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DEVELOPMENT OF VACUUM TECHNOLOGIES FOR THE PREPARATION
OF HIGH-PURITY THIN FILMS IN SIMPLE SYSTEMS

by

RAAD A. SWADY

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award
of Doctor of Philosophy of the Loughborough University of Technology

August 1992

Supervisor : Professor R. P. Howson

Director of Research : Professor K. Ziebeck

Department of Physics

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IN THE NAME OF ALLAH THE MOST GRACIOUS, MOST MERCIFUL

"The birds can fly and leave their nests but the Iraqi can never forget his love"

DEDICATION: To

IRAQ: I shall continue to cry tears and blood till your wounds and my wounds are over

All Iraqi children

The memory of my father (Abdulsada) and my brother (Zuhair), may Allah rest them in Heaven

My great mother: You have always taught me not to compromise on principles and have always given me the strength. Your pray has always been the spot of light that brightens all the moments of darkness I have experienced out of my country. I hope I can give back something of huge debts to you. All I can say now is that I give up my life to you "my holly mum"

My brothers and sisters, Thank you for your support and belief
SUMMARY

It has been demonstrated that reactive magnetron sputtering can be controlled in low pumping speed vacuum system through observation of the spectral line emission by the plasma emission monitor (PEM). Confining the deposition process in an enclosed volume has provided the gettering-pumping action needed to deposit films with good quality reducing the active contamination that low pumping vacuum system suffers. TiN films of specular quality has been optimised by observing the emission line of the sputtered titanium. It was shown that optimum TiN film is formed when the consumption of nitrogen flow at the metal line set point is a maximum. This optimisation is characterised by a clear minima of ultimate resistivity and better selective optical properties. Films of TiN deposited using the balanced magnetron source had higher resistivity than the metal titanium in contrast to its bulk properties. That was explained by their lower densities. The lack of activation energy of the growing film during deposition resulted in a columnar structure separated by voids which is a normal microstructure of low film density. By adding activation energy, from an unbalanced magnetron source, a plasma beam was leaked to the substrate subjecting the growing film to energetic ions of sufficient energy to modify the structure of the film. Films were shown to have resistivities lower than the metal titanium. This characterisation was verified by examining their structure by SEM which showed dense films.

The reactive gas consumption gave also a good indication of the process control and the optimisation of dielectric films of TiO₂ and ZrO₂. Optimum films characterised by lowest absorption and high refractive index were shown to form when the consumption of oxygen is low at the lowest metal line set point within the limit of the plasma emission monitor. This shift occurred because the much tighter control of reactive gas pressure which is consequently higher for oxides than for nitrides.
Films of TiN were also deposited at a low magnetron potential. Increasing electron injection reduced the operating potential of the sputtered titanium resulting eventually in a reduction of sputtering rate and consequently a reduction in nitrogen consumption. Films made at lower target potentials had lower resistivities due to the enhanced reactivity and increasing ion current density bombarding the film.
ACKNOWLEDGEMENTS

1- To a personality of great honour, pride, scientific capability and responsibility

Professor K. Ziebeck head of department and my director of research

I can not express my deep gratitude and respect to you in the way that the Iraqi nation does because my words are falling short of that of huge great traditions. All words can not fully give a description of your stand supporting me in the worst time I spent in this country of my entire life. Your single support amused many people especially those who wished my departure. You have taught them (if they are able to learn) many great lessons in scientific responsibility and morality. You did not discriminate and confronted the forces of lies by your awareness of what was going on. You did not leave an innocent student to be disrupted by a brutal campaign of accusation. Your continuous visits weekly bringing food and fruit and offering money reminded me in our great Iraqi traditional values. Some people when looking at their eyes or when speaking indirectly to me did not understand the real values of life as far as your attitude is concerned. They forgot that you understand the mentality and behaviour of Iraqi student very well whom they can never stab you or anybody from behind. I wish I could include your amazing letter to the" Panel Game " which you attended with me in "Wormwood Scrobs" prison in London, as one of the documents of this project. You asked that panel to release me in the condition that I live with your family as a guarantee turning down their accusation of terrorism. Your honourable attitude and scientific supervision have to be taught as a separate course by countries taking overseas students on. You released me from prison and made my life possible after to continue my research. Your remarkable support and honest intention are medals of honour which suits the Iraqis very well. Thank you very much for reading and correcting the manuscript. Please forgive me if I have not given you the description you deserve.
2- I am also grateful to my supervisor Professor R. Howson for his fruitful discussions. I thank him for arranging for me to present our paper in the international conference which was held at Loughborough University in April 1992. My thanks to Dr A. Spencer for his scientific suggestions. His visit to the prison gave another example of ethical responsibility. I would like also to thank Mr M. Stenelake for his technical assistance and Mr J. Bates from metallurgical department who spent many hours with me doing the SEM investigation and printing the photograph. My thanks also go to Mr G. Critchlow for doing the Auger analysis of some of the samples.

I would like also to thank the Ministry of Higher Education and Scientific Research of Republic of Iraq for the financial support. At last I would like to thank all the Iraqi students and especially Mr A. Al-Ashaab who supported me towards the continuation of my research and visiting me regularly during my imprisonment. Mr Al-Ashaab has given the friendship and brotherhood the meaning they deserve.

"Something has to be said"
"My 50 days of unjust and inhuman captivity in this country"

Please note that writing this statement should not be regarded as an exploitation of pure scientific field to raise a political issue. If the right was given to exploit my life as a student by jailing me, I see no reason why I should not express my calm anger and condemnation in a civilised manner as always do. I feel it is my historical duty to report my feelings honestly and condemn that action done against me. We were locked up in individual cells for 19 hours a day and treated like criminals. They accused us of being "TERRORISTS" and I find that accusation to be cheap, sick and does not suit countries called "GREAT". From my knowledge in history I know that great nations are those which possess great ethical values. I belong to a nation which has never stabbed anybody
from behind and this nation has always been stabbed from behind. This nation if you read history very well has the oldest civilisation in the history which taught other nations all fields of sciences and above all, ethical values. I am always ready to sacrifice myself for the sake of my beloved IRAQ but when I know my real enemy very well in the fighting front which he tries to attack my dear people. I belong to a great nation which always appreciates the generosity (even if it does not exist materialistically) and has never been disgraceful or violated or threatened any country opened his door for scientific research. I was jailed simply because I did not insult Iraq or let my head down by expressing my opinions openly in civilised manner when other people opened such discussion. I did not know that people living in society called democratic did not like somebody like me who knows something of history as far as others are concerned. It seemed however that explaining the truth in English language for people who can not answer back and hide their intention inside had upset them. I have been here to complete my postgraduate studies but I am bound to carry my national identity and feelings wherever I go. I really regret that some people were very pleased for my suffering of imprisonment who wished to be deported but the voice of GOD and the determination and support of head of department Professor K. Ziebeck disappointed and overcome the voice of short sightness. At last and the most important is not the least I would like to say "I may forgive but God will never forget".
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Conclusions
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<table>
<thead>
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<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>( A_p )</td>
<td>Area of the probe</td>
</tr>
<tr>
<td>( B )</td>
<td>Full width at half height of a Bragg peak</td>
</tr>
<tr>
<td>( c )</td>
<td>Speed of light in free space</td>
</tr>
<tr>
<td>( d )</td>
<td>Lattice plane spacing</td>
</tr>
<tr>
<td>( D )</td>
<td>Complex dielectric displacement</td>
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<tr>
<td>( E )</td>
<td>Ion bombardment energy</td>
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<tr>
<td>( E_r )</td>
<td>Relaxation energy</td>
</tr>
<tr>
<td>( E_0 )</td>
<td>Intensity or amplitude of light perpendicular to the complex wave vector</td>
</tr>
<tr>
<td>( E_2 )</td>
<td>Additional electric field acting on the bound electrons in the Lorentz model</td>
</tr>
<tr>
<td>( h )</td>
<td>Planck's constant</td>
</tr>
<tr>
<td>( H )</td>
<td>Magnetic field</td>
</tr>
<tr>
<td>( i )</td>
<td>Complex number</td>
</tr>
<tr>
<td>( i^- )</td>
<td>Electron current of the cathode</td>
</tr>
<tr>
<td>( I )</td>
<td>Electric current</td>
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<tr>
<td>( J )</td>
<td>Current density</td>
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<tr>
<td>( k )</td>
<td>Extinction coefficient</td>
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<tr>
<td>( K )</td>
<td>Boltzmann's constant</td>
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<tr>
<td>( L_0 )</td>
<td>Distance between the photographic plate and the sample (camera distance)</td>
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<tr>
<td>( m )</td>
<td>Mass of the electron or ion</td>
</tr>
<tr>
<td>( M )</td>
<td>Weight loss of the sputtered target</td>
</tr>
<tr>
<td>( M_i )</td>
<td>Ion mass</td>
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<tr>
<td>( n )</td>
<td>Number density of particles (Section 2.2)</td>
</tr>
<tr>
<td>( n )</td>
<td>Refractive index (Section 2.9)</td>
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<tr>
<td>( N )</td>
<td>Number density of electrons or ions</td>
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Nd : Number of particles participating in screening the perturbed region of the plasma

N_{is} : Number density of ions at the plasma-sheath interface

N_0 : Number density of electrons or ions in an unperturbed plasma

n\lambda : Order of reflection of an X-ray diffracted by a crystal

P : Dipole moment

q : Complex wave vector of the light

r : Distance of over which light travels in a medium

r_0 : Radius of diffraction ring

S : Sputtering yield

t : Average grain size of the crystal

T_e : Electron temperature

U : Electron or ion average velocity

V_B : Breakdown voltage

V_f : Floating potential

V_s : Bias voltage

x : Separation distance between two electrodes

X_s : Sheath thickness

\bar{\alpha} : Frequency-dependent atomic polarizability

\rho : Density of space charge

\lambda : Debye length

\gamma : Secondary electron emission

\omega : Frequency of the medium acting on the electron

\omega_0 : Frequency of electron

\omega_p : Plasma frequency
\( \Gamma : \) Damping of electron (frequency) (Lorentz model)
\( \varepsilon : \) Complex dielectric constant
\( \varepsilon_0 : \) Permittivity of free space
\( \varepsilon_1 : \) Real part of complex dielectric constant
\( \varepsilon_2 : \) Imaginary part of complex dielectric constant
\( \sigma : \) Optical conductivity
\( \lambda_0 : \) Wavelength of light in free space
\( \alpha : \) Absorption coefficient
\( \tau : \) Relaxation time
\( \theta : \) Angle of diffraction
\( \varepsilon_\infty : \) Polarizability resulted from electronic excitation (section 2.9.3)
CHAPTER ONE
INTRODUCTION

1.1 The Aim of this Project

The objective of this work was to deposit TiN by reactive magnetron sputtering in low pumping speed vacuum system. In such poor quality of vacuum it was suggested to contain the reactive process in an enclosed volume of the getter box within the vacuum chamber. The reactive process inside the getter box is controlled by an observation of the spectral line of the sputtered target by a plasma emission monitor (PEM).

Three stages of investigations were made throughout this project. In the first stage a balanced magnetron with a rectangular source was operated. The second stage involves operating the unbalanced magnetron of a circular source to bombard the film by a dense leaked plasma beam. The last stage involves operating the unbalanced magnetron (stage two) at low sputtering voltage using a filament.

Films of ZrN, TiO₂ and ZrO₂ were also deposited using the unbalanced magnetron within the getter box by observing the metal line.

1.2 TiN

The transition metals of carbides and nitrides have received enormous attention for the last two decades and in particular TiN due to the combination of mechanical, electrical and optical properties that it possesses. The metal titanium belongs to the IVa group of the transition metals in the periodic table. In vacuum deposition when titanium vapour is reacted with nitrogen the resulting optimum compound exhibits golden appearance.
TiN crystallises in NaCl structure (f. c. c) which exists over a wide range of composition ratio (nitrogen to titanium ratio = 0.62-1.16) (Ref. 1).

Due to its high hardness and resistance against erosion and abrasion it was applied in the form of thick coating in industrial applications as a hard, protective and decorative coatings (Refs. 2-9). As a protective coatings TiN was also deposited on the vacuum chamber by S. Komiya et al (Ref. 10). They showed that the outgassing rate released by desorption from a bare stainless surface was reduced to fifth when TiN was applied to it.

The extreme hardness and high melting temperature of TiN (2970 C°) due to strong metallic bonding are responsible for the metallic behaviour which is characterised by high conductive properties.

The electrical properties of TiN characterised by high conductivity (low contact resistance) attracted large number of investigations to be done for its application in IC technology (Refs. 11-16). M. Wittmer studied the diffusion barrier properties of TiN in contact systems for silicon devices (Refs. 12,13).

The integration of TiN as a metal possessing interesting optical properties has also brought a great deal of investigation of such selective properties in order to characterise and assess the best optical films in thin forms which could be used as optical filters of solar control films. In the last decade intensive studies have been made on the optical properties of TiN. In the Drude model the metal of ideal free electrons shows reflectivity approaching unity below the plasma frequency (Ref. 17). The optical properties of conducting materials are featured for their free charge carriers by a plasma frequency. The sharp transition from minima reflection (dielectric behaviour) to a higher reflection is determined by the free carrier relaxation time which is most
pronounced at higher values. All metals do not have significant transmission at low wave length because of considerable residual interband absorption (Ref. 18). The excitations or interband transitions can occur in metals only, since insulators do not have partially filled states below Fermi level and this explains why the insulators are non-conducting (Ref. 17).

The capability of formation of solid solutions e.g TiC\textsubscript{x}N\textsubscript{y} and the unusual properties of 4b transition metal nitrides such as their hardness and chemical stability are special characteristics for their bonding mechanism (Ref. 19). The clear overlap of Ti 3d and N 2p states below Fermi level shows covalent bonding in TiN (Ref. 20). The material also exhibits d-band metallic conductivity (Ref. 21). Charge transfer from N to Ti gives also small contribution of ionic bonding (Ref. 22). Because of the atomic selection rule interband transitions between d-d states are suppressed while transitions between p-d states are allowed (Ref. 23).

In recent years particular attention has been dedicated to deposit TiN by reactive magnetron sputtering and the possibility of using it as a heat mirror. In space 98% of the total energy radiated by the sun lies between the wave lengths 0.25-3 \mu m (Ref. 24). In hot season where considerable heat radiation through the window glass to the inside buildings occurs, a coating is needed which can allow the visible light to come through and reject the harmful infrared heat. By applying such coating the cost of cooling system can be reduced. In cold weather a coating is needed which gives a wider range of transmission for the wavelengths 0.3-3 \mu m and suppressing the light at higher wavelengths. It was suggested to use TiN as a stable alternative to noble metals for heat mirrors applications (Ref. 25). The inclusion of TiN among other materials and multilayers as a heat reflecting surface in solar control system and Low-Emissive conservation system need very well controlled films with stoichiometry character at
optimum condition that could compete with those of noble metal. The weakness of TiN in such mentioned systems comes from high absorption due to interband transitions or very low and almost zero transmission in the visible part of the spectrum. The possibility to obtain high transmission in the visible through highly absorbing opaque film is to make it thinner. The implications of making thinner films lead to a decrease in IR reflection although the transmission is risen in the visible. M. Georgson compared the optical properties of two thin films of TiN and silver prepared at the same thickness (Ref. 19). He showed that transmission of TiN in the visible was not as sharp as silver and the increase of reflection (high extinction coefficient K) at longer wave length was lower and not as rapid as silver. Consequently TiN in thin form shows more absorbing character rather than being highly reflective surface. TiN and other transition metals carbides and nitrides are very sensitive to impurities such as oxygen and carbon due to their strong affinity (Ref. 1). The presence of these impurities reduces the number of energy states to which the electrons can be excited by yellow light (Ref. 26). It is these electrons which on relaxation emit yellow light and their number is a measure of brightness.

In the third world there is a potentiality of optical solar films due to intensive solar heat emitted over long period of the year.

1.3 Film Deposition Techniques
Physical vapor deposition (PVD) techniques such as ion plating, evaporation and sputtering are versatile deposition methods for both optical thin films and hard thick coatings. PVD has many advantages over chemical vapor deposition (CVD). The parameters which govern the deposition process such as transportation of evaporated atoms or deposition of a compound by reaction between the source atoms and the
injected reactive gas, the path of that transportation from the source (target) to the substrate and finally the condensation of these atoms and the following nucleation and film growth can all be controlled individually in PVD systems. One of the outstanding deposition process which emerged as reliable candidate for controlled film stoichiometry of a compound of high purity and high deposition rates is reactive sputtering. This process involves the sputtering of a metal (target) in the presence of reactive gas. The advantages of reactive sputtering are: possibility of forming complex compound from easy fabricated metal targets. Besides insulating compounds e.g TiO\textsubscript{x} and ZrO\textsubscript{x} can be easily deposited with a dc power or rf power at wide composition.

Conventional sputtering systems results in intensive heat by electron bombardment striking the substrate.

The problem of heat and the loss of electrons can be suppressed in the so called magnetron sputtering. The configuration of electric and magnetic field causes the secondary electrons emitted from the cathode (target) to be trapped in a long spiral path increasing the ionisation efficiency of the working gas atoms. This technique offers a high deposition rate, low substrate heating and low gas pressure. Another advantage emerging from magnetron sputtering is its flexibility in terms of building a small sputtering unit for laboratory research and building a big production plant of coating at large substrate areas for industrial applications.

In general reactive sputtering is a slow deposition process due to the target coverage of reactive gas. Consequently the deposition rate is reduced sharply at certain pressure of reactive gas which in turn results in poor film quality. A closed-loop feed back control system with d.c magnetron sputtering system using the nitrogen peak height (partial pressure of reactive gas) controlled by a mass spectrophotometer resulted in good deposition control even without pulsing (Refs. 27,28). The rate of deposition of TiN
with and without pulsing was the same as that of pure Ti. Stabilising of reactive process by monitoring the emission intensity of the Ti line during reactive magnetron sputtering of TiN was advocated by S. Schiller et al (Ref. 29).

J. E. Sundgren et al also devoted intensive studies on TiN throughout the mechanism of reactive sputtering characterising the influence of process parameters upon film composition (Ref. 30), morphology and structure (Ref. 31) and the influence of substrate bias on composition and structure (Ref. 32). It was shown that the amount of gas incorporated into the growing film depends on whether a compound is formed on the target surface (Ref. 30). TiN films deposited by r.f sputtering and d.c magnetron sputtering at the same composition, substrate temperature and gas pressure were found to be different in terms of deposition rate and structure (Ref. 33). The deposition rate was much higher for magnetron sputtering while the film possessed many voids and a wide range of grain sizes and shapes rather than the r.f sputtered film which was dense and homogeneous.

TiN in thick form film > 3 μm has been applied intensively besides other refractory compounds as a tribological and protective coatings by chemical vapour deposition (CVD). CVD process involves a chemical reactions taking place in the gas phase under controlled high temperature > 1000 °C and high pressure < 1 atm, activated by radiation or heat to form solid product for industrial application and volatile byproducts (Ref. 34). This process results in highly corrosive atmosphere of background product which can determine the life of the vacuum pumps and in particular the rotary pumps, in contrary to the clean environment offered by a relatively cold process such as magnetron sputtering. However CVD has been used for protection against wear and corrosion on forming tools, bearing, gears, aeronautics, nuclear reactor, weapons etc.
As optical thin films TiN can be easily deposited by reactive magnetron sputtering. The factors which influence the characterisation of TiN are: composition, power levels, impurity levels (residual background pressure), bias voltage, ion current density, substrate temperature and working gas pressure. The more satisfactory approach for modifying the properties is to add activation energy to the growing film in order to disrupt the columnar growth densifying the film by strengthening the grain boundaries without heating the substrate (Ref. 35). In the case of conducting layers such as metals, the film growth can be modified by biasing the substrate to attract positive ions that may be present in the vapor stream (Refs. 36,37). The depositing atoms themselves may have sufficient energy to modify growth as in ion-beam deposition or ion-cluster beam deposition (Ref. 38).

The plasma in the deposition chamber in magnetron sputtering can be manipulated in such a way that it leaks to the substrate providing high ion current density and consequent bombardment to the substrate. This can be done by concentrating more magnetic material on the outer magnets and less material in the centre pole. As a result a beam of plasma confined by the magnetic field in the vicinity of the cathode leaks away to the substrate. By placing a probe in place of the substrate and powering it by external power supply, the ion current density and the ion energy reaching the substrate can be measured. This modified configuration of magnetron is called the unbalanced magnetron (UM) (Refs. 39-41). The bias voltage or the energy of ion bombardment can be further increased when a coil is placed behind the substrate.

The ability to provide a controllable ion flux from a planar magnetron while retaining the many other desirable features (simplicity, high deposition rate, geometric versatility, toleration of reactive gas) would assist in the implementation of ion beam assisted deposition in both research and production (Ref. 9). High optical and electrical quality
of TiN was produced using low energy ions by the unbalanced magnetron (Ref. 41). High optical reflection as high as 82% at (λ= 800 nm) was achieved. Ion bombardment during growth of simple metal films is known to reduce optical scattering and lead to very smooth surfaces (Ref. 42). N. Savvides and B. Window also deposited stoichiometric TiN films of 0.6-2 μm thick onto glass substrate at different substrate temperatures and ion energies. Films deposited at 500 °C and energy of 40 eV were golden in color and their resistivities reached minimum value of 26.2 Ω cm (Ref. 40).

Ion bombardment during growth can lead to a build up of stresses in TiN films (Refs. 43-46). These stresses are more pronounced when insulating substrate (glass) is used at low substrate temperature. The stress was always compressive and for deposition temperature 100 °C and 300 °C at increased ion energy up to 30 eV the films spalled either during deposition or on cooling down to room temperature and exposure to the atmosphere (Ref. 41).

Due to the need of high reactivity in reactive deposition and high particle flux bombarding the substrate it is necessary to assist the deposition process by ions that originate from the cathode (source) itself. This can be accomplished when a high current is given to the cathode at lower voltages. The principle of achieving high flux of ionised metal source is met in arc evaporation source. The energies of the metal particles bombarding the substrate were about 20 times larger than that for magnetron sputtering (Ref. 46). The highly percentage of ionised cathode material in the arc evaporation is generated at areas known as cathode spots of high current density. Optical emission spectroscopy revealed that the neutral or Ti emission is produced by particles with energies of the order of 0.4 eV and ionised Ti emission is produced by particles at energy about 3 eV (Ref. 47).
In sputtering the degree of ionisation of Ti sputtered from a clean surface was of order of 0.1 % (Ref. 48). The ionised fraction of the condensing titanium vapor during TiN deposition by arc evaporation was about 84 % (Ref. 49). The cathodic arc plasma deposition process was considered to be unsuitable for decorative applications owing to the presence of macroparticles in the film (Ref. 50). The vapor pressure in the plasma cloud can cause splashing of the molten metal. The amount of droplets emitted was shown to be higher when the melting point and/or the vapor pressure at the melting point is lower (Ref. 51). During reactive deposition of nitride films it was observed that increasing the nitrogen partial pressure reduces the amount of droplets emitted (Ref. 52).

