It is usually established in a vacuum system in which an inert gas pressure of 10-100 mTorr is maintained and a voltage of 1-6 kV is applied between two planar electrodes about 5 cm apart. Figure (2.6) shows an exaggerated cross-sectional view of a DC plasma discharge. It consists of several dark and glowing or light-emitting regions. These regions will be described in terms of the behaviour of charge carriers moving through them.

Secondary electrons generated at the surface of the cathode due to ion-bombardment, are accelerated away from it as a result of the repulsive force established by the electric field near to the cathode body. At such an early stage, the energy of the electrons is so low (~1 eV) that they are unable to cause ionisation of, or even excitation, to background gas atoms. This region is referred to as "Aston dark space". Adjacent to the Aston dark space is a glowing region known as "the cathode glow". The light emitted depends on the incident ions and the cathode material\(^\text{21}\). There are two possible causes of the cathode glow\(^\text{21}\). First, still being at low energy, the slowly moving secondary electrons from the cathode are involved in excitation collisions with gas atoms, followed by the photon-emitting relaxation of the excited atoms. Secondly, electrons from the cathode recombine with incoming ions with the resultant emission of photons.

Beyond the cathode glow there is a region of faint luminosity called the "Crookes' dark space". It is the most important region in the glow discharge characterised by a high electric field, established by a space charge of positive ions, across which almost all the applied voltage appears. In passing through this region, secondary electrons
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Dark Spaces

Aston Substrate Anode

Crookes Faraday

Cathode glow Negative glow Positive column Anode glow

Luminous regions

Figure (2.6): Regions, luminous intensity, potential, electric field, space charge density and current density across a low pressure gas discharge. Reproduced from references 11,15 and 23.
are rapidly accelerated to energies equal to or exceeding that necessary for the ionisation of the background gas atoms. Thus, ionising collisions are more probable than exciting ones which are followed by the subsequent emission of photons. On the other hand, if a collision happens to take energy away from an electron and slow it down, the high electric field quickly accelerates the electron back to a high energy. Thus recombination followed by the subsequent photon emission is similarly unlikely. This lack of both relaxation and recombination processes may account for the faint luminosity of this region.

Ions produced in the Crookes' dark space are accelerated by the high electric field of this region towards the cathode to create new secondaries. However, the flux of these ions is not sufficient to sustain the discharge. This is because in most glow discharge sputtering systems, the mean free path of ions is smaller than the thickness of Crookes' dark space, hence they suffer many charge exchange collisions on their way to the cathode. The number of these collisions is determined by the ratio \( L/\lambda_i \) (\( \approx 10^{-15} \)) which is proportional to pressure according to equations (A1.24), (A1.27) and (2.8). Hence, very few of the ions that cross the dark space are able to assume the full applied voltage present there. This is the conclusion of the work carried out by Davis and Vanderslice on the energy distribution of ions striking the cathode in an abnormal glow discharge. They found that an ion moving in its own gas transfers its charge to a neutral in a charge-transfer collision (see A1.4.4). The original ion which becomes a neutral maintains its momentum prior to charge transfer, whereas the new ion, formerly a neutral, carries on with only its thermal energy. This affects the energy distribution of ions (i.e., the percentage of the number of ions reaching the cathode as a function of the percentage of their energies, normalised to the cathode fall or, to a very good approximation, the applied voltage) as shown in figure (2.7), which is for \( \text{Ar}^+ \) moving in the dark space of a glow discharge having an applied voltage of 600 V in an argon pressure of 60 mTorr. Their results indicate that most of the ions strike the cathode with virtually zero energy, about 0.5% strike it with energies close to that of the applied voltage, while almost 50% strike it with energies as low as 10% of that of applied voltage. Meanwhile, in addition to causing sputtering, the new neutrals (formerly ions) have a high probability of being reflected with little or no loss of energy and hence generating too few secondary electrons to sustain the discharge. All these observations imply that for the glow discharge to be self-sustained, ions have to be produced elsewhere in addition to those produced in the Crookes' dark space.
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Figure (2.7): Percentage of ions reaching the cathode as a function of their energy normalised to cathode fall. Reproduced from reference 22.

Upon leaving Crookes' dark space which has the positive space charge and high electric field, the energetic electrons enter a new region of extremely weak electric field called "the negative glow". The dominance of positive space charge drops drastically and the region is neutral, consisting of approximately equal number of electrons and ions; it is a plasma. The drift velocities of these electrons are quickly randomised by either ionising or exciting collisions with gas atoms, depending on the distance from the cathode. The glow in this region is due to relaxation and recombination processes and is characteristic of the gas involved. Ions produced in the negative glow are accelerated towards the cathode and produce secondary electrons to sustain the discharge. They also involved in charge transfer collisions, as described by Davis and Vanderslice, during their passage through Crookes' dark space.

To conclude, ions are produced predominantly in both the Crookes' dark space and negative glow regions. In the case of a normal glow discharge the largest fraction of ions is produced in the Crookes' dark space, whereas in an abnormal glow discharge the largest fraction is produced in the negative glow\textsuperscript{22}. Meanwhile, before moving to other
regions, where ion production becomes far less probable, it is useful to mention that the electron current density to the anode \( J_{de} \) is equal to the ion current density \( J_{di} \) to the cathode plus the current density resulting from the secondary electrons \( \gamma_i \cdot J_{di} \). That is \( J_{de} = J_{di}(1+\gamma_i) \).

After losing most of their energy in the negative glow, the "exhausted" electrons enter another dark region called the "Faraday dark space". In this region, electrons are unable even to excite gas atoms. They begin to accumulate there forming a region of slightly negative space charge, moving by diffusion.

Electrons are then accelerated towards the anode. When they gain enough energy to excite and ionise gas atoms, a region of low luminosity called the "positive column", begins. It is characterised by the absence of net space charge and a very low electric field through which the electrons diffuse in a similar manner to that described by equation (2.6) until the final region, "the anode sheath" is reached.

The area of the anode relative to that of the positive column cross section, determines whether the potential across the anode sheath is positive or negative with respect to the plasma potential. The basis of this dependence lies in the balance that should exist between electron current to the anode and that required by the discharge. If the area of the anode is large, which it is in most cases, the potential across the anode sheath is negative with respect to that of the plasma allowing less current (electrons) to the anode and leaving the plasma more positive than the most positive surface in contact with it. The voltage distribution across DC glow discharge is shown in figure (2.8). Conversely, if the area of the anode is small, the potential across the anode sheath is positive with respect to the plasma potential, allowing more current to the anode.

The exact location of the anode in a self-sustained glow discharge is, up to a certain distance from the cathode, of little importance as far as the electrical characteristics of the glow is concerned. This is because in such a discharge, ions, and the subsequent secondaries, are created near the boundary between Crookes' dark space and the negative glow and hence in the vicinity of the cathode. Thus, if the anode is moved toward the cathode consuming the positive column, the Faraday dark space and the negative glow, only a small effect can be observed on the electrical characteristics of the glow. If, however, the anode is pushed as far as Crookes' dark space, a considerable increase in the potential across the electrodes is needed to maintain the discharge current (corresponding to an ascent on the left-hand portion of figure 2.5.a) because the number of the ions being produced then decreases. This is called "the obstructed glow". Finally, if the anode is pushed into Crookes' dark space, no ions can be produced and no glow can be maintained even for very high applied voltages.
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Figure (2.8): Voltage distribution across a dc glow discharge. Reproduced from references 11 and 17.

The cathode-to-substrate distance plays a decisive role in determining the amount of sputtered material deposited on the substrate. The amount of material collected by a substrate is inversely proportional to this distance. Therefore, in most sputtering systems the substrate, which is often also the anode, is placed inside the negative glow just far enough away from the cathode to not obstruct the glow\textsuperscript{16,20}.

2.3. Mechanisms of charged particles-surface interaction

Bombardment of solid surfaces by energetic particles give rise to many phenomena\textsuperscript{23,24} as shown in figure (2.9). These phenomena essentially depend on: (i) The mass, energy and angle of incidence of the bombarding particle; (ii) The masses of the bombarded atoms; (iii) The texture and orientation of the bombarded surface. As a consequence of that, the bombardment of solid surfaces with ions gives rise to the production of more species than does bombarding them with electrons, due to the great difference in mass. With the former, the collision is between particles of approximately equal mass leading to the energy transfer function approaching unity, as equation (A1.33) indicates. With the latter, the energy transfer function is very small and virtually no transfer of kinetic energy can take place, though there may be a substantial transfer of potential energy to the massive body\textsuperscript{11,18}. 

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Although the ejection of cathode material (sputtering) in a neutral atomic form is the most important phenomenon, at least for the purpose of this work, other phenomena are also of great importance for maintaining the discharge, their effects on the growth of the sputtered film or as means of controlling some other glow discharge processes such as reactive sputtering.

2.3.1. Secondary electrons

For an ion approaching a clean conducting surface, there is a high probability that it will capture a field-emitted electron just before impact\textsuperscript{23}. The neutralisation or recombination energy may then be released as kinetic energy given to a third carrier\textsuperscript{25}, usually a lattice conduction band electron, causing the ejection of a secondary electron. This process is called radiationless Auger-type recombination or Auger emission. Upon approaching the cathode, an argon ion for example, is seen by the conduction band electrons of the lattice as a potential well\textsuperscript{26,27} of a depth equal to the ionisation energy of argon (i.e., 15.8 eV) as shown in figure (2.10). The minimum energy required for a lattice electron to flee the cathode surface is $e\phi$ (~3-5 eV for metals), where $\phi$ is the work function of the cathode material.
A lattice electron may then tunnel into the argon ion potential well to recombine with the argon ion. The energy difference (i.e., \(\sim 10.8 \text{ eV}\)) is released in the form of a photon. If the photon is absorbed by another lattice electron near the surface, the electron may then acquire enough energy to be emitted from the surface. This electron is called an "Auger electron". The probability of this process is low, therefore more than one ion is needed to release one electron. The secondary electron emission coefficient, \(\gamma_i\), for metals is in the range 0.1-0.3 for incident ions of energy less than 1 keV\(^{11}\). In insulators, \(\gamma_i\), is higher\(^{26,28}\). Since \(J_{de} = J_{di} (1 + \gamma_i)\) as discussed in section (2.2.7), for the same discharge current density \(J_{de}\), the ion current density to the cathode \(J_{di}\), is smaller in the case of insulators (e.g., oxides) than metals. This indicates that for the same discharge current density, insulators would sputter more slowly than metals. This conclusion is of great importance in reactive sputtering as will be seen in a later chapter. The yield, \(\gamma_i\), for inert gas ion-bombardment using ion energies of less than 1 keV, the region where most glow discharge sputtering experiments take place, is almost insensitive to ion energy\(^{23}\) and decreases with the mass of the bombarding ions\(^{11}\). For ion energies in the range 1-10 keV, where most ion beam sputter deposition experiments are carried out, \(\gamma_i\) increases with ion energy\(^{29}\) and depend on the bombarded crystal face\(^{11}\). The average ejection energy of these secondaries is a few eV.

As mentioned earlier, these electrons are essential in a glow discharge. They are accelerated by the strong electric field of the Crookes' dark space and are involved in ionising collisions to produce enough ions to sustain the discharge. Eventually they
approach the anode and strike it. Ball\cite{10} suggested that electron-bombardment of the anode is the source of anode heating. He found that about 40% of the applied power density is dissipated at the anode due to secondary electron-bombardment, whereas only about 1% of anode heating is due to the arrival and condensation energy of the sputtered species.

Similarly, the bombardment of a solid surface by a beam of primary electrons gives rise to the emission of secondary electrons. Some of these secondaries result from elastically or inelastically scattered primaries leaving the surface at higher energy, and the remainder are "true secondaries"\cite{11,28} leaving the surface at a mean energy around 10 eV.

**Figure (2.11): The energy distribution of secondary electrons emitted by electron-bombarded silver target. Reproduced from reference 11.**

Figure (2.11) shows the energy distribution of secondary electrons emitted by silver. The secondary electron emission coefficient due to electron-bombardment, $\gamma_e$, is greater than unity in the case of metal surfaces and may reach even higher values for oxides\cite{11,26,28}. So the coefficient is higher than that for ion-bombardment, partly due to the greater penetration depth of an incident electron into a surface\cite{18}, which is about 30 nm for 1 keV electrons\cite{28}, compared with 1 nm for 1 keV ions\cite{24}. The penetrating electron is involved in many ionising collisions with the lattice atoms giving rise to the production of more electrons. Some of these electrons which are generated within a certain depth,
the escape depth, may leave the surface. The escape depth is characteristic of the bombarded surface and of the electron energy.

2.3.2. Ejection of surface material

The two surfaces of interest in a vacuum discharge sputter deposition chamber are the cathode and the substrate surface; the former as a source of material, the latter as a base for material "landing" as well as a film modification medium.

In a glow discharge, electrons cannot reach the cathode. If this cathode is bombarded with low energy ions with kinetic energies less than 5 eV, the bombarding ions are reflected or come into thermal equilibrium with the surface to be evaporated later\textsuperscript{24,26}. When the kinetic energy of the bombarding ions exceeds the binding energy of the lattice atoms and reaches a certain value, the sputtering threshold, the material of the cathode is ejected and sputtering is said to have occurred. Sputtering threshold is about four times the heat of sublimation of the surface material and is of the order of 15-40 eV\textsuperscript{24}, sufficiently large to cause displacement of lattice atoms.

At kinetic energies above about 100 eV, ions begin to be trapped or implanted in the lattice to a depth dependant on crystal structure and orientation of the bombarded surface, until an equilibrium state is reached in which the trapped bombarding ions are sputtered in the same manner as the lattice atoms of the cathode. The trapping probability increases with incident ion energy and, at a given ion energy, the trapping probability is inversely proportional to the mass of the bombarding ion\textsuperscript{23}.

Although some details concerning the mechanisms by which atoms are ejected during ion-bombardment are reasonably well known and described in terms of the momentum transfer model, the exact mechanisms are not well understood and are rather complicated. This lack of understanding is due to the number of parameters involved, including kinetic energy and mass of ions, as well as lattice structure and binding energy of the bombarded surface.

Historically, it was believed that energetic ion-bombardment of a surface originates a localised increase in surface temperature, or "hot spot", which causes surface material to evaporate\textsuperscript{31,32}. According to this theory, it was thought that sputtering rate and sputtering yield, that is the number of ejected atoms from a cathode per incident ion, depend on both the kinetic energy of bombarding ions and the heat of sublimation of surface material. It was also thought that sputtered atoms adhere to a cosine distribution law.
The experiments which led to these conclusions were carried out using self-sustained glow discharge sputtering systems, which are not suitable for such basic studies for the following reasons: (i) As the pressure required to sustain the discharge can not be reduced below a certain level (Paschen's law), the mean free path of ions in glow discharge systems is not large enough (see section A1.2), hence ions strike the cathode with a wide range of energies and angles of incidence due to multiple collisions. Similarly, the mean free path of sputtered atoms is also so small that not all these atoms reach the substrate to be accounted for and measured. Some of these atoms diffuse back to the cathode; (ii) Ion current, ion energy and gas pressure can not be controlled, and hence investigated, independently; (iii) Determination of thresholds, or working around them, require the use of ions of lower energies (i.e., lower applied voltages). Unfortunately, a self-sustained glow discharge can not be maintained below a characteristic voltage; (iv) The dominance of the charge transfer mechanism in the cathode region\textsuperscript{22} (see section 2.2.7) adds more difficulties to interpretation of results\textsuperscript{34,35}.

Due to the above limitations of a glow discharge in fundamental studies, it was replaced by ion beam or other discharge-supporting methods, which provide independent alternatives of ion generation. This eliminates any controversy involving ion generation to sustain a glow discharge on the one hand, and ion acceleration to sputter cathode material, on the other. For example, to verify the effect of bombarding-ion energy on sputtering yield, Guntherschulze and Meyer\textsuperscript{34,35} used a thermionic oxide cathode and an anode to create a dense plasma at a gas pressure below 10 mTorr. The target material was biased negatively and immersed in the plasma as a third independent electrode (this system is now known as triode sputtering). Such a pressure allowed the mean free path of ions or sputtered atoms to be comparable with, or even larger than the chamber dimensions. These experiments and many others tried to solve mysteries surrounding the hot spot theory. It was then found that

1. The energy of sputtered particles is higher than that of evaporated ones. For example\textsuperscript{36}, the average ejection energy of Ge atoms under 1.2 keV Ar ion-bombardment is about 15 eV compared to only about 0.1 eV for evaporated Ge. In sputtering systems, cathode-to-substrate distance is relatively small (less than a few mean free paths), to secure maximum deposition rate. This implies that the energy distribution of sputtered particles upon striking the substrate will be almost the same as that of ejected particles.

2. In contradiction to evaporation, no thermionic electron emission is observed\textsuperscript{34}.

3. Sputtering yields are independent of both the thermal conductivity and the temperature of cathode material. They increase for more oblique angles of
incidence of bombarding ions. Sputtered atoms are ejected in the forward direction under oblique low-energy ion-bombardment.

4. Sputtering yields are dependant on crystal orientation\(^{37,38}\). Unlike polycrystalline and amorphous cathodes with no preferred crystal plane orientation, the distribution of sputtered atoms from a single crystal cathode is not governed by the cosine law (i.e., \( j_\delta = j_0 \cos \delta \)), where \( j_\delta \) is the current density of sputtered atoms ejected at an angle \( \delta \) with respect to the normal of the cathode surface, and \( j_0 \) is the current density of atoms ejected perpendicular to the cathode surface implying that if the substrate is opposite to the cathode, the thickest film would be deposited onto it), but concentrates in the close-packed-crystal directions. Furthermore, even in single crystal cathodes, the adherence to preferred ejection directions occurs only when the temperature of the cathode is higher than a characteristic value which depends, for a given cathode, on ion mass and energy, and rate of bombardment\(^{39,40}\). This is because such a high temperature secures quick annealing of any surface damage caused by ion-bombardment. Otherwise the surface damage results in an amorphous structure without any preferred ejection direction.

5. Sputtering yields of single crystals show maxima and minima that vary with the angle of incidence of the bombarding ions. These maxima and minima correspond to the lattice directions in which the crystal shows maximum or minimum transparency.

6. Sputtering yields depend not only on the energy, but also on the mass of bombarding ions, and increase with it.

7. At very high ion energies, sputtering yields decrease due to ion implantation.

These contradictions to the hot spot evaporation theory, paved the way for a more realistic theory, the momentum transfer theory, first suggested by Stark\(^41\) and later supported by the observations of Wehner\(^{36,42}\) and other workers\(^{33,43}\). In this theory, the momentum of an incident ion is directly transferred, upon collision, to the atoms of the bombarded surface, forcing them to move from their equilibrium positions and to be involved in more collisions. This series of binary collisions in the bombarded surface, which is called a "collision cascade", may eventually lead to the ejection of atoms from that surface. The diameter of a typical cascade is 20 nm and sputtering barely occurs as a result of collision sequences initiated more than five atomic layers below the bombarded surface\(^44\).
Sputtering is often described as a game of three-dimensional billiards played with atoms as shown in figure (2.12).

The bombarding ion, represented by the cue ball, strikes the arranged assembly of balls, representing the atomic array of the bombarded surface. The balls, or bombarded atoms, are caused to scatter in every direction, including, but not necessarily, some backwards in the direction of the player, that is out of the bombarded surface. This implies that the ejection of an atom from the surface would require at least two collisions. Furthermore, this ejection of atoms is not inevitable. The cascade may carry on inside the bombarded surface dissipating the energy of the primary impact to the surrounding lattice in form of heat. This accounts for the fact that sputtering is a very inefficient process\textsuperscript{11,24,26}. Only a small fraction of the incident energy causes the dislodging of atoms from the surface and then appears as the energy of the sputtered atoms (~1%). The rest appears as heat and lattice damage.

Although the atoms are not simple balls, but are subjected to interatomic repulsion or attraction potentials that vary with separation, this analogy is still quite acceptable\textsuperscript{11}. 

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{sputtering_diagram.pdf}
\caption{The atomic billiard model of sputtering.\textsuperscript{11} Reproduced from reference 11.}
\end{figure}
This model implies that the "cue balls" can be ions, electrons, or neutrals. As mentioned before, the electron-atom energy transfer function is too small leading to inefficient sputtering process, neutrals are avoided due to the difficulty in accelerating them. Therefore, ions are the only reasonable candidate to be "cue balls", though they are neutralised by field-emitted electrons just before striking the cathode, as described earlier. Sigmund pointed out that the collision cascade mechanism is most dominant when metallic surfaces are bombarded during cathode sputtering.

In addition to sputtered neutrals, cathode material can be emitted in the form of positive and negative secondary ions. The high electric field of the cathode sheath draws the positive ions, which form less than 1% of the sputtered flux, back to the cathode surface, whereas it accelerates the negative ions towards the substrate. The negative ions, which also constitute a small fraction of the flux, involve in electron stripping collisions and strike the substrate as energetic neutrals. The sputtered material may also leave the cathode in an excited state and emit, upon relaxation, characteristic photons. Similarly, incident ions are reflected in the form of neutrals, as discussed earlier, as well as in the form of positive ions, negative ions and excited atoms. Finally ultraviolet and x-ray radiation may also be emitted, which may be a problem if the substrates used are sensitive to these radiations.

Once leaving the cathode surface (usually with initial energies of 10-40 eV), sputtered material in a glow discharge is subject to the same conditions as those of sputtering gas atoms. The sputtered atoms, in their passage through the plasma, are involved in many collisions with the atoms of the sputtering gas and other sputtered species. The number of these collisions is dependant on the kinetic energy of the sputtered atoms on one hand, and on their mean free path, and hence the chamber pressure, on the other. As a result of these collisions, the sputtered atoms may lose part or all of their initial energy, or, they will participate in ionising and exciting collisions. In the former case, the sputtered atoms may either arrive at the substrate with reduced energy (~1-2 eV), be backscattered to the surrounding surfaces including the cathode, or come into thermal equilibrium with gas atoms by losing enough energy, and thereafter diffuse in the same manner as sputtering gas atoms. In the latter situation, the positively ionised sputtered atoms are accelerated, by the electric field of the Crookes' dark space, back towards the cathode leading to the phenomena of self-sputtering. Using a high density argon plasma to sputter aluminium at high rates, Hosokawa et al found that the aluminium cathode was bombarded not only with Ar ions but also with Al ions. They concluded that a significant number of the sputtered atoms must be ionised upon passing through the plasma and these ions are accelerated back to the cathode. They estimated that more than 18% of the total ion current is due to ionised sputtered aluminium atoms. Clearly,
such interfering phenomena may affect the accuracy of the measured values of sputtering yields. Finally, the involvement of a sputtered atom (or a gas atom) in an exciting collision is usually followed by relaxation of the excited sputtered atom to a lower energy state emitting a characteristic photon\textsuperscript{51}. These form the base of a very important technique used as a controlling method of reactive sputtering processes\textsuperscript{52,53,54}, as will be described in a coming chapter.

2.4. Sputtering yield and threshold

The three-dimensional billiards model of sputtering discussed previously implies that the sputtering yield should depend on the mass, $m_i$, energy, $E_i$, and angle of incidence of the bombarding ions, and also on the mass, $m_t$, of the bombarded surface atoms as well as the binding energy, $U_0$, of this surface. As mentioned earlier, although this model is quite accurate, it does not take into account the interatomic repulsion or attraction potentials to which atoms are subjected. On the other hand, according to Sigmund's theory of sputtering\textsuperscript{55}, incoming ions deposit their energies in the near surface region of the cathode and sputtered atoms are ejected only from the outermost layers of the surface (within about five atomic layers below the surface\textsuperscript{44}). Thus these potentials play a significant role in the process of sputtering and should be included in any expression of sputtering yield. This was achieved by including the nuclear stopping power, $S(E)$. Sigmund obtained the following formula of $S(E)$, for bombardment energy up to 1 keV:

$$S(E) = \frac{m_t m_i}{(m_i + m_t)^2} E_i \cdot \text{constant} \quad [2.10]$$

Clearly, the sputtering yield should be proportional to the stopping power. The last formula can then be used to predict the sputtering yield, $Y$, from the following expression:

$$Y = \frac{3\beta}{4\pi^2} \frac{4m_i m_t E_i}{(m_i + m_t)^2 U_0} \quad [2.11]$$

where $\beta$ is a function of $m_t/m_i$ and the angle of incidence, but independent of the ion energy $E_i$. This expression indicates that sputtering yield increases linearly with ion energy. Experimental results show that this is true up to above 1 keV\textsuperscript{11,23}, but at higher energies, the sputtering yield becomes almost independent of ion energy\textsuperscript{11,23,56}. Furthermore, experimental data shows that sputtering yield actually decreases at very high ion energy\textsuperscript{11,23,57}, due to the increasing probability of ions being implanted, and hence sputtered along with the original cathode material. For bombarding energies above 1 keV, Sigmund introduced a modified expression\textsuperscript{55,55} of sputtering yield.
Sigmund's theory works well for ion energies above 1 keV\textsuperscript{11} but is not applicable in the low energy range because of uncertainties in the relevant collision cross sections\textsuperscript{18}. Using computer modelling, Biersack and Eckstein\textsuperscript{19} also concluded that Sigmund's formula is not valid below 500 eV. Steinbruchel\textsuperscript{18} simplified Sigmund's theory and used an accurate expression of nuclear stopping cross section. He gave a more convenient formula of sputtering yield, for low energy sputtering (i.e., roughly 0.1-1 keV), by combining results of various workers like Zalm\textsuperscript{60}, Andersen and Bay\textsuperscript{61}, and others including Sigmund\textsuperscript{45,55}. His formula is:

\[ Y = \frac{5.2}{U_0} \left( \frac{Z_i}{Z_i^{2/3} + Z_t^{2/3}} \right)^{3/4} \left( \frac{Z_i}{Z_t + Z_i} \right)^{2/3} E_i^{1/2} \]  \hspace{1cm} \text{[2.12]}

where \( Z_i \) and \( Z_t \) are the atomic number of bombarding ions and bombarded surface atoms, respectively. \( U_0 \) is the binding energy, in eV, of the bombarded surface and \( E_i \) is the ion energy, in keV.

It is interesting to note that according to the previous formulas, one should not expect a maximum sputtering yield when \( m_i \approx m_t \), as the energy transfer function (equation A1.33) would suggest, if the three-dimensional billiards model of sputtering was applied alone. This expectation is supported by the experimental results of Almen and Bruce\textsuperscript{56} who measured the sputtering yield of copper, using an electromagnetic isotope separator, over a wide range of ion energies for various noble gas ions. They found that sputtering yield increases with atomic mass of bombarding ions, and does not reach a maximum when Cu (atomic mass, \( A_m \), equals to 64) is bombarded with Kr (\( A_m = 83 \)) or Ar (\( A_m = 40 \)), but does with Xe (\( A_m = 131 \)), despite the atomic masses of Kr and Ar being closer to the atomic mass of Cu than that of Xe. The same conclusions were reached when Cu was replaced with Ag, Pd, Sn or Mo. Always Xe secures maximum sputtering yield.

It is also interesting to note the immediate conclusion that can be drawn when equation (2.12) is applied in reactive sputtering. In this process, the reaction products, of cathode material and reactive gas, form a stable compound layer\textsuperscript{42} (i.e., one with negative heat of formation) on the surface of the cathode. This indicates that the binding energy of such a layer is higher than that of reacting species (e.g., the original cathode material). Since sputtering takes place within the uppermost surface layers, and since sputtering yield is inversely proportional to surface binding energy, it can be concluded that the arrival of reactive gas at the cathode gives rise to a reduction in the sputtering yield. This reduction will be more for the highly reactive systems (e.g., Al + O\textsubscript{2} or Ti + O\textsubscript{2}) which form compounds with greater negative heat of formations, and hence higher surface binding energies.
Assuming that there is no backscattering or self-sputtering of the sputtered species, an approximate expression for the sputtering yield of an element can be derived as follows: If \( J \) is the discharge current density in \( \text{A/m}^2 \), \( J_i \) the ion current density upon bombarding the cathode in \( \text{A/m}^2 \), \( \gamma_i \) the secondary electron emission coefficient of cathode material, \( N_i \) the number of ions bombarding a unit area of the cathode per second, \( N_m \) the number of sputtered cathode atoms from a unit area of the cathode per second, \( \Delta W \) is the decrease of cathode mass per unit area, in \( \text{kg/m}^2 \), after being sputtered for \( t \) seconds, \( \Delta W \) is the atomic mass of cathode atoms, \( e \) is the electronic charge, and \( N_{Av} = 6.022 \times 10^{23} \) atoms/mol is Avogadro number, then:

\[
N_i = \frac{J_i}{e} = \frac{J}{e(1 + \gamma_i)} \tag{2.13}
\]

Since \( Y = \frac{N_m}{N_i} \) by definition, then using equation (2.13):

\[
Y = \frac{e(1 + \gamma_i)N_m}{J} \tag{2.14}
\]

but:

\[
N_m = \frac{N_{Av} \Delta W}{A_m \cdot t} \tag{2.15}
\]

hence, using equation (2.14) and (2.15), and substituting \( e \) and \( N_{Av} \) with their values give:

\[
Y = 10^5 \frac{(1 + \gamma_i)\Delta W}{A_m \cdot J \cdot t} \tag{2.16}
\]

It is worth mentioning that tables give the sputtering yields of pure elements, at certain values of energies of bombarding ions, can only be used as rough guides. This can be attributed to two reasons: (i) In glow discharge sputtering, the bombarding ions are not at all monoenergetic; (ii) Pure elemental cathodes are hardly found in sputtering. These cathodes are usually contaminated with implanted sputtering gas atoms, oxide layers, etc., which are sputtered along with cathode material. Also, these cathodes often intentionally consist of alloys, compounds or mixtures.

Sputtering threshold, which is about four times the heat of sublimation of the surface material, seems to be more characteristic of cathode material and varies little with the type of bombarding ions. This is the conclusion of the work carried out by Stuart and Wehner. They measured the threshold energies of a wide range of elements when bombarded with different ions. For example, the threshold energy for Cr is 22, 22, 18, 20 and 23 eV when it is bombarded with Ne, Ar, Kr, Xe or Hg ions, respectively. On
They measured the threshold energies of a wide range of elements when bombarded with different ions. For example, the threshold energy for Cr is 22, 22, 18, 20 and 23 eV when it is bombarded with Ne, Ar, Kr, Xe or Hg ions, respectively. On the other hand, the threshold energy of Al, Nb and W when bombarded with Ar ions is 13 eV, 25 eV and 33 eV respectively.

2.5. Sputtering rate

Deposition rate, $R_{\text{dep}}$, can be defined as the amount of sputtered material deposited on a unit area of substrate in unit time. It is proportional, but not equal, to the sputtering rate, $R_{\text{sput}}$, which can be defined as the amount of sputtered material from a unit area of the cathode per unit time. The reason why these two rates are not equal lies in the fact that not all sputtered material can reach the substrate due to collision with sputtering gas atoms that give rise to backscattering and self-sputtering phenomena, as described in section (2.3.2). Also, not all material reaching the substrate adheres to it, due to resputtering and other phenomena that accompany film growth. From the definition, $R_{\text{sput}} = \Delta W/t$. Using equation (2.16), one gets:

$$R_{\text{sput}} = 10^{-5} \frac{A_m \cdot Y_j}{(1 + \gamma_j)}$$  \[2.17\]

According to Wasa and Hayakawa\textsuperscript{64}, the amount of sputtered material that reaches the unit area of the substrate, $W_i$, is inversely proportional to the product $p_d$, and is given by the following approximate equation:

$$W_i \approx k_1 \frac{\Delta W}{p_d}$$  \[2.18\]

where $k_1$ is a constant. Since $R_{\text{dep}} = W_i/t$ by definition, then by using equations (2.16) and (2.18), the following equation of deposition rate can be obtained:

$$R_{\text{dep}} \approx 10^{-5} k_1 \frac{A_m \cdot J}{(1 + \gamma_j) p_d}$$  \[2.19\]

In practice, it is customary in thin film processes to express the deposition rate of a film in terms of its thickness divided by deposition time, assuming a uniform film. In most industrial applications, it is favourable to deposit at the highest rate. According to the former equation, for a given deposition system and cathode material, this can be achieved by increasing both $Y$ and $J$, where $J \propto p^2$ for a given voltage (equation 2.9). The yield can be increased by raising the discharge voltage (equation 2.12), but such an increase is relatively slow and almost saturates at higher voltages\textsuperscript{64}. Increasing the
discharge current density, independently of pressure, is limited by the capability of the power supply. In practice, a power supply with limitless capability does not exist. Finally, although increasing the discharge current density, by raising the pressure in the chamber at constant voltage (power), leads to a linear increase in the deposition rate, it also encourages the incorporation of sputtering gas atoms into the growing films with resultant contamination. Furthermore, such an increase of deposition rate with pressure is not limitless either. At still higher pressures, the yield, and hence the deposition rate decreases sharply due to backscattering. For example, above about 130 mTorr, more than 50% of the sputtered material diffuses back to the cathode. In addition, the thickness of Crookes' dark space decreases with pressure (equation 2.8). This makes the shielding of the cathode (which will be described in chapter three) more difficult, which in turn increases film contamination, due to the sputtering of the cathode body. Many workers found that the best compromise argon pressure in glow discharge sputtering is in the range 50 mTorr-60 mTorr.

To summarise, in order to deposit at high rates and low pressures, using available power supplies with their limited outputs, it is best to sputter at high current densities and low voltages. This can be accomplished by the manipulation of new glow discharge sputtering systems, that is thermionically (triode sputtering) or magnetically (magnetron sputtering) supported glow discharge. These systems will be described in the next chapter.

2.6. Preferential sputtering

Despite the difference in the sputtering yields of its components, it is possible to sputter-deposit a film, from a multi component cathode, with the same composition as that of the cathode from which it was sputtered. This is called "preferential sputtering". In the initial stages, the components of higher yields will be removed faster giving rise to an altered layer (~100 nm to 1000 nm thick) to be formed at the cathode surface. The composition of such a layer is different than that of bulk material. It becomes deficient in the higher sputtering yield components and vice versa. After about 15-30 minutes of ion-bombardment, a steady state is reached in which, the surface composition of a multicomponent cathode will adjust itself to balance the elemental sputtering yields, that is:

\[
\frac{Y_1}{C_{b_1}} = \frac{Y_2}{C_{b_2}} = \cdots = \frac{Y_n}{C_{b_n}} \tag{2.20}
\]

where \( Y_1, Y_2, \ldots, Y_n, C_{b_1}, C_{b_2}, \ldots, C_{b_n} \) are the yield, surface concentration, and bulk concentration of component 1, 2, ...n, respectively.
However, compositional differences between sputtered films and the cathodes from which they were sputtered may be observed. These differences are attributed to: (i) Inefficient cooling of the cathode, which may not only cause diffusion of some material into the altered layer and change its composition, but also allow the evaporation of some components from the cathode if they have a significant vapour pressure; (ii) Some part of the cathode is covered with oxides, which causes the steady state to be not for the original components but for their oxides; (iii) Backscattering of some sputtered atoms to the cathode; (iv) Resputtering of the film (e.g., during bias sputtering), where the components of higher yields will be removed faster from the film.

2.7. Evaluation of sputter-deposition process

Behind the revolutionary change in the reputation of sputtering, from an unwanted, annoying effect that consumes cathodes and contaminates plasmas, to an irreplaceable technique in some applications of today's thin film technology (e.g., VLSI), lies the intensive effort of many scientists. Their collaborative efforts helped in the development of a better understanding of the advantages, and of course, disadvantages of this process. A summary of both is given in this section. The sputtering process enjoys the following advantages:

1. The possibility to sputter-deposit metals, semiconductors, or insulators using DC or RF sputtering, both reactively (e.g., to form oxidised, nitrided or carbided films) and non-reactively. Furthermore, it is even possible to deposit materials of complicated composition such as stainless steel and Pyrex glass provided that cathode cooling is secured. Vacuum evaporation of these materials is almost impossible.

2. The unique possibility of sputter-cleaning the surface of the substrate, just before deposition, by bombarding it with ions in vacuum. The substrate need not be exposed again to ambient after cleaning.

3. The possibility of sputtering from large area cathodes simplifies the problem of obtaining films with homogeneous thicknesses over large substrates. It also helps to minimise shadowing effects due to dust particles, with the resultant pinholes in films.

4. The relative simplicity of film thickness control. Once the process parameters to obtain a measurable thickness are determined, any other desired thickness can be achieved by maintaining these parameters and changing only deposition time.
5. Values of sputtering yields, compared to the values of vapour pressures of various materials are closer to each other. This makes the deposition of multilayer films more controllable by sputtering.

6. In most cathodes, there is enough material to last for many deposition runs before replacement of the target becomes necessary.

7. As sputtering is an atom-by-atom process, unlike vacuum evaporation, there are no problems with "spitting" (i.e., the ejection of larger agglomerates) from the cathode.

8. The possibility of shaping the plasma by external magnetic fields, leads to lower thermal stresses on the substrates caused by electron-bombardment. It also improves the density and thickness uniformity of sputtered films.

9. As mentioned in section (2.3.2), the ejection energy of sputtered particles is about 100-300 times higher than that of evaporated ones\textsuperscript{30,36}. If glow discharge sputtering is performed at pressures less than 5 mTorr, where the mean free path of sputtered atoms (calculated using equations A1.27 and A1.24) is comparable with cathode-to-substrate distance, the sputtered atoms arrive at the substrate with their high ejection energy (~10-15 eV). They penetrate one or two atomic layers into the surface of substrate\textsuperscript{69}, which results in superior adhesion of sputtered films compared to vacuum evaporated films\textsuperscript{69}.

10. From the point of view of film structure and growth, the high arrival energies of sputtered atoms at the substrates, just mentioned, help in cleaning the surface of the substrate, and can be accommodated by the substrate\textsuperscript{70}. This gives rise to the growth of epitaxial films at lower temperatures. Also, denser films were obtained with higher sputtering voltages (i.e., higher ejection energies). Finally, some of sputtered atoms may penetrate into the surface of the substrate and generate point defects that act as nucleation sites for the formation of stable nuclei\textsuperscript{24}.

11. Unlike vacuum evaporation, the presence of the plasma during sputter-deposition adds a unique advantage. Biasing the substrate and varying its temperature during deposition help in controlling film properties (e.g., step coverage and grain structure), through ion-bombardment of the growing film. This will be discussed in detail later in this chapter.

On the other hand, sputtering process suffers the following disadvantages:

1. High capital equipment costs.
2. Sputtered films can be more contaminated than vacuum evaporated ones. As it is performed in partial vacuum due to the presence of a sputtering gas, working pressures are higher in sputtering than in high vacuum evaporation. This increases the possibility of impurity incorporation (e.g., the sputtering gas atoms) into the deposited films.

3. Sputtering rates are lower than evaporation rates\textsuperscript{20}. Also taking into account the backscattering of some sputtered atoms due to the presence of a sputtering gas, lower deposition rates are obtained by sputtering than by vacuum evaporation.

4. Not all materials can be sputter-deposited. Some materials (e.g., organic solids) degrade under ion-bombardment.

\textbf{2.8. The sequence of thin film nucleation and growth}

Figure (2.13) shows the stages of thin film growth. The sputtered materials arrive at the substrate in the form of atoms or molecules. To be attached to the surface of the substrate, the atom must lose its impact velocity component normal to the surface by transferring it to the lattice atoms of the substrate\textsuperscript{64,71}. An adsorbed atom diffuses around the surface of the substrate in a motion influenced by its impact velocity component parallel to the surface, its binding energy to the surface and the nature as well as temperature of the surface\textsuperscript{11}. Higher substrate temperature means higher mobility of the atom. This leads to the trapping of the atom in the most energetically favourable sites. It also leads to the desorption of loosely sorbed atoms as well as the sublimation of volatile species.
Figure (2.13): Schematic of stages of thin film growth.
The ultimate result of this motion is either an interaction with another diffusing atom to form a doublet, or re-evaporation. The probability of forming such a cluster increases with the density of adatoms on the surface, and hence with the deposition rate. The mobility of a cluster is smaller than its constituent atoms, so the probability for it to move or re-evaporate is lower. As the adatoms diffuse around the surface they join the cluster to form a bigger and hence more stable one. The "nucleation" occurs when the diameter of the cluster, or as it is called the nuclei, reaches a critical value. Otherwise, the cluster re-evaporates. In both evaporation and sputtering the diameter of such a nuclei was found by Chopra\textsuperscript{70} to be 10-20 Å. He also found that the nucleation density of sputtered Ag, Pt, Ni, Au or Au/Ag films is higher than that of the corresponding evaporated films, although the order of magnitude is the same (\textasciitilde 10\textsuperscript{11} nuclei/cm\textsuperscript{2}) for both deposition methods. The higher density was attributed to the higher number of point defects generated on the surface of the substrate in sputter-deposition (see section 2.7).

The next stage is the growth of nuclei to form islands. Although a nuclei grows in three dimensions, its growth in the direction parallel to the surface of the substrate is more than that in the normal direction. This is because adatoms diffuse around the surface. The directional inconsistency in growth is more observable in sputtering than evaporation due to continuous ion-bombardment in the former which retards the growth in the normal direction. Eventually, the islands grow large enough to touch each other, or to "coalesce", in a liquid-like behaviour, marking the coalescence stage. This stage is characterised by an increase in the height of all islands on account of the simultaneous decrease in their total area. Following coalescence, the uncovered surface area of the substrate becomes larger, allowing more room for secondary nucleation and growth processes to take place as fresh material lands on the substrate. Following nucleation and coalescence, the large islands continue to grow, leaving behind narrow channels of exposed surface. These channels are bridged, with the aid of secondary nucleation and growth, to form holes which are then filled in the same way to result in a continuous film.

Prior to the coalescence stage, an island is usually single crystal, or contains only a few crystallites. A polycrystalline substrate does not influence the orientation of each island. Islands will be randomly oriented and the deposited film will be polycrystalline. The situation is totally reversed when deposition is carried out on a single crystal substrate, where a single crystal film can be obtained. Meanwhile, substrate temperature and deposition rate play a significant role in both cases. As mentioned earlier, a higher substrate temperature leads to higher mobilities of deposited atoms, which helps them to find more stable nucleation sites. This routine of finding the most energetically
favourable sites takes time, which should be allowed for by deposition at lower rates. To conclude, higher substrate temperature and lower deposition rate encourage the growth of single crystal films, as well as improving the quality of polycrystalline films (e.g., larger grain size and lower density of crystal defects).

2.9. Structure-zone models of thin films

Movchan and Demchishin\textsuperscript{72} studied the microstructure of 0.3-2000 µm-thick electron-beam evaporated films of Ti, Ni, W, ZrO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}. They were the pioneers in expressing their results in terms of what they called the "structure zone diagram" or (SZD). The SZD is a schematic representation of structural forms or zones, as a function of the ratio of the substrate temperature, \( T_s \), to the melting point of film-material, \( T_m \), where both temperatures are in K. The model proposed, as shown in figure (2.14), that the film structure can be divided into three structural zones, each with its own characteristic structure and physical properties\textsuperscript{15,73-75}.

- **Zone 1** \((T_s/T_m < 0.22 - 0.3)\): Consisting of tapered crystallites with domed tops, which are formed due to low adatom mobility, separated by voided boundaries. These open boundaries are due to the shadowing effect, in which higher points on the growing film receive more material than lower ones. This effect is encouraged by a more oblique flux, lower substrate temperature and hence adatoms mobility. The diameter of the crystallites increases with substrate temperature. Metallic films have a great hardness but little lateral strength.

- **Zone 2** \((0.22 - 0.3 < T_s/T_m < 0.45 - 0.5)\): Consisting of columnar grains with smooth granular tops, separated by distinct dense intercrystalline boundaries. Grain sizes increase with temperature and may extend through the film thickness at high temperatures. The surface has a matt appearance. The transition between this zone and the next one is gradual, as shown in figure (2.14). Metallic films have properties similar to cast metals.

- **Zone 3** \((0.45 - 0.5 < T_s/T_m < 1)\): Consisting of equiaxial grains with a polyhedral structure. The surface is smooth and has a bright appearance. The diameter of the grains increase with temperature. The structure and properties correspond to a fully annealed metal.
Figure (2.14): Structure zone diagrams of Movchan and Demchishin (reference 72).

Figure (2.15): Structure zone diagrams of Thornton (reference 76).
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This two-dimensional model of structural features was further developed in 1974 by Thomton\textsuperscript{76} to include sputtering conditions, in which the presence of a working gas is inevitable. Thomton, who carried out his investigation on the morphology of 25-250 μm-thick sputtered films of Mo, Cr, Ti, Fe, Cu and Al-alloy deposited onto glass and metallic substrates\textsuperscript{77}, added a third axis to the model of Movchan and Demchishin to accommodate variations in the pressure of the working gas. Figure (2.15) shows the Thomton SZD. It can be observed that at higher sputtering pressure, the structure of zone 1 persists to higher substrate temperature. This is because of the reduction in the adatoms mobility by adsorbed gas atoms, the number of which increases with pressure. This effect of pressure on the structures is very limited at high substrate temperatures due to the lower residence time of adsorbed gas atoms at elevated temperatures\textsuperscript{9}. The Thomton SZD contains a transition zone (i.e., zone T) between zone 1 and zone 2, not reported by Movchan and Demchishin, consisting of a dense structure of poorly defined fibrous grains without voided boundaries\textsuperscript{73,75}.

2.10. Modification of thin films by ion-bombardment

The significantly higher surface-to-volume ratio, impurity incorporation, density variations with thickness, etc., make the optical, electrical, structural, mechanical, and chemical properties of deposited films highly surface-dependent and different from that of the bulk material from which they were deposited\textsuperscript{26,78}. These properties are influenced by the deposition method specifics (e.g., deposition rate, substrate temperature and crystal structure, etc.), as well as fundamental processes such as energetic particle bombardment.

In addition to the sputtered atoms of cathode material, growing films are subject to bombardment by a variety of energetic particles such as ions and electrons from the plasma, negative ions of cathode material\textsuperscript{76} and contaminants, neutralised sputtering gas atoms reflected from the cathode surface, and charge exchange neutrals. Such an energetic bombardment induces structural and thus physical changes in the growing film\textsuperscript{80}.

As mentioned in section (2.7), if sputtering can be performed at pressures lower than 5 mTorr (e.g., magnetron sputtering), where the mean free path of sputtered atoms and reflected gas atoms is comparable with cathode-to-substrate distance, the atoms strike the substrate with very high energies compared to thermal ones. At higher pressures (e.g., diode sputtering), such atoms arrive at the substrate after having lost most of their initial energies in collisions\textsuperscript{81}. 

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In DC, RF, or even magnetron sputtering, the substrate is immersed in the plasma. As indicated in section (2.2.4), the energy of the ions striking the substrate is \(-e(V_f - V_p)\), if the substrate is made floating in the plasma (i.e., self-biased). The main technique for self-biasing the substrate is to use what is called "unbalanced magnetron" which will be described in the next chapter. On the other hand, the energy of these ions is \(eV_p\) when the substrate is grounded. Although the plasma potential is very small and of the order of \((\sim 3-5 \text{ eV})\), ions accelerated in the sheath of the grounded substrate will have energies an order of magnitude higher than the thermal species\(^2\). Since nucleation and growth processes are very sensitive to ion-bombardment, it is very common to deliberately bias the substrate (i.e., bias sputtering) with a negative DC (or RF) voltage with respect to the plasma, \(V_{\text{Bias}}\), to be able to control the flux and energy of ions bombarding the substrate. Figure (2.16) shows the energy distribution in a bias sputtering system. The sheath potential difference in the vicinity of the substrate is \(V_{\text{Bias}} - V_p\). For small values of \(V_{\text{Bias}}\), the sheath thickness will also be small (equations 2.9 and 2.8), and ions suffer no collisions in passing through the substrate sheath. Such ions strike the substrate with energy equal to \(-e(V_{\text{Bias}} - V_p)\). For highly negative bias voltages, the situation is reversed. Ions are involved in charge exchange collisions in the sheath, which attenuate their energy, according to the conclusions of Davis and Vanderslice\(^2\) (see section 2.2.7). As a result, the same changes in film properties may be achieved at less negative values of bias voltage.

\[\text{Potential distribution in bias sputtering.}\]

\[\text{Reproduced from reference 11.}\]

Low energy ion-bombardment\(^9\) (about 100 eV or less) during deposition often leads to film properties characteristic of deposition in the absence of ion-bombardment, but at significantly higher substrate temperature\(^8\). It encourages adatom mobility to overcome the shadowing effects of films deposited at low substrate temperatures. Low energy ion-bombardment affects the properties of thin films in many respects. Among them: (i)
Increasing film density\textsuperscript{84}, sometimes to near bulk values, by altering the columnar structure (caused by the shadowing that results from low adatom mobility as described in section 2.9), resulting in smaller grain size\textsuperscript{85,86} and less voided boundaries. This leads to less porous films which are crucial in obtaining more environmentally durable optical films\textsuperscript{87}; (ii) Altering preferred grain orientation\textsuperscript{85,88}; (iii) Altering the size (atoms from resputtered smaller clusters may diffuse to supply larger more stable islands), distribution (to a more uniform one) and density of nuclei\textsuperscript{89-91}; (iv) Lowering epitaxial temperature\textsuperscript{92-94}; (v) Altering the density of dislocations\textsuperscript{95}; (vi) Controlling gas incorporation (e.g., Ar) in films. Ion-bombardment, at lower values bias voltages (~50 V), has been shown to increase the purity of deposited films by reducing the concentration of adsorbed gas atoms due to the preferential resputtering of these atoms\textsuperscript{96}. On the other hand, the concentration of gas atoms in the film has been shown to increase at higher values of bias voltages (~100 V) due to gas atoms being implanted\textsuperscript{97}; (vii) Improving film adhesion to substrate\textsuperscript{98}; (viii) Increasing the coverage of the depositing films over steps\textsuperscript{90,92,100}. This is either due to the more rapid resputtering of the topographical features, which extend up from the rest of the surface plane, than flat surfaces, or to the increase in adatoms mobility\textsuperscript{101}, or both. The surface migration model is more supported since the energies of bombarding ions is believed to be too small to cause efficient resputtering\textsuperscript{26,88}; (ix) Altering the type of thermal stress\textsuperscript{83,99,102} in the films, which already exists due to thermal expansion mismatch with the substrate\textsuperscript{82}, from tensile (occurs at low substrate temperature leading to contraction of films parallel to substrate and added to total stress), passing through zero, to compressive (occurs at higher substrate temperature, and proportional to the melting point of the film material, leading to expansion of films parallel to substrate and subtracted from total stress). The total stress (which is the sum of thermal, external, and intrinsic stresses) is then reduced\textsuperscript{26}; (x) Altering the optical properties of films\textsuperscript{74,103}, such as increasing the refractive indices\textsuperscript{104}, due to changes in density. Also lower absorptances\textsuperscript{99,105} were observed; (xi) Lowering film resistivity\textsuperscript{83,86,88,106-108}. It is generally attributed to\textsuperscript{83,86,96} significant change in film stress, reduction in grain size and the resultant higher density of the film, as well as improvement in film purity\textsuperscript{109} by preferential sputtering of contaminants (e.g., bombarding gas atoms, oxygen, etc.); (xii) Influencing the composition and stoichiometry of films as well as activating the reaction at the substrate. In addition to controlling inert gas incorporation, ion-bombardment helps in cleaning the substrate before deposition, and in reducing contamination of films during deposition to produce purer films. According to Winters and Sigmund\textsuperscript{110}, the chemisorbed impurities of low atomic number atoms (such as O, N and C) were found to be resputtered with higher probability compared to higher atomic number atoms (e.g., metal atoms). For example, despite the high binding energy (~6.7 eV/atom) in the case of nitrogen chemisorbed on W, the sputtering yield of nitrogen atoms was found to be high and the
threshold energy low. In addition, ion-bombardment of compound films during deposition alters the relative composition of these films due to preferential sputtering in a similar way to that seen at the cathode where an altered layer is formed during sputtering of compound cathodes. Literature is rich with examples of the role of ion-bombardment in the motivation of chemical reactions at the substrate and control of the stoichiometry of deposited films\textsuperscript{102,106,111-114}. For instance, Brett and Parsons\textsuperscript{115} reactivity sputter-deposited transparent conducting films of ZnO onto RF-biased substrates. They found that biasing the substrate more negatively (from -7 eV to -40 eV) changes the composition of the film from the dark brown ZnO\textsubscript{0.76} to the light brown ZnO, that is decreasing the zinc content of the film. This was attributed to: (i) Preferential Zn re-emission (i.e., resputtering and re-evaporation) of loosely bound surface atoms, bearing in mind the slow oxidisation process of Zn which means that adatoms may remain unreacted and mobile on the surface of a growing film for longer periods of time, which in turn leads to a higher probability of re-emission; (ii) Energetic bombardment of the substrate by Ar\textsuperscript{+} and oxygen ions (O\textsubscript{2}\textsuperscript{+} and O\textsuperscript{+}) and/or the creation of excited and atomic oxygen species due to collision processes (oxygen activation) which increases the oxygen content of the growing film. In another example, Spencer \textit{et al}\textsuperscript{116} used an unbalanced magnetron to reactively deposit indium oxide.

