Studies of p-type semiconductor photoelectrodes for tandem solar cells

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Studies of p-type Semiconductor
Photoelectrodes for Tandem Solar Cells

Thesis

Thomas Smith

Department of Chemistry
Loughborough University

Supervisor
Dr Upul Wijayantha
Acknowledgments

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Abstract

Photoelectrodes and photovoltaic devices have been prepared via multiple thin film deposition methods. Aerosol assisted chemical vapour deposition (AACVD), electrodeposition (ED), chemical bath deposition (CBD) and doctor blade technique (DB) have been used to deposit binary and ternary metal oxide films on FTO glass substrates. The prepared thin films were characterised by a combination of SEM (Scanning Electron Microscopy), powder X-ray diffraction, mechanical strength tests and photochemical measurements.

Nickel oxide (NiO) thin films prepared by AACVD were determined to have good mechanical strength with a photocurrent of 7.6 μA cm$^{-2}$ at 0 V and an onset potential of about 0.10 V. This contrasted with the dark current density of 0.3 μA cm$^{-2}$ at 0 V. These NiO samples have very high porosity with crystalline columns evidenced by SEM. In comparison with the AACVD methodology, NiO films prepared using a combination of ED and DB show good mechanical strength but a higher photocurrent of 24 μA cm$^{-2}$ at 0 V and an onset potential of about 0.10 V with a significantly greater dark current density of 7 μA cm$^{-2}$ at 0 V. The characteristic features shown in the SEM are smaller pores compared to the AACVD method.

Copper (II) oxide (CuO) and copper (I) oxide (Cu$_2$O) films were fabricated by AACVD by varying the annealing temperature between 100-325°C in air using a fixed annealing time of 30 min. It was shown by photocurrent density (J-V) measurements that CuO produced at 325 °C was most stable and provided the highest photocurrent of 173 μA cm$^{-2}$ at 0 V with an onset potential of about 0.23 V.

The alignment of zinc oxide (ZnO) nano-rods and nano-tubes fabricated by CBD have been shown to be strongly affected by the seed layer on the FTO substrate. SEM images showed that AACVD provided the best seed layer for aligning the growth of the nano-rods perpendicular to the surface. Nano-rods were successfully altered into nano-tubes using a potassium chloride bath etching method.

NiO prepared by both AACVD and the combined ED/DB method were sensitized to absorb more of the solar spectrum using AACVD to deposit CuO over the NiO. A large increase in the photocurrent was observed for the p-type photoelectrode. These p-type photoelectrode showed a photocurrent density of approximately 100 μA cm$^{-2}$ at 0 V and an onset potential of 0.3 V. This photocathode was then used as a base to produce a solid state p-type solar cell. For the construction of the solid state solar cells several n-type semiconductors were used, these were ZnO, WO$_3$ and BiVO$_4$. WO$_3$ and BiVO$_4$ were successfully produced with BiVO$_4$ proving to be the optimum choice. This cell was then studied more in depth and optimised by controlling the thickness of each layer and annealing temperatures. The best solid state solar cell produced had a J$_{sc}$ of 0.541 μA cm$^{-2}$ (541 nA) and a V$_{oc}$ of 0.14 V, TX146 made up of NiO 20 min, CuFe$_2$O$_4$ 50 min, CuO 10 min, BiVO$_4$ 27 min, using AACVD and then annealed for 30 min at 600 °C.
## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>AACVD</td>
<td>Aerosol assisted chemical vapour deposition</td>
</tr>
<tr>
<td>AM</td>
<td>Air mass coefficient</td>
</tr>
<tr>
<td>AM 1.5</td>
<td>Solar spectrum after travelling through 1.5 times the Earth’s atmosphere</td>
</tr>
<tr>
<td>CBD</td>
<td>Chemical bath deposition</td>
</tr>
<tr>
<td>DB</td>
<td>Doctor Blade</td>
</tr>
<tr>
<td>ED</td>
<td>Electrochemical deposition</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Energy gap or band gap</td>
</tr>
<tr>
<td>FF</td>
<td>Fill factor</td>
</tr>
<tr>
<td>FTO</td>
<td>Fluorine doped Tin Oxide</td>
</tr>
<tr>
<td>IPCE</td>
<td>Incident Photon Conversion Efficiency</td>
</tr>
<tr>
<td>J</td>
<td>Current density</td>
</tr>
<tr>
<td>$J_{sc}$</td>
<td>Short circuit current density</td>
</tr>
<tr>
<td>PEC</td>
<td>Photoelectrochemical cell</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>T</td>
<td>Tera = $10^{12}$</td>
</tr>
<tr>
<td>$V_{fb}$</td>
<td>Flat band potential</td>
</tr>
<tr>
<td>$V_{oc}$</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>$\eta$</td>
<td>Efficiency</td>
</tr>
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Chapter One: Introduction

1.1 Aim of this Doctoral Study

The study of solar energy conversion is a task that is becoming a necessity due to the need for an alternative to fossil fuel energy resources. Photovoltaic cells are one option in the pursuit of supplying energy as cost effectively and cleanly as possible. To further this subject matter this thesis will examine the fabrication of light harnessing devices with the aspiration of an efficient cost effective solar cell.