In ion plating and magnetron sputtering deposition systems the processes control of the partial pressure of the reactive gas is required as compared with control of the total pressure in the chamber in the cathodic arc system (Ref. 53).

The composition ratio of N/Ti of stoichiometric TiN (0.95-1) is dependent on nitrogen pressure and is obtained in a narrow nitrogen pressure ($4 \times 10^{-2} - 5 \times 10^{-2}$) Pa in reactive magnetron sputtering (RMS). Stoichiometric films of TiN deposited at the same conditions by reactive arc evaporation (RAE) were obtained at wider range of N$_2$ pressure ($4 \times 10^{-2} - 2 \times 10^{-1}$) Pa (Ref. 46). As a result the optical and electrical properties of TiN are more sensitive to the change of nitrogen pressure than that of the films deposited by RAE. At higher nitrogen pressure more nitrogen than Ti is incorporated in the lattice during RMS. Besides there is high probability for titanium and nitrogen atoms to incorporate in the lattice without reaction due to their lower mobilities, this results in a poor quality films.
1.4 The Getter Action of Surfaces

A major difficulty with conventional sputtering and other vacuum deposition systems results from the contamination of the growing film caused by residual gases such as \( \text{H}_2\text{O}, \text{CO}, \text{O}_2, \) and \( \text{N}_2, \) in the coating equipment (Ref. 54). To eliminate the reactive component of residual gases a means is needed to purify the deposition zone between the cathode and the substrate from these active contaminations, this method of purification is called gettering. In more practical getter-sputtering arrangements, the cathode is of finite size but the walls of the sputtering chamber are arranged to be as close as possible to both the substrate and cathode, subject only to not interfering with the glow discharge (Ref. 55). Getter sputtering was used to prepare superconducting-normal metal couples of Pb-Cu and Pb-Pt. This method also neglects the use of ultra high vacuum for preparing superconductive materials which are very sensitive to residual contaminations (Ref. 56). Getter action by sputtering was also utilised to deposit high-purity aluminium films providing a sufficiently low partial pressure of reactive gas in the deposition chamber (Ref. 57). R. Howson and V. Malina (Refs. 58,59) modified the three temperature method (the simultaneous evaporation of the source elements onto hot substrate) to provide the getter action. A semi-closed system was used to allow material, initially evaporated on to the cooled container walls, to getter the residual gas of active impurities before exposing the substrate to coming evaporated flux. This modification was performed to prepare InAs, InSb and Cd\(_3\)As\(_2\) thin films.

By designing the getter surfaces the level of contaminations of residual gases can be minimised by continuous gettering-pumping action performed by the sputtered atoms of the target which deposit these contaminations on sacrificial surfaces of enclosed volume. This can provide the pumping required to deposit pure films by pure deposition atmosphere. In reactive sputtering process which the reactive gas atoms
form the deposited compound film, another problem appears resulted from enormous reactivity of the reactive gas at the target surface reducing its capability of gettering and increasing reactive gas pressure. It was shown that deposition in a boxed-in chamber shifts the operating points of partial pressure of reactive gas to a stable position (Refs. 60,61).

S. Schiller et al (Ref. 62) built a shield surrounding the target. This closed wall confines the plasma in the reaction chamber and acts as a getter surfaces whose pumping capacities are larger than that of the target. With a voltage control the increase of partial pressure of oxygen near the target can be prevented.
1.5 References


CHAPTER TWO
BACKGROUND AND THEORY

2.1 The Glow Discharge

2.1.1 Characteristics of a Gas Discharge
A discharge initiates when a gas is ionised in the presence of an electric field applied across two electrodes. To distinguish between different kinds of discharge, Figure 2.1 shows a diagram of discharge generated in a gas of low pressure with d.c power (Refs. 1,2). Initially when a voltage is applied between two electrodes, a very small current will be detected. This is due to the presence of a small number of ions and electrons. Here the current is constant and is limited by the small number of charged particles which do not have sufficient energy to regenerate more ions and electrons by collisions. When the voltage is increased these particles will gain enough energy so that they can produce more charged particles by collisions with the electrodes (i.e. emission of secondary electrons) and with neutral gas atoms. If it is assumed that the electrons contributing to the charges are produced only by ionisation within the gas (i.e. ignoring electron production by the electrodes) and neglecting any recombination effects of free electrons with other ionised atoms, then the current density $J$ is given by: (Ref. 2),

$$J = xe \frac{dn}{dt}$$

where:

- $e$ : is the charge of the electron
- $x$ : is the separation between two electrodes
- $dn/dt$ : is the ionisation rate per unit volume
Fig. 2.1 Discharge generated by a d.c power supply (Ref. 1)
If the production rate $\frac{dn}{dt}$ of the ions is constant, any increase in the voltage causes the current to saturate as may be seen in Fig. 2.1. After saturation, when the voltage is further increased, the charged particles will generate more particles and as a result the current starts to rise. As more secondary electrons are emitted and further ionisation takes place the current increases rapidly causing a Breakdown voltage $V_B$ to occur. The rapid increase in current just prior to the breakdown occurrence is called a Townsend Discharge which was first investigated by Townsend (Ref. 3).

The ions generated are accelerated by the electric field towards the cathode striking it and releasing secondary electrons. These electrons (now called primary electrons) in turn ionise the neutral gas atoms and more secondary electrons are emitted. When the primary electrons are just sufficient to generate enough ions which are capable of generating the same number of electrons, a Self-Sustaining discharge occurs and the gas begins to glow. The voltage then drops and the current rises abruptly. This type of discharge is called Normal Discharge, in which the ion bombardment of the cathode surface is not uniform. As the power increases the bombardment becomes uniform covering the cathode surface and a near uniform current density can be achieved. Continuous increase in power then causes both an increase in voltage and current, this region of discharge is known as "Abnormal Glow" and is used in all other glow discharge systems including sputtering. If the cathode is not cooled an emission of thermionic electrons occurs in addition to the secondary electrons. Further emission reduces the impedance drastically and the voltage drops accordingly. The low-voltage high-current discharge is the principle by which arc discharge systems operate.

An important aspect of the abnormal discharge is the breakdown voltage $V_B$. $V_B$ of a gas depends on parameters such as: gas purity, gas pressure, type of gas, electrode spacing, type of materials used in electrodes and container, and the shape of the electrodes and containers (Ref. 2). For a fixed system, if the gas pressure is very low
or the separation distance is too small the secondary electrons will strike the anode with maximum velocity without making a sufficient number of ions by collisions with the neutral atoms. Very high gas pressures or a very large separation of the electrodes decreases the energy of the ions generated because of inelastic collisions, thus reducing the ion bombardment energy which gives rise to a reduction of secondary electron emission.

2.1.2 Basic Collisions in a Gas Discharge

The discharge of gas is composed of different particles such as, electrons, ions, neutral atoms and photons. Most collisions that occur in a discharge are inelastic in which the kinetic energy and the internal or potential energy of the colliding particles are changed. In elastic collisions involving electron scattering in a gas, the electron will change only its direction but maintain the same kinetic energy (Refs. 4,5).

The most important and frequent impact of particles within the discharge is the electron-neutral atom impact. It is this process which maintains the discharge by continuous ionisation of neutral gas atoms by electrons. In this collision process the primary electron removes a bound electron on an atom producing a positive ion and two electrons. These electrons are then accelerated through an electrical field generating further ionisation. Ionisation can also occur when a photon collides with a neutral gas atom in the ground state or with the atoms in the wall of the chamber. This is called photoionisation. If an electron possesses enough energy to displace a bound electron of an atom to an orbit of higher energy, the atom will be in an excited state and this process of collision is called excitation. In this case the atom usually remains in this state for a short period of time about $10^{-8}$ second, the displaced electron then returns to its normal orbit and in doing so releases energy in form of radiation i.e photons. The glow characteristic of a discharge is due to this emission process. Since the electron of
an excited atom is not removed completely from the atom the energy required for excitation is less than that for ionisation. For argon atoms the excitation potential is 11.6 eV whilst the ionisation potential is 15.7 eV. There are certain energy levels corresponding to particular orbits to which an electron may be displaced but from which it cannot easily return to its original level. The atom may remain in this excited metastable state for a long time ($10^{-3}$-1) seconds. On account of their long life time metastable atoms have a good chance of receiving sufficient energy from subsequent electron impact to ionise them. There is a possibility that a neutral gas atom can be ionised by impact with a metastable atom, this collision process is called Penning ionisation. As a result of Penning ionisation the metastable atom returns to its normal ground state. Ionisation can also be achieved when two metastable atoms collide with each other. The major ionisation of metastable atoms are caused by the impact with electrons since the energy required is only 27% of ionisation energy as in the argon case.

The increase or the accumulation of difference sources of ionisation in the discharge is balanced by losses through recombination processes. An electron coalesces with a positive ion in the presence of either a wall or another gas atom. Another source of losses is through particle impact on the walls of the chamber which conveys the resulting heat to the surrounding atmosphere.

2.1.3 The Regions of Glow Discharge
It has been mentioned earlier that a discharge can be created when an electric field is applied between two electrodes at sufficient separation in the presence of a gas. Many of the electron-atom collisions are of the type that results in excitation of an orbital electron to a higher state with subsequent decay to the ground state with the emission of photons. As a result there is considerable light emitted by the discharge. The general
appearance of the discharge is depicted in Fig. 2.2 (Ref. 4). There is a thin sheet of very high luminosity which is in contact with the cathode surface, this region is called the cathode glow. There are two possible types of glow. One possibility is associated with the electrons ejected from the cathode surface as a result of the interaction between the incident ions and the lattice electrons. The electrons from the surface have low energies and experience collisions with the gas atom near the cathode surface and cause excitations. The second possibility is due to the neutralisation of Ar ions which may gain an orbital electron in an excited state of an atom and in decaying to the ground state will emit a photon (Ref. 6). Next to the cathode glow is a region of much lower luminosity known as the cathode dark space or the Crookes dark space. Electron-atom collisions in the dark space do not take place, therefore the lack of excitations and emission of photons is responsible for the dark appearance of this zone. The secondary electrons emitted from the cathode are accelerated through the high electric field in this zone with a very high velocity characterised by their low mass. Since the mobility of ions is very much less than that of electrons, the predominant particles in the dark space are ions (Ref. 7). Consequently the net space charge in this region is positive. Electrons which may be slowed down in the dark space, immediately gain a high acceleration by the field. Electrons just approaching the end of the dark space enter a new region where they collide and ionise the neutral gas atoms at distances corresponding to their mean free path. This new zone is the most luminous one in the discharge and is known as the negative glow. Most electrons give up a great amount of energy due to the collisions with neutral atoms even before they have passed through the region. Consequently the electric field in the negative glow decreases. Further along the discharge there is a region of much less luminosity and nearly zero electric field strength, this is called the Faraday dark space. Electrons reaching this region have already given up most of their energy, therefore they have too little energy to cause further excitation of the neutral atoms. The final space represents a field free space of equal number density of electrons and ions i.e. a plasma which fills the region from the
Fig. 2.2 General appearance of a discharge (Ref. 4)
Faraday space to the anode. Most of the probe investigations and substrate placement are made in the positive column.

2.2 The Plasma

A plasma is an ionised gas composed of different charged particles such as electrons and ions. The presence of neutral atoms is important in order to generate sufficient ions and electrons in the discharge. A simple plasma can be identified by equal number density of ions and electrons i.e. $N_e = N_i$, electron temperature $T_e$, ion temperature $T_i$ and Debye length $\lambda$.

Plasma research was developed from the study of low density ionised gases contained in discharged tubes. W. Crooks was the first who named the ionised medium, the fourth state of matter and paved the way towards understanding the discharge (Ref. 8). However it was not until 63 years ago that the term Plasma was introduced by I L. Tonks and I Langmuir (Ref. 9) in connection with their studies of oscillations in an ionised gas.

2.2.1 Characterisation of the Plasma

The plasma properties such as electron temperature, density and Debye length etc. can be measured by placing an isolated probe or substrate of small surface area in the plasma. This probe will acquire an equal current density of ions and electrons i.e $I = 0$ at a potential called the floating potential $V_f$. The potential difference between the plasma $V_p$ and $V_f$ causes repulsion of the electrons from reaching the probe. This leads to a generation of a net positive charge around it forming a sheath.
2.2.1.1 Plasma Sheath and Wall Potential

When a body or probe is immersed in a plasma it will acquire a negative potential. Near the wall of the probe there is a boundary layer in which the potential increases monotonically from a negative value on the wall to a zero value which corresponds to an unperturbed plasma. This boundary layer is called the plasma sheath. The transition from macroscopic electrical neutrality caused by the presence of a charge induced electrical field exists over a distance or radius called the Debye length (Ref. 10). Fig. 2.3 illustrates the plasma sheath and the variation of the potential and the number densities inside the sheath (Ref. 10).

The probability of macroscopic particles existing in the plasma is proportional to \( \exp\left(\frac{eV}{kT}\right) \). The number densities of ions and electrons are obtained from a Maxwellian distribution as follows:

\[
N_e(x) = N_0 \exp\left(\frac{eV(x)}{kT}\right) \\
N_i(x) = N_0 \exp\left(-\frac{eV(x)}{kT}\right)
\]

The current densities \( I_e \) and \( I_i \) for the electrons and the ions caused by their random motions can be obtained from the kinetic gas theory (Ref. 11) these are expressed by:

\[
I_e = \frac{1}{4} N_e U_e \\
I_i = \frac{1}{4} N_i U_i
\]

Where \( U_i \) and \( U_e \) are the average velocity of ions and electrons.
under equilibrium conditions,

\[ I_e = I_i \quad \text{at} \quad x = 0 \tag{2.4} \]

When \( x = 0 \), \( V(0) = V_w \) and \( x = \infty \), \( V(\infty) = 0 \) \tag{2.5}

If the average energies of the random ions and electrons are equal:

\[ \frac{1}{2} m_e U_e^2 = \frac{1}{2} m_i U_i^2 \tag{2.6} \]

where:

\[ U : \text{is the average particle velocity} = \frac{8 kT \frac{1}{2}}{\pi m} \]

By re-arranging equation 2.6,

\[ \frac{U_i}{U_e} = \left( \frac{m_e}{m_i} \right)^{\frac{1}{2}} \]

Substituting equation 2.2 into 2.3 and their combination into 2.4, and equation 2.6 into the latter new combination yields:

\[ \exp \left( -\frac{2 V_w}{kT} \right) = \left( \frac{m_i}{m_e} \right)^{\frac{1}{2}} \]

By taking the natural logarithm, the wall potential can be computed as follows:

\[ V(w) = -\frac{kT}{4e} \ln \left( \frac{m_i}{m_e} \right) \tag{2.7} \]
2.2.1.2 Sheath Thickness

The sheath thickness can be approximately determined assuming that the electron density is negligible compared with the ion density. The sheath that is formed on the anode as well as that on the cathode is a positive space charge, therefore the major population in the sheath are ions. Fig. 2.4 shows a schematic diagram of the variation of the electric potential near the surface of a negatively biased probe (Ref. 12). The same sheath mechanism but in a much thicker is formed near the cathode surface (Ref. 1).

The absolute ion velocity can be expressed as follows:

$$U_i = \frac{2eV}{m_i^{1/2}}$$

2.8

The total ion current crossing a surface of area A around the probe is:

$$J_i = A N_i U_i = \text{constant}$$

2.9

By applying Poissons equation,

$$\frac{d^2 V}{dx^2} = -\frac{\rho}{\varepsilon_0} = -\frac{e}{\varepsilon_0} (N_i - N_e)$$

2.10

For a positive space charge, $N_e = 0$; and substituting eq. 2.9 into 2.10 yields,

$$\frac{d^2 V}{dx^2} = \left(\frac{-eJ}{\varepsilon_0A}\right) \left(\frac{m_i^{1/2}}{2eV}\right)$$

2.11
Fig. 2.3 Plasma sheath and the variation of potential and the number densities inside the sheath (Ref. 10)

Fig. 2.4 The variation of potential near the surface of a negatively biased probe (Ref. 12)
Integrating eq. 2.11, yields:

\[
\frac{d^2 V}{dx^2} = \frac{2 J}{\varepsilon_0 A} \left( \frac{1}{2} \right) \left( -\frac{1}{2} \right) \left( -\frac{1}{2} \right) (V - V_s)^\frac{1}{2}
\]

2.12

The current density of the ions across the sheath can be obtained as follow: Since the ions follows a Maxwellian Distribution, their probability of existence is proportional to the Boltzmann factor \( \exp \left( \frac{-eV}{kT_e} \right) \).

\[
J = A_s N_{i0} U_{is} = A_s N_{i0} \exp \left( \frac{eV}{kT_e} \right) \left( \frac{2eV_s}{m_i} \right)^\frac{1}{2}
\]

2.13

At the plasma-sheath interface, and as illustrated in Fig. 2.4 the voltage \( V_s \) can be expressed as: (Refs. 11,12)

\[
V_s = -\frac{kT_e}{2e}
\]

2.14

Substituting eq. 2.14 into 2.13 results.

\[
J = \exp \left( -\frac{1}{2} \right) A_s N_{i0} \left( \frac{T_e}{m_i} \right)^\frac{1}{2}
\]

2.15

The floating potential \( V_f \) can be obtained by setting the total current drawn by the probe to zero. Since most electrons are repelled, the random electron current reduced by Boltzmann factor is.
The total electric current is:

\[ I_t = I_e + I_i \]

\[ I_i \] is obtained from eq. 2.15 where \( I = eJ \), so that,

\[ I_i = \frac{1}{4} e A_s N_0 \exp \left( \frac{eV}{kT} \right) U_e \] (2.16)

Integration of eq. 2.12 and making the substitution of eqs. 2.14 and 2.18 in it yields:

(Ref. 12),
\[
\frac{X_s}{\lambda} = \frac{2}{3} \left( \frac{2}{\exp(-1)} \right)^{\frac{1}{2}} \left[ \left( \frac{eV_0}{kT_e} \right)^2 - (\sqrt{2}) \right]^{\frac{1}{2}} \left[ \left( \frac{eV_0}{kT_e} \right)^2 + \sqrt{2} \right]^{\frac{1}{2}}
\]

2.19

where:

\( X_s \): is the approximate Sheath Thickness

\( \lambda \): is the Debye Length

2.2.1.3 Electron Temperature

The most satisfactory method of determining the electron temperature is to use the slope of the plasma I-V characteristics as follow:

Since the electrons follow Maxwellian distribution,

\[
I_e = I_{e0} \exp \left( -\frac{eV}{kT} \right)
\]

\[
\ln \frac{I_e}{I_{e0}} = -\frac{eV}{kT}
\]

the derivative of this equation yields

\[
\frac{d\ln I_e/I_{e0}}{dV} = -\frac{e}{kT}
\]

2.21

The electron temperature can be calculated experimentally from the linear dependence of the probe voltage on the logarithmic electron current contribution.
2.2.1.4 Plasma Density

The total electric current drawn by an electrically isolated probe is:

\[ I = -\frac{1}{4} e A_p N_i U_i + \frac{1}{4} e A_p N_e U_e \]  

When the probe approaches the space plasma potential at \( V = 0 \) the electron current collected by the probe will saturate and the ion current decreases rapidly. Since the average thermal velocity of the electrons is much greater than that of ions, the electron current is much greater than the ion current. Eliminating ion current contribution from the above equation yields:

\[ \frac{I_e}{A_p} = \frac{1}{4} e N_e U_e \]  

where:

- \( I_e/A_p \) : is the electron current density
- \( e \) : is the electron Charge
- \( U_e \) : is the average electron velocity = \( (8KT/m_e)^{1/2} \)
- \( A_p \) : is Area of the probe

2.2.1.5 Debye Length

The potential field around a charged particle is effectively screened by the cloud of other charged particles, its range of force is now confined within a certain characteristic length determined by the density and the temperature of the plasma (Ref. 13). The Debye length is defined as the minimum distance which charged particles with different signs can maintain electrical neutrality (Ref. 14). The effect of a potential perturbed charge can be deduced from Poissons equation:
The charge density is given by

\[ \rho = e \left( N_i - N_e \right) \]

Both electrons and ions densities can be determined by the Boltzmann factor

\[ N_i(x) = N_{i0} \exp \left( \frac{eV}{kT} \right), \quad N_e(x) = N_{e0} \exp \left( \frac{eV}{kT} \right) \]

\[ \rho = -2 \sinh \left( \frac{eV}{kT} \right) \]

where, \( \sinh(x) = \frac{1}{2} (\exp(x) - \exp(-x)) \)

If there is no perturbation: \( N_{i0} = N_{e0} \)

\[ \frac{d^2V}{dx^2} = 2 \frac{N_{e0}}{\varepsilon_0} \sinh \left( \frac{eV}{kT} \right) \]

Since \( kT \gg eV \), \( \sinh(eV/kT) = eV/kT \), so that:

\[ \frac{d^2V}{dx^2} = 2 \frac{V}{\lambda^2} \]
where \( \lambda \) is the Debye Length,

\[
\lambda = \left( \frac{\frac{e}{N_e} k T_e}{N_e^2} \right)^{\frac{1}{2}}
\]  \hspace{1cm} 2.27

The solution of the above equation for a sphere symmetry with the boundary condition that \( V(r) \) vanishes at \( R \) approaches \( \infty \) is: (Ref. 13)

\[
V(r) = A \exp \left( - \frac{r}{\lambda} \right) \hspace{1cm} \text{Where } A \text{ is a constant} \hspace{1cm} 2.28
\]

This solution shows the exponential dependence upon distance far from the charge, with \( \lambda \) the characteristic length. The physical meaning of eq. 2.28 reveals that for distances larger than \( \lambda \) the potential field decreases exponentially. The potential field around a point charge is effectively screened out by the induced space charge field in the electron gas for distances greater than the Debye length \( \lambda \) (Ref. 13). This range depends on the number of particles \( N_d \) that can contain the charge. If a sphere is considered, it has a radius of \( \lambda \) centred on the point charge, known as the Debye sphere, its volume is \( \frac{4}{3} \pi \lambda^3 \). The number of particles that can be contained within \( \lambda \) and participate in screening the charge leaving the rest of the plasma neutral can be computed as follows: (Ref. 15),

\[
N_d = \frac{4}{3} \pi^3 \lambda N_e
\]  \hspace{1cm} 2.29

Practical results can be deduced from the plasma properties mentioned before, at Argon pressure of 3 mtorr and for an unbalanced magnetron current of 3 A, the following quantitative plasma characteristics have been obtained:
$T_e = 42000 \text{ K}$

$V_p = 3 \text{ V}$

$V_f = V_0 = -14.5 \text{ V}$ Practical

$N_e = 1.19 \times 10^{11} \text{ cm}^{-3}$

$\lambda = 0.4 \text{ mm}$

$V(w) = -10.2 \text{ V}$ Theoretical

$X_s = 1.98 \text{ mm}$

$N_d = 3.4 \times 10^7 \text{ Particles}$
2.3 Sputtering

The term sputtering refers to an ejection of atoms from the a cathode (target) due to the impact of particles such as ions upon it. This phenomenon occurs in a glow discharge of ionised heavy inert gas atoms e.g. argon, due to electron impact in a vacuum across a potential applied between two electrodes. Sputtering was first discovered in 1852 by W. R. Grove who noticed metallic deposits on the glass walls of the discharge tube during studies of electrical conductivity of gases (Ref. 16). W. Crookes interpreted the heating of the cathode in the plasma during deposition of different materials was the cause of material ejection and not the ion bombardment (Ref. 17). A quantitative description of sputtering was initially begun in 1961 and the following years (Refs. 18-20).