![Deposition rate as a function of oxygen partial pressure](image)

**Figure (2.17): Deposition rate as a function of oxygen partial pressure, for conducting indium oxide films made with and without plasma bombardment. Replotted from reference 116.**

They controlled the plasma beam to the substrate by either placing an auxiliary electrode in the beam and varying the resistance of this to earth, or placing magnets behind the substrate to make the beam more concentrated or dispersed. Their results are replotted in figure (2.17) and indicate that, for a constant stoichiometry, a given deposition rate
(which is a measure of how much oxygen is incorporated into the growing film at constant stoichiometry) occurs at lower oxygen partial pressure (which is an indicator of the oxygen arrival rate at growing film at constant gas pressure) with a plasma beam to the substrate, compared with no beam. They interpreted that in terms of an increased (or more efficient) utilisation of oxygen by films with more bombardment, due to activation of the indium/oxygen reaction. They attributed this activation to be due either to direct action of the plasma beam on the substrate with a resultant increase in adatom energy or heating, or to an action on the reactive gas such as ionisation, excitation, dissociation or heating.
REFERENCES


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CHAPTER THREE

SPUTTER DEPOSITION SYSTEM
CONFIGURATIONS

3.1. Introduction

Several sputtering systems have been developed to meet the rapidly increasing demands to produce high quality films for very wide range of applications at high deposition rates. Several configurations of sputter deposition systems will be reviewed in this chapter, with special emphasis on DC planar magnetron sputtering which has proved to be very efficient and been used throughout this work.

3.2. Glow discharge diode sputtering

Most aspects of diode sputtering have been discussed in chapter two. In this section the limitations of diode sputtering will be mentioned. The concepts of DC, AC and RF diode sputtering will be summarised.

3.2.1. Direct current (DC) diode sputtering

A DC diode sputtering system is an evacuated chamber containing a target, which is a plate of the material to be deposited, connected to a negative voltage supply and a substrate facing the target and connected to the anode. The chamber, which is connected to a series of vacuum pumps, is evacuated to a pressure level (~10^4-10^7 Torr), called "the base pressure", well below the desired working pressure to minimise the presence of contaminants such as water vapour, O, C, N,... etc. The chamber is then backfilled with a "working gas", commonly inert, to the desired working pressure usually ranging from 10 to 100 mTorr\textsuperscript{1,2}. Figure (3.1) shows a cross-section of such a system.
Figure (3.1): A schematic representation of a DC diode sputtering system and the plasma in it. Reproduced from reference 1.

Voltages in the range of 500 V to 5 kV are applied across the electrodes and current densities in the range of 1 mA/cm² to 10 mA/cm² run between the electrodes. As discussed in chapter two, a self-sustained glow discharge is achieved by ions of the working gas striking the cathode causing the emission of an appropriate number of secondary electrons. Ion-bombardment of the cathode also causes the ejection of its material which is then deposited onto the substrate with a rate of the order of 40 nm/min. This method of sputtering is extremely inefficient. Only about 1% of the energy incident on the cathode surface is used for the ejection of sputtered particles including secondary electrons. Whereas about 75% of that energy is dissipated at the cathode surface in the form of heat causing the temperature of the cathode to rise, the
remainder of the incident energy is dissipated by the secondary electrons at the anode (including the substrate) upon striking it. This implies the need of the cathode, and sometimes the substrate, to be cooled. This is usually done by forcing the cooling water to circulate directly underneath the target (which is attached to a backing plate to avoid thermal cracking) through channels machined in the body of the cathode. Another point of concern is the need to prevent sputtering of the cathode assembly itself. This is achieved by using a ground shield which is contoured around all the surfaces of the cathode (excluding the target plate) at a distance less than that of the Crookes' dark space. At such a separation, no discharge will take place between the cathode body and the ground shield which acts as an auxiliary anode. In other words, no ions can be produced there and no sputtering of these parts can occur. Instead of ground shields, dielectric materials may be employed to suppress sputtering, but the difficulties in shaping them and the danger of outgassing make the use of dielectrics far less popular. The theory behind the ground shield was discussed in the end of section (2.2.7).

The limitations of DC diode systems were discussed in section (2.5). In principle, they are: (i) The pressures required to sustain the discharge are relatively high (more than 10 mTorr). This is to enable a primary electron, before being lost to the anode, to produce enough ions to generate a new secondary electron upon striking the cathode. As a result of the high pressure, the mean free paths of ions are too short. They participate in many collisions and charge exchange collisions (see section 2.2.7) and strike the cathodes with relatively low energies. This can result in a lower sputtering rate; (ii) Secondary electrons are accelerated away from the cathode. This lack of confinement of electrons near the cathode causes the production of ions to take place far from the cathode and hence the probability of them being thermalised, due to collisions, before reaching the cathode is high. The poor ionisation efficiency and high working pressure affect the sputtering processes as well as the properties of the deposited films in many aspects, among them:

1. Low deposition rate due to both low discharge current density (i.e., lower sputtering rate) and high working pressure (i.e., more backscattering of sputtered atoms) as discussed in section (2.5), and as equation (2.19) indicated. Attempts to increase the discharge current density by increasing the discharge voltage would fail as ionisation cross-section decreases with increasing electron energy above 100 eV (section A1.4.1).

2. Contamination of deposited films by the working gas. This contamination would be predicted to decrease if the working pressure could be decreased. Unfortunately, high pressure operation is a necessary feature of this process.
3. Heating the substrate due to electron-bombardment. The poor confinement of plasma near the cathode leads to most secondary electrons that are emitted from the cathode, instead of causing ionisation, being collected by the anode (including the substrate which is immersed in the plasma) where they cause an undesirable heating.

4. Reduced film adhesion as a result of the low energy with which the sputtered material arrives at the substrate. Due to the high pressure of operation, the mean free path of sputtered species is short. They participate in many collisions on their way to the substrate and arrive at it after having lost part or all of their initial (i.e., ejection) energy (section 2.3.2). This also results in less film density and poorer film properties (e.g., step coverage, voids... etc.).

Finally, the use of simple DC diode sputtering systems is almost entirely restricted to research purposes rather than industry, or to situations where high sputtering rate is not a necessity in the growth of special films.

3.2.2. Radio frequency (RF) diode sputtering

DC glow discharge can not be used to sputter insulators. This is because when either or both of the two electrodes is covered with an insulating material (e.g., an oxide), the DC glow discharge can not be sustained. The reason behind that can be explained as follows: When an ion strikes the cathode of a DC glow discharge system, it is neutralised by an electron removed from the cathode surface (see section 2.3.1). If the cathode material is a conductor, the stripped electron can be substituted by electrical conduction and the cathode surface maintains the negative potential required to sustain the discharge. If the cathode material is an insulator, such a substitution is not probable since electrical conduction from the interior of an insulator to its surface is not possible. Thus, a positive charge is accumulated on the front surface of the cathode and increased with time of exposure to ion-bombardment. This leads to a reduction in the potential difference between the cathode and the anode with time until a point is reached (after about 1-10 μs) where the potential difference becomes no longer sufficient to sustain the discharge.

The charge build-up can be interrupted by the simultaneous bombardment of the insulating electrode with ions and electrons. A sputtering method of insulators was then first proposed by Anderson et al. When an AC signal below about 50 kHz is applied to the electrodes, ions are sufficiently mobile so there is an adequate time to establish a complete DC discharge at each electrode on each half-cycle. The system behaves as if there were two cathodes with a dark space in front of each electrode. The discharge is
essentially the same as the previously described DC one (in fact it is a series of brief DC discharges of alternating polarity) and is still sustained by the emission of secondary electrons from the two electrodes. Hence it requires the same pressure to be sustained as the equivalent DC discharge. The main difference is that sputtering is now possible from the two electrodes.

As indicated earlier, the time required by the insulator surface to be positively charged, so the discharge is extinguished, is about 1-10 µs which corresponds to an AC signal to the electrodes in the range of 0.1-1 MHz. Therefore, low frequency AC signals (e.g., the 50 Hz which is the conventional mains frequency corresponds to a charging time of 20 ms) are inadequate at sustaining such a discharge. Most systems are operated at a frequency of 13.56 MHz which has been allocated by the Federal Communications Commission (FCC) for industrial, scientific and medical applications to prevent interference with other radio-transmitted signals. Operation at another frequency requires careful shielding.

If the frequency of the applied voltage is increased above about 50 kHz, it is observed that the minimum pressure required to sustain the discharge is decreased, and levels off for frequencies above a few megahertz which implies that secondary electrons emitted from the electrodes are not the only source of ionisation. The additional source of ionisation is that electrons oscillating in the radio frequency field participate in elastic collisions with gas atoms and they may gain enough energy from the field to cause ionisation of these atoms. Initially, a free electron in vacuum oscillates, along an x-axis, under the influence of an alternating field \( E = E_0 \cos \omega t \), where \( \omega \) is the angular frequency and \( E_0 \) is the amplitude, with a velocity \( v = eE_0 / m_\epsilon \omega \cdot \cos(\omega t + \pi / 2) \) which is \( \pi / 2 \) radians out of phase with \( E \). This means that \( v \) is a maximum when \( E = 0 \) and the electron gains no energy from the field. If the electron, however, has in an elastic collision with a gas atom and the direction of its motion is reversed by the collision (see section A1.4) at the precise moment the RF field changes its direction (i.e., \( E = 0 \) and \( v \) is maximum), the kinetic energy of the electron keeps increasing and may become sufficient to cause ionisation. Thus, the high applied voltage which is required for the production of secondary electrons to sustain a DC discharge is no longer necessary to sustain an RF discharge. Due to random collisions, electrons may scatter out of the inter-electrode space. These electrons are no longer influenced by the RF field and hence unable to oscillate since the applied RF field is confined between the two electrodes. Therefore, these electrons will not acquire enough energy to cause ionisation and hence will be lost to the glow. But the application of a magnetic field parallel to the RF field can help in trapping these electrons, and hence, reducing the probability of them being lost.
On the other hand, in addition to the lower operating voltages, the massive ions can not follow the short-lived variations in the applied RF voltages so, unlike electrons, they acquire relatively little energy directly from an RF field. The important question now is 'how can these low-energy ions cause sputtering?'. The answer to that lies in the phenomenon of self-bias which occurs at the surfaces of electrodes. Because the mobility of electrons is much higher than that of ions, the number of electrons reaching a particular electrode during the positive half-cycle is higher than the number of ions that does so during the negative half-cycle. Thus, the plasma of an RF discharge develops a positive potential, with respect to the two electrodes, which appears across the two dark spaces. The build-up of a negative charge at the surface of the electrodes increases during the first few cycles, and the electrodes are then able to repel some electrons in the positive half-cycle and to attract positive ions more effectively in the negative half-cycle. A steady state prevails when the number of ions and electrons which bombard a particular electrode during each complete cycle is equal. The electrodes are said to have negatively self-biased, and the ion sheath developed in front of each electrode is analogous to the Crookes' dark space in DC sputtering. If the potential difference between the plasma and the self-biased electrode is adequate, then ions are accelerated in the sheaths and sputtering occurs. The self-bias voltage is almost equal to the peak voltage of the RF input signal. This is due to the significant displacement of the voltage waveform towards the negative.

**Figure (3.2): A schematic diagram of an RF glow discharge circuit. Reproduced from reference 10.**
Figure (3.2) shows a schematic diagram of an RF glow discharge circuit. The role of the blocking capacitor will be explained later. The capacitor is initially uncharged. When a square wave is applied to the circuit (figure 3.3), $V_2$ will follow the drop of $V_1$ towards the negative peak (say -1000 V) of the square wave (part a to b in figure 3.3). The glow is then initiated and ions strike the upper electrode leading $V_2$ to rise towards zero and...
also the capacitor to charge positively. Because of the high frequency used, the increase in the value of $V_2$ (part b to c in figure 3.3) will be limited to a voltage which is slightly less negative (say -800 V) than the voltage at b (i.e., -1000 V). When $V_1$ rises (part c to d in figure 3.3) by 2000 V, $V_2$ will instantly follow it (to -800+2000 = 1200 V). This positive voltage will attract the more mobile electrons more efficiently causing $V_2$ to decrease more rapidly than ions did in the negative part b to c, say to 100 V, (part d to e in figure 3.3). Then $V_1$ will drop by 2000 V (part e to f in figure 3.3) making $V_2$ at f (100-2000 = -1900 V) even more negative than at b. But since ion current is small, $V_2$ will not rise much before a new rise by 2000 V occurs. After a few cycles, the voltage waveform will become repetitive, and almost entirely suppressed towards the negative. Hence, the self-bias voltage (DC offset) is almost equal to the peak voltage of the RF input signal. On the other hand, the combination of lower mobilities and higher potential difference that the ions are subjected to, compared with the electrons, makes the ion and electron current to a particular electrode equal. A similar effect holds for a conventional sine wave\textsuperscript{12}. The ion-bombardment of electrodes is virtually uninterrupted since $V_2$ is positive for only a very short fraction of each cycle, as figure (3.4) demonstrates.

Unfortunately, self-biasing followed by sputtering can take place at the two electrodes, as well as at any surface in contact with the plasma (e.g., the chamber). In order to suppress sputtering at all surfaces, excluding the target surface, the sheath voltage in
front of the target has to be made much larger than that of any other surface in contact with the plasma.

Figure (3.5): Voltage distribution between electrodes.
Reproduced from reference 10.

Figure (3.5) shows the voltage distribution between the electrodes in an RF discharge, where \( V_1 \) and \( V_2 \), \( L_1 \) and \( L_2 \), are the sheath voltages and the sheath thicknesses at the electrodes, respectively. \( A_1 \) and \( A_2 \) are the areas of the two electrodes, and \( V_p \) is the plasma potential. Since \( V_1 \) and \( V_2 \) are the only DC voltages in this circuit, they should be equal and opposite provided that the plasma is equipotential\(^{10,11}\). A blocking capacitor is added to the circuit to eliminate this equality. The relationship between the current

\[
\left( \frac{V_1}{V_2} \right) = \left( \frac{A_2}{A_1} \right)^4
\]
density of the ions through the sheath and the voltage across it, is given by the Child-Langmuir law (equation 2.5). Since the current density of the ions must be equal at both electrodes, then \( V_1^{3/2}/L_1^2 = V_2^{3/2}/L_2^2 \). On the other hand, the high voltage drop across the sheath implies that the sheath is a region of very high resistivity, and hence, the combination of an electrode, sheath, and plasma can be modelled as a capacitor with a capacitance \( C \propto A/L \). The RF voltage is capacitively divided between the two sheaths so \( V_1/V_2 = C_2/C_1 \). Combining the above equations gives:

\[
\frac{V_1}{V_2} = \left( \frac{A_2}{A_1} \right)^4
\]  

[3.1]

The fourth power that appears in this equation is not observed in practical systems. Horwitz\(^\text{13}\) and Coburn and Kay\(^\text{14}\) investigated this dependency. Although all concluded that the sheath voltage is inversely proportional to the area of the relevant electrode, Coburn and Kay\(^\text{14}\), for instance, found that the power is of the order of unity. Thus, to restrict sputtering to the target material, it should be attached to the smaller electrode. In practice, the substrate holder and the vacuum chamber are grounded acting as a large electrode, whereas the target material is connected to the smaller electrode. On the other hand, since it is desirable that \( V_1 \neq V_2 \) and the plasma is equipotential, a DC voltage will then exist between the electrodes leading to leakage through or around the edges of the target in the presence of the plasma, especially when the target is a conductor. The blocking capacitor will aid in preventing any such leakage.

![Diagram](image)

Figure (3.6): A typical network for impedance matching between an RF power supply and the discharge. Reproduced from references 4 and 10.

In addition, a variable impedance matching network is used between the discharge and the RF power supply to maximise the power dissipation in the discharge. Power supplies are made to possess a virtually resistive output (commonly 50 \( \Omega \)) to prevent large RF currents flowing round the circuit, whereas the impedance of the discharge is larger and partially capacitive. The variable matching network is added, as can be seen in figure
(3.6), and tuned so as the load of the combination "matching network-discharge" is equal to the virtually resistive output of the generator.

Besides the high cost of equipment, the power losses and the complexity in setting up an RF-powered sputtering system, the two principal disadvantages of RF diode sputtering are: (i) Low deposition rates compared to DC sputtering. Tutea et al. prepared films of indium-tin oxide (ITO) with deposition rates in the range of 0.1-0.28 nm/s depending on the relative concentration of O\textsubscript{2} in the chamber with respect to that of Ar. Valentini et al. obtained films of ZnO with deposition rates as low as 0.03 nm/s. However, the deposition rates of films prepared by RF magnetron sputtering techniques are higher. For instance, deposition rates of ZnO films deposited using this technique are in the range of 0.04-0.41 nm/s\textsuperscript{17}, and 0.7 nm/s\textsuperscript{18} in another case; (ii) Films adhere to the stoichiometry and composition of the target since the material of the target is in pressed powder form\textsuperscript{19-22} of well defined composition and stoichiometry.

### 3.3. Other non-magnetron sputtering configurations

In this section a summary of the principles of three non-magnetron types of sputtering systems will be given, namely: triode, getter, and ion beam sputtering.

#### 3.3.1. Triode sputtering

Triode sputtering is an alternative method for overcoming the main limitations of diode sputtering, particularly the low ionisation efficiency with the resultant poor sputtering rate, and high operational pressure required to maintain the discharge with the resultant reduction in the mean free path of sputtered particles which leads to a poor deposition rate. Therefore, it is beneficial to create a sputtering system in which the discharge parameters (current density, voltage and pressure) are independent and hence have the capability of forming a dense plasma at a low gas pressure\textsuperscript{23,24}. This is achieved by supplying the discharge with additional electrons, from an independent source, other than those secondaries emitted from the target cathode which are considered to be responsible of maintaining the discharge. The discharge is established between a thermionic cathode (usually a heated tungsten filament that can survive ion-bombardment for long duration) which emits electrons, and an anode. A magnetic field, supplied by external coils, is used to confine the plasma between the thermionic cathode and the anode. The target cathode is immersed in the plasma and is biased separately (by a DC or RF power supply) to a potential more negative than that of the anode. Ions from the plasma are then extracted and accelerated towards the target cathode causing
the ejection of its material which is then deposited onto a substrate. Figure (3.7) shows a schematic representation of a triode sputtering system.

![Triode Sputtering System Diagram]

**Figure (3.7): A schematic representation of a triode sputtering system.**

The anode is biased positively (commonly ~50-100 V) with respect to the usually grounded substrate to prevent the thermionically emitted electrons from being collected by the substrate which would upset the homogeneities of plasma density at the target cathode as well as causing the substrate temperature to rise. The density of ions in the plasma can be manipulated by either varying the current of the thermionically emitted electrons, or the voltage used to accelerate them. The energy of the sputtering ions can be governed by adjusting the voltage of the target cathode. Consequently, a high ionisation density is maintained at a much lower pressure (~0.5-1 mTorr) compared with DC diode systems. This is achieved by providing additional electrons, from a third electrode, at appropriate energies be able to cause efficient ionisation. Deposition rates up to several hundred nm/min can be obtained\(^\text{25}\).
Films of metals\textsuperscript{26-28}, alloys\textsuperscript{29}, and semiconductors\textsuperscript{30} were deposited using triode sputtering. Unfortunately, triode sputtering suffers from three disadvantages: (i) It is difficult to produce uniform deposits from very large targets due to the problems encountered in obtaining a uniform thermionic discharge on a large scale\textsuperscript{4}; (ii) It is difficult to obtain reproducible results because the ranges of the parameters are much wider than those of the self-maintained discharges\textsuperscript{31}; (iii) The heated filament acts as source of contamination and radiant heat\textsuperscript{32}.

3.3.2. Getter sputtering

Whether they were initially resident or produced as a result of outgassing from the walls of the vacuum chamber, the presence of active gas contaminants, such as O\textsubscript{2}, H\textsubscript{2}O, N\textsubscript{2}, H\textsubscript{2} and CO, in the sputtering gas risks the purity of the growing films. Getter sputtering is an alternative to the otherwise expensive option of using ultra high vacuum to obtain thin films of high purity. Developed by Theuerer and Hauser\textsuperscript{33,34} in the mid-sixties, the getter sputtering technique relies on the fact that a freshly deposited film is an active 'getter' of impurities. Before reaching the region where the required film is being deposited, the sputtering gas is cleansed up by forcing it to move over other areas of deposited film that are continually refreshed. The active gas contaminants are then chemisorbed or react with the deposited film (especially with metals like Al, Ta, Ti,...etc.) to form a chemical compound (e.g., an oxide of the film material) whereas the atoms of inert gases are just physisorbed and are not easily entrapped. This gettering effect also leads to a reduction in the process pressure.

In order to permit a large gettering area around it, the substrate is mounted at the centre of a very large substrate holder opposite to and coaxial with an adequately large cathode. The sputtering gas inlet to the chamber is placed as remote as possible from the substrate to enable the impurity atoms present in the sputtering gas to have as many collisions as possible with the depositing film material, and hence have a high probability of being removed, before arriving at the central zone where the substrate is located. Thus, the material that is deposited at the centre of the substrate holder (i.e., at the substrate) will be free from the impurities. In reality, the cathode in a getter sputtering system is of limited size and contained, along with the substrate, in a compact and reasonably gas-tight sputtering chamber which is held at a positive pressure of sputtering gas and placed within the main vacuum chamber. The compactness of the sputtering chamber is accomplished by arranging its walls to be very close to both the cathode and the substrate without interfering with the glow discharge. The positive pressure inside the sputtering chamber has the advantage of reducing any tendency of contaminants and
oil vapour from the pumping system, present in the main chamber, to enter the sputtering chamber.

Figure (3.8): A schematic diagram of a simple getter sputtering system.

Figure (3.8) shows a schematic diagram of a simple getter sputtering system. A compact sputtering chamber, containing two symmetrically arranged cathodes of the material to be sputtered, is placed inside the main vacuum chamber. The gas inlet to the system is placed at the bottom of the sputtering chamber and the greatest gettering activity takes place at the lower cathode. The sputtering gas is also cleansed by passing over the continually refreshed films deposited onto the walls of the sputtering chamber where impurities are buried. Following sputtering for an appropriate period of time to ensure that all impurities have been gettered, the shutter is removed to allow the material sputtered from the upper cathode to be deposited onto the substrate.
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High purity thin films of different material have been prepared using this technique. For examples, Theuerer and Hauser\textsuperscript{33,34} have prepared superconducting films of materials such as Ta, Nb, V\textsubscript{2}Si, V\textsubscript{3}Ge, V\textsubscript{3}Ga, Pb-Cu and Pb-Pt. Magnetic films of the rare-earth alloys of Co-Cu-Sm series\textsuperscript{35} and amorphous GdCo\textsuperscript{36} have also been prepared using getter sputtering. Cook \textit{et al}\textsuperscript{37} reported the successful deposition of high quality Al films with resistivities approaching those of bulk material. Finally, using a DC magnetron cathode within a getter box, Howson \textit{et al}\textsuperscript{38} sputtered Al films of high specular reflectance (\textasciitilde92\% @ 633 nm) at high deposition rates.

3.3.3. Ion beam sputtering

![Figure (3.9): A simple schematic of ion beam sputtering system.](image)

Self-sustained glow discharge systems are not suitable for basic studies concerning the sputtering processes, for the reasons mentioned in section (2.3.2). It is, therefore, replaced by the ion beam technique which provides an independent alternative for ion generation, and hence eliminates any controversy involving ion generation to sustain a glow discharge on the one hand, and ion acceleration to sputter cathode material, on the other. In addition, the high background pressure of the sputtering gas, which is required to sustain the discharge, makes films prepared by this method suffer from high levels of contamination due to the inclusion of the gas molecules in them.
Figure (3.9) shows a simple schematic of ion beam sputtering system. It can be divided into two main parts: (i) An external ion beam source in which a glow discharge is established, at a gas pressure of the order of $10^{-4}$ Torr, and ions are generated; (ii) A process chamber containing both the target and the substrate in a virtually field-free high vacuum environment ($\sim 10^{-5}$ Torr). Some of the ions, which are produced by the ion beam source, are extracted by a series of grids, and accelerated into the process chamber towards the target where sputtering occurs. The current density of ions that can be extracted by the extraction voltage is governed by the Child-Langmuir law (equation 2.5), and is about $1 \text{ mA/cm}^2$ at 1000 eV. The ion beam is prevented from being expanded, due to Coulomb repulsion, by using a neutralisation filament that thermionically emits electrons to neutralise the beam. The ion beam sputtering technique enjoys the following advantages: (i) It allows an independent control of ion beam current and energy; (ii) The narrow spread of the energy of ion beams enables investigators to study the sputtering yield as a function of ion energy; (iii) It is possible to vary the angle of incidence of the beam on the target and the angle of deposition on the substrate; (iv) As the beam is neutralised, it is possible to sputter insulators without them charging up; (v) It can be carried out at a lower pressure, compared with glow discharge sputtering, which leads to less incorporation of gas molecules into the growing films, and also to less scattering of sputtered species allowing them to arrive at the substrate with a high energy that is almost equal to their ejection energy; (vi) It allows greater isolation of the substrates and targets from the glow discharge generation process. Thus, the electron-bombardment of the substrate, which leads to heating it, is minimised.

The major drawback of this sputtering method is the small ion beam diameter ($\sim 1 \text{ cm}$), and hence the small area of the bombarded target. Accordingly, the deposition rate in this technique is small (from a few up to tens of nm/min) and the production of films of uniform thicknesses over large substrate areas is difficult. However, later developments have provided ion sources with ion beams of the order of $38 \text{ cm}^2$ in diameter, but the high product cost and the lack of reproducibility, which are attributed to operational problems, are believed to constitute the major obstacle to the widespread use of broad ion-beam ion sources.

Many high purity materials have been deposited using ion beam sputtering. For example, high purity superconducting films (e.g., Nb), semiconductor materials (e.g., Si, GaAs, InSb,... etc.) have been successfully produced using this technique.
3.4. DC planar magnetron sputtering

Magnetron sputtering sources can be defined as diode devices in which magnetic fields are used in concert with the cathode surface to form electron traps which are configured so that the $E \times B$ electron drift currents (also called Hall drift) close on themselves. The magnetic fields lengthen the electron residence time (or its path length) in the vicinity of the cathode, before being collected by the anode, and thus increase the probability of ionisation collisions taking place near the cathode at lower operating pressures (~1 mTorr) compared with those required to sustain conventional diode systems. This leads to denser plasmas of much lower impedances, larger discharge current densities (10-200 mA/cm²), lower operating voltages (less than 1000 V) and increased deposition rates (~1 μm/min for Al). In addition, reduced substrate heating is another important feature of magnetron sputtering. Instead of bombarding the substrate, electrons which have been accelerated in the cathode dark space, will be trapped near the cathode due to the presence of a magnetic field, as will be described in section (3.4.1.2). Even those electrons which can escape the confinement after being involved in ionising or other collisional processes can not bombard the substrate either. They are virtually thermalised, as a result of these collisions, and easily collected by an anode neighbouring the cathode. On the other hand, as a result of lower operating pressures, less contaminated and higher quality films can be obtained at lower substrate temperatures. The latter (i.e., the higher quality) is due to the higher arrival energy of sputtered species at the substrate (see section 2.7). Furthermore, magnetron sputtering...
is capable of producing films of uniform thicknesses on large area substrates. These films are of same composition as cathode for alloy or multi-element cathodes.

**Figure (3.11): A schematic of a cylindrical magnetron sputtering system. Reproduced from reference 53.**

The essential principle of all magnetically supported sputtering techniques was discovered by Penning\(^{46}\) in 1939. Figure (3.10) shows the Penning magnetron. A magnetic field is applied parallel to a cylinder and electrons within the cylinder are forced to travel small cycloidal paths in large circles around the axis of the cylinder where the cathode is located. When an electron participates in collisions with gas atoms, it moves away from the cathode and is eventually collected by the anode. Thus, before reaching the anode, the electrons must participate in ionising collisions. As a result, the operating pressures required to maintain the discharge are very low, and the discharge current densities are very high. The work of Penning was subsequently developed by many workers\(^{47-51}\), resulting in the cylindrical magnetron\(^{52}\) which is shown in figure (3.11)\(^{53}\). If the inner cylinder is the target, the arrangement is called post-cathode\(^{49}\) and can be scaled to large sizes, permitting relatively large areas to be uniformly coated\(^{54}\). If the inside of the outer cylinder is the target, the arrangement is called an inverted magnetron or hollow-cathode\(^{48}\) and is effective for coating substrates of complex shapes\(^{54}\). As a result of the crossed electric and magnetic fields, the radial motion of electrons is confined in cycloidal paths around the axis of the cylinder with the resultant
reduction in substrate plasma bombardment, whereas their axial motion is not. Therefore, electrons can escape the plasma through the end of the target (end-losses) with the resultant decrease in plasma density (leading to reduced discharge currents and deposition rates) and increase in the minimum operating pressure and voltage. Another disadvantage of cylindrical systems is that they are not appropriate to accommodate very large area substrates which have to be placed inside the cylinder.

The first description of a planar magnetron device was that of Kesaev and Pashkova\textsuperscript{59} in 1959. After about fifteen years, the principle was reintroduced in the form of the planar magnetron by Chapin\textsuperscript{66}. Figure (3.12) demonstrates a case when a magnetic field is oriented horizontally (into the plane of the page), and perpendicular to the electric field. The electron $\mathbf{E} \times \mathbf{B}$ drift current, as will be described in section (3.4.1.2), is horizontal from left to right. Electrons will tend to accumulate at one side of the plasma, and will likely be lost. Such losses can be minimised by properly orienting the magnetic field so as to force the electron $\mathbf{E} \times \mathbf{B}$ drift current to form a closed loop.

![Diagram of electron drift due to crossed electric and magnetic fields](image)

**Figure (3.12):** Electron drift to one side due to crossed electric and magnetic fields. Reproduced from reference 61.

Hence, instead of being lost, the drifting electrons will be confined and circulating\textsuperscript{6}, in the vicinity of the cathode, above the closed loop in the absence of collisions. This can be achieved by placing permanent magnets or electromagnets\textsuperscript{57,58} directly behind the cathode. The magnetic field, in the electromagnets, can be controlled by the adjustment of the current flowing through coils placed around the circumference and with a separate supply feeding a coil around the centre pole. The magnets are arranged so that there
exists at least one region in front of the cathode where the locus of magnetic field lines parallel to cathode is a closed path.

If the rectangular magnetron which is shown in figure (3.13) is taken as an example, the magnetic field lines first emanate normal to the cathode (line of exit, where the field is most intense), then bend approximately parallel to the cathode surface (perpendicular to the electric field), and finally return into the cathode (line of entry) completing the magnetic circuit. The maximum transverse component of magnetic field in front of the cathode is in the range of 200-500 Gauss, that is about 0.02-0.05 Tesla.

The region beneath the approximately parabolic (or domed) magnetic field lines, between the line of exit and line of entry, is called the "erosion zone" or the "race track", a term suggested by its appearance. It represents the closed loop designed to minimise end-losses. Secondary electrons emitted from the cathode as a consequence of ion-bombardment are almost trapped in this zone, resulting in increased ionisation and higher sputtering rate. The erosion zone is of a "V" shape which implies that the erosion rate is not uniform across it and has a maximum value.

This can be explained with the help of figure (3.14). If $\alpha$ is the angle between the magnetic field and the cathode surface, away from the central region of the cathode, and
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\( v \) is the velocity acquired by a secondary electron in its passage through the dark space, then the component of velocity parallel to the magnetic field is \( v' = v \sin \alpha \). This velocity component will drive the electron along the magnetic field line to the summit of the dome and down in the direction of the cathode surface once again. Secondaries emitted or reflected from a point on the cathode surface where the magnetic field is parallel to the cathode surface (corresponding to \( \alpha = 0 \) or to a very small \( \alpha \)) will have a very small velocity \( v' \) across the dome. Conversely, secondaries emitted or reflected from a point on the cathode surface where \( \alpha \neq 0 \) will move across the dome passing the region where the magnetic field is parallel to the cathode. Thus, assuming that the massive ions do not move far from their point of creation, it can be concluded then that the highest electron density, and hence the highest ion density and erosion rate, is beneath the region where the magnetic field is parallel to the cathode.

\[
\begin{align*}
\text{Target} \\
\text{Dark space}
\end{align*}
\]

Figure (3.14): The electron motion in an inclined magnetic field.

The range of target thicknesses that can be used in magnetron sputtering is broad. The maximum target thickness is determined by the ability to sustain an adequate magnetic field strength, and secure a sufficient cooling rate at the surface of the cathode. On the other hand, there is no minimum target thickness. It is possible to sputter from thin foils fixed to a backing plate, or even from deposited films.

The main disadvantage of magnetron sputtering is the poor utilisation of the target material due to the non-uniform erosion across the target. The target utilisation is typically about 25\% to 35\% of the starting target material. The lifetime of the target can be extended by shaping the magnetic field or by providing relative motion of the target with respect to the magnets. Spencer et al. have modified the magnetic field distribution by placing the poles of the magnetic circuit in front of the target surface.
flatter erosion profile has resulted with a target utilisation of 50%. Wright and Beardow\(^6\) reported a target utilisation of 90% by rotating a tubular target around a fixed magnet array. Another disadvantage of magnetron sputtering, which is related to the non-uniform erosion of the target, is the non-uniform deposition pattern. The deposition profile can be an image of the erosion track particularly when the target-to-substrate distance is small. In the case of a long narrow rectangular magnetron, the erosion profile, which looks like a racetrack, is "seen" by the substrate as two parallel line sources. To achieve film thickness uniformity in the case of a planar magnetron, it is usually necessary to rotate (or translate) the substrate over the cathode/s (or more precisely the two line sources). Alternatively, the magnet array behind the cathode is moved\(^6\). In the course of this work, the substrate was rotated passing over two magnetrons, as will be seen in a coming chapter.

Magnetrons are more sensitive to arcing than other conventional systems, and this is provoked by the low voltage, high current power supplies which are required to drive the low impedance discharges\(^6\). The diffused magnetron plasma turns into a bright concentrated beam of arc discharge accompanied by a drastic drop in voltage. Arcs are formed by charge build-up on small oxide islands, spikes, sharp points or other irregularities on the cathode surface which lead to a local increase in current density and hence increase the probability of arc initiation. Arcs cause regional melting of cathode material due to the concentration of almost all the discharge current, and hence power, into a very small area of the cathode. Two types of local arcs have been observed, racetrack and looping arcs\(^5,6\). In the former, the evaporated charged particles of cathode material move rapidly around the erosion area, whereas in the latter, they move following the domed magnetic field lines and can be suppressed by extending the ground shield slightly over the outside edge of the cathode. Arcs, which can be particularly severe in reactive sputtering as will be discussed in section (4.6.1), result in reducing the cathode voltage, for a fraction of second to several seconds, and the main discharge is then extinguished. Power supplies are equipped with arc suppression circuits. Upon sensing a reduction in voltage (arc formation), the current is terminated for a specific period of time before the discharge is reignited.

As indicated in sections (2.3.2) and (3.2.1), sputtering is a very inefficient process, and a large fraction of the incident energy (~75%) appears as heat and lattice damage at the cathode surface causing the temperature of the cathode to rise. In magnetron sputtering, the typical limiting factor to the maximum deposition rate (i.e., the maximum power that can be applied without damaging the cathode) is the ability to cool the cathode. Therefore, efficient cooling of the cathode is crucial to prevent the cathode from being melted, cracked or warped. When a cooling system is designed (e.g., the geometry of
the system; the coolant material, pressure and flow rate, etc.), several factors have to be considered. Among them: (i) The amount of maximum power that is intended to be applied; (ii) The physical properties of the cathode material to be sputtered such as thermal conductivity, structural stability and melting point. The configuration of the cooling system is described in section (3.2.1).

Similar to diodes (see section 3.2.1), the use of a ground shields in magnetrons to prevent sputtering of the magnetron body itself is also imperative. The shield should be made from a non-magnetic material. As a rule, excluding the magnetic circuit, which consists of the magnets and the poles, all materials used to form the magnetron unit (e.g., the magnetron body, earth shield, clamping rings and screws, etc.) should be non-magnetic (e.g., stainless steel, copper, aluminium, etc.). This prevents any interference with the magnetic field like short-circuiting it in some points, and changing its shape and/or strength.

As has been just mentioned, the magnetic circuit consists of the magnets as well as the rear and sometimes front poles. The poles, which are used to redirect the magnetic field, are made from magnetic materials like mild steel. The use of the rear pole is to complete the 'magnetic circuit' by directing the magnetic field to increase the intensity of the magnetic field in the front of the cathode and decrease it in the back to minimise back-sputtering. It has to be sufficiently thick to avoid saturation by the magnetic field passing through it. On the other hand, the use of the front pole is to redirect the magnetic field to make it flatter in front of the target which leads to a less sharp race track (flatter erosion zone). The main drawback of the front pole is sputtering from it, if the magnetic field is not very well designed, hence causing Fe contamination in the sputtered films.

Magnetrons can be oriented in three ways. In sputter-up operation, any flakes of coating material fall back to the cathode which prevents any contamination of the substrate by these flakes, but can result in shorting-out of the magnetron should they bridge the gap between earth shield and magnetron body. In sputter-down operation, there is no danger of magnetron shorting due to flakes, but film contamination is likely. Finally in sideways operation, any combination of last two may happen.

3.4.1. Electron trapping and plasma confinement in \( \vec{E} \times \vec{B} \) fields

3.4.1.1. Electron motion in a magnetic field

The magnetic force \( F_m \) on an electron with mass \( m_e \) and charge \( e \) moving with velocity \( v \) in a uniform magnetic field \( \vec{B} \) is \( F_m = ev\vec{B}\sin \alpha \), where \( \alpha \) is the smaller angle between
\( \vec{v} \) and \( \vec{B} \). Because \( F_m \), \( \vec{v} \) and \( \vec{B} \) are vectors, the former equation can be written as a vector product:

\[
\vec{F}_m = e\vec{v} \times \vec{B} \tag{3.2}
\]

The SI unit of \( \vec{B} \) is Tesla, where 1 Tesla = \( 10^4 \) Gauss. As it is always the case for a vector product, \( \vec{F}_m \) is perpendicular to the plane formed by \( \vec{v} \) and \( \vec{B} \). Thus \( \vec{F}_m \) is always perpendicular to \( \vec{v} \), and is always a sideways deflecting force. It can not change the magnitude of \( \vec{v} \), only its direction. It should be noted that \( \vec{F}_m \) disappears when \( \vec{v} \) is parallel or anti-parallel to the direction of \( \vec{B} \) (i.e., \( \alpha = 0^\circ \) or \( 180^\circ \)) and has its maximum magnitude, equal to \( evB \), when \( \vec{v} \) is at right angles to \( \vec{B} \).

Figure (3.15): An electron moving with a constant speed in a plane perpendicular to a uniform magnetic field (into the plane of the page).

Figure (3.15) shows an electron moving with a constant speed \( \vec{v} \) in a plane perpendicular to uniform magnetic field \( \vec{B} \) (into the plane of the page). Since \( \vec{v} \perp \vec{B} \), the magnitude of the magnetic force on the electron is \( F_m = evB \), and acts always perpendicular to its path. Consequently, the electron moves in a circle, and if the radius of the circle is \( r_m \), the electron must have a constant centripetal acceleration \( \frac{v^2}{r_m} \) towards the centre of the circle. Therefore, from Newton's second law:

\[
evB = m \frac{v^2}{r_m} \tag{3.3}
\]
where \( E \) is the kinetic energy of the electron. Due to their high masses compared to electrons, ions are almost unaffected by magnetic fields of the strengths used in magnetron sputtering. The orbit of the ion is usually ignored because it is often much larger than the chamber. The angular velocity, \( \omega_c \), of the circular motion is:

\[
\omega_c = \frac{v}{r_m} = \frac{eB}{m_e}
\]

which is known as the cyclotron frequency.

The motion of an electron whose velocity is inclined to a magnetic field is shown in figure (3.16).

**Figure (3.16): The motion of an electron whose velocity is inclined to the magnetic field.**

The electron enters a uniform magnetic field \( \mathbf{B} \) with its velocity \( \mathbf{v} \) at an angle \( \alpha \) to the field. Its component of velocity parallel to the field, \( v \cos \alpha \), carries the electron along the magnetic field, whereas its component of velocity perpendicular to the field, \( v \sin \alpha \), makes it describe circles in planes perpendicular to the field. Thus, the electron assumes a helical path of radius \( r_m \), where:

\[
e(v \sin \alpha)B = m_e \frac{(v \sin \alpha)^2}{r_m}
\]

or

\[
r_m = \frac{m_e v \sin \alpha}{eB}
\]
and the angular velocity, $\omega_C$, of the circular motion is the same as that of equation (3.5). The period of the rotation is $T = 2\pi/\omega = 2\pi m_e/eB$, and the pitch, $d_{\text{pit}}$, of the helical is equal to $(v \cos \alpha)T$ or

$$d_{\text{pit}} = \frac{2\pi m_e}{eB} v \cos \alpha$$

[3.8]

3.4.1.2. Electron motion in electric and magnetic fields

If a uniform electric field $\vec{E}$ is applied parallel to a uniform magnetic field $\vec{B}$, the helical motion with constant radius occurs, but because of electron acceleration in the electric field, the pitch of the helix lengthens with time.

As mentioned earlier, in magnetrons, electron confinement near the cathode is achieved by a magnetic field oriented parallel to the cathode surface and perpendicular to the electric field. Figure (3.17) shows an electron moving with a velocity $\vec{v}$ perpendicular to a uniform magnetic field $\vec{B}$ (into the plane of the page). The electron, which is emitted from the cathode, is accelerated in the cathode dark space towards the anode. As the speed of the electron increases, it undergoes an increasing force due to the magnetic field (since $F_m = evB$), which deflects its path more and more from the vertical. The electron keeps acquiring kinetic energy while rising through the electric field, and its speed reaches maximum when it advances parallel to the cathode. It can not acquire any more kinetic energy when its line of motion is perpendicular to the line of the electric field (an equipotential path). The electromagnetic force on it is then vertically directed towards the cathode, and the electron returns to it following a symmetrical path and losing the kinetic energy gained in the first half of its route (i.e., the arrival velocity of the electron at the cathode is equal to the velocity at which it was emitted from the it). The electron is then emitted again towards the anode following the same route and so on. Hence, the path of the electron is a series of semicircles (or cycloid), provided it does not collide en route. Consequently, the effect of the magnetic field is to trap the electron near the cathode from which it was emitted.
The next step is to prove that the motion of an electron in crossed electrical and magnetic fields is cycloidal. If both an electric field \( \mathbf{E} \) and a magnetic field \( \mathbf{B} \) act on a particle of a charge \( q \), the total force on it can be expressed as

\[
\mathbf{F} = q\mathbf{E} + q\mathbf{v} \times \mathbf{B}
\]  

[3.9]

which is the well-known Lorentz force. The components of the Lorentz force are:

---

Figure (3.17): The motion of an electron in crossed electric and magnetic fields.
Returning to figure (3.17), it can be deduced that $E_x = E_z = 0$ and $E_y = -E$, whereas $B_x = B_y = 0$ and $B_z = -B$. Substituting the resulting force components into Newton's second law, with $q = -e$, one gets:

\[
\begin{align*}
F_x &= m_e \ddot{x} = ev_y B \\
F_y &= m_e \ddot{y} = eE - ev_x B \\
F_z &= m_e \ddot{z} = 0
\end{align*}
\]

Hence, no forces act along the z-axis, and only motion in the xy-plane can occur. The solution of the differential equations (3.13) and (3.14) gives:

\[
\begin{align*}
x &= \frac{m_e E}{eB^2}(\omega_e t - \sin \omega_e t) \\
y &= \frac{m_e E}{eB^2}(1 - \cos \omega_e t)
\end{align*}
\]

where $\omega_e = eB/m_e$, as equation (3.5) indicates. Equations (3.16) and (3.17) are those of a cycloid, which is the curve traced out by a point on the circumference of a circle of a radius $r$ as it rolls along a plane, where

\[
r = \frac{m_e E}{eB^2}
\]

As indicated earlier, the electrons undergo a drift in a direction perpendicular to both $\bar{E}$ and $\bar{B}$ (see figure 3.13). This motion is known as the $\bar{E} \times \bar{B}$ drift. Thus, the drifting electrons experience no force in the y-direction (see figure 3.17). Setting $F_y = 0$ and $v_x = v_d$, where $v_d$ is the drift velocity, in equation (3.14), one gets:

\[
v_d = \frac{E}{B}
\]

According to equation (3.17), since the minimum value of $\cos \omega_e$ is -1, the maximum excursion, $y_{\text{max}}$, of the electron from the cathode occurs when $(1 - \cos \omega_e) = 2$. Hence:

\[
y_{\text{max}} = \frac{2m_e E}{eB^2} = 2r
\]
This equation holds either if the electric field is uniform between the two electrodes, which is not the case in magnetron sputtering systems, or if \( y_{\text{max}} \) occurs within the cathode dark space of a magnetron, where \( E \neq 0 \). In magnetrons, \( y_{\text{max}} \) may occur outside the cathode dark space. For example, in planar magnetron sputtering systems, the width of the dark space at typical sputtering pressures is about 0.5 mm. Using equation (3.18), assuming that the operating voltage and the magnetic field are about 500 V and 0.05 T respectively, the radius of the circular component is then \( r = 2.2 \text{ mm} \). Thus, \( y_{\text{max}} = 2r = 4.4 \text{ mm} \), which is much greater than the width of the cathode dark space, as shown in figure (3.18). Green and Chapman\(^5\), have derived a general form of \( y_{\text{max}} \) which holds both inside and outside the dark space.

\[ E \times \frac{\partial}{\partial x} X \]

**Figure (3.18): The approximate trajectory of an electron in the cathode region. Dimensions are not to scale.**

They equated the decrease in the potential energy of the electron to the increase in its kinetic energy:

\[ \frac{1}{2} m_e \dot{x}^2_{\text{max}} = e(V_{\text{max}} - V_c) \]  

[3.21]

where \( V_{\text{max}} \) and \( V_c \) are the potential at \( y_{\text{max}} \) and at the cathode surface, respectively. By integrating equation (3.13), which can be written as \( \dot{x} = eB/m_e \), it can be found that \( \dot{x} = eB/m_e \) or \( \dot{x}_{\text{max}} = ey_{\text{max}}B/m_e \). By substituting in equation (3.21), one gets

\[ y_{\text{max}} = \sqrt{\frac{2m_e (V_{\text{max}} - V_c)}{eB^2}} \]  

[3.22]

Equation (3.20) can be derived by substituting \( V_{\text{max}} - V_c = Ey_{\text{max}} \) in equation (3.22).
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It should be noted that since in cathode sputtering systems almost all the applied electric field appears across the cathode dark space (see section 2.2.7), electrons execute a cycloidal motion only within the cathode dark space where both the electric and magnetic fields are present. Meanwhile, the magnitude of the electric field, within the narrow dark space of the magnetron, overcomes the magnetic field\(^7\). As a result, instead of being ejected from the cathode surface at a small angle to normal, electrons are ejected in a direction virtually normal to the cathode surface across the full width of the dark space. When electrons reach the negative glow region where the electric field is very small, they become mainly influenced by the magnetic field, and hence, execute a circular motion before collisions may propel them back into the dark space or forward toward the anode. Figure (3.19) shows the motion of an electron in the cathode region of a planar magnetron.

![Figure (3.19): The motion of an electron in the cathode region of a planar magnetron.](image)

\[
\text{Circular motion} + \text{Linear motion} = \text{Cycloid}
\]

### 3.4.2. I-V characteristics of magnetrons

The empirical relationship between the cathode current \(I\) and the cathode potential \(V\) observed in a typical planar magnetron (i.e., an optimum magnetic field intensity and shape) is given by\(^6\)

\[
I = kV^n \quad [3.23]
\]

where \(k\) is a constant. The exponent \(n\) is in the range of 3 to 15\(^6\). It increases with the efficiency of the electron confinement\(^6\). As equation (3.23) indicates, the higher the value of \(n\), the slower the change of \(V\) for large changes of \(I\), and can be neglected. Both \(k\) and \(n\) are dependant on the magnetron design (e.g., the type of the magnetron and the magnetic field shape and strength...etc.), the cathode material and the sputtering...
gas type and pressure\textsuperscript{59}. It is worth mentioning that the current density in the erosion zone may reach four times the average current density given by equation (3.23).

The exact values of these constants, for a particular magnetron design and target material as well as sputtering gas type and pressure, can be obtained experimentally by plotting $\ln I$ against $\ln V$. Since $\ln I = \ln k + n \ln V$, the resultant curve is a straight line with an intercept equals to $\ln k$ and a slope equals to $n$.

Rossnagel and Kaufman\textsuperscript{64} and Rossnagel\textsuperscript{65} related the discharge voltage and sheath thickness, $L$, in magnetrons by

$$L = cV^m$$

[3.24]

where $c$ is a constant, and $m$ an exponent. For example, $m$ is equal to -3.9 and -5.8 at an Ar pressure of 3 and 10 mTorr respectively, when sputtering Cu. The magnetron current and voltage, as well as the sheath thickness are expected to obey Child-Langmuir Law (equation 2.5) in which $I \propto V^{3/2}/L^2$. Substituting equation (3.24) into equation (2.5) gives a result similar to the empirical relation given by equation (3.23). It can be concluded then that the sheath is certainly a positive space charge similar to that of a simple diode.

3.4.3. Sputtering gas rarefaction phenomenon

Plasmas in magnetron sputtering are characterised by a high flux of energetic atoms sputtered from the cathode, as well as neutralised sputtering gas atoms which are reflected from the cathode surface with much higher energies. The presence of such species leads to local perturbations in the gas density near the cathode\textsuperscript{66}. This is because these energetic species are thermalised, upon elastically colliding with gas atoms, and considerable amounts of energy are delivered to the gas atoms. This, in turn, leads to a substantial rise in the gas temperature, and hence, to a decrease in the local density of the gas in the near-cathode region where the energies of such energetic species are high. Reductions as high as 85\% of the original gas density were observed at 3 kW\textsuperscript{67}.