Sensitised solar cells are a cheap and easily manufactured technology. They can be produced from cheap materials or small quantities of more expensive materials. This gives a good opportunity to produce a low cost solar cell which can produce a cheap source of electricity. One such method is to produce a tandem dye sensitised solar cell, which could improve the efficiency while maintaining low cost. Quantum dots can also be used as sensitisers. Quantum dots are desirable because of the quantum confinement effect which can be used to control the band gap. This gives one the ability to manage the light absorption of the solar cells to maximise efficiency. One design for tandem solar cells incorporated the ideas of dye sensitised solar cells and quantum dots. Figures 1.1a and b show the band diagram for the materials necessary to produce the cheap solar cell this is similar to the design reported by J. He et al.¹ This works by increasing the voltage by combining it from each half cell and therefore increasing the total voltage produced by the solar cell.
Figure 1.1a A schematic diagram of Q Dot sensitised Tandem Solar Cell.

Figure 1.1b A diagram of the band energies for a low cost tandem solar cell with the voltage produced from each photo electrode giving the total voltage of the complete cell.
The overall aim of this project is to work towards and produce a low cost tandem solar cell. This will be undertaken in collaboration with Jason Riley’s (DJR) group at Imperial College London and David Fermin’s (DJF) group at Bristol University. This will be carried out by developing a Tandem Solar Cell that employs Q-dot sensitization of the photoanode and the photocathode that harvest different specific regions of the solar spectrum. The area of focus for this PhD is the cathodic side of the tandem cell.

DJR’s group at Imperial College will focus on anodic photoelectrodes based on nanostructured titanium dioxide (TiO\textsubscript{2}) sensitised with a quantum dot semiconductor like cadmium selenide (CdSe).

DJF’s group at Bristol University will focus on production of quantum dots controlling the band gap by choosing different binary and ternary semiconductors and constraining the size of the particles so that the quantum confinement effect can occur. This can be carried out using colloidal synthesis and analysed by microscopic and spectroscopic techniques.

UW’s group at Loughborough University is working on the cathodic photoelectrode for the tandem solar cell. The first part of the project is to use a wide band gap cathodic semiconductor to prepare nanostructured electrodes. The nanostructured electrodes are then used as a base for a suitable absorber semiconductor or quantum dot colloid semiconductor. Nanostructured electrodes have a huge surface area compared to volume which improves the semiconductor-semiconductor interface. Having a large semiconductor-semiconductor interface improves the photoactivity of the electrode due to higher charge separation of electron-hole pairs at the interface. The second part of the project is to find and use a suitable cathodic light absorber to sensitise the nanostructured cathode. The absorber semiconductor must be compatible with the band positions of the nanostructured cathode semiconductor electrode so that the charge separation can be achieved.
1.2 Outline of the Thesis

In this work construction of a cathodic photoelectrode which could be used in a tandem solar cell and solid state cathodic solar cells is discussed. This thesis is divided into eight chapters. The first chapter consists of background, history of energy and theory of photovoltaic devices. The second chapter consists of experimental methods for fabricating thin films and the techniques. The third chapter consists of material characterisation techniques. The fourth chapter consists of results and discussion of each photocathodes and the solid state solar cells. The fifth chapter consists of the conclusions gained from the results and discussion. The sixth chapter consists of suggestions for future work related to this thesis. The seventh chapter describes how the results were disseminated. The eighth chapter consists of the references of all the chapters.
1.3 Energy

1.3.1 Energy demand throughout history

Energy is in ever growing demand; humanity uses it in larger and larger quantities as our quest for a better quality of life is always present. Throughout history humans have used their ingenuity to satisfy this energy demand. Humanity started out using the same energy sources as other animals, solar energy for light and heat, food and an individual or group muscle power. Over time humanity used their skills to harness energy in available biomass (dry plant material) to create or maintain fire. There is a debated evidence for fire use about 1.5 million years ago in Africa.\textsuperscript{2, 3} There is firmer evidence for fire use was found in present day Israel that is dated 780 thousand years BC.\textsuperscript{4} Animal muscle power was then used about 15 thousand years BC start of the domestication of wolves (dogs) for hunting.\textsuperscript{5} Then later about 12000-11000 years BC, cattle were first domesticated in southwest Asia.\textsuperscript{6} In 5000-4000 BC in Afro-Eurasia secondary animal products were harnessed (milk) and large domesticated animals strength was used to do work (riding, pulling ploughs and carts).\textsuperscript{6} Geothermal power was harnessed 10000 years ago by Paleo-Indians, using hot springs for warming themselves, later Roman baths used geothermal hot springs.\textsuperscript{7} Solar power was harnessed in 8000 BC in the south of France, where equipment was found that used the Sun to dry food.\textsuperscript{8} 287 – 212 BC in ancient Greece, Archimedes burnt the Roman fleet in the bay of Syracuse using the Sun’s energy by focusing it using mirrors.\textsuperscript{9} Later in 1774 the first solar furnace that focused the Sun’s energy was made with glass lens made by A. Lavoisier which could reach temperatures of 1750 °C.\textsuperscript{8, 10} In 1839, Alexandre-Edmond Becquerel in France first discovered the photoelectric effect and this was observed between two different metal plates in a liquid exposed to sunlight.\textsuperscript{11} In 1883, the first hot air engine was made using solar energy made by J. Ericsson.\textsuperscript{8, 12} Wind power was harnessed in about 4000-3500 BC by Egyptians using sail boats to travel the Nile.\textsuperscript{13, 14} Later in 200 BC, vertical windmills in the Persian-Afghan borders were used to grind grain.\textsuperscript{15} Manpower was harnessed on a large scale in 3200 BC when the first city states in Mesopotamia were established, then later in Egypt in 3100 BC which shows usage of man power in large groups as a work force or/and slavery.\textsuperscript{6} Fossil fuels were harnessed in China; natural gas was used for heating cooking and light by the Chinese before
1000 BC,\textsuperscript{16} coal mined in Fu-shun in north-eastern China before 1000 BC was being used in smelting copper.\textsuperscript{17} Water power was harnessed in about 500 BC by water wheels that powered Roman and Greek grain mills.\textsuperscript{14} As it can be seen, none of these power sources are new and have been exploited for thousands of years. Newer methods have been used to harness these power sources for energy conversion. Nuclear fission is the only new power source which was discovered in 1938 by Lise Meitner, Otto Hahn and Fritz Strassmann.\textsuperscript{18} In Idaho, USA, on the 20th December 1951, for the first time a nuclear reactor was used to produce enough electricity to power four 25 W light bulbs.\textsuperscript{19}