The ions of working gas atoms are accelerated by the electric potential towards the target, bombarding it and causing ejection of neutral atoms, atoms in excited states, secondary electron emission and photons. The secondary electrons are thereafter accelerated by the same target potential ionising the gas atoms again (self-sustained discharge). In normal sputtering systems the emitted electrons have high energy and speed up towards the anode subjecting it to an enormous heat. When the ion approaching the target surface is neutralised before the impact by interaction with the lattice electrons of the surface. One lattice electron is captured by the ion as an orbital electron, thus neutralising the ion. The second electron will gain the excess energy and momentum given up by the neutralising electron and may as a result be ejected from the surface (Ref. 6). This kind of emission as mentioned before is called secondary electron emission. The latter has a great role in sustaining the discharge in conventional and enhanced sputtering systems. Solid surfaces are generally sputtered when bombarded by energetic particles, namely neutral atoms/molecules, ions, electrons or
photons (Ref. 21). The sputtering process presents several variants now known as collisional, thermal, electronic and exfolitational sputtering. In the surface of a solid two groups of changes take place because of the impact of ions, these are emission and changes in the target zone (Ref. 22). As a result of this impact photons are emitted together with the emission of atomic and molecular particles and electrons. The emitted atomic and molecular particles may be in a neutral or charged (secondary ions) states. Most of the data on ion emission from solids due to primary ion bombardment has been exploited in secondary ion mass spectroscopy (SIMS). However in a glow discharge sputtering it is unlikely that a positive ion formed at the target surface has the capability to accelerate or escape through the negative potential towards the anode. It is also highly improbable that secondary negative ions are generated during inert gas ion bombardment of pure metal surfaces (Ref. 1). Negative ions result mainly from the sputtering of compounds (Refs. 23-26) and high electron affinity components of alloys (Refs. 27,28). Negative ions, like secondary electrons are accelerated by the cathode potential away towards the anode (substrate) giving rise to substrate bombardment. These ions can be neutralised by electron stripping collisions when travelling through the glow discharge regions (Ref. 1). The emitted photons are generated in front of the surface in the surface area and in the bulk of the target (Refs. 29,30). Different processes such as de-excitation (relaxation) and neutralisation are responsible for the appearance of this emission. Ion induced photon emission carries important information concerning the emitted surface atoms e.g. the chemical composition of the surface. Ions striking the target may penetrate a certain distance into the surface if they have very high energy (few KeV) and remain trapped there. When ions have a sufficient high energy to overcome the binding energy of the target atoms to cause collisional cascade within the surface, the atoms can be sputtered due to the momentum transfer of the neighbouring atoms. If this cascade heads off into the interior of the
target the energy of the primary impact will be dissipated by the lattice vibrations i.e. heat. The energy binding the atoms in a crystal surface influences sputtering in two ways. First, it provides a barrier which must be surmounted by escaping atoms and hence plays an important part in determining the yield of the sputtered atoms. Second, its directional properties are a significant influence on the directions taken by the ejected atoms (Ref. 31). The interaction of primary ions with the surface atoms can also result in their reflection (Ref. 32). A direct energy transfer process from the incoming primary ion to a surface atom in a single collision can also result in the emission of a surface particle with relatively high energy, this ejection process is called recoil sputtering. In the collisional cascade most of the energy of the ion is dissipated through this interaction and only a fraction of this energy causes ejection of atoms. It was found that 1% of the energy incident on a target surface results in ejection of atoms whereas 75% subjects the target to damage from heat and the rest dissipates as a source of secondary electrons and other kinds of radiation (Ref. 1). Fig. 2.5 shows the effect of primary ions interaction on the surface of the target (Ref. 4).
Incident Ions & Neutrals

Reflected Ions

Secondary Electrons

Sputtered Atoms

Surface

Collision Sequence:

Bombarding Ions

May Be Implanted

Structural Changes Possible

May Terminate Within The Target

or

Result In The Ejection Of A Target Atom (Sputtering)

Fig. 2.5 Interaction of primary ions on the target surface (Ref. 4)
2.4 Sputtering Yield

An important parameter which normally appears as an indication of the sputtering rate is the sputtering yield $S$. It is defined as the number of the target atoms ejected from the target surface per incident ion. Sputtering yield is a function of many parameter such as, relative masses, energy of incident particle, structure and crystallographic orientation of the target, target material, angle of incident of bombarding particle, and sputtering pressure (Ref. 33). P. Sigmund formulated the sputtering yield in this equation: (Ref. 20),

$$S = \frac{3 \alpha M_i M_t E}{4 \pi^2 (M_i + M_t)^2 U_0}$$  \hspace{1cm} 2.30

where:

- $\alpha$ : monotonic increasing function of $M_t/M_i$
- $E$ : ion bombardment energy
- $M_i$ : ion mass
- $M_t$ : mass of target atom
- $U_0$ : surface binding energy of the target material or the sublimation energy

The sputtering yield can experimentally be measured by the weight loss of the target after bombardment (Ref. 6). This method was used for targets sputtered in triode systems. The yield is expressed by this equation:

$$S = \frac{9.64 \times 10^4 \ m \ (1 + \gamma)}{M_t}$$  \hspace{1cm} 2.31
where:

\[ m \] : weight loss
\[ M \] : atomic weight of the target material
\[ t \] : sputtering time
\[ i^- \] : electron current
\[ \gamma \] : secondary electron emission

If the above method is applicable in our unbalanced magnetron sputtering system we can make an approximation of the sputtering yield. For Ti target of atomic weight 47.90, magnetron potential of 350 V, current of 3 A and sputtering time of 43 minutes assuming secondary emission of 0.1, the sputtering yield is about 0.27 atoms/ion. For deposition of TiN by optical emission, since the sputtering rate is proportional to the emission intensity of the metal line we can assume a sputtering rate ratio of TiN/Ti at 60% of Ti line to be 0.6. Therefore for such controlled reactive deposition process the yield of the target is 0.16. It can be realised by observing the state of the target after deposition in reactive environment that a nitride or oxide layer is formed at the target surface reducing the sputtering yield of the target.

2.5 Magnetron Sputtering

The previous intensive investigations dedicated on deposition techniques led to find an effective deposition process that can offer higher deposition rate, high ionisation efficiency by the secondary electrons, and low substrate heating comparing with conventional sputtering systems. These requirements were met in magnetron sputtering sources. Magnetron sputtering source can be defined as a diode device in which magnetic fields are used in concert with the cathode surface to form electron traps.
which are so configured that $E \times B$ electron-drift current can close on themselves (Ref. 1). The trapping of the secondary electrons emitted from the cathode (now called primary) in a well designed magnetron is sufficiently effective so that these electrons are able to transfer most of their energy to the plasma causing the generation of ions before they are lost from the system (Ref. 34). Different shapes of magnetrons were designed which have the same principle of electron trapment, these are cylindrical-post, planar and gun type magnetrons. Cylindrical-post and rectangular planar magnetrons have the advantage of being scaled to long lengths to ease large deposition areas for industrial production (Ref. 35). Because of the low pressure offered by the magnetron sputtering the sputtered atoms undergo a near-collisionless line-of-sight transport to the substrate (Ref. 36). The substrates in this deposition system are generally subjected to the heat originating from condensation, sputtered atoms kinetic energy, plasma radiation, and energetic working gas atoms which are reflected at the cathode (Ref. 37). Substrates positioned in front of planar magnetron were claimed to be subjected to less bombardment by energetic reflected working gas atoms because they are reflected passing to the side and miss the substrates (Ref. 34). Substrate heating in the planar magnetron seems to take place due to the plasma radiation (Ref. 38).

The magnetron sputtering systems operate at discharge voltages between 300-800 volt with a magnetic field strength of few hundred gauss. At high magnetron currents the voltage was shown to increase slightly. This was interpreted to energy losses from the primary electrons to other charged species via collisions and plasma oscillations or to increased electron losses from the magnetic trap via cooperative effects (Ref. 34). Magnetron sputtering was shown as an attractive deposition technique for solar cell application because of its potential for providing uniform coatings over large areas (Ref. 39). Multi films can be deposited by dc multi-source magnetron sputtering sources (Ref. 40). Super hard and magnetic coatings can also be deposited by a high rate magnetron sputtering (Refs. 41,42). For insulating targets magnetron source
operated by radio frequency power can be used. Magnetron dc reactive sputtering of TiN and ITO was shown to be sensitive to the design and operating parameters of the magnetron. Plasma confinement, current density, voltage, water cooling of the target, and the ratio of argon to the reactive gas are the important operating parameters (Ref. 43). Non-uniformity of the magnetic fields in the magnetron device can lead to an escape of electrons especially at the centre of target area causing substantial heat load to the substrate. When the escaping electrons are confined again the discharge can be maintained at lower gas pressure than usual magnetron sputtering system. This requirement can be achieved by facing two targets. A planar magnetron sputtering system with facing two targets was presented to produce AlN films by K. Tominaga (Ref. 44). The ionisation of gas atoms was shown to be higher in facing two target systems than single target system. A self-sputtering mode magnetron source was presented which combined the productivity of e-gun evaporators with the larger quality of sputter magnetrons (Ref. 45). The ability to run a self-sputtering mode can be used for the production of very pure layers without incorporation of argon gas.

The planar magnetron sputtering device was combined with a hollow cathode arc electron source to form a triode magnetron (Ref. 46). The hollow cathode was chosen in place of a filament for high emission current at low energy, life time, and ease of operation in high magnetic fields and reactive gases. The hollow cathode enhanced magnetron discharges were also capable of high current operation at voltages down to 20 V, which is below the sputter threshold.
2.6 Triode Sputtering

The Triode sputtering system is a modification of conventional diode device with additional cathode normally a hot filament which serves as a support of the discharge. When the argon gas is bled into the system, the hot filament is electrically heated to emit thermionic electrons which are accelerated to the anode ionising the argon atoms and initiating a plasma discharge between the anode and the filament. The target is negatively biased so as to attract the ions to cause ejection of atoms by sputtering. Due to the high ionisation efficiency, this system can operate at low-voltage (50 V), high currents (5-20) A arc discharge between a thermionic filament and a main anode (Ref. 1). The very high ion current density obtainable in this technique allows operation at much lower pressures than a two-terminal glow discharge and allows control of the target current density independently of the target voltage. In this system the energetic neutral gas atoms which are generated at the cathode surface by neutralisation and reflection of ions can pass to the substrate with little loss of kinetic energy (Ref. 36). These reflected atoms can then be trapped in the growing film when the substrate temperature is low. It was found that the amount of trapped argon atoms in coatings deposited by the triode sputtering technique was larger than those coatings deposited by conventional diode sputtering system (Ref. 47).

A supported discharge by thermionic enhancement was designed to reduce the required power to the hot cathode of the filament. It used an auxiliary target to continually deposit a fresh low work function material such as thorium onto cathode filament (Ref. 48). Recent modification in deposition systems has combined the triode sputtering with the addition of magnetic enhancement (Ref. 49). The marriage of magnetron and triode sputtering (Tri-Mag) systems offered larger target utilisation of 70% because the magnetic flux lines are parallel to the entire surface of the target. Fig. 2.6 shows the Tri-Mag sputtering technique.
Fig. 2.6 Tri-Mag sputtering system (Ref. 46)
2.7 Reactive Sputtering

Several models were presented concerning the reaction of reactive gases with target surfaces (Refs. 50-53). The reactive deposition process involves a sputtering of target in the presence of reactive gas to form compounds of oxides, nitrides, carbides etc. The percentage in which the target coverage by the reactive gas shifts the operating optimisation causing a failure of obtaining the stoichiometry of concerned compounds at high deposition rates. The deposition of a compound with a mixture of argon and reactive gases requires a high process control of the reaction inside the deposition chamber in unstable mode called transition mode. When the reactive gas is admitted to the working chamber during sputtering the target and increased, the reactive gas pressure rises abruptly at specific flow rate characterised by target switching from metallic to reactive condition. When this happens the target sputtering rate drops sharply i.e. target poisoning. To understand this phenomena practically Figures 2.7a, 2.7b, and 2.7c show the influence of oxygen flow on: the emission intensity of Ti at 499.1 nm, chamber pressure, the profile of cathode discharge respectively in dc reactive magnetron sputtering of low pumping vacuum systems. When the oxygen flow is increased to 8 sccm the intensity of Ti is decreased to about 7% due to the reaction at the cathode. At flow of 43 sccm it can be seen a reduction of intensity of about 22%. This decrease is accompanied by an increase of target potential (Fig. 2.7c) but the emission of secondary electrons is capable of retaining the target in the metallic mode. It can be seen that a pure Ti is sputtered at the target for oxygen flow less than the peak. The latter can be also seen by the unchanged of the chamber pressure (total pressure = argon pressure). This means that the target is capable of gettering the reactive gas atoms incident on its surface. Further increase in oxygen flow at 46 sccm causes an extreme reaction of oxygen atoms on the target surface and dramatic decrease in sputtering rate takes place. This causes an abrupt reduction of intensity and a sharp increase of chamber pressure and a clear maxima of magnetron potential. This rapid
Fig. 2.7 Influence of oxygen flow rate on the emission intensity of Ti (Fig. a), chamber pressure (Fig. b), magnetron potential (Fig. c)
target switching from metallic mode to the reactive mode is called the transition mode. J. Heller presented model of reactive sputtering of metals in oxidising atmospheres (Ref. 54). He showed that the ratio of sputtering rate to the oxidation rate is decisive for the oxide growth on the target surface. He explained that the formation of oxide was due to its dependence upon the threshold of reactive gas pressure. At value prior to the threshold the sputtering rate of the metal is constant and at higher value the sputtering rate decreases with increasing reactive gas pressure.

It was shown that if the cathode is sputtered at a certain power and the oxygen flow is increased the pressure does not increase with oxygen flow until a threshold amount of oxygen is reached (Ref. 55). It was also shown as the oxygen flow is increased from zero, titanium metal is sputtered from the target and deposited on available surfaces. The oxygen reacts with the freshly deposited titanium target, but there is insufficient oxygen available to form an oxide on the target surface until the threshold value of oxygen flow is reached. At this reactive mode the target is almost completely covered by the reactive gas atoms and can not getter them leading to a significant reduction of secondary electron emission. Meanwhile any further increase in oxygen flow beyond the threshold results in the formation of more oxide on the target surface at an increasing rate until target oxidation is complete. This available surplus or excess oxygen present in the discharge chamber causes no further decrease of intensity but continuous increase of reactive gas pressure. This is correlated with a reduction of magnetron potential. S. Schiller et al observed that at a constant power, voltage increases with increasing oxygen partial pressure, reaches a maximum at a specific pressure ratio and then decreases again (Ref. 56). This is a typical of reactive d.c. magnetron sputtering in mixtures of argon-oxygen and features the sputtering conditions at the target.

When the flow is decreased by taking a backward path the magnetron potential increases again. This increase of potential at lower flow rate can be explained by longer
residence time or longer relaxation time of reactive gas atoms which is determined by the small pumping capacity and the geometry of the deposition chamber. Another probability is due to the transfer of reactive gas atom from the surplus in the discharge and the chamber wall which could compensate the oxide layer that could have been sputtered from the surface. It should be noted that the state of target potential is dependent upon the recovery time i.e. at specific sputtering time different values of potentials could be obtained at single and narrow range of time at single value of reactive gas pressure. Decreasing the oxygen flow shows oxide resistance to be sputtered to continue to a level of 20 sccm causing the appearance of another peak potential where behind it there is no sufficient oxygen to be consumed on the target surface and the target retains its metallic character again. At this stage a sharp increase of intensity and a rapid drop of system pressure take place and the target potential drops systematically. The potential exhibits a steplike decrease to its original values at time which can be called the relaxation or recovery time. As can be clearly seen the drop of reactive gas pressure reaching zero and the consequent sputtering of pure metal occur at lower flow of reactive gas, this leaves a hysteresis loop behind which represents the presence of surplus reactive gas which can not be pumped away.

T Abe and T Yamashina also presented a model giving the deposition rate of metals in atmosphere of oxygen and nitrogen in an argon plasma. They found that there was a limiting pressure at which the sputtering rate begins to decrease drastically for all the processes in Mo-O₂, Mo-N₂, Ti-O₂, and Ti-N₂ sputtering systems. In the case of Ti-N₂ system they found two limiting values of pressure which were interpreted by formation of two different chemical compounds (Ref. 57).

2.7.1 Control Techniques of Reactive Process

The problem which the reactive process generated has so far attracted many researchers to identify the cause and to find the proper method to control the pressure instability
The mismatch of flow consumption value between the admitted and the pumped flow of reactive gas plays an important role in assessing the percentage of target coverage and thereafter the pressure instability. In low pumped vacuum system target poisoning can not be prevented due to the domination of the excess gas which acts as a poisoning source covering the target surface. The high reactivity during sharp increase of reactive pressure can be overcome by suitable chamber geometry and proper method of feedback loop between the deposition chamber and the gas supply (Ref. 58).

A Spencer and R Howson designed a dynamic control for reactive magnetron sputtering system (Ref. 59). This control allowed the consumption of reactive gas by the vacuum pump to dominate the reactive gas consumption by the growing film. They showed that breaking the cycle which causes target poisoning by matching the admission and consumption rates to give zero surplus, can give a better controlled film properties and higher deposition rates. Since the sputtering rate is directly linked to the plasma emission intensity, the reactive gas partial pressure and therefore the degree of target poisoning can be suitably adjusted via the emission intensity (Refs. 63,64). The emission intensity, normalised to sputtering in pure argon is inversely proportional to the reactive gas partial pressure. The plasma emission monitor (PEM) was performed in conjunction with the getter box in low pumped vacuum system by R Howson et al (Ref. 65). Two plasma emission monitors were also used to control the reactive dc magnetron sputtering in In-Line sputtering production plant for double-side coating of glass substrates (Ref. 58). S Kadlec et al (Refs. 66,67) and A Okamoto and Serikawa (Ref. 68) presented models in which explanation of the hysteresis phenomena and solutions were detailed. The solution was using high pumping speeds with a reactive gas control. This high pumping throughput can pump the excess reactive gas and shrink the hysteresis loop providing stable operation of reactive gas pressure in the transition mode. In spite of the stability the deposition rate of TiN was less than the rate of pure metal. It was shown that the high pumping speed and throughput capability
attainable with a cryogenic vacuum pumping system provided the stable operation conditions necessary to produce quality of TiO$_x$ films in a predictable manner and with a high level of repeatability (Ref. 69). The cryogenic pump can also provide a minimal amount of water vapour in the chamber background. A. S. Penfold linked the hysteresis loop to the sizes of the substrate and the cathode (Ref. 70). He found that the effect of doubling the cathode and substrate sizes can be exactly offset by quadrupling the pump size.

S. Berg et al (Ref. 71) performed both the mass spectrometry (MS) and optical emission spectroscopy (OES) to investigate the reactive sputtering of TiN and ZrN films. The nitrogen signal was used as a process control in various R.F powers by keeping the nitrogen mass flow constant to identify the position of the sputter rate drop. They concluded that stoichiometric films can be formed at optimum processing point at nitrogen supply level where exactly all nitrogen is consumed by the sputter eroded targets. They also showed that the deposition rate is directly proportional to the nitrogen gas supply. W. Sproul used an automatic feedback control to produce TiN (Refs. 72, 73). This control provides a feedback signal which is a representative of the nitrogen peak height (partial pressure of reactive gas) from the mass spectrometer to the gas flow controller and to keep constant power on the target. The deposition rate of TiN resulted by such loop either with fast pulsing or with continuous gas flow was the same as that of pure Ti. The percentage of reaction of reactive gases on the target surfaces can also be minimised by using a baffle (Ref. 74). Utilisation of baffle can enhance the reactivity on the substrate and act as a getter surface close to the target surface and also restrict the flow of reactive gas into the target area. Consequently the target surface can be kept metallic while a significant partial pressure of reactive gas exists near the substrate.

In conclusion, several methods have been employed to control the reactive gas pressure in the transition mode suppressing the percentage of target coverage allowing the
reaction to take place a way from the target surface or maintaining a gradual control of reactive gas pressure along the concerned transition mode.

2.8 Ion Sources for Films Depositions and Modifications

There has been a revolution in investigations of ion beam processing to extend the process control of deposition to contain a wide range of control of ion energies and ion current densities. By applying a very well controlled ion beam before or during deposition the mechanical, electrical and optical properties of films can be improved remarkably.