The predominant source of gas heating and rarefaction is collisions with sputtered atoms ejected from the cathode surface, rather than the reflected neutrals from the cathode\textsuperscript{64}. This conclusion is attributed to: (i) The momentum-transfer cross-section for the energetic reflected neutrals, whose energies are generally between 400-800 eV (see section 2.2.7), is about 5-10 times lower than that of sputtered atoms (~3-20 eV); (ii) The amount of reduction in the gas density depends on the cathode material and the type of the sputtering gas. It increases with the sputtering yield of the cathode and with the atomic mass of the sputtering gas; (iii) Unlike the energetic reflected neutrals which have
low collision cross-sections due to their high energies\(^{10}\) and hence long mean free paths, the mean free paths of the sputtered atoms, in the range of pressure used in magnetron sputtering, is generally less than the cathode-to-substrate distance. Thus the probability of sputtered atoms being involved in collisions with gas atoms is higher.

Rossnagel\(^6\) found that the gas density, \(n_\text{H}\), in the region of a magnetron cathode is inversely proportional to magnetron current \(I\), the sputtering yield of the cathode \(Y\), the average ejection energy per sputtered atom \(E_a\), and the cross-section for momentum transfer of the sputtered atom \(\sigma_{\text{mt}}\). He also found that \(n_\text{H}\) is proportional to the thermal conductivity of the gas \(K_\text{th}\), the original chamber gas density \(n_0\) which is in turn proportional to the chamber pressure, as equation (A1.27) indicates, and the bulk temperature of the gas (wall temperature) \(T_\text{w}\). The equation he obtained is:

\[
\frac{2\pi n_0 T_\text{w} K_\text{th} f}{E_a Y \sigma_{\text{mt}}} = n_\text{H} \quad [3.25]
\]

where \(f\) is equal to the number of mean free paths away from the cathode chosen to be the distance over which the kinetic energy of the sputtered atoms is absorbed. In Rossnagel's work\(^6\) a value of \(f = 3\) was assumed.

The local alteration of the gas density in the vicinity of the magnetron cathode affects both the plasma and the deposition process. The decrease in the gas density near the cathode reduces the probability of ionisation of gas atoms, since such a probability is proportional to gas density. As a result, the plasma becomes more resistive. Thus, according to equation (3.25), the impedance of the plasma will be high (i.e., the gas rarefaction effect will be strong) when the sputtering yield of the cathode is high or when the thermal conductivity of the sputtering gas is low. Therefore, the discharge voltage, which is the product of the plasma impedance and the discharge current, should rise to a larger degree with increasing current than in equivalent cases with smaller gas rarefaction effects. Consequently, the current-voltage empirical relationship of equation (3.23) can be modified, for a particular magnetron, by changing the type of the sputtering gas or the material of the cathode to be sputtered. The exponent \(n\) in equation (3.23) should be small when the gas rarefaction is strong (e.g., Zn sputtered with Ar), and as large as 25-75 or more when the gas rarefaction is weak\(^{67}\) (e.g., W sputtered with He).

On the other hand, the gas rarefaction phenomenon also affects the scattering of sputtered atoms. Increasing the discharge current reduces the gas density near the cathode (see equation 3.25). This leads the amount of backscattered material to the cathode, at a fixed chamber pressure and cathode-to-substrate distance, to decrease, and
thus, minimises compositional change in films when sputtering from an alloy target (section 2.6). Finally, the approximately linear relationship between the emission intensity from the neutral background gas atoms and the discharge current at fairly low power levels, becomes non-linear (proportional to the square root of current) at high power levels, mainly because of the reduction of gas species near the cathode (see equation 3.25).

3.4.4. The unbalanced magnetron

A balanced magnetron is defined as one in which the intensities of the magnetic flux through the pole faces of the outer and inner magnets are identical or comparable. In reality, it is very difficult to construct an ideally balanced magnetron because magnetic field lines are hard to focus. The plasma in the balanced (conventional) magnetron is confined near the cathode, which is beneficial for high rate sputtering of the cathode, but results in an inability to achieve high levels of bias current to the substrate and, hence, the ion-bombardment of the growing film is minimised.

On the other hand, ion-bombardment of the growing films helps in obtaining thin films of improved properties, as discussed in section (2.10). The unbalanced magnetron sputtering technique offers such a possibility. It has been used for the concurrent deposition and ion-bombardment of films. The potential of this technique was first reported by Fraser and Cook in 1977, who used an auxiliary magnet placed behind the substrate to set up opposing or aiding magnetic fields to control the ion flux to the substrate. The birth of the terms "balanced" and "unbalanced" magnetron was in 1986 when Window and Savvides published a series of papers describing various magnetic field configurations and reporting the self-biasing voltages of the substrates, the ion currents to substrates and the potential applications of these devices. Soon after, the unbalanced magnetron technique was used at Loughborough University of Technology in the UK to successfully produce thin films of diamond-like carbon (hard carbon), dense optical coatings, films of transparent conducting oxides and magnetic films, as well as for the etching of polymer surfaces in an O₂ atmosphere using a carbon target. Also, the Institute of Physics in Prague and D. G. Teer Coating Service Ltd. in the UK have become involved in ion-assisted sputtering of thin films using the unbalanced magnetron technique.

In the unbalanced magnetron, the plasma is intentionally "leaked" out to impinge on the substrate by permitting a portion of the confining magnetic field lines, which are parallel to the cathode surface in the balanced magnetron, to become normal to the cathode surface. Consequently, some of the electrons ejected from the cathode surface are allowed to escape the cathode region, along those normal field lines, drawing ions with
them by electrostatic forces. This creates a plasma beam that is directed onto the substrate surface, subjecting it, and the growing film surfaces, to bombardment by the ions of the sputtering gas. As discussed in section (2.2.4), because the electrons are very much more mobile, and have a longer mean free path (equation A1.26) than the ions, the surface of an insulating or isolated substrate, which is immersed in this dense plasma, will acquire a negative charge and negative potential with respect to the plasma until the fluxes of the electrons and ions are equal. This floating (or self-biasing) potential accelerates the ions to bombard the substrate.

Any strengthening or weakening of the outer or inner set of magnets leads the balanced magnetron to become unbalanced. Window and Savvides\textsuperscript{72} reported two types of unbalanced magnetrons, as shown in figure (3.20). In type I, the flux from the inner set of magnets is larger than that of the outer set. In other words, all the field lines originate from the inner set of magnets, with some not passing into the outer set. In type II, the flux from the inner set of magnets is less than that of the outer set. In other words, all the field lines originate from the outer set of magnets, with some not passing into the inner set. Type II enjoys the following advantages over type I\textsuperscript{72,73}: (i) The ion currents to the substrate are 3-10 mA/cm\textsuperscript{2} (i.e., about 100 times higher than that of type I). Thus, the ion fluxes at the substrate are much larger (up to 10 times\textsuperscript{24}) than that of the sputtered atoms, whereas it is typically 5-10% of the sputtered atoms in balanced magnetrons\textsuperscript{92}; (ii) The self-bias voltages are higher, ranging from 20 to 30 V\textsuperscript{83,93}, compared to 7 V in type I. Therefore, the energy delivered by ions to insulating films is about 400 times (i.e., 100* (30/7) = 400) higher than that in type I.

Howson and Ja'Fer\textsuperscript{41} have placed a hot-filament, just above the racetrack of a circular unbalanced magnetron, for supplying the discharge with additional electrons. The filament was operated at the cathode potential from an isolated AC low voltage resistance heating supply. Besides allowing the operation of the system at much lower voltages and pressures (0.2 mTorr), this resulted in a bombardment energy of films growing on isolated substrate was in the range up to 100 eV, with associated currents of up to 100 mA/cm\textsuperscript{2}. However, the energy of the bombarding ions can be altered by DC or RF biasing the substrates or the growing films, according to the electrical properties of the substrate and the growing film. The upper limit to the ion energy is determined by respattering of the depositing film, when the film is subjected to a bombardment by ions whose energy is in excess of the sputtering threshold of the film. This respattering has been used to clean substrates before deposition.
In practice, type I is more suitable, than the otherwise more popular type II, to be used for coating heat-sensitive substrates (e.g., polymers). However, Window and Savvides\textsuperscript{72} suggested to start deposition using type II mode to clean the substrate, to assist

Figure (3.20): Magnetic field patterns of magnetrons.
adhesion or to produce preferred orientation, and then to switch to type I mode to aid the growth of a columnar structure. In practice, such a switching can be accomplished by using either one magnetron with electromagnets or two magnetrons with permanent magnets.

The self-bias voltage is dependent on magnetic field configurations. In type II unbalanced magnetrons, the self-bias voltage is almost independent of discharge current (or power), target material and gas composition (e.g., Ar/He or Ar/N₂)\(^7\), whereas it decreases with gas pressure\(^7,76,94\). However, in gas systems containing oxygen (e.g., Ar/O₂), the self-bias voltage is dependent on the gas composition. It increases with O₂ partial pressure\(^73,94\), due to the increasing probability of the formation of O⁺ ions, which are accelerated by the electric field of the cathode sheath and collide with the substrate\(^95,97\).

The ion current to the substrate is also dependent on the magnetic field configurations. In type II unbalanced magnetrons, this current is almost proportional to discharge current (or power) and substrate bias, at typical cathode-to-substrate distances, and almost independent on target material and gas composition (e.g., Ar/He or Ar/N₂)\(^7\). The ion current, at a constant bias voltage, generally decreases with gas pressure, but it is almost constant at the pressures which are usually used in magnetrons (i.e., 0.3-5 mTorr)\(^73,79\). However, in gas systems containing oxygen (e.g., Ar/O₂), the ion current to the substrate is very dependent on the gas composition at moderate to high values of O₂ partial pressure. It is then almost proportional to the O₂ partial pressure\(^73,94\), due to the increasing probability of the formation of O⁺ ions and the consequent increase in the self-bias voltages of substrates, as discussed earlier. On the other hand, both the self-bias voltage and ion current to the substrate decrease with increasing cathode-to-substrate distance\(^72\), and the radial distributions of the self-bias voltage, ion current to the substrate and deposition rate, across a circular planar unbalanced magnetron, are maximum at the centre of the target\(^72,77,79\).

To summarise, since DC biasing in balanced magnetrons is ineffective due to the confinement of the plasma in the cathode region, unbalanced magnetrons are a compromise between a high sputter flux from the cathode and reduced operating pressures, on one hand, and the ability to impose a DC sheath in front of the substrate, on the other.

Finally, although ion-bombardment of the substrate helps to obtain denser and higher quality films, it might have, in some cases, negative effects such as resputtering the substrate (if the bombarding ion current/energy is too high), increasing the substrate...
temperature to an undesired value...etc. Altering the ion-bombardment (increasing or decreasing it) can be achieved by:

1. Altering the distribution of the magnetic field by either placing a permanent magnet behind the substrate with its north or south directed in the desired way to oppose or aid the magnetic field lines of the magnetron, or by placing a coil with its current in the needed direction.\(^7\)

2. Altering the power of the magnetron.
REFERENCES


2- George J. (1992), Preparation Of Thin Films. Marcel Dekker, Inc.


Chapter Three


CHAPTER FOUR

DC REACTIVE MAGNETRON SPUTTERING

4.1. Introduction

Reactive sputtering can be defined as the sputtering of elemental targets in the presence of chemically reactive gases that react with the ejected target material. It has become a very popular technique, in today's search for new material properties, for the deposition of a very wide range of compound and alloy thin films including oxides, nitrides, carbides, fluorides or arsenides. Besides the improved properties of non-reactively sputtered films, which were discussed in the previous chapters, the popularity of DC reactive sputtering from elemental targets can be attributed to several factors, among them: (i) It is capable of producing thin compound films of virtually optional stoichiometries and compositions, at high deposition rates and on an industrial scale; (ii) Elemental targets are more easily purified, and hence, high purity films can be produced; (iii) The complexity and expense of RF systems can be avoided since non-compound targets are generally electrically conductive, and hence, DC power can be applied; (iv) Elemental targets are usually easy to machine and bond; (v) Metallic targets are thermally conductive, which makes the cooling of these targets more efficient. Thus, the range of the applied power can be extended (e.g., ~50 W/cm²) without the fear of being cracked; (vi) Films are deposited at temperatures less than 300 °C.

Although reactive sputtering is conceptually simple, it is in fact, a complex and non-linear process which involves many interdependent parameters. The presence of the reactive gas at both the cathode surface and the substrate results in strong interactions of the reactive gas not only with the condensing material but also with the cathode surface, the so called target poisoning. Reactions in the gas phase are ruled out for the same
reasons that ions can not be neutralised in the gas phase (see section A1.4.1). These cathode reactions are seen to increase suddenly at some rate of reactive gas flow. They are marked by a change in the impedance of the operating plasma, an abrupt increase in the system pressure (or more precisely, in the reactive gas pressure), a drastic drop in the deposition rate and a change in the film from metal-rich to gas-rich (i.e., a change in the stoichiometry).

In this chapter, attention will be paid to DC reactive magnetron sputtering and its implications such as the hysteresis effect and the instability in the reactive gas pressure, as well as the methods used to control the process with a special concentration on the techniques used in the course of this work.

4.2. The hysteresis effect and process instability

Figure (4.1.a) shows schematically the famous and important feature of reactive sputtering at a constant partial pressure of non-reactive gas: A hysteresis curve of the reactive gas partial pressure, \( P_r \), as a function of the reactive gas flow rate, \( f_r \), at a constant sputtering power (or as a function of sputtering power at a constant reactive gas flow rate). First, consider the line representing the dependence of \( P_r \) on \( f_r \) when the discharge is off. Obviously, \( P_r \) increases linearly with \( f_r \) because of the constant pumping speed of the system.

Now, consider what happens when the discharge is on. At low values of \( f_r \) (e.g., point A in figure 4.1.a), almost all the available reactive gas is gettered at the condensation sites (e.g., the substrate and the chamber walls). As a result, no essential change in \( P_r \) is observed from the background level and the deposited film is metal-rich. This situation prevails until \( f_r \) reaches a critical value, \( f_r^c \) (point B in figure 4.1.a), where the flow rate of the reactive gas into the chamber becomes higher than the gettering rate of the sputtered metal. The reactive gas reacts, then, with the target surface to form a layer of the gas-metal compound. Sputtering rates from compound targets are less than that of pure metallic targets, by a factor of 10-20, for mainly two reasons (see equation 2.17):

(i) The sputtering yield of metal atoms from a compound on the target surface is less than that from a pure metallic target (see section 2.4).

(ii) Compounds have higher secondary electron emission coefficients than metals (see section 2.3.1) and hence most of the energy of the incident ions is utilised to create and accelerate secondary electrons.
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(a): Hysteresis behaviour of reactive gas pressure

\[ \Delta P_r = P_{r1} - P_{r2} \]

Reactive gas pressure

Reactive mode

Discharge off

Metallic mode

\[ P_r \]

\[ P_{r1} \]

\[ P_{r2} \]

\[ P_a \]

Reactive gas flow rate

(b): Hysteresis behaviour of reactive gas consumption

Metallic mode

Reactive mode

Reactive gas flow rate

(c): Hysteresis behaviour of sputtering rate or cathode voltage.

Metallic mode

Reactive mode

Sputtering rate or Cathode voltage

Reactive gas flow rate

Figure (4.1): The hysteresis behaviour of reactive magnetron sputtering.
Consequently, less metal atoms are sputtered and less reactive gas is consumed in the reaction, and a sudden and sharp rise in the reactive gas partial pressure to a new value, $P_r$, occurs (point C in figure 4.1.a). The deposited film is then gas-rich. If the discharge was off, the value of $P_r$ corresponding to $f_r$ would be $P_{s_e}$, so that $\Delta P_r = P_{s_e} - P_r$ is the decrease in the reactive gas partial pressure due to the gettering effect of metal atoms. Any further increase in the reactive gas flow rate beyond $f_r$ results in a linear increase in $P_r$ so as $\Delta P_r$ is constant. If $f_r$ is reduced following an increase in $P_r$ to a high level, $P_r$ will not decrease following the same trajectory as it increased. $\Delta P_r$ will stay constant until some value $f_{r_a}$ (point D in figure 4.1.a) where it abruptly increases and the reactive gas pressure decreases to the background level. This is because the reactive gas pressure remains high until the compound layer on the surface of the target is removed and metal is exposed to be sputtered once more. As a result, the consumption of the reactive gas increases and the deposited film is metal-rich again. The dependence of both reactive gas consumption and deposition rate on reactive gas flow rate are seen in figures (4.1.b) and (4.1.c), respectively. On the other hand, since compounds have higher secondary electron emission coefficients than metals and since $J_{de} = J_{di} (1 + \gamma_i)$ as discussed in section (2.2.7), Ohm's law suggests that the plasma impedance decreases when the target is poisoned\(^9\). This is seen in the hysteresis curve of the cathode voltage versus reactive gas flow rate, at a constant discharge current, as shown in figure (4.1.c).

The hysteresis effect is a result of two opposing processes: The sputtering of reaction products off the target surface, and the formation (or coverage) of reaction products on that surface\(^11\). The hysteresis curve, therefore, represents two stable states\(^12\) of the system with rapid transitions between them:

(i) **State I (metallic mode):** There is an insignificant change in the reactive gas partial pressure with $f_r$. Basically, all available amount of reactive gas is consumed by the deposited film. Hence, state I is that in which the sputtered metal is doped with reactive gas and is characterised by a high deposition rate. The discharge voltage and current hardly differ from the values for sputtering in the absence of the reactive gas.

(ii) **State II (reactive mode):** The target is entirely poisoned. There is a linear dependence of reactive gas partial pressure on $f_r$, but is lower by $\Delta P_r$ than that observed if the discharge was off. Thus, a constant amount of reactive gas is consumed, independent of $f_r$, and there is a surplus of reactive gas available which makes the formation of a stable stoichiometric compound is preferable. State II is characterised by a much lower deposition rate and sometimes severe arcing. The discharge voltage and current do differ from the values for sputtering in the metallic mode.
For example, Smith et al. found during the production of transparent conducting films of ITO that operation in state I (lower curve) results in deposition of a metal-rich film which requires annealing in an \( \text{O}_2 \) atmosphere to become transparent, whereas operation in state II (upper curve) results in deposition of an oxidised film which requires annealing in a reducing atmosphere to become conductive.

The transition between the two states is much more slower or smoother (i.e., lower slope of the lines BC and DA in figure 4.1.a) when the system target material-gas is less chemically reactive (e.g., nitrides when they are compared with oxides; the reactions in the former are endothermic whereas in the latter are exothermic). This is due to the relatively higher sputtering yield of metal from such a category of compound targets (see section 2.4), and hence to the higher gettering rate of reactive gas by the sputtered metal atoms (i.e., higher \( \Delta P_r \)). Maniv and Westwood studied the transition rates for In\(_{0.9}\)Sn\(_{0.1}\) and Al targets, sputtered in an \( \text{Ar}/\text{O}_2 \) atmosphere, and found that the transition is much more slower in the In\(_{0.9}\)Sn\(_{0.1}\) case. On the other hand, if the degree of reaction, \( d_{\text{rel}} = b/a \), of the compound M\(_x\)R\(_y\) (where M and R are the metal and the reactive gas, respectively) is high, the value of \( f_r \) in figure (4.1.a) will be also high at a given target size and power density. It can be concluded then, that the shape of the hysteresis curve depends not only on the discharge conditions, but also on the kinetics of compound formation on the target surface.

The hysteresis effect is very undesirable and has to be eliminated, because the process is unstable inside this region. At one value of \( f_r \), it is likely to deposit compound films of different stoichiometries and thus physical properties. This is due to the existence of two stable operating states corresponding to an individual value of \( f_r \), when \( f_r \) is in the region of hysteresis. Fast and sophisticated process control systems are required in order to operate inside this region.

4.3. Differential poisoning of magnetron cathode

All the discussion so far has been related to diode sputtering systems which are characterised by a uniform plasma density across the cathode surface. This is not the case in magnetron cathodes (see section 3.4), in which the plasma is highly localised in the racetrack region leading to an inhomogeneous discharge current density across the cathode. As a result, Schiller et al. pointed out that metal sputter rate, \( R_{\text{sput}} \), and oxidation rate, \( R_{\text{ox}} \), are not constant over the target surface but show a noticeable site-
Figure (4.2): Differential poisoning of magnetron cathode. Reproduced from references 4 and 16.
dependence. Consequently, the degree of oxide coverage, $\Theta_{ox}$, on the target surface must also be site-dependent leading to the possibility of the simultaneous existence of three states on the target surface; fully metal, fully oxidised or partially oxidised.

Figure (4.2.a) represents a plot of $R_{sput}(x)/R_{sput}(x=0)$ as a function of the distance, $x$, from the centre of the erosion zone. It appears that $R_{sput}$ is highly site-dependent and shows a peak at $x = 0$. Also shown in figure (4.2.a), the fairly uniform distribution of $R_{ox}(x)/R_{ox}(x=0)$ as a function of $x$. This means that at a moderate O$_2$ partial pressure, $P_{O_2}$, $R_{sput} > R_{ox}$ in the centre of the erosion zone and the difference between these two values decreases as $x$ increases until a certain point where $R_{sput} < R_{ox}$. It should be mentioned that even in the erosion zone, oxides are continually formed and then destroyed.

If sputtering takes place in a very high $P_{O_2}$, and/or quite low discharge power, $P$, almost all the target surface will be covered by the reaction products (i.e., $\Theta_{ox} \approx 1$), as can be seen in figure (4.2.b). Under these conditions, oxides are deposited onto the substrate with an extremely low rate due to the much lower sputtering yield of metal from an oxide target (see section 4.2).

With decreasing $P_{O_2}$ and/or increasing $P$, $\Theta_{ox}$ decreases according to the distribution of the discharge current (or power) density within the discharge zone (figure 4.2.c) until the target region corresponding to maximum discharge current density (i.e., where $x = 0$) becomes entirely free from oxides (i.e., metallic with $\Theta_{ox} \approx 0$), as figure (4.2.d) shows. If $P_{O_2}$ is further decreased and/or $P$ is further increased, the width of the oxide-free zone on the target also increases, as shown in figure (4.2.e).

Finally, adjacent to the metallic zone, on both sides, there are transition regions within which $\Theta_{ox}$ increases from zero to unity. Outside the transition regions a macroscopically thick oxide film then grows on the target surface.

Despite the differential poisoning at a given reactive gas pressure, the hysteresis effect, discussed earlier, was also observed in magnetron cathodes.$^{8-10,17,18}$

4.4. Methods of process stabilisation

The best film properties and the highest deposition rate can be achieved by forming the desired film at the substrate while sputtering from a metallic magnetron surface.$^{19}$ Thus, it is beneficial to operate the magnetron cathode with its surface either fully or partially metallic, while maintaining an adequately high partial pressure of the reactive gas at the substrate to form the desired compound film. As discussed in section (4.2), this is not
always possible because if the flow rate of the reactive gas is manually increased, the reaction between the reactive gas and the metallic target becomes inevitable. This in turn leads to the hysteresis behaviour, which is marked by an uncontrollable change-over (or instability) between a metallic and a poisoned target\(^{17,20-23}\), exactly in the pressure range where a stoichiometric film is formed\(^{13,20}\). Methods of process control to get rid of the ambiguous non-unique value of the reactive gas flow rate, reactive gas partial pressure, or sputtering rate, will be summarised below.

### 4.4.1. Varying the pumping speed

One solution to eliminate the hysteresis effect is simply to "overpump" the deposition chamber\(^{2,3,7,11,20,24-30}\). This is achieved by providing a pumping system with a pumping speed that is sufficiently high so that the consumption of the reactive gas by the pumping system dominates that by the growing film. As a result, a gradual transition between the metallic (state I) and reactive (state II) modes takes place. Kadlec et al.\(^{11}\) stated that during reactive sputtering, the reactive gas flowing into the deposition chamber, with a rate \(f_r\), is either gettered by the sputtered material or removed by the pumping system. The equilibrium state is given by:

\[
f_r = f_{rm} + P_r S_r \tag{4.1}
\]

where \(f_{rm}\) is the flow rate of the reactive gas gettered by the sputtered material, \(P_r\) is the reactive gas partial pressure and \(S_r\) is the pumping speed of the pumping system for the reactive gas. Meanwhile, according to Spencer et al.\(^{20}\), instability or hysteresis occurs when the target becomes poisoned at reactive gas pressures where a stoichiometric film is formed. Consequently, the consumption of reactive gas decreases due to the lower sputtering yield from compound targets. This leads to a surplus in the reactive gas (in the deposition chamber) causing its partial pressure to rise. The cycle that leads to instability or hysteresis is seen in figure (4.3). It can be concluded then that the deposition system becomes unstable if an increase in the reactive gas pressure results in a decrease in the reactive gas consumption (i.e., \(df_r/dP_r < 0\)). For a stable system, the last inequality becomes: \(df_r/dP_r > 0\). Applying this condition to equation (4.1), one gets\(^{28}\)

\[
\frac{df_{rm}}{dP_r} + S_r > 0 \tag{4.2}
\]

If the critical pumping speed, \(S_c\), is defined as\(^{11}\)

\[
S_c = -\frac{df_{rm}}{dP_r} \tag{4.3}
\]
the condition for the deposition system to become stable (i.e., to eliminate the hysteresis effect) is then

\[ S_r > S_c \]  \hspace{1cm} [4.4] \]

That is, the pumping speed of the pumping system should be greater than a critical value \( S_c \).

Spencer et al.\(^{20}\) examined the above condition during the deposition of conducting films of indium oxide at a constant Ar partial pressure. They measured the \( \text{O}_2 \) consumption in the system when the magnetron was on (i.e., the total \( \text{O}_2 \) flow rate to both the growing film and the pumps), and when the magnetron was off (i.e., the \( \text{O}_2 \) flow rate to the pumps which was 240 l/s). From these measurements they obtained the consumption of \( \text{O}_2 \) by the film. Their results are reproduced in figure (4.4). The stability condition implied that \( S_r > 150 \text{ l/s} \). To examine this, they baffled the vacuum pump to give an \( \text{O}_2 \) pumping speed of 120 l/s. The results, which are reproduced in figure (4.5), indicated that the system became unstable with an uncontrollable rise in the \( \text{O}_2 \) partial pressure accompanied by a similar rise in the magnetron potential. The latter is a clear indication of a change in the state of the target (i.e., from metallic to oxidised). Furthermore, to prove that their results were independent of their system or the material used, they carried out the same experiments in another vacuum system to deposit tin oxide. They reached the same conclusion, that is, instability occurs due to an insufficient pumping speed of the reactive gas by the pumping system. In the same paper, Spencer et al.\(^{20}\) proposed a conceptual model of the reactive sputtering process.
Figure (4.4): The consumption of oxygen in a stable system depositing indium oxide. Reproduced from reference 20.

Figure (4.5): The system of figure (4.4) made unstable by reducing the pumping speed. Reproduced from reference 20.
They first treated the effects of raising the reactive gas partial pressure at the target and the substrate independently, and then combined both effects to propose a model of the reactive gas consumption by the film. At the target, the surface is continuously being poisoned and sputter-cleaned. A partially poisoned surface results when the poisoning rate is higher than the cleaning rate. The area of the target surface that is poisoned increases with increasing the partial pressure of the reactive gas. Since the sputtering yield of metal atoms from a poisoned surface is less than that from a pure metallic target (see section 2.4), the metal flux from the target decreases with increasing reactive gas partial pressure until the entire target is poisoned, as can be seen in figure (4.6.a). At the substrate, when the reactive gas partial pressure is low, the formation rate of the compound film is limited by the impact rate and utilisation of the reactive gas atoms and hence a metal-rich, or sub-stoichiometric, film is deposited. Since the impact rate of the reactive gas atoms increases with its partial pressure, the reactive gas-content of the compound film increases with the reactive gas partial pressure until a gas-rich, or over-stoichiometric (saturated), film is deposited (figure 4.6.b). The combination of the processes, at the target and substrate, produces the curve of the reactive gas consumption by the film which is shown in figure (4.6.c).

Okamoto and Serikawa\(^7\) reactively sputtered Si in an Ar/N\(_2\) atmosphere using RF magnetron technique at a constant Ar partial pressure. The pressure of the sputtering gas was controlled by throttling a baffle valve located above the diffusion pump. They varied the pumping speed, by a factor of 20, by changing the flow rate of Ar from 5 SCCM to 100 SCCM. At 5 SCCM, a well-defined hysteresis curve, between nitrogen partial pressure and flow rate, was obtained, and the deposition rate decreased from 15 to 3 nm. At 100 SCCM, the hysteresis effect disappeared completely, although the deposition rate decreased to about 6 nm. However, the critical Ar flow rate was 62 SCCM. Thus, the suppression of the hysteresis effect does not grant any significant benefits as far as the deposition rate is concerned. This conclusion was also reached by Berg et al\(^24\), who also found that the introduction of the reactive gas very close to the substrate (i.e., the creation of a gradient in the reactive gas partial pressure in the chamber\(^22\)) decreased the poisoning of the target. They suggested this to be combined with a feedback control system, for the reactive gas partial pressure versus the reactive gas flow rate, to be also able to operate within the instability where the most favourable conditions exist. These arrangements increase the deposition rate of compound films to a level virtually equal to that from metallic targets.
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(a): At the target

- Metal sputter rate
- Target poisoning
- Sputtering rate of poisoned target

Reactive gas pressure

(b): At the substrate

- Atomic ratio gas/metal in film
- Gas rich
- Stoichiometry
- Metal rich

Reactive gas pressure

(c): The resulting reactive gas consumption

- Film effect
- Target effect
- Arrival rate and utilisation of reactive gas at the substrate
- Target poisoning
- Sputtering rate of poisoned target

Reactive gas pressure

Figure (4.6): The origins of the reactive gas consumption. Reproduced from reference 20.
Finally, Danroc et al. found, during the reactive magnetron sputtering of TiN, that the shape of the hysteresis curve changes as a function of both the pumping speed and the position of the N₂ inlet. The width of the hysteresis curve decreased as the N₂ inlet was made closer to the turbomolecular pump entrance. The problem with increasing the pumping speed lies in adding costs at the building stage of new machines, and can be difficult to adopt in existing ones.

4.4.2. Varying the target-to-substrate distance

Another method to reduce target poisoning is to make the target-to-substrate distance large. This effect was investigated experimentally by Schiller et al. and published in a paper covering many important aspects of controlling the deposition process between the metallic and the reactive modes of the target. They found, during the DC reactive magnetron sputtering of Ti in an Ar/O₂ atmosphere, that when the target-to-substrate
distance was small, over-stoichiometric or gas-rich films of TiO$_{2.4}$ were formed. This is because at such small distances, the flux density of sputtered Ti was high and hence a high O$_2$ partial pressure, P$_{O_2}$, was needed for the reaction to take place. The high P$_{O_2}$ caused the target to switch to the reactive (or poisoned) mode, which is characterised by a low sputtering rate and gas-rich films. This indicates that optimum film properties can not be achieved from a poisoned target. When the target-to-substrate distance was made larger, the stoichiometric film of TiO$_2$ was formed at a lower P$_{O_2}$, and hence the probability of total poisoning of the target was reduced. The lower P$_{O_2}$ is because the flux density of sputtered Ti was then lower due to the cosine distribution law. On the other hand, in the same paper Schiller et al$^{12}$ investigated the variation of plasma emission intensity as a function of reactive gas flow rate. They found that the dependence exhibits a similar hysteresis curve to that of reactive gas partial pressure versus reactive gas flow rate, as shown in figure (4.7), and concluded that plasma emission can be used to control the process within the instability. This important idea is not elaborated on until later papers by Schiller and his co-workers.

4.4.3. Obstructing reactive gas flow to the cathode

![Figure (4.8): Schematic of baffled magnetron sputtering system.](image)
Maniv et al\textsuperscript{11} suggested a different solution to prevent magnetron target poisoning and hence hysteresis instability, while producing transparent conducting films of Cd\textsubscript{2}SnO\textsubscript{4} by reactive magnetron sputtering of Cd\textsubscript{2}Sn alloy target. They modified the magnetron system to reduce the oxidation rate at the target relative to the substrate by introducing a baffle between the substrate and the target, with O\textsubscript{2} inlet to the system on the substrate side, as can be seen in figure (4.8). The baffle also provided additional gettering surfaces for O\textsubscript{2} in the proximity of the target\textsuperscript{20}. With this arrangement, it was possible to deposit stoichiometric films, on RF-biased substrates, before oxidation of the target was complete (i.e., before transition from state I to state II takes place). Maniv et al\textsuperscript{11} also used a baffle to obtain transparent conducting ZnO without RF coupling to the substrate. Many workers reported the successful use of this technique for the production of compound films. For example, Scherer and Wirz\textsuperscript{33} for Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, SnO\textsubscript{2} and Ta\textsubscript{2}O\textsubscript{5}, Este and Westwood\textsuperscript{34,35} for Al\textsubscript{2}O\textsubscript{3}, AlN and TiN, Czternastek et al\textsuperscript{11} for ZnO doped with In (ZIO), Brett et al\textsuperscript{17} for ITO and ZnO and Brett and Parsons\textsuperscript{38} for ZnO. However, the necessity for frequent cleaning of the baffle, the reduction of the metal flux to the substrate and the reduction of plasma-bombardment of the substrate, if the baffle is grounded, are the principal drawbacks of this technique. The last problem may be solved by either placing a positively-biased electrode in the substrate region to pull the plasma out of baffle, or by biasing the substrate.

4.4.4. Pulsed reactive gas flow

Aronson et al\textsuperscript{17} and later Sproul\textsuperscript{19} proposed, during the DC reactive magnetron sputtering of Ti to deposit films of TiN, another method to maintain a stable operation in the metallic mode (i.e., at a constant N\textsubscript{2} partial pressure). They employed a pulsed reactive gas flow technique in which the reactive gas flow switches on and off periodically for short times. Two timers were used to independently control the pulse 'on' and 'off' times of a piezoelectric valve. The switching off is to allow the removal of any traces of compound formed onto the target surface before it accumulates and hence the target becomes irreversibly poisoned. Thus, the target switches between state I and state II, and the average target condition is then intermediate between the two states (i.e., the target continuously operating between the metallic and reactive modes around the knee of the hysteresis curve). Clearly, the pulsing time can not be too long otherwise the deposited film would be of alternate layers of compound and metal. Sproul\textsuperscript{40} reported the successful deposition of TiN at a rate of about 50\% of that of metallic Ti when N\textsubscript{2} was pulsed on and off at a rate of 3 s each. He also reported that the deposition rate of TiN, at the same cathode power, became virtually equal to that of metallic Ti when the pulsing rate was increased to 0.2 s. The pulse technique was also employed by Howson et al\textsuperscript{11} to deposit films of TiO\textsubscript{2}. The main disadvantages of this technique are:
(i) The need for an extensive amount of process optimisation prior to reproducibly depositing films with the required stoichiometry; (ii) The need for a continuous monitoring and adjustment of the process parameters. For example, it is not possible to deposit stoichiometric films at high rates unless the reactive gas flow is controlled manually to maintain a constant reactive gas partial pressure. Otherwise, either stoichiometric or over-stoichiometric films would be deposited at low rates accompanied by a rise in the reactive gas partial pressure, or sub-stoichiometric films would be deposited at high rates.

4.5. Methods of control to prevent instability

It is obvious that a stable operation in the metallic mode of the target is necessary to produce films of the desired stoichiometries at high deposition rates. This implies the need to operate at the knee of the hysteresis curve (i.e., in the transition mode at $f_t$), which is usually very difficult to achieve because any major disturbance in the reactive gas partial pressure will shift the process to either extreme of the metallic or reactive mode. For example, any increase in the reactive gas partial pressure will drive the process to the reactive mode. Such a transition is irreversible since it will be impossible then to retrieve the desired set-point without tracing out the hysteresis curve, with the resultant deposition of inhomogeneous films. Consequently, a very fast feedback method has to be employed to automatically control the flow rate of the reactive gas into the system, or the discharge power, to maintain the desired set-point. This is accomplished by the continuous monitoring of any change in the operating point, using a process parameter representative of the target state, and providing a feedback signal, in the control loop, to adjust either the flow rate of the reactive gas or the discharge power accordingly. Several parameters, that continuously characterise the state of the process, have been used as monitors. Cathode current, cathode voltage, reactive gas partial pressure, system pressure, deposition rate, film properties and light emitted from the plasma are the parameters which change rapidly near the critical flow $f_t$, and been used measure the process\textsuperscript{15,22,30,42-51}. Unfortunately, not all these parameters allow the required degree of accuracy for process control. For example, reactive gas partial pressure is too slow because pressure measurements take place away from the region of interest (i.e., target region). Furthermore, partial pressure is an equilibrium measurement, whereas in the case of controlling reactive sputtering, a transient process that keeps changing very rapidly when controlling within the instability region is confronted. Mass spectrometry of a high pressure process is quite complex and requires differential pumping through an orifice\textsuperscript{22,40,42}. Also, it is installed far from the target due to the size of the required pumping system\textsuperscript{43}, so its response to changes in the target status is too slow\textsuperscript{44}. Of these parameters, Plasma Emission Monitoring (PEM) and Voltage Control techniques have

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proved to be very reliable in controlling reactive sputtering processes. The PEM and voltage control equipment and parameters specific to the system used in the course of this work will be described in a coming chapter. They have been used in the course of this work and will be described below. Other methods of control, including Successive Plasma Anodistion (SPA) and Successive Pulsed Plasma Anodistion (SPPA) will also be described.

4.5.1. Plasma emission monitoring

Although the use of light emitted from DC plasma discharges, as a diagnostic tool, is not new, the real re-birth of plasma emission monitoring was in the semiconductor industry for end-point detection in plasma etching. After that, a US patent covering the utilisation of spectral emission lines from the plasma to control reactive sputtering in the region of instability was granted in 1979, but the general use of this technique was very limited until 1987 when it was re-introduced by Schiller et al after they had alluded to it in 1984.

Excitation and relaxation mechanisms in glow discharge plasmas are discussed in section (A1.4.2). In summary, the relaxation of an excited atom, following an inelastic collision with an electron in the gas phase, causes the emission of a photon. Although these photons extend from deep ultraviolet to far infrared, they are typically in the visible and ultraviolet region of the electromagnetic spectrum and have precise wavelengths that are characteristic of the atom. The emission intensity, $I_{em}(x)$, at any position $x$ in the discharge, corresponding to the transition $i \rightarrow j$ is given by

$$I_{em}(x) = N(x) P_i(x) T_{ij} g(\lambda) \tag{4.5}$$

where $N(x)$ is the number density of relevant species. $T_{ij}$ is the probability that the electron will decay back from state $i$ to state $j$ through the radiative transition of interest, and is a constant determined by quantum mechanics. $g(\lambda)$ is the fraction of emitted photons corresponding to this transition that are detected, and is a function of plasma transmission, detector sensitivity and system geometry. $P_i(x)$ is the probability of exciting an atom to state $i$, and is given by

$$P_i(x) = \int n_e(x, v_e) \sigma_{exc}(v_e) \, dv_e \tag{4.6}$$

where $n_e$ and $v_e$ are the electron density and velocity, respectively. $\sigma_{exc}$ is the excitation cross-section. By substituting $v_e = (2E_e/m_e)^{1/2}$ in equation (4.6), where $E_e$ and $m_e$ are the electron kinetic energy and mass respectively, one gets
Equation (4.5) implies that \( I_{em}(x) \propto N(x)P_1(x) \), where the product \( N(x)P_1(x) \) represents the density of the excited species. The determination of both \( T_{ij} \) and \( g(\lambda) \) is very complicated and they are constant at given experimental conditions. \( P_1(x) \) is a function of electron density and energy distribution, as equation (4.7) indicates, and it is generally not known. Greene\textsuperscript{59} gave examples in which \( P_1(x) \) was a constant with respect to either sputtering conditions or sample composition. It was concluded, therefore, that the emission intensity, \( I_{em}(x) \), can provide direct quantitative diagnostic information and can be used for process monitoring on an empirical basis.

\[
P_1(x) = \frac{1}{(2m_e)^{1/2}} \int E_e^{-1/2} n_e(x,E_e) \sigma_{exc}(E_e) \, dE_e \tag{4.7}
\]

**Figure (4.9): Normalised emission intensities of As, Ga and Ar peaks as a function of distance between anode and cathode. Reproduced from reference 60.**

\( I_{em}(x) \) exhibits a pronounced decrease with distance from the cathode\textsuperscript{60,61}, as can be seen in figure (4.9). Since \( N(x) \) should not change significantly with the distance from the cathode, the decrease in \( I_{em}(x) \) is attributed to the sharp decrease in \( P_1(x) \). This is because, when an electron loses its energy as a result of an inelastic collision with a gas atom, after having left the cathode dark space, it will not regain sufficient energy, on its
way to the anode, to participate in another exciting collision since almost all the applied voltage appears across the cathode dark space.

Schiller et al have experimentally studied the relation between the emission intensity of the Ta line at 481 nm and the magnetron discharge parameters in a non-reactive atmosphere. They found that \( I_{em}(x) \) is virtually linearly proportional to magnetron current, magnetron power and deposition rate, at a given pressure. In addition, a strong pressure dependence (i.e., \( I_{em}(x) \propto P_a \), where \( P_a \) is the non-reactive gas pressure) was observed, at given discharge parameters. In a reactive atmosphere, a pronounced drop in the emission intensity of the Ta line at 481 nm was observed as \( O_2 \) partial pressure increased due to the coverage of the target surface with the reaction products which leads to a reduction in the metal sputtering rate. Furthermore, it was also observed that \( I_{em}(x) \) stays relatively high even if the \( O_2 \) content of the discharge gas is more than 50%. Similar results to those of Ta were obtained using Al, Cu, Ti and In (90%-Sn (10%) targets. Blom et al also found, during the reactive deposition of ZrN films, that the nitrogen emission intensity increases linearly with the nitrogen flow rate.

It can be deduced from the above results, which have also been confirmed by many other workers, that the dependence of the emission intensity on the discharge parameters is evident. This made the emission intensity a valid control parameter to be utilised in controlling the reactive sputtering processes.

In PEM, the reactive gas inlet to the system is placed close to the target, the target-to-substrate distance is decreased and the creation of a plasma shield toward the chamber is encouraged. These arrangements improve the excitation of the reactants at the substrate, and hence, lower the flow rate of the reactive gas at which the desired degree of reaction occurs (i.e., \( f_q \) and \( f_q \) in the hysteresis curve are moved closer to each other). Thus, in contrast to the methods discussed earlier which tried to separate the event taking place at target and substrate, this method encourages such coupling in a way that the process would be unstable without it.

Spencer and Howson developed a dynamic control for reactive magnetron sputtering to operate the magnetron in the instability region to produce films of better properties at higher deposition rates. They suggested that this can be achieved by breaking the feedback cycle, in figure (4.3), through matching the reactive gas admission rate to the system and the consumption rate (by the film and the pumps) for the surplus of the reactive gas, which causes target poisoning, to be zero. A solution to the instability, in systems of limited pumping capacities, was obtained by providing a control of the partial pressure of the reactive gas with a rapid feedback. This was achieved by using an observation of the spectral line emission of the sputtered metallic atoms or the gas, in
the plasma, as a signal representing the poisoning of the target or the partial pressure of
the reactive gas in the chamber to control the admission rate of the reactive gas into the
sputtering system. Such a method of control allows the production of films of
carefully controlled stoichiometries even at intermediate points that would be impossible
to reach by ordinary pressure control apparatus.

Figure (4.10) shows a PEM control loop. The light from the plasma usually contains the
emission lines corresponding to the sputtering gas, the target material, the reactive gas
and the contaminants such as hydrogen and oxygen due to water vapour dissociation, as
well as carbon, nitrogen,...etc. It is viewed through a relatively long tube into which an
optical fibre bundle is inserted. The tube, which is used to prevent the surface of the
fibre bundle from being coated with sputtered material, is directed into the centre of the
magnetron to avoid deceptive indications of the target mode due to the simultaneous
existence of three states across the magnetron cathode; fully metal, fully oxidised or
partially oxidised (see section 4.3). The light is passed on through an optical fibre system
to an appropriate optical filter (or a monochromator) which selects only the requested
line emission. The selected wavelength is chosen so that the signal it passes (of the
target material, the sputtering gas, or the reactive gas) is not influenced by the
neighbouring lines of other elements in the plasma which may interfere with the wanted
signal. The obtained optical signal is converted into an electrical signal, proportional to
the density of the corresponding element in the plasma, by a photomultiplier. In summary, this device is based on secondary electron emission due to photoelectric effect. It consists of a photocathode made of material with a low work function coated on the inside of a glass tube, a series of dynodes with increasing positive potentials and hence secondary electron emission coefficient and an anode to collect the resultant emitted electrons. The electrical signal is then applied to the PEM controller which is connected to a piezoelectric control valve of a very fast response. The controller compares the input signal to it with the desired set-point and gives the appropriate command to the piezoelectric gas flow control valve to admit/disallow a flow of the reactive gas to the system until the magnitudes of both, the set-point and the input signal, are equal.

To conclude, the PEM is a powerful technique for monitoring and controlling the reactive sputtering processes for the production of high quality films reproducibly. It samples from the region where the reaction is actually taking place, the information may be obtained in real time without disturbing the discharge and several peaks emission intensities can be proportionally related to the sputtered metal flux and the partial pressure of the reactive gas\textsuperscript{45}.

4.5.2. Voltage control

An alternative parameter that continuously characterises the state of the reactive sputtering process and changes rapidly near the critical flow $f_n$ is the cathode voltage\textsuperscript{36,51}. The cathode voltage is a measure of the degree of reaction at the cathode surface (i.e., target coverage) because it varies with the secondary electron emission coefficient from this surface, which is in turn sensitive to the surface conditions. For example, the secondary electron emission coefficients from oxide compounds are generally higher than their metal constituents (see sections 2.3.1 and 4.2). Consequently, as these compounds are formed on the surface of the cathode, the cathode voltage will be changed. The cathode voltage may be measured and used to supply an electrical signal to the process controller to control the partial pressure of the reactive gas by adjusting the admission rate of the reactive gas to the system in a similar manner to that of PEM.

Voltage control is a less conventional method and may be employed in certain reactive sputtering conditions. These conditions are:

1. The difference between the cathode voltage of the metallic target material and that of the reaction product should be sufficiently large\textsuperscript{57} and positive\textsuperscript{35,67}. For example, the cathode voltage in the case of a pure Si target is \textasciitilde700 V versus \textasciitilde200
V when SiO₂ is formed on the target surface, whereas the cathode voltage in the case of a metallic In (90%)-Sn (10%) target is ~385 V and the oxide is ~360 V. In the first case, the cathode voltage has been found to be a good indicator of the degree of reaction, whereas in the second case the range is too small and hence voltage control cannot be utilised.

2. The cathode voltage as a function of the reactive gas flow rate, or its partial pressure, should be single valued (e.g., In-Sn sputtered in Ar/O₂ is not)⁵⁷.⁶⁷.

Voltage control has been used in this work in the cases of Al, Zn, Cu and Pb when they were sputtered in an Ar/O₂ atmosphere.

### 4.5.3. Successive plasma anodisation (SPA)

An alternative to the simultaneous delivery of the constituent parts of a compound material (e.g., oxides) to the growing film, is to provide them separately, at different times, and react them together on the substrate⁶⁸. Obviously, this can be achieved more easily on very thin layers of metal and the compound thin film can be built as an assembly of these.

In practice, this can be achieved by using two magnetrons, one to deposit a thin layer of metal and the other, which is strongly unbalanced, to oxidise the metallic layer in an Ar/O₂ plasma. The self-bias that appears on the isolated substrate, due to being immersed in the plasma that leaks from the unbalanced magnetron, helps in activating the reaction on the substrate by ion-bombardment and hence oxidising all of the metal. This process is repeated, to give the total thickness of oxide that is required, by placing the substrate on a rotating table. A spinning rate of around one revolution per second is used.

### 4.5.4. Successive pulsed plasma anodisation (SPPA)

The SPA process, mentioned in section (4.5.3), was developed to use just one unbalanced planar magnetron to both sputter the metal and oxidise it in Ar/O₂ plasma⁶⁸. This was achieved by pulsing the admission of the reactive gas in response to a signal indicating the state of the cathode surface. In practice, an intermediate circuit was designed to obtain a minimum 0 V and a maximum 1 V settings corresponding to the signals proportional to the partial pressure of oxygen at the onset of fully poisoned and fully metallic target states, respectively. PEM or voltage control signals can be used. With the cathode operating in a fully poisoned mode, the output signal from the circuit to the reactive gas pressure controller was offset to 0 V. Then, with the reactive gas
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switched off and the cathode returned to the metal state, the output signal was set to 1 V. An electronic switching unit was designed to control the pulsing of the reactive gas into the chamber. Selection of two voltage threshold levels determined the open and closed states of a driver valve, which directed the reactive gas either to the process chamber or elsewhere. Admission of a reactive gas pulse to the chamber forces the signal below the selected 'lower threshold' (e.g., 0.2 V) and shuts off the reactive gas supply to the chamber, by diverting the flow, allowing the cathode to clean. The signal then rises above the 'upper threshold' (e.g., 0.8 V) where reactive gas is diverted back to the chamber and the target poisons once more. Repetition of this cycle was found to enable continuously variable and controllable target status.

With no reactive gas admitted, metal is sputtered. When oxygen is admitted, the target is poisoned and the just-deposited metallic layer is oxidised by the Ar/O₂ plasma. Again, the self-bias that appears on the isolated substrate, due to being immersed in the plasma that leaked from the unbalanced magnetron, helps in activating the reaction on the substrate by ion-bombardment and hence oxidises all of the metal. Howson⁶⁸ found that a switching time of about one second was appropriate for the deposition of a few atomic layers and their oxidation.

4.6. Arcing and methods of avoiding it

Highly insulating films (e.g., Al₂O₃, SiO₂ and TiO₂) have been traditionally deposited using RF diode or magnetron sputtering from compound targets⁶⁹-⁷². However, the drawbacks of the RF technique (see section 3.2.2) and the advantages of reactive sputtering from metallic targets (see section 4.1), have encouraged workers to think of alternative methods for the production of such films. The serious problem encountered during the reactive deposition of highly insulating films from metallic targets, using DC magnetron sputtering technique, is the build-up of an electrically insulating layer on the cathode surface with the resultant charge accumulation and arcing.

In the following sections, the causes of arc initiation will be summarised. The destructive effects of arcing on the deposition process, the coating properties and the target lifetime will be also discussed. Finally, methods of avoiding arcs will be described.

4.6.1. Arcs initiation and their destructive effects

When a highly insulating compound is deposited, using DC reactive magnetron sputtering, both the metallic and the insulating states exist simultaneously on the cathode surface due to the differential poisoning of magnetron cathodes (see section 4.3). Since sputtering is a momentum transfer process, ion-bombardment of the cathode causes
sputtering of both the insulating layers (Ins) and the metallic parts of the cathode (Met). However, unlike those that strike the metallic parts of the cathode, ions striking the surface of the insulating layers (Surf) can not be neutralised by electrons from the cathode. Besides sputtering insulating layers, they only attract an equal number of electrons on the metallic surface of the cathode underneath the insulating layers, as can be seen in figure (4.11). From an electrical standpoint, the combination "Surf-Ins-Met" represents a capacitor which keeps charging up as ions impinge on the surface of the insulating layer causing the voltage, $V_{\text{ins}}$, across the insulating layer to increase. Since the output voltage of the power supply is predetermined, the voltage across the cathode dark space should be reduced by $V_{\text{ins}}$, provided that the dielectric strength of the insulating layer is sufficiently high. This continues until the voltage across the cathode dark space becomes zero (i.e., the surface potential of the insulating layer is equal to the plasma potential). At this stage, no ions can acquire sufficient energy to further sputter the layer.