1.3.2 Problems with Energy

With each power source there are associated advantages and disadvantages, some of these problems can be solved with technological advancement whilst others are more complicated. Presently the world’s main source of energy is fossil fuels. Increasing issues over the use of fossil fuels have led a drive to find cleaner and more abundant energy sources. Many realise that using fossil fuels at a greater rate than they are being generated, so logically they are a finite source. This means at some point fossil fuels will run out of if consumption continues at this rate. If people don’t reduce their use we will have to go to more extreme methods of extraction until it gets to the point of it no longer be financially viable and other sources of energy will be required.\textsuperscript{20} There are also issues of the environmental damage caused by the use of fossil fuels on this scale.\textsuperscript{21} The first world scaled attempt to realise the need to move from fossil fuels was the Kyoto protocol.\textsuperscript{22} The Kyoto protocol restricts emissions of developed countries and therefore to meet this, a change in energy generation and an increase in efficiency will be required.\textsuperscript{22} All these factors have led to a need for other sources of energy to be used. There are many alternatives that are being considered and researched so they can be ascertained as to their suitability. Therefore a new source of energy is needed which produce less or no carbon dioxide (CO\textsubscript{2}) as a by-product and the possible options available are nuclear and renewable sources.
Nuclear energy has benefits in being a secure and controllable manner with less CO₂ emissions. The infrastructure needed for nuclear power stations is similar to what is already used by fossil fuel power stations, so significant changes to the infrastructure would not be required. Nuclear energy is a non-renewable energy source relying on fissile materials such as uranium (²³⁵U) and plutonium (²³⁹Pu). There are also public worries over nuclear safety and radiation which can occur accidently or deliberately. One such recent accident was the release of radioactive material from the Fukushima nuclear plant in Japan due to a tsunami on 11th March 2011. This was classed as a major accident with a severity rating of 7.²³ Political forces also attempt to ban the use of nuclear energy for some countries due to the threat of making nuclear weapons.

Renewable energy covers a large number of energy sources such as kinetic, chemical, electromagnetic and thermal. Currently they are not being fully harnessed to fulfil the energy need. For example the UK in 2012 energy statistics show renewable and waste energy sources accounts for about 4.1 % of the primary energy demand and about 11.3 % of primary and secondary electricity production. The UK’s renewables can be broken down to 73.7 % Biomass, 18.0 % Wind, 4.9 % wave, tidal and Hydro (large and small scale), 0.6 % Geothermal and heat pumps, 2.7 % Solar PV and active solar heating.²⁴ ²⁵ There are many advantages and disadvantages with all of these renewable energy sources as indicated in table 1.3.2a.²⁶
Table 1.3.2a Advantages and disadvantages of renewable energy sources.\(^{26}\)

<table>
<thead>
<tr>
<th>Energy Source</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
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<tbody>
<tr>
<td><strong>Solar</strong></td>
<td>Does not produce carbon dioxide. Abundant and readily available all over the world especially near the equator.</td>
<td>Affected by the weather conditions and cloud cover.</td>
</tr>
<tr>
<td><strong>Biomass and Biofuels</strong></td>
<td>Easy to convert conventional systems to incinerate biomass.</td>
<td>Releases carbon dioxide as it burns to release its energy. Land can be used for growing fuel crops however this conflicts with the growth of crops for food.</td>
</tr>
<tr>
<td><strong>Wind</strong></td>
<td>Does not produce carbon dioxide. Abundant and readily available especially in the UK.</td>
<td>Some people think that they are noisy. Some people think that they are an eyesore. They interfere with radar signals as indistinguishable from that of aircraft. Affected by the weather wind speed and direction.</td>
</tr>
<tr>
<td><strong>Hydro</strong></td>
<td>Does not produce carbon dioxide. It is reliable and controllable.</td>
<td>Can only be used in specific hilly/deep valley locations.</td>
</tr>
<tr>
<td><strong>Wave</strong></td>
<td>Does not produce carbon dioxide.</td>
<td>Affected by the weather, wave frequency, height and force linked to wind. Can only be used in specific locations with the sea.</td>
</tr>
<tr>
<td><strong>Tidal</strong></td>
<td>Does not produce carbon dioxide. It is reliable and predictable.</td>
<td>Can only be used in specific locations with the sea.</td>
</tr>
<tr>
<td><strong>Geothermal</strong></td>
<td>Does not produce carbon dioxide. It is reliable and controllable.</td>
<td>Can only be used in specific locations due to geological conditions and crust thickness.</td>
</tr>
</tbody>
</table>
Biomass and biofuel can be formed from energy crops, animal by-products, anaerobic digestion and wastes including landfill, sewage gas and other combustible waste. Current methods for gaining energy from these sources are well established using incinerators and gas burners. Energy crops compete for agricultural land and resources like fertiliser, while waste is already generated and needs to be converted to a suitable form for energy production.