2.8.1 Ion Plating

The deposition technique of ion plating combines both evaporation of the source material and applying a negative voltage to the substrate. The ionisation of the material takes place by plasma above the evaporation source (thermal evaporation). The ions are accelerated by the electric field of the substrate bombarding it. The ion bombardment can be done in an inert, reactive or mixed gas radio frequency discharge system where the substrate is made a discharge electrode (Ref. 75). Transparent films of indium oxide (In$_2$O$_3$) and ITO were deposited on plastics by ion plating technique (Refs. 75,76). These films had a high electrical conductivity. The metal sources were sputtered and evaporated by magnetron sputtering and induction heating. Films of ITO were also deposited on room temperature glass substrate which exhibited high conductivities comparing with those reported for films deposited at substrate temperature 450 C and higher (Ref. 77). Results of In$_2$O$_3$ films doped with fluorine deposited also on room temperature glass substrate showed relatively high conductivities (Ref. 78). Dielectric optical thin films of Y$_2$O$_3$, Ta$_2$O$_5$, ZnSe, and BaF$_2$ were also synthesised by ion plating (Ref. 79).
2.8.2 Ion Beam Sputtering  IBS

The ion beam sputtering deposition technique is a method by which a film is generally deposited with the assistance of ion beam to sputter the target or to bombard the growing film or to use both actions in the deposition chamber. The high intensity Kaufman ion source is routinely used to sputter elemental, alloy or compound targets and the sputtered material deposited as thin film. The IBS method offers advantages which can be summarised: the growing film is not exposed to large fluxes of electrons, the processing may be carried out in high vacuum conditions (typically $10^{-4} - 10^{-5}$ Torr), the ion beam can be focussed or apertured into a defined shape, and finally the depositing atoms have a mean energy of $3-10$ eV (compared to $0.1$ eV or so in thermal evaporation) and the resulting film adhesion and the structure are generally improved (Ref. 80). The ion beam can be used as a source needed for the surface modification and deposition process (Ref. 21). Ions from the material to be deposited can also be used as the main source of deposition (Ref. 81). When two ion sources are used, one to sputter the target and the other uses an inert gas ion to form a single film or reactive gas ion to form a compound film, such system is termed Dual ion beam deposition DIBD. This system was adopted by C. Weissmantel (Ref. 82). The broad beam was used as a source providing reactive nitrogen ions $N_2^+$ to form a compound and as a high energetic ions bombarding the substrate during sputtering the Al target by another ion beam (Ref. 83). By using the former beam the arrival rate of reactive gas to the target atoms can be controlled. The Kaufman source can provide up to several mA of 1 KeV gaseous ions with sputter coating material onto the substrate and when the thickness of the film reaches an optimum value the second ion source is switched on to irradiate the growing film. Any sputtering caused by the latter source can be compensated by increasing the current in the Kaufman source. This method of deposition is called Dynamic recoil mixing DRM (Refs. 84,85).
The DIBS deposition technique was also extended to include the synthesis and study of others films such as Ag (Refs. 86-88), Cu (Ref. 89), Mo (Ref. 90), Nb (Ref. 91) and dielectric compounds TiO$_2$ and SiO$_2$ (Ref. 92). Figure 2.8 shows a schematic diagram of DIMD.

2.8.3 Ionised Cluster Beam Deposition ICBD

This technique was developed by Takagi et al (Refs. 93,94). It involves evaporation of source material at high temperature. the vapour of the evaporant is ejected through a nozzle of the crucible into a high vacuum atmosphere. In this process the particles of the vapour gather into clusters by adiabatic expansion, cooling to a supersaturated state. Energetic electrons are used to positively ionise some of the clusters (500-2000 atoms) which may then be subsequently accelerated to the substrate by an applied electric field. The growing film is also bombarded with neutral clusters, atoms and ions. Ionised clusters enhance the chemical reaction and assist the nucleation for the film formation, while the kinetic energy provided by the acceleration voltage contributes to the surface cleaning in the deposition process (Ref. 95). On their arrival to the substrate the clusters are broken up into the atomic state and the incident momentum of the clusters is transformed into the surface diffusion energy of each atom. The migration effect of adatom due to this enhanced surface diffusion energy contributes to form good quality films (Ref. 96). Anti-reflection coatings of zinc sulfide ZnS on Germanium Ge for transmission windows were deposited by ICBD technique (Ref. 95).

2.8.4 Radio-Frequency Bias Sputtering RFBS

In this technique the target especially an insulator is driven by RF power to sustain a
Fig. 2.8 Dual ion beam deposition (Ref. 83)
glow discharge plasma in the working gas. Many of the effects of ion bombardment during deposition were demonstrated using radio-frequency bias sputtering RFBS and later observed in other deposition systems (Ref. 21). Ions are accelerated across the cathode dark space to sputter atoms from the target surface. At a typical pressure of 4 Pa (30 mtorr), the sputtered atoms rapidly lose their ejection energy by collisions with the background gas and diffuse to the substrate at essentially thermal energy (Ref. 97). Ion bombardment of the substrate can be provided by a bias voltage applied to the substrate (anode) which develops a negative bias relative to the glow discharge. This potential difference accelerates ions from the plasma to the substrate providing ion bombardment of the film during deposition. The growing film can also be bombarded by ions that are neutralised at the target surface and reflected as atoms and by secondary electrons accelerated from the the target across the dark space. Other sources of bombardment could happen by negative ions emitted from the target (Ref. 30) and charged exchange neutrals formed in the anode dark space (Ref. 7).

2.8.5 The Unbalanced Magnetron UM
The ion bombardment can also be achieved when a deposition source is modified resulting in substantial ion fluxes striking the substrate. This effective self-bombardment source is called the unbalanced magnetron. It is well known that the magnetic field in the balanced magnetron source follow a closed path that forms a trap to the secondary electrons emitted due to the ion bombardment of the target. When more magnetic material is added to the magnetic assembly (outer Pole) the closed path is violated and a beam of electrons (as well as ions due to an electrostatic movement) leaks towards the substrate adding activation energy to the deposited atoms and enhancing their mobilities within the surface of the film.
Electromagnetron type source was performed to alter the bias voltage for deposition of TiO$_2$ (Ref. 98). Placement of an auxiliary magnet beneath the substrate can also alter the ion bombardment of the growing film (Ref. 99). The need for high ion bombardment was investigated by B. Window and N. Savvides (Ref. 100) and N. Savvides and B. Window (Ref. 101) who designed a magnetron sputter source based on an unbalanced magnetic field (UM-gun). They found that the fluxes to probes at typical substrate distances are proportional to the discharge current, independent of pressure and independent of gas mixture (Ref. 101). The amount of ion current bombarding the growing film can be controlled by controlling the plasma beam through placing an electrode in the beam and varying the resistance of this to earth (Refs. 1,102). The ion current reaching the substrate located in a large distance from the magnetron can be increased even at higher pressure (P=5 Pa) by using the double site sustained discharge (DSSD) (Ref. 103). By performing such unbalanced magnetron (UM) in the DSSD mode higher ratio of the arrival rate of ions to the arrival rate of a metal as high as 10 can be achieved. S. Kadlec et al designed a sputtering system with a multipolar magnetic plasma confinement (Ref. 104). This magnetically enhanced ionisation for ion plating of TiN films produced higher ion current densities than the UM operated in the DSSD system.

2.8.6 Other Sources of Ion Beams
Laser beam can also be used to evaporate material creating energetic ions. Multilayer systems can be deposited without interrupting the vacuum (Ref. 105). Laser was also used to irradiate the substrate resulting in a decrease of absorption for dielectric films due to the desorption of impurities from the substrate surface during the laser
pretreatment process. It was also performed as a controlled energy to modify thin film properties. The transmission of SiO$_x$ was shown to increase when the layer was irradiated. The evaporation rate of the laser was found to be larger than that achieved by electron beam.

Recent development in ion processing based on the unbalanced magnetron mode has led to its use as source providing high ion current density. If this source is directed to another independent biased target the latter can be sputtered and consequently a film can be deposited. At bias voltage of 150 V a deposition rate of 1 nm/sec was achieved for copper (Ref. 106).

2.8.6 Effects of Ion Bombardment

It has been about two decades since ion bombardment first was used to modify the properties of deposited films (Ref. 107). The mechanism of densification by the ion assisted deposition can largely be understood in terms of ion-atom and atom-atom collisions in the growing film. An ion with an energy of about 1 KeV can penetrate the surface of a material to an average depth of a few nanometers and produces a collision cascade of knock-on atoms (Ref. 108). The displacement of target atoms results in the formation of vacancies at or close to the surface of the film and forward recoil atoms pushed into interstitial sites deeper in the material. The effect is to deplete the surface of atoms and densify the film at greater depths. The depleted area then is partially replenished by arriving atoms from the vapour stream and the process repeated.
2.8.6.1 Optical Properties

Significant improvement in the optical properties of dielectric and conducting materials was made by bombarding the growing film with low energy ions. The refractive index of ZrO₂ was increased from 1.85 to 2.15 when the ion current density was increased to 50 μA/cm² and reaching a constant value of 2.17 above 100 μA/cm² (Ref. 109). Vacuum evaporated dielectric films are characterised by a columnar film structure with below bulk density, reduced index of refraction, high porosity and relatively low stability, due to the adsorption of water vapour (Ref. 110). The voids between the columns can absorb water resulting in an effective change in the refractive index. The ion bombardment accomplished by the ion assisted deposition technique can alter the film structure as well as the stoichiometry. A variety of dielectric films were produced by this technique. The general effect is that the ion bombardment alters the columnar structure of the film, reducing the number of voids and subsequently increasing the film density (Refs. 111-115). Accordingly this reduces the absorption of water vapour into the film (Ref. 116).

Highly transparent In-10% Sn oxide films were deposited on rf biased plastic sheets using the roll to roll apparatus (Ref. 76). Plasma assisted ion plating was shown to be effective for depositing dielectric films of low optical scattering (Ref. 79).

2.8.6.2 Adhesion

Adhesion is defined by the work done to separate atoms or molecules of the interface between the film and the substrate (Ref. 117). This interface can be identified in terms of mechanical, monolayer-on-monolayer, chemical bonding, diffusion and pseudo-diffusion interface layers. Adhesion of the film to the substrate can be improved remarkably by ion bombardment. Gold films deposited on various
substrates and bombarded by 5 KeV argon ions were shown to have a very good adhesion (Ref. 118). J. Salim and F. Sequeda showed an increase of gold adhesion to silicon and glass when the substrate was irradiated with oxygen ions (Ref. 119). The failure loadings of scratch tests for gold on glass and silicon substrates was shown to rise from 2g to 2 Kg when these substrate were irradiated by oxygen ions assisted deposition (Ref. 120). Very good adhesion between the deposited metal film and the plastic substrates can also be achieved by ion plating technique (Ref. 75).

During the deposition process by triode ion plating the ionic bombardment allows the deposited atoms to migrate resulting in formation of a more homogeneous and adherent films (Ref. 121).

Low energy ion bombardment of the substrate and the growing film can lead, in addition to sputter cleaning, to a fundamental change in the nucleation kinetics. These include preferred adsorption sites, trapping or implanting of incident species in the near-surface region, the dissociation of small clusters during the early stages of growth, enhanced adatom diffusion, and local electric field effects due to charging (Ref. 122).

2.8.6.3 Structure
The energy and the current density of ions play an important role in modification of film properties. It has been mentioned in the previous section that the optical and electrical properties are strongly related to film densification as a result of ions bombarding the growing film. Thin films deposited by physical vapour deposition techniques frequently have properties dissimilar to those of bulk materials (Ref. 80).
Among such properties the most important are composition, stoichiometry, defect density and grain size. Ion bombardment during deposition often leads to film properties characteristic of depositions in the absence of ion bombardment but at significantly higher substrate temperature (Ref. 123). The microstructure of films can be explained depending on the modified structural zone presented by J. A. Thornton (Ref. 124). This model (Figure 2.9) shows the effect of gas pressure and temperature ratio of the substrate to the melting temperature \( T_s/T_m \) on the morphology of the coating material. At temperature ratio of \( T_s/T_m < 0.3 \) a porous structure consisting of tapered crystallites separated by voids is formed. At \( T_s/T_m \) between 0.3-0.5 a region of smooth topped granular structure is formed. The third zone shows a recrystallised grain structure. Between zones 1 and 2 there is a transitional region consists of densely packed fibrous grains.

D. S. Rickerby observed an increase of internal compressive stress in TiN films with increasing the bias voltage to the substrate (Ref. 125). This was explained to changes in the density of the coating. The refinement of structure of TiN during bombarding the surface by low energy ion is accompanied by removal of impurities such as oxygen because of preferential resputtering of these impurities from the growing films (Ref. 126). One of the effects of structural changes due to the ion bombardment is the improvement in the electrical resistivity. By applying a bias voltage of -100 Volt to the substrate the resistivity of TiN was shown to decrease to 0.24 \( \Omega \) \( \mu \)m (Ref. 127).

Zone 1 is a typical structure with voids located both along the column boundaries and in the interior of each column (Ref. 128). The number density of voids and pores can be decreased drastically with increasing ion energy or ion flux for insulating and conducting films (Ref. 80). The density of tantalium Ta films was shown to increase
Fig. 2.9 The dependence of morphology of films on the gas pressure and substrate temperature (Ref. 124)
linearly with increasing the substrate bias reaching 16.3 g/m/cm$^3$ at bias voltage of -500Volt (Ref. 129).

2.8.6.4 Stresses Induced Ion Bombardment

The properties of films which have so far been mentioned are so often related to stresses. Two parameters that affect or cause stresses, these are adhesion and morphology. These in turn have a pronounced effect on the mechanical, optical and electrical properties. Stresses induced by ion bombardment or bias voltage can lead to adhesion failure (film spalling). This failure is a result of internal stresses which are classified by intrinsic stresses caused by grown defects or structural mismatch between the film and the substrate, and thermal stresses caused by different expansion coefficients of the film and the substrate (Ref. 125). This imply that adhesion of the film is dependent on the material of the substrate. The general trend of stress is not dependent on deposition technique. In rf bias sputtering and evaporation a transition from tensile to compressive stresses can be observed as the bias voltage increases (Ref. 21). In magnetron sputtering the films showed the same analogue of transitional stress from tensile to compression as the gas pressure was decreased (Ref. 130). That was interpreted to an increase of the energetic bombardment of the growing film. At low argon pressures the neutralised reflected ion have a high energy and mean free path larger than the separation distance and can strike the growing film conveying a substantial thermal heat. At high argon pressure the mean free path of the energetic particles is shorter than the separation distance due to the collisions with the gas atoms and this causes them to scatter and their energy can be lost before reaching the substrate.

The unbiased coatings have a high level of adherence due to their lower stresses and
the hardness of these open voided microstructures is low but increases with bias voltage as dense intercrystalline boundaries are formed (Ref. 126). The intrinsic stress can be influenced by proper adjustment of the ratio of the impacting ions to condensing atoms. It was observed a critical ratio of I/A in which the overall stress of the system is zero. At lower and higher ratios tensile and compressive stresses were observed respectively for boron B and chromium Cr films (Ref. 131). It was also found that compressive stresses were caused by the presence of the bombarding ions Ar⁺ in the lattice of these films. Resistivity of Nb films was shown to decrease remarkably as the ion flux increases due to a transitional stress to a compression (Ref. 132). A peak of optical reflection for Cr films was seen at maximum compression stress (Ref. 133). A critical ion to atom ratio was also observed during concurrent bombardment of higher energy ions.
2.9 Optical Properties of Thin Films

2.9.1 Lorentz Model

The Lorentz model of an oscillator can be regarded as a small mass bound to a large mass by a spring. The small and large masses resemble the electrons and the nucleus of an atom respectively. The motion of an electron bound to the nucleus is then described by the following equation:

\[
\frac{d^2r}{dt^2} + m\Gamma \frac{dr}{dt} + m\omega_0^2r = -eE
\]

where \( m \) is the electronic mass and \( e \) is the magnitude of electronic charge. The field \( E \) is the macroscopic local field which is acting on the electron as a driving force. The term \( m\Gamma \frac{dr}{dt} \) represents the viscous damping and provides for an energy loss mechanism. This loss mechanism can arise from radiation damping or from various scattering mechanisms in a solid. The term \( m\omega_0^2r \) represents restoring force obeying Hooke's law.

In equation 2.32 it is assumed that the mass of the nucleus is infinite. It is also assumed that the velocity of the electrons is small in comparison with the velocity of light \( c \) in a vacuum, so that the contribution of the magnetic field \(-ev \times b/c\) is neglected in the expression for the Lorentz model. Taking \( E \) to vary with time as \( \text{EXP}(i\omega t) \), where \( \omega \) is the angular frequency of the incident field, the solution of eq. 2.32 is: (Ref. 134),

\[
r = \frac{-eE}{m(\omega_0^2 - \omega^2) - i\Gamma \omega}
\]
Each electron contributes to the polarisation a moment $P$. The displacement of a charge corresponding to an induced dipole moment is:

$$\hat{P} = -e \mathbf{r} \quad 2.34$$

Substituting eq. 2.33 in eq. 2.34 yields,

$$\bar{P} = -\frac{e^2 E}{m (\omega_0^2 - \omega^2) - i \Gamma \omega} \quad 2.35$$

There is a contribution from the nuclei, but since the nuclear masses are heavy in comparison with the masses of the electrons, their contribution can be neglected. Since the displacement $r$ is assumed to be sufficiently small that a linear relationship can exist between the electric field $E$ and the dipole moment $P$, so that:

$$P = \alpha E \quad 2.36$$

Where $\alpha$ is the frequency-dependent atomic polarizability.

From eqs. 2.35 and 2.36 the polarisation of one electron is:

$$\bar{\alpha} = \frac{e^2}{m (\omega_0^2 - \omega^2) - i \Gamma \omega} \quad 2.37$$

As can be seen $\alpha$ is complex due to the inclusion of a damping term. The total
displacement of a charge density $n$ to an induced dipole moment is:

$$P_t = \vec{P} \cdot \vec{n} = \frac{n e^2 E}{m (\omega_0^2 - \omega^2) - i \Gamma \omega} \quad 2.38$$

The complex electric displacement $D$ can be expressed as,

$$D = \varepsilon_0 \vec{\varepsilon} \cdot \vec{E} = \varepsilon_0 \vec{E} + P_t \quad 2.39$$

Where $\varepsilon$ is the complex dielectric constant and $\varepsilon_0$ is the permittivity of the free space.

Substituting $P_t$ from eq. 2.39 in eq. 2.38 gives the complex dielectric constant $\varepsilon$ as follows:

$$\varepsilon = 1 + \frac{n e^2}{\varepsilon_0 m (\omega_0^2 - \omega^2) - i \omega \Gamma} \quad 2.40$$

The real $\varepsilon_1$ and imaginary $\varepsilon_2$ parts of the complex dielectric constant $\varepsilon$ can be split giving:

$$\varepsilon_1 = 1 + \frac{n e^2 (\omega_0^2 + \omega^2)}{\varepsilon_0 m (\omega_0^2 - \omega^2)^2 + \omega^2 \Gamma^2} \quad 2.41$$

$$\varepsilon_2 = \frac{n e^2 \omega \Gamma}{\varepsilon_0 m (\omega_0^2 - \omega^2)^2 + \omega^2 \Gamma^2} \quad 2.42$$
If classical atoms with more than one electron per atom are considered, then the complex dielectric constant for electrons of density $N_j$ and bound with a resonance frequency $\omega_j$ is:

$$
\tilde{\varepsilon} = 1 + \frac{e^2}{\varepsilon_0 m} \sum_j \frac{N_j}{(\omega_j^2 + \omega^2) - i \Gamma_j \omega}
$$

It should be noted that the local field acting on the electrons which was inserted in the equation of motion is equal to the mean field $E$ within the insulator plus the field $E_2$ which is produced by the free ends of dipole chains that terminate on the wall of a fictitious sphere. This field was calculated by Lorentz using.

$$
E_2 = \frac{P}{3} \varepsilon_0
$$

### 2.9.1.1 Theory of Dispersion

From equation 2.41 and 2.42 several criteria can be extracted by consideration of the frequency dependence of $\varepsilon_1$ and $\varepsilon_2$ for a solid made of a collection of single electron classical atoms. The following criteria are seen in Figure 2.10:

1. The variation of $\varepsilon_1$ with frequency $\omega$ constitutes a phenomenon called the dispersion. It can be seen that $\varepsilon_1$ is an increasing function of the frequency, this kind of dispersion is called Normal. There is a sharp maximum of $\varepsilon_1$ at
value of $\omega$ which is lower than $\omega_0$ and sharp minimum at a value higher than $\omega_0$. Between the maximum and minimum the function $\varepsilon_1$ decreases with increasing frequency $\omega$. The latter phenomena of dispersion is called Anomalous. Therefore light of shorter wavelengths is refracted less than those of longer wavelengths.

2. The width of the anomalous dispersion can be obtained by differentiating equation 2.41 and then setting it to zero. Here the maximum and minimum of $\varepsilon_1$ can be identified by the frequency $\omega_m$ as follows:

\[ (\omega_0^2 - \omega_m^2)^2 = \omega_m^2 \Gamma^2 \tag{2.45} \]

As seen from Figure 2.10 when the effect of damping is not taken into the account, there is one singularity at the resonance frequency $\omega_0$, here:

\[ \omega_0 = \omega \text{ (maximum)} = \omega \text{ (minimum)} \]

If the damping is considered,

\[ \omega_{\text{max}} = \omega_0 - \frac{\Gamma}{2}, \quad \text{and} \quad \omega_{\text{min}} = \omega_0 + \frac{\Gamma}{2} \]

3. From equation 2.42 the maximum value of $\varepsilon_2$ can be seen at $\omega = \omega_0$, thus:

\[ \varepsilon_2 \text{ (maximum)} = \frac{n \epsilon^2}{\epsilon_0 m \Gamma \omega_0} \tag{2.46} \]
Fig. 2.10 The frequency dependence of $\varepsilon_1$ and $\varepsilon_2$ (Ref. 134)

Fig. 2.11 The dependence of electronic polarizability on frequency (Ref. 134).

(a) permanent dipoles (microwave), (b) ionic lattice vibrations (infrared), and (c) displacement of electrons (visible and ultraviolet).
The full width of $\varepsilon_2$ at half maximum is $\Gamma$.

4 The contribution of the electronic polarizability to the dielectric constant can also come from other sources as represented in Figure 2.11. There is an effect of the nuclei motion and ionic lattice vibrations which take place at very long wavelengths (short frequencies-Infrared). The electrons follow the field almost instantly up to rather high frequencies including in many cases those of the whole visible spectrum. The nuclear masses on the other hand are so heavy that they can not follow the field in the high frequency region i.e. $\varepsilon_1 = 0$ for the visible light.

2.9.1.2 Frequency Dependent Behaviour of Solids

The Lorentz oscillator can be used to analyse whether a material mainly exhibits reflecting, absorbing, or transparent behaviour. These differences can be explained by the dependence of $\varepsilon_1$ and $\varepsilon_2$ on the frequency or photon energy as shown in Figure 2.12. The conclusions which can be extracted from this Figure are:

1 At frequency $\omega << \omega_0$, the material shows insulating character where the absorption coefficient $k$ is zero. This leads to a real complex dielectric function $\varepsilon$ where $\varepsilon_2$ can be omitted in equation 2.43 and $\varepsilon_1$ equal to $n^2$. Expressions relating refractive index $n$ to the absorption coefficient $k$ are given in the next section, which deals with $k$. Region 1 as shown in Figure 2.12 is characterised by high transmission, no absorption, and a small reflectivity as expected for insulator.
Fig. 2.12 The frequency dependence of the optical behaviour of a dielectric material (Ref. 134)
Region 2 can be identified by strong absorption. Although the values of n and k may be high, leading to appreciable reflection, the light that is not reflected is strongly absorbed in the material.