![Diagram of plasma and cathode with positive surface charge and insulating layer](image)

**Figure (4.11): Positive charge accumulation on the surface of an insulating layer.**
However, if the dielectric strength of the insulating layer is not sufficiently high, the layer breaks down when the electric field across it reaches its dielectric strength. A dielectric has a very small electrical conductivity at temperatures above 0 K which means the presence of few electrons in its conduction band. If a very high voltage is applied, those electrons are accelerated and gain sufficient energies to participate in ionising collisions with atoms, causing other electrons to jump from the valence to the conduction band. These electrons are in turn accelerated by the applied voltage and ionise other atoms. Ultimately, an avalanche effect (i.e., a stream of electrons) occurs which results in a sharp increase in the current and hence temperature. The latter may produce local evaporation of target material. 

On the other hand, any low impedance state (i.e., a high current and low voltage) observed at the output of the power supply caused by the process can be called an arc. The most important sources of arcs at low gas pressures are field emission of electrons and macro particles. Thermionic electron emission from the cathode as a result of heating it (e.g., cooling failure), outgassing from the cathode or the existence of a sufficiently high voltage gradient at the cathode are among the probable causes of field emission of electrons. The other source of arcing is attributed to the accelerated macro particles which are detached from the cathode. If their energies are sufficiently high upon striking the anode, they cause local evaporation of its material. Due to the confinement of charged particles in magnetrons, these macro particles may end their lives at the cathode surface itself causing evaporation to its material.

It can be concluded from the above discussion, that a unipolar arc may be initiated by the breakdown of an insulating layer which builds up outside the racetrack of a magnetron cathode. Schiller et al. found that only 0.1% of these unipolar arcs may result in a bipolar arc. The undesired effects of arcing in reactive sputtering may be summarised as follows: (i) Driving the process to become unstable, this can be attributed to the disability of the system to recover its original state, after switching off the power supply temporarily to supress an arc, due to the hysteresis effect; (ii) Reducing the target lifetime. The target surface may be damaged due to the concentration of the entire discharge current in a very small spot of the cathode (with a diameter ranges from 1 µm to about 50 µm) causing local melting of the target; (iii) Creating defects in the coatings. This is due to the incorporation of droplets of molten target material, which are ejected from the target surface when an arc occurs, in the growing film. For example, arcing causes absorption losses in SiO₂ films prepared by reactive DC magnetron sputtering, because the emitted material usually contains a large number of metallic atoms which are not all completely oxidised.
4.6.2. Time required for arcs to occur

As has been stated in section (4.6.1), the combination "Surf-Ins-Met" represents a capacitor which continues to charge up as ions impinge on the surface of the insulating layer. If a small area, \( A \), of the insulating layer with a thickness, \( d \), is bombarded by an ion current density, \( J_i \), the capacitance, \( C \), of the capacitor is

\[
C = \frac{\varepsilon_r \varepsilon_0 A}{d} \tag{4.8}
\]

where \( \varepsilon_r \) is the dielectric constant of the insulating layer, and \( \varepsilon_0 = 8.85 \times 10^{-12} \text{ C}^2 \text{/N.m}^2 \) is the permittivity of free space. The electric charge, \( q \), on the area \( A \) of this capacitor is

\[
q = J_i At = CV \tag{4.9}
\]

where \( V \) is the voltage across the capacitor, and \( t \) is the time since it was last discharged. Since the electric field across the insulating layer is \( E = V/d \), then by combining equations (4.8) and (4.9), one gets

\[
t = \frac{\varepsilon_r \varepsilon_0 E}{J_i} \tag{4.10}
\]

The required time to charge the capacitor for the breakdown to occur, \( t_B \), can be obtained by substituting \( E \), in equation (4.10), with the value of the dielectric strength of the insulating layer, \( E_B \)

\[
t_B = \varepsilon_r \varepsilon_0 \frac{E_B}{J_i} \tag{4.11}
\]

Thus, breakdown can be prevented if the insulating layer can be discharged periodically with a period less than \( t_B \), or a frequency greater than \( 1/t_B \). Equation (4.11) indicates that \( t_B \) is dependent on the material involved and the deposition system. It also indicates that \( t_B \) is independent of variations in the thickness of the insulating layer across the magnetron (see section 4.3). This implies that all regions of the insulating layer break down instantly. In magnetrons, however, the current density across the cathode is not uniform. It is higher near the thinner regions of the insulating layer (see section 3.4). Thus, according to equation (4.11), thinner regions break down first.

To get an idea about the approximate value of \( t_B \), and hence the frequency, which are required to prevent arcing, the reactive magnetron sputtering of Si to produce films of SiO\(_2\) will be taken as an example. In SiO\(_2\), \( \varepsilon_r = 3.7 \) and \( E_B = 3 \times 10^7 \text{ V/m} \). If \( J_i = 10 \text{ A/m}^2 \) in the border of the erosion zone, the discharging period, according to
equation (4.11), should be $t_B < 100 \mu s$, which corresponds to a discharging frequency greater than 10 kHz.

On the other hand, Este and Westwood\textsuperscript{97} studied the dependence of the sputtering rate on the frequency of the power supply, at a given power, during magnetron sputtering from Al targets. They measured the deposition rates at 60 kHz, 80 kHz, 500 kHz and 13.56 MHz and found that these rates were: 100%, 85%, 70% and 55% of that of the DC one, respectively. Consequently, the upper limit of frequency should not exceed 60-80 kHz. They also found that the deposition rate of AlN films at 100 kHz is 80% higher than that at 13.56 MHz.

As a conclusion, to secure an efficient avoidance of arc formation without affecting the deposition rate, the discharging frequencies of the insulating layers should be between about 10-70 kHz.

4.6.3. Methods of avoiding arcs

Tremendous efforts have been exerted by power supplies manufacturers to shorten both the detection time of an arc, and the switching off time of the power supply\textsuperscript{86,88,89}. Although it helps to minimise the undesired effects of arcs, the rapid switching off of a power supply, upon detecting an arc, for a predetermined period of time followed by an automatic reignition of the discharge have been found to be insufficient to maintain the stability and the high deposition rate of the reactive sputtering processes of highly insulating materials\textsuperscript{77-79,83}. As a result, attention has been focused, in recent years, on finding practical methods for preventing the formation of arcs instead of suppressing the already existing ones.

As discussed earlier, an arc may be initiated by the breakdown of an insulating layer on the surface of the magnetron cathode. Such a breakdown is attributed to the accumulation of positive charges on the surface of the insulating layer to such an extent that permits the electric field across the layer to reach the value of its dielectric strength. Consequently, arcing can then be eliminated by not allowing such a degree of positive charge to accumulate, and hence, keeping the electric field across the insulating layer lower than its dielectric strength. In other words, arcing can be prevented by periodically discharging the charge build-up on the surface of the insulating layer before breakdown occurs. This can be achieved by the employment of the so-called "pulsing technique", in which a low frequency power is utilised.

In the following sections, the two ways of applying the pulsing technique, namely: the unipolar and bipolar pulsing, will be discussed.
4.6.3.1. Unipolar pulsed magnetron sputtering

![Diagram of unipolar pulsed magnetron sputtering]

**Figure (4.12): The basic arrangement for unipolar pulsed magnetron sputtering. Reproduced from reference 78.**

The basic arrangement for unipolar pulsed magnetron sputtering is shown in figure (4.12). The charge build-up on the surface of the insulating layer is restricted so that the electric field across the layer is kept below its dielectric strength. During the pulse-on time, sputtering of target material occurs and is accompanied by charge accumulation on the surface of the insulating layer. During the pulse-off time, the accumulated charge is discharged through the plasma (i.e., the charging potential is lowered via the plasma). For example, Frach et al. utilized medium frequency pulsed power input into the discharge to reactively deposit films of Al₂O₃. A DC power supply was connected to the magnetron via an electronic switching device and a "special network", as it was called, to periodically provide a pulse-on time for about 10-20 μs and a pulse-off time for about 10 μs. With this arrangement, a good process stability, a lower arcing frequency and a good film quality were attained.

Another example about effectiveness of this technique is the work carried out by Pond et al. They reactively deposited films of Ta₂O₅, Nb₂O₅ and SiO₂ as well as multilayer films of Ta₂O₅/SiO₂ (a 23-layer) to be used as an optical bandpass filter. They used the dual magnetron system which is shown simplified in figure (4.13). Since the reactive sputtering of Si in an Ar/O₂ atmosphere is accompanied by a severe arcing, the Si target was sputtered using a pulsed voltage formed by a modulator circuit and waveform generator, whereas Ta and Nb were reactively sputtered from the other target using...
normal DC voltage. The DC power supply was connected to a modulator circuit containing several switching transistors which switch the voltage from the power supply on and off according to the output of a waveform generator. The output voltage from the modulator to the Si target was modulated at 18 kHz with its most negative value equal to the output of the DC power supply, and its most positive value equal to zero. Again, good results, as far as process stability, arcing frequency and film quality are concerned, were achieved.

![Figure (4.13): Schematic of the modulated DC sputtering system. Reproduced from references 83 and 84.](image-url)
4.6.3.2. Bipolar pulsed magnetron sputtering

Instead of switching off the magnetron for a certain period of time to discharge the charged surface of the insulating layer via the plasma, as was the case in the unipolar pulsed magnetron sputtering, the surface of the insulating layer, in the bipolar mode, is discharged as a result of electron-bombardment when the polarity of the magnetron is reversed. Bipolar pulsed magnetron sputtering can be carried out using one magnetron or two magnetrons.

I. Bipolar pulsed magnetron sputtering using one magnetron

Historically, Cormia et al. were the pioneers in using the low frequency AC technique in reactive magnetron sputtering. As mentioned in section (3.2.2), at such frequencies, the system behaves as if there were two cathodes with a dark space in front of each electrode. They deposited films of TiO₂. Using a conventional AC power supply, a 10 kHz-AC potential was applied between a Ti target and a counter electrode which was, in their method, a conventional anode (a cylindrical bar along one edge of the target). During one half-cycle, the potential of the Ti target is more negative than the plasma potential and sputtering of its material occurs. In addition, the surface of the insulating layer is charged positively. In the other half-cycle, the surface of the insulating layer is discharged, due to electron-bombardment, as the polarity is reversed. The main disadvantage of Cormia's method can be explained as follows: To avoid arcing, ion and electron currents to the target must be the same (i.e., the average target current should be zero). As a result, a plasma has to be ignited even when the target is charged positively. Such a plasma is then sustained in the diode mode since the counter electrode, which now represents the cathode of the system, is a non-magnetron electrode. This requires, therefore, a very large positive voltage on the target on each half-cycle accompanied by sputtering of the counter electrode. In addition to the probable contamination of the deposited films, such an arrangement causes the electrodes to operate asymmetrically which results in an insufficient discharging of the surface of the insulating layer (e.g., SiO₂) and hence arcing, although some improvement of process stability can be achieved.

Graham and Sproul employed the bipolar pulse technique to reactively deposit films of TiO₂. They used a power supply, made by Magtron, and was capable of controlling the pulse parameters such as unipolar or bipolar mode, positive and negative pulse-on and pulse-off times, and frequency. They connected one side of the bipolar unit to the target and the other side to the chamber. The negative part of the cycle was on for 25 μs and off for 10 μs, whereas the positive part of the cycle was on for 5 μs and off for 10 μs. A reduction in the deposition rate, compared to that of the DC at the same power, was
observed. It was attributed to the time of the positive part of the cycle as well as to the pulse-off time. Alternatively, Scholl\textsuperscript{74} has designed a circuit contained an electronic switch, which may be controlled by a waveform generator, and a transformer. The output voltage of the transformer was about -0.1 of its input. The circuit periodically reverses the negative DC voltage, applied to the target, to a value about -0.1 of the operating target voltage. This voltage, which is slightly more positive than the plasma potential, allows electrons from the plasma to bombard the target and hence to discharge the insulating layer. The reversal time was about 5 $\mu$s, and the time between reversals was 50 $\mu$s. With such arrangements, Scholl\textsuperscript{74} have reactively deposited highly insulating films, including Al$_2$O$_3$ and SiO$_2$.

Finally, a problem emerged during the non-reactive DC sputtering of carbon as an overcoat for computer disks. The origin of the problem was the formation of insulating islands, called "nodules", on the carbon target which then could not be sputtered using the DC power. These nodules resulted from the implantation of hydrogen, formed by the disassociation of H$_2$O vapour presented in the vacuum chamber, into carbon. The application of low frequency AC power, as had been suggested by Cormia et al\textsuperscript{77}, could solve the problem but the deposition rate was not satisfactory. This is because the deposition rate is proportional to the sputtering yield (see equation 2.19) which is in turn proportional to the energy of the bombarding ions. Such an energy is proportional to the self-bias, and at the frequency suggested by Cormia, little negative self-bias can be achieved as the period was large compared with the transit time of the ions across the sheath (see section 3.2.2). What is needed is a sufficiently small period, compared with the transit time of the ions across the sheath, so that ions do not have sufficient time to reach the cathode and neutralise the acquired negative charge. However, increasing the frequency leads to a significant increase in the deposition rate, but this solution is not cost effective since the cost of high frequency AC power is higher than that of the DC power. To solve the problem, Scholl\textsuperscript{91} suggested adding the AC (at 400 kHz) and the DC powers together through a "combiner" which consisted of a high-pass filter in series with the AC power supply, and a low-pass filter in series with the DC power supply. High deposition rates were reported in the case of carbon. However, the deposition rate in the case of reactive sputtering of SiO$_2$ was quite low, and this was attributed to the low levels of power that can be applied in this system and to the small size of the cathode compared with that of the substrate.

\textbf{II. Bipolar pulsed magnetron sputtering using two magnetrons}

To overcome the already mentioned drawbacks of Cormia's method, a sufficient number of electrons has to be made available to bombard the target when it is biased positively.
In other words, an effective discharging of the insulating layer should be guaranteed for the sputtering process to be arc-free. On the other hand, the deposition of an insulating film also imposes another problem since the anode of the system will also be coated with the insulating material being deposited\textsuperscript{1, 74, 79, 81}. The anode, which may be the walls of the vacuum chamber or a separate electrode, acts as a collector of those electrons escaped from the plasma. The current they carry represents the return current to the power supply. Therefore, the increasing coverage of the anode with insulating layers, causes potential fluctuations and hence significant changes in the discharge parameters (i.e., an irretrievable drift in the desired set-point). Eventually, the discharge will extinguish due to the loss of an effective anode (i.e., the power supply comes to its voltage limit as a result of the increasing impedance). This problem becomes dominant in the industrial-scale production of optical films, such as SiO\textsubscript{2} and TiO\textsubscript{2}. Therefore, the coating process has to be terminated periodically to allow the anode to be cleaned. Obviously, a well-defined DC conducting anode is required for an AC sputtering process to be stable at a given set-point.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.14.png}
\caption{Bipolar pulsed magnetron sputtering using two floating magnetrons.}
\end{figure}

The above requirements can be fulfilled by using a mid-frequency AC power supply to drive two magnetrons, which are decoupled from the sputtering chamber, side-by-side in a floating manner. The electrodes are then operated symmetrically. According to figure (4.14), in each half-cycle, one of magnetrons behaves as a temporary anode while the other behaves as a temporary cathode. The voltage waveform of the two electrodes are identical, provided that the material and the oxidation state of the two targets are also identical, but are always 180° out of phase (regardless of the material and the oxidation state) as will be seen in the experimental chapters of this thesis. This conclusion has also been supported by the work of Glocker\textsuperscript{80} and Scherer \textit{et al.}\textsuperscript{82}.
Figure (4.15): Voltage between one cathode and ground during AC reactive sputtering of AlN. Reproduced from reference 79.

Figure (4.15) shows the voltage waveform between one electrode and ground during the reactive deposition of AlN from two Al targets, using a 35 kHz-AC power supply. The waveform of the other electrode, which does not appear in the figure, is identical but 180° out of phase. As discussed in section (2.2.7), if the area of the temporary anode is small, which is the case here, the potential across the anode sheath is positive with respect to the plasma potential, allowing more current to the anode. In fact, the potential of the temporary anode, in this technique, is usually of the order of only several tens of volts and is more positive than the positive plasma potential (usually of the order of several volts). Such a relatively small potential difference is sufficient for electrons, which are very mobile, to bombard the surface of the insulating layer to discharge it from the positive charge which had accumulated, during the negative half-cycle, as a result of bombardment by the very less mobile ions subjected to a relatively much higher negative potential difference. Thus, the requirement that, to avoid arcing ion and electron currents to the target must be the same, is fulfilled. Meanwhile, besides being sputtered, the temporary cathode provides the required electrons to discharge the surface of the insulating layer on the temporary anode. This periodical sputtering from each electrode results in a self-cleaning effect which leaves the centre of the erosion zone to be highly DC conducting which results in well-defined anodes and cathodes. Furthermore, such an arrangement allows for an effective decoupling of the processes on the electrodes from those on the substrate and the walls of the chamber. This is of great importance for the stability a sputtering process in which the substrate is moving in front of the cathode.

Glocker has studied the difference between 35 kHz-AC and DC plasmas, during the reactive magnetron sputtering of AlN. His calorimetric measurements, at a total power
of 500 W, revealed that the substrate temperature in the AC case was somewhat higher than that of the DC. In terms of figures, he found that the average deposition rate and the energy delivered to the substrate per atom, in the DC case, were 0.82 nm/s and 20 eV, respectively, and 0.70 nm/s and 32.8 eV in the AC case. To find out the reason behind that, he used Langmuir probe. His Langmuir probe measurements, under his experimental conditions, revealed:

1. The electron energies in the AC plasmas (3.2 eV) are slightly higher than in the DC plasmas (2.4 eV).

2. The differences between the plasma and the floating potentials are comparable (7 V in the AC case and 6.7 V in the DC case).

3. The average ion densities in the AC plasma is about four times that of the DC plasma.

The last difference, between the AC and the DC plasmas, is the most significant. According to optical emission measurements, the plasma extinguishes on each half-cycle and has to be reignited. The increase in ion densities in the AC plasma was attributed to target voltage spikes during the reignition of the plasma on each half-cycle, as it is evident on the negative-going part of each cycle (see figure 4.15). Such spikes cause rapid electron acceleration in the presheath region leading to significantly more efficient ionisation of gas and hence much higher plasma bombardment.

This emerging technique has been utilised recently by a few workers. The results were very promising. For example, Szczyrbowski and Braatz have reactively deposited films of SiO₂ at high rates using 40 kHz-AC power applied between two Si magnetrons. In addition to the excellent optical and mechanical properties of the deposited films, no arcing was observed during the entire lifetime of the target which was more than a week. Schiller et al. have reactively deposited films of Al₂O₃ from two Al magnetrons using an AC power at different frequencies ranged from 50 Hz to 164 kHz. They reported a significant decrease in the defect density of the deposited films with increasing frequency. The curve, for non-absorbing films, saturated at frequencies greater than 50 kHz which was an indication of an arc-free process beyond this frequency. They also reported a deposition rate of about 60% of that of metallic Al. The rate was almost independent of the frequency in the range they investigated. Scherer et al. have also adopted the two cathodes technique to reactively deposit films of Al₂O₃, SiO₂ and Si₃N₄ using 40 kHz-AC power. They reported deposition rates comparable to those obtained with the DC power.
To summarise, bipolar pulsed magnetron sputtering technique, using two magnetrons, enjoys the following advantages:

1. The periodical effective discharging of the insulating layer, due to the symmetrical operation of the electrodes, allows the reactive sputtering process to be arc-free\textsuperscript{82}. Consequently, the defect density in insulating films is reduced by orders of magnitude\textsuperscript{79} in comparison with the DC technique.

2. The well-defined DC conducting anode allows the sputtering process to be stable at a given set-point.

3. The high deposition rates obtained are comparable with those of the DC technique\textsuperscript{74,78,82}.

4. Unlike the additional complexity of the RF technique, the coupling of the AC power to the cathodes, in the frequency range used, is simple. Consequently, the AC technique can be easily adopted for sputtering from larger area cathodes\textsuperscript{82}.

5. It is important to note that the deposition of highly insulating films creates another problem regarding ion-bombardment of the growing film. The accumulation of positive charge on the surface of the film prevents any further bombardment. The AC technique helps in discharging the surface of the growing film during the positive half-cycle, allowing continuous bombardment\textsuperscript{1}.

6. The substrate temperature in AC plasmas is higher than that in similar DC plasmas\textsuperscript{80}.
REFERENCES


CHAPTER FIVE

EXPERIMENTAL: SYSTEM AND PROCESS CONSIDERATIONS

5.1. Introduction

A spinning disc multiple station system was used throughout this work to sputter-deposit a variety of oxide films. To identify optimum films one should have a stable and continuously operating system. Stability was achieved by using PEM or voltage control. Both DC and 40 kHz-AC power have been used and combined together in a novel way to allow the reactive sputtering process to be arc-free. Dopants were added as metals which were subsequently oxidised in the SPA process created by circulating the substrate between two magnetrons (section 4.5.3). Activation of oxygen to provide higher reactivity on the substrate was achieved by the use of unbalanced magnetrons. Continuous operation for maintaining conditions while iterative changes were made to determine optimum films was allowed by using airlock entering for substrates.

In this chapter, a detailed description of this system as well as modifications carried out on it, in order to serve the purpose of this work, will be given. Methods of control of reactive gas admission and methods of power application which were utilised will be discussed. Finally, the deposition procedure and process will also be described.

5.2. The deposition system

Figure (5.1) shows photographs of the deposition system used in the course of this work. A schematic of the system is seen in figure (5.2). The various parts of this system will be reviewed in the following sections.

5.2.1. The deposition chamber

Figure (5.3) shows photographs of the inside of the deposition chamber. A side and overhead view of the chamber are shown in figures (5.4) and (5.5), respectively.
Figure (5.1): Photographs of the deposition system used in this work.
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<td>6030B, .2 Meter</td>
<td>Rofin Limited, Verity Instruments</td>
</tr>
<tr>
<td>26, 27</td>
<td>Digital voltmeters</td>
<td>PM 2517 X</td>
<td>Philips</td>
</tr>
<tr>
<td>28</td>
<td>Pirani gauge for the chamber</td>
<td>GP-210 C</td>
<td>Bendix</td>
</tr>
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</table>
Figure (5.2) : A schematic diagram of the sputtering system.
Figure (5.3): Photographs of the inside of the deposition chamber.
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<td>3</td>
<td>Opening in the rotating platen to accommodate the substrate holder</td>
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<td>Vacuum chamber-turbomolecular pump interface</td>
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<td>6</td>
<td>Shaft attached to the platen and connected to the DC motor (stainless steel)</td>
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Figure (5.4): A side view of the deposition chamber.
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<td>2</td>
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<td>8</td>
<td>Secondary magnetron</td>
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<tr>
<td>9</td>
<td>Shaft attached to the platen and connected to the DC motor</td>
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</tbody>
</table>

**Figure (5.5):** An overhead view of the deposition chamber.
The chamber, labelled '4' in figure (5.4), comprised a 42 cm diameter stainless steel chamber, 12 cm deep internally, giving a short pump down time compared with conventional bell-jar systems. The chamber base accommodated two identical magnetrons. The magnetron, which had both the oxygen inlet to the chamber and the optical fibre input tip of PEM control loop, labelled '10' and '12' respectively in figure (5.4), attached to its pod will be, henceforth, called 'main magnetron'. The target attached to it is called 'main target'. It is labelled '7' in figure (5.4). The other magnetron, which was connected to the argon inlet to the chamber, labelled '14' in figure (5.4), will be, henceforth, called 'secondary magnetron' and the target attached to it called 'secondary target'. It is labelled '18' in figure (5.4).

Deposition was in a "sputter up" orientation to prevent flakes of loose material falling onto the substrate during the process. It was felt that it is more beneficial to prevent film contamination in this way, even though it might allow flakes to fall back to the cathode, leading to short-circuits of the magnetrons.

An axially mounted aluminium platen, labelled '2' in figure (5.4), was located above the magnetron cathode surfaces, and it was onto this platen, which was floating, that substrates were loaded from the airlock allowing a target-to-substrate distance of about 40 mm. The centrally-oriented metal shaft, labelled '6' in figure (5.4), was attached to the platen so that it could be rotated around this axis by the application of up to 30 V to a DC motor, labelled '12' in figure (5.2). This achieved a rotation speed of up to 60 r.p.m. In order to transmit mechanical movement from atmosphere into the vacuum system, the highly polished rotary shaft was passed through a hole, in a greased and suitably supported elastomer, whose diameter was 20-35% smaller than that of the shaft (Wilson seal)\(^1\).\(^2\).

Base and process pressures were monitored using Penning and Pirani gauge sensors, respectively. Both sensors were located at the base of the chamber.

### 5.2.2. The airlock system

The system was airlocked, that is, the main deposition chamber always remained under vacuum whilst the samples could be loaded/unloaded via a separately pumped airlock. The airlock system is labelled '22' in figure (5.2). A manual vacuum gate valve, series 12, manufactured by VAT Vacuum Products was used, a photograph of it is seen in figure (5.6). The airlock was a 10 cm in diameter and 4.6 cm deep, had a 0.361 l volume, and could typically be evacuated from atmosphere to approximately 40 mTorr in about 2 minutes, via an E2M2 two-stage rotary pump, labelled '15' in figure (5.2), with a pumping speed of 0.783 l/s.
Figure (5.6): A photograph of the manual vacuum gate valve used in the airlock system.

Figure (5.7): A photograph of the perspex plate and the loading arm used in the airlock system.
The pressure in the airlock chamber was measured via a Monitorr 101 Pirani gauge, labelled '24' in figure (5.2), using a PR 10-K sensor, labelled '23' in figure (5.2). The pump, the gauge and the sensor were manufactured and supplied by Edwards.

Samples were mounted singly in a jig, which was then attached to the end of a loading arm. A perspex plate sealed against a rubber 'o-ring' recessed into the surface of the airlock. The 1/4" rotary/linear shaft of the loading arm was free to move through a double Wilson-type vacuum seals, mounted off axis (2.2 cm from the centre) in the perspex window plate, without affecting the integrity of the process vacuum. These seals were designed to transmit mechanical movement from atmosphere into the vacuum chamber. Figure (5.7) shows a photograph of the perspex plate and the loading arm.

Airlock systems offer a great advantage, especially for iterative reactive processing, in which the partial pressure of the reactive gas is varied gradually until the desired film properties are attained.

5.2.3. The pumping system

The pumping system consisted of a turbomolecular pump backed by a two-stage rotary pump. A rotary pump influences gas transport by a rotating cylinder which trap and carry out a volume of gas. Turbomolecular pumps are generally used in applications where high throughput and lowest oil contamination are needed. A turbomolecular pump contains a high speed rotor (tip speeds of about 400 m/s) with several rotating rows of blades alternating with stationary blades. A coolant is, therefore, required for the bearings. Pumping is accomplished by momentum transfer from the rotating blades to molecules of the pumped gas. If the pressure in the pump is maintained sufficiently low so that molecular gas flow (i.e., where the mean free path of molecules is larger than the spacing between opposite surfaces) prevails, efficient momentum transfer from the rotating blades to gas molecules occurs since molecule-blade collisions dominate and the turbomolecular pump operates efficiently. On the contrary, if the pressure in the pump is high, viscous gas flow prevails where intermolecular collisions dominate and the turbomolecular pump operates inefficiently. Thus, backing the turbomolecular pump (e.g., using a rotary pump) is required to hold the outlet of the pump at sufficiently low pressure, generally below 10 mTorr, to maintain molecular flow throughout the turbomolecular pump. Above such a pressure, an abrupt decrease in the pumping speed of the turbomolecular pump occurs.
In the system used in this work, a base pressure of $2 \cdot 10^{-6}$ Torr was achieved in less than three hours by the use of a Turbovac 360 turbomolecular pump, labelled '16' in figure (5.2), having a rotation speed of 45000 r.p.m. and a pumping speed of 345 l/s for N$_2$. The turbomolecular pump was backed by an LH Trivac D16 B two-stage rotary pump, labelled '20' in figure (5.2), with a rotation speed of 1500 r.p.m. and a pumping speed of 4.6 l/s for air. Both pumps were manufactured and supplied by Leybold-Heraeus™. The rotary pump was reducing the pressure from atmospheric to about 10 mTorr in approximately 4 minutes. Around this value of pressure the water-cooled turbomolecular pump was started.

5.2.4. Pressure measurements

Due to the wide range of pressure measured in vacuum technology, a large number of vacuum gauges have been developed. Each gauge has a specific measuring range. In this work, two types of vacuum gauges were used. A Pirani gauge for pressures higher than millitorr order, and a cold cathode vacuum gauge (Penning gauge) for pressures lower than millitorr order.

5.2.4.1. Pirani gauge

The basic principle of this gauge depends on the fact that, in the molecular flow regime, the thermal conductivity of a gas increases with increasing pressure (whereas it is independent of pressure in the viscous regime). The Pirani gauge sensor contains a tungsten wire enclosed in a glass or metal envelop and is connected to the work chamber to form one arm of a Wheatstone bridge. A reference, which forms another arm of the bridge, is made by enclosing an identical wire in another envelope which is highly evacuated. A constant voltage is applied to the bridge and hence the same current is passed through both wires as long as the pressure is sufficiently low. The other two resistors in the bridge are adjusted so that the current in the central branch of the bridge is zero. At higher pressures, where the thermal conductivity of the gas increases, the temperature of the sensing wire and hence its resistance decrease. This upsets the balance of the bridge. The current through the unbalanced bridge is used as a measure of the change in pressure. These gauges are not effective at pressures below about $10^{-3}$ Torr, because at such low pressures, heat from the wire is transferred mainly by radiation, which is a pressure independent mechanism. Calibration of thermal conductivity gauges, including the Pirani gauge, is necessary since its sensitivity changes with gas type. This calibration is commonly carried out for N$_2$ or dry air as their thermal conductivities are almost identical. If the pressure of another gas (e.g., Ar) is to be measured, readings of the gauge can be converted into corrected values by using calibration curves.
Two Pirani gauges were employed, in this work, to measure the chamber pressure: (i) A Leybold Inficon™ CC3 cold cathode vacuum gauge controller precalibrated for N₂ or Ar, labelled '4' in figure (5.2), with a Leybold Inficon™ LH DE 968 Pirani sensor, labelled '13' in figure (5.2), to measure the chamber pressure as it was being rough pumped during pump down (using the rotary pump), before the turbomolecular pump was started; (ii) A Bendix GP-210 C, labelled '28' in figure (5.2), precalibrated for Ar, to measure the process pressure.

It is worth mentioning the difficulty in measuring oxygen partial pressure in this system in most stoichiometric regions because it was very low (unless it was very high in the insulating oxides regions) due to:

1. The very efficient control system (see section 5.2.8).
2. The existence of the pods which confined the oxygen to a very small region over the target.
3. The very high pumping speed, due to the turbomolecular pump, and the position of oxygen inlet to the chamber close to the pump's baffle.
4. The very small volume of the chamber.

5.2.4.2. Cold cathode vacuum gauge (Penning gauge)

High vacuum Penning gauges uses the current of a glow discharge, which is the sum of ion and electron currents, as a measure of the gas pressure. A magnetron discharge is used because it can be sustained at a very low pressure and hence pressures of the order of 10⁻⁶ Torr can be measured. Crossed electric and magnetic fields of about 2 kV and 600 Gauss, respectively, are usually applied. The penning gauge should never be utilised at higher pressures (of the order of 10⁻³ Torr) because of the risk of sputtering from its cathode.

The base pressure was measured via a CC3 cold cathode vacuum gauge controller, labelled '4' in figure (5.2), using a P/N 850-610-G1 Penning sensor, labelled '10' in figure (5.2). When the system pressure rose above threshold, the cold cathode gauge would automatically turn off and the display changed over to the Pirani sensor. Both the gauge and the sensor were manufactured and supplied by LH Leybold Inficon™.

5.2.5. Gas admission and flow measurements

All components marked with an asterisk in the this section were manufactured and supplied by Vacuum General.
5.2.5.1. Inert gas arrangements

An Ultra Flow® mass flow controller, labelled '18' in figure (5.2), with a built-in solenoid valve, was connected to an 80-55° flow command and display module, labelled '19' in figure (5.2). With the set-point of the latter indicating the desired mass flow, a potential is applied to the valve allowing it to open and admit an initial flow rate of inert gas to the chamber. The measured flow rate is passed from the mass flow controller back to the flow command module, where it is compared with the set-point. The closed loop circuitry admits inert gas until the two are equal, the desired flow rate henceforth maintained by the comparator.

5.2.5.2. Reactive gas (oxygen) arrangements

The same concept of inert gas admission to the chamber can be applied to reactive gas admission with some exceptions:

1. The solenoid valve was replaced by a piezoelectric valve which had a faster response, to cope with much faster changes in the desired supply of reactive gas required to maintain a certain cathode status compared with that of inert gas. A 77-10 M° piezoelectric valve, labelled '8' in figure (5.2), with a response time of less than 2 ms was connected to a 77-360-1000 RF® (FM 360) mass flow controller, labelled '7' in figure (5.2), which acted in this work, only as a mass flow meter (after removing the solenoid valve). Upon entering the device, the turbulent flow from the storage bottle is converted into laminar flow. A small part of this flow is then diverted through a glass sensing tube, in which two heated resistance thermometers are located. When the gas flows across the tube, the amount of heat which is removed by the gas from the first thermometer in line is greater than that removed from the second, leading to a temperature imbalance between the two thermometers. This imbalance is converted into an electrical signal which is linearly proportional to the mass flow rate.

2. The 80-55° module used as a command and display unit for the inert gas was replaced for admission of reactive gas by: (i) An 80-4° flow/ratio controller, labelled '2' in figure (5.2), acting only as a mass flow display, and connected to the mass flow meter '7'; (ii) An 80-1° automatic pressure controller, labelled '1' in figure (5.2), functioning as a controller of reactive gas flow rate to the chamber (henceforth, 'process controller'), using the feedback signal derived from the controlling technique used (PEM or voltage control).

At the outset, the internal diameters of the admission pipes for both inert and reactive gases were 1.5 mm. Despite admission through a piezoelectric valve, which has a very
fast response time, the time constant for adjustment and maintenance of \( \text{O}_2 \) partial pressure in the chamber, to alter oxygen flow rate according to the target status, was too long. This made the control of the process almost impossible.

The inside diameter of the reactive gas pipe was increased, taking into account the limits allowed by the fitting of the chamber and availability of materials, to 4.2 mm. This increased the flow cross section by a factor of about 7.8. Assuming an equal pressure difference between the ends in both pipes, ability to deliver reactive gas was increased by about 8-60 times (flow rate \( \propto \) area for turbulent flow and flow rate \( \propto \) area^2 for laminar flow).

Conversely, the total distance between the reactive gas pipe exit in the chamber and the piezoelectric valve was minimised (to about 22 cm) to help reduce the time constant of the pipe.

These modifications, allied with the pipe outlet being very close to the target in the very confined volume provided by the gettering pods, labelled '8' and '17' in figure (5.4), and other factors, such as the high pumping speed of the system and low volume of the vacuum chamber enabled very efficient control of the reactive deposition processes.

5.2.6. Magnetron design

The implications of magnetron design and the materials used to construct magnetrons have been discussed, in general, in section (3.4). In this section, the concentration will be on the particular design of the magnetrons used in this work.

Two circular planar magnetrons were used and onto each was mounted a 4" (i.e., \(~10.2\) cm)-diameter target. A schematic and a photograph of one of the two identical magnetrons are shown in figures (5.8) and (5.9), respectively.

The magnetic field was obtained by the use of concentric rings of magnets, sitting in the water channel. The seven inner magnets were cylindrical, each with a diameter of 5 mm and height of 10 mm which were made of bonded neodymium-iron-boron. In the outer ammulus, the magnets were sintered samarium cobalt. The dimensions of each outer magnet were 10 x 10 x 3 mm and they were assembled in 24 groups, each of three magnets, with total dimensions of 10 x 10 x 9 mm.
Figure (5.8): A cross section of the magnetron used in this work.

Figure (5.9): A photograph of one of the two identical magnetrons.
All magnets were made by Magnet Developments Limited. A homemade Gaussmeter, with flux probe which measures the magnetic flux perpendicular to its plane, was used to measure the magnetic field and the zero point of the magnetic field. The magnetic field in front of the magnetron was measured by making the plane of the probe normal to the magnetron surface and in contact with it. The probe was then moved along the radius of the magnetron. The maximum transverse component of the magnetic field was 400 Gauss parallel to the magnetron surface at the centre of the erosion zone. Figure (5.10) shows a photograph of an eroded Zn target with an image of the erosion profile, and another photograph of the same target after being completely eroded. It can be seen that the entire surface area of the target was subject to erosion, except for 18 mm diameter central disc and a 6 mm wide peripheral zone, the latter due to earth shield masking. Maximum erosion within the racetrack was seen at a diameter of 62 mm (i.e., at 31 mm from the centre of the target).

On the other hand, to determine the zero point of the magnetic field (the null-point), the plane of the probe was made parallel to the magnetron surface, opposite to its centre, and moved away from the magnetron surface along a line normal to its surface. The zero point of the magnetic field was about 57 mm from the centre of the magnetron. This implies that the substrate, which was about 40 mm from the magnetron surface, was immersed in the plasma but below the null-point. Figure (5.11) shows a photograph of the magnetic field lines of the magnetron using iron filings. The solid line in the photograph represents the actual position of the substrate.

As mentioned in section (3.4), the magnetic circuit consists of the magnets as well as the rear and sometimes front poles. In the magnetrons used in this work, the rear poles were made from mild steel (< 0.6% carbon), which is a magnetic material. Conversely, in order to prevent contamination of deposited films, no front poles were used. This was on account of the target utilisation which was found to be about 23% by weighing the target before and after sputtering through to the rear surface.

The target was water-cooled via a 0.25 mm thick stainless steel diaphragm to avoid a direct contact between the rear of the target and cooling water. Although it generally increases the cooling efficiency, direct contact encourages ruining of the 'o-ring' as a result of successive substitution of targets, causing water leaks due to the accumulation of calcium from the water on the rear of the target and, most important, increases the risk of flooding of the deposition chamber with water if the target is sputtered through to the back surface.

The pressure, input temperature and flow rate of the cooling water were $3 \times 10^5$ N/m$^2$, 7.9°C and 0.0385 l/s (i.e., 0.0385 kg/s), respectively.
Figure (5.10): A photograph of an eroded Zn target with an image of the erosion profile, and another photograph of the same target after being completely eroded.
Figure (5.11): A photograph of the magnetic field lines of the magnetron using iron filings. The solid line in the photograph represents the actual position of the substrate.

The output temperature of the cooling water was 10.7°C when one target was operated at 500 W. The amount of heat, $Q_w$, removed by the cooling water is given by:

$$Q_w = m_w c_w \Delta T,$$

where $m_w$, $c_w = 4190$ J/kg·K and $\Delta T$ are the mass, specific heat capacity and the change in the water temperature, respectively. Thus, ignoring heat transfer by radiation, the amount of heat removed by the cooling water per second was about 451 W which was about 90% of the applied power. The remaining 10% of the applied power goes mainly to ions, to sputter the target material and to bombard the substrate when the magnetron is unbalanced, and to electrons to bombard the anode of the system. This result provides experimental evidence about sputtering being an inefficient process, as mentioned in chapters two and three.

The magnetron body was made from copper. The earth shield, clamping ring and screws were made from stainless steel. The pod, which was an extension of the earth shield, was made from aluminium. Copper, stainless steel and aluminium are non-magnetic materials.
5.2.7. Methods of power application

For coating composition to be controlled, the sputtering rate from each magnetron has to be flexibly and independently manipulated. This can be achieved by controlling the current (or power) to each magnetron (see equation 2.17).

Three different methods have been used, in this work, to apply power to the magnetrons. These methods will be discussed in the following sections.

5.2.7.1. Independently DC powered magnetrons

In this method, the two magnetrons were powered independently, using two identical DC magnetron power supplies. The DC power supply used throughout this work was an MDX 2500-W Magnetron Drive, which was manufactured and supplied by Advanced Energy Industries, Inc. The MDX power supply, which was connected to the magnetron using a coaxial UHF cable with the inner core carrying the negative potential and the shield securing earth protection, provides about 0-1000 V at a current dependent on the power rating of the supply. The MDX power supply allows three modes of regulation: constant current, voltage or power, and throughout the work, the latter was selected. Upon sensing a large current spike due an arc, a shut down circuitry within the MDX power supply shuts off the power to the magnetron for 5-10 ms, to substantially reduce the energy delivered to the arc to allow it to extinguish. This followed by an automatic reignition of the discharge. The MDX power supply also has a ramp button which allows one to pre-program the time taken to go from zero output to the desired set-point. This is very useful, for example, when starting a newly cast target or targets that are prone to arcing (e.g., Al and Ti).

5.2.7.2. Mid-frequency AC powered magnetrons in floating mode without a DC bias

The theoretical justifications behind using the mid-frequency AC sputtering technique have been reviewed in section (4.6). The theory of the bipolar pulsed magnetron sputtering technique, using two magnetrons, has been discussed in section (4.6.3.2-II).

The AC magnetron power supply used throughout this work was a PE 2500 Generator, which was manufactured and supplied by Advanced Energy Industries, Inc. The output frequency and power of the PE power supply are 40 kHz ± 100 Hz and 2500 W at 550 V nominal output, respectively. When an arc occurs, the PE supply turns off within 0.1 ms of sensing it, and reignites the discharge in 3 ms. This power supply regulates power. The output power remains constant while the current and voltage vary within the ranges specified by the internal circuitry. One can only specify the desired power level using a
Chapter Five

10-turn potentiometer, and the PE power supply calculates the actual output power and displays it (i.e., the power supply does not display the desired set-point). If both powers are within 0.2% of each other, the power supply is then operating within set-point and the set-point LED is lit. Otherwise, the set-point LED flashes and the unit is out of set-point.

The current and voltage readings from the PE supply are the root-mean-square (or effective) values $I_{\text{r.m.s.}} = I_m / \sqrt{2}$ and $V_{\text{r.m.s.}} = V_m / \sqrt{2}$, respectively, where $I_m$ and $V_m$ are the amplitude of the current and the voltage waves, respectively. The power reading is the average power, $\bar{P}$, which is given by: $\bar{P} = I_{\text{r.m.s.}} V_{\text{r.m.s.}} \cos \phi = \frac{P_{\text{max}}}{2} \cos \phi$, where $\cos \phi$ is the power factor and $P_{\text{max}} = I_m V_m$ is the maximum power.

The PE power supply is normally connected to the magnetron using a coaxial UHF cable with the inner core carrying the electrical signal (i.e., the voltage waveform) and the shield securing earth protection. Alternatively, the output of the supply can be floating (i.e., to allow the current to swing between the two magnetrons) by disconnecting the link between the output connector ground and the supply case. To operate the two magnetrons in floating mode, each of the two lines of the output was connected to the inner of a standard UHF square socket. The two sockets were mounted in a metal box whose body was connected to the earthed case of the power supply. This provided full earth protection of the output to minimise electrical interference with other equipment. A standard coaxial UHF cable was then connected to each socket to power one of the magnetrons with the inner core carrying the electrical signal and the shield providing earth protection. These arrangements are seen in figure (5.12). In addition, two built-in potential dividers (do not appear in the figure) with a division ratio of 1/100 each, were added to the box to allow for oscilloscope monitoring at the output of the PE power supply through two standard BNC sockets.

The first attempt to operate in the floating mode used the pods as well as the platen (see figures 5.4 and 5.8). Unfortunately, no discharge occurred. However, the discharge did occur when either the pods or the platen were omitted. In fact, the distance between the surface of the pods and the platen was only about 7 mm (i.e., the difference between the target-to-substrate distance, which was about 40 mm, and the pod height, which was about 33 mm). This distance was increased to about 18 mm by reducing the height of the pods from 33 mm to 22 mm to allow the electrodes to 'see' each other more effectively and hence the AC discharge between the two floating electrodes to strike.

Using oscilloscope monitoring, two important experiments were carried out to find out the voltage waveform that comes out of the PE supply to feed each magnetron, and the phase shift between these waveforms. In all these experiments, the base pressure was

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Figure (5.12): The arrangements used to allow the two magnetrons to be operated in the floating mode.
2.10⁻⁶ Torr, the working pressure was 2.10⁻³ Torr and the applied AC power was 1 kW floating between the two magnetrons. In the first experiment, two Al targets were sputtered in an inert (Ar) atmosphere. A reproduction of the photograph taken from the oscilloscope, for the voltage waveforms of the two floating outputs of the PE supply relative to ground, is shown in figure (5.13). It is obvious that the two waveforms are identical with each one running from a maximum of ~ +300 V to a minimum of ~ -1130 V at a frequency of 40 kHz (i.e., 25 μs period), but are always 180° out of phase. In another experiment, the Al target of the main magnetron was replaced by a Zn one, keeping other conditions the same. Although the voltage waveforms of the two cathodes were still 180° out of phase, they were no longer identical, as can be seen in figure (5.14). The main magnetron (Zn) was running between ~ +420 V and ~ -1260 V, whereas the secondary magnetron (Al) was running between ~ +270 V and ~ -1100 V.

Figure (5.13): A reproduction of the photograph taken from the oscilloscope for the voltage waveforms of the two floating outputs of the PE supply relative to ground. Note that the period was 25 microseconds corresponding to a frequency of 40 kHz.
Operating the magnetrons in the floating mode, on its own, was not enough to vary the composition to reach that desired for reactively sputtered coatings from elemental targets. The reason behind this lies in the fact that the applied power to the floating magnetrons $P_{M+S}$ by the AC power supply will have the following formula

$$P_{M+S} = P_M + P_S$$  \[5.1\]

where $P_M$ and $P_S$ are the powers received by the main and the secondary magnetron, respectively. As will be discussed later, the same current $I$ flows in the circuit. If $V_M$ and $V_S$ are the voltages of the two magnetrons, respectively, then

$$P_{M+S} = I(V_M + V_S)$$ \[5.2\]

Equation (5.2) indicates that the distribution of the applied AC power between the magnetrons depends mainly on the ratio $V_M/V_S$, which was considered too limiting to control coating composition. In the special case where the target materials, of the two identical magnetrons, are the same, the applied power is equally shared between the two magnetrons\(^{16}\), since $V_M$ is then equal to $V_S$.

5.2.7.3. Mid-frequency AC powered magnetrons in floating mode with a DC bias

The above discussion implies that, for coating composition to be easily controlled, the amount of power (or current) received by one/both of the floating magnetrons has to be flexibly and independently varied. This was achieved by DC-biasing one of these magnetrons. In most cases, the two floating magnetrons were held at a constant AC power, using the 40 kHz PE supply, whereas the DC power applied to one of the magnetrons was varied, using the MDX supply. Such a method of combined AC and DC power application enjoys the following major advantages:

1. It paves the way for producing coatings of virtually any desired composition by simply varying the ratio of the applied DC and AC powers.

2. It retains the advantages of applying mid-frequency AC power, between two floating magnetrons, which has been mentioned in section (4.6.3.2-II).

3. It also retains the advantages of applying DC power, such as high deposition rates onto large area substrates.

The major obstacle which had to be considered, before being able to practically employ the combined AC and DC technique, was how could the AC and the DC power supplies be protected from each other?
Figure (5.14): The filter used to protect the DC power supply from AC currents.
There was, however, no problem with protecting the AC power supply from the DC current. A built-in capacitor at the output stage of the AC power supply blocks such a DC current. Conversely, a filter had to be designed to protect the DC power supply from the AC current. Figure (5.14) shows a schematic diagram of the arrangements used in the combined AC and DC technique. The impedance of each L branch of the filter is $X_L = \sum \omega L = 0(\omega L) = 8.45 \, \text{kΩ}$, where $L = 5.6 \, \text{mH}$ is the inductance of each inductor and $\omega = 2\pi v$ is the angular frequency in (rad/s), where $v = 40 \cdot 10^{-3} \, \text{Hz}$ is the frequency of the AC power supply. The impedance of the C branch of the filter, at this frequency, is $X_C = 1/\omega C = 8.45 \, \text{kΩ}$, where $C = 0.47 \cdot 10^{-6} \, \text{F}$ is the capacitance of the capacitor. The filter allows virtually all the DC current ($\omega = 0$) to reach the biased magnetron ($X_L = 0$ and $X_C = \infty$), whereas it prevents the AC current from reaching the DC power supply. For example, ignoring the internal resistance of both power supplies, the equivalent impedance of the filter is $Z_{\text{eqv}} = X_L + [X_L X_C/(X_L + X_C)]$. Since $X_L \gg X_C$, then $Z_{\text{eqv}} \approx X_L \approx 8.45 \, \text{kΩ}$. If, for instance, the applied AC voltage at the point 'a' in figure (5.14) is $V_a = 600 \, \text{V}$, which represents the full-scale output voltage of the PE power supply, the AC current $I_1$ is $I_1 = V_a / Z_{\text{eqv}} = 71 \, \text{mA}$. On the other hand, the AC current to earth, through the capacitor, is $I_2 = V_c / X_C$ and the remaining AC current to the DC power supply is $I_3 = V_c / X_L$, where $V_c$ is the voltage at the point 'c'. Since $I_1 = I_2 + I_3$, then $V_c \approx 0.6 \, \text{V}$, $I_2 \approx 71 \, \text{mA}$ and $I_3 \approx 71 \, \mu\text{A}$. This very insignificant value of $I_3$ proves that the filter is very effective in attenuating (or even blocking) the current from the AC power supply to the DC one.

It was very important to verify that, when the above arrangement was used, the DC bias was virtually applied to one magnetron and not the other (i.e., a variable sputtering rate with the DC bias from one magnetron and not the other). It should be emphasised first that the plasma was earthed, otherwise no DC current could flow in the DC part of the circuit in figure (5.14). The experiments were carried out with two Al targets, sputtered in an Ar atmosphere. It was difficult to measure the current using a clamp because of coaxial shielding effects. In addition, it was difficult to measure the current using the oscilloscope, the easiest method being the use of a current probe, but even with this, there were difficulties in connecting the live probe head in line with the magnetron. Above all, this current probe was unavailable for this work. Alternatively, an oscilloscope was used to measure the DC potential developed on the magnetrons, relative to earth, in the following cases:

(i) On one of the magnetrons when the applied power was 100 W AC floating between the two magnetrons (figure 5.15.a).
(a) On one of the magnetrons when the applied power was 100 W AC floating between the two magnetrons

(b) On the biased magnetron when the 100 W AC floating was combined with 300 W DC

(c) On the non-biased magnetron when the 100 W AC floating was combined with 300 W DC

Figure (5.15): A reproduction of the photographs taken from the oscilloscope for the DC potentials, relative to earth, developed on a floating, biased and non-biased Al magnetrons
(ii) On both the biased (figure 5.15.b) and the non-biased (figure 5.15.c) magnetrons, when the 100 W AC floating was combined with a 300 W DC power to bias one of the magnetrons (a common case).