Geothermal energy is a very good form of renewable energy because it is reliable and controllable source. The geothermal energy is acquired by pumping water into the ground where the geothermal heat is present. The heated water is collected as hot water at ~60 °C or as supercritical steam at ~120 °C. This hot water used for heating and supercritical steam is used to generate electricity. Unfortunately there are few suitable sites for geothermal as it requires very specific geology and geological activity however, it has proven to be a reliable energy source.

Hydro comes in two main categories large scale and small scale. Large scale has a capacity of above 5 MW and small scale is below 5 MW. Large scale normally requires a reservoir and a dam which allows water to flow to power turbines. The reservoir needs a specific location which cannot be used everywhere. The small scale does not require a large reservoir and uses water stream of a river.

Tidal power is a very reliable and predictable energy source because it caused by the gravitational pull of the moon and the Sun. It is normally harnessed using a similar technology to wind power. Tidal power for UK is about 20-30 TWh/year.

Wave power is caused by the wind passing over the surface of the sea. This can be harnessed by using floating barriers attached to the sea bed. The UK has higher wave power levels and an estimated exploitable electricity generated is about 40-50 TWh/year.

Wind energy can be harnessed using wind turbines. Wind turbines have successfully been linked to the grid in many countries and have seen a rapid market growth since 1991. Wind has drawbacks of fluctuations with wind
conditions, so location is critical for wind farms. Wind power can be on shore or off shore.

Many energy sources including wind, wave, hydro, biomass and fossil fuel are all derived from solar energy. The wind is produced when solar energy heats up earth’s surface unevenly. This creates places with high and low pressures in the earth atmosphere which drives air to move to equalise the pressures. Waves are produced when wind travels over the surface of water and as already discussed wind is derived from the solar energy. Hydro-power is produced by water flowing down to the ocean. Water is heated by the Sun and evaporates and forms clouds, when they hit cooler air, it causes to condense and precipitate. Precipitation occurs over land and then the water makes its way back to the ocean or lakes in rivers. This process is continuous to maintain the water cycle. Plants absorb and convert solar light into sugars which are then used as the source of energy to grow. The plants are then harvested and converted into biomass and biofuel. Fossil fuels were created in the same way as biomass but over millions of years, where they were fossilised, plants giving coal and animal matter giving oil and natural gas. This shows that solar power is the original source of energy for many energy sources, so the energy quantities available from solar energy must be vast and would be a good source to harness.
1.4 Solar Cells and Solar Energy

Solar energy is the most abundant energy source in the world and this can be harnessed almost anywhere. Solar energy is one of the sources being studied due to its wide availability all over the globe and its sheer abundance. The potential energy that could be supplied by solar radiation is about $8.33 \times 10^{17}$ kWh per annum which is over 15000 times the amount of the global primary energy consumption of 2012. The true figure for 2012 was $5.49 \times 10^{13}$ kWh per annum (12476.6 million tonnes of oil equivalent). Hence, only need to convert a fraction of available solar energy to meet our energy needs. Photovoltaics (PV) and Thermal are two ways of utilising the solar energy. Today there is a pressing need for novel, low-cost and efficient PV configurations to harness solar energy. Thermal uses the entire solar spectrum to generate heat in a liquid or molten salt, which can be used for heating, cooking, drying or to generate electricity. Thermal energy from the Sun is converted into electricity by turning water into steam and use steam to power turbines. There are many different designs for thermal conversion such as the solar power tower and solar concentrators.

---

**Fig 1.4a Power Tower schematic.**

Solar power towers use the Sun’s thermal energy. The tower holds liquids or molten salts which are heated by mirrors call heliostats that surround the tower. The heliostats focus the light onto the tower which boils or superheats the salt...
solution or liquid. This is then used to boil water to turn a steam turbine. A schematic of a solar power tower is shown in figure 1.4a.

![Schematic of a solar power tower](image)

**Fig 1.4b Parabolic Trough schematic.**

Solar concentrators also use solar thermal energy. Solar concentrators use parabolic mirrors to focus light onto a tube where a liquid or molten salt flowing through the pipe is heated. This is then used to boil water to turn a steam turbine. A schematic of a solar concentrators is illustrated in figure 1.4b.

Photovoltaics are another option that harness light. These convert light directly into electricity by absorbing photons. The photons have to have enough energy to excite an electron to cross the band gap and move into the conduction band. The electrons are then collected and circulated around the external circuit to generate electricity.
1.4.1 World Solar

The World’s energy usage has been increasing on average with the demands of growing populations, businesses and industries. The World’s primary energy consumption can be seen for the period of 1965 to 2011 in figure 1.4.1a. The energy usage will not be sustainable unless we harness energy from multiple sources. One of the promising energy sources to meet these challenges is solar energy.

![Figure 1.4.1a The world's primary energy consumption in Terawatt hours per year.](image)

The increase in world installed PV capacity has been almost exponential in recent years as shown in figure 1.4.1b. This has been due to the world effort to reduce carbon dioxide after the Kyoto agreement in 1997.
Due to the curvature of the planet, a higher intensity of solar energy near the equator and lower intensity near the poles is expected. This is because the same quantity of solar energy is spread over a larger area which can be seen in figure 1.4.1c. It can also be seen that the Sahara, the Middle East, India and central Australia have the highest potential solar energy available to harness.