In region 3 where $\omega \gg \omega_0$ the electrons of the insulator respond as if they were free electrons. This is due to the photon energy which is much greater than the binding energy of the electrons. Consequently a metallic behaviour is shown in this region. For good insulator this region lies well into the ultraviolet region.

The onset of region 4 is defined by $\varepsilon_1 = 0$. This happens at a frequency called the plasma frequency $\omega_p$. Substituting $\varepsilon_1 = 0$ in equation 2.41 and assuming $\omega >> \omega_0 >> \Gamma \omega_p$ can be written as:

$$\omega_p^2 = \frac{N e^2}{\varepsilon_0 m}$$  \hspace{1cm} 2.47

2.9.2 Absorption Coefficient

The relationship of the microscopic properties of matter to the macroscopic optical properties can be explained by understanding the microscopic form of Maxwell's equations. In the absence of an external source or a net charge density the external current density and the charge density can be set to zero in the first and fourth Maxwell's equations. The new form of Maxwell's equations after setting $\mu$ to 1 for non-magnetic materials are:
\text{div} \ E = 0 \hfill 2.48

\text{Curl} \ E = - \left( \frac{1}{c} \right) \frac{\text{d}H}{\text{d}t} \hfill 2.49

\text{div} \ H = 0 \hfill 2.50

\nabla \times H = \left( \frac{\varepsilon}{c} \right) \frac{\partial E}{\partial t} + \left( \frac{\sigma}{\varepsilon_0 c} \right) E \hfill 2.51

Taking the curl of equation 2.49 yields:

\nabla \times \nabla \times E = - \left( \frac{1}{c} \right) \frac{\partial}{\partial t} (\nabla \times H) \hfill 2.52

Substituting eq. 2.51 into eq. 2.52 results in,

\nabla \times \nabla \times E = - \left( \frac{\varepsilon}{c^2} \right) \left( \frac{\partial^2 E}{\partial t^2} \right) - \left( \frac{\sigma}{\varepsilon_0 c^2} \right) \frac{\partial E}{\partial t} \hfill 2.53

The left hand side of eq. 2.53 can be transformed using the vector identity as follows:

\nabla \times (\nabla \times E) = \nabla (\nabla \cdot E) - \nabla \cdot (\nabla E) \hfill 2.54

By setting \text{div} \ E equal to zero as stated in eq. 2.48 (in the absence of a net charge density) and equating eqs. 2.53 and 2.54 yields:
\[ \nabla^2 E = \left( \frac{\varepsilon}{c^2} \right) \frac{\partial^2 E}{\partial t^2} + \left( \frac{\sigma}{\varepsilon_0 c^2} \right) \frac{\partial E}{\partial t} \]  

2.55

The plane complex wave describing the energy dissipation of the wave can be expressed as:

\[ E = E_0 \exp\left( i (q r - \omega t) \right) \]  

2.56

Where, \( E_0 \) is perpendicular to the complex wave vector \( q \) and \( \omega \) is the frequency.

From substitution of eq. 2.56 into 2.55 a relationship between the complex wave vector and frequency in the medium can be found as follows:

\[ q^2 = \left( \frac{\omega^2}{c^2} \right) \left[ \left( \varepsilon + i \frac{\sigma}{\varepsilon_0 \omega} \right) \right] \]  

2.57

The complex refractive index \( n \) is related to the complex dielectric constant by this equation: (Ref. 135),

\[ \bar{n} = \sqrt{\varepsilon} = \sqrt{\varepsilon_1 + i \varepsilon_2} \]  

2.58

Where \( \varepsilon_1 \) and \( \varepsilon_2 \) are seen in eq. 2.43

For absorbing material \( n \) consists of two parts, a real part and an imaginary part i.e \( \bar{n} = n + i k \) where \( k \) is the extinction coefficient.

The complex refractive index \( \bar{n} \) can be defined as follows:
From eqs. 2.57 and 2.59 expressions for $\varepsilon_1$ and the optical conductivity $\sigma$ in terms of $n$ and $k$ can be obtained, thus:

\[
\varepsilon_1 = n^2 - k^2 \quad 2.60
\]

\[
\varepsilon_2 = 2nk = \frac{\sigma}{\varepsilon_0 \omega} \quad 2.61
\]

The absolute value of $\varepsilon$ is given by this relation

\[
|\varepsilon| = (\varepsilon_1^2 + \varepsilon_2^2)^{1/2} \quad 2.62
\]

When a highly transparent material or dielectric is considered, $k$ can be set to zero. This forms eqs. 2.58, 2.59 and 2.60 as $n = \sqrt{\varepsilon_1}$, $q = \omega n/c$ and $\varepsilon_2 = 0$.

Equation 2.56 can now be rewritten to include the complex wave vector $\bar{q}$ in its new form as:

\[
E = E_0 \exp \left( i \frac{\bar{\omega}}{c} r \right) \exp i \left[ \frac{\bar{\omega}}{c} \left( r - \omega t \right) \right] \quad 2.63
\]

The first exponential factor in the eq. 2.63 describes the amplitude attenuation of the wave with distance. The absorption coefficient $\alpha$ explains the fractional decrease in intensity $I$ with distance and can be expressed as:
Integrating eq. 2.64 yields:

\[ \alpha = - \left( \frac{1}{I_0} \right) \frac{dI}{dr} \]

From eqs. 2.64 and 2.66 it can be found,

\[ \alpha = \frac{2 \omega k}{c} = \frac{4\pi k}{\lambda_0} \]

where \( \omega = 2 \pi f = 2 \pi c/\lambda_0 \)

\[ \exp - \alpha r = \frac{1}{I_0} \]

The intensity \( I \) is proportional to the square of the wave amplitude or to the square of the electric field, i.e

\[ I \alpha E^2 \]

\[ I = E_0 \exp - \left( \frac{2\omega}{c} \right) k r \]

2.9.3 Drude Model for Metals

Since the conduction electrons of the metal are not subjected to any force, the Drude model for metals can be obtained by omitting the expression of the restoring force m
\( \omega_0^2 \Gamma \) from the Lorentz oscillator model in equation 2.32. Therefore from eqs. 2.41 and 2.42 by setting \( \omega_0 \) to 0 we can obtain:

\[
\varepsilon_1 = 1 - \frac{N e^2}{m \varepsilon_0 (\omega^2 + \Gamma^2)} \tag{2.68}
\]

\[
\varepsilon_2 = \frac{N e^2 \Gamma}{M \varepsilon_0 (\omega^2 + \Gamma^2)} \tag{2.69}
\]

The appearance of the damping term \( \Gamma \) for a free electron metal is an indication of the ordinary scattering of electrons. The mean free time of scattering between collisions of the conduction electrons is the inverse of \( \Gamma \) i.e. \( \Gamma = r^{-1} \), where \( r \) is the mean free or the relaxation time. After substituting of equation 2.47, the above equations become:

\[
\varepsilon_1 = 1 - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2} \tag{2.70}
\]

\[
\varepsilon_2 = \frac{\omega_p^2 \tau^2}{\omega (1 + \omega^2 \tau^2)} \tag{2.71}
\]

In real Drude metal the metal exhibits reflection of 100% at frequency below the plasma frequency \( \omega_p \). At \( \omega_p \) a sharp reduction of reflection occurs and the metal becomes transparent at higher frequencies. Figure 2.13 shows the reflection spectra of a real Drude metal. The Drude model which underlines the free electron like can
Fig. 2.13 Reflection spectra for a real Drude metal (Ref. 134)
describe the optical behaviour of Ag and TiN (Refs. 87, 137). To obtain the Drude parameters equations 2.70 and 2.71 can now be rewritten as:

\[
\varepsilon_1(\omega) = \varepsilon_\infty - \frac{\omega_p^2 \tau^2}{1 + \omega^2 \tau^2}
\]

2.72

\[
\varepsilon_2(\omega) = \frac{\omega_p^2 \tau}{\omega (1 + \omega^2 \tau^2)}
\]

2.73

where \(\varepsilon_\infty\) is the polarizability resulted from electronic excitation.

Substituting equation 2.73 into 2.72 yields after re-arrangement:

\[
\varepsilon_1 = \varepsilon_\infty - \frac{\tau}{\hbar} \varepsilon_2 \hbar \omega
\]

2.74

From the linear dependence of \(\varepsilon_2 \hbar \omega\) on \(-\varepsilon_1\) an important parameter can be obtained from the slope which characterises the conductivity and reflection of TiN, this parameter as mentioned above called the relaxation time \(\tau\). Another related important entity of conductive material can also be derived from the relaxation time, this is called the plasma energy \(\hbar \omega_p^2\). This can be obtained from the substitution of \(\tau\) into equation 2.72 and after re-arrangement:

\[
\varepsilon_1 = \varepsilon_\infty - \frac{(\hbar \omega_p)^2}{E^2 / \tau + E^2}
\]

2.75

where:
\( E_\tau : \) is the relaxation Energy = \( h / \tau \)
\( E : \) is the photon energy

From the above expressions it can be concluded that obtaining longer relaxation time means a reduction in the number of scattering of conduction electrons (reduction in \( \Gamma \)). This implies a better optical and electrical quality of TiN film characterised by higher conductivity and higher plasma reflection edge or higher infrared reflection and consequently lower reflection minima in the middle of the visible part of the spectrum.
2.10 References

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CHAPTER THREE
EXPERIMENTAL TECHNIQUES

3.1 Vacuum System

A simple vacuum pumping system has been used throughout all the experiments consisting of a two stage rotary pump, a mechanical booster pump and a polycold Meissner trap to remove the water vapour from the chamber. Fig. 3.1 shows the vacuum chamber. The 0.2 m³ chamber can be evacuated giving a pressure of $4 \times 10^{-5}$ mbar in 10 minutes. The superpump system used incorporates an external oil filtration unit and an outlet mist filter, and so permits reliable pumping of corrosive gases. The external oil filter delivers the supply of clean decontaminated oil directly to the vacuum pump oil circuit. Any excess oil backflushes the internal filter keeping it clear of particulates. An easy release and self-seal mechanism allows the filter container to be taken to a safe area for elemental cleaning. Regular Superpump systems feature sealing and lubrication with perfluoropolyether (PFPE) fluids and are also supplied with a complete control system. The electrical control box houses the main isolator, pump motor stators, the external oil filter switch, the gas ballast solenoid switch and the mist filter and drain control (Ref. 1).

Condensation of contaminating vapours in the pump can be prevented by use of a dry nitrogen gas ballast facility incorporated in the Superpump. Gas ballast involves injecting dry nitrogen into the stator during compression of the second stage of the rotary pump (high pressure) in order to reduce the partial pressure of the pumped vapour below its saturated vapour pressure preventing the condensation. This can be achieved by adjusting the ratio between the volumetric rate of the gas allowed by the
gas ballast device and the pumping speed of the pump, this ratio on a two stage rotary pump is $0.1 < B/s < 0.2$ (Ref. 2)

The roots pump is a mechanical gas transfer pump that uses positive displacement as the pumping method. It has a very high volumetric capacity because of its physical size. Gases entering the pump inlet are swept to the discharge side by a pair of lobed rotors that have no sealing or rubbing contact with the stator wall and can thus rotate at high speed (1500 to 3600 rpm). The internal clearances between the lobed rotors are between (0.1-0.3) mm. The hydrokinetic fluid coupling, which is built integral with the booster permits the simultaneous starting of the booster with the backing pump from atmospheric pressure, prevents motor overload and helps to accelerate pumpdown time. Another alternative which also permits starting the booster from atmospheric pressure is to fit a bypass line which a part of the gas can recirculate when the gas load is high (Ref. 3).

The gauges used to read the vacuum pressure are: a head gauge which reads the pressure from below the atmosphere up to $10^{-3}$ mbar and an ionisation gauge which reads the vacuum pressure up to $10^{-6}$ mbar.

### 3.2 The Getter Box

A closed deposition chamber was designed to meet the requirement of purification to minimise the contaminations of active residual gases present in the system. The getter box provides a sacrificial surfaces in which contaminations are embedded during sputtering-cleaning process of the deposited material. The requirement of a self-gettering system are fulfilled by creating a low conductance for the sputtering gas with the self-gettering pumping speed for active contaminants by the deposited material. The substrate is carried by a sliding lid which can allow the initial sputtering-cleaning
process from the planar magnetron to take place without exposing the sample to the discharge. The inner volume of the box was of sheet aluminium with overlapping joints designed to limit the conductances. A discharge can also be initiated outside the volume using air or argon at pressure of 80 mtorr to bombard and clean the glass substrate before deposition. Rectangular and circular getter boxes were designed, one to accommodate the balanced magnetron and the other to accommodate the unbalanced magnetron. The separation distance between the target and the substrate was 6 cm. The argon gas is bled into the main vacuum chamber through a manifold while the reactive gas is flown directly inside the getter box through two manifolds. Fig. 3.2a shows a photograph of the rectangular getter box. A diagram of the vacuum chamber including the getter box and plasma pick up positions is shown in Fig. 3.2b.

3.3 Mass Flow Controller Units
The sputtering gas of purity as high as 99.999% is controlled by a mass flow sensor. This is connected to a display unit type (80-55) to display the desired value of the mass flow on a panel. The front panel is also used to adjust the calibration factor (for argon this is 1.45). This unit is provided with a set point to show the gas which was fixed at first value before terminating the flow and also to change the gas flow. Zero function is also available to terminate the flow.

With respect to the reactive gas few units of flow control are set up, these are:

1. Display unit type (80-5) shows the flow rate which has been controlled, this has a zero function.
2. Pressure controller type (80-1) which possesses manual and automatic control of
Fig. 3.1  The vacuum chamber

Fig. 3.2a  The getter box
Fig. 3.2b The deposition chamber
the reactive gas.

3. Mass flow sensor connected to the display unit.

4. Piezoelectric valve of fast response time to control the reactive gas admission when the pressure controller is set to an auto-mode.

5. Photomultiplier serves as detector for the metal line from the plasma.

When a 80-1 automatic pressure controller is incorporated with a 80-5 flow display, the 80-1 controls the main gas flow and the 80-5 displays the main gas flow. The signal or emission intensity of the metal line is passed from the getter box via an optical fibre to the optical filter which provides stable filtration of the transmitted light of the metal line concerned. This signal is transferred to the photomultiplier that is connected to the pressure controller unit (80-1). By adjusting the percentage of the metal line set point from 80-1, the piezoelectric valve will control the reactive gas consumption which will be displayed on 80-5 display unit and that percentage will be displayed as an output signal from the photomultiplier in terms of mvolt. This signal can also be transformed to a percentage of the Ti line set point. Figure 3.3 illustrates a diagram of the closed loop of a reactive process control performed by the plasma monitor.

3.4 Film Analysis and Measurements

In order to evaluate the quality of deposited films several techniques were employed to identify their optical and electrical properties as well as their structures, these are:

3.4.1 The Thickness Measurement by Stylus Technique

The thickness of the film is one of the most important parameter which determine the properties of the films. This can be measured by a talystep. This device consists of a
Fig. 3.3 PEM
fine diamond tip with radius of about 50 μm which is moved over the surface. The vertical motion of the tip caused by irregularities of the surface is converted to an electrical signal which is then amplified and recorded on the paper according to the profile of metal strips on the substrate. The film is simply scratched and the profile obtained is an indication to the depth or thickness of the film. The Talystep is also provided with divisions of magnification to meet the change of film thicknesses. Each division recorded on the paper multiplied by the desired magnification gives the film thickness. The sensitivity of the talystep has important role in having accurate profile of the scratched film. A problem arose due the fragmentations of the edges of the scratched TiN film which caused strong irregularities or profiles when the tip moved over the surface even after cleaning and removing these fragments we have still obtained misleading thickness values.

3.4.2 Determination of Densities by Microbalance

A sensitive balance was used to weigh the sample before and after deposition. This method was also used to determine the film thickness which depends on the density as an important parameter. To determine the film thickness there must exist data which can provide values of the density at different compositions of nitrogen along Ti line set point. It must however be born in mind that the bulk density of TiN can not be taken as a standard value for our TiN films because simply they have lower densities. But we can use the linear dependence of the sputtering rate or thickness on Ti line set point to estimate the film thickness and the corresponding densities. This can be done as follows:

1. Films of TiN were made at different composition (N/T > 1 - N/T = 0). In order to
plot a straight line another point is needed besides the origin point. Here we have two options to find this point. One is to determine the thickness of one of the films by another method such as (talystep or SEM), and when doing so we can extrapolate the straight line to find the thickness of other points. From those points we can determine the film densities as well since their collected masses are available. Secondly we can assume a density of pure titanium film since the error should be smaller than that when TiN is assumed. From that and by using the collected mass of pure Ti film, its thickness can be estimated and this in turn leads us to find the thicknesses and corresponding densities of other films at other compositions. The second option gave rise to big error because the thicknesses determined were less and this produced high densities of films which were not consistent with the structure of these films. To reduce the error all films were fractured and their thicknesses were determined by SEM.

3.4.3 Ellipsometry

It was established that thin films can be detected on surfaces by the change in elliptically of a beam of light following its reflection from the surface (Refs. 4-7). Figure 3.4 shows a schematic diagram of the ellipsometer. Today however, ellipsometry is the common optical technique for the determination of the thickness and refractive index of thin homogeneous films. When a plane polarised light interacts with a surface at some angle, it is resolved into its parallel and perpendicular components (s- and p-polarised, respectively). These components are reflected from the surface producing a change in their amplitude and phase. When the s- and p-polarised reflected light are combined, the result is elliptically polarised light. Ellipsometry uses this phenomenon to estimate the thickness and the refractive index of a transition region between the surface and air by
Fig. 3.4 A schematic diagram of the ellipsometer
measuring the ratio \( r \) between \( r_p \) and \( r_s \), the reflection coefficient of the p- and s-polarised light, respectively. In a typical ellipsometer a light source of helium:neon laser is plane polarised (\( P = \) angle of polarisation) and impinges on the surface. A compensator changes the reflected beam that is elliptically polarised to plane-polarised (\( A = \) angle of polarisation). The analyser then determines the angle \( A \), by which the compensator polarised the beam. These two angles \( P \) and \( A \) give the phase shift between the parallel and perpendicular components \( \Delta \), and the change in the ratio of the amplitudes of the two components \((\tan \psi)\). \( \Delta \) and \( \psi \) are related to known values such as the angle of incidence in the ambient medium, the wavelength of the light, the refractive index of the substrate and unknown values to be determined which are the thickness and the refractive index of the film.

3.4.4 Sheet Resistance

The sheet resistance of a conducting film deposited on an insulating substrate can be measured by a four point probe method (Ref. 8,9). These four probes are connected by a spring which allows them to press against the film. The potential difference \( V \) is read between the inner probes while a known current \( I \) flows between the outer pair of probes and this allows the calculation of the surface resistance and therefore the film resistivity. Fig.3.5 shows a schematic diagram for the four probe. If distances between the probes are equal i.e \( S_1=S_2=S_3=S_4 \) and \( S >> \) film thickness \( d \), the sheet resistance can be obtained by the following equation: (Ref. 8),

\[
R_s = \frac{V\pi}{I\ln 2}
\] 

3.1
Fig. 3.5 Measurement of sheet resistance by a four probe method
3.4.5 X-Ray Diffraction XRD

This technique was used to obtain orientation, lattice parameter and the average crystal size for TiN films. A schematic diagram of the diffraction of X-ray by a crystal is shown in Figure 3.6. When X-ray of a wavelength $\lambda$ is directed to a crystal at an angle $\theta$, it will be diffracted by parallel atomic planes of separation $d$. The amplitude then of the diffracted ray will be a maximum when the path difference between rays reflected from successive planes is equal to a whole number of wavelengths ($n\lambda$). The relation which applies to this condition is called the Bragg law Which is: (Ref. 10),

$$n \lambda = 2d \sin \theta$$

The particle size can be calculated using Scherrer formula from the full width at half the maximum intensity $B$ of a Bragg peak at the orientation concerned, this is given by:

$$t = \frac{0.9 \lambda}{B \cos \theta}$$

The X-ray diffractometer used for the investigation was (RIGAKU DENKI K.K.,) and the radiation source was CuK$\alpha$. The current applied was 30 mA and the acceleration voltage was 40 KV.

3.4.6 Scanning and Transmission Electron Microscopy SEM and TEM

The scanning microscope was originally designed for the visual examination of specimens, using secondary or back-scattered electrons leaving the surface on which
Fig. 3.6 Diffraction of X-rays by a crystal
the incident electron probe impinged (Ref. 11). The machine used to scan the TiN samples was (JEOL-JEM100CX). This machine is equipped with scanning unit in order to generate a surface image by secondary electrons. This machine also combines both techniques SEM and TEM because it offers a better resolution than normal scanning methods.

Diffraction patterns of TiN on glass were not possible because the electron beam cannot transmit through the glass and therefore thin films of TiN were deposited on Potassium Bromide (KBr) substrates because they can be easily removed when dissolved in water. These films were then placed on a specimen support grid of copper. The camera distance $L_0$ was calibrated using an evaporated Al film because it has a very fine crystal size and accordingly $L_0$ was measured and taken as a standard camera length for our measurements. The plane spacing $d$ was calculated using the following equation: (Ref. 12),

$$d = \frac{\lambda L_0}{r_0}$$  

Where:

- $\lambda$ : is the wavelength of electron at accelerating voltage of 100 KV = 0.037 A$\text{o}$
- $L_0$ : is the camera distance = 72.31 cm
- $r_0$ : is the radius of diffraction ring in cm

When the plane spacings $d$ were found, they were compared with standard tables (Ref. 13) and their Miller indices hkl were also obtained. The images were generated by bright field using a normal imaging mode in TEM by using an objective aperture in the
plane of the diffraction patterns (aperture around the transmitted beam spot). The planes which diffract the beam strongly were shown to produce black spotted grains while those which diffract weakly showed areas of white grains.

TiN films deposited on glass were scanned to obtain their structures as well as their thicknesses. These films were broken and selected area of 1 mm in height was gold coated thickness (5-10 nm) by dc sputtering technique. The deposition was necessary because the glass due to its insulating nature charges up when subjected to an electron beam, therefore to prevent such problem the substrate supporting the film had to be conducting.