A similarity can be noticed between figures (5.15.a) and (5.15.c). To understand the reason behind that, the reader is referred to figure (5.14). The capacitor shown in the AC part of the circuitry is an internal component of the output stage of the AC power supply. Its purpose is to block any DC component of current, should there be any, emanating from the AC power supply, and has two-fold ramifications. The first is that the current, in the AC part of the circuit, is forced to be the same in both directions when a DC bias is applied. Secondly, without a DC bias, the capacitor is charged/discharged following the voltage waveform of the AC power supply. Alternatively, when a DC bias is applied to one of the magnetrons, the capacitor is charged/discharged (via the biased magnetron) following the voltage difference $V_a - V_b$, where $V_a$ is the fixed DC voltage and $V_b$ is the alternating AC one. This leads to a slight change in the AC current in the AC part of the circuit from that when only the AC power was applied. As a result, a slight change in the voltage of the non-biased magnetron should also occur to maintain AC current magnitude in both directions. In other words, for periods when the AC current flow is in the same direction to the DC current, the capacitor will charge due to the latter. This accumulated charge is discharged onto the biased magnetron. In order to maintain AC current magnitude in both directions, the non-biased magnetron must develop an appropriate bias, as can be noticed by comparing the positive voltage regions of figures (5.15.a) and (5.15.c). Consequently, figure (5.15.a) can be regarded as a representative voltage waveform for such a circuit. Comparing figures (5.15.a) and (5.15.c), it is suggested that the AC current (in the AC part of the circuit) is indeed approximately equal in both cases. The magnitude in both directions are approximately equal, within the biased magnetron arrangement.

On the other hand, as previously stated, whenever the DC potential of the magnetron is negative with respect to the plasma potential (earth potential in this case), sputtering will occur. It is easy to see, then, from figure (5.15.b), that the biased magnetron is sputtering continuously, albeit to various degrees. Figure (5.15.c) shows that the non-biased cathode is not sputtering continuously; although it attains a potential of about -550 V, these periods are short compared to the 'off times', when its potential goes positive with respect to plasma potential.

To summarise, the above paragraphs have shown, in sequence, that
Chapter Five

1. The biased magnetron is tied to a DC potential. The current to it is the sum of the DC current driven from the DC power supply and the current that is driven from the AC power supply. The existence of a DC bias means that the plasma has to be earthed to allow the DC current to flow.

2. The non-biased magnetron will adjust its voltage so as the AC current flowing around the AC part of the arrangement is approximately equal in magnitude for both current directions (i.e., to both magnetrons). This results in a constant AC power applied to each cathode, provided the target materials are identical.

3. The DC voltage figures illustrate that the biased magnetron is sputtering continuously, and that the magnitude of its DC potential does not appear on the non-biased magnetron in any discernible form.

To conclude, then, the non-biased magnetron has been shown to be independent of the DC-biased one, confirming the experimental observations of continuously variable dopant (i.e., bias-induced) concentrations.

5.2.8. Methods of control

Two methods, were used in this work, to control the admission rate of oxygen into the deposition chamber for the production of thin films of reactively sputtered oxides. The theoretical background of these methods has been reviewed in section (4.5). The arrangements for oxygen admission to the deposition chamber have been described in section (5.2.5.2). The first of these method was the PEM (section 4.5.1), and used to control the reactive sputter-deposition of In, Zn, W, V, Mo and Ti oxide. The second method was the voltage control (section 4.5.2), and used to control the reactive sputter-deposition of Zn, Cu, Pb and Al oxide.

In this section, the equipment of PEM and voltage control as well as parameters, specific to the system used in this work, will be described.

5.2.8.1. Plasma emission monitoring (PEM)

Figure (4.10) shows a schematic of a PEM control loop. A band pass filter, attached to a 6030B photomultiplier tube (PMT), which was manufactured and supplied by Rofin Limited, was used in this work. It is labelled '25' in figure (5.2), and is suitable for operation in the 200 nm to 930 nm wavelength range with a resolution of 2.5 nm. The inside (or active) diameter of the optical fibre cord of PEM control loop was about 2.3 mm. In the course of this work, the plasma contained mainly the emission lines corresponding to argon, oxygen and the target material. Therefore, to control on the
emission line/s of one of these elements, the optical filter had to be chosen so that either the wavelength/s of light it transmitted was unique to this element, or the emission intensity at the selected wavelength/s was sufficiently higher than the corresponding ones of the other two elements.

In the light of the above discussion, two different optical filters, manufactured and supplied by Ealing Electro-optics, were utilised. Figure (5.16) shows the measured transmittance of these filters versus wavelength, using Hitachi's U-2000 double-beam spectrophotometer. This spectrophotometer will be described in the next chapter. The first filter was a band pass filter and was used for controlling on the In emission line at 451.1 nm for the reactive sputter-deposition of In oxide. The intensity of this emission line is 18000. Sufficient signals up to about 150 mV were obtained at applied powers of the order of 300 W. At this wavelength, there is neither an argon nor an oxygen-line, sufficiently intense, to interfere with the In one.

The other filter was a high-pass filter with a cut-off wavelength at about 620 nm. It was successfully used to control the reactive sputter-deposition of W, V, Mo and Ti oxide. Signals up to about 1.5-2 V were obtained at applied powers of the order of 300 W. The question is 'to what element this powerful signal does belong?'. At wavelengths greater than about 620 nm, the intensities of the emission lines of these metals are very weak. The most intense lines are 45 at 629.20 nm for W, 710 at 624.31 nm for V, 230 at 661.91 nm for Mo and 490 at 843.49 nm for Ti. Thus, the transmitted signal by this filter is either due to argon or oxygen-lines.
<table>
<thead>
<tr>
<th>λ&lt;sub&gt;em&lt;/sub&gt; (nm)</th>
<th>Intensity (arb.)</th>
<th>λ&lt;sub&gt;em&lt;/sub&gt; (nm)</th>
<th>Intensity (arb.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>696.54</td>
<td>10000</td>
<td>777.19</td>
<td>870</td>
</tr>
<tr>
<td>706.72</td>
<td>10000</td>
<td>777.41</td>
<td>810</td>
</tr>
<tr>
<td>738.39</td>
<td>10000</td>
<td>777.53</td>
<td>750</td>
</tr>
<tr>
<td>750.38</td>
<td>20000</td>
<td>844.62</td>
<td>810</td>
</tr>
<tr>
<td>751.46</td>
<td>15000</td>
<td>844.63</td>
<td>1000</td>
</tr>
<tr>
<td>763.51</td>
<td>25000</td>
<td>844.67</td>
<td>935</td>
</tr>
<tr>
<td>772.37</td>
<td>15000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>772.42</td>
<td>10000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>794.81</td>
<td>20000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>800.61</td>
<td>20000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>801.47</td>
<td>25000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>810.36</td>
<td>20000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>811.53</td>
<td>35000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>826.45</td>
<td>10000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>840.82</td>
<td>15000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>842.46</td>
<td>20000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>852.14</td>
<td>15000</td>
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<td>866.79</td>
<td>4500</td>
<td></td>
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</tr>
<tr>
<td>912.29</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>922.44</td>
<td>15000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table (5.1): The most intense emission lines of argon and oxygen at wavelengths range from 620 nm to 930 nm\textsuperscript{10}
In fact, although some oxygen-lines do exist in this range, their intensities are very much smaller than those of argon. Table (5.1) shows the most intense emission lines of argon and oxygen at wavelengths, $\lambda_{em}$, ranging from 620 nm to 930 nm (i.e., the working range of the combination filter-photomultiplier). It can be concluded then that, the strong signal was due to argon and the control was carried out on the argon-lines.

Finally, no optical filter with a sufficient transmittance (or signal) was available, for this work, to control on a zinc or an oxygen-line for the reactive sputter-deposition of Zn oxide. Therefore, to make use of its high capability of magnifying signals, the band pass filter and 6030B photomultiplier tube (PMT) was replaced by a 2 Meter monochromator/detector, manufactured and supplied by Verity Instruments. The monochromator was tuned to the oxygen-lines at 777 nm and the control was carried out on these lines.

5.2.8.2. Voltage control

![Diagram of Voltage Control System](image)

**Figure (5.17): Voltage control (VC) system used in controlling reactive magnetron sputtering processes.**

Figure (5.17) shows a schematic of a voltage control loop. A user connector, located on the rear panel of the Advanced Energy™ power supplies which was used in this work, provides a 0-5 V DC analogue signal representing the cathode voltage (i.e., the output voltage of the power supply). The DC signal was 0 V when the output voltage of the supply was also 0 V and it was 5 V at the full-scale output voltage of the supply. This 0-5 V-DC signal was used as an input to a voltage controller. As will be explained soon,
the signal was taken through two controls, one of which backs it off against another potential to provide a zero reference. The difference from this zero signal was then amplified by a variable gain amplifier to give an output ranging from 0 to 1 V. The output signal from the voltage controller was then applied to a standard pressure controller (process controller) which was connected to a piezoelectric control valve of a very fast response. The types and manufacturers of both the pressure controller and the piezoelectric valve were the same as indicated before. The process controller worked then in a similar manner to that in the case of the PEM control (see the end of section 4.5.1).

A schematic of the voltage controller is shown in figure (5.18). The input DC voltage to the controller, \( V_i = 0 - 5 \) V, is divided (by the potential divider \( R_7, R_8 \) and \( R_9 \)) for the digital voltmeter, D.V.M.1, which measures up to 200.0 mV, to be able to display it. The division ratio of this divider is 1/67, and can be obtained by tuning the variable resistor \( R_9 \). Since \( V_i = i_1(R_7 + R_8 + R_9) \) and \( V_{D,V.M.1} = i_1(R_8 + R_9) \), where \( i_1 \) is the current in this part of the circuit and \( V_{D,V.M.1} \) is the voltage which is read by D.V.M.1, \( R_9 \) can then be calculated from the equation

\[
V_{D,V.M.1}/V_i = (R_8 + R_9)/(R_7 + R_8 + R_9) = 1/67 \tag{5.3}
\]

and found to be about 32 \( \Omega \).

The voltage \( V_4 = V_i \) is divided by the potential divider \( R_6 \) and \( R_{10} \). Since \( V_4 = V_i = i_2(R_6 + R_{10}) \) and \( V_5 = i_2R_{10} \), then

\[
V_5/V_i = R_{10}/(R_6 + R_{10}) = 0.1754 \tag{5.4}
\]

Similarly, \( V_1 - V_3 = (R_2/(R_1 + R_2 + R_3))(V_A - V_B) = 2.92 \) V. If, for example, the wiper of the resistor \( R_2 \) is in the middle, its voltage \( V_2 = 0 \) and hence \( V_1 = +1.46 \) V and \( V_3 = -1.46 \) V. The signal is fed first to a differential amplifier, whose output is\(^{12}\)

\[
V_7 = V_8 = V_5[1+(R_5/R_4)] - V_2(R_5/R_4) \tag{5.5}
\]

and then to an amplifier with an adjustable gain, whose input 2 is grounded through the resistor \( R_{13} \). The output of this amplifier is

\[
V_{10} = V_{11} = V_8[1+(R_{17}/R_{13})] \tag{5.6}
\]
Figure (5.18): A schematic of the voltage controller.
amplifier is then $V_5 = 263.1 \text{ mV}$ (equation 5.4). The bias knob (i.e., the wiper of the resistor $R_2$) will be adjusted so that $V_7 = 0 \text{ V}$, which appears on D.V.M.2 (equation 5.7). This means that $V_2 = 526.2 \text{ mV}$ (equation 5.5). In the second case (i.e., $V_i = 4 \text{ V}$), the D.V.M.1 will read 59.7 mV (equation 5.3). The input and output voltages to the differential amplifier are then $V_5 = 701.6 \text{ mV}$ (equation 5.4) and $V_7 = 877 \text{ mV}$ (equation 5.5), respectively. The gain knob (i.e., the variable resistor $R_{17}$) of the second amplifier will be adjusted so that its output voltage $V_{10} = 1 \text{ V}$. The D.V.M.2 will read 100.0 mV (equation 5.7). The value of $R_{17}$ can then be calculated from equation (5.6) and is found to be $R_{17} = 140.25 \Omega$. If one takes the middle of the user's scale (i.e., $V_i = 2.75 \text{ V}$), for example, then following the above procedure, the D.V.M.1 will read 41.0 mV, $V_5 = 482.35 \text{ mV}$, $V_7 = 438.5 \text{ mV}$, $V_{10} = 499.99 \text{ mV}$ and the D.V.M.2 will read 50.0 mV which is also in the middle of 0 and 100.0 mV.

The input to the voltage controller was taken from the DC power supply, when it was used, as it represented the dominating power applied to the main magnetron relative to the floating power applied by the AC power supply. This arrangement provided better control.

5.3. The deposition procedure

5.3.1. Targets properties and preparation

Due to the nature of this research, a relatively large number of circular planar targets, of different elements, was used. Table (5.2) summarises the preparation method, purity and thickness of these targets. Al and Cu targets were prepared from commercially available sheets by only cutting to size. Mo, Nb, V, W, Ta and Ti targets were available, for this work, as sputtering targets. However, the low sputtering yields of these elements, which range from about 1 to 1.25 atoms/ion for 500 eV argon ions, allow these targets to last for a relatively long time.

The increasing demands on In made it a relatively expensive element with a cost of about £475 per kg in 1993. Because of that, it was not cost effective to replace each target when it wears through having only utilised 23% of the volume due to the tight erosion zone (see section 5.2.6). Because of its physical properties (low melting point, MP, of 156.6 °C), it was able to be recast in an aluminium case, using a thermostatic hot plate, to maximise utilisation of material. The material which has been used in this work was replenished from a supply which had previously been recast several times.
<table>
<thead>
<tr>
<th>No.</th>
<th>Target</th>
<th>Preparation</th>
<th>Purity</th>
<th>Total thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al</td>
<td>Cutting a commercially available sheet to size</td>
<td>Commercial engineering grade</td>
<td>7.5</td>
</tr>
<tr>
<td>2</td>
<td>Bi</td>
<td>Cast locally in an aluminium case</td>
<td>99.5%</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>Cu</td>
<td>Cutting a commercially available sheet to size</td>
<td>Commercial engineering grade</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>In</td>
<td>Cast locally in an aluminium case</td>
<td>Recast from originally 99.99% material</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>Mo</td>
<td>Available as a sputtering target</td>
<td>99.9%</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>Nb</td>
<td>Available as a sputtering target</td>
<td>99.8%</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>Pb</td>
<td>Cast locally in a stainless steel case</td>
<td>Commercial engineering grade</td>
<td>8</td>
</tr>
<tr>
<td>8</td>
<td>Sn</td>
<td>Cast locally in an aluminium case</td>
<td>99.99%</td>
<td>8</td>
</tr>
<tr>
<td>9</td>
<td>Ta</td>
<td>Available as a sputtering target</td>
<td>99.9%</td>
<td>2</td>
</tr>
<tr>
<td>10</td>
<td>Ti</td>
<td>Available as a sputtering target</td>
<td>99.6%</td>
<td>6</td>
</tr>
<tr>
<td>11</td>
<td>V</td>
<td>Available as a sputtering target</td>
<td>99.7%</td>
<td>6.5</td>
</tr>
<tr>
<td>12</td>
<td>W</td>
<td>Available as a sputtering target</td>
<td>99.7%</td>
<td>6.5</td>
</tr>
<tr>
<td>13</td>
<td>Zn</td>
<td>Cutting a commercially available sheet to size and binding it to a copper base using indium</td>
<td>Commercial engineering grade</td>
<td>10</td>
</tr>
</tbody>
</table>

Table (5.2): Preparation, purity and thickness of the targets which were used in this work. The diameter of all targets was 4" (i.e., 10.2 cm).

It should be emphasised that mechanical abrading of the inside of the aluminium case, during the recast process, was essential to achieve good wetting and hence avoid the otherwise poor mechanical, thermal and electrical contact.
Other low melting point elements were also recast, following the above procedure; Sn (MP = 231.9 °C) and Bi (MP = 271.3 °C) targets were recast in aluminium cases; Pb target was recast in a stainless steel case, instead of an aluminium one, to avoid the deformation of the case due to the higher melting point of Pb (MP = 327.5 °C). Active flux was used for binding the molten Pb to the case.

(a) A Zn target prepared from commercially available sheets by cutting to size.

(b) Bending of the Zn target.

(c) Binding a Zn sheet to a Cu base using molten In as a binder.

Figure (5.19): Preparation of zinc targets to overcome the problem of bending.

Finally, Zn targets were initially prepared from commercially available sheets by only cutting to size. Unfortunately, a major problem appeared after sputtering such targets for only one or two days. The cooling water used to leak to the vacuum system as a result of an easily recognisable bending of these targets. In general, such a bending may be due to the difference in the thermal loads applied to the upper and lower surface of the target. Due to ion bombardment, the upper surface is usually much hotter than the lower one, which is in contact with the cooling water. Consequently, the upper surface is then subjected to expansion forces, whereas the lower one is subjected to contraction forces. The resultant force acts as to bend the target, as can be seen in figure (5.19). The question now is ' if the above explanation is correct, why the bending problem was so
severe in Zn targets and was not as obvious, for example, in the case of Cu, Al or Ta targets? In addition to being not a very hard metal, like for example Ti and W, the severe bending of Zn targets was probably due to the combination of two factors:

1. Relatively very high linear expansion coefficient of Zn (31·10⁻⁶ K⁻¹ @ 0-100 °C), compared with 17·10⁻⁶ K⁻¹ for Cu, 23.5·10⁻⁶ K⁻¹ for Al and 6.5·10⁻⁶ K⁻¹ for Ta, in the same range of temperature.

2. Relatively low thermal conductivity of Zn (116 W/m.K @ 0-100 °C), compared with 401 W/m.K for Cu, 237 W/m.K for Al and 57.5 W/m.K for Ta, in the same range of temperature.

To overcome this problem, Zn targets were prepared by binding Zn sheets to Cu bases using molten In as a binder. In addition to holding the Zn sheet to prevent it from being bent, this method helps in reducing the temperature difference between the upper and lower surface of the Zn sheet by eliminating the direct contact between the cooling source and the lower surface of the sheet. The major disadvantage of this method is reducing the cooling efficiency of the target. However, in the power range used in this work, which was of the order of few hundreds of watts, such a disadvantage was not so important.

5.3.2. The sequence of deposition process

Unless otherwise stated, 38 x 26 x 1.1 mm commercial grade microscope glass slides were used in this work as substrates with a coated area of 29 x 23 mm. A few experiments, however, were carried out on silicon, stainless steel or aluminium substrates, having the same dimensions. Once the desired base pressure of approximately 2·10⁻⁶ - 4·10⁻⁶ Torr was achieved (see section 5.2.3), a constant flow rate of argon, of about 240 sccm, was allowed to the chamber as an inert backfill for the magnetron discharge to strike. Such a flow rate of argon secured a working pressure of about 2·10⁻³ Torr.

As mentioned in section (5.2.2), the substrate was mounted singly in the jig, which was then attached to the end of the loading arm. This was followed by evacuation of the airlock from atmosphere to approximately 40 mTorr. Such a pressure was adequately low to have no significant effect on chamber pressure when the gate valve was opened to insert the jig into its position, labelled '3' in figure (5.4), onto the axially mounted aluminium platen which was described in section (5.2.1). When this pressure had been achieved, and prior to opening the gate valve, the airlock pump was switched off and the valve between this pump and the airlock chamber was closed to avoid backstreaming of
oil into the deposition chamber. Following the insertion of the jig, the substrate was manually rotated to a predetermined intermediate position (approximately opposite the vacuum chamber-turbomolecular pump interface, labelled 'S' in figure 5.4) so that it was not facing any of the magnetrons. This was to prevent any deposition onto the substrate until the desired set-points (e.g., applied power/s, automatic feedback control signal or \( \text{O}_2 \) flow rate in manual control,...etc.) had been achieved. Thus, this movement of the substrate played the same role as the shutter in conventional deposition systems. The loading arm was then withdrawn to allow the gate valve to be closed again to guarantee that the integrity of the high vacuum system was not entirely dependent on the perspex/o-ring interface.

In both control methods (i.e., PEM and voltage control), the deposition process was started when the targets were in the metallic mode so that a 100\% reference signal can be determined. Therefore, before starting the sputtering process, the targets were sputter-cleaned, for few minutes, to remove the contaminated surface-layers. Reaching a constant cathode voltage was an indication of the removal of these layers. Such a cleaning process was occasionally accompanied by a severe arcing which was overcome by using the ramp button on the MDX power supply (see section 5.2.7.1). This was followed by decreasing the signal gradually (or increasing it when control was on an oxygen-line) allowing oxygen to be controllably admitted until the desired film properties (i.e., high visible transparency and low resistivity) were achieved. Once the desired set-points were attained, the substrate was rotated at a speed of 60 r.p.m. by switching on the DC motor (section 5.2.1). At exactly this moment, timing of deposition was started. Unless otherwise stated, deposition time was 3 min in the case of the oxides of high sputtering yield metals (In, Zn, Cu and Pb), and 6 min in the case of the oxides of low sputtering yield metals (V, W, Ti and Mo). Finally, it should be emphasised that all reported results are for as deposited films since no post-deposition annealing of any kind has been carried out on any of the films deposited in this work. Furthermore, deposition was carried out at room temperature and without any external bias applied to substrate.

5.4. The deposition process

5.4.1. Material-based targets distribution

Unless otherwise stated, the main magnetron was used as a source for the deposition of the main oxide materials (e.g., the In magnetron in the case of ITO) where a higher power should be applied, whereas the secondary magnetron was used as a source for the
deposition of the dopant materials (e.g., the Sn magnetron in the case of ITO) where a relatively lower power should be applied.

To explain the reason behind that, the matter will be discussed in terms of the standard molar enthalpies of formation, $\Delta H_f^\circ$, of the oxides of the two materials (i.e., the host and dopant material) to be deposited. $\Delta H_f^\circ$ can be defined as the enthalpy changes, in kJ/mol, that occur when unit amount of the compound (i.e., the oxide in this case) in its standard state (i.e., at a pressure of 1 atm and the temperature specified, which is often but not necessarily, 298.15 K) is formed from its elements in their standard states\(^\text{14}\). Although reactions in reactive sputtering take place in a vacuum chamber at much lower pressures than 1 atm, $\Delta H_f^\circ$ is still valid to give a qualitative idea about the relative easiness of an oxide to be formed inside chamber. It should be noted that the more negative $\Delta H_f^\circ$ is the more the metal, which forms the oxide, is keen to react with oxygen.

1. Let $\Delta H_f^\circ$ of the oxides of the two metals in concern be comparable, and let the material meant to be the main oxide material, with a higher power applied to its magnetron, be deposited from the secondary magnetron, and the dopant material from the main magnetron. Then, controlling the stoichiometry would be very difficult and the resultant films would be almost metallic. This is because, when any method of feedback control is used, the oxygen provided to the chamber would be solely determined according to the amount of sputtered material, which is in this case quite small (lower power, hence less sputtered material and lower oxygen requirement for oxidisation). The main stream of the unoxidised material would be coming from the secondary magnetron where the main oxide material would be sputtered with relatively much higher power applied. This would cause a large deficiency of oxygen over the main magnetron as the feedback control can not cope with a high flux of material coming from the other magnetron, whereas the control and consequent oxygen supplied are according to the dopant material of the main magnetron.

2. If the $\Delta H_f^\circ$ of the two oxides of the metals in concern, are very different (e.g., In$_2$O$_3$ or ZnO doped with Al or Ti), then the material of the lower (or more negative) $\Delta H_f^\circ$ (e.g., Al and Ti), which are usually the dopant material, should be sputtered from the secondary magnetron, away from oxygen. This is to prevent its target from being poisoned and the consequent drastic decrease of the sputtering rate from such a target. This, in turn, would make the composition control of the coatings almost impossible. In some special cases, this arrangement was used to deposit the oxide of the material in the secondary magnetron (e.g., In or Sn) doped with material of the main magnetron (e.g., Ti).
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5.4.2. Substrate rotation mode

5.4.2.1. Atomic level deposition mechanism

If the case of In and Sn is considered, it was a very common feature in this process that about 165 nm-thick films of ITO could be obtained, in a deposition time of 3 min, at applied powers to In and Sn cathodes equal to 300 W and 40 W, respectively. If the substrate rotation speed is 60 r.p.m., which was the case throughout this work, the number of revolutions the substrate made during the 3 min was 180. Thus, during each revolution, about 0.92 nm-thick film were deposited from both magnetrons. The diameters of In and Sn atoms are almost identical, averaging 0.315 nm. This means that an average of about 3 layers of both In and Sn atoms were deposited, per revolution, from both magnetrons. It can be concluded then that the number of atomic layers deposited, per revolution, from one magnetron, was less than 3 layers.

The above discussion may suggest some idea about the deposition mechanism. Each revolution, when the substrate passes over the main magnetron which was used as the source of the deposition of the element of the main or host oxide (i.e., the In magnetron in the case of ITO), very few layers of the metal atoms were deposited and oxidised on it. Then the substrate would pass over the secondary magnetron which was used as the source of the deposition of the dopant element (i.e., the Sn magnetron in the case of ITO), where even fewer dopant metal atomic layers were deposited. These dopant atoms would be oxidised by the oxygen plasma of the main magnetron upon passing over the main magnetron during next revolution.

5.4.2.2. Measured and actual deposition rate

A unique feature of this system was that, unlike the vast majority of sputtering systems, the rotating substrate did not continuously face the target/s, and hence did not receive the sputtered material, during the entire deposition time. Therefore, the measured deposition rate, $R_{\text{dep}}^m$, of a film was less than, $R_{\text{dep}}^a$, the actual one. The latter reflects the conditions (e.g., the effectiveness of both the plasma confinement near the magnetron cathode and the control system of the reactive gas) at which the reactive sputtering process took place (see section 2.5). The percentage of time the substrate actually spends over each magnetron can be calculated as follows: During each revolution, the substrate travels a distance approximately equal to the circumference of the circle which has a radius equal to the distance between the centrally-oriented shaft, labelled '6' in figure (5.4), and the centre of the opening in the rotating platen, labelled '3' in the same figure, into which the substrate holder is inserted. In the system used in this work, this radius is equal to 9.3 cm, and the circumference of the circle is then about 58.4 cm.
Since the rotation speed of the substrate is 60 r.p.m. (i.e., 1 revolution/s), the linear speed of the substrate is, therefore, about 58.4 cm/s. As a result, the substrate traverses the target, which has a diameter of 4" (10.2 cm), in about 0.175 s. Ignoring the secondary magnetron due to the relatively lower power applied to it compared to that applied to the main one, the actual deposition time is then about 0.175 of the measured one. Consequently, the actual and measured deposition rates may be related to each other as follows

\[ R_{\text{dep}}^a \approx R_{\text{dep}}^m / 0.175 \approx 5.71 R_{\text{dep}}^m \]  

[5.8]

Considering, for example, the case of indium oxide in which about 158 nm-thick films could be obtained in a deposition time of 3 min at 300 W applied to the main cathode only (i.e., the In one), then \( R_{\text{dep}}^m \approx 0.88 \text{ nm/s} \) and \( R_{\text{dep}}^a \approx 5 \text{ nm/s} \). The high deposition rate is an indication that the sputtering arrangements, including the control system, are very efficient.

5.4.3. Substrate condition probe

The theory of current-voltage characteristic of diode plasmas has been reviewed in section (2.2.5). However, the theory of probes in magnetron plasmas is more complex, due to the presence of a magnetic field\(^{15,16}\), and it is out of the scope of this thesis.

A true Langmuir probe was not necessary for the purpose of this work, as the only point of interest was knowing the conditions that the substrate was subject to and those which directly affected the film properties. These were the ion current density to the substrate and its floating potential. In other words, the number and energy of ions that bombarded the growing films. Such a probe was termed a "substrate condition probe". Figure (5.20) shows a cross-sectional and a bottom view (i.e., the surface with a direct contact with the plasma) of this probe. It essentially consisted of a central cylindrical head, whose diameter was 6 mm, surrounded by a 25 x 37 mm guard. The guard, which was entirely isolated from the head, was utilised to minimise the plasma edge-effect from the probe head. Such an effect was caused by ion flux passing around the head in a similar manner to liquid molecules passing around a flat object placed normal to a stream of the liquid. The probe was placed in the plane of the substrate following the same procedure of placing a substrate; it was mounted in the jig which was in turn inserted into the platen.
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The I-V characteristics was then obtained by biasing the probe head, using an ordinary DC power supply. The current to the guard was excluded. A schematic of the circuit which was used for this purpose can be seen in figure (5.21).

Probe measurements were performed using In and Sn targets attached to the main and secondary magnetrons, respectively. Keeping the working pressure at $2 \times 10^{-3}$ Torr, two sets of experiments were carried. The first was when the probe was held opposite to the centre of the In magnetron using different DC powers (i.e., at 100, 200 and 300 W). In addition, the characteristics of the probe when it was facing the erosion zone of the In magnetron, when the applied power was 300 W, was also plotted for comparison. The results are shown in figures (5.22) and (5.23). In the second set of experiments, the probe was held opposite the centre of the In magnetron throughout. The applied powers were, 50 W and 100 W AC floating between the two magnetrons, and 300 W DC combined with 100 W AC. The results are shown in figure (5.24).
Figure (5.21): The arrangements of probe measurements.

Figure (5.22): The T-V characteristics of the probe when an In magnetron was held at 300W DC and the probe was held opposite the centre of the magnetron.
The following remarks can be deduced from these figures:

1. The ion-current to the probe increased with the applied DC power to the magnetron (figure 5.23). On the other hand, at a fixed DC power (e.g., 300 W), such a current was higher when the probe was held opposite the centre of the magnetron than when it was opposite the erosion zone. Similarly, the ion-current to the probe also increased with the applied floating AC power (figure 5.24).

2. At a fixed magnitude of power (e.g., 100 W), the ion-current to the probe was lower in the DC case (figure 5.23) than in the floating AC one (figure 5.24).
Furthermore, the ion-current to the probe in the case of the 100 W AC combined with 300 W DC was the highest (figure 5.24).

3. The floating potential of the probe was almost independent of the applied AC power (figure 5.24) and slightly dependent on the DC power (figure 5.23). However, the order of magnitude of these floating potentials was slightly lower when DC powers were applied.

The above conclusions are in very good agreement with the results obtained by Window and Savvides\textsuperscript{7} (section 3.4.4), and the results of Glocker\textsuperscript{10} (section 4.6.3.2-II). In addition, the ion-current and floating potential when the probe was opposite to the erosion zone are less than the corresponding values when the probe was opposite to the centre of the magnetron (figure 5.23), under the same conditions (i.e., applied power). This result is also with a good agreement with those of Howson \textit{et al}\textsuperscript{18} and Spencer \textit{et al}\textsuperscript{9}.

It is informative, however, to compute the arrival ratio of Ar ions to metal atoms at the substrate. Assuming a uniform ion flux, the number of ions bombarding 1 cm\(^2\) of the substrate per second, \(N_i\), is given by

\[
N_i = \frac{J_i}{e} \cdot 10^{-3}
\]  

[5.9]

where \(J_i\) is the ion current density to the substrate in mA/cm\(^2\) and \(e\) is the electronic charge in C.

On the other hand, neglecting the dopant concentration in the deposited films and assuming that all these films are uniform and stoichiometric, the number of deposited metal atoms on 1 cm\(^2\) of the substrate per second (in atoms/cm\(^2\)s) is then given by

\[
N_{m}^a = \alpha N_{mole}^a
\]  

[5.10]

where \(\alpha\) is the number of metal atoms in the compound molecule (e.g., \(\alpha = 2\) in stoichiometric In\(_2\)O\(_3\)) and \(N_{mole}^a\) is the number of deposited compound molecules on 1 cm\(^2\) of the substrate per second (in molecules/cm\(^2\)s). By definition, \(N_{mole}^a\) is given by

\[
N_{mole}^a = \frac{N_{Av} W_{film}}{M_w}
\]  

[5.11]

where \(W_{film}\) is the mass of the film deposited on 1 cm\(^2\) of the substrate in unit time (in g/cm\(^2\)s), \(M_w\) is the molecular mass of film material (in g) and \(N_{Av}\) is Avogadro's number. \(W_{film}\) in turn is given by
where $S_w$ is the density of film material (in g/cm$^3$) and $V_{film}$ is the volume of the film deposited on 1 cm$^2$ of the substrate in unit time (in cm$^3$/cm$^2$s). $V_{film}$ is the product of the film area (which is 1 cm$^2$ in this case) and film thickness, $d_{film}$ in nm, deposited in unit time (i.e., the deposition rate, $R_{dep}$ in nm/s) and is given by

$$V_{film} = \frac{d_{film}}{t} \cdot 10^{-7} = R_{dep} \cdot 10^{-7}$$

where $t$ is the deposition time in second. Using equations (5.11), (5.12) and (5.13) and substituting in equation (5.10), one gets

$$N_m^s = 6.022 \cdot 10^{16} \frac{\alpha S_w d_{film}}{M_w t} = 6.022 \cdot 10^{16} \frac{\alpha S_w R_{dep}}{M_w}$$

By dividing equation (5.9) by equation (5.14) side by side, one finds that

$$\frac{N_i^s}{N_m^s} = 0.1 \frac{M_w}{\alpha S_w d_{film}} J_i^s = 0.1 \frac{M_w}{\alpha S_w R_{dep}} J_i^s$$

Returning now to figure (5.22) in which the applied power to the magnetron was 300 W DC. The ion current density to the substrate, the floating potential of the substrate and the plasma potential were $J_i^s = 0.9$ mA/cm$^2$, $V_f = -8$ V and $V_p \approx 20$ V, respectively.

Considering the case of indium oxide, as an example, and assuming that the density of the film was equal to that of bulk material, then $M_w = 278$ g, $S_w = 7.179$ g/cm$^3$ and $\alpha = 2$. Using equation (5.15), and considering the experimental values $t = 180$ s and $d_{film} = 158$ nm, it was found that $N_i^s/N_m^s = 2$ and the energy delivered to the substrate by ions per In atom was about 60 eV. Since the actual deposition time was about 0.175 of the measured one for each magnetron (section 5.4.2.2), then $N_i^s/N_m^s = 0.7$ and the energy delivered to the substrate by ions per In atom was about 21 eV.

On the other hand, according to figure (5.24), $J_i^s = 7.1$ mA/cm$^2$, $V_f = -17$ V and $V_p = 0$ V (see section 5.2.7.3) in the case when the applied power to the magnetron was 300 W DC combined with 100 W AC. Considering the case of indium oxide again (with $d_{film} = 152$ nm) and following the above procedure, it was found that $N_i^s/N_m^s = 5.7$ and the energy delivered to the substrate by ions per In atom was about 100 eV.

Although the two magnetrons were unbalanced in the system used in this work, the measured floating potentials of the substrate were relatively low, whereas, the measured ion current densities were moderate. This could be due to the fact that target-to-substrate distance is less than the null-point of the magnetrons (section 5.2.6), which means that, at such low distance, ions can not acquire high kinetic energies when they...
impinge on the substrate, with the lower floating potential that the substrates have. The small target-to-substrate distance also affects, but less severely, the ion current density, as the substrate can not collect all ions available because it is not in the way of the focused beam leaking from the cathode, rather it is in the base of that beam.

5.5. Advantages of the deposition technique

According to the above discussion, the deposition technique, employed in the course of this work, enjoys the following major advantages

1. Substrate rotation enhanced atomic level mixing of the film constituents. The stoichiometry of the film was controlled by PEM or voltage control on one magnetron, and dopants were added by sputtering from the other magnetron. This means that the former magnetron serve two purposes; the first is to sputter metal and oxidise it, and the second purpose is to oxidise the metal sputtered from the other magnetron.

2. The ability to obtain a sputter-deposited coating of an alloy or multi-element compound which is either difficult or impossible to be formed from a single target.

3. The use of an airlocked, feedback controlled reactive system allows the implementation of an iterative deposition process to vary coating stoichiometry, and simple variation of applied power type (AC/DC) and magnitude to control coating composition. Hence, information regarding different composition and stoichiometry can be attained rapidly without cathode acquisition or preparation.

4. The system, described in this work, is superior to the dual magnetron technique described by Lewin and Howson in 1987, where two concentric cathode annuli of different materials (with separate magnetic fields) comprise one magnetron device (see figures 5.25 and 5.26), in that the two sources sputter independently of each other. The latter technique, of Lewin and Howson, permits variable compositions to be selected only to a limited extent in a reactive environment, the limit being reached when differential poisoning of the two cathode materials dominates. Clearly, precise stoichiometry control also suffers from this problem as a direct result of the close proximity of the cathode.
Figure (5.25): A reproduction of a cross-sectional view of the dual magnetron.

Figure (5.26): A photograph of the dual magnetron.
REFERENCES


Chapter Six

CHAPTER SIX

TECHNIQUES AND INSTRUMENTATION USED FOR THE CHARACTERISATION OF THE THIN FILMS DEPOSITED IN THIS WORK

6.1. Introduction

Electrical, optical and compositional properties are of great importance to performance of thin films, especially when these films are intended to be electrically conducting and visibly transparent. Information about these properties is crucial in considering a film to be used in a particular application such as heterojunction solar cells, gas sensors, electronic displays...etc. In this chapter, the techniques and instrumentation employed in the course of this work, to perform such assessments will be described.

6.2. Electrical measurements

Due to the nature of this work, it was extremely important to be able to evaluate rapidly the electrical performance of films produced during iterative reactive deposition processes. This was achieved by measuring the sheet resistance of the film as the sample was removed from the deposition chamber. Such a measurement verified quantitatively whether the film was electrically worse or better (i.e., less or more conducting, respectively) than the one deposited in the previous run.

To introduce the concept of sheet resistance, the reader is referred to figure (6.1.a). The resistance, \( R \), of a rectangular shaped section of film of length, \( L \), width, \( W \), and thickness, \( d_{\text{film}} \), measured in a direction parallel to the film, is given by

-191-
(a) The concept of sheet resistance

(b) Direct measurement of sheet resistance

(c) Measurement of sheet resistance using four-point probe technique

*Figure (6.1): The concept of sheet resistance and methods of measuring it.*
where $R_y$ is the resistivity of the film. The unit of $R_y$ is $\Omega.m$, provided that $L$, $W$ and $d_{film}$ are in meters and $R$ is in $\Omega$. If the case of a square is considered (i.e., $L = W$), then equation (6.1) becomes

$$R = \frac{R_y L}{W d_{film}}$$

[6.1]

where $R_y$ is the sheet resistance of the film, in ohms per square ($\Omega/\square$). It is evident from equation (6.2) that $R_x$ is independent of the edge dimension of the square and depends only on $R_y$ and $d_{film}$. Obviously, if $R_x$ and $d_{film}$ are known, the film resistivity is then given by

$$R_y = R_x d_{film}$$

[6.3]

However, the technique used in this work to measure film thicknesses will be described in section (6.3.2.4). On the other hand, as the definition implies, $R_x$ can be determined simply by preparing a rectangular film (figure 6.1.b), calculating its resistance by measuring the voltage drop across a distance of the film as a current is driven through the film and dividing by the number of squares that lie between the voltage terminals. This simple and direct method suffers from the following disadvantages: (i) The need for fabricating special samples makes it impractical for instant evaluation of films during a deposition run; (ii) When the thickness of the film is not uniform, measuring $R_x$ at different parts of the substrate becomes a necessity. This requires the preparation of a large number of small rectangular samples which is very impractical.

In a paper published in 1954, Valdes described a very convenient method, called "four-point probe", to measure $R_x$. In this technique, which has become very popular, the probes are lightly pressed into the surface of a film as shown in figure (6.1.c). To make a measurement, a known current, $I$, is forced between the outer two probes and the voltage drop, $V$, between the two inner probes is measured. Valdes showed that if the film is semi-infinite compared with probe spacing ($S_1$, $S_2$ and $S_3$), the resistivity is given by

$$R_y = \frac{V}{I} \left( \frac{2 \pi}{\frac{1}{S_1} + \frac{1}{S_3} - \frac{1}{S_1 + S_2} - \frac{1}{S_2 + S_3}} \right)$$

[6.4]

When $S_1 = S_2 = S_3 = S$, equation (6.4) becomes
\[ R_y = \frac{V}{I} 2\pi \sigma \]  

Valdes also showed that if the material is an infinitely thin slice resting on an insulating substrate, then resistivity is given by

\[ R_y = \frac{V \pi d_{\text{film}}}{I \ln 2} \]  

and the sheet resistance is given by

\[ R_s = \frac{R_y}{d_{\text{film}}} = 4.532 \frac{V}{I} \]

In this work, sheet resistance measurements were carried out using a microprocessor voltmeter, type Datastore, manufactured by Schlumberger/Solarton Limited. The voltmeter was connected to four pins (probes). The pins, which were 15 mm long and 1.7 mm in diameter with \( S = 2.5 \text{ mm} \) at the needle tips, were connected by springs to allow them to press against the film. They were mounted in a PVC holder to secure equal contact pressure to the film. The voltmeter was auto-ranging and was sensitive to 1 \( \mu \text{V} \). Furthermore, the multiplication factor 4.532 was also included in the program so that \( R_s \) was automatically and instantly displayed.

The major disadvantage of this technique was the penetration of pins into soft films (e.g., \( \text{In}_2\text{O}_3 \)) leading to the creation of voids in these films with the resultant increase in sheet resistance. Consequently, only the first reading, at the same position, could be considered reliable in such cases.

6.3. Optical measurements

6.3.1. Ellipsometric measurements

6.3.1.1. The ellipsometer

Ellipsometry is a more than 100 year-old technique for measuring the thickness, \( d_{\text{film}} \), and refractive index, \( n_{\text{film}} \), of thin films\(^4\). The availability of computers for process automation and data processing, since about 1970, has widely increased the popularity of this technique\(^5\).

Ellipsometers are optical instruments which measure changes in the state of polarisation of collimated beams of monochromatic polarised light caused by reflection from the surfaces of substances\(^6,7\). An ellipsometric measurement involves irradiating the surface of a sample, at a known angle of incidence, with a collimated beam of monochromatic...
light having a known, controllable state of polarisation, and determining the differences between the states of polarisation of the incident and reflected beams caused by the sample. From these differences, various properties of the reflecting surface can often be computed. For example, for a substrate coated with a transparent film, $d_{\text{film}}$ and $n_{\text{film}}$ can be computed, provided the optical constants of the substrate are known. This powerful, non-contact, non-destructive technique is capable of observing changes in film thickness of 0.007 nm.

The electric fields of both the incident and the reflected beams can each be resolved into two orthogonal linearly polarised components; one of these components is parallel to the plane of incidence (designated 'p') and the other is perpendicular to this surface (designated 's'). The p and s components of each beam may have different phases (designated $\beta_p$) and different amplitudes (designated $E_0$). The state of polarisation of a beam is determined by the amplitude ratio, $E_p/E_s$, and the phase difference, $\beta_p - \beta_s$, of the p and s components (e.g., the beam is linearly polarised if the phase difference is either $0^\circ$ or $180^\circ$, otherwise the beam is elliptically polarised). When the incident beam is reflected, the state of the polarisation of the beam undergoes changes (i.e., changes in the amplitude ratio and the phase difference of the p and s components). The ellipsometer measures two angles $\Delta$ and $\Psi$. The angle $\Delta$ is defined as the change in phase upon reflection and is given by

$$
\Delta = (\beta_p - \beta_s)_{\text{reflected}} - (\beta_p - \beta_s)_{\text{incident}} \tag{6.8}
$$

whereas the angle $\Psi$ is defined as the arc-tangent of the factor by which the amplitude ratio changes and is given by

$$
\Psi = \arctan \left[ \frac{(E_p/E_s)_{\text{reflected}}}{(E_p/E_s)_{\text{incident}}} \right] \tag{6.9}
$$

The changes in the state of the polarisation of the beam upon reflection (i.e., indicated by the angles $\Delta$ and $\Psi$) are dependent on:

1. The optical constants of the substrate, that is, the refractive index, $n_{\text{subs}}$, and extinction factor, $k_{\text{subs}}$.
2. The angle of incidence, $\theta$.
3. The wavelength, $\lambda$, of the incident light.
4. The refractive index, $n_{\text{amb}}$, of the ambient medium.
5. The optical constants of the film, that is, the refractive index, $n_{\text{film}}$, and extinction factor, $k_{\text{film}}$.

6. The film thickness, $d_{\text{film}}$.

In fact, $n_{\text{film}}$ and $d_{\text{film}}$ can be calculated from equations (6.8) and (6.9) provided that: (i) A monochromatic light with a known $\lambda$ and $\theta$ is used; (ii) $n_{\text{subs}}$, $k_{\text{subs}}$ and $n_{\text{amb}}$ are known; (iii) The film is non-absorbing (i.e., $k_{\text{film}} = 0$). Unfortunately, equations (6.8) and (6.9) cannot be inverted to obtain $n_{\text{film}}$ and $d_{\text{film}}$. Instead, a numerical technique has to be employed, using computer, to determine them.

The ellipsometer used in this work was a Gaertner L117. The angle of incidence was 50°. The monochromatic light, at $\lambda = 632.8$ nm, from a HeNe laser is first linearly polarised by passing through a polariser and then elliptically polarised by passing through a quarter-wave plate compensator. After being reflected from the film under study, the light passes first through an analyser and then through a filter to remove irrelevant background light and finally through a photodetector to be indicated by the variable gain extinction meter. In practice, the polariser and analyser are rotated until the light intensity at the detector is minimum, indicated by the extinction meter. At this point, the ellipticity caused by the polariser-analyser combination is the exact opposite of that produced by the film. In other words, there are certain settings of the polariser that cause the light reflecting from the film to become linearly polarised. When the polariser is at one of these settings, $p_1$, the analyser can be rotated to a position, $a_1$, where almost no light is detected by the photodetector. A second polariser setting, $p_2$, and the corresponding analyser position, $a_2$, gives a second set of values. The values $p_1$, $p_2$, $a_1$ and $a_2$ are used in a computer program, along with $n_{\text{subs}}$ and $k_{\text{subs}}$, to obtain the values of $n_{\text{film}}$ and $d_{\text{film}}$. On the other hand, some difficulties arise when the substrate is transparent (e.g., glass), which is the case in this work. The reflected beam from the back surface of the substrate is also sensed by the photodetector. Consequently, the complete extinction of light is almost impossible. In addition, the interference between the two beams affects ellipsometric parameters leading to incorrect measurements. A typical solution to overcome this problem is to blacken or to abrade the back surface of the substrate in order to eliminate back reflection. Another solution, which was followed in this work, is to sufficiently separate the two reflected beams by increasing the apparent thickness of the substrate. This was achieved by placing the glass substrate, whose $n_{\text{subs}} = 1.5$ and $k_{\text{subs}} = -0.005$, on a 10 mm thick glass plate. Continuity was attained by putting a drop of oil, whose refractive index was also 1.5, between the two surfaces.
6.3.1.2. Uncertainties of the results

Ellipsometric measurements were carried out, at the early stages of this work, to determine $n_{\text{film}}$ and $d_{\text{film}}$ of reactively deposited films of ITO and zinc oxide doped with aluminium (ZAO) produced then. During these measurements, the laser spot was directed at the visually estimated centre of the sample. Unfortunately, when these measurements were repeated on several samples, due to some doubts concerning their accuracy, irreproducible results were obtained. The irreproducibility, however, was not significant when the sample had not been removed from its position during repeated measurements. Conversely, the irreproducibility was quite obvious when the sample was removed and remounted, keeping the laser spot at its estimated centre. It was felt then that, although the results were reproducible at a fixed point of the film, they were site-dependent since the centre of sample was only visually estimated. To verify that, the refractive index and thickness of a transparent conducting film of ITO, deposited on a glass substrate at about 31% of In-line set-point for 3 min, were measured at different sites on the film. The transmittance and sheet resistance of the film were 90% and 37 $\Omega/\square$, respectively. The results are summarised in figure (6.2). Furthermore, to eliminate the effect of the substrate (e.g., back reflection), these measurements were also carried out on a second ITO film deposited, under the same conditions, on a single crystal silicon substrate whose $n_{\text{subs}} = 3.858$ and $k_{\text{subs}} = 0.018$. The results are summarised in figure (6.3). It is obvious from these two figures, that the ellipsometric measurements were very site-dependant. This may be attributed to film inhomogeneity (i.e., variation in refractive index through the thickness of the film) and to the existence of slight absorption in the film. In addition, ellipsometric measurements are very time-consuming, especially if the number of samples to be measured is large. This was the case in this work, where about 1500 samples had to be measured. For all these reasons, it was decided to use another method to determine the thickness and refractive index of films.

6.3.2. Spectrophotometric measurements

Information concerning optical transmittance and reflectance spectra are crucial in evaluating the optical performance of conducting oxide-films. Spectrophotometry is another non-contact, non-destructive technique often employed for thin film characterisation. In addition to a brief review of the spectrophotometer and the procedure followed in measuring the transmittance and reflectance spectra of the films produced in this work, the method used for determining refractive indices and thicknesses of these films from the reflectance spectra will also be detailed.
Figure (6.2): A 3-D view of refractive index and thickness distribution of an ITO film deposited on a glass substrate.
Figure (6.3): A 3-D view of refractive index and thickness distribution around the centre of an ITO film deposited on a single crystal silicon substrate.
6.3.2.1. The spectrophotometer

Transmittance and reflectance spectra of transparent films, produced in this work, were measured using a Hitachi U-2000 double-beam spectrophotometer. This machine, which has a photometric accuracy of better than ±0.004, is designed primarily for measuring transmittance and absorptance of liquids, solids and gases in ultraviolet and visible spectral regions. The wavelength range it covers is from 190 nm to 1100 nm in increments of 0.1 nm. It can be either operated in interactive mode or driven by an ordinary personal computer using Hitachi’s U-2000 Manager software program. The latter was chosen in this work due to the large number of samples which had to be measured. The measured spectra, with a list interval of 5 nm, were stored as ASCII files.

Figure (6.4) shows the optical system, for the transmittance mode, of the U-2000 spectrophotometer. The system is capable of switching between two light sources according to the wavelength being studied. A tungsten iodide lamp is employed for measurements in the visible range and a deuterium lamp for measurements in the ultraviolet range. The light emitted from the light source is condensed and reflected by the condensing mirror (M₁) to feed a monochromator utilising the diffraction grating (G). The monochromatic beam is passed through a filter (F), reflected by the mirror (M₂) and then separated by the half mirror (HM) into a reference beam and a sample beam. The two beams are absolutely identical to permit accurate measurements. After being focused by the lens (L₂), the reference beam goes directly to a silicon photodetector (D₂) where it is converted into an electrical signal, whereas the sample beam passes first through the sample being examined and then to the lens (L₁) and the photodetector (D₁) to be also converted into another electrical signal. The result of a measurement is obtained by comparing the two electrical signals using an appropriate electronic circuit. Finally, the light beam that irradiates the sample is of a rectangular shape with an area of about 10.8 mm².

6.3.2.2. Transmittance and reflectance measurements

In spectrophotometric measurements carried out in this work, both transmittance and reflectance spectra were measured in the spectral range 350-750 nm with a scanning speed of 400 nm/min.

After setting the desired conditions of measurements (e.g., wavelength range and scan speed), the spectrophotometer had to be calibrated (i.e., calibrating the 100% and 0% over the wavelength range of interest).
This was achieved by conducting the user baseline measurements under the currently defined conditions. Therefore, efficient correction could be made using the same conditions as those set in the actual measurement. To obtain transmittance spectra,
baseline measurements were carried out in air. This means that the reported transmittances of the deposited films were approximately 8% lower than the actual values since the transmittance of the uncoated glass, used throughout this work, was only about 92% in the visible region as can be seen in figure (6.5). Evaluation of the transmittance spectrum of a sample was then achieved by inserting the coated substrate into the transmittance mounting jig and scanning through the defined spectral range.