Figure 1.4.1b The world’s cumulative Installed PV capacity in Terawatts hours per year.\textsuperscript{30}

Figure 1.4.1c World map of solar energy potential.\textsuperscript{32}
1.4.2 Solar in the UK

The UK commonly uses passive solar energy in buildings via windows and skylights saving energy for heating and lighting. At a rough estimate this account for 145 TWh/a. Active solar heating uses solar collectors to heat water for domestic use and is estimated to account for 252 GWh and for swimming pools it is estimated to be 1082 GWh in 2012.

In the UK there has been a drastic increase in installed PV capacity since April 2010, due to the UK government introduced a feed in tariff. This is clearly seen from the cumulative installed PV capacity plot as shown in figure 1.4.2a. These feed in tariffs gives regular payments for generated electricity regardless of it being used or feed into the grid. The tariffs are linked to the retail price index and for individual schemes will be supported for 25 years. Specific tariffs have been reduced in March 2012 and the altered again in August 2012 and March 2013.

![Figure 1.4.2a The cumulative Installed PV capacity in the UK.](image)

The UK’s primary energy consumption in 2012 was $8.96 \times 10^{11}$ kWh/a and calculations with the lowest solar irradiation of 750 kWh/m²/a (~$1.81 \times 10^{14}$ kWh/a) show that even using solar cells of 10 % efficiency, covering about 5 % of the UK
landmass. This supplies sufficient energy to meet all our demands if the energy can be efficiently stored. Solar Irradiance is the measurement of sunlight, direct and diffused, and can also be calculated by taking into account many factors including meteorological data as shown in figure 1.4.2b. Global average annual horizontal surface irradiance is approximately 170 W/m² while in the UK the average is approximately 105 W/m².\textsuperscript{33}

Figure 1.4.2b The yearly global horizontal irradiation for the UK and Ireland in kWh/m².\textsuperscript{34}
1.5 History of Photovoltaics

The history of photovoltaics begins over 170 years ago and owes its development and understanding to many people.

### PV Timeline

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>1839</td>
<td>Alexandre-Edmond Becquerel in France who first discovered the photoelectric effect this was observed between two different metal plates in a liquid exposed to sunlight.(^{11})</td>
</tr>
<tr>
<td>1860</td>
<td>Charles Fritts develops solar cell using selenium.</td>
</tr>
<tr>
<td>1876</td>
<td>Lenard observes variation in electron energy.</td>
</tr>
<tr>
<td>1883</td>
<td>Goldman and Brodsky reported the semiconductor metal interface (rectifying action).(^{11})</td>
</tr>
<tr>
<td>1888</td>
<td>The phenomenon previously known as part of the photoelectric effect was referred to as photovoltaic effect.(^{11})</td>
</tr>
<tr>
<td>1894</td>
<td>Walter Schottky and Neville Mott reported the theory of metal semiconductor barrier layers.(^{11})</td>
</tr>
<tr>
<td>1902</td>
<td>A grown p-n junction enabled the production of a single crystal cell of germanium.</td>
</tr>
<tr>
<td>1905</td>
<td>Daryl Chapin and Calvin Fuller from Bell Laboratories made a 6% solar cell using arsenic doped silicon coated with boron.(^{11})</td>
</tr>
<tr>
<td>1914</td>
<td>The US Navy launched the “Vanguard I” which was the first solar powered satellite, The Soviet Union launched “Sputnik III” three weeks later that was also powered by solar. This proved to the world that satellites could and should be powered by photovoltaic modules.(^{11})</td>
</tr>
<tr>
<td>1916</td>
<td>Willboughby Smith discovered that light affected the conductivity of crystalline selenium.(^{11})</td>
</tr>
<tr>
<td>1920's</td>
<td>William Adams and Richard Day discovered the photoelectric effect in selenium.(^{11})</td>
</tr>
<tr>
<td>1923</td>
<td>Weston invents and patents saturated cadmium cell.</td>
</tr>
<tr>
<td>1930</td>
<td>Charles Fritts made the first large area selenium solar cell.(^{11})</td>
</tr>
<tr>
<td>1941</td>
<td>Albert Einstein released a paper describing the photoelectric effect.</td>
</tr>
<tr>
<td>1914</td>
<td>Milikan provided experimental proof of the photoelectric effect.</td>
</tr>
<tr>
<td>1916</td>
<td>Albert Einstein received the Nobel Prize for his contribution on the photoelectric effect.</td>
</tr>
<tr>
<td>1923</td>
<td>Calvin Fuller and Gerald Pearson from Bell Laboratories made a good quality solar cell using lithium and gallium doped silicon.(^{11})</td>
</tr>
<tr>
<td>1930</td>
<td>Daryl Chapin and Gerald Pearson from Bell Laboratories made a 4% solar cell with silicon and thin phosphorous with an antireflective plastic covering.(^{11})</td>
</tr>
<tr>
<td>1951</td>
<td>After many sales attempts from Western Electric, National Fabricated Products and Hoffman Electronics to bring solar cells to a large market were unsuccessful due to the production costs. This resulted in solar powered toys and radios were only successful.(^{11})</td>
</tr>
</tbody>
</table>
### PV Timeline continued