3.4.7 Auger Electron Spectroscopy AES
Two complementary techniques still dominate surface analysis, these are Auger electron spectroscopy (AES) and X-ray photo-electron spectroscopy (XPS or ESCA) (Ref. 14). Since the heart of either technique is an electron energy analyser, AES and XPS are frequently found in combination. AES in the form of high resolution scanning Auger microscopy adds the surface compositional dimension to scanning electron microscopy. The addition of an ion source for sputter removal of surface layers allows either XPS or AES to perform composition depth profiling.

The Auger process involves an ejection of electron from K level by an incident electron whose energy E must be greater than the binding energy $E_k$ of an electron in K. This could follow a creation of a hole in the level K, the atom relaxes by filling the hole via a transition from an outer level L2. As a result of that transition the energy difference $(E_k-E_{L2})$ becomes available as excess kinetic energy, and this excess can be given to
another electron from level L₃, whereupon the second electron is ejected. The energy of the ejected Auger electron is therefore:

\[ E = E_k - E_{L2} - E_{L3} \]

This Auger energy expressed by the above equation is a function only of atomic energy levels, so that for each element in the periodic table there is an unique set of Auger energies, there being no two elements with the same set of atomic binding energies. This analysis of Auger energies directly leads to elemental identification.

3.4.8 Spectrophotometry

The transmission and reflection spectra and the corresponding absorption of the films were obtained using the scanning spectrophotometer model (323 UV-VIS-NIR) recording spectrophotometer. This spectrophotometer covers the wavelength of light in the regions of: Far UV (170-210 nm), UV (210-340 nm), Visible (340-700 nm), and Near infrared NR (600-2600 nm). The wavelengths of interest were mainly in the visible and near infrared where the light source used was a tungsten lamp and the detectors used were a photomultiplier tube for the visible and lead sulphide PbS cell for the near infrared. Figure 3.7 shows a schematic diagram of the scanning spectrophotometer (Ref. 15) together with an attachment (broken lines) to obtain the reflection spectra. This attachment reflects the beam up to a reference mirror and the sample and then redirects the beam back to the original optical path. The reference sample was a deposited aluminium mirror. Corrections had to be performed when obtaining the reflection spectra because the reflection was too high, this was due to the
Fig. 3.7 Optical layout of the scanning spectrophotometer
Al reference mirror which gave less reflection than it should i.e about 92%. The correction involved comparing the reflection from an uncoated glass substrate and set it to give 8% (ambient-glass and glass-ambient). This correcting ratio was then used to get accurate reflection spectra for the films.

3.5 Samples Preparation and Deposition Procedure

Glass of size $25 \times 75 \times 1 \text{ mm}^3$ was used as substrates throughout the whole investigations but exceptionally for the investigations by TEM, those TiN films were deposited on KBr substrates. All samples were cleaned by ethanol and many of them were ultrasonically cleaned using a detergent solution. Two sources of magnetron were used: one was a planar rectangular source with target dimensions $250 \times 100 \times 3 \text{ mm}^3$ and the other was an unbalanced source with effective diameter of target of 78 mm. Each sample was inserted and fixed on the slot of the sliding lid and the vacuum system was pumped to pressure better than $5 \times 10^{-5} \text{ mbar}$. The deposition procedure is simply as follows:

1. The argon pressure was adjusted as desired by adjusting the argon gas flow which is controlled by a means of a mass flow controller.

2. The target was then sputtered-cleaned for about 10-15 minutes to remove the contaminating layer to give a constant voltage which is an indication of the removal of such layer. Sometimes arcing took place and this was overcome by reducing the power for some time and then increasing it gradually.
3. When the optical emission unit was set up, the intensity of the sputtered target (Ti or Zr) at percentage of 100 (pure metal) was allowed to stabilise by observing the output signal in mvolt, and then the pressure controller model 80-1 was used to fix the metal line at the required percentage.

4. When the flow rate of reactive gas was under control, the deposition process was left to stabilise again by monitoring the magnetron potential, output signal and system pressure. Once that settled the lid of the getter box was let down completely to expose the sample to the incoming flux. Extreme care was needed when doing the latter stage because fluctuations could cause changes in output signal and nitrogen consumption. This happened because a freshly coated area of the lid is exposed to the plasma, changing the pumping rate.

5. Repeating steps 1,2,3,4 with new substrates at increased Ti line set point up to 100%.

6. Many samples were made using the repeated steps at different magnetron currents and argon pressures and different thicknesses.
CHAPTER 4 RESULTS AND DISCUSSIONS

4.1 The Balanced Magnetron

A rectangular planar magnetron with commercial titanium target of dimensions $250 \times 100 \times 3$ mm$^3$ was used as a sputtering source. Figure 4.1a shows a schematic diagram of cross section of the planar magnetron. The target is cooled by direct contact of cooling water through channel paths between the poles and the centre magnet. The contact between the housing body of the magnet assembly and the target is sealed by O-ring. The target utilisation is about 35% of the total area due to the high magnetic concentration at narrow areas between the centre magnet and the pole piece. This leads to high concentration of ion bombardment which is responsible for producing a V-shape race track. Figure 4.1b shows the motion of electron in a crossed electric and magnetic fields.

4.1.1 Characterisation of TiN

Films of TiN were optimised by using different settings of Ti line as described in section 3.5. Figs. 4.2a and 4.2b shows the relationships between nitrogen consumption and Ti line set point for films deposited at magnetron currents 1, 2 and 3, 4 Amperes respectively. When Ti line increases the nitrogen consumption increases and the corresponding film possesses high nitrogen concentration $N/T > 1$ (high nitrogen partial pressure). As Ti line further increases the flow rises up to a maximum revealing a formation of well specified golden colour of TiN as shall be seen later on. Further increase of the metal line causes a reduction of nitrogen flow which implies a high incorporation of titanium in the film reaching 1 at Ti line of 100% and flow rate of 0. From these curves it can be clearly seen that a higher nitrogen consumptions are
Fig. 4.1a A cross section of the planar magnetron (balanced)

Fig. 4.1b Motion of electrons in crossed electric and magnetic fields
Fig. 4.2a Characterisation of TiN films for magnetron currents of 1A and 2A and an argon pressure of 3 mtorr

Fig. 4.2b Characterisation of TiN films for magnetron currents of 3A and 4A and an argon pressure of 5 mtorr
needed with higher currents due to the higher sputtering rate or Ti emission which require a higher flow of reactive gas to form a compound. Fig. 4.2c shows a plot of thickness versus Ti line set point for films prepared at currents 3,4 A as an example to the linear dependence of the sputtering rate or the thickness of the film on the emission intensity of the metal line. This figure demonstrates that the arrival rate of titanium to the substrate plays a decisive role in forming TiN when the emission of the metal line is chosen. The specification of colours along Ti line set points at magnetron current 4A can be seen in Fig. 4.2d where a golden appearance of TiN film lies between flow rates of 4.2 and 4.4 corresponding to percentages of 60% and 70% for the Ti line.

4.1.1.1- Electrical and Optical Properties
The influence of the Ti line set points and nitrogen consumption on resistivity at these points is shown in Figs. 4.2e and 4.2f for films prepared at currents of 3A and 4A. As the Ti line increases the resistivity decreases due to the increase in sputtering rate, change in film composition and structure (Fig. 4.2e). The resistivity reaches a minima at a Ti line of 70% (Fig. 4.2f) and for maximum consumption of nitrogen 3.1 sccm and 4.4 sccm for currents 3A and 4A respectively. The resistivity shows generally a slight increase up to a Ti line of 90% and then decreases reaching a lower value than for the optimum film at a full percentage of the Ti line and zero nitrogen consumption. This decrease can be expected since the density of optimum TiN is low and this can be verified when discussing the morphology and density. To compare the resistivity values of these room temperature deposited films it can be seen from Tables 1 and 2 that the resistivity ratios of the best TiN (electrically) to metal titanium is about 1.2 (Table 1) and 1.5 (Table 2). The corresponding condensation ratio is about 0.5 (Table 1) and 0.7 (Table 2). S. Schiller et al (Refs. 16,17) reported a ratio of condensation of
Fig. 4.2c The dependence of thickness on the Ti line set point for TiN films deposited at currents of 3A and 4A.

Fig. 4.2d Colour specification of TiN films with the Ti line set point for a magnetron current of 4A.
Fig. 4.2e The dependence of resistivity of TiN films on the Ti line set point for currents of 3A and 4A

Fig. 4.2f The dependence of resistivity of TiN films on the nitrogen consumption at the set point of Ti line
<table>
<thead>
<tr>
<th>Sample</th>
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<th>Current A</th>
<th>N2 Flow sccm</th>
<th>Thickness nm</th>
<th>Resistivity</th>
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<table>
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<td>6</td>
<td>1.81</td>
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</table>

Table 1 Preparation parameters and electrical and optical data for selected TiN films deposited at magnetron currents of 1A and 2A

<table>
<thead>
<tr>
<th>Sample</th>
<th>Current A</th>
<th>Ti Line %</th>
<th>N2 Flow sccm</th>
<th>Thickness nm</th>
<th>Resistivity</th>
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<th>Argon Pressure mtorr</th>
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</tr>
<tr>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 2 Preparation parameters and electrical and optical data for selected TiN films deposited at magnetron currents of 3A and 4A
C. Ribbing and E. Valkonen (Ref. 18) found that the resistivity of crystalline TiN prepared with a heated substrate was about half that of pure titanium. Heating the substrate during deposition can improve the density, adhesion and the related optical and electrical properties TiN. S. Schiller et al also found this ratio to be 0.4 (Ref. 16).

TiN is a sensitive compound which is aggressively influenced by any contamination present in the deposition chamber (getter box) or even during sample preparation. The dominant contaminations include nonmetal impurities such as oxygen and carbon. These impurities can not be avoided due to their enormous affinity with TiN (Ref. 19). The effect of changes in the background elemental composition on the colour of TiN prepared by reactive magnetron sputtering was investigated by A. Mumtaz and W. Class (Ref. 20). They specified colour by Auger analysis and found that the brighter the film the lower the oxygen content. The incorporation of oxygen causes deviation from stoichiometry due to the electron scattering in the highly contaminated films. Such electrons which are responsible for the conductivity of TiN can not be excited to energy states where they can emit the yellow light which is responsible for the golden appearance of TiN.

The appearance and the optical properties can also determine the quality of the TiN films. Figs. 4.2g and 4.2h show plots of reflection spectra for selected TiN films prepared at different TiN line set points at magnetron currents of 1,2 Amperes and 3,4 Amperes respectively. From these two figures it can be concluded that films prepared at a current 2A and a Ti line of 40% and at a current of 4A and a Ti line of 60% are the best films (optically). A clear reflection minima of about 17% at 430 nm and sharp plasma reflection edge at the end of the visible region increasing the reflection in the near infrared is exhibited by the former film. The latter thicker film shows a
Fig. 4.2g Reflection spectra in the visible region for selective TiN films prepared at different settings of the Ti line and for currents of 1A and 2A.

Fig. 4.2h Reflection spectra in the visible region for selective TiN films prepared at different settings of the Ti line and for currents of 3A and 4A.
pronounced reflection minima of about 18% at 440 nm and a very pronounced plasma reflection edge giving a reflection value of about 76% at 700 nm. The optical data for this investigation is also included in Table 1 and Table 2.

4.1.1.2 Effect of Magnetron Current on Films Properties

TiN films were deposited at different magnetron currents and thicknesses and their impurities, electrical and optical properties were obtained. The impurities were determined by Auger electron spectroscopy. Fig. 4.3a shows the relationship between the resistivity and oxygen content versus magnetron current. As shown there is a clear drop in resistivity up to magnetron current of 5A, whereas the oxygen content decreases slightly at lower currents and then decreases sharply reaching 3.7% at a magnetron current of 5A. This is expected since at higher sputtering rates the active impurity such as oxygen is pumped faster by the deposited metal on the getter box walls. This drop of film resistivity at higher currents is correlated with a decrease of refractive index and an increase in extinction coefficient. Table 3 lists the numerical optical results for this investigation.

Comparing the refractive index values $n$ of our best TiN films with other references reveal their quality. $n$ for thick films made on glass at room temperature by activated reactive evaporation had a value of 1.7 at a wavelength of 600 nm (Ref. 21), whereas for thinner films the $n$ values were ranged from below 1 to just below 1.6 (Ref. 22). The minimum $n$ value for an opaque TiN film deposited on heated glass substrates was as low as 0.85 (Ref. 18). It has to be mentioned that making such sensitive compound at high cathode powers destabilises the deposition process (fluctuation of the output signal). The other effect was film spalling due to the enormous heat coming from the
plasma. Increasing the energy of sputtered atoms means conveying considerable heat radiation to the substrate through the impact. This as a result could affect the measurement of refractive index as stated in Table 3 where sample made at magnetron current of 5A shows a slight increase in refractive index. Although some heat is transferred from the plasma through the lid to the substrate, the glass substrate due to its lower expansion coefficient can not overcome the difference between the heat coming from the plasma during deposition and that heat it receives before deposition. The dependence of nitrogen consumption and thickness on magnetron current is shown in Figs. 4.3b and 4.3c. Due to higher sputtering rate implied by higher currents, the reactive gas consumption has to increase accordingly (section 4.1.1).

4.1.1.3 Effects of Various Deposition Parameters on Films Quality

In order to expand our investigations on the electrical and optical properties of TiN films, it was necessitated more work to be done to study the effects of power, argon pressure and thickness. The results of this investigation are tabulated in Table 4. Several points can be extracted from Table 4, these are:

1. With increasing argon pressure the resistivity as well as the refractive index \( n \) both increase, the extinction coefficient \( k \) decreases. This proves that the quality of TiN is improved since having lower \( n \) and higher \( k \) means that the reflection minima in the visible region is lower and the reflection in the near infrared is higher. This can be concluded from samples 1 and 3.

2. The faster the samples can be made the better the quality of the films, this is represented by samples 1 and 2, 4 and 6, 8 and 9.
Fig. 4.3a Influence of magnetron current on the resistivity and related oxygen contamination of TiN

Fig. 4.3b The dependence of the nitrogen consumption of TiN films on magnetron current
### Table 3: The composition and contamination content obtained by the Auger analysis and optical data for TiN films deposited at different magnetron currents

<table>
<thead>
<tr>
<th>Magnetron Current</th>
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<th>Nitrogen Content</th>
<th>Carbon Content</th>
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<td>2.11</td>
<td>48.4</td>
<td>40.2</td>
<td>7.4</td>
</tr>
</tbody>
</table>
Table 4 The effect of various deposition parameters on the optical and electrical properties of TiN films
3. From samples 5, 6 and 7 it can be shown that with increasing film thickness the resistivity shows a slight increase and the refractive index shows a slight decrease but the extinction coefficient remain unchanged. It should be pointed out that the target utilisation or erosion changes the characteristics of the operating voltage which in turn has an effect on the consumption of reactive gas.

4.1.1.4 Electrical and Optical Properties of Semitransparent Films

The optical and electrical properties of TiN Films were shown to improve when they are made thinner or semi-transparent (Ref. 22) and when substrates are heated (Ref. 18). Since better films can be obtained at higher magnetron currents and lower argon pressures, for this investigation a magnetron current of 5A was applied and the argon pressure was 4 mtorr. This experimental deposition process were taken as the upper limit after which the films can suffer high stresses and total spalling. Fig. 4.4a shows the effect on resistivity as the thickness of the film increases. The film thicknesses were estimated using the method described by O. H. Heavens (Ref. 23). The resistivity reaches a minima of about 1 \( \Omega \mu m \) at a thickness of 66 nm. The refractive index and the extinction coefficient of this film had the lowest and the highest value which were 1.31 and 2.23 respectively. As the the exposure time progresses the resistivity increases reaching about 1.35 \( \Omega \mu m \) at a thickness of 118 nm. Here two points have to be mentioned from the experimental observations:

1. As the exposure time increases the observed value of nitrogen consumption of about 6.3 sccm which gave optimum TiN shifted to a lower value. This decrease in optimum nitrogen consumption became apparent at higher exposure times after which the best film of 66 nm thick was deposited at 30 second. Consequently
Fig. 4.3c The dependence of thickness of TiN films on the magnetron current

Fig. 4.4a Effect of thickness on the resistivity of TiN films
the position of optimum film electrically and optically could take place at longer exposure time than that of the latter film. It is evident from the optical data in these thicker films which showed higher values of refractive index and lower values of extinction coefficient as mentioned briefly in the previous discussion. As an example for a 118 nm thick film the n and k values were 1.4 and 2.05 respectively.

2. Due to higher plasma radiation the films suffered stresses with increasing sputtering time. This could affect the sheet resistance values of thicker films.

3. It is known that the structure of TiN is related to collective effects of density, resistivity and optical quality. As the film thickness progresses there is a point where a better structure is obtained which characterised by a low surface resistance, which is related to a specific density at best optical quality. Then if the density does not change as the surface resistance does, the key factor here is the film thickness which if it increases the resistivity will increase. Increasing the film thickness could not change the density remarkably since the mass of the film increases accordingly. From that we can conclude for one given composition the density can not change remarkably but the resistivity can. This point should be regarded as a separate consequence of thickness since points 1 and 2 concern a probable different composition due to change of reactive gas consumption.

Fig. 4.4b shows the transmission and reflection spectra for two semi-transparent films of approximate thicknesses 8 nm 22 nm. As shown for the thinner film, there is a reflection minima of 16% and transmission peak of 55% at a wavelength 500 nm. For thicker film there is a reflection minima of 24% and a transmission peak of 31% . This
also demonstrates that although the transmission in the visible region is increased when the film is made thinner its infrared reflection is lowered. C. Ribbing and E. Valkonen investigated the optical properties of TiN and other noble metals (Ref. 18). They showed that TiN films can not be comparable to gold films due to their lower infrared reflection and quite high absorption when the infrared reflection was plotted versus normalised transmission weighted by the solar spectrum. They also concluded that TiN thin films prepared by reactive magnetron sputtering technique had a lower infrared reflection than opaque films sputtered using similar conditions. That was attributed to the vacancies and voids due to oxygen affinity accompanying the formation of very thin films.

In order to investigate the effect of thickness on the absorption of the film Fig. 4.4c shows a plot of absorption at 1000 nm versus thickness for a set of samples. From the classical Drude theory metals in the near infrared when \( k \gg n \) their absorption exhibit a maxima as a function of thickness (Refs. 22, 24). With regard to these two references they showed an absorption maxima at a critical thickness of 15 nm. As can be seen from Fig. 4.4c the maximum absorption is about 38% at thickness of 8 nm. This value is also higher than those values stated in References 22 and 24 because our film is simply thinner and also deposited at room temperature on a glass substrate. Fig. 4.4d shows reflection spectra for a 66 nm thick TiN film. From the previous discussion it can be verified that obtaining a lower resistivity of TiN is correlated with a decreased minima in the visible reflection and an increase of IR reflection.

The influence of heating the substrate on the performance of TiN films as heat mirrors and resistivity were investigated by E. Valconen et al (Ref. 22). They showed that heating the substrate to 400 °C improved the optical and electrical properties by
Fig. 4.4b Transmission and reflection spectra in the visible and near infrared regions for two semitransparent TiN films of thicknesses 8 nm and 22 nm.

Fig. 4.4c Effect of thickness on the absorption of TiN films.
Fig. 4.4d Reflection spectra in the visible and near infrared regions for a 66 nm thick TiN film prepared at magnetron current of 5A.
producing dense films, increasing the IR reflection and decreasing the resistivity. The performance of noble metals as heat mirrors can also be improved when a thin metal layer is embedded between two dielectric selective films which serves as an antireflection coating and provides a hard and good chemical surface at the interfaces (Ref. 25). It was suggested that by changing the active gas between oxygen and nitrogen a sandwich filter can be made from one titanium target to give a structure consisting of a metal layer between two oxide layers of that metal (Ref. 26). The ideal heat mirror transmits all the visible light and reflects all the solar radiation at longer wavelengths i.e. infrared region. The performance of heat mirrors can be valued by plotting the infrared reflection against visible transmission. The ideal surface should occur in the top right hand corner of that plot (100% IR reflection at 100% visible transmission) (Ref. 27). Because of the reduction in IR reflection when TiN was made thinner it was antireflected by two of high refractive index of TiO₂ of selective optical properties (Refs. 27-29). A. G. Spencer et al (Ref. 27) and Y. Claesson et al (Ref. 28) obtained values of Visible transmission and IR reflection of 55%, 64% and 60%, 70% respectively. The performance of heat mirrors can also be improved at increased discharge currents (Ref. 28).

When the silver layer was made too thin for the optical filter ZnS/Ag/ZnS, it was found not to be IR reflecting but more or less absorbing and even the thick silver films were still reflecting in the visible (Ref. 25).

4.1.1.5 Morphology of TiN

Fig. 4.5a shows micrographs of a fractured cross section for two TiN films deposited at Ti line set points of 60% and 70% and a magnetron current of 3A. The thicknesses
Note: The scale of all SEM micrographs is 1 cm = 100 nm

Fig. 4.5a Micrographs cross-sections made by SEM of two TiN films deposited at Ti lines of 60% and 70%
Argon pressure = 5 mTorr

Fig. 4.5b Micrographs cross-sections made by SEM of two TiN films deposited at a current of 3A and with argon pressures of 5 mTorr and 7 mTorr

Argon pressure = 7 mTorr
Fig. 4.5c  Typical region of surface made by SEM for TiN film deposited on glass substrate
are about 175 nm and 210 nm respectively. As seen from these two micrographs, the poor density characterised by columns separated by voids is an indication of deficiency in the activation energy accompanying deposition without substrate heating or ion bombardment. At low temperature ratio of the substrate T S to the melting point of the film T m i.e. T S/T m < 0.3, this structure is very common phase in TiN. Fig. 4.5b shows another two micrographs for relatively equal thicknesses about 350 nm deposited at two different argon pressures 5 mTorr and 7 mTorr. The increase in argon pressure has the effect of decreasing the density of the film giving a more loosely packed structure and this is also shown through the accumulation of broken columns due to loss of energy during deposition which can act as bonds strengthening the grain boundaries and filling the gaps between the voids. Fig. 4.5c also shows a micrograph made by SEM of a 400 nm thick TiN film. An average grain size of 50 nm was estimated from this micrograph. The glass supporting the film was not gold coated in this case.