![Transmittance spectrum of glass substrate used in this work.](image)

Figure (6.6) shows the optical part of the reflectance mounting jig used to measure the reflectance spectra. The sample light beam, of figure (6.4), was reflected by a newly sputter-deposited aluminium mirror to irradiate the sample. The reflected beam from the sample was reflected again by another newly sputter-deposited aluminium mirror before being focused by the lens ($L_1$), which does not appear in figure (6.6), to go to the photodetector ($D_1$). Before evaluating the reflectance spectra of samples, baseline measurements were also carried out, but this time by using a freshly prepared aluminium mirror located in the place of the sample to serve as a reference mirror.

There were three problems associated with the use of the reflectance mounting jig which made the measured reflectances higher than the actual ones: (i) The reflectance of the reference aluminium mirror, in the visible region, was not 100%, but about 92%\cite{1}; (ii) The incorporated increase in the optical path which resulted in an optical lever, altering the focus of the resultant beam going to the photodetector ($D_1$) and causing errors in the measurements; (iii) The reflected beam from the back surface of the substrate which was also sensed by the photodetector.
Corrections of the measured reflectance spectra of the deposited films had to be made, taking into account each of the above mentioned problems. The corrections involved:

1. Measuring the reflectance spectrum of the bottom surface of an uncoated glass substrate in order to subtract it from the measured values of reflectance. This was achieved by treating the bottom surface of an uncoated glass substrate with emery paper so virtually eliminating reflection from it, as figure (6.7) indicates. The reflectance spectra of the untreated (or top) surface and that of an ordinary glass substrate were then measured (figure 6.7). The reflectance spectrum of the back...
surface was obtained by subtracting the reflectance values of the top surface from those of the ordinary substrate, and were averaged to be 5%.

2. Measuring the reflectance spectrum of a single crystal silicon wafer and comparing it with a calculated one\(^2\), as seen in figure (6.8), to derive a correction curve of the measured reflectance in order to obtain the absolute reflectance of the coatings. The correction ratio was, on average, 0.76.

![Image](Figure 6.8: Calculated and experimental reflectance spectra of a single crystal silicon wafer. Also shown the correction ratio as a function of wavelength. Data of the calculated curve are from reference 11.)

Thus, the relation between the measured reflectance, \( R_{\text{measur}} \), and the actual one, \( R \), is

\[
R \approx 0.76(R_{\text{measur}} - 5\%) \tag{6.10}
\]

or

\[
R \approx 0.76R_{\text{measur}} - 4\% \tag{6.11}
\]

As a result, if \( R_{\text{max}} \) is the measured value of a reflectance maximum, the corresponding actual value, \( R_{\text{max}} \), is given by

\[
R_{\text{max}} \approx 0.76R_{\text{max}} - 4\% \tag{6.12}
\]

6.3.2.3. Calculations of refractive indices from reflectance spectra

In this section, the case of transparent non-absorbing films deposited on transparent substrates will be considered. It should be mentioned first that the wavelength \( \lambda \) of the incident light is chosen so that it is comparable to the film thickness \( d_{\text{film}} \) to allow interference effects to occur\(^3\).
As can be seen in figure (6.9), when light of wavelength $\lambda$ coming from a medium of index $n_{\text{amb}}$ is incident at an angle $\theta_0$ on a parallel-sided, isotropic film of index $n_{\text{film}}$ deposited on a plane substrate of index $n_{\text{subs}}$, the reflectance can be expressed in terms of the Fresnel coefficients of reflection at the $n_{\text{amb}}/n_{\text{film}}$ and $n_{\text{film}}/n_{\text{subs}}$ interfaces\textsuperscript{4}. At the $n_{\text{amb}}/n_{\text{film}}$ interface, the Fresnel reflection coefficients are

\begin{align}
    r_1 &= \frac{n_{\text{film}} \cos \theta_0 - n_{\text{amb}} \cos \theta_{\text{i}}}{n_{\text{film}} \cos \theta_0 + n_{\text{amb}} \cos \theta_{\text{i}}} \tag{6.13} \\
    r_2 &= \frac{n_{\text{film}} \cos \theta_{\text{i}} - n_{\text{amb}} \cos \theta_0}{n_{\text{film}} \cos \theta_{\text{i}} + n_{\text{amb}} \cos \theta_0} \tag{6.14}
\end{align}

where $r_1$ and $r_2$ are the components parallel and perpendicular to the plane of incidence. Similarly, the Fresnel reflection coefficients at the $n_{\text{film}}/n_{\text{subs}}$ interface are

\begin{align}
    r_1 &= \frac{n_{\text{subs}} \cos \theta_1 - n_{\text{film}} \cos \theta_0}{n_{\text{subs}} \cos \theta_1 + n_{\text{film}} \cos \theta_0} \tag{6.15} \\
    r_2 &= \frac{n_{\text{subs}} \cos \theta_2 - n_{\text{film}} \cos \theta_1}{n_{\text{subs}} \cos \theta_2 + n_{\text{film}} \cos \theta_1} \tag{6.16}
\end{align}

If $n_{\text{film}} \geq n_{\text{amb}}$ and $n_{\text{film}} \geq n_{\text{subs}}$, and if the case of normal incidence (i.e., $\theta_0 = \theta_1 = \theta_2 = 0$) is considered, then equations (3.13)-(3.16) become
The amplitude reflectance is obtained by summing multiply reflected beams, and given by

\[
R = \frac{r_1^2 + r_2^2 + 2r_1r_2 \cos \delta}{1 + r_1^2r_2^2 + 2r_1r_2 \cos \delta}
\]  

where \( \delta = (2\pi/\lambda)(\text{Path difference}) \) is the phase difference. Since the total path difference is equal to \( 2n_{\text{film}}d_{\text{film}} \), then

\[
\delta = 4\pi n_{\text{film}}d_{\text{film}}/\lambda
\]  

On the other hand, when reflection occurs at an optically denser medium (i.e., higher refractive index), which is the case here since it was assumed that \( n_{\text{film}} \geq n_{\text{amb}} \), the reflected wave \( (r_1) \) undergoes a phase change by \( \pi \) radians, whereas \( (r_2) \) does not. Thus, \( \delta \), in equation (6.19), should be replaced by \( \delta + \pi \). The resultant equation is then

\[
R = \frac{r_1^2 + r_2^2 - 2r_1r_2 \cos \delta}{1 + r_1^2r_2^2 - 2r_1r_2 \cos \delta}
\]  

From equation (6.21), maxima in the reflectance spectra occur when \( \cos \delta = -1 \) and are given by

\[
R_{\text{max}} = \left( \frac{r_1 + r_2}{1 + r_1r_2} \right)^2
\]  

This implies that \( \delta = (2k + 1)\pi \), where \( k \) is an integer. Using equation (6.20), one gets

\[
n_{\text{film}}d_{\text{film}} = (2k + 1)\frac{\lambda_{\text{max}}}{4}
\]  

where \( \lambda_{\text{max}} \) is a wavelength at which a reflectance maximum occurs. Similarly, minima in the reflectance spectra occur when \( \cos \delta = 1 \) and are given by

\[
R_{\text{min}} = \left( \frac{r_1 - r_2}{1 + r_1r_2} \right)^2
\]  

This means that \( \delta = 2k\pi \), where \( k \) is an integer. Using equation (6.20), one gets
where $\lambda_{\text{min}}$ is a wavelength at which a reflectance minimum occurs. In practice, it is more convenient to express $R_{\text{max}}$ and $R_{\text{min}}$ in terms of refractive indices. This can be achieved by substituting equations (6.17) and (6.18) in equations (6.22) and (6.24). This yields the following two equations:

$$R_{\text{max}} = \left( \frac{n_{\text{film}}^2 - n_{\text{amb}} n_{\text{subs}}}{n_{\text{film}}^2 + n_{\text{amb}} n_{\text{subs}}} \right)^2$$  \[6.26\]

$$R_{\text{min}} = \left( \frac{n_{\text{subs}} - n_{\text{amb}}}{n_{\text{subs}} + n_{\text{amb}}} \right)^2$$  \[6.27\]

By solving equation (6.26) for $n_{\text{film}}$, one gets

$$n_{\text{film}} = \left( n_{\text{amb}} n_{\text{subs}} \frac{1 + \sqrt{R_{\text{max}}}}{1 - \sqrt{R_{\text{max}}}} \right)^{1/2}$$  \[6.28\]

The relative precision of $n_{\text{film}}$ is given by

$$\frac{\Delta n_{\text{film}}}{n_{\text{film}}} = \frac{\sqrt{R_{\text{max}}}}{2(1 - R_{\text{max}})} \frac{\Delta R_{\text{max}}}{R_{\text{max}}}$$  \[6.29\]

For example, if $R_{\text{max}} = 36\%$, it is then sufficient to measure $R_{\text{max}}$ to an accuracy of about 2% (i.e., $\Delta R_{\text{max}} = 0.7\%$) so that the relative error for $n_{\text{film}}$ is not larger than 1%.

In this work, films were deposited on glass substrates with $n_{\text{subs}} = 1.525$ and the spectrophotometric measurements were carried out in air (i.e., $n_{\text{amb}} = 1$). Thus, by substituting the value of $R_{\text{max}}$ from equation (6.12) in equation (6.28), one gets

$$n_{\text{film}} = \left( 1.525 \frac{1 + \sqrt{0.76 \text{measur}} - 0.04}{1 - \sqrt{0.76 \text{measur}} - 0.04} \right)^{1/2}$$  \[6.30\]

Instead of ellipsometry, equation (6.30) was used to calculate refractive indices of films produced in the course of this work, for the following reasons:

1. It is independent of optical thicknesses of coatings and consequently gives consistent results for variable optical thicknesses.
2. The possibility of obtaining refractive indices over many wavelengths rather than at 632.8 nm using the ellipsometer.

3. The ratio of the area of light beam of the spectrophotometer (~10.8 mm²) and that of the laser beam of the ellipsometer (~0.8 mm²) is about 14. This gives better integration over the coated area of the substrate.

4. There was no point in doing ellipsometric measurements for a very large number of samples (~1500) as their reflectance spectra are already available.

5. It is quicker than ellipsometric measurements.

6.3.2.4. Calculations of thicknesses from reflectance spectra using interference methods

After calculating $n_{\text{film}}$, using equation (6.30), the film thickness could be calculated using equations (6.23) and (6.25). The calculation procedure depended on the shape of the reflectance spectrum of interest.

If there were two consecutive maxima in the scanned spectral range, then the equation (6.23) for the first maximum is $4n_{\text{film}}d_{\text{film}} = (2k+1)\lambda_{\text{max}_1}$ and that for the second maximum is $4n_{\text{film}}d_{\text{film}} = [2(k-1)+1]\lambda_{\text{max}_2}$. By solving these two equations, it is found that

$$d_{\text{film}} = \frac{\lambda_{\text{max}_1} - \lambda_{\text{max}_2}}{2n_{\text{film}}(\lambda_{\text{max}_2} - \lambda_{\text{max}_1})}$$

Equation (6.31) is also valid in the case of two consecutive minima. The problem of this equation is that it ignores changes of $n_{\text{film}}$ with wavelength. However, it was considered to be sufficiently accurate for the estimation of $d_{\text{film}}$ for the purpose of this work, especially in the relatively narrow range of wavelength studied where variations in $n_{\text{film}}$ were not expected to be so significant. When only one maximum (or minimum) existed in the reflectance spectrum, the value of $k$ was estimated and then substituted in the appropriate equation (i.e., equation 6.23 for a maximum and equation 6.25 for a minimum). The estimation of $k$ in such cases was based on knowing the order of thicknesses of films prepared under close conditions in another deposition run and/or the sputtering rates of the elements involved.

Finally, it should be indicated that the results of the thickness measurements were satisfactorily consistent in the course of this work.
6.4. Compositional measurements using Auger electron spectroscopy

Auger electron spectroscopy (AES) is one of the most common techniques of surface analysis. It is able to give qualitative and quantitative information concerning elements in the outermost atomic layers of a solid surface\textsuperscript{15-18}.

Auger electrons are generated by bombarding the surface of a solid with an energetic beam of electrons (up to 20 keV\textsuperscript{18}). To explain that, the case of figure (6.10) will be considered as an example. A primary electron from such a beam ionises an inner atomic level (e.g., K) of a surface atom leaving a hole in this level, provided that the energy of the primary electron is greater than the binding energy of the ejected one. Once it is ionised, the atom must relax by filling the hole in the K level with an electron from an outer level (e.g., L\textsubscript{2}), and emitting the excess energy in the form of an X-ray photon. This photon may either escape the atom (a radiative process) or cause the ejection of an "Auger" electron from a lower energy level (e.g., L\textsubscript{3}) in a non-radiative process. The latter process was first discovered by Auger\textsuperscript{19} and named after him. The measured energy of the Auger electron, \(E_{\text{Auger}}\), in this case is approximately

\[
E_{\text{Auger}} = E_K - E_{L_2} - E_{L_3} - \phi_A,
\]

where \(E_K\), \(E_{L_2}\) and \(E_{L_3}\) are the energies corresponding to the atomic levels K, L\textsubscript{2} and L\textsubscript{3}, respectively, and \(\phi_A\) is the work function of the analyser material which is constant for a given analyser. Consequently, \(E_{\text{Auger}}\) is a
function only of the atomic energy levels taking part in the process, and is thus characteristic of the parent atom. Such an Auger electron is termed as a KLL Auger electron. Other Auger electrons may be created from LMM, MNN and other transitions. It is quite obvious that since the emission of an Auger electron is a three-electron process, elements such as H and He, whose atomic number is less than three, can not be detected.

Most Auger electrons posses energies in the range 20-2500 eV. Their mean free paths are in the range of about 1-3 nm (i.e., a few atomic layers). Consequently, Auger electrons generated at deeper distances below the surface have a low probability of reaching the surface, escaping and being detected. They only contribute to the general secondary electron background on which the meaningful signal is superimposed. This background distribution (i.e., N(E) versus E) varies slowly with energy, therefore, permitting the Auger peaks to be emphasised by the first derivative of the spectrum.

As it is a surface sensitive technique, an AES analysis is performed in an ultra-high vacuum environment in the range of $10^{-9}-10^{-10}$ Torr in order to prevent the sample surface from becoming contaminated. In addition to the electron gun which produces an electrostatically focused beam of energetic electrons, an Auger spectrometer contains an electron energy analyser and detection system. Furthermore, modern instruments are airlocked and equipped with a differentially-pumped ion gun for cleaning samples and obtaining depth profiles.

The main advantage of AES technique over SEM, in the determination of the relative concentrations of elements in the film, is that the penetration depth (sampling depth) of SEM is about 1-2 μm whereas that of AES is about 1-3 nm. Thicknesses of films deposited in this work were of the order of 200 nm. This implies that the electron probe in SEM would penetrate to the glass substrate and analyse the substrate rather than the film itself.

A Varian 10 keV scanning Auger electron spectrometer, with a base pressure of less than $10^{-8}$ Torr, was used. The primary electron beam current and energy were 1.1 μA and 3 keV, respectively, with a spot diameter of about 100 μm. The working gas in the ion gun was Ar at a pressure of $8 \times 10^{-5}$ Torr. The ion current density and energy of the gun were 50 μA/cm² and 3 keV, respectively. Sub-surface compositions were determined at two depths (after 15 and 30 seconds ion etching) in each analysed sample. In all cases, similar compositions were observed at each depth indicating that the bulk of the film had been reached. The numerical results will be given in the relevant section.
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CHAPTER SEVEN

RESULTS AND DISCUSSION: INDIUM OXIDE AND ITS DOPANTS

7.1. Introduction

Visibly transparent and electrically conducting thin films can be obtained, in general, by either depositing very thin metal films (~10 nm-thick) or depositing transparent conducting oxides. In addition to their partial transparency, the conductivity of metallic thin films (e.g., Au, Ag and Cu) is sometimes several orders of magnitude lower than that of bulk material. The latter is due to the considerably reduced mobility of charge carriers which is attributed to metallic and/or oxide impurities which act as scattering sites of the carriers (i.e., Coulomb scattering from ionised impurities), and also to scattering of the carriers by the surface potential of the film. Moreover, environmental stability and mechanical robustness of metallic thin films are quite limited.

High transparency, in the visible region, and good electrical conductivity can only be achieved by creating electron degeneracy in a wide band gap semiconducting oxide. The minimum semiconductor band gap which is required for transmitting visible light may be calculated as follows: The relation between the photon energy, $E_{\text{photon}}$, and its wavelength, $\lambda_{\text{photon}}$, is given by

$$E_{\text{photon}} (\text{eV}) = \frac{1241}{\lambda_{\text{photon}} (\text{nm})} \quad [7.1]$$

In the range of visible light 400 nm $\leq \lambda_{\text{visible}}$ $\leq$ 700 nm. Using equation (7.1), gives $3.10 \text{ eV} \geq E_{\text{visible}} \geq 1.77 \text{ eV}$, which means that any semiconductor with a band gap in this range will act as an optical filter transmitting all photons with energies lower than
its band gap and absorbing photons with higher energies. Thus, for any semiconductor to be transparent in the visible region, its band gap should be greater than or rather equal 3.10 eV.

Transparent conducting oxides are n-type degenerate semiconductors\(^4\). The high conductivity is due to high electron concentration since the mobility of the carriers in such films is less than that in bulk material. This high conductivity of these oxides make them highly reflective at longer wavelengths (i.e., in the infrared region of the spectrum) and hence able to minimise the exchange of heat transferred by radiation\(^5\). The origin of conducting electrons in undoped and heavily doped oxides is different.

In undoped oxides (e.g., \(\text{In}_2\text{O}_3\)), high electron concentration (~10\(^{17}-10^{21}\) per cm\(^3\)) is achieved by stoichiometric deviation owing to oxygen deficiency (e.g., \(\text{In}_2\text{O}_{3-x}\)) or excess metal atoms (e.g., \(\text{In}_{2+y}\text{O}_3\)). Under reducing conditions, an oxygen atom is removed leaving two electrons in the crystal which may then be excited and moved away from the vacancy to contribute in conduction. As a result, the vacancy becomes positively charged and hence a site for electron trapping. This implies that the density of these trapping sites, and hence the number of conduction electrons, has to be made small (less than 0.01) for conduction to be high\(^6\). This is an uneasy task since these oxides are easily oxidised and reduced due to the relatively low standard molar enthalpies of formation (section 5.4.1). It was observed in this work, and in many other works\(^7,8\), that any small deviation from a certain volume fraction of oxygen vacancies may severely affect the conductivity of undoped oxide films.

In doped oxides, the high electron concentration is an outcome of the substitutional incorporation of cations, or anions, into the host lattice. There are several requirements which have to be met in order to create free electrons, so enhancing n-type conductivity. These requirements are:

1. The doping cation should posses a higher valance (e.g., \(\text{Sn}^{4+}\) in ITO) than that of the host (e.g., \(\text{In}^{3+}\) in \(\text{In}_2\text{O}_3\)) which necessitates the addition of an electron in order to maintain overall charge neutrality. In fact, lower valency cations create holes which act as traps for electrons in the n-type semiconductors and reduce conductivity. On the contrary, the doping anion should posses a lower valance than that of oxygen (e.g., \(\text{F}^{-}\) in the case of tin oxide doped with fluorine).

2. The diameter of the doping cation should be smaller than or equal to the diameter of the host ion it substitutes, otherwise it would be incorporated as an interstitial and act as a scattering site.
3. The dopant oxide and the host oxide should not be able to form any compound or solid solution with each other.

On the other hand, the conductivity of transparent oxide films is also affected by the virtually permanent supply of cations, from glass substrates, which diffuse into the films. Clearly, such a contaminating effect increases with substrate temperature since the diffusion process does the same. Unfortunately, among these cations there are: (i) Cations whose ionic diameters are sufficiently small so they can substitutionally incorporate into deposited oxides and produce holes which act as traps for electrons (e.g., Li\(^+\)). (ii) Cations whose ionic diameters are large so they can be incorporated into deposited oxides as interstitials and act as scattering sites (e.g., Ca\(^{2+}\)).

In general, the window of appropriate stoichiometries, or the "process window", which may be defined as the range of oxygen partial pressure, or any of its representatives (e.g., the percentage of control signal in PEM control, or the percentage of cathode voltage in voltage control), through which transparent conducting oxide films occur, is very narrow. This makes the curve of sheet resistance (or resistivity) versus oxygen partial pressure (or any of its representatives) almost a "V"-shape. In addition, this window is usually within the pressure instability region discussed in chapter four. Consequently, any tiny change of oxygen partial pressure results in a significant change in sheet resistance. This reflects the difficulty in producing high quality films of conducting oxides and implies the need for an optimum oxygen content, and hence very efficient control of oxygen admission rate to the chamber, to deposit such films with minimum sheet resistance.

Due to their unique optical and electrical properties, as well as their good mechanical resistance, excellent adherence to the substrate and environmental stability\(^9,10\), transparent conducting oxides have gained an increasing interest and have been adopted in a wide variety of applications in modern technology. Among them: (i) Energy-efficient windows in buildings\(^5,6,11-13\); (ii) Heat mirrors in front of the absorbers in solar collectors\(^5,14,15\); (iii) Heat mirrors in incandescent lamps for reducing the energy required to heat the tungsten filament, by reflecting this heat back to the filament, and also for minimising the unwanted heat radiation in the area illuminated by such lamps\(^5\); (iv) As they are n-type semiconductors, they can be deposited onto p-type single crystal semiconductors (e.g., p-Si and p-InP) in heterojunction photovoltaic solar cells\(^16-19\). In addition to forming the junction required to provide the bending of energy bands necessary to generate photocurrent in a practically easier manner than that of conventional diffused p-n junctions, these oxides permit the direct transmission of solar radiation to the active region (i.e., the p-n junction) with minimised attenuation. Furthermore, such a film can serve simultaneously as a low resistance contact to the
junction and as an antireflection coating\textsuperscript{4,20}; (v) Transmitting electrodes for optoelectronics, which include light emitting diodes\textsuperscript{21} and display devices\textsuperscript{22-24}; (vi) Gas sensors in which an oxide film is deposited on an insulating substrate with two metal electrodes. Attributed mainly to direct transfer of electrons from the adsorbed gas to the oxide film, the electron concentration, and hence conductivity, in semiconductor sensors may vary almost linearly with gas pressure\textsuperscript{2}; (vii) Other applications also include, thin film resistors due to their high degree of stability with temperature, low friction wear resistant coatings for glass containers, laser-resistant coatings\textsuperscript{25,26}, antistatic coatings\textsuperscript{17} (e.g., for satellites) and as transparent heating elements to prevent the formation of ice and moisture on aircrafts and automobiles windshield\textsuperscript{23}.

This chapter will concentrate on the techniques, used in this work, to sputter-deposit and characterise transparent conducting films of indium oxide doped with tin as well as some other new alloys such as indium zinc oxide and indium oxide doped with titanium or aluminium. In general, information concerning targets preparations, deposition procedures, methods of power application and methods of control of the admission rate of oxygen into the sputtering chamber were described in chapter five. In addition, the techniques and instrumentation used for the characterisation of the produced films were discussed in chapter six. Finally, it should be emphasised that the combinations of powers reported throughout this work were not the only ones investigated. In fact, they were the ones that gave the most promising results.

7.2. Indium oxide doped with tin (ITO)

Indium oxide, especially when it is doped with tin to form ITO films, has been virtually the most extensively utilised transparent conducting oxide due to its excellent electrical and optical properties. The band gap, electron mobility, carrier concentration and refractive index of undoped indium oxide films are about 3.5-3.7 eV, 10-75 cm\textsuperscript{2}/V.s, \(10^{19}-10^{20}\) cm\textsuperscript{-3} and 1.9-2.08, respectively. The corresponding values for ITO films are greater than \(-3.7\) eV, \(-15-40\) cm\textsuperscript{2}/V.s, \(-10^{21}\) cm\textsuperscript{-3} and \(-1.8-2.1\), respectively\textsuperscript{2,5,6,30}. In practice, large numbers of deposition techniques (e.g., reactive evaporation\textsuperscript{6,16,20,27}, DC reactive magnetron sputtering\textsuperscript{7,9,12,28-34}, RF sputtering\textsuperscript{10,24,26,35-37} and other methods\textsuperscript{38}) and procedures (e.g., varying the substrate temperature, biasing the substrate, post-deposition annealing in different atmospheres...etc.) have been applied to produce high quality films. Examples of some of these techniques and procedures, along with the optical and electrical properties of the resultant films, are summarised in table (7.1). In fact, most deposition processes which have been adopted to produce good quality ITO films (and other conducting oxide films) suffer from, at least one, of the following disadvantages
<table>
<thead>
<tr>
<th>Depos. method</th>
<th>Subs. temp. (°C)</th>
<th>Subs. bias (V)</th>
<th>Post-deposition annealing temperature (°C) and duration (min)</th>
<th>$R_y$ (μΩm) or $R_y$ (Ω/□)</th>
<th>$T$ (%)</th>
<th>Depos. rate (nm/min)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>RE</td>
<td>400</td>
<td>-</td>
<td>-</td>
<td>$R_y=2$</td>
<td>85</td>
<td>0.08</td>
<td>27</td>
</tr>
<tr>
<td>RE</td>
<td>&gt;150</td>
<td>-</td>
<td>-</td>
<td>$R_y=2$</td>
<td>78</td>
<td>0.20</td>
<td>6</td>
</tr>
<tr>
<td>RE</td>
<td>300-400</td>
<td>-</td>
<td>-</td>
<td>$R_y=2$</td>
<td>80</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>RE</td>
<td>350-400</td>
<td>-</td>
<td>in H$_2$ (neither temperature nor duration was stated)</td>
<td>$R_y=2$</td>
<td>86</td>
<td>0.11</td>
<td>16</td>
</tr>
<tr>
<td>DCRMS</td>
<td>&lt;60</td>
<td>RF</td>
<td>-</td>
<td>$R_y=9$</td>
<td>90</td>
<td>1.25 @ ?</td>
<td>12</td>
</tr>
<tr>
<td>DCRMS</td>
<td>Room</td>
<td>Float.</td>
<td>-</td>
<td>$R_y=6$</td>
<td>82</td>
<td>0.16 @ 250W</td>
<td>28</td>
</tr>
<tr>
<td>DCRMS</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>$R_y=4$</td>
<td>High</td>
<td>4.16 @ 3A</td>
<td>29</td>
</tr>
<tr>
<td>DCRMS</td>
<td>Room</td>
<td>-</td>
<td>320-480 °C in air according to film thickness (no duration was stated)</td>
<td>$R_y=4.5$</td>
<td>&gt;90</td>
<td>4 @ 1.25KW</td>
<td>30</td>
</tr>
<tr>
<td>DCRMS</td>
<td>Room</td>
<td>5</td>
<td>-</td>
<td>$R_y=1$</td>
<td>79</td>
<td>0.8 @ 820W</td>
<td>31</td>
</tr>
<tr>
<td>DCRMS</td>
<td>200-400</td>
<td>-</td>
<td>400 °C in 90% N$_2$ and 10% H$_2$ for 60 min</td>
<td>$R_y=2.5$</td>
<td>80-90</td>
<td>0.08</td>
<td>32</td>
</tr>
<tr>
<td>DCRMS</td>
<td>-</td>
<td>-</td>
<td>300-500 °C in air for metal-rich films, and in 95% N$_2$ and 5% H$_2$ for oxidised films for up to 80 min</td>
<td>$R_y&lt;40$</td>
<td>&gt;90</td>
<td>-</td>
<td>33</td>
</tr>
<tr>
<td>DCRMS</td>
<td>Room</td>
<td>2 kV RF</td>
<td>-</td>
<td>$R_y=6$</td>
<td>85</td>
<td>25 @ 3A</td>
<td>7</td>
</tr>
<tr>
<td>DCRMS</td>
<td>Room</td>
<td>-80V</td>
<td>350-500 °C in vacuum for 40 min</td>
<td>$R_y=3$</td>
<td>85</td>
<td>-</td>
<td>34</td>
</tr>
<tr>
<td>DCRMS</td>
<td>Room</td>
<td>-</td>
<td>-</td>
<td>$R_y=6.8$</td>
<td>85</td>
<td>-</td>
<td>9</td>
</tr>
</tbody>
</table>

*Table (7.1): Electrical and optical properties of ITO films prepared by reactive evaporation (RE) and DC reactive magnetron sputtering (DCRMS).*
1. A narrow process window which makes the identification of optimum electrically conducting and visually transparent films a very difficult task.

2. A low deposition rate which means that the production of these films, on a large-scale, is a slow and/or a power-consuming process.

3. Raising the substrate temperature during deposition adds complexity to the process and may affect heat-sensitive substrates.

4. Biasing the substrate, usually with an independent RF power, adds complexity to the process.

5. In addition to being a time-consuming process, annealing of deposited films in an oxidising or reducing atmosphere may affect heat-sensitive substrates.

Three different methods were used, in this work, to deposit ITO films. They were

7.2.1. Independently DC powered magnetrons without PEM control

The main and secondary targets (section 5.2.1) were, in this method of preparation, Sn and In, respectively. Using the independently DC powered magnetrons method, described in section (5.2.7.1), the power to the Sn cathode, $P_{Sn}^{DC}$, was held constant at 300 W throughout, whereas the power applied to the In cathode, $P_{In}^{DC}$, was varied taking the values 200, 230, 250 and 270 W. For each $P_{Sn}^{DC}$-$P_{In}^{DC}$ combination, oxygen was manually admitted to the chamber (i.e., without PEM control) and its flow rate, $f_{O_2}$, was gradually increased, starting from metallic targets. At each value of $f_{O_2}$, a film was deposited and its sheet resistance, $R_s$, transmittance spectrum, refractive index, $n_{film}$, thickness, $d_{film}$, and resistivity, $R_y$, were determined. It should be emphasised that the transmittance, $T_{550}$, in the middle of the visible range (i.e., at 550 nm), where the human eye is most sensitive, has been considered in this work instead of the maximum transmittance which may occur at any wavelength in that range.

Figure (7.1) shows variations of voltages of Sn and In cathodes versus $f_{O_2}$ when $P_{In}^{DC}$ was 200, 230 and 250 W. At relatively low values of $f_{O_2}$, the Sn cathode was rapidly oxidised whereas the In cathode remained almost metallic, a result of the $O_2$ inlet to the chamber being attached to the pod of the Sn cathode (section 5.2.1). At higher values of $f_{O_2}$, both cathodes were oxidised.
Figure (7.1) shows the variations of volteages of Sn and In cathodes versus the manually admitted oxygen flow rate. The power to the Sn cathode was held constant at 300W. The power to the In cathode was 200, 230 and 250W.

Figure (7.2) shows the variations of $R_y$ and $T_{550}$ with $f_{O_2}$, at the above mentioned combinations of powers. Excluding those corresponding to $P_{In}^{DC} = 200$ W, both $R_y$ and $T$ of these films started to decrease at some higher values of $f_{O_2}$.

This was quite an abnormal behaviour since increasing $f_{O_2}$, beyond some critical value at which films of minimum $R_y$ and high $T_{550}$ were obtained, was usually accompanied by films of higher $R_y$ and $T_{550}$. In fact, it was visually observable that at such higher values of $f_{O_2}$, some spots of metallic appearance, possibly due to insufficient oxidisation of sputtered In, started to deposit, an indication of $O_2$ deficiency in the system. Figure (7.3) shows the minimum $f_{O_2}$, and the corresponding chamber total
pressure, at which the 'shadowed' transparent conducting films of ITO started to appear as functions of $P^{\text{DC}}_{\text{In}}$. Obviously, the 'shadowed' films appeared at lower values of $f_{\text{O}_2}$ and total pressure, as $P^{\text{DC}}_{\text{In}}$ was increased. A probable explanation of that could be the formation of SnO$_2$, instead of SnO, at the Sn cathode at some critical value of $O_2$ partial pressure with the resultant increase in $O_2$ consumption leaving the chamber $O_2$-deficient since the $O_2$ supply to it was fixed by the manually controlled flow rate of oxygen. When $P^{\text{DC}}_{\text{In}}$ was high, the sputtering rate from the In cathode (equation 2.17) and hence the amount of oxygen required to oxidise it were both high. Consequently, the 'shadowed' films appeared at a lower value of $f_{\text{O}_2}$. Note that no 'shadowed' films was observed when $P^{\text{DC}}_{\text{In}} = 200$ W.

![Figure (7.3): Minimum oxygen flow rate, and the corresponding chamber total pressure, at which the 'shadowed' transparent conducting films of ITO started to appear as functions of power applied to the In cathode.](image)

Figure (7.3) shows the transmittance spectra of the best transparent conducting ITO films at different powers applied to the In cathode. Oxygen flow rates, at which the best transparent conducting ITO films occur are plotted in figure (7.5) versus $P^{\text{DC}}_{\text{In}}$. The percentage of Sn in these films, obtained by AES (section 6.4), is also plotted in the figure. Finally, $R_y$ and $T_{550}$ of the best ITO films are plotted in figure (7.6) as functions of $P^{\text{DC}}_{\text{In}}$. The following remarks can be deduced provided that $P^{\text{Sn}}_{\text{In}}$ is constant

1. The Sn content of the film decreases linearly with $P^{\text{DC}}_{\text{In}}$ (figure 7.5).

2. The best transparent conducting films occur at higher $f_{\text{O}_2}$ as $P^{\text{DC}}_{\text{In}}$ increases (figure 7.5).

3. The resistivity of these films decreases as $P^{\text{DC}}_{\text{In}}$ increases (i.e., when the Sn content of the film decreases), whereas the corresponding transmittance increases

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first and then decreases (figures 7.4 and 7.6). Such a decrease in transmittance was probably due to the inability of the system to oxidise the sputtered metallic In at high powers, as discussed earlier. However, it was impossible for O\textsubscript{2} partial pressure in the system to greatly exceed that of Ar as such an increase might endanger the turbomolecular pump.

**Figure (7.4):** Transmittance spectra of the best transparent conducting ITO films at different powers to the In cathode. The Sn cathode was held constant at 300 W throughout. Oxygen flow rate was manually controlled.

**Figure (7.5):** The occurrence of the best transparent conducting ITO films as a function of power applied to the indium cathode. The percentage of tin in these films is also plotted. Oxygen flow rate was manually controlled.
Table (7.2) summarises the properties of the best transparent conducting films prepared by this technique. Remember that the deposition rate, $R_{\text{dep}}$, mentioned in the table is the measured deposition rate (section 5.4.2.2).

In addition to the relatively narrow process window, the resistivities of ITO films prepared by this method were somewhat high and could not be further improved due to the constraints imposed by the sputtering system. Therefore, some other methods were considered to improve the quality of the deposited films.

<table>
<thead>
<tr>
<th>$P_{\text{In}}^{\text{DC}}$ (W)</th>
<th>$R_\parallel$ (Ω/□)</th>
<th>$R_\perp$ (Ω·m)</th>
<th>$n_{\text{film}}$</th>
<th>$T_{550}$ (%)</th>
<th>$R_{\text{dep}}^\text{In}$ (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>74</td>
<td>$19.0 \times 10^{-6}$</td>
<td>2.00</td>
<td>80.9</td>
<td>1.43</td>
</tr>
<tr>
<td>230</td>
<td>74</td>
<td>$18.8 \times 10^{-6}$</td>
<td>2.07</td>
<td>86.6</td>
<td>1.41</td>
</tr>
<tr>
<td>250</td>
<td>43</td>
<td>$10.8 \times 10^{-6}$</td>
<td>2.07</td>
<td>86.2</td>
<td>1.40</td>
</tr>
<tr>
<td>270</td>
<td>38</td>
<td>$9.4 \times 10^{-6}$</td>
<td>2.04</td>
<td>82.9</td>
<td>1.38</td>
</tr>
</tbody>
</table>

Table (7.2): Properties of the best transparent conducting films of ITO prepared by independently DC powered magnetrons without PEM control.

7.2.2. Independently DC powered magnetrons with PEM control

In this method, the main and secondary targets (section 5.2.1) were In and Sn, respectively. Using the independently DC powered magnetrons method (section 5.2.7.1), the power to the In cathode, $P_{\text{In}}^{\text{DC}}$, was held constant at 300 W throughout, whereas the power applied to the Sn cathode, $P_{\text{Sn}}^{\text{DC}}$, was varied taking the values 0 (i.e., undoped indium oxide), 10, 20, 30, 40, 50, 100 and 200 W. PEM control, on the In emission line at 451.1 nm, was used (sections 4.5.1 and 5.2.8.1). For each $P_{\text{In}}^{\text{DC}}$, $P_{\text{Sn}}^{\text{DC}}$
combination, the percentage of In line set-point, $\text{In}^\%_{\text{pem}}$, was gradually decreased by the automatic admission of the appropriate flow rate of oxygen to the chamber, starting from metallic targets. At each value of $\text{In}^\%_{\text{pem}}$, a film was deposited and characterised.

Figures (7.7) and (7.8) show variations of voltages of the In and Sn cathodes, respectively, versus $\text{In}^\%_{\text{pem}}$, when $P_{\text{Sn}}^{\text{DC}}$ was 10, 50, 100 and 200 W. The In cathode (figure 7.7) was oxidised regardless of the power applied to the Sn one, but the degree of oxidisation increased with $P_{\text{Sn}}^{\text{DC}}$. This may be understood in terms of the sputtering rate from the Sn cathode which is proportional to $P_{\text{Sn}}^{\text{DC}}$ (equation 2.17). At higher $P_{\text{Sn}}^{\text{DC}}$ the amount of sputtered Sn was high and thus $\text{In}^\%_{\text{pem}}$ should be lower to secure sufficient O$_2$ partial pressure to oxidise such an amount of metallic Sn with the plasma of the In cathode. As a result, the degree of oxidation of the In cathode would be higher. On the other hand, the Sn cathode (figure 7.8) remained almost metallic when $P_{\text{Sn}}^{\text{DC}}$ was low (e.g., 10 and 50 W) but its degree of oxidisation was higher when $P_{\text{Sn}}^{\text{DC}}$ was increased (e.g., 100 and 200 W). As already discussed, the latter could be attributed to the higher O$_2$ partial pressure required to oxidise the relatively large amount of sputtered Sn which in turn oxidised the Sn cathode.

Figure (7.7): Variations of the voltage of the In cathode versus the percentage of In line set-point at different powers applied to the Sn cathode. The power to the In cathode was fixed at 300 W.

![Figure (7.7): Variations of the voltage of the In cathode versus the percentage of In line set-point at different powers applied to the Sn cathode. The power to the In cathode was fixed at 300 W.](image)

Figure (7.9) supports the above explanation. In this figure, $R_y$ and $f_{O_2}$ are plotted versus $\text{In}^\%_{\text{pem}}$ for the transparent conducting films of undoped indium oxide (i.e., the power to the Sn cathode was switched off) and the corresponding ITO films when $P_{\text{Sn}}^{\text{DC}} = 50$ W. It can be seen that the values of $f_{O_2}$ in the case of undoped indium oxide were lower than the corresponding ones of ITO. The difference may be due to the amount of O$_2$ required to oxidise the sputtered Sn. On the other hand, this figure also
shows the very wide process window at which conducting ITO films can be deposited by this technique.

Figure (7.8): Variations of the voltage of the Sn cathode versus the percentage of In line set-point at different powers applied to the Sn cathode. The power to the In cathode was fixed at 300 W.

Figure (7.9): A plot of resistivity and oxygen flow rate versus the percentage of In line set-point for transparent conducting films of undoped indium oxide and the corresponding ITO films when the Sn cathode was held at 50W.

Figure (7.10) shows the dependence of $R_y$ and $T_{550}$ of the transparent conducting films of undoped indium oxide and ITO on $In_{pcm}$. The applied power was 300 W to the In cathode and 20, 30, 40, 50 and 100 W to the Sn cathode. Again, the very wide process windows were quite obvious. They were about 6.5% at $P_{Sn}^{PC} = 40$ W and 5% at $P_{Sn}^{PC} = 50$ W. The percentages of In line set-point, at which the best transparent conducting films occur, along with the corresponding resistivities, are plotted in figure (7.11) versus $P_{Sn}^{PC}$, whereas $T_{550}$ and $R_y$ of these films are plotted in figure (7.12)
versus $P^{\text{DC}}_{\text{Sn}}$. Finally, the transmittance spectra of the best films at different powers applied to the Sn cathode are plotted in figure (7.13). Provided that $P^{\text{DC}}_{\text{In}}$ is constant, these figures imply

1. The best transparent conducting films occur at lower $\text{In}^{\%}_{\text{pcm}}$ as $P^{\text{DC}}_{\text{Sn}}$ increases (figure 7.11). This may be to achieve sufficient $O_2$ partial pressure to oxidise the increasing amount of sputtered metallic Sn.

-225-
2. The resistivity of these films increases as $P_{Sn}^{DC}$ increases, whereas the corresponding $T_{550}$ generally decreases (figure 7.12). The transmittance, $T_{550}$, of these films and their thickness, $d_{film}$, are plotted in figure (7.14) versus $P_{Sn}^{DC}$. At lower values of $P_{Sn}^{DC}$ (i.e., $P_{Sn}^{DC} \leq 50$ W), $T_{550}$ behaves in an opposite way to that of $d_{film}$, whereas at higher values of $P_{Sn}^{DC}$, both $T_{550}$ and $d_{film}$ decrease. The former could mean that the decrease in $T_{550}$ was due to increasing film thickness, whereas the latter was probably due to the higher Sn content of the films. However, the ranges of thickness and transmittance were quite limited.
3. These films show a very high transmission in the red (~88-91%) and an increasing absorption in the blue as $P_{Sn}^{DC}$ increases (figure 7.14).

Figure (7.14): Transmittance at 550nm and thickness of the best transparent conducting films of undoped indium oxide and ITO versus power applied to the Sn cathode. PEM control was used.

In addition, AES results revealed that the percentage of Sn in the best ITO films was between 3.4% and 3.7%. Table (7.3) presents a summary of the properties of the best transparent conducting films prepared by this method. As mentioned before, the high deposition rate is evidence about the efficiency of this deposition technique and PEM control.

<table>
<thead>
<tr>
<th>$P_{Sn}^{DC}$ (W)</th>
<th>$R_s$ (Ω/□)</th>
<th>$R_y$ (Ω.m)</th>
<th>$n_{film}$</th>
<th>$T_{550}$ (%)</th>
<th>$R_s^{gapp}$ (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>25</td>
<td>$3.9 \times 10^{-6}$</td>
<td>2.06</td>
<td>82.4</td>
<td>0.88</td>
</tr>
<tr>
<td>10</td>
<td>29</td>
<td>$4.5 \times 10^{-6}$</td>
<td>2.11</td>
<td>85.9</td>
<td>0.86</td>
</tr>
<tr>
<td>20</td>
<td>34</td>
<td>$5.2 \times 10^{-6}$</td>
<td>2.14</td>
<td>84.3</td>
<td>0.86</td>
</tr>
<tr>
<td>30</td>
<td>32</td>
<td>$5.0 \times 10^{-6}$</td>
<td>2.10</td>
<td>80.9</td>
<td>0.88</td>
</tr>
<tr>
<td>40</td>
<td>30</td>
<td>$4.9 \times 10^{-6}$</td>
<td>2.04</td>
<td>79.5</td>
<td>0.91</td>
</tr>
<tr>
<td>50</td>
<td>35</td>
<td>$5.8 \times 10^{-6}$</td>
<td>2.00</td>
<td>78.4</td>
<td>0.93</td>
</tr>
<tr>
<td>100</td>
<td>42</td>
<td>$6.9 \times 10^{-6}$</td>
<td>2.08</td>
<td>77.3</td>
<td>0.91</td>
</tr>
<tr>
<td>200</td>
<td>120</td>
<td>$19.0 \times 10^{-6}$</td>
<td>2.07</td>
<td>76.6</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Table (7.3): Properties of the best transparent conducting films of undoped indium oxide and ITO prepared by independently DC powered magnetrons with PEM control.
7.2.3. Mid-frequency AC powered magnetrons in floating mode with a DC bias to indium magnetron and PEM control

As in section (7.2.2), the main and secondary targets were In and Sn, respectively. The two magnetrons were operated in the floating mode using the 40 kHz PE supply, at $P_{\text{AC}}^{\text{In+Sn}} = 100$ W, as described in section (5.2.7.2), where $P_{\text{AC}}^{\text{In+Sn}}$ is the floating AC power between the two magnetrons. In addition, the In magnetron was DC-biased using the MDX supply, as described in section (5.2.7.3). The DC power applied to the In magnetron, $P_{\text{DC}}^{\text{In}}$, was varied taking the values 200, 300, 350, 370, 400 and 450 W. As in the previous technique, PEM control on In emission line at 451.1 nm was used, $\text{In}_{\text{pem}}$ was gradually decreased for each $P_{\text{AC}}^{\text{In+Sn}} - P_{\text{DC}}^{\text{In}}$ combination, and a film was deposited and characterised at each value of $\text{In}_{\text{pem}}$. Before presenting the results, it is worth mentioning that the general behaviour of the biased magnetron (i.e., the In one), as figure (7.15) indicates, was similar to that seen in figure (7.7) where no AC power was applied (section 7.2.2). This implied that the effect of the DC bias, for the combinations of $P_{\text{AC}}^{\text{In+Sn}} - P_{\text{DC}}^{\text{In}}$ used, was overwhelming. Figure (7.16) shows the dependence of $R_y$ and $T_{550}$ of the transparent conducting films of ITO on $\text{In}_{\text{pem}}$. A wide process window, of about 4.5%, was observed at $P_{\text{DC}}^{\text{In}} = 370$ W. The percentages of In line set-point, at which the best transparent conducting films occur, along with the corresponding resistivities, are plotted in figure (7.17) versus $P_{\text{DC}}^{\text{In}}$. Figure (7.18) shows $\text{In}_{\text{pem}}$, and the corresponding $f_0$, at which the best transparent conducting films occur versus $P_{\text{DC}}^{\text{In}}$, whereas figure (7.19) shows the dependence of $T_{550}$ and $R_y$ of these films on $P_{\text{DC}}^{\text{In}}$. 

**Figure (7.15): Voltage of the DC-biased In magnetron versus the percentage of In line set-point at different DC powers. The In and Sn magnetrons were floating at 100 W AC. PEM control was used.**
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Figure (7.16): Resistivity and transmittance of transparent conducting films of ITO versus the percentage of In line set-point. The floating AC power between the two magnetrons was 100W. The In magnetron was biased with 200, 300, 350, 370, 400 and 450W.

- Resistivity (Ry) (GΩm)
- Transmittance at 550nm

Percentage of Indium Line Set-Point (%)

2.1E-5
1.9E-5
1.7E-5
1.5E-5
1.3E-5
1.1E-5
9.0E-6
7.0E-6

Provided that $P_{In \rightarrow Sn}^{AC}$ is constant, these figures imply

1. The best transparent conducting films occur at lower $In_{pcm}^{%}$ and higher $fO_2$ as $P_{in}^{DC}$ increases (figures 7.17 and 7.18). This is probably to attain sufficient $O_2$ partial pressure to oxidise the increasing amount of sputtered metallic In.

2. The resistivity and transmittance of the best films decrease with $P_{in}^{DC}$ until $P_{in}^{DC} = 400$ W, and then increase (figure 7.19). The slight increase in $R_y$ above 400 W could be due to the very small level of Sn doping at higher values of $P_{in}^{DC}$.
However, the change of the best $R_y$ in the range $350 \leq P_{In}^{DC} \leq 450$ W is quite limited, an indication of reaching appropriate stoichiometries and compositions. On the other hand, the decrease in $T_{550}$ below 400 W could be attributed to the substantial increase in thickness, as figure (7.20) indicates, whereas the increase in $T_{550}$ above 400 W could be due to the higher In content of the film.

![Figure (7.18): The percentage of In line set-point, and the corresponding oxygen flow rate, at which the best transparent conducting films of ITO occur vs. the DC bias applied to the In magnetron. The floating AC power between the two magnetrons was 100W.](image)

![Figure (7.19): Transmittance at 550nm and resistivity of the best transparent conducting films of ITO versus the DC bias applied to the In magnetron. The floating AC power between the two magnetrons was 100W. PEM control was used.](image)
Figure (7.20): Transmittance at 550nm and thickness of the best transparent conducting films of ITO versus the DC bias applied to the In magnetron. The floating AC power between the two magnetrons was 100W. PEM control was used.

Table (7.4) presents a summary of the properties of the best transparent conducting films prepared by this technique.

<table>
<thead>
<tr>
<th>$P_{In}^{DC}$ (W)</th>
<th>$R_s$ (Ω/□)</th>
<th>$R_y$ (Ω·m)</th>
<th>$n_{film}$</th>
<th>$T_{550}$ (%)</th>
<th>$R_{sep}^m$ (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>127</td>
<td>$15.7 \times 10^{-6}$</td>
<td>2.06</td>
<td>88.0</td>
<td>0.68</td>
</tr>
<tr>
<td>300</td>
<td>91</td>
<td>$13.9 \times 10^{-6}$</td>
<td>2.10</td>
<td>84.0</td>
<td>0.84</td>
</tr>
<tr>
<td>350</td>
<td>40</td>
<td>$8.2 \times 10^{-6}$</td>
<td>2.03</td>
<td>81.8</td>
<td>1.14</td>
</tr>
<tr>
<td>370</td>
<td>32</td>
<td>$7.7 \times 10^{-6}$</td>
<td>2.07</td>
<td>80.7</td>
<td>1.34</td>
</tr>
<tr>
<td>400</td>
<td>31</td>
<td>$7.4 \times 10^{-6}$</td>
<td>2.07</td>
<td>78.2</td>
<td>1.33</td>
</tr>
<tr>
<td>450</td>
<td>36</td>
<td>$8.7 \times 10^{-6}$</td>
<td>2.04</td>
<td>84.2</td>
<td>1.34</td>
</tr>
</tbody>
</table>

Table (7.4): Properties of the best transparent conducting films of ITO prepared by mid-frequency AC powered magnetrons in floating mode with a DC bias to indium magnetron and PEM control.

To conclude, the first deposition technique, in which oxygen flow rate was manually controlled (section 7.2.1), gave relatively the worst results as far as resistivity is concerned, due to system constraints. The widest process windows, lowest resistivities and highest transmittances could be achieved by employing the independently DC powered magnetrons technique with PEM control (section 7.2.2), in which the energy delivered to the substrate by ions per In atom was moderate (~21 eV), as found in section (5.4.3). However, a wide process window was also observed when the combined AC and DC technique (section 7.2.3) was employed, but the resistivities of the films were slightly higher. The latter could be attributed to the substantially higher
energy delivered to the substrate by ions per In atom, which was about 100 eV, as found in section (5.4.3).

7.3. Indium zinc oxide (IZO)

No references were found in the literature about IZO films. These transparent conducting films were prepared in this work using two different techniques. They were

7.3.1. Independently DC powered magnetrons with PEM control

In this method of preparation, the main and secondary targets were In and Zn, respectively. The power to the In cathode, $P_{In}^{DC}$, was held constant at 300 W throughout, whereas the power applied to the Zn cathode, $P_{Zn}^{DC}$, was changed taking the values 0, 50, 60, 70, 80, 90, 100 and 120 W. PEM control, on In emission line at 451.1 nm, was used. For each $P_{In}^{DC}$-$P_{Zn}^{DC}$ combination, the percentage of In line set-point, $In_{\%_{pem}}$, was gradually decreased, starting from metallic targets. At each value of $In_{\%_{pem}}$, a film was deposited and characterised.