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>1960's</td>
<td>Akira Fujishima discovered the Honda-Fujishima effect (titanium dioxide electrodes decompose water to hydrogen and oxygen by photoillumination).&lt;sup&gt;35&lt;/sup&gt;</td>
</tr>
<tr>
<td>1969</td>
<td>Zhores Alferov creates GaAs solar cells.</td>
</tr>
<tr>
<td>1970</td>
<td>Scientists at the Solar Power Corporation made silicon solar modules for approximately $10 per Watt.&lt;sup&gt;11&lt;/sup&gt;</td>
</tr>
<tr>
<td>1973</td>
<td>World’s first solar power building.</td>
</tr>
<tr>
<td>1974</td>
<td>Almost all of the world’s oil rig lights, light houses and buoys had been converted to photovoltaics.</td>
</tr>
<tr>
<td>1977</td>
<td>Telecom industries in America and Australia converted remote communication systems like microwave repeaters to photovoltaics.&lt;sup&gt;11&lt;/sup&gt;</td>
</tr>
<tr>
<td>1980's</td>
<td>Mali Aqua Viva (photovoltaic water pump company) and Telecom Australia were the largest commercial buyers of solar cells in the world for this year.&lt;sup&gt;11&lt;/sup&gt;</td>
</tr>
<tr>
<td>1980</td>
<td>The foundation of solar development cooperative.</td>
</tr>
<tr>
<td>1981</td>
<td>Bush installed Building Integrated photovoltaic (Bi-PV) solar electric generators.</td>
</tr>
<tr>
<td>1990's</td>
<td>Andre Borschberg flew the first overnight flight for a manned solar powered plane lasting 26 hours.&lt;sup&gt;38&lt;/sup&gt;</td>
</tr>
<tr>
<td>1991</td>
<td>First Perovskite solar cell fabricated by Akihiro Kojima Kenjiro Teshima, Yasuo Shirai, and Tsutomu Miyasaka.&lt;sup&gt;38&lt;/sup&gt;</td>
</tr>
<tr>
<td>1992</td>
<td>Michael Grätzel and Brian O’Regan published in Nature a high efficiency, low cost solar cell using TiO&lt;sub&gt;2&lt;/sub&gt; and dye, called a Dye Sensitised Solar Cell (DSSC) or Grätzel cell.&lt;sup&gt;37&lt;/sup&gt;</td>
</tr>
<tr>
<td>2002</td>
<td>Due to the concern of global warming by anthropogenic carbon dioxide led research into green energy technologies.&lt;sup&gt;36&lt;/sup&gt;</td>
</tr>
<tr>
<td>2009</td>
<td>The space race led to more and more improvements in photovoltaic modules as the US government spent over 50 million dollars competing with the Soviet Union.&lt;sup&gt;11&lt;/sup&gt;</td>
</tr>
<tr>
<td>2010</td>
<td>Elliot Berman decided space and earth based applications had different priorities, extra-terrestrial needed efficiency and durability while terrestrial needed low cost.</td>
</tr>
</tbody>
</table>

---

The development of the first thin film solar cell.

President Carter installed solar panels on the White House.

Middle Eastern instability and a break down in political relations led to an increase in oil prices and the western world concerned about its dependence on oil, this led to a lot of interest into “Alternative energy sources” and funding of demonstration projects from the Energy Research and Development Agency.<sup>11</sup>

Due to the concern of global warming by anthropogenic carbon dioxide led research into green energy technologies.<sup>36</sup>
1.6 Theory

1.6.1 Light

Light is the visible part of the electromagnetic spectrum which also consists of γ-rays, X-rays, ultraviolet, infrared, microwaves and radio waves. Light can be considered to be a wave or as a discrete packet of energy called a photon. Photons are a more accurate way of thinking of light rather than a continuous wave. This is due to the way light is formed. This occurs when electrons in atoms that have excess energy release the energy as an electromagnetic wave of a discrete energy that is equal to the loss in energy by the electron. As it drops into a lower energy level to conserve energy a photon is released as shown in figure 1.6.1a.

![Figure 1.6.1a A schematic of an atom releasing a photon.](image)

The solar spectrum is derived from the photons released by the Sun. The solar spectrum is shown in figure 1.6.1b. According to the equation 1.6.1a, the wavelength is inversely proportional to the energy, therefore, absorption of blue light results in more energy. However, due to the narrow wavelength region up to the blue light, low current densities are observed due to the low population of photons with required energy for the excitation in the solar spectrum.

\[ E = \frac{hc}{\lambda} \]  

(eq. 1.6.1a)

E is energy of the photon, \( h \) is Planck's constant, \( c \) is the speed of light in a vacuum and \( \lambda \) is the wavelength of the photon. Whilst harnessing a red light
means the energy is lower but the current population is higher due to a larger number of photons with the required energy. The characteristics of the solar cells are greatly affected by the materials' light absorbing properties.

Figure 1.6.1b The solar spectrum AM1.5 and AM0.\textsuperscript{35}

The atmosphere absorbs and scatters light as shown by the difference between AM0 and AM1.5 seen in figure 1.6.1b. The Air Mass (AM) coefficient is where AM0 is the solar light spectrum without any absorption from the earth's atmosphere. AM1 is the solar light spectrum when it has travelled through the thickness of the earth's atmosphere to the earth's surface when the Sun is directly overhead. AM1.5 is the solar light spectrum when it has travelled through 1.5
times the thickness of the earth's atmosphere to the earth's surface when the Sun is at about 42° above the horizon as shown in figure 1.6.1c.

Figure 1.6.1c A schematic explanation of Air Mass coefficients, AM0, AM1 and AM1.5.