4.1.1.6 X-ray Diffraction

Four films of TiN deposited at different Ti line set points were prepared to investigate their orientation and lattice parameter. Fig. 4.6 shows XRD for TiN prepared at Ti lines of 50%, 60%, 70% and 80%. Table 5 lists the numerical results for this investigation. As shown from this table mixed textures of 111 and 222 orientations were only found for samples made at Ti lines of 50% and 60% (Fig. 4.6a and 4.6b). The (200) diffraction peak which occurs at an angle of 42.64° also appeared in this film (Fig. 4.6c) revealing formation of a stoichiometric compound of TiN (at maximum consumption of nitrogen). It is also seen an increase of relative intensity but in a pronounced manner at Ti line of 70% for texture 111 (Fig. 4.6c). The estimated
Fig. 4.6 X-ray diffraction pattern of TiN films deposited at different settings of the Ti line with current of 3A and an argon pressure of 5 mtorr.
<table>
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<th>Orientation</th>
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<th>Lattice Parameter</th>
<th>Relative Intensity</th>
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Table 5: The lattice parameter, orientation and grain size for TiN films deposited at different settings of the Ti line with magnetron current of 3A.
grain size for film deposited at Ti Line of 70% was about 46 nm using the (111) diffraction peak corresponding to an angle of 36.64°. It can be shown from Fig. 4.6 that as the sputtering rate increases (an increase in film thickness) the peak intensity of (111) increases but the line width becomes narrower (an increase in grain size) at Ti line of 70% and then wider again at Ti line of 80% implying a decrease again in grain size. A (222) peak has also appeared in all of these films with a slight increase of intensity at Ti lines of 60% and 70%. The lattice parameter, grain size and relative intensity are shown in Table 5 where the maximum intensity of the reflection (111) for a Ti line of 70% was taken as a reference for other peak intensities.

### 4.1.1.7 Density and Related Resistivity

A set of samples were deposited using a current of 3A at Ti lines ranging from 30% to 100% and their mass difference before and after deposition were obtained using a microbalance. Film thicknesses were estimated by SEM. Fig. 4.7 shows a plot of resistivity and density versus Ti line. As the Ti line increases the resistivity reaches a minimum and the density reaches maximum at a point where the optimum film was formed i.e. maximum consumption of reactive gas at a Ti line of 70%. The resistivity starts to increase and decrease again reaches value less than the optimum. This behaviour of resistivity is understandable when comparing its general effect on density for TiN as discussed in previous sections. The density for pure Ti shows value less than the optimum although its resistivity is slightly lower. This argument is consistent with the results presented by E. Sundgren et al (Ref. 30). We can conclude that the density value for the optimum film 4.5 gm/cm³ should be lower. It should be noted that within the limit of resistivity ratio of TiN to pure Ti films which is about 1.15, this value can be valid especially for films having very low masses and thicknesses. The
Fig. 4.7 The dependence of resistivity and related density on the percentage of Ti line set point
difference in density value can be explained due to errors in measurement involving weighing the samples since samples were shown to lose some weight under vacuum. Another possible source of errors come from the determination of thicknesses. All these factors have a profound influence on the estimation of density by the weighing method. However the experimental value of density obtained for the optimum film which is about 4.5 gm/cm$^3$ is lower than the bulk value 5.2 gm/cm$^3$. This value is expected for such poorly columnar structures of TiN.
4.2 Unbalanced Magnetron

Recently techniques of providing low voltage ion bombardment of a growing film have appeared which have been shown to result in improved properties for the films that are made. They involve placing the insulating or isolated substrate in a dense DC plasma, the self bias that appears on the surface (Ref. 31), due to the need for electron and ion currents to equalize, causes the ions to be accelerated through voltages of up to 100 volts. This bombardment is of particular importance in reactive processing and has been used with plasmas produced by low voltage electron beam guns in evaporation systems (Ref. 32), the highly ionised product of arc evaporation (Ref. 33) and by redirecting the plasma created in a planar magnetron onto the substrate, by unbalancing the magnetic field which confines it (Ref. 34).

A circular planar magnetron, with concentric poles is a natural system to be unbalanced either with magnetic material at each pole or with magnetic material concentrated at the periphery, with the magnetic return circuit being made with high permeability material. This is because of the ease in providing magnetic material volume at the extreme edge of the circle. The ion bombardment can be increased by placing a coil behind the substrate. Such configuration with the electric circuit of the coil is shown in Fig. 4.8. The effective diameter of the target was 78 mm. Electrons trapped in the planar magnetron field, which is parallel to the surface can be scattered into this unbalanced field and be directed towards the substrate. They will take ions with them by electro-static forces to give a plasma beam directed onto the substrate surface. If the substrate is insulating or isolated it's surface will acquire a charge, when immersed in this dense plasma, so as to equalise the electron and ion currents that flow to it. The electrons are much more mobile and have a longer mean free path, so that the surface acquires a negative charge and potential. This accelerates the ions which constitutes the equalising, positive-charge current, to give bombardment of the substrate. This bombardment can be assessed using
Fig. 4.8 A cross section of the unbalanced magnetron
a biased probe to give the acceleration potential and the ion current density (Ref. 31).

4.2.1 I-V Plasma Characteristics

Fig. 4.9 shows a plot of ion current versus bias voltage for a 1 centimetre square probe at a discharge current of 3 A and at different argon pressures. As the pressure is decreased both the floating potential $V_f$ and the plasma potential $V_p$ respectively become more negative and more positive with respect to the ground leading to higher substrate potentials (Ref. 35). The ion current density is increased as the pressure is decreased due to the higher ionisation. When the ion current becomes zero at $V_f$ the probe current is dominated by electron contribution. When the probe voltage reaches the ionisation potential of the gas atoms, the probe current increases rapidly (is not seen here).

4.2.2 Control of the Ion Bombardment by Coil

The use of the ion bombardment, arising from the use of unbalanced magnetron can be controlled by an additional coil placed behind the substrate with the results shown in Figs. 4.10a, 4.10b, 4.10c, and 4.10d. As the coil current is increased positively (auxiliary magnetic field) both the ion current and the floating potential increase due to an increase of magnetic field leakage which in turn increases the density and the acceleration of the plasma beam striking the substrate (Figure a). In the same way by changing the polarity of the coil, a plot of self bias voltage and ion current density versus coil current is shown in (Figure b). From Fig. 4.10b a heat load in terms of power input to the probe can be calculated, this is shown in Fig. 4.10c. As can be seen the power input represents the heat which is conveyed to the glass substrate supporting the film, and for example, at a current of $+2A$ the heat load to substrate is about 5.4 watt/cm² which in
Fig. 4.9 I-V Plasma characteristics at different argon pressures

Fig. 4.10a I-V Plasma characteristics at coil currents of +1A and +2A
Fig. 4.10b Influence of the coil current on ion bombardment

Fig. 4.10c Heat load to the probe as a function of coil current
Fig. 4.10d  I-V Plasma characteristics at a coil current of -2A.
fact is very large to form films with a very good adhesion on a room temperature glass substrate. The I-V plasma characteristics for balancing the unbalanced magnetron is also shown in (Figure d) where the bias voltage can be reduced to zero when a current of -2A is applied to the coil. Fig. 4.11 shows the influence of placing an auxiliary magnet behind the substrate on the plasma shape (Ref. 35). Using an opposing magnet disperses the plasma or the ion beam away from the substrate while using a supporting magnetic field increases the confinement of plasma towards the substrate.

4.2.3 Iron and Oxygen Impurities
In order to investigate the impurity levels within the deposition chamber of the getter box a plasma monitor model (1451) (Princeton Applied Research) was used as a spectrum analyser which cover the intensities of interest at wavelengths between 400 to 700 nm. The light signal of the plasma is transferred by an optical fibre located through a hole made on the wall of the getter box. An extension was fitted to the optical fibre to prevent it from being coated. This signal is magnified by a photomultiplier which is connected to the plasma monitor. A recording facility is available to plot the spectra. Different spectra were taken at different magnetron powers. Fig. 4.12 shows the iron and oxygen impurities expressed as a percentage of total counts (intensity) versus magnetron power at wavelengths of 421 nm and 616 nm respectively and an argon pressure of 3 mtorr. As can be seen, as the power increases these impurities decrease reaching a minimum value at 1.5 KW. This can be explained as follows: since the emission of Ti expressed as a sputtering rate increases with power (but not linearly as shall be seen in the next section), a higher percentage of impurities are deposited and pumped by the sacrificed surface of the getter box, this leads to a purer deposition environment or simply better film quality. The origin of oxygen is well known and is due to the dissociation of
Fig. 4.11 Influence of an auxiliary magnet beneath the substrate
water vapour molecules into hydrogen and oxygen. The oxygen as a result compete with the mother atoms of the coating material and incorporate into the film and settles in the lattice structure. The origin of iron is obvious and comes from the outer pole of the unbalanced magnetron which is bombarded by the accelerated argon ions and as a result is sputtered and deposited onto the substrate. This contribution will be discussed in more detail when analysing some films using Auger spectroscopy.

4.2.4 The Dependence of Ti Emission on Magnetron Power

The Plasma Monitor was also used to investigate the relationship between the emission of excited states of neutral Ti atoms and the target power. Fig. 4.13 shows the dependence of the emission intensity I of Ti on the discharge power P at a wavelength of 499.5 nm. This relationship follows this equation:

\[ I = A P^{1.61} \]  

Where :

A : is a constant

It was found that the emission intensity of tantalium sputtered in pure argon was nearly linearly proportional to the discharge power over a large range of powers (Ref. 36). This variation obtained from the equation above is consistent with that shown in reference (37) who attributed it to the power variation of the electron excitation frequency.
Fig. 4.12 Iron and oxygen impurities

Fig. 4.13 The dependence of emission intensity of Ti on the discharge power
4.2.5 TiN

4.2.5.1 Dependence of the Sputtering Rate on Ti Line Set Point

In section 2.6 of chapter 2 an explanation of the target poisoning and control processes of reactive gas partial pressure were given. In reactive magnetron sputtering a constant rate of delivery of the sputtered target material while maintaining the reactive gas partial pressure at each point of that rate is needed to assess the position where optimum TiN is formed. This has been done in our work through the optical and electrical characterisation of TiN. The plasma monitor was used to show how the sputtering rate responds to the variation of Ti line set point in a deposition environment of argon and nitrogen. At each point of the Ti line the deposition process was monitored and the corresponding spectra was recorded. Two central peaks of Ti intensities were observed through out these investigations at wave lengths of 499.5 nm and 505.5 nm. Here the emission intensity of the central peak at 505.5 nm was compared each time with the intensity of a discharge occurring in argon only. Fig. 4.14a shows the spectra for percentages of Ti line set points of: 34% (Fig. 1) (high nitrogen partial pressure), 65% (Fig. 2) (optimisation area at flow rate around the maximum of 3.3 sccm), and 100% (Fig. 3) (zero nitrogen partial pressure). As can be seen when the Ti line increases the intensity of the central peak increases. If we divide this intensity of (1) and (2) by that of metallic Ti (3) we obtain relative intensities of 0.35 and 0.63 which in fact represents the relative emission lines of 0.34 and 0.63. This gives us evidence of the process control. Increasing the intensity with increasing Ti line means a generation of higher sputtering rate or higher deposition rate at the substrate. As a result the deposition rate ratio of the film in question (TiN) to that of a fully metallic film (100% of Ti line) is equal to the ratio of intensity of a specific Ti line (TiN) to that of pure Ti. The deposition rate of Indium tin oxide (ITO) films deposited by reactive d.c planar magnetron
Fig. 4.14a Spectra made by the plasma monitor showing the effect of Ti line set point on the emission intensity of Ti at 505.5 nm
Fig. 4.14b The dependence of emission intensity of Ti on the Ti line set point (sputtering rate)
sputtering was also shown to increase linearly with increasing the emission intensity of Indium (Ref. 38). It should be pointed out that when analysing the spectra using the plasma monitor the target had to be sputtered-cleaned and a new spectra of the residual background had to be scanned as well, because continuous operation of the Ti line with changing the reactive gas changes the target history (counts or emission intensity per unit of time) with background concentration. Fig. 4.14b shows the linear dependence of the central peak on the Ti line set point.

4.2.5.2 Electrical Properties

Since the characterisation of TiN in terms of the dependence of nitrogen consumption and thickness on the Ti line set point discussed early when the balanced magnetron was used can repeat itself here, plots of resistivity versus Ti line set point and nitrogen consumption are only shown in Figs. 4.15a and 4.15b respectively. At low percentages of the Ti line the sputtering rate is low (gas rich) (transparent film) while at higher percentage (above the stoichiometry) the rate is higher (metal rich). Between these two positions a collection of graded golden films was formed. The partial pressure of nitrogen at which this is obtained is taken as that which gives stoichiometric titanium nitride. In fact the optimisation as discussed earlier can be characterised when investigating the optical and electrical properties. The percentages of the Ti line were set at very close intervals and because of that we can see a group of graded stoichiometric TiN films occupying a resistivity minima. These films have little difference in sheet resistance and the difference in their thicknesses is small as well. The unbalanced magnetron that was used resulted in a bias of about -15 volts with an ion current of 9 mAmps per square centimetre when operated at an argon pressure of 5 mtorr, with the magnetron operating at 3 Amps and about 350 volts. From figures 4.15a and 4.15b two
Fig. 4.15a The dependence of resistivity of TiN films on the Ti line set point (unbalanced magnetron)

Fig. 4.15b The dependence of resistivity of TiN films on nitrogen consumption at the set point of the Ti line (unbalanced magnetron)
points can be extracted which are:

1. The influence of the ion bombardment is to give films of lower ultimate electrical resistivity, which is lower than that of titanium metal. The decrease in the resistivity obtained with ion bombardment is attributed to the increased density, which can be seen in the cross section electron micrographs later on. The resistivity ratio of optimum TiN to that of metal titanium is \(\approx 0.7\) which is about half of that ratio obtained by the balanced magnetron.

2. The formation of optimum TiN occurs when the nitrogen consumption within the system is a maximum.

It should be mentioned that some of these films peeled off because of the high ion dose striking the growing film. Films spalling became more pronounced when the reactive gas was increased revealing the sensitive nature of TiN towards reactive gas incorporation.

4.2.5.3 Effects of Bias Voltage on Electrical and Optical Properties.

Three films of TiN were deposited at different bias voltages by using a coil behind the substrate. Figs. 4.16a,b and c show the sheet resistance of these films as a function of the nitrogen gas flow at the set point of Ti deposited at biases of 0, -7 and -15 volts respectively. It can be clearly seen that as the bias voltage decreases to 0 volts the sheet resistance of TiN becomes higher than that of metallic titanium giving the same resistivity behaviour of that of the rectangular balanced magnetron source. The density of TiN is strongly correlated with the resistivity. Figs. 4.16d,e and f shows the
Fig. 4.16 a,b and c The behaviour of sheet resistance versus nitrogen consumption at the set point of the Ti line for TiN films deposited at different biases.
Fig. 4.16 d, e and f: The behaviour of resistivity versus nitrogen consumption for TiN films shown in Fig. 4.16a, b and c.
Fig. 4.16g Effect of bias voltage on the resistivity at the set point of Ti line for TiN films

Fig. 4.16h Reflection spectra in the visible region for three selective TiN films deposited at different biases
corresponding resistivity for the same films presented in Figs. a,b and c respectively. The conclusion which can be drawn from these figures is that although the films are made at bias voltages of 0 and -7 volts, their TiN resistivity is still lower than the metal titanium due to the increase of films thicknesses. It can be clearly seen as presented in Fig. 4.16g that the resistivity of TiN deposited at bias voltage of -15 volt is lower, this has been demonstrated and attributed to an increase in film density. The improvement in optical selectivity can be seen with films made at higher biases (Fig. 4.16h) where the reflection minima is lower in the middle of the visible and higher in the red region.

4.2.5.4 Morphology

The best method to demonstrate the improvement of TiN films due to the effect of subjecting the growing film to a dense plasma beam, is to show the cross section electron micrographs made by SEM for these films. Fig. 4.17a show micrographs for two films deposited at percentage of the Ti line of 55% and 70% respectively. The improvement in film density characterised by diminished voids is clearly evident compared with those films prepared by the balanced magnetron. The energetic particles striking the growing film transfer their energy and momentum to the atoms in the coating lattice, these knock-on atoms of the coating material are driven further into the bulk where they fill the microvoides which are the characteristics of formation zone I structure defined by J. A. Thornton (Ref. 39). This bombardment caused by the unbalanced magnetron UM promotes formation of a zone T structure. The latter is accompanied by denser films of lower resistivity (Ref. 30). It should be pointed out that some samples exhibited blisters due to the high ion dose striking the growing films. Blistering is attributed to a sudden coalescence of bubbles within the range distribution of the incident ions (Ref. 40). The formulated models of stresses and information
Fig. 4.17a Micrographs cross-sections made by SEM of two TiN films deposited at Ti lines of 55% and 70% (unbalanced magnetron)
Fig. 4.17b  SEM micrograph showing blisters
describing this phenomenon are detailed in Ch. 1 of reference 40. A micrograph showing blisters is seen in Fig. 4.17b.

4.2.5.5 TEM

Very thin TiN films were deposited on potassium bromide KBr substrates for transmission electron microscopy investigation. The magnetron was operated at a current of 4A and the argon pressure was 5 mtorr. These films were deposited at percentages of the Ti line ranging from 36% to 100%. Fig. 4.18 shows the diffraction patterns and the corresponding transmission electron micrographs made by the bright field image for three films. Fig. 4.18a for film deposited at percentages of Ti line set point of 36% (high nitrogen concentration) at flow rate of 2.8 sccm, Fig. 4.18b at Ti line of 59% (optimum film) at maximum flow of 3.7 sccm, and Fig. 4.18c at Ti line of 100%. Since the diffracted beams are stopped off by the objective aperture, dark grains correspond to areas which are in a strong diffracting position. Fig. 4.18d shows a plot of nitrogen consumption and grain size versus percentage of Ti line set point. The average grain size is clearly shown to increase reaching a maximum of about 8 nm at a Ti line of 59% (at maximum nitrogen consumption). Behind this point it decreases to about 0.8 nm at Ti line of 78%. At higher Ti line percentages up to 100% the grain size diminishes revealing formation of an amorphous phase of Ti and this can be seen through an observation of the increased width of the diffracted ring. Tables 6a and 6b list the lattice plane spacing and the corresponding orientation for two TiN films deposited at percentages of the Ti line of 36% (high nitrogen partial pressure) and 59% (optimum film) respectively.
Note: The scale of all electron diffraction patterns is reduced to 70%.

Note: The scale of all transmission micrographs is 1 cm = 26 nm.

Fig. 4.18a Electron diffraction pattern and the corresponding micrograph for TiN film deposited at the Ti line of 36% (high nitrogen concentration).
Fig. 4.18.b Electron diffraction pattern and the corresponding micrograph for TiN film deposited at the Ti line of 59% (stoichiometric film)
Fig. 4.18c Electron diffraction pattern and the corresponding micrograph for metallic Ti film (amorphous film)
Fig. 4.18d The dependence of nitrogen consumption and related average grain size on the Ti line set point.
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Table 6a Lattice plane spacings and orientations for TiN film deposited at Ti line of 36% (high nitrogen content)

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<td>9</td>
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Table 6b Lattice plane spacings and orientations for TiN film deposited at Ti line of 59% (stoichiometric film)
4.2.5.6 Auger Analysis

The impurity and stoichiometry concentration of the TiN films was obtained by Auger electron spectroscopy (AES). The analysis was carried out using a Varian 10 KeV Auger electron spectrometer. The primary electron beam current was 0.9 μA at 3 KeV. A rastered argon ion beam of current density of 25 μA/cm² at 3 KeV was used to sputter etch the films prior to analysis. Table 7 lists the numerical results of the AES investigation for three TiN films deposited at bias voltages of -15, -7 and 0 volts and at Ti line of about 61%. Fig. 4.19 shows an Auger spectrum obtained from sample of thickness of 230 nm deposited at a bias voltage of -7 volts and at depth profile of 30 nm. As can be seen there are two peaks for titanium at electron energies of 380 eV and 417 eV. There is a nitrogen peak at 380 eV which overlaps with titanium peak. There are signals corresponding to impurities for carbon and oxygen at energies of 272 eV, 510 eV. Three peaks of iron can also be seen at energies of 598 eV, 656 eV and 703 eV. As shown from Table 7 and Fig. 4.19 the iron impurity decreases with increasing the bias voltage reaching 1.9% at depth profile of 60 nm and bias of -15 volts. Since these films were deposited at the same experimental conditions, the low iron content can be attributed to the change of plasma shape and the effect of high acceleration energy and large ion dose or ion current density which was about 9 mA/cm². While that for films deposited at biases of -7 and 0, the ion current density was about 3 mA/cm². This means that some of the iron atoms sputtered from the outer pole are removed by the momentum transfer of energy of incident higher ion doses.

4.2.6 ZrN

Films of ZrN were deposited using the same units of the plasma emission monitor. The emission line of zirconium at a wavelength of 467.8 nm was chosen as input signal for
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<th>Titanium Content (%)</th>
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<td>37.2</td>
<td>45.0</td>
<td>1.9</td>
<td>3.8</td>
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Table 7  The composition at two depth profiles obtained by the Auger analysis for selective TiN films deposited at bias voltages of 0, -7 and -15 Volts
Fig. 4.19 An Auger spectrum for a 230 nm thick TiN film deposited at bias voltage of -7 Volt
the process control. A variable wavelength instrument was used as a detector. The current applied to the magnetron was 2A and the argon pressure was 8 mtorr, this gave target potential of about 290 volts. This current and pressure was the upper limit after which the films suffered severe stresses during deposition. Sample were deposited at increased percentage of the Zr line set point from 20% to 100%. The percentage of 20% (very high nitrogen partial pressure) was the lowest level achievable so far within the response time and the limit of the optical emission controller. The output signal (ZrN) was very stable.

4.2.6.1 Electrical and Optical Properties

The relationship between resistivity versus Zr line set point and nitrogen consumption are shown in Figs. 4.20a and 4.20b respectively. At (20%) percentage of Zr line of the film showed insulating character and this is illustrated by extending the resistivity curves to infinity. Although the film thickness as estimated by examining the fracture cross section was about 110 nm the sheet resistance was very high and almost non-measurable. This is attributed to the high nitrogen concentration of this film. B. Johansson et al (Ref. 41) reported formation of higher nitrides of hafnium and zirconium corresponding to Hf3N4 and Zr3N4 by nitrogen ion bombardment of a deposited metal film (ion-assisted deposition technique). These metastable phases were transparent and insulating in contrast to the golden-coloured highly conducting mononitrides. The new nitride phase Zr3N4 which crystallises with NaCl structure was first discovered and reported by V. Juza et al in 1964 (Ref. 42). V. Juza et al (Ref. 43) also showed that this compound had no metallic conductivity and was diamagnetic and the Zr sublattice is only partially occupied. On the bases of this discussion simple metastable structures should be expected because there is insufficient time for the growth of a structure with a complex unit cell (Ref. 44). J. Cuomo et al (Ref. 45) produced an
Fig. 4.20a Resistivity of ZrN films versus the Zr line set point

Fig. 4.20b Resistivity of ZrN films versus nitrogen consumption at the set point of the Zr line
insulating hafinium nitride film that is transparent with straw like colour by sputtering HfC in a pure nitrogen atmosphere. B. Johansson et al (Ref. 46) also reported by X-ray measurement of higher nitride film prepared by magnetron sputtering. The value of resistivity of ZrN prepared by r.f bias reactive sputtering in pure nitrogen atmosphere was reported to be infinite at substrate temperature of 20°C and had a value of 500 Ω µm at 200°C (Ref. 47). This behaviour was attributed to the higher nitrogen content which causes the defect structure and metal vacancies. This reference also showed that there is a critical temperature for forming an insulating phase in ZrN, HfN and TiN which was 25°C, 200°C and ≤-196°C respectively. ZrN prepared by R.F and dual ion beam depositions was also shown to exhibit insulating character when 100% nitrogen gas was used (Ref. 48).