![Figure (7.21): A plot of resistivity and oxygen flow rate versus the percentage of In line set-point for transparent conducting films of undoped indium oxide and the corresponding films of IZO when the Zn cathode was held at 80W.](image)

The deposition mechanism of IZO films, using this technique, is similar to that of ITO films described in section (7.2.2). In figure (7.21), $R_s$ and $f_{O_2}$ are plotted versus $In_{\%_{pem}}$ for the transparent conducting films of undoped indium oxide and the corresponding IZO films when $P_{Zn}^{DC} = 80$ W (see figure 7.9 for comparison). Obviously, the values of $f_{O_2}$ in the case of IZO were higher than the corresponding ones of undoped indium oxide. The difference may again be attributed to the amount of $O_2$ required to oxidise the sputtered Zn. Note that this difference is lower in figure (7.9) which is probably due
to the lower sputtering yield of Sn ($Y_{Sn} = \sim 2.7$ atoms/ion for 500 eV Ar ions whereas $Y_{Zn} = \sim 5.07$ atoms/ion at the same ion energy)\textsuperscript{40}.

**Figure (7.22):** A plot of resistivity and transmittance of transparent conducting films of undoped indium oxide and IZO versus the percentage of In line set-point. The applied power was 300 W to the In cathode and 50, 70, 80 and 90 W to the Zn cathode.

**Figure (7.23):** The occurrence and resistivity of the best transparent conducting films of undoped indium oxide and IZO versus power applied to the Zn cathode.

Figure (7.22) shows the dependence of $R_y$ and $T_{550}$ of the transparent conducting films of undoped indium oxide and IZO on $In_{pen}^\%$. The applied power was 300 W to the In cathode and 50, 70, 80 and 90 W to the Zn cathode. A very wide process window of about 9% was observed at $P_{Zn}^{DC} = 80$ W. The percentages of In line set-point, at which the best transparent conducting films occur, as well as the corresponding resistivities, are plotted in figure (7.23) versus $P_{Zn}^{DC}$. 

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On the other hand, $T_{550}$ and $R_y$ of these films are plotted in figure (7.24) against $P_{Zn}^{DC}$. Finally, the transmittance spectra of the best films at different powers applied to the Zn cathode are plotted in figure (7.25).

As far as the deposition process is concerned, the conclusions which could be drawn from these figures are in the same general sense as those of ITO films (section 7.2.2). That is

1. In order to achieve sufficient $O_2$ partial pressure to oxidise the increasing amount of sputtered metallic Zn, the best transparent conducting films occur at lower $In_{per}^{*}$ as $P_{Zn}^{DC}$ increases (figure 7.23).
2. The resistivities of these films increase as $P_{Zn}^{DC}$ increases, whereas their transmittances at 550 nm decrease first with increasing $P_{Zn}^{DC}$ (figure 7.24) and then almost stabilise at higher values (i.e., $P_{Zn}^{DC} \geq 70$ W).

AES analysis of the best IZO films indicated that the percentage of Zn in these films was 22.1% and 41.9% for samples prepared at 50 and 70 W, respectively. Table (7.5) summarises the properties of the best transparent conducting IZO films obtained by the independently DC powered magnetrons technique.

<table>
<thead>
<tr>
<th>$P_{Zn}^{DC}$ (W)</th>
<th>$R_s$ (Ω/□)</th>
<th>$R_y$ (Ω.m)</th>
<th>$n_{film}$</th>
<th>$T_{550}$ (%)</th>
<th>$R_{dep}^{in}$ (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>25</td>
<td>3.9 x 10^{-6}</td>
<td>2.06</td>
<td>82.4</td>
<td>0.88</td>
</tr>
<tr>
<td>50</td>
<td>53</td>
<td>8.1 x 10^{-6}</td>
<td>2.06</td>
<td>78.2</td>
<td>0.85</td>
</tr>
<tr>
<td>70</td>
<td>66</td>
<td>13.7 x 10^{-6}</td>
<td>1.99</td>
<td>70.3</td>
<td>1.15</td>
</tr>
<tr>
<td>80</td>
<td>94</td>
<td>19.4 x 10^{-6}</td>
<td>2.02</td>
<td>68.9</td>
<td>1.15</td>
</tr>
<tr>
<td>90</td>
<td>183</td>
<td>38.0 x 10^{-6}</td>
<td>1.95</td>
<td>69.1</td>
<td>1.15</td>
</tr>
<tr>
<td>100</td>
<td>440</td>
<td>99.0 x 10^{-6}</td>
<td>1.90</td>
<td>70.0</td>
<td>1.25</td>
</tr>
<tr>
<td>120</td>
<td>520</td>
<td>121.5 x 10^{-6}</td>
<td>1.92</td>
<td>67.2</td>
<td>1.29</td>
</tr>
<tr>
<td>150</td>
<td>2000</td>
<td>430.2 x 10^{-6}</td>
<td>1.88</td>
<td>71.4</td>
<td>1.19</td>
</tr>
</tbody>
</table>

Table (7.5): Properties of the best transparent conducting films of undoped indium oxide and IZO prepared by independently DC powered magnetrons with PEM control.

7.3.2. Mid-frequency AC powered magnetrons in floating mode with a DC bias to indium magnetron and PEM control

The main and secondary targets were kept as In and Zn, respectively. The two magnetrons were operated in the floating mode at $P_{In+Zn}^{AC} = 100$ W, as described in section (5.2.7.2). The DC-bias applied to the In magnetron, $P_{In}^{DC}$, was varied taking the values 100, 200, 300 and 400 W (section 5.2.7.3). As in the previous technique, PEM control on In emission line at 451.1 nm was used, In$_{pec}^{%}$ was gradually decreased for each $P_{In+Zn}^{AC}$-$P_{In}^{DC}$ combination, and a film was deposited and characterised at each value of In$_{pec}^{%}$.

Figure (7.26) shows the dependence of $R_y$ and $T_{550}$ of the transparent conducting films of IZO on In$_{pec}^{%}$. Wide process windows, of about 4%, were observed when $P_{In}^{DC}$ was 200 and 300 W. The percentages of In line set-point, at which the best transparent
Figure (7.26): Resistivity and transmittance of transparent conducting films of IZO versus the percentage of In line set-point. The floating AC power between the two magnetrons was 100W. The In magnetron was biased with 100, 200, 300 and 400W.

Figure (7.27): The occurrence and resistivity of the best transparent conducting films of IZO versus the DC bias applied to the In magnetron. The floating AC power between the In and Sn magnetrons was 100W. PEM control was used.

conducting films occur, and their resistivities, are plotted in figure (7.27) versus $P_{\text{in}}^{\text{DC}}$, whereas figure (7.28) shows the variation of $\text{In}_{\text{pem}}^{\%}$ and $f_{\text{O}_2}$, at which these films occur, with $P_{\text{in}}^{\text{DC}}$. Figure (7.29) shows the dependence of $T_{550}$ and $R_y$ of these films on $P_{\text{in}}^{\text{DC}}$. Provided that $P_{\text{in}+\text{Zn}}^{\text{AC}}$ is constant, these figures imply

1. The best transparent conducting films occur at lower $\text{In}_{\text{pem}}^{\%}$ and higher $f_{\text{O}_2}$ as $P_{\text{in}}^{\text{DC}}$ increases (figures 7.27 and 7.28). As in the case of ITO (section 7.2.3), this could be attributed to the need to attain sufficient $O_2$ partial pressure to oxidise the increasing amount of sputtered metallic In.
Figure (7.28): The percentage of In line set-point, and the corresponding oxygen flow rate, at which the best transparent conducting films of IZO occur vs. the DC bias applied to the In magnetron. The floating AC power between the two magnetrons was 100W.

2. The resistivity of the best films decreases with $P_{In}^{DC}$. Such a decrease in $R_y$ is sharper when $P_{In}^{DC} \leq 200$ W (figure 7.29). However, the very small decrease in the best $R_y$ in the range $200 \leq P_{In}^{DC} \leq 400$ W is an indication of attaining appropriate stoichiometries and compositions.

3. The transmittance at 550 nm of the best conducting films decreases with $P_{In}^{DC}$ below 300 W which might be due to the substantial increase in thickness, as figure (7.30) shows, whereas the increase in $T_{550}$ above 300 W could be due to the higher In content of the film.
Figure (7.30): Transmittance at 550nm and thickness of the best transparent conducting films of IZO versus the DC bias applied to the In magnetron. The floating AC power between the two magnetrons was 100W. PEM control was used.

Table (7.6) presents a summary of the properties of the best transparent conducting IZO films prepared by the combined AC and DC technique.

<table>
<thead>
<tr>
<th>$P_{\text{in}}^{\text{DC}}$ (W)</th>
<th>$R_s$ (Ω/□)</th>
<th>$R_x$ (Ω/m)</th>
<th>$n_{\text{film}}$</th>
<th>$T_{550}$ (%)</th>
<th>$R_{\text{dep}}$ (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>199</td>
<td>$18.3 \times 10^{-6}$</td>
<td>1.94</td>
<td>81.4</td>
<td>0.51</td>
</tr>
<tr>
<td>200</td>
<td>53</td>
<td>$8.6 \times 10^{-6}$</td>
<td>2.06</td>
<td>79.4</td>
<td>0.90</td>
</tr>
<tr>
<td>300</td>
<td>37</td>
<td>$8.5 \times 10^{-6}$</td>
<td>2.00</td>
<td>74.2</td>
<td>1.27</td>
</tr>
<tr>
<td>400</td>
<td>31</td>
<td>$8.2 \times 10^{-6}$</td>
<td>1.96</td>
<td>86.5</td>
<td>1.47</td>
</tr>
</tbody>
</table>

Table (7.6): Properties of the best transparent conducting films of IZO prepared by mid-frequency AC powered magnetrons in floating mode with a DC bias to indium magnetron and PEM control.

To conclude, wide process windows were attained in both deposition techniques. However, lower resistivities, higher transmittances and higher deposition rates could be achieved, and in a wide range of bias power to In magnetron, by utilising the combined AC and DC technique (section 7.3.2). This could be due to the higher energy delivered to the substrate by ions per deposited atom (section 5.4.3).

7.4. Indium oxide doped with titanium (ITiO)

The two known attempts to deposit transparent conducting films of ITiO were not very promising\(^{35,41}\). Groth\(^{41}\) investigated the electrical and optical properties of spray-hydrolysed ITiO films and found them of no interest as transparent conductors. Vossen\(^{35}\) deposited these films using RF sputtering technique. The targets he used were
prepared by dry mixing, pressing and sintering (at about 900 °C in air) of \( \text{In}_2\text{O}_3 \) and \( \text{TiO}_2 \) powders. The resistivity and average transmission, over the visible range, of these films were \( 7.5 \times 10^{-3} \ \Omega \cdot \text{m} \) and 96%, respectively. Perhaps, he assumed that transmittance of the substrate was 100% (section 6.3.2.2). Apparently, such unpromising results as well as the impossibility to prepare these films from alloy targets containing In and Ti due to the inability of forming an alloy of them\(^4\), led \( \text{ITiO} \) films to be deserted.

\( \text{ITiO} \) films were produced in this work by employing the combined AC and DC technique (section 5.2.7.3) rather than the independently DC powered magnetrons technique (section 5.2.7.1) which would result in severe arcing (section 4.6) during prolonged deposition times. This is because of the low standard molar enthalpy of formation, \( \Delta H_f \), of titanium oxide (section 5.4.1) which increases the probability of oxide formation on the surface of the Ti target during the reactive sputtering processes. The main and secondary targets were In and Ti, respectively. The two magnetrons were run in the floating mode at \( P_{\text{AC}}^{\text{In-Ti}} = 100 \ \text{W} \). The DC-bias applied to the In magnetron, \( P_{\text{DC}}^{\text{In}} \), was varied taking the values 150, 200, 250 and 300 W. As before, PEM control on In emission line at 451.1 nm was used, \( \text{In}_{\text{PEM}} \) was gradually decreased for each \( P_{\text{AC}}^{\text{In-Ti}} - P_{\text{DC}}^{\text{In}} \) combination, and a film was deposited and characterised at each value of \( \text{In}_{\text{PEM}} \).

Figure (7.31) shows the dependence of \( R_y \) and \( T_{550} \) of the transparent conducting films of \( \text{ITiO} \) on \( \text{In}_{\text{PEM}} \). Wide process windows, of about 4%, were observed when \( P_{\text{DC}}^{\text{In}} = 250 \ \text{W} \). The percentages of In line set-point, at which the best transparent
conducting films occur, and their resistivities, versus $P_{in}^{DC}$ are plotted in figure (7.32), whereas figure (7.33) shows the dependence of $R_y$ and $T_{550}$ of these films on $P_{in}^{DC}$.

**Figure (7.32):** The occurrence and resistivity of the best transparent conducting films of ITiO versus the DC bias applied to the In magnetron. The floating AC power between the In and Ti magnetrons was 100W. PEM control was used.

**Figure (7.33):** Resistivity and transmittance at 550nm of the best transparent conducting films of ITiO versus the DC bias applied to the In magnetron. The floating AC power between the two magnetrons was 100W. PEM control was used.

These figures indicate that

1. The best transparent conducting films occur at lower In$^{\%}$ as $P_{in}^{DC}$ increases (figure 7.32). As in the previous cases, this may be due to the need to secure sufficient O$_2$ partial pressure to oxidise the increasing amount of sputtered In.

2. The resistivity of the best films decreases first with $P_{in}^{DC}$ and then increases with a minimum at $P_{in}^{DC} = 200$ W (figure 7.33). The increase in $R_y$ could be
attributed to the lower Ti content of the films at higher values of $P_{in}^{DC}$. It should be noticed that such a minimum occurred at $P_{in}^{DC} = 400$ W in the case of ITO (figure 7.19). The difference in $P_{in}^{DC}$ between the ITO and ITiO cases, at which $R_y$ minimum occurred, could be due to the much lower sputtering yield of Ti ($Y_{Ti} = \sim 1.25$ atoms/ion for 500 eV Ar ions)\(^49\) compared to that of Sn ($Y_{Sn} = \sim 2.7$ atoms/ion).

3. The transmittance at 550 nm of the best conducting films decreases with $P_{in}^{DC}$ below 250 W which might be attributed to the increase in thickness, as figure (7.34) shows, whereas the increase in $T_{550}$ above 250 W could be due to the higher In content of the film.

![Figure (7.34): Transmittance at 550nm and resistivity of the best transparent conducting films of ITiO versus the DC bias applied to the In magnetron. The floating AC power between the two magnetrons was 100W. PEM control was used.](image)

<table>
<thead>
<tr>
<th>$P_{in}^{DC}$ (W)</th>
<th>$R_s$ ($\Omega/\square$)</th>
<th>$R_y$ ($\Omega.m$)</th>
<th>$n_{film}$</th>
<th>$T_{550}$ (%)</th>
<th>$R_{dep}^{in}$ (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>51</td>
<td>$6.0 \times 10^{-6}$</td>
<td>1.89</td>
<td>84.6</td>
<td>0.65</td>
</tr>
<tr>
<td>200</td>
<td>33</td>
<td>$4.6 \times 10^{-6}$</td>
<td>2.07</td>
<td>82.1</td>
<td>0.78</td>
</tr>
<tr>
<td>250</td>
<td>32</td>
<td>$4.9 \times 10^{-6}$</td>
<td>2.04</td>
<td>81.2</td>
<td>0.85</td>
</tr>
<tr>
<td>300</td>
<td>37</td>
<td>$5.9 \times 10^{-6}$</td>
<td>2.03</td>
<td>82.5</td>
<td>0.89</td>
</tr>
</tbody>
</table>

Table (7.7): Properties of the best transparent conducting films of ITiO prepared by mid-frequency AC powered magnetrons in floating mode with a DC bias to indium magnetron and PEM control.
AES analysis of the best ITiO films revealed that the percentage of Ti in these films was between 1% and 1.55%. Such values were quite predictable since the corresponding Sn ones in ITO were between 3.4% and 3.7% (section 7.2.2), bearing in mind the higher sputtering yield of Sn. Table (7.7) summarises the properties of the best transparent conducting ITiO films obtained in this work.

Such very promising results created some concern about the various possibilities behind the properties of ITiO films. These possibilities could be

1. Plasma annealing when the substrate passes over the Ti target. This plasma activation may improve the film properties. However, such a possibility was not only inherent to ITiO films, but also to all other films prepared by this technique.

2. Ti target may behave like a buffer in consuming any surplus of oxygen in the system and maintaining the process stable.

3. These properties are due to indium oxide being doped with Ti.

To verify the effect of Ti on the film properties and the conditions of preparation (e.g., the window of appropriate stoichiometry), it was first thought to implant Ti flakes into melted indium in order to sputter-deposit these films from a single target and compare the results with those of undoped indium oxide. Such a thought followed many unsuccessful attempts to prepare these films from a compound target containing In and Ti due to the impossibility of forming an alloy of them. However, it was feared that the Ti-implantation method may cause difficulties in controlling the composition of the films, which seemed to be a key factor in the properties (especially the electrical ones) of obtained films as will be seen soon, bearing in mind that the discharge in magnetron sputtering is not uniform over the cathode. This means that if the relative area covered by Ti was to fulfil a certain composition, it should have been calculated according to the profile of the race track, which appeared to be a very difficult task. On the other hand, even if that calculation could have been made possible, $\Delta H^\circ$ of indium oxide and titanium oxide are very disparate, which means, in turn, that during oxygen admission, Ti flakes would be poisoned, resulting in a very low sputtering rate for titanium, whereas indium remained metal. Hence, it was felt that implanting flakes may lead to misleading results and has been excluded.

In another experiment, the Ti target was replaced by an In one (i.e., the main and secondary targets were made In). The two magnetrons were run in the floating mode at $P_{\text{In}} = 100$ W. The DC-bias applied to the main In magnetron was 250 W. This
combination of AC and DC powers was chosen because it gave the widest process window in the case of ITiO films, as seen earlier. Other conditions were kept the same.

Figure (7.35): Resistivity and transmittance of transparent conducting films of ITiO and undoped indium oxide versus the percentage of In line set-point. In both cases, the floating AC power was 100W and the main In magnetron was biased with 250W DC.

Figure (7.35) shows the dependence of $R_y$ and $T_{550}$ of the transparent conducting films of undoped indium oxide prepared by this method on In. Also plotted in the figure, the corresponding results of ITiO films for comparison. Obviously, ITiO films possess much wider process window, lower resistivities and higher transmittances, though the latter could partially be attributed to the slightly lower thicknesses (~155 nm compared to ~170 nm in the case of undoped indium oxide).

Figure (7.36): Transmittance spectra of transparent conducting films of ITiO and undoped indium oxide versus the percentage of In line set-point. In both cases, the floating AC power was 100W and the main In magnetron was biased with 250W DC.
Finally, the shape of the transmittance spectra of the films, shown in figure (7.36), are different at wavelengths lower than about 500 nm with the undoped indium oxide film having a peak at about 425 nm. Thus, it may be concluded that the incorporation of Ti in the films improved their optical and electrical properties as well as the conditions of preparation (e.g., the window of appropriate stoichiometry).

Furthermore, the effect of the doping level on the electrical and optical properties of these films was also investigated. In this set of experiments the main and secondary targets were Ti and In, respectively. The two magnetrons were operated in the floating mode at $P_{AC}^{Ti+In} = 100$ W. The DC-bias applied to the Ti magnetron, $P_{DC}^T$, was varied taking the values 100, 200, 300, 400 and 500 W. PEM control on Ar emission lines was used (section 5.2.8.1). The percentage of Ar lines set-point, $Ar_{pem}^\%$, was gradually decreased for each $P_{AC}^{Ti+In}-P_{DC}^T$ combination, and a film was deposited and characterised at each value of $Ar_{pem}^\%$. The deposition time was 6 minutes.

Figure (7.37) shows the dependence of $R_y$ and $T_{550}$ of the transparent conducting films of ITiO on $Ar_{pem}^\%$. Again, wide process windows, up to about 8.5%, were observed. Figure (7.38) shows the dependence of $T_{550}$ and $R_y$ of these films on $P_{DC}^T$. Obviously, the resistivities of these films are about an order of magnitude higher than those of figure (7.33), whereas the corresponding transmittances are slightly higher. Finally, figure (7.39) shows the transmittance spectra of the best films. It is clear from this figure that a transmittance peak appears at a higher wavelength as $P_{DC}^T$ increases. On the other hand, AES analysis of the best ITiO films deposited in this series of experiments revealed that the percentage of Ti in these films was between 3.8% and 4.9%. Such values are quite higher than those obtained earlier.
Figure (7.38): Resistivity and transmittance at 550 nm of the best transparent conducting films of ITiO versus the DC bias applied to the Ti magnetron. The floating AC power between the two magnetrons was 100 W. PEM control was used.

Figure (7.39): Transmittance spectra of the best transparent conducting ITiO films at different powers to the Ti magnetron. The floating AC power between the two magnetrons was 100 W. PEM control was used.

<table>
<thead>
<tr>
<th>P_{DC}^{Ti} (W)</th>
<th>R_s (Ω/□)</th>
<th>R_y (Ω.m)</th>
<th>n_{film}</th>
<th>T_{550} (%)</th>
<th>R_{dep}^{eff} (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>148</td>
<td>16.3 x 10^{-6}</td>
<td>2.00</td>
<td>83.4</td>
<td>0.30</td>
</tr>
<tr>
<td>200</td>
<td>144</td>
<td>17.5 x 10^{-6}</td>
<td>2.09</td>
<td>89.3</td>
<td>0.33</td>
</tr>
<tr>
<td>300</td>
<td>126</td>
<td>18.2 x 10^{-6}</td>
<td>2.12</td>
<td>86.6</td>
<td>0.40</td>
</tr>
<tr>
<td>400</td>
<td>149</td>
<td>24.2 x 10^{-6}</td>
<td>2.09</td>
<td>76.7</td>
<td>0.45</td>
</tr>
<tr>
<td>500</td>
<td>230</td>
<td>40.7 x 10^{-6}</td>
<td>2.08</td>
<td>73.3</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Table (7.8): Properties of the best transparent conducting films of ITiO prepared by mid-frequency AC powered magnetrons in floating mode with a DC bias to titanium magnetron and PEM control.
Table (7.8) summarises the properties of the best transparent conducting \text{ITiO} films obtained in this set of experiments. It can be concluded then that the properties of \text{ITiO} films, especially the electrical ones, are influenced by the percentage of Ti in the films.

The above experiments indicate that the optical and electrical properties of these films are largely due to indium oxide being doped with Ti but do not entirely exclude the potential influence of the other effects.

### 7.5. Indium oxide doped with aluminium (IAO)

No references were found, in the literature, to IAO films. These transparent conducting films were prepared in this work using the combined AC and DC technique (section 5.2.7.3) for the same reasons mentioned in section (7.4). The main and secondary targets were In and Al, respectively. The two magnetrons were operated in the floating mode at $P_{\text{in+Al}}^\text{AC} = 100$ W. The DC-bias applied to the In magnetron, $P_{\text{in}}^\text{DC}$, was varied taking the values 150, 200, 250, 300, 350 and 400 W. The rest was as in section (7.4).

![Figure (7.40): Resistivity and transmittance of transparent conducting films of IAO versus the percentage of In line set-point. The floating AC power between the two magnetrons was 100 W. The In magnetron was biased with 150, 200, 250, 300 and 350 W.](image)

Figure (7.40) shows the dependence of $R_y$ and $T_{550}$ of the transparent conducting films of IAO on In\%$_{\text{in}}$. Wide process windows were quite obvious. They were about 5% at $P_{\text{in}}^\text{DC} = 200$ W and 4% at $P_{\text{in}}^\text{DC} = 250$ W. The percentage of In line set-point, at which the best transparent conducting films occur, and the corresponding $f_{\text{O}}$, versus $P_{\text{in}}^\text{DC}$ are plotted in figure (7.41), whereas figure (7.42) shows the dependence of $R_y$ and $T_{550}$ of these films on $P_{\text{in}}^\text{DC}$. Finally, figure (7.43) shows the transmittance spectra of the best films. Clearly, transmittance peaks appear at higher wavelengths as $P_{\text{in}}^\text{DC}$ increases.
The following remarks could be deduced from the previous figures:

1. In order to achieve sufficient $O_2$ partial pressure to oxidise the increasing amount of sputtered metallic In, the best transparent conducting films occur at lower $In_{\%}$ and higher $f_{O_2}$ as $P_{In}^{DC}$ increases (figure 7.41).

2. The resistivity of the best films decreases first slightly with $P_{In}^{DC}$ and then increases with a minimum at $P_{In}^{DC} = 250$ W (figure 7.42). The increase in $R_y$ probably due to the lower Al content of the films at higher values of $P_{In}^{DC}$.
3. The transmittance at 550 nm of the best conducting films generally decreases with $P_{\text{In}}^{\text{DC}}$ which might be attributed mainly to the increase in thickness, as figure (7.44) shows.

AES analysis of the best IAO films revealed that the percentage of Al in these films was between 2.2% and 3%. The properties of the best transparent conducting IAO films, obtained in this work, are summarised in table (7.9).
<table>
<thead>
<tr>
<th>$P_{in}^{DC}$ (W)</th>
<th>$R_{s}$ ($\Omega/\square$)</th>
<th>$R_{y}$ ($\Omega.m$)</th>
<th>$n_{film}$</th>
<th>$T_{550}$ (%)</th>
<th>$R_{dep}^{in}$ (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>53</td>
<td>$5.88 \times 10^{-6}$</td>
<td>1.93</td>
<td>82.5</td>
<td>0.61</td>
</tr>
<tr>
<td>200</td>
<td>47</td>
<td>$5.73 \times 10^{-6}$</td>
<td>2.04</td>
<td>86.0</td>
<td>0.67</td>
</tr>
<tr>
<td>250</td>
<td>42</td>
<td>$5.71 \times 10^{-6}$</td>
<td>2.04</td>
<td>84.5</td>
<td>0.75</td>
</tr>
<tr>
<td>300</td>
<td>38</td>
<td>$5.97 \times 10^{-6}$</td>
<td>2.01</td>
<td>75.4</td>
<td>0.87</td>
</tr>
<tr>
<td>350</td>
<td>38</td>
<td>$6.48 \times 10^{-6}$</td>
<td>1.99</td>
<td>72.7</td>
<td>0.94</td>
</tr>
<tr>
<td>400</td>
<td>32</td>
<td>$6.94 \times 10^{-6}$</td>
<td>1.96</td>
<td>70.7</td>
<td>1.20</td>
</tr>
</tbody>
</table>

Table (7.9): Properties of the best transparent conducting films of IAO prepared by mid-frequency AC powered magnetrons in floating mode with a DC bias to aluminium magnetron and PEM control.
REFERENCES


CHAPTER EIGHT

RESULTS AND DISCUSSION: ZINC OXIDE AND ITS DOPANTS

8.1. Introduction

Zinc oxide is a low cost n-type semiconductor. The band gap, electron mobility and carrier concentration of undoped zinc oxide films are about 3.3 eV, 8-38 cm²/V.s and \(10^{18}-10^{20}\) cm⁻³, respectively. The semiconducting properties of ZnO is attributed to a small non-stoichiometry which results in interstitial zinc atoms and/or oxygen vacancies occupied by electrons and acting as donor states. Transparent conducting films of undoped zinc oxide have been prepared by a variety of techniques including reactive evaporation, spray pyrolysis, dual ion beam sputtering, RF magnetron sputtering and DC magnetron sputtering. Examples of some of these techniques and deposition conditions, as well as the best optical and electrical properties of the produced films, are summarised in table (8.1). High substrate temperature, post-deposition annealing at a high temperature and/or biasing the substrate are a common feature in order to obtain good transparent conducting films.

Several dopants (e.g., Al, In, Ti, Sn and Cu) have been investigated in this work in order to enhance the transparent conducting properties of ZnO films taking advantage of the developed technique. No promising results, as far as the electrical conductivity is concerned, were observed when ZnO was doped with Cu. On the other hand, it should be emphasised again that the results shown in this thesis are for as-deposited films and where deposition was carried out at room temperature without any external bias applied to substrate. Finally, information concerning system and process details and film characterisation were discussed in chapters five and six, respectively.
### Table 8.1: Electrical and optical properties of zinc oxide films prepared by reactive evaporation (RE), spray pyrolysis (SP), RF reactive magnetron sputtering (RFRMS) and DC reactive magnetron sputtering (DCRMS).

<table>
<thead>
<tr>
<th>Depos. method</th>
<th>Subs. temp. (°C)</th>
<th>Subs. bias (V)</th>
<th>Post-deposition annealing temperature (°C) and duration (min)</th>
<th>$R_s$ (µΩ.m)</th>
<th>T (%)</th>
<th>Depos. rate (nm/s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>RE</td>
<td>&lt;200</td>
<td>-</td>
<td>-</td>
<td>11</td>
<td>90</td>
<td>0.2-0.8</td>
<td>3</td>
</tr>
<tr>
<td>SP</td>
<td>420</td>
<td>-</td>
<td>450 °C in H$_2$ for 5 min</td>
<td>10</td>
<td>85</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>RFRMS</td>
<td>&lt;60</td>
<td>-</td>
<td>-</td>
<td>4.5</td>
<td>90</td>
<td>0.1 @ 43W</td>
<td>7</td>
</tr>
<tr>
<td>DCRMS</td>
<td>&lt;60</td>
<td>-85</td>
<td>-</td>
<td>40</td>
<td>90</td>
<td>1.25 @ ?</td>
<td>9</td>
</tr>
</tbody>
</table>

Table (8.2): Electrical and optical properties of ZAO films prepared by RF magnetron sputtering (RFMS), RF reactive magnetron sputtering (RFRMS) and DC reactive magnetron sputtering (DCRMS).

<table>
<thead>
<tr>
<th>Depos. method</th>
<th>Subs. temp. (°C)</th>
<th>Subs. bias (V)</th>
<th>Post-deposition annealing temperature (°C) and duration (min)</th>
<th>$R_s$ (µΩ.m)</th>
<th>T (%)</th>
<th>Depos. rate (nm/s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>RFMS</td>
<td>200-350</td>
<td>-</td>
<td>-</td>
<td>&lt;3</td>
<td>90</td>
<td>0.04 @ 40W</td>
<td>13</td>
</tr>
<tr>
<td>DCRMS</td>
<td>&gt;250</td>
<td>-</td>
<td>-</td>
<td>2.7</td>
<td>85</td>
<td>-</td>
<td>15</td>
</tr>
<tr>
<td>DCRMS</td>
<td>≥180</td>
<td>-50</td>
<td>-</td>
<td>5</td>
<td>85</td>
<td>~1.66 @ 105W</td>
<td>16</td>
</tr>
<tr>
<td>DCRMS</td>
<td>350</td>
<td>-</td>
<td>-</td>
<td>3-6</td>
<td>85</td>
<td>0.26-0.58 @ 80W</td>
<td>17</td>
</tr>
<tr>
<td>DCRMS</td>
<td>350</td>
<td>-</td>
<td>300 °C in H$_2$ for 30 min</td>
<td>2-5.5</td>
<td>80-85</td>
<td>0.23-0.58 @ 80W</td>
<td>18, 19</td>
</tr>
<tr>
<td>DCRMS</td>
<td>Room</td>
<td>-</td>
<td>400 °C in N$_2$ or air for 5 min</td>
<td>5</td>
<td>90</td>
<td>2 @ 100W</td>
<td>20</td>
</tr>
<tr>
<td>RFRMS</td>
<td>&lt;100</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>90</td>
<td>0.12 @ 150W</td>
<td>22</td>
</tr>
</tbody>
</table>

-254-
8.2. Zinc oxide doped with aluminium (ZAO)

Depending on the Al content, the band gap of ZAO films ranges from about 3.55 to 3.90 eV, whereas the carrier concentration is of the order of $10^{20}-10^{21}$ cm$^{-3}$. Transparent conducting ZAO films have been prepared by many workers using several techniques including RF magnetron sputtering, DC magnetron sputtering and the so called "dual-target magnetron sputtering" with an RF power applied to a ZnO target and a DC power applied to an Al target. In the latter, the rotating substrate was placed perpendicular to the plane of the target in order to minimise ion and neutral bombardment of the growing films which is considered to be responsible for degrading the ZnO-based films. Table (8.2) summarises the deposition conditions as well as the optical and electrical properties of some of the sputtered films. Again, high substrate temperature, post-deposition annealing and/or biasing of the substrate are necessary to obtain good transparent conducting films.

In this work, two different techniques were used to sputter-deposit ZAO films. They were

8.2.1. Independently DC powered magnetrons with PEM control

It should be mentioned first that this deposition method had been used in the early stages of this work before the combined AC and DC technique was developed. In fact, arcing from the Al cathode did take place during prolonged deposition times. In this method of preparation, the main and secondary targets were Zn and Al, respectively. The power to the Zn cathode, $P_{Zn}^{DC}$, was held constant at 300 W throughout, whereas the power applied to the Al cathode, $P_{Al}^{DC}$, was varied taking the values 0, 30, 40, 50, 60 and 70 W. PEM control, on oxygen emission lines at 777 nm, was used (sections 4.5.1 and 5.2.8.1). The 100% oxygen emission intensity, at a certain $P_{Zn}^{DC}-P_{Al}^{DC}$ combination, was defined as the reading, in mV, from the D.V.M., labelled '26' in figure (5.2), that corresponded to a chamber total pressure of 6 mTorr obtained by admitting oxygen to the chamber in which the argon pressure was 2 mTorr (i.e., completely poisoned targets). For each $P_{Zn}^{DC}-P_{Al}^{DC}$ combination, the percentage of oxygen lines set-point, $O_{pen}^{\%}$, was gradually increased by the automatic admission of the appropriate flow rate of oxygen to the chamber, starting from metallic targets. At each value of $O_{pen}^{\%}$, a film was deposited and characterised.

Figure (8.1) shows the dependence of $R_y$ and $T_{550}$ of the transparent conducting films of undoped zinc oxide and ZAO on $O_{pen}^{\%}$. Process windows of about 0.5% can be achieved at 30, 40 and 50 W to the Al cathode. The percentages of oxygen lines set-
point, at which the best transparent conducting films occur, as well as the corresponding resistivities, are plotted in figure (8.2) versus $P_{\text{AI}}^{\text{DC}}$.

**Figure (8.1): Resistivity and transmittance of transparent conducting films of undoped zinc oxide and ZAO versus the percentage of oxygen line set-point.** The applied power was 300W to the Zn cathode and 30, 40, 50, 60 and 70W to the Al cathode.

**Figure (8.2): The occurrence and resistivity of the best transparent conducting films of undoped zinc oxide and ZAO versus power applied to the Al cathode.**

Finally, figure (8.3) shows the dependence of resistivity and transmittance at 550 nm of these films on $P_{\text{AI}}^{\text{DC}}$, whereas figure (8.4) shows the transmittance spectra of the best films at different powers applied to the Al cathode. The following remarks may be deduced from these figures.

-256-
1. The best transparent conducting films occur at higher $O_{\text{pm}}^\%$ as $P_{\text{Al}}^{\text{DC}}$ increases (figure 8.2). This may be attributed to the need to secure sufficient $O_2$ partial pressure in order to oxidise the increasing amount of sputtered metallic Al.

2. The resistivity of the best films decreases with $P_{\text{Al}}^{\text{DC}}$ until $P_{\text{Al}}^{\text{DC}} = 50$ W, and then increases (figure 8.3). The increase in $R_y$ above 50 W could be due to the higher level of Al atoms in the films which may act as scattering sites of the carriers. However, the change of the best $R_y$ in the range $40 \leq P_{\text{Al}}^{\text{DC}} \leq 60$ W is very small, an indication of the attainment of suitable stoichiometries and compositions. On the other hand, the transmittance at 550 nm of the best films
increases with $P_{Al}^{DC}$ until $P_{Al}^{DC} = 40$ W, and then slightly decreases. The decrease could be attributed to the slight increase in thickness and/or higher Al content of the films.

3. These films possess a high transmission in the red and a slight absorption in the blue (figure 8.4).

On the other hand, AES results revealed that the percentage of Al in the best ZAO films was 2.5%, 8.7% and 12% corresponding to 40, 60 and 70 W to the Al cathode, respectively. Table (8.3) presents a summary of the properties of the best transparent conducting films of undoped zinc oxide and ZAO prepared by this method.

<table>
<thead>
<tr>
<th>$P_{Al}^{DC}$ (W)</th>
<th>$R_x$ (Ω/□)</th>
<th>$R_y$ (Ω.m)</th>
<th>$n_{film}$</th>
<th>$T_{550}$ (%)</th>
<th>$R_{dep}^m$ (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1000</td>
<td>237.6 x 10^{-6}</td>
<td>1.88</td>
<td>39.7</td>
<td>1.32</td>
</tr>
<tr>
<td>30</td>
<td>1064</td>
<td>185.8 x 10^{-6}</td>
<td>1.94</td>
<td>70.5</td>
<td>0.97</td>
</tr>
<tr>
<td>40</td>
<td>194</td>
<td>34.6 x 10^{-6}</td>
<td>1.82</td>
<td>84.2</td>
<td>0.99</td>
</tr>
<tr>
<td>50</td>
<td>92</td>
<td>17.0 x 10^{-6}</td>
<td>1.85</td>
<td>79.1</td>
<td>1.03</td>
</tr>
<tr>
<td>60</td>
<td>149</td>
<td>25.2 x 10^{-6}</td>
<td>1.91</td>
<td>77.8</td>
<td>0.94</td>
</tr>
<tr>
<td>70</td>
<td>850</td>
<td>156.2 x 10^{-6}</td>
<td>1.80</td>
<td>80.4</td>
<td>1.02</td>
</tr>
</tbody>
</table>

Table (8.3): Properties of the best transparent conducting films of undoped zinc oxide and ZAO prepared by independently DC powered magnetrons with PEM control.

8.2.2. Mid-frequency AC powered magnetrons in floating mode with a DC bias to zinc magnetron and voltage control

The main and secondary targets were kept as Zn and Al, respectively. The two magnetrons were operated in the floating mode at $P_{Zn+Al}^{AC} = 100$ W, as described in section (5.2.7.2). The DC-bias applied to the Zn magnetron, $P_{Zn}^{DC}$, was varied taking the values 300, 350, 400, 450, 500 and 550 W (section 5.2.7.3). Voltage control on Zn magnetron was used (sections 4.5.2 and 5.2.8.2). The percentage of zinc magnetron voltage set-point, $Zn^{\%}$, was gradually decreased for each $P_{Zn+Al}^{AC}$-$P_{Zn}^{DC}$ combination, and a film was deposited and characterised at each value of $Zn^{\%}$.

Figures (8.5) and (8.6) show the dependence of $R_y$ and $T_{550}$ of the transparent conducting films of ZAO on $Zn^{\%}$, respectively. A wide process window, of about 4%, was observed at $P_{Zn}^{DC} = 500$ W. Such a window is much wider than that of the previous case when PEM control was used. The percentage of zinc magnetron voltage set-point, at which the best transparent conducting films occur, and their resistivities, are plotted
in figure (8.7) versus $P_{Zn}^{DC}$, whereas figure (8.8) shows the variation of $Zn_{w}$ and $f_{O_{2}}$, at which these films occur, with $P_{Zn}^{DC}$.

**Figure (8.5): Resistivity of transparent conducting films of ZAO vs. the percentage of Zn magnetron voltage set-point. The floating AC power between the two magnetrons was 100W. The Zn magnetron was biased with 300, 350, 400, 450 and 500W.**

![Resistivity graph](image)

**Figure (8.6): Transmittance at 550nm of transparent conducting films of ZAO vs. the percentage of Zn magnetron voltage set-point. The floating AC power between the two magnetrons was 100W. The Zn magnetron was biased with 300, 350, 400, 450 and 500W.**

![Transmittance graph](image)

Finally, figure (8.9) shows the dependence of resistivity and transmittance at 550 nm of these films on $P_{Zn}^{DC}$, whereas figure (8.10) shows the transmittance spectra of the best films at different powers applied to the Zn magnetron. Obviously, these films are absorbing in the blue. Provided that $P_{Zn+Al}^{AC}$ is constant, these figures imply that
1. As in similar cases, the best transparent conducting films occur at lower $Z_{ni}^{56}$ and higher $f_{O_2}$ as $P_{Zn}^{DC}$ increases (figures 8.7 and 8.8) in order to attain sufficient $O_2$ partial pressure to oxidise the increasing amount of sputtered metallic Zn.

2. The resistivity of the best films decreases with $P_{Zn}^{DC}$ until $P_{Zn}^{DC} = 350$ W, and then increases (figure 8.9). The increase in $R_y$ above 350 W could be due to the lower level of Al in the films. However, the best $R_y$ varies slightly in the range
350 ≤ P_{Zn}^{DC} ≤ 500 W, an evidence of achieving suitable stoichiometries and compositions in this range. Figure (8.9) also indicates that the transmittance at 550 nm of the best films increases with P_{Zn}^{DC} until P_{Zn}^{DC} = 500 W, and then slightly decreases. A lower Al content of the film and/or an increase in its thickness could be responsible for such a decrease.

Table (8.4) summarises the properties of the best transparent conducting ZAO films prepared by the combined AC and DC technique. The above results may indicate that regardless of the technique used for deposition, the best resistivities of undoped zinc oxide and ZAO films prepared in this work were
about an order of magnitude higher than the best reported results (table 8.2) with similar transmittances. This is because, the reported results in the literature are for films deposited on heated substrates, annealed films and/or for films deposited on substrates facing the targets in a non-parallel way to reduce ion-bombardment, whereas the properties of the films produced in this work were for as-deposited films grown at room temperature with the substrate parallel to the plane of targets.

<table>
<thead>
<tr>
<th>$P_{Zn}^{DC}$ (W)</th>
<th>$R_s$ (Ω/□)</th>
<th>$R_y$ (Ω.m)</th>
<th>$n_{film}$</th>
<th>$T_{550}$ (%)</th>
<th>$R_{dep}$ (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>200</td>
<td>46.1 x 10^{-6}</td>
<td>1.92</td>
<td>71.8</td>
<td>1.28</td>
</tr>
<tr>
<td>350</td>
<td>138</td>
<td>32.2 x 10^{-6}</td>
<td>1.89</td>
<td>71.2</td>
<td>1.29</td>
</tr>
<tr>
<td>400</td>
<td>131</td>
<td>33.1 x 10^{-6}</td>
<td>1.87</td>
<td>78.2</td>
<td>1.40</td>
</tr>
<tr>
<td>450</td>
<td>126</td>
<td>33.5 x 10^{-6}</td>
<td>1.93</td>
<td>80.5</td>
<td>1.48</td>
</tr>
<tr>
<td>500</td>
<td>115</td>
<td>35.9 x 10^{-6}</td>
<td>1.90</td>
<td>82.3</td>
<td>1.73</td>
</tr>
<tr>
<td>550</td>
<td>113</td>
<td>46.9 x 10^{-6}</td>
<td>1.87</td>
<td>62.6</td>
<td>2.30</td>
</tr>
</tbody>
</table>

Table (8.4): Properties of the best transparent conducting films of ZAO prepared by mid-frequency AC powered magnetrons in floating mode with a DC bias to zinc magnetron and voltage control.

Furthermore, the resistivity of the best ZAO film prepared by the combined AC and DC technique (section 8.2.2) was about two times that prepared by the independently DC powered magnetrons technique (section 8.2.1). This could be understood in terms of ion-bombardment of the growing films. Following the calculations of section (5.4.3), which were based on equation (5.15), and considering the case of ZnO in which $M_w = 81$ g, $S_w = 5.606$ g/cm$^3$ and $\alpha = 1$, the energy delivered to the substrate by ions per In atom was about 15 eV in the case DC power, whereas it was about 50 eV in the case of combined AC and DC technique.

8.3. Zinc indium oxide (ZIO)

The band gap, electron mobility, carrier concentration and refractive index of transparent conducting films of ZIO are about 3.3 eV, 2-15 cm$^2$/V.s, $10^{19}$-$10^{20}$ cm$^{-3}$ and 1.9, respectively$^{2,23}$. Several techniques have been utilised to deposit these films including spray pyrolysis$^2$, RF magnetron sputtering$^{24}$ and DC reactive magnetron sputtering$^{16,25,27-30}$. Table (8.5) presents a summary of the deposition conditions, along with the optical and electrical properties of the resultant films. Once more, high substrate temperature, post-deposition annealing and/or biasing the substrate are essential to produce high quality transparent conducting films.
ZIO films were deposited in this work by applying the combined AC and DC technique (section 5.2.7.3). The main and secondary targets were Zn and In, respectively. The two magnetrons were run in the floating mode at $P_{Zn+In}^{AC} = 100$ W.

<table>
<thead>
<tr>
<th>Depos. method</th>
<th>Subs. temp. (°C)</th>
<th>Subs. bias (V)</th>
<th>Post-deposition annealing temperature (°C) and duration (min)</th>
<th>$R_y$ ($\mu\Omega\cdot m$)</th>
<th>$T$ (%)</th>
<th>Depos. rate (nm/s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP</td>
<td>High</td>
<td>-</td>
<td>-</td>
<td>8</td>
<td>80</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>RFMS</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>~50</td>
<td>70 @ 500nm 60W</td>
<td>0.44 @ 35W</td>
<td>26</td>
</tr>
<tr>
<td>DCRMS ≥280</td>
<td>-50</td>
<td>-</td>
<td>-</td>
<td>14</td>
<td>Low</td>
<td>0.66 @ 35W</td>
<td>16</td>
</tr>
<tr>
<td>DCRMS</td>
<td>In H$_2$ for 30 min (annealing temperature was not stated)</td>
<td>440</td>
<td>80</td>
<td>0.12-0.20</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DCRMS</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>225</td>
<td>-</td>
<td>-</td>
<td>27</td>
</tr>
<tr>
<td>DCRMS</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>40</td>
<td>80</td>
<td>1.2</td>
<td>28</td>
</tr>
<tr>
<td>DCRMS</td>
<td>-24</td>
<td>400 °C in Ar for 2 hours</td>
<td>34</td>
<td>~87</td>
<td>2.2</td>
<td>29</td>
<td></td>
</tr>
</tbody>
</table>

Table (8.5): Electrical and optical properties of ZIO films prepared by spray pyrolysis (SP), RF magnetron sputtering (RFMS) and DC reactive magnetron sputtering (DCRMS).

The DC-bias applied to the Zn magnetron, $P_{Zn}^{DC}$, was varied taking the values 200, 250, 300, 350, 400, 450 and 500 W. Voltage control on Zn magnetron was used (sections 4.5.2 and 5.2.8.2). The percentage of zinc magnetron voltage set-point, $Zn_{pc}$, was gradually decreased for each $P_{Zn}^{AC}$\textsuperscript{-}P$_{Zn}^{DC}$ combination, and a film was deposited and characterised at each value of $Zn_{pc}$.

Figures (8.11) and (8.12) show the variation of $R_y$ and $T_{550}$ of the transparent conducting films of ZIO with $Zn_{pc}$, respectively. Process windows, of about 2.5%-4.5%, were observed. Figure (8.13) shows the occurrence and resistivity of the best transparent conducting films of ZIO versus $P_{Zn}^{DC}$, whereas figure (8.14) presents the dependence of $Zn_{pc}$ and $f_{O_2}$, at which these films occur, on $P_{Zn}^{DC}$. Finally, the dependence of $R_y$ and $T_{550}$ of these films on $P_{Zn}^{DC}$ is shown in figure (8.15), whereas the transmittance spectra of the best films at different powers applied to the Zn
magnetron are seen in figure (8.16). It is clear from figure (8.16) that a transmittance peak appears at a higher wavelength as $P_{Zn}^{DC}$ increases. Provided that $P_{Zn+In}^{AC}$ is constant, these figures imply that

Figure (8.11): Resistivity of transparent conducting films of ZIO versus the percentage of zinc cathode voltage set-point. The floating AC power was 100W. The Zn magnetron was biased with 200, 250, 300, 350, 400, 450 and 500W.

<table>
<thead>
<tr>
<th>Percentage of zinc cathode voltage set-point (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.5</td>
</tr>
<tr>
<td>6.0E-5</td>
</tr>
</tbody>
</table>

As in previous cases, for $O_2$ partial pressure to be adequate for oxidisation of the increasing amount of sputtered Zn, the best transparent conducting films occur at lower Zn$_{ve}$ and higher $f_{O_2}$ as $P_{Zn}^{DC}$ increases (figures 8.13 and 8.14).
2. The resistivity of the best films increases with $P_{Zn}^{DC}$ (figure 8.15). This could be due to the decreasing In content of the films as $P_{Zn}^{DC}$ increases. In fact, AES analysis revealed that the percentage of indium in the best ZIO films was 50.6%, 47.2% and 31.5% corresponding to a DC bias to the Zn magnetron of 200, 250 and 350 W, respectively. On the other hand, $T_{550}$ of these films decreases with $P_{Zn}^{DC}$ reaching a critical value at $P_{Zn}^{DC} = 300$ W and then increases until $P_{Zn}^{DC} = 400$ W. The decrease in $T_{550}$ above 400 W could be due to decreasing In content of the films and/or increasing thicknesses.

Figure (8.13): The occurrence and resistivity of the best transparent conducting films of ZIO versus the DC bias applied to the Zn magnetron. The floating AC power between the Zn and In magnetrons was 100 W.

Figure (8.14): The percentage of zinc magnetron voltage set-point and the corresponding oxygen flow rate at which the best transparent conducting films of ZIO occur versus the DC bias applied to the Zn magnetron. The floating AC power was 100 W.
Table (8.6) summarises the properties of the best transparent conducting ZIO films produced in this work.

![Figure (8.15): Resistivity and transmittance at 550nm of the best transparent conducting films of ZIO versus the DC bias applied to the Zn magnetron. The floating AC power between the two magnetrons was 100W.](image)

![Figure (8.16): Transmittance spectra of the best transparent conducting ZIO films at different powers to the Zn magnetron. The floating AC power between the two magnetrons was 100W.](image)
Table (8.6): Properties of the best transparent conducting films of ZIO prepared by mid-frequency AC powered magnetrons in floating mode with a DC bias to zinc magnetron and voltage control.

8.4. Zinc oxide doped with titanium (ZTiO)

No references were found in literature about ZTiO films. These transparent conducting films were prepared in this work using the combined AC and DC technique (section 5.2.7.3) for the same reasons mentioned in section (7.4). The main and secondary targets were Zn and Ti, respectively. The two magnetrons were operated in the floating mode at $P_{Zn+Ti}^{AC} = 100$ W. The DC-bias applied to the Zn magnetron, $P_{Zn}^{DC}$, was varied taking the values 300, 400 and 500 W. The rest was as in section (8.3).

Figure (8.17): Resistivity and transmittance of transparent conducting films of ZIO versus the percentage of zinc magnetron voltage set-point. The floating AC power was 100 W. The Zn magnetron was biased with 300, 400 and 500 W.
Figure (8.17) shows the dependence of $R_y$ and $T_{550}$ of the transparent conducting films of ZTiO on Zn\%\text{\textcopyright}. Process windows, of about 3.5%, was observed at biases of 400 and 500 W to the Zn magnetron. Figure (8.18) shows a plot of Zn\%\text{\textcopyright}, at which the best transparent conducting films occur, and the corresponding $f_{O_2}$, as functions of $P_{Zn}^{DC}$, whereas figure (8.19) shows the dependence of $R_y$ and $T_{550}$ of these films on $P_{Zn}^{DC}$.