Photovoltaics are one solution for harnessing this abundant energy source which is naturally available. This method converts light directly into electricity because of the photoelectric effect and the quantum nature of electrons in matter. The Photoelectric effect was discovered by Alexandre-Edmond Becquerel in 1839 and later described by Albert Einstein in 1905.\textsuperscript{11,36} The quantum nature of electron energy in matter was first proposed by Max Planck in 1900, who suggested that there are discrete energies in matter. This theory was later harnessed to model an atom's structure by Niels Bohr in 1913.\textsuperscript{37}
1.6.2 Semiconductors

Semiconductors are elements or compounds that have electrical conductivity which increases with increasing temperature. This occurs as the band gap is small enough for valence electrons to be excited into the conduction band (CB) from the valence band (VB) through thermal excitation. Conductors have no band gap and some have band overlap. Insulators have large band gaps where electrons cannot be excited to cross the gap as shown in figure 1.6.2a. Semiconductors are materials that can act as an insulator or a conductor depending on the energy conditions (e.g. temperature and light). The separation of the valence band and the conduction band is called the band gap, energy greater than the band gap must be absorbed by an electron to change from insulator to conductor. To be classed as a semiconductor the band gap has to be approximately between 0.5 and 5 eV. This can be broken down further to wide band gap and narrow band gap semiconductors with band gaps greater than 3 eV considered to be wide band gaps.

![Figure 1.6.2a Band gaps for conductor, semiconductor and insulator.](image)

Direct band gap is where the conduction band minimum and the valence band maximum occurs at the same value for wavevector \( \mathbf{k} \) which is parallel to the Miller indices \( \mathbf{k} \) which describes the unit cell of the crystal lattice. Indirect band gap is where the conduction band minimum and the valence band maximum occurs at different values of \( \mathbf{k} \). This means that a photon with energy the same as the minimum energy of the band gap is no longer sufficient to promote an electron into the conduction band as there needs to be a change in momentum as well as an
increase in energy. As a photon has hardly any momentum this must come from another source; it is thought to come from a phonon which is a lattice vibration. Both of these have to occur at the same instant, so the correct momentum must be supplied to an electron in the maximum valence band, as a photon of an equal energy level to that of the band gap is absorbed. So this relies on two processes happening simultaneously to promote the electron so absorption is weaker for indirect band gap materials than direct band gap materials as shown in figure 1.6.2b.

\[ E_g \]

\[ k \]

**Figure 1.6.2b A schematic of direct and indirect band gap.**

Electrons (e\textsuperscript{-}) are negatively charged subatomic particles that orbit atomic nuclei. They can be involved in bonding or as free electrons. When an electron in a semiconductor is promoted into the conduction band it creates a vacancy which is called a hole (h\textsuperscript{+}). The hole is the absence of an electron in the valence band. So there is an electron missing in the chemical bond this means that an electron from an adjoining bond can move into the space and this can be repeated so therefore it can be easier to think of it as a positive charge moving in the opposite direction to the electron. The electron and the hole move around as an exciton until they can be separated. Fermi level energy (E\textsubscript{F}) is the energy at which states are filled by electrons at a given temperature. If the temperature is at absolute zero the electrons would have no kinetic energy and would only fill the lowest available energy state filling the lowest first. As it is not at 0 K the electrons have kinetic energy and therefore some will have enough energy to be excited to a higher
energy state. The minimum amount of energy required for an electron to be promoted is the difference in energy between the highest occupied energy state to the lowest unoccupied energy state.

Semiconductors fall into three main categories Intrinsic, n-type and p-type as shown in 1.6.2c. Intrinsic semiconductors are perfect crystal lattices with no impurities and therefore the only discrete energy levels allowed. The energy levels that occur in intrinsic semiconductors are well established and can be calculated from the molecular orbital energies that are occupied or unoccupied. The Fermi level energy in intrinsic semiconductors is half way between the valence band and the conduction band. n-type semiconductors are electron accepting or negative charge carriers, this is usually done by doping the crystal lattice with electron rich atoms so it has more valence electrons for the crystal lattice. In n-type semiconductors the Fermi level energy is close to the conduction band due to a donor level which is from doping or inherent in the semiconductor. p-type semiconductors are hole acceptors or positive charge carriers, this is done by doping the crystal lattice with electron deficient atoms so there are less valence electrons for the crystal lattice. p-type semiconductors the Fermi level energy is close to the valence band due to an acceptor level which is from doping or inherent in the semiconductor. This also shows why in p-type semiconductors the majority charge carrier is the positively charged hole (h+) as when an electron is exited out of the valence band leaving a positive charge in the lattice which can now move through the lattice to transport charge through the semiconductor. While the excited electron can be trapped in the acceptor level and not be able to transport charge.40, 41

![Figure 1.6.2c Intrinsic, n-type and p-type semiconductors.](image-url)
1.6.3 Semiconductor Interfaces

When an electrode is in contact with an electrolyte the charge on the electrode effects the concentration of the anions and cations compared to that in the bulk solution, this is known as diffuse double layer. A visualisation of this is shown by the Grahame model in figure 1.6.3a. The effect of the electrical potential falls away exponentially with distance from the electrode which is shown by the white line, IHP indicates the inner Helmholtz layer, which cuts through the centre of adsorbed species on the surface of the charged electrode. OHP indicates the outer Helmholtz layer which is the closest distance of approach of the ions because of the solvation sphere around them, therefore the type of solvent and type of ion and charge greatly affect the size of the solvation sphere. The diffuse double layer shows where the ion concentrations approach the bulk solution, this occurs over a finite space from the electrode and helps take into account thermal fluctuations in the solution.