Going back to Figs. 4.20a and 4.20b and as the emission of Zr line (thickness) increases the resistivity reaches a minimum value of 2.4 Ω µm. This film as shown in Fig. 4.20b is positioned at a localised maxima of nitrogen consumption. After this point increasing the sputtering rate of the metal is accompanied by a decrease in nitrogen content leading to a rise in resistivity. Further increase in the Zr line set point up to the deposition of metallic Zr only causes reduction in resistivity. Although the ZrN films have been deposited by the unbalanced magnetron it seems that the metal film is superior in terms of conductivity. Another factor which could be behind obtaining higher resistivity of ZrN film is due to iron impurities which has been shown to increase with decreasing magnetron power. R. Duckworth and I. Wilson (Ref. 49) prepared ZrN by hot rod r.f reactive sputtering. They obtained a resistivity for Zr and ZrN of 1.06 Ω µm and 6 Ω µm respectively. The deposition rate ratio of metallic Zr to ZrN film was 5.8.

Fig. 4.20c shows reflection spectra for two ZrN films of thicknesses 160 nm and 240 nm. The reflection is lower in the middle of the visible region exhibiting a minima and higher in the red and near infrared regions for the thicker film (240 nm). The resistivity

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for the 160 nm thick film was 3.7 $\Omega \mu m$ while for the 240 thick film it was 2.4 $\Omega \mu m$. It seems from that, although the 160 nm thick film is opaque its density or structure still did not reach stable phase where the resistivity does not increase remarkably. That led us to conclude that TiN can gain a more stable structure or density at a much lower thickness than ZrN film.

4.2.7 Deposition of TiO$_2$ Using a Wide Band Gap Optical Filter

TiO$_2$ as a dielectric film has in particular been investigated by many researchers because of its high refractive index (2.3-2.55), high transmission and its chemical stability and hardness. The optical properties of TiO$_2$ are clearly affected by the deposition technique. The substrate temperature and the degree of oxidation of the film play an important role in identifying the stoichiometry or composition (Ref. 50).

Films of TiO$_2$ were synthesised by reactive sputtering from the unbalanced magnetron. The optical filter which was attached to the photomultiplier to provide an input signal of the metal line had a wide band gap. The magnetron current and the argon pressure were 4 A and 5 mtorr respectively.

4.2.7.1 Characterisation of Films

Fig. 4.21a shows a plot of oxygen flow rate and deposition rate versus Ti line set point. Three areas can be distinguished from this Figure. At percentages of the Ti line below 30% pressure instability is very dominant and the optical emission controller can not be used, this is the first area. At percentages of the Ti line from 35% to 73% transparent films with graded absorption were deposited. As the Ti line increases the deposition rate decreases reaching a minima at a Ti line of 54% and then increases for higher Ti lines. A drop in oxygen consumption can clearly be seen as the percentage of the Ti line (sputtering rate) increases. The third area is represented by a dramatic increase in both
Fig. 4.20c  Reflection spectra in the visible region for two ZrN films of thicknesses 160 and 240 nm

Fig. 4.21a  The dependence of oxygen consumption and the deposition rate of TiO$_2$ films on the Ti line set point
the deposition rate and the reactive gas consumption at percentages of the Ti line higher than 73% revealing the formation of absorbing films (metal rich) (formation of Ti and TiO₂ films). Although the total pressure was unchanged as indicated by the constant output signal of Ti line, this means that as the sputtering rate of the metal increases the effect of the pump was to remove or pump more reactive gas from the deposition chamber which was needed to form a compound. Fig. 4.21b shows the relationship between absorption (1-R-T) at 400 nm and the refractive index at 633 nm versus Ti line set point. The optimum TiO₂ film is formed at a Ti line of 54% and the absorption and the refractive index of this film are 1% and 2.34 respectively.
4.2.8 Deposition of TiO₂ Films Using a Narrow Band Optical Filter

In this section the films were deposited using the same optical emission controller but a narrow band optical filter was attached within the photomultiplier unit. This filter was used because it allowed a better filtration signal of the emission of the metal line at 451 nm for both deposition of TiN and TiO₂ films. The filter mentioned in the previous section showed no control for all gain stages of the pressure controller during the deposition of TiN and this could be attributed to the transmission of mixed signals of Ti and N₂ lines or to the overlapping both signals of titanium and nitrogen. The magnetron current and the argon pressure used in these experiments were 4 A and 5 mtorr.

4.2.8.1 Characterisation of the Films

The behaviour of the oxygen flow rate when using this optical filter is different from that presented in the previous section, and is shown in Fig. 4.22. At a very narrow region of the Ti line set point of 16% an optimum transparent TiO₂ film was deposited which is characterised by the lowest absorption 1% and high refractive index of 2.32 at 633 nm. The thickness of this film is 42 nm. The absorption (1-R-T) at 400 nm versus the Ti line set point in % is also seen in Fig. 4.22. As the sputtering rate increases the absorption of the films increases revealing the incorporation of mixed regions of Ti and TiₓOᵧ in the growing film. The absorption reaches a maxima of 90% at a Ti line of 73%. When the sputtering rate is further increased the incorporation of metallic titanium increases and the absorption decreases implying the disappearance of the phase TiₓOᵧ due to the decrease of oxygen content in the film which reaches zero at a Ti line of 100%. The absorption in dielectric films are caused by impurities or deviation from stoichiometry (Ref. 51). H. K. Pulker (Ref. 52) investigated the
Fig. 4.21b The dependence of absorption and related refractive index of TiO$_2$ films on the Ti line set point.

Fig. 4.22 The dependence of oxygen consumption and related absorption of TiO$_2$ films on the Ti line set point.
optical losses in single layers of TiO₂, ZrO₂, Al₂O₃, SiO₂ as well as in multilayers. He attributed these losses to scattering, and the change in film deposition process from thermal evaporation to sputtering tended to produce films with considerably lower losses.

Comparing the refractive indices of our TiO₂ films (n= 2.32-2.34) prepared in the getter box with other references it can be concluded that these values are not superior but reasonable for films deposited at temperatures very close to ambient temperature. M. Georgson et al (Ref. 29) reported values of n at wave lengths of 600 nm and 650 nm of 2.27 and 2.28 respectively for films deposited at a magnetron current of 6 A onto room temperature glass substrate. They also obtained a n value of 2.41 at 650 nm for TiO₂ film grown on a 300 C° substrate. These films prepared at elevated temperatures showed narrower X-ray diffracted peaks indicating increased grain size and consequently higher density. However taking into account the power or current levels and substrate heating used by reference 29 it can be revealed that the improvement of our films is due to the effect of the unbalanced magnetron which provides a plasma ion beam of Ar-O₂ that leaks to the substrate bombarding the growing film during deposition. A fraction of oxygen atoms are ionised and contribute to this ion bombardment. R. P. Howson (Ref. 53) has performed extensive investigations on TiO₂ films, produced by r.f bias ion plating using electron beam evaporated titanium metal giving a refractive index close to 2.5. This ion bombardment competes with those films deposited by reactive evaporation and r.f sputtering onto heated substrates (Refs. 54,55). TiO₂ films were also deposited by three deposition techniques which were reactive evaporation (RE), Ion assisted deposition (IAD) and ion beam sputtering (Ref. 50). Indices of refraction obtained by these depositions were 2.27, 2.43 and 2.49 respectively at 625 nm. The high n value
for ion beam sputtered films was attributed to increased film density. The indices of refraction for our films are allocated between those prepared by RE and IAD. Giving the limited (low) ion energy striking the substrates by the unbalanced magnetron the quality of films deposited by IAD are better since the range of ion energies are higher.

4.2.9 ZrO$_2$

The process control of optical emission when depositing ZrN was used to optimise ZrO$_2$. The argon pressure was 3 mtorr and the magnetron current was 2 A. This gave a stable potential of about 290 volts.

4.2.9.1 Characterisation of Films

Fig. 4.23a shows the oxygen consumption and absorption at 633 nm versus Zr line set point. The film characterisation is similar to that discussed earlier for reactively sputtered TiO$_2$ films. At low sputtering rates (low percentage of Zr line of 20%) and low oxygen consumption an optimum ZrO$_2$ film characterised by low absorption (0.8-1)\% and high refractive index of 2.134 for a film of about 96 nm thick. The absorption at 500 nm was $\approx$ 1.1. Fig. 4.23b shows the transmission and reflection spectra for this film. A transmission peak of 89\% is clearly seen at 440 nm. Such a high transmittance can be very useful in antireflecting coating if thinner films can retain similar transmission. Consequently the embedded thin metal film can reflect the infrared solar radiation while the highly transparent film suppresses the reflection from the metal film increasing the transmission in the visible, this is the performance of a heat mirror. ZrO$_2$ is a hard material with a high refractive index that is highly sensitive to the deposition conditions (Ref. 50). It can be shown from Fig. 4.23b that the
Fig. 4.23a The dependence of oxygen consumption and related absorption of ZrO₂ films on the Zr line set point

Fig. 4.23b Transmission and reflection spectra in the visible region for a ZrO₂ film
absorption is increased and extended from the green part of the visible to the UV region of the spectrum. W. Pawlewicz et al (Ref. 51) stated that the proximity of the 250 nm wavelength to the optical band edge of ZrO₂ appeared to result in absorption losses, since all other oxides with higher band gaps show a 2-3% loss which can be presumed to be caused by scattering due to surface roughness of the film. The UV absorption in ZrO₂ can be minimised by improving the stoichiometry or eliminating impurities. They also reported absorption plus scattering loss in their best coating to be 9% at 250 nm which is close to the optical band edge at 240 nm in UV region. ZrO₂ films prepared by ion-assisted deposition under oxygen ion bombardment was shown to have higher refractive index due to a reduction of microvoid density which is otherwise high in conventionally evaporated films (Refs. 56,57). These films produced under oxygen bombardment had higher refractive index of 2.19 than those films deposited by argon ion bombardment (n=2.138). K. Muller et al (Ref. 58) studied the effect of ion assisted deposition on evaporated ZrO₂ films. The refractive index of the initial evaporated layer was 1.76 and that for the assisted layer was 2.08 at wavelength of 633 nm. The latter improvement was due to higher density caused by the ion bombardment. Comparing the refractive index of our film with those films reported by the previous references and giving the limitation of ion energy it can be concluded that the ion bombardment performed by the unbalanced magnetron has improved the quality of ZrO₂.
4.3 The Reactive Sputtering of Thin Films of TiN at Low Target Potentials

Thin films of TiN were deposited on low temperature substrates by the DC reactive sputtering of titanium. The same unbalanced magnetron used in our previous investigations was used in an enclosed volume within a vacuum chamber, into which nitrogen was admitted. The energy of the incident particles could be adjusted by operating the magnetron at different potentials allowed by using electron injection into the race-track of the magnetron from a resistance-heated filament. When the energy of the depositing atoms is reduced their radiation damage can be reduced resulting in less stresses which are so common in sensitive compounds such as TiN.

It was observed and formalised that the enclosure of a high rate process will saturate the contaminations in the system, arising from desorption from the walls of the chamber, to give a greater purity to the films that are made (Refs. 59, 60). It was decided to produce films of TiN in a tightly enclosed volume, using the self-gettering effect to give greater purity, plasma-emission-monitoring (PEM) control (Ref. 61) to provide stability for the reactive sputtering process, and an unbalanced magnetron (UM), with electron injection to allow operation at low cathode potentials (Ref. 62). Fig. 4.24 shows the front and side cross sections of the deposition system indicating the position of the filament and the power supplies of the filament and the magnetron.

4.3.1 Influence of Filament Current on Deposition Parameters

Fig. 4.25 shows the effect of increasing the AC filament current on the operating parameters of the unbalanced magnetron and the energy and current density of ion bombardment at constant power of 0.5 KW and argon pressure of 5 mtorr. It is
Fig. 4.24 Front and side cross sections of the unbalanced magnetron showing the position of the filament.
obvious that the effect of electron injection is to increase the excitation (emission) of Ti atoms which causes reduction in magnetron potential and increasing the ion current density bombarding the substrate at a range depending upon the ionisation threshold of argon atoms by injected electron current. Fig. 4.26 also shows the operating parameters of the unbalanced magnetron, the ion bombardment of the substrate and the thickness of the titanium films that were produced as a function of the electron emission into the race track of the magnetron. These investigations were performed using the same power but at an argon pressure of 2 mtorr. The bias voltages at each point with increasing filament current were 12, 13.5, 15.3 and 18 volts respectively. It should be mentioned that the bias voltage at higher argon pressure was quite unstable and that reduction shown in Fig. 4.25 above could be attributed to the change of plasma characteristics with electron injection. This change at lower argon pressure was also seen but the average bias voltage at each point was taken at a period of time where stable readings were obtained. As shown in Fig. 4.26 as the filament current increases the sputtering rate begins to decrease at a point where the number of excited Ti atoms begins to increase. This can be remarkably seen at a filament current of 38 A where a dramatic drop in sputtering rate (thickness of the film) took place when the emission (output signal) and magnetron current increased rapidly. This point represents the lower limit of the operating potential within the limit of the power supply (5 A, 100 V). In order to reach a lower levels of magnetron potential by which no sputtering can take place (sputtering threshold) power supply of higher current must be used.

It was shown by J. E. Greene and F. S. Oserio (Ref. 63) that the maximum concentration of sputtered atoms occurs in the cathode fall region where the electron energy is high and the relative probability of electron collision excitation is small, this
Fig. 4.25 The effect of electron injection from the filament on the operating parameters of an unbalanced magnetron (argon pressure = 5 mTorr)

Fig. 4.26 The effect of electron injection from the filament on the deposition parameters of pure Ti (argon pressure = 2 mTorr)
is represented by the high energy tail of the cross-section curve in (Fig. 4.27). In our experiments the probability of excitation is higher and the energy of electrons is lower giving rise to the excitation cross section of Ti atoms. The maximum cross section for electron impact excitation of neutral atoms usually occurs in the range of 50 eV or less (Ref. 63).

The relation between emission intensity and number density of target atoms is given by this equation: (Ref. 64),

\[ I(x) = N(x) \cdot P_i(x) \cdot T_{ij} \cdot g(\lambda) \]

Where:

- \( N(x) \) is the number density of sputtered target atoms
- \( P_i(x) \) is the probability of exciting an atom to state \( i \)
- \( T_{ij} \) is the probability that the electron will decay back to state \( j \) through the radiative transition of interest
- \( g(\lambda) \) is the fraction of emitted photons corresponding to the transition \( (T_{ij}) \)

This equation assumes that the emission intensity is proportional to the sputtering rate of the target atoms since the excitation probability does not change at higher electron energies (Fig. 4.27). From our experiments it has been shown that the emission increases as target potential decreases due to the increase number density of excited Ti atoms or due to the decrease in number density of neutral atoms (drop in film thickness). The relationship between the emission of Ti and target potential is shown in Fig. 4.28 for an argon pressure of 2 mtorr. It is clearly seen at the end of the tail that the emission starts to become flat at higher potential because of increasing number
Fig. 4.27 Electron excitation cross section for neutral Ti atoms as a function of electron energy

Fig. 4.28 Effect of target potential on the emission of excited Ti atoms (argon pressure=2 mTorr)
of Ti neutral atoms or decreasing number of excited Ti atoms.

4.3.2 Characterisation of TiN Films at Low Magnetron Potentials
Three sets of TiN films were deposited at different magnetron potentials. Fig. 4.29 shows the nitrogen consumption (a), the thickness of TiN films (b), and the resistivity (c) as a function of the setting of the PEM controller and the operating potential of the magnetron. From Fig (a) as the potential decreases the nitrogen consumption decreases as well, due to:

1. Increasing the number of excited Ti neutral atoms, decreasing the sputtering rate of the metal Ti, enhancement of reactivity of nitrogen and titanium atoms, increasing number of ionised nitrogen.

2. The observation that the nitrogen is totally consumed in the deposition process i.e there was no reaction at the target surface. This means less nitrogen consumption was needed since the available areas in the getter box where the nitrogen atoms impinged and reacted were reduced leading to a lower flow rate of reactive gas.

From Fig (c) it can be seen that the resistivity is lower for films made at a lower potential of 120 volts. This is attributed to the enhanced reactivity of depositing particles on the growing film and an increase of the ion bombardment to the substrate. The ion current density at 120 volt was 6 mA/cm² while at 200 and 300 volts was 4 mA/cm². Recently highly transparent and conducting Indium tin oxide (ITO) films were deposited at a lower target potential in dc magnetron sputtering system (Ref. 65).
The reduced resistivity at low sputtering voltage was explained by a smaller collision energy of negative ions (oxygen ions) entering the ITO film, resulting in a smaller damage. That reduction in resistivity was also attributed to an increase in carrier concentration. To investigate the effect of decreasing the target potential further, Fig. 4.29d shows a plot of resistivity and target current as a function of target potential at an increased injection of electrons from the filament for TiN films deposited at the same power (0.5 Kw) but at a low argon pressure of 2 mtorr. At lower potential limited by the power supply, a lower resistivity is obtained at higher target current. Although TiN film deposited at potential of 100 Volt is very thin about 20 nm, its resistivity is lower than those of the thicker films. The high reactivity which can be further achieved at decreased argon pressure shifts the sputtering rate to a lower value at lower potential.
Fig. 4.29a Effect of target potential on nitrogen consumption at the set point of the Ti line for TiN films (argon pressure=5 mTorr)

Fig. 4.29b Effect of target potential on the thickness of TiN films at the set point of the Ti line
Fig. 4.29c Effect of target potential on the resistivity of TiN films at the set point of Ti line

Fig. 4.29d Effect of target potential on the resistivity of TiN films and magnetron current (argon pressure=2 mTorr)
4.4 References of chapters 3 and 4

1- Leybold-Heraeus, "Vacuum technology, its foundations formula and tables", GMBH.
13- Joint committe on powder diffraction standards (ASTM), 1973, TiN, Table No. 6-0642

CHAPTER FIVE
CONCLUSIONS

It has been demonstrated that reactive magnetron sputtering process can be controlled in low pumping speed vacuum system. Confining such process in an enclosed volume of the getter box and performing the plasma emission monitor of the spectral line of the sputtered target shifted the operating points to a stable conditions where the optimum TiN films can be deposited. Observing the sputtering rate of the target gave a very good indication of the process control of reactive gas pressure. The sputtering rate was shown to be linearly proportional to the percentage of Ti line set point. Films of TiN and ZrN with a specular quality were shown to form when the nitrogen consumption at the metal line set point is a maximum. This was correlated with golden appearance and selective optical and electrical properties. The stoichiometry was also shown to occur at maximum consumption when TiN films were investigated by X-ray diffraction pattern (XRD) and Transmission electron microscopy (TEM). It was shown that polycrystalline film of larger grain size and higher diffracted peak intensity was deposited at Ti line set point where the consumption of nitrogen is maximum. Films of TiN deposited at maximum nitrogen consumption had lowest ultimate resistivity. When using the balanced magnetron source the resistivity of TiN was higher than the metal titanium. That was attributed to the lower film density which was also verified very clearly when examining the micrographs of cross section made by SEM. The deposition of TiN on a room temperature insulating substrate without adding activation energy to the growing film caused low adatom mobility which can not fill the voids between the dominant columnar structure. This is a characteristics of low density films.
Increasing the magnetron current was shown to enhance the electrical and optical
properties of TiN due to the reduction of active contamination of oxygen but not enough to densify the films significantly since the sputtering rate is increased.

By adding activation energy from the unbalanced magnetron source, a plasma beam leaked to the substrate subjecting the growing film to energy of ions that is necessary to reduce the voids increasing the mobility of deposited atoms and consequently increases the density of films. That was remarkably shown when the resistivity of optimum TiN was lower than the metal titanium. This was also verified when examining the morphology of TiN where denser films were deposited.

The impurity of films obtained by Auger electron spectroscopy showed a decrease with increasing magnetron power and that was consistence with impurities obtained by observing their spectral lines by the plasma monitor.

The consumption of reactive gas at the metal line set point gave also a very good indication of the stoichiometry for dielectric compounds. For films like TiO₂ and ZrO₂ the optimum compound was formed at low consumption of oxygen. This can be explained by a much tighter control of reactive gas pressure. That means because of the pronounced reactivity of oxygen the optimisation shifts to a much a higher reactive gas pressure or to a lower metal line set point. This is also related to the binding energy of oxygen atoms which are higher than that of nitrogen atoms. This reactivity can be realised very clearly when observing the target potential which showed a maxima at the point where stoichiometric compound was formed although the process was under control. It is worthwhile to mention that there is no specific or obvious point where the consumption of oxygen can be regarded as a minima in contrast to the clear maximum of nitrogen consumption. If films of TiO₂ are made below the point which
gives optimum transparent film the oxygen flow is still in decrease but these films are absorbing and lie below the limit of plasma emission controller.

The optical and electrical properties of TiN was shown to improve with increasing the ion energy that bombards the film during deposition. Lower resistivity and higher reflectivity were obtained at higher bias voltages.

TiN films prepared at low target potentials were shown to have lower resistivity. The injection of electrons from the filament decreased the target potential increasing the number of excited Ti atoms which can be seen by an increase of emission of Ti line of the output signal of the plasma emission monitor. This generated a lower sputtering rate and lower nitrogen consumption due to the enhancement of reactivity of deposited atoms. The consumption of nitrogen at lowest target potential which gave the lowest ultimate resistivity was not maximum and occur at lower value, this new characteristic can be explained again to better reactivity and higher utilisation of reactive gas and to increased percentage of ionised nitrogen atoms. This was also observed when this shift occurred at higher percentage of Ti line set point comparing with films deposited at higher target potential and lower set point of Ti.