Finally, figure (8.20) shows the transmittance spectra of the best films. All films show absorption in the blue. The following remarks could be deduced from the previous figures.
1. As before, the best transparent conducting films occur at lower $Zn_{\text{voc}}$ and higher $f_o$, as $P_{Zn}^{\text{dc}}$ increases (figure 8.18).

2. The resistivity of the best films increases first slightly with $P_{Zn}^{\text{dc}}$ and then decreases, whereas $T_{550}$ behaves in an opposite manner (figure 8.19). The drop in resistivity, and the increase in $T_{550}$, above 400 W is expected to be a result of a significant decrease of Ti content of the film. However, the transparent conducting properties of this film ($R_y = 7.7 \times 10^{-5} \, \Omega \cdot m$ and $T_{550} = 83.5\%$) were much better than the corresponding properties of undoped ZnO film ($R_y = 24 \times 10^{-5} \, \Omega \cdot m$ and $T_{550} = 39.7\%$) prepared in section (8.2.1), an indication of some level of doping of this film with Ti.

The properties of the best transparent conducting ZTiO films, obtained in this work, are summarised in table (8.7).

<table>
<thead>
<tr>
<th>$P_{Zn}^{\text{dc}}$ (W)</th>
<th>$R_s$ (Ω/□)</th>
<th>$R_y$ (Ω.m)</th>
<th>$n_{\text{film}}$</th>
<th>$T_{550}$ (%)</th>
<th>$R_{2\mu}^{\text{ep}}$ (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>500</td>
<td>85.2 x 10^{-6}</td>
<td>1.97</td>
<td>82.3</td>
<td>0.95</td>
</tr>
<tr>
<td>400</td>
<td>325</td>
<td>94.7 x 10^{-6}</td>
<td>1.88</td>
<td>78.5</td>
<td>1.62</td>
</tr>
<tr>
<td>500</td>
<td>239</td>
<td>76.8 x 10^{-6}</td>
<td>1.92</td>
<td>83.5</td>
<td>1.78</td>
</tr>
</tbody>
</table>

Table (8.7): Properties of the best transparent conducting films of ZTiO prepared by mid-frequency AC powered magnetrons in floating mode with a DC bias to zinc magnetron and voltage control.
8.5. Zinc oxide doped with tin (ZTO)

Halla\textsuperscript{30} tried to deposit transparent conducting films of ZTO in 1993 using reactive magnetron sputtering technique from a single target. In order to vary the film composition, his target was made of strips of Sn cut to widths in increasing units of 5 mm and fixed across the diameter of a Zn target using an In:Sn alloy 'glue', melting at 114 °C. A computer calculation was used to work out the Sn target coverage as a percentage of the active Zn target area (e.g., a 25 mm wide strip corresponded to a nominal area doping of ZnO:33%Sn). Films were deposited at 400 W for one minute using PEM control. The minimum sheet resistance he obtained was 8.6 M\(\Omega/\square\) at a nominal area doping of ZnO:33%Sn and an oxygen flow rate of 21.5 SCCM. He did not report any optical data of such films.

In this work, transparent conducting films were prepared using the combined AC and DC technique (section 5.2.7.3). The main and secondary targets were Zn and Sn, respectively. The two magnetrons were operated in the floating mode at \(P^{AC}_{\text{Zn+Sn}} = 100\) W. The DC-bias applied to the Zn magnetron, \(P^{DC}_{\text{Zn}}\), was varied taking the values 150, 300, 450 and 600 W. The rest was as in section (8.3).

All transparent films deposited at \(P^{DC}_{\text{Zn}} = 150\) W were insulators, whereas, at \(P^{DC}_{\text{Zn}} = 300\) W the only non-insulating film was obtained at \(Zn_{Zn}^{\%} = 18.25\%\) with a sheet resistance of 1.2 M\(\Omega/\square\). At higher values of \(P^{DC}_{\text{Zn}}\) better conductivities were achieved.

**Figure (8.21): Resistivity and transmittance of transparent conducting films of ZTO versus the percentage of zinc magnetron voltage set-point. The floating AC power was 100W. The Zn magnetron was biased with 450 and 600W.**
Figure (8.21) shows the dependence of $R_y$ and $T_{550}$ of the transparent conducting films of ZTO on $Zn_{dc}$ at DC biases to the Zn magnetrons equal to 450 and 600 W. A process window, of about 3.5%, was observed at 450 W to the Zn magnetron. Figure (8.22) shows the dependence of $Zn_{dc}$ and $f_{O_2}$, at which these films occur, on $P_{Zn}^{DC}$, whereas figure (8.23) shows the dependence of $R_y$ and $T_{550}$ of these films on $P_{Zn}^{DC}$.

Finally, figure (8.24) shows the transmittance spectra of the best films. The following remarks could be deduced from these figures:

1. The best transparent conducting films occur at lower $Zn_{dc}$ and higher $f_{O_2}$ as $P_{Zn}^{DC}$ increases (figure 8.22).
2. The resistivity and transmittance at 550 nm of the best films decrease first with $P_{Zn}^{DC}$ (figure 8.23) and then decreases almost stabilise at higher values (i.e., $P_{Zn}^{DC} \geq 450$ W), an indication of reaching appropriate stoichiometries and compositions.

![Transmittance spectra of the best transparent conducting ZTO films at different powers to the Zn magnetron. The floating AC power between the two magnetrons was 100W.](image)

Table (8.8) summarises the properties of the best transparent conducting ZTO films obtained in this work.

<table>
<thead>
<tr>
<th>$P_{Zn}^{DC}$ (W)</th>
<th>$R_s$ (kΩ/□)</th>
<th>$R_y$ (Ω.m)</th>
<th>$n_{film}$</th>
<th>$T_{550}$ (%)</th>
<th>$R_{exp}^p$ (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1200</td>
<td>$1.8 \times 10^{-1}$</td>
<td>1.99</td>
<td>85.1</td>
<td>0.86</td>
</tr>
<tr>
<td>450</td>
<td>27</td>
<td>$6.5 \times 10^{-3}$</td>
<td>1.96</td>
<td>75.0</td>
<td>1.35</td>
</tr>
<tr>
<td>600</td>
<td>16</td>
<td>$5.0 \times 10^{-3}$</td>
<td>1.95</td>
<td>74.2</td>
<td>1.76</td>
</tr>
</tbody>
</table>

Table (8.8): Properties of the best transparent conducting films of ZTO prepared by mid-frequency AC powered magnetrons in floating mode with a DC bias to zinc magnetron and voltage control.
REFERENCES


CHAPTER NINE

RESULTS AND DISCUSSION: OTHER OXIDES

9.1. Introduction

The ability of the sputtering system, used in this work, to flexibly and independently control the composition and stoichiometry of alloy oxide films deposited using an arc-free reactive magnetron sputtering process (sections 5.2.7.3 and 5.5) has paved the way to investigate a large number of alloy oxides in search of new transparent conducting films. Oxide films of Mo, W, V, Pb, Ti, Sn and Cu doped with dopants such as Zn, Sn, Ti, Nb, Ta, Mo or Bi have been deposited, at different combinations of powers, and characterised. The most promising transparent conducting films of these were tin oxide doped with titanium and vanadium molybdenum oxide. However, the insulating oxide films produced were also of great interest for optical applications.

This chapter will concentrate on the conditions under which these films were deposited as well as on their electrical and optical properties.

On the other hand, it being very difficult to be sputter-deposited in a reactive atmosphere due to arcing, aluminium oxide was chosen to be deposited in the early stages of this work in order to

1. Evaluate the performance of the sputtering system when two aluminium magnetrons were operated in the floating mode, using the 40 kHz AC power supply (section 5.2.7.2), in a reactive atmosphere.

2. Assess the efficiency of the automatic feedback voltage control of the admission rate of oxygen into the deposition chamber.
Although aluminium oxide is a transparent insulator and hence it is out of the scope of this work, it is thought that the interesting results obtained are worth mentioning.

9.2. Tin oxide doped with titanium (TTiO)

The band gap, electron mobility, carrier concentration and refractive index of undoped tin oxide films are about 3.83-4.3 eV, 5-30 cm²/V.s, 10¹⁸-10²⁰ cm⁻³ and 1.8-2.2, respectively¹⁻⁴. In addition to being extremely resistant to chemical etching, these films possess excellent hardness, excellent adherence to the substrate and very good environmental stability¹. Transparent conducting films of undoped tin oxide have been prepared using various deposition techniques such as spray pyrolysis \((R_y = 5 \cdot 10^{-5} \, \Omega \cdot m\) and \(T = 80-90\%\), after annealing in Ar at 400 °C¹), reactive evaporation \((R_y = 2 \cdot 10^{-5} \, \Omega \cdot m\) and \(T = 85\%\), at a substrate temperature of 490 °C⁴) and reactive magnetron sputtering²⁻³. In the latter, Lewin et al⁵ produced films deposited onto plastic substrates at room temperature with \(R_y = 1.11 \cdot 10^{-4} \, \Omega \cdot m\) without reporting the optical transmittance, whereas De and Ray⁹ reported the production of undoped tin oxide at a substrate temperature of 450 °C with \(R_y = 6.1 \cdot 10^{-5} \, \Omega \cdot m\) and \(T \approx 84\%\). The most popular dopants of tin oxide are antimony and fluorine¹⁻². In the case of Sb, a resistivity and transmittance of about \(10^{-5} \, \Omega \cdot m\) and 80-90%, respectively was obtained using spray pyrolysis technique at high substrate temperature¹, whereas Lewin et al⁵ reactively-sputtered these films onto plastic substrates at room temperature with \(R_y = 3.75 \cdot 10^{-3} \, \Omega \cdot m\) without reporting the optical transmittance. In the case of F doped tin oxide, however, a resistivity as low as \(4.6 \cdot 10^{-6} \, \Omega \cdot m\) and a transmittance in the range 80-90% was achieved using spray pyrolysis technique at a high substrate temperature¹.

In this investigation, attention was paid to the deposition of transparent conducting films of TTiO. No references were found in literature about these films. They were prepared in this work using the combined AC and DC technique (section 5.2.7.3). The main and secondary targets were Ti and Sn, respectively. The two magnetrons were operated in the floating mode at \(P_{AC_{Ti+Sn}} = 50 \, W\). The DC-bias applied to the Ti magnetron, \(P_{DC_{Ti}}\), was varied taking the values 150, 200, 250 and 300 W. PEM control on Ar emission lines was used (section 5.2.8.1). The percentage of Ar lines set-point, \(Ar_{pem}^\%\), was gradually decreased for each \(P_{AC_{Ti+Sn}}\), \(P_{DC_{Ti}}\) combination, and a film was deposited and characterised at each value of \(Ar_{pem}^\%\). The deposition time was 6 minutes.
Figure (9.1): Resistivity and transmittance of transparent conducting films of TTiO versus the percentage of Ar lines set-point. The floating AC power was 50W. The Ti magnetron was biased with 150, 200, 250 and 300W.

Figure (9.1) shows the dependence of $R_y$ and $T_{550}$ of the transparent conducting films of TTiO on $\text{Ar}_{\text{pen}}$. Wide process windows of about 3%-7% were observed.

The percentages of Ar lines set-point, at which the best transparent conducting films occur, as well as the corresponding oxygen flow rates, are plotted in figure (9.2) versus $P_{\text{Ti}}^{\text{DC}}$, whereas figure (9.3) shows the dependence of $R_y$ and $T_{550}$ of these films on $P_{\text{Ti}}^{\text{DC}}$. Finally, the transmittance spectra of the best films at different powers applied to the Ti magnetron are plotted in figure (9.4). Films become more absorbing as $P_{\text{Ti}}^{\text{DC}}$ increases.
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Figure (9.3): Resistivity and transmittance at 550nm of the best transparent conducting films of TTIO versus the DC bias applied to the Ti magnetron. The floating AC power between the two magnetrons was 50W. PEM control was used.

Figure (9.4): Transmittance spectra of the best transparent conducting TTIO films at different powers to the Ti magnetron. The floating AC power between the two magnetrons was 50W. PEM control was used.

Provided that $P_{\text{Tot}}$ is constant, the following remarks could be deduced from these figures:

1. The best transparent conducting films occur at lower $A_p$ and higher $f_0$ as $P_{\text{DC}}$ increases to secure oxidisation of the increasing amount of sputtered Ti (figure 9.2).

2. The resistivity of the best films decreases first with $P_{\text{DC}}$ and then increases with a minimum at $P_{\text{DC}} = 200$ W (figure 9.3). The increase in $R_y$ could be attributed to the higher level of Ti atoms in the films which may act as scattering sites of the carriers. However, the change of the best $R_y$ at the combinations of
power studied is very small, indicating the attainment of suitable stoichiometries and compositions. On the other hand, the transmittance at 550 nm of the best films increases first slightly with $P_{\text{ni}}$ until $P_{\text{ni}} = 200$ W, and then decreases. The decrease could be attributed to the slight increase in thickness and/or higher Ti content of the films.

Table (9.1) presents a summary of the properties of the best transparent conducting TTiO films prepared by this technique.

<table>
<thead>
<tr>
<th>$P_{\text{ni}}$ (W)</th>
<th>$R_i$ (Ω/□)</th>
<th>$R_y$ (Ω.m)</th>
<th>$n_{\text{film}}$</th>
<th>$T_{550}$ (%)</th>
<th>$R_{\text{app}}$ (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>1349</td>
<td>154.1 x 10^{-6}</td>
<td>2.00</td>
<td>82.4</td>
<td>0.31</td>
</tr>
<tr>
<td>200</td>
<td>749</td>
<td>107.1 x 10^{-6}</td>
<td>2.01</td>
<td>84.5</td>
<td>0.39</td>
</tr>
<tr>
<td>250</td>
<td>819</td>
<td>132.9 x 10^{-6}</td>
<td>2.03</td>
<td>80.5</td>
<td>0.45</td>
</tr>
<tr>
<td>300</td>
<td>869</td>
<td>159.8 x 10^{-6}</td>
<td>2.02</td>
<td>74.6</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Table (9.1): Properties of the best transparent conducting films of TTiO prepared by mid-frequency AC powered magnetrons in floating mode with a DC bias to titanium magnetron and PEM control.

### 9.3. Vanadium molybdenum oxide (VMO)

VMO films were prepared using the combined AC and DC technique (section 5.2.7.3). The main and secondary targets were V and Mo, respectively. The two magnetrons were operated in the floating mode at $P_{\text{V}+\text{Mo}} = 100$ W. The DC-bias applied to the V magnetron, $P_{\text{DC}}$, was varied taking the values 100, 200 and 300 W. PEM control on Ar emission lines was used (section 5.2.8.1). The percentage of Ar lines set-point, $Ar_{\text{pem}}$, was gradually decreased for each $P_{\text{V}+\text{Mo}}-P_{\text{DC}}$ combination, and a film was deposited and characterised at each value of $Ar_{\text{pem}}$. The deposition time was 6 minutes. Figure (9.5) shows the dependence of resistivity and transmittance at 550 nm of the best transparent conducting films on $P_{\text{DC}}$. It can be seen from this figure that $R_y$ increases with $P_{\text{DC}}$ whereas $T_{550}$ decreases. This is probably due to the decreasing concentration of Mo in the films as $P_{\text{DC}}$ increased. On the other hand, oxygen flow rates at which these films occurred were 0.5, 1.2 and 2 SCCM corresponding to 100, 200 and 300 W DC-biases to the V magnetron, respectively. Finally, figure (9.6) shows the transmittance spectra of the best films at different powers applied to the V magnetron. Films become more absorbing as $P_{\text{DC}}$ increases.

Table (9.2) summarises the properties of the best transparent conducting VMO films produced in this work.
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Figure (9.5): Resistivity and transmittance at 550nm of the best transparent conducting films of VMO versus the DC bias applied to the vanadium magnetron. The floating AC power between the two magnetrons was 100W, PEM control was used.

Figure (9.6): Transmittance spectra of the best transparent conducting VMO films at different powers to the vanadium magnetron. The floating AC power between the two magnetrons was 100W, PEM control was used.

<table>
<thead>
<tr>
<th>$P_{V}^{DC}$ (W)</th>
<th>$R_{x}$ (Ω/□)</th>
<th>$R_{f}$ (Ω.m)</th>
<th>$n_{film}$</th>
<th>$T_{550}$ (%)</th>
<th>$R_{dep}^{\text{film}}$ (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>200</td>
<td>509.3 $\times$ 10$^{-6}$</td>
<td>1.773</td>
<td>76.8</td>
<td>0.70</td>
</tr>
<tr>
<td>200</td>
<td>1800</td>
<td>747.5 $\times$ 10$^{-6}$</td>
<td>1.735</td>
<td>69.1</td>
<td>1.15</td>
</tr>
<tr>
<td>300</td>
<td>7321</td>
<td>3478 $\times$ 10$^{-6}$</td>
<td>1.734</td>
<td>67.9</td>
<td>1.31</td>
</tr>
</tbody>
</table>

Table (9.2): Properties of the best transparent conducting films of VMO prepared by mid-frequency AC powered magnetrons in floating mode with a DC bias to vanadium magnetron and PEM control.
9.4. Aluminium and other insulating oxides

Aluminium oxide films are of great importance in the electronic industry (e.g., passivation layers in integrated circuits and piezoelectric layers in surface acoustic wave devices) and in the optical industry (e.g., antireflection layers in solar cells) as dielectric, wear resistant, low refractive index and transparent films.\textsuperscript{10} Although high deposition rates, of the order of 30-60 nm/s, can be achieved when these films are prepared by evaporation at high substrate temperatures, such films usually suffer from porous microstructures as a result of the low kinetic energy of the condensed species\textsuperscript{12} (see section 2.3.2). On the contrary, RF sputtered \textit{Al}_2\textit{O}_3 films suffer from low deposition rates (-0.16-0.58 nm/s)\textsuperscript{13,14}. Using a baffle to separate the reaction of \textit{O}_2 at the substrate from that at the target surface (see section 4.4.3), Scherer and Wirz\textsuperscript{8} have DC-sputtered \textit{Al}_2\textit{O}_3 films in a reactive atmosphere with a rate of 3.6 nm/s at a power density of 12 W/cm\textsuperscript{2}. Alternatively, several workers have successfully used mid-frequency AC reactive magnetron sputtering for high rate deposition of \textit{Al}_2\textit{O}_3 films. For example, Frach \textit{et al}\textsuperscript{7} have used unipolar pulsed magnetron sputtering (see section 4.6.3.1) at a substrate temperature of 50 °C. The deposition rate and transmittance at 550 nm of the produced films were about 4 nm/s at 2.5 kW and 87%, respectively. Scherer \textit{et al}\textsuperscript{8} have adopted bipolar pulsed magnetron sputtering technique using two magnetrons operated in the floating mode (see section 4.6.3.2.II) at a power of 7 kW. The substrates were passed in front of the targets in a translational motion with a constant speed. The deposition rate and transmittance at 550 nm of the produced films were about 3.3 nm/s and 88%, respectively. Also, Schiller \textit{et al}\textsuperscript{15} have deposited these films using the same technique at a rate of 4 nm/s at 2 kW. Finally, the reported values of refractive index of \textit{Al}_2\textit{O}_3 films are in the range\textsuperscript{16} 1.51-1.73. A higher refractive index means a denser film and hence higher resistivity to chemical etching.

In this work, \textit{Al}_2\textit{O}_3 films were prepared using the mid-frequency AC powered magnetrons technique of section (5.2.7.2). The main and secondary targets were both Al and the two magnetrons were operated in the floating mode at \textit{P}_{\textit{Al}_{2}\textit{O}_3}=1 \textit{kW}. Substrates were held static over the main magnetron. Voltage control on the main Al magnetron was used (sections 4.5.2 and 5.2.8.2). The percentage of aluminium magnetron voltage set-point, \textit{Al}_{\%}, was gradually decreased and a film was deposited and characterised at each value of \textit{Al}_{\%}. The deposition time was 3 minutes. Figure (9.7) shows the dependence of \textit{T}_{550} of the visibly transparent \textit{Al}_2\textit{O}_3 films, and the corresponding deposition rate, on \textit{Al}_{\%}. Obviously, films of higher \textit{T}_{550} are deposited at lower rates. The percentage of Al magnetron voltage set-point, and the corresponding \textit{O}_2 flow rate, at which the best \textit{Al}_2\textit{O}_3 film occurred (i.e., the one of the highest transmittance and deposition rate) were 73.7% and 3.6 SCCM, respectively. The
transmittance at 550 nm, refractive index and deposition rate of this film were 89.5%, 1.67 and 2.02 nm/s, respectively. Clearly, such a result is comparable with the best reported results\(^{8,15}\) taking into account that the applied power in this work was only 1 kW. Finally, figure (9.8) shows the transmittance and reflectance spectra of the best film. The transmittance and reflectance spectra of the best Al\(_2\)O\(_3\) film are shown in figure (9.8). Finally, it is worth mentioning that in addition to glass, aluminium oxide films have also been deposited, using this technique, on stainless steel and single crystal silicon substrates for extended periods of time (up to 45 minutes) and at high rates without any sign of arcing.

**Figure (9.7):** Transmittance at 550 nm and the corresponding deposition rate versus the percentage of aluminium magnetron voltage set-point of visibly transparent films of aluminium oxide. The floating AC power between the two Al magnetrons was 1 kW.

**Figure (9.8):** Transmittance and reflectance spectra of the best transparent Al oxide film which occurred at 73.7% of Al magnetron voltage set-point. The floating AC power was 1 kW. The relevant spectra of an uncoated glass substrate are also plotted.
Finally, a large number of oxide films of Mo, W, V, Pb, Ti, Sn and Cu doped with dopants such as Zn, Sn, Ti, Nb, Ta, Mo or Bi has been deposited, at different combinations of powers and at different stoichiometries, and characterised. They were initially investigated for conductivity. Although the transparent films were insulating under the deposition conditions and procedures followed (i.e., unintentional heating or biasing of substrates and no post-deposition heat treatment), their optical properties (e.g., a very wide range of refractive indices) are of great interest in optical applications.

Table (9.3) summarises the preparation conditions and the optical properties of some of the transparent insulating oxide films prepared in this work, where $P_{Cu}^{DC}$, $P_{W}^{DC}$, $P_{V}^{DC}$, $P_{Mo}^{DC}$ and $P_{Pb}^{DC}$ are the DC biasing powers applied to the floating Cu, W, V, Mo and Pb magnetrons, respectively, and $Cu_{wC}$ and $Pb_{wC}$ are the percentages of metallic Cu and Pb magnetrons voltages set-points, respectively. The floating AC power and deposition time were 100 W and 6 min, respectively, throughout.
Table (9.3): A summary of the preparation conditions and optical properties of some of the transparent insulating oxide films prepared in this work. The floating AC power was 100 W throughout.
REFERENCES


Problems associated with reactive magnetron sputtering from elemental targets have been successfully solved in this work. The elements of this achievement may be summarised as follows:

1. The use of mid-frequency (i.e., 40 kHz) AC power in the floating mode allowed the reactive sputtering process to be arc-free and hence eliminating the undesired effects of arcing in reactive sputtering such as driving the process to become unstable, creating defects in the films and reducing the target lifetime.

2. The combination of DC and mid-frequency AC power in a novel way using a filter to protect the DC power supply from the AC one (or the independently DC powered magnetrons method) permitted the composition of the produced films to be easily and independently manipulated by varying the magnitude of power applied to each magnetron.

3. Depending on the materials involved, the use of very fast feedback methods to automatically control the admission rate of oxygen into the sputtering chamber (i.e., PEM and voltage control) allowed the stoichiometry of the deposited films to be independently controlled. The very efficient control of the admission rate of oxygen also allowed the deposition rate of reactively sputtered films to be high.

4. Sputtering from two magnetrons made the production of alloys or multi-element compounds, which are either difficult or impossible to be formed from single targets, an easy task.
5. Substrate rotation enhanced atomic level mixing of the film constituents. The stoichiometry of the film was controlled by PEM or voltage control on one magnetron, and dopants were added by sputtering from the other magnetron. This means that the former magnetron served two purposes; the first was to sputter metal and oxidise it, and the second purpose was to oxidise the metal sputtered from the other magnetron.

Using this technique, a large range of alloy-oxide films were deposited at high rates. In fact, the independent control of both the metallic composition and stoichiometry was very valuable in identifying optimum electrically conducting and visually transparent films. Consequently, this novel technique opens the door wide for investigating virtually all potentially promising oxides (e.g., zinc oxide doped with gallium). In addition, this technique is also capable of being used in producing films of insulating oxides of any composition giving transparent films of different refractive indices for optical applications. Furthermore, such a technique may also be capable of investigating other types of thin films (e.g., hard coatings, semiconducting films, superconducting films,...etc.).

Well-known films such as ITO, ZAO and ZIO were deposited at wide windows of appropriate stoichiometries (about 4-6.5% of the control signal in PEM control or of the metallic cathode voltage in voltage control). In addition, new types of oxide films, which have great promise, have been successfully identified including ITiO, IAO, IZO, ZTiO, ZTO, TTiO and VMO. In general, the windows of appropriate stoichiometries were also wide (about 3.5-9% of the control signal). Electrical and optical properties of the produced films were determined by measuring the sheet resistance, using a four-point probe, and the transmittance and reflectance spectra of the visibly transparent films, using a spectrophotometer. In addition, the refractive indices and thicknesses of the films were calculated from their reflectance spectra, so that the resistivity of the films could be determined. Finally, compositional measurements were carried out using Auger electron spectroscopy.

It was found that the dopant content of the film increased with the DC power applied to its magnetron, when the independently DC powered magnetrons method was employed, whereas it decreased with the magnitude of the DC bias applied to the magnetron of the host material when the combined AC and DC technique was used.

It was also found that, in the case of the independently DC powered magnetrons method, the best transparent conducting films occurred at a lower percentage of metal line emission set-point or higher percentage of oxygen line emission set-point of the host material when PEM control was used (or at a lower percentage of metallic
magnetron voltage set-point in voltage control) as the power applied to dopant magnetron was increased (e.g., see figures 7.11, 7.23 and 8.2). Similarly, the same behaviour was observed in the case of the combined AC and DC technique when the DC bias applied to the magnetron of the host material was increased (e.g., see figures 7.17, 7.27 and 8.7). This may be attributed to the need to secure sufficient oxygen partial pressure in order to oxidise the increasing amount of sputtered metals.

In general, it was observed that in indium oxide-based films, the amount of dopant was not critical and gave inferior properties to those obtained with undoped oxide using stoichiometry control but made the production of transparent conducting films easier (e.g., see figure 7.12). On the contrary, a precise amount of dopant was required in zinc oxide-based films to achieve optimum properties which could not be obtained using stoichiometry control (e.g., see figure 8.2).

Table (10.1) summarises the properties of the best transparent conducting films of alloy oxides prepared in this work. Remember that no intentional heating or external biasing were applied to substrate and no post-deposition annealing of any kind was carried out on any of the deposited films. However, it is recommended that these factors be investigated, along with the effect of varying the rotation speed of the platen, in a future work. In addition, it is also recommended to investigate films properties in a greater detail (e.g., Hall mobility, carrier concentration and band gap) since this was out of the scope of this work.

<table>
<thead>
<tr>
<th>Material</th>
<th>$R_s$ (Ω/□)</th>
<th>$R_y$ (Ω.m)</th>
<th>$n_{film}$</th>
<th>$T_{550}$ (%)</th>
<th>$R_{opt}^n$ (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IAO</td>
<td>42</td>
<td>$5.7 \times 10^{-6}$</td>
<td>2.04</td>
<td>84.5</td>
<td>0.75</td>
</tr>
<tr>
<td>ITiO</td>
<td>33</td>
<td>$4.6 \times 10^{-6}$</td>
<td>2.07</td>
<td>82.1</td>
<td>0.78</td>
</tr>
<tr>
<td>ITO</td>
<td>30</td>
<td>$4.9 \times 10^{-6}$</td>
<td>2.04</td>
<td>79.5</td>
<td>0.91</td>
</tr>
<tr>
<td>IZO</td>
<td>31</td>
<td>$8.2 \times 10^{-6}$</td>
<td>1.96</td>
<td>86.5</td>
<td>1.47</td>
</tr>
<tr>
<td>TTiO</td>
<td>749</td>
<td>$107.1 \times 10^{-6}$</td>
<td>2.01</td>
<td>84.5</td>
<td>0.39</td>
</tr>
<tr>
<td>VMO</td>
<td>200</td>
<td>$509.3 \times 10^{-6}$</td>
<td>1.77</td>
<td>76.8</td>
<td>0.70</td>
</tr>
<tr>
<td>ZAO</td>
<td>92</td>
<td>$17.0 \times 10^{-6}$</td>
<td>1.85</td>
<td>79.1</td>
<td>1.03</td>
</tr>
<tr>
<td>ZIO</td>
<td>84</td>
<td>$11.7 \times 10^{-6}$</td>
<td>2.07</td>
<td>86.4</td>
<td>0.77</td>
</tr>
<tr>
<td>ZTiO</td>
<td>239</td>
<td>$76.8 \times 10^{-6}$</td>
<td>1.92</td>
<td>83.5</td>
<td>1.78</td>
</tr>
<tr>
<td>ZTO</td>
<td>16000</td>
<td>$5.0 \times 10^{-3}$</td>
<td>1.95</td>
<td>74.2</td>
<td>1.76</td>
</tr>
</tbody>
</table>

Table (10.1): Properties of the best transparent conducting films of alloy oxides prepared in this work.

On the other hand, oxide films of Mo, W, V, Pb, Ti, Sn and Cu doped with dopants such as Zn, Sn, Ti, Nb, Ta, Mo or Bi have been deposited, at different combinations of powers, and characterised. They were originally investigated for conductivity. Although
the transparent films were insulating under the deposition conditions and procedures followed, their optical properties (e.g., a very wide range of refractive indices between about 1.6 and 2.6) are of interest in optical applications.

Finally, it is believed that the independent biasing of each floating magnetron with a DC power supply, using two filters, may lead to a more precise control of film composition and it is suggested to be considered in future work.
SUMMARY OF PLASMA FUNDAMENTALS

A1.1. Electron and ion temperature, average speed and random thermal current density

A gas in thermal equilibrium has particles of all velocities. The most probable distribution of these velocities is known as the Maxwell-Boltzmann distribution. If, for simplicity, a gas particle constrained to dimension, say $x$, is considered, the Maxwell-Boltzmann distribution is:

$$f(u) = A_x \cdot \exp\left(-\frac{1}{2} \frac{mu^2}{kT}\right)$$  \hspace{1cm} [A1.1]

where $f \, du$ is the number of particles in unit volume (density) with velocity between $u$ and $u + du$, $m$ is the particle mass, and $k$ is the Boltzmann's constant. The number density, $n$, is given by:

$$n = \int_{-\infty}^{\infty} f(u) \cdot du$$  \hspace{1cm} [A1.2]

By applying equation (A1.2), the constant $A_x$ is found to be:

$$A_x = n \left(\frac{m}{2\pi kT}\right)^{1/2}$$  \hspace{1cm} [A1.3]

The average kinetic energy of particles, $E_{xv}$, associated with motion in the $x$ direction according to this distribution is:
\[ E_{av} = \frac{1}{2} \mu u^2 \]  

Alternatively, the average kinetic energy of particles can be expressed in terms of \( \bar{u}^2 \), the mean-square velocity of those particles:

\[ E_{av} = \frac{1}{2} \mu \bar{u}^2 \]  

where \( \bar{u}^2 \) is:

\[ \bar{u}^2 = \frac{\sum u^2}{N} \]

with \( N \) the total number of gas particles. From equations (A1.4) and (A1.5), it is obvious that:

\[ E_{av} = \frac{1}{2} \mu \bar{u}^2 = \frac{1}{2} kT \]

Following the same approach, the average kinetic energy of particles, \( E_{av} \), in three dimensions can be obtained. Maxwell-Boltzmann distribution is then:

\[ f(u, v, w) = A \cdot \exp\left[-\frac{1}{2} m(u^2 + v^2 + w^2)/kT\right] \]

where:

\[ A = n \left( \frac{m}{2\pi kT} \right)^{3/2} \]

With similar calculations to those of one dimension, \( E_{av} \) is:

\[ E_{av} = \frac{1}{2} mc^2 = \frac{3}{2} kT \]

where \( c^2 \) is the mean-square speed of those particles given by:

\[ c^2 = \frac{\sum c^2}{N} = \frac{\sum u^2 + v^2 + w^2}{N} = \frac{\bar{u}^2 + \bar{v}^2 + \bar{w}^2}{N} \]

Since \( T \) and \( E_{av} \) are so closely related, it is customary in plasma physics to give temperatures in units of energy. To avoid confusion on the number of dimensions involved, it is not \( E_{av} \) but the energy corresponding to \( kT \) that is used to denote the
Appendix One

temperature. For \( kT = 1 \text{eV} \Rightarrow T = \frac{1}{8.62 \times 10^{-5}} = 11600 \text{ K} \). So the term 2 eV plasma indicates an average kinetic energy \( E_{av} = 3 \text{eV} \).

As mentioned earlier in this section, the Maxwell-Boltzmann distribution is valid at thermal equilibrium, so can it be applied to energetic electrons? Assuming a large number of electron-electron collisions and other interactions, and very efficient energy sharing amongst the electrons (the energy transfer function, which is described in section A1.4, is between 0 and 1), the Maxwell-Boltzmann distribution will be quite reasonable, and the average electron energy, \( E_e \), can be expressed in terms of electron temperature \( T_e \) using the following equation:

\[
E_e = \frac{1}{2} m_e \overline{c^2_e} = \frac{3}{2} kT_e \quad [A1.12]
\]

where \( m_e \) and \( \overline{c^2_e} \) are electron mass and mean-square speed respectively. Similarly, the average ion energy, \( E_i \), is:

\[
E_i = \frac{1}{2} m_i \overline{c^2_i} = \frac{3}{2} kT_i \quad [A1.13]
\]

where \( m_i \), \( \overline{c^2_i} \), and \( T_i \) are ion mass, mean-square speed, and temperature respectively. Measurements on plasmas give average electron and ion energies around 2 eV and 0.043 eV respectively, which correspond to \( T_e = 23200 \text{ K} \) and \( T_i = 500 \text{ K} \).

A more useful parameter is the average speed of particles, \( \overline{c} \), is defined as:

\[
\overline{c} = \frac{\sum c}{N} = \frac{1}{N} \int c \cdot dN_c \quad [A1.14]
\]

where \( dN_c \) is the number of particles whose speeds lie between \( c \) and \( c + dc \). From the kinetic theory one can get:

\[
\overline{c} = \left( \frac{8kT}{\pi m} \right)^{1/2} \quad [A1.15]
\]

Equation (A1.15) for electrons becomes:

\[
\overline{c_e} = \left( \frac{8kT_e}{\pi m_e} \right)^{1/2} \quad [A1.16]
\]

where \( \overline{c_e} \) is the average electrons speed. Similarly, for ions:
where $\overline{c}_i$ is the average ions speed. When $T_e >> T_i$ and $m_e << m_i$, then it is obvious from equations (A1.16) and (A1.17) that $c_e >> \overline{c}_i$.

Kinetic theory also shows that the random thermal current density, $J_r$, of a gas is given by:

$$J_r = \frac{en\overline{c}}{4} = en\left(\frac{kT}{2\pi m}\right)^{1/2}$$

where $en/4$ is the gas flux. Denoting $n_e$ as the electron density, and applying equation (A1.18) to the case of electrons give:

$$J_{re} = \frac{en_e\overline{c}_e}{4} = en_e\left(\frac{kT_e}{2\pi m_e}\right)^{1/2}$$

where $J_{re}$ is the electrons random thermal current density. Similarly, the ion random thermal current density $J_{ri}$ is given by:

$$J_{ri} = \frac{en_i\overline{c}_i}{4} = en_i\left(\frac{kT_i}{2\pi m_i}\right)^{1/2}$$

where $n_i$ is the ion density. Bearing in mind that in a plasma $n_i = n_p = n$, taking the values of $T_e = 23200$ K and $T_i = 500$ K mentioned before, as an example, and taking $m_i = 6.6 \cdot 10^{-23}$ g and $m_e = 9.1 \cdot 10^{-28}$ g, then it is found that $J_{re}/J_{ri} = 1835$. It may be deduced then, that the random thermal current density of electrons is much higher than that of ions.

**A1.2. Electron and ion mean free path**

The mean free path of a molecule, $\lambda$, in a gas can be defined as the average distance which it travels between collisions. Initially, it is assumed, for simplicity, that all molecules but one are at rest. Then the one moving molecule will strike all those whose centres lie within a distance $\sigma$ of its path, where $\sigma$ is the molecule diameter. In a time $\Delta t$, the moving molecule will cover an average distance $\overline{c}\Delta t$ and make a number of collisions equals to $n_{col}$. The mean free path is then $\lambda = \overline{c}\Delta t/n_{col}$. On the other hand, $n_{col} = n(\pi\sigma^2)(\overline{c}\Delta t)$, where $n$ is the number of molecules in the unit volume of the gas. From the last two equations one can get:
If the relative motion of molecules is considered, equation (A1.21) becomes:

\[ \lambda = \frac{1}{\pi \sigma^2 n} \] [A1.21]

Since the diameter of an ion is almost equal to that of a neutral molecule, the ionic mean free path, \( \lambda_i \), is almost equal to that of a molecule in equation (A1.22):

\[ \lambda_i = \frac{1}{\pi \sigma^2 n \sqrt{2}} \] [A1.23]

If \( r \) is the radius of a gas-molecule, then \( \sigma = 2r \) and equation (A1.23) becomes:

\[ \lambda_i = \frac{1}{4\pi r^2 n \sqrt{2}} \] [A1.24]

To find the electronic mean free path, \( \lambda_e \), two assumptions should be made:

1. An electron is much smaller than an ion. Therefore, the radius of the electron may be neglected. It may be said that, to strike a gas molecule, an electron must approach the centre of the molecule within a distance equal to the molecule’s radius, \( r \).

2. In applying an electric field, electrons reach a speed much greater than the mean thermal speed of the gas-molecules. Therefore, the latter can be considered at rest in comparison to electrons.

Accordingly, equation (A1.21) is valid after replacing \( \sigma \) with \( r \), hence:

\[ \lambda_e = \frac{1}{\pi r^2 n} \] [A1.25]

The quantity \( \pi r^2 \) is called the collision cross-section of the molecule for electrons. If equation (A1.25) is divided by equation (A1.24), it is found that the mean free path of electrons in a plasma is about six times longer than that of ions:

\[ \frac{\lambda_e}{\lambda_i} = 4\sqrt{2} = 5.65 \] [A1.26]

On the other hand, the number of gas molecules per cm\(^3\), \( n \), can be obtained from the ideal gas laws. If the pressure \( p \) is in Torr, and \( T \) is the absolute temperature then:
This equation means that the mean free path (for ions or molecules) is proportional to the ratio \( T/p \).

**A1.3. Electron and ion mobility and drift current**

A charged particle, in an electric field, travelling through a conductor (e.g., metal or plasma) makes a finite number of collisions\(^2\). If ions or electrons form a swarm so that the velocities of individual particles are equally distributed in all directions about an average velocity, then an electric field acting on the swarm will move it bodily. The average speed with which the centre of the swarm moves in the direction of the field is called the drift velocity \( \nu_d \). On the other hand, the mobility, \( \mu \), of charged particles is defined as the drift velocity in unit electric field, that is \( \mu = \nu_d/E \), where \( E \) is the electric field.

When an ion collides with a gas molecule, the ion may lose much of its kinetic energy to the molecule due to the almost equal mass of the ion and molecule. After the collision the ion gains energy again from the electric field to lose some of it in the next collision. This process carries on until the ion settles down to a quasisteady motion, in which the average energy lost by collisions equals that gained between them\(^3\). Consider an ion having a positive charge \( e \), and a mass \( m_i \), moving in an electric field \( E \). The acceleration of the ion in the direction of the field is then \( a_i = eE/m_i \). Assuming that the average drift velocity is much less than the average random thermal speed \( c_i \), and the ion starts from rest after each collision, the velocity gained by the ion between collision is \( \nu_i = \alpha \tau_i = 2\nu_d \), (or the average drift velocity of the ion is half the velocity it gains between collisions) where \( \tau_i = \lambda_i/c_i \) is the time between collisions. Using equation (A1.24) gives:

\[
\mu_i = \frac{1}{8\pi\sqrt{2}} \frac{e}{nm_i r^2 c_i} \quad [A1.28]
\]

When electrons pass through a gas, they may make elastic and inelastic collisions (this will be discussed in the next section). In an elastic collision, an electron can lose only a small fraction of its kinetic energy, but in an inelastic collision, it may lose much or all of that energy. Therefore, the detailed motion of electrons through a plasma is complicated, but it is believed that this motion is quasisteady. In similar treatment to that of ions, the mobility of electrons, \( \mu_e \), is given by:
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\[ \mu_e = \frac{1}{2\pi n m e r^2 c_e} \] \hspace{1cm} \text{[A1.29]}

According to equation (A1.27), both \( \mu_i \) and \( \mu_e \) are proportional to the ratio \( T/p \).

If equation (A1.29) is divided by equation (A1.28), and equations (A1.16) and (A1.17) are used one obtains:

\[ \frac{\mu_e}{\mu_i} = 5.65 \left( \frac{m_i T_i}{m_e T_e} \right)^{1/2} \] \hspace{1cm} \text{[A1.30]}

Considering again the values of \( T_e = 23200 \) K and \( T_i = 500 \) K mentioned before, as an example, and taking \( m_i = 6.6 \cdot 10^{-23} \) g and \( m_e = 9.1 \cdot 10^{-28} \) g, the above ratio becomes \( \mu_e/\mu_i \approx 225 \). It may be deduced then, that the mobility of electrons is much higher than that of ions.

The drift of ions and electrons through a glow discharge, which is superimposed on their random thermal motion, carries the electric current which flows through the discharge from the anode to the cathode. The current density carried by ions is \( J_{di} = n_i e v_{di} \) or \( J_{di} = n_i e \mu_i E \), and that carried by electrons is \( J_{de} = n_e e \mu_e E \). The discharge current density is therefore \( J_d = J_i + J_e \), or:

\[ J_d = eE \left( n_i \mu_i + n_e \mu_e \right) \] \hspace{1cm} \text{[A1.31]}

In a plasma \( n_i = n_e = n \), therefore:

\[ \frac{J_{de}}{J_{di}} = \frac{\mu_e}{\mu_i} \] \hspace{1cm} \text{[A1.32]}

which implies that most of the current in a plasma is carried by electrons.

**A1.4. Collision processes**

There are many types of species in a glow discharge. The presence of electrons, ions, neutral atoms and/or molecules, and photons give rise to a wide range of elastic and inelastic collision processes. The most important processes will be summarised here.

It is beneficial, before describing the elastic collisions, to establish the so called "energy transfer function". Applying the definition of the elastic collision, where momentum and kinetic energy are conserved, for two particles, one of which is stationary with a mass \( M \) and the velocity of the other is \( v_0 \) with a mass \( m \) gives:
\[
\frac{1}{2} m(v_b^2 - v_a^2) = \frac{1}{2} m v_b^2 \frac{4mM}{(m+M)^2} \cos^2 \varphi
\]

where \(v_a\) is the velocity of the particle of the mass \(m\) after collision, and \(\varphi\) is the angle of collision. The term \(\left[\frac{4mM}{(m+M)^2}\right] \cos^2 \varphi\) is the energy transfer function.

If an electron collides elastically with an atom, it bounces off it in any direction without a major change in its kinetic energy, whereas the atom is almost unaffected. This is because the energy transfer function in this is too small (\(m \ll M\)). These sort of collisions restrict the velocities of electrons in the direction of the electric field.

There are many types of inelastic collisions in a glow discharge in which the kinetic energy is not conserved. Among these collisions:

**A1.4.1. Ionisation and recombination**

The collision of an electron with an atom may ionise the atom (a bound electron being ejected from the atom) provided that the energy of the striking electron is higher than ionisation potential of the atom. In such a collision, the electron loses much more than the atom gains. (e.g., \(e^- + \text{Ar} \rightarrow 2e^- + \text{Ar}^+\)). This means that each electron, upon ionisation, produces another electron and both of them contribute to the discharge. It is fairly typical, in inert gases, for the ionisation cross-section to increase with electron energy, for energies above the threshold, to a maximum at around 100eV and then drops. Ionisation can also be produced by any suitable energy input such as thermal activation (by impact with neutral ground state gas atoms or with the atoms of the walls) which is less likely in cold discharges, and by photon activation (photoionisation). Photo-ionisation cross-section behaves in a similar way to ionisation cross-section.

Recombination is the inverse of ionisation and may happen at the walls of the chamber, the so called "wall losses". Ions can not be neutralised in the gas phase because there is no mechanism which can dissipate the heat of neutralisation to conserve both momentum and energy in a two body system. Therefore it can only happen at a surface. Recombination can also result in either radiation being emitted, the so called "radiative recombination" (e.g., \(\text{Ar}^+ + e^- \rightarrow \text{Ar} + h\nu\)), or the forming of two neutrals (e.g., \(\text{A}^- + \text{A}^+ \rightarrow 2\text{A}\)). The latter is not very likely, especially in inert gases where the outermost shell is saturated and hence forming a negative ion is quite a remote possibility.
A1.4.2. Excitation and relaxation

The collision of an electron having an energy lower than that needed for ionisation with an atom may result in excitation (a bound electron is enabled to jump to a higher energy level within the atom) provided that the energy of the striking electron is higher than the excitation potential of the atom (e.g., $e^- + Ar \rightarrow Ar^* + e^-$), where the asterisk represents the excited state. For example, the excitation potential of argon is 11.56 eV, whereas its ionisation potential is 15.8 eV. Like ionisation, excitation can also result from photoexcitation and thermal excitation, although the latter is rare in cold discharges. Finally, excitation and photoexcitation cross-sections behave in a similar way to the corresponding ionisation ones.

Relaxation is the inverse of excitation. As the excited states are rather unstable with relatively short lifetimes, an excited electron returns to its ground state in a single or multiple transitions, emitting a photon of energy specific to each transition, and equal to the difference between the relevant energy levels (e.g., $Ar^* \rightarrow Ar + hv$). These photons are responsible for the "glow" in glow discharges.

A1.4.3. Metastable collisions

Most excited states have a lifetime of $10^{-10} - 10^{-7}$ s. Some other excited states, known as metastable excited atoms, have a longer lifetime of $10^{-4} - 1s^{23}$ which may increase the probability of the involvement of such excited atoms in collisions. Argon, for instance, has metastable states at 11.5 eV and 11.7 eV.

There are many collision processes in which metastable excited atoms are involved. They are:

- **Metastable-neutral ionisation**: (e.g., $Ar^* + Ar \rightarrow Ar^+ + Ar + e^-$). This is also called Penning ionisation.

- **Metastable-metastable ionisation**: (e.g., $Ar^* + Ar^* \rightarrow Ar^+ + Ar + e^-$)

- **Electron-metastable ionisation**: (e.g., $e^- + Ar^* \rightarrow Ar^+ + e^- + e^-$)

A1.4.4. Other collisions

- **Ion-neutral collisions**: If the kinetic energy of the ion or the neutral is sufficient, a new ion can be produced. This type of collision can also be elastic where an ion and a neutral exchange charge (known as charge transfer). Charge transfer can be symmetrical, when the exchange of the charge is between an atom and an ion of
the same atom, or asymmetrical, if it between an atom and an ion of another atom.

- **Electron attachment and dissociation**: In electron attachment the striking electron may join the atom to form a negative ion. This type of collision is rare in inert gases since the outer electron shell is already filled. Dissociation is possible in the case of molecules (e.g., $e^- + O_2 \rightarrow e^- + O + O$) if the energy of the striking electron is higher than the bond energy of the molecule. Sometimes, dissociation is accompanied by ionisation (e.g., $e^- + O_2 \rightarrow O^+ + O + 2e^-$) and is called dissociative ionisation.

Finally, the total collision cross-section is the sum of the above mentioned individual cross-sections of various collision processes.

**A1.5. Debye length $\lambda_D$**

![Figure (A1.1): Potential distribution in the proximity of a grid in a plasma. Reproduced from reference 1.](image)

Suppose a perfectly transparent grid is planted, in a plasma, on the plane $x = 0$ and held at a potential $\phi_0$, as in figure (A1.1). To find $\lambda_D$, the potential distribution $\phi = f(x)$, near the grid has to be determined by solving Poisson's equation. To do so, it is assumed that the ratio $m_i/m_e$ is large enough that the inertia of ions prevents them from moving significantly, hence forming a positively charged and uniform background in which electrons move. This implies that $n_i = n$ anywhere in the plasma and the grid potential affects $n_e$ only. Poisson's equation in one dimension is:

$$\varepsilon_0 \nabla^2 \phi = -e(n_i - n_e) \quad \text{[A1.34]}$$

where $\varepsilon_0$ is the permittivity of free space. To find $n_e$, the Maxwell-Boltzmann distribution is used. In the presence of a potential $\phi$, the distribution function of electrons (equation A1.1) is:

$$f(u) = A \cdot \exp\left[-\left(\frac{u}{2m_e^u} + \frac{q\phi}{kT_e}\right)\right] \quad \text{[A1.35]}$$
where \( q = -e \). Using equation (A1.2), and noting that \( n_e = n \) when \( \phi \to 0 \), one gets:

\[
    n_e = n \cdot \exp\left(\frac{e\phi}{kT_e}\right)
\]  \hspace{1cm} [A1.36]

Substituting for \( n_i \) and \( n_e \) in equation (A1.34) gives:

\[
    \varepsilon_0 \nabla^2 \phi = \varepsilon_0 \frac{d^2\phi}{dx^2} = en \left\{ \left[ \exp\left( \frac{e\phi}{kT_e} \right) \right] - 1 \right\}
\]  \hspace{1cm} [A1.37]

The region close to the grid, where \( |e\phi| \gg kT_e \), does not contribute greatly to the value of \( \lambda_D \), since only very energetic particles can reach there. If \( |e\phi| \ll kT_e \), then the Taylor series can be used, and the above equation becomes:

\[
    \varepsilon_0 \frac{d^2\phi}{dx^2} = en \left[ \frac{e\phi}{kT_e} + \frac{1}{2} \left( \frac{e\phi}{kT_e} \right)^2 + \ldots \right]
\]  \hspace{1cm} [A1.38]

Omitting the non-linear terms gives:

\[
    \frac{d^2\phi}{dx^2} = \frac{n_e^2}{\varepsilon_0 kT_e} \phi
\]  \hspace{1cm} [A1.39]

Defining:

\[
    \lambda_D = \left( \frac{\varepsilon_0 kT_e}{n_e^2} \right)^{1/2}
\]  \hspace{1cm} [A1.40]

equation (A1.39) can be written as:

\[
    \frac{d^2\phi}{dx^2} = \frac{1}{\lambda_D^2} \phi
\]  \hspace{1cm} [A1.41]

which has a solution:

\[
    \phi = \phi_0 \cdot \exp\left( -|x|/\lambda_D \right)
\]  \hspace{1cm} [A1.42]
REFERENCES


APPENDIX TWO

LIST OF PUBLICATIONS


4- Safi I., and Howson R. P. (1997), Reactive sputtering of mixed insulating oxides, to be published.


6- Safi I., and Howson R. P. (1997), The doping of indium oxide with titanium and aluminium to create better transparent conducting coatings, to be published.