Figure 1.6.3a A schematic of the interaction of an electrode in contact with an electrolyte using the Grahame model.
The metal or electrolyte energy level can be altered by applying a voltage. Maintaining the voltage to give the same energy level as the Fermi level energy of the semiconductor is known as the flat band potential where no band bending occurs is shown in figure 1.6.3b.

![Figure 1.6.3b A schematic for flat band potential.](image)

When the energy levels do not match, band bending occurs. This can cause accumulation and depletion regions near the interface in contact with an electrolyte, metal or another semiconductor. For the purposes of demonstration, semiconductor metal interfaces shall be used. Interaction of a high work function metal and an n-type semiconductor leading to band bending causing a depletion region in the semiconductor near the metal semiconductor interface is shown in figure 1.6.3c.

![Figure 1.6.3c A schematic of band bending occurring at the high work function metal and n-type semiconductor interface.](image)

The interaction of a low work function metal and an n-type semiconductor leading to an accumulation region in the semiconductor near the metal semiconductor interface is shown in figure 1.6.3d.
The interaction of a low work function metal and a p-type semiconductor leading to a depletion region in the semiconductor near the metal semiconductor interface is shown in figure 1.6.3e.

The interaction of a high work function metal and a p-type semiconductor leading to an accumulation region in the semiconductor near the metal semiconductor interface is shown in figure 1.6.3f.

---

**Figure 1.6.3d** A schematic of band bending occurring at the low work function metal and n-type semiconductor interface.\(^{41}\)

**Figure 1.6.3e** A schematic of band bending occurring at the low work function metal and p-type semiconductor interface.\(^{41}\)

**Figure 1.6.3f** A schematic of band bending occurring at the high work function metal and p-type semiconductor interface.\(^{41}\)
1.6.4 Solar Cell Parameters

Solar cells have many parameters which provide useful information about the cells or modules. Power that is generated by a solar cell can be calculated by equation 1.6.4a

\[ P = IV \]  \hspace{1cm} \text{(eq. 1.6.4a)}

Where \( P \) is power, \( I \) is current and \( V \) is voltage.

Fill factor is calculated by equation 1.6.4b

\[ FF = \frac{J_mV_m}{J_{sc}V_{oc}} \]  \hspace{1cm} \text{(eq. 1.6.4b)}

\( FF \) is the fill factor, \( J_m \) is the maximum current density, \( V_m \) is the maximum voltage, \( J_{sc} \) is the short circuit current density; this occurs when the voltage is equal to zero. \( V_{oc} \) is the open circuit voltage; this occurs when the current is equal to zero.

The ideal electrical behaviour in light and dark conditions for a photovoltaic cell is shown by figure 1.6.4a. These current voltage curves can be used to gain information about the solar cell including the \( V_{oc}, J_{sc} \) as well as the \( J_m \) and \( V_m \). These can be used to gain other useful information as described later 1.6.5.
Chapter 1 Introduction

Figure 1.6.4a A current density vs. voltage for ideal photodiode behaviour for light and dark conditions.

Photovoltaic cells are actually non-ideal so can be described more accurately using the circuit shown in figure 1.6.4b with the resistors corresponding to $R_s$ series resistance and $R_p$ parallel (shunt) resistance.

Figure 1.6.4b A circuit diagram that represents the electronic characteristics of a solar cell a symbol for a solar cell.
1.6.5 Solar Cell Efficiency

The efficiency of a solar cell ($\eta$) is how much light energy is converted to electrical energy. This is calculated by equation 1.6.5a.

$$\eta = \frac{P_{out}}{P_{in}}$$  \hspace{1cm} (eq. 1.6.5a)

$P_{out}$ is the power given out by the system, $P_{in}$ is the incident power into the system.

By combining and rearranging equation 1.6.4a and 1.6.5a to give equation 1.6.5b.

$$\eta = \frac{I_mV_m}{P_{in}}$$  \hspace{1cm} (eq. 1.6.5b)

Rearranging 1.6.4b and combining with equation 1.6.5b to give equation 1.6.5c which makes it easier to calculate efficiency as the parameters are simpler to deal with.

$$\eta = \frac{I_{sc}V_{oc}FF}{P_{in}}$$  \hspace{1cm} (eq. 1.6.5c)

1.6.6 Recombination and Parasitic Resistance

Recombination can occur in many ways including when a conduction band electron recombines with a valence band hole. This can happen in a metal by loss of energy through vibration. In a semiconductor the band gap is too large to do this so it must undergo spontaneous emission of a photon.

There are two types of parasitic resistance; parallel (shunt) and series resistance. In the ideal case parallel resistance should be close to infinity so no current can travel in an unfavourable direction, these are linked to pin holes and defects in the layers. Conversely the ideal case for series resistance should be a value as close to zero as possible so current is not lost through being converted into heat. This is due to the resistance of the semiconductor films as well as resistance between layers and particles. A schematic of these resistances are shown in figure 1.6.4b.
Figure 1.6.6a Non-ideal photodiode behaviour due to increased series resistance $R_s$.

Figure 1.6.6b Non-ideal photodiode behaviour due to decreased parallel resistance $R_p$. 
Figures 1.6.6a and 1.6.6b show the effects of changing these parasitic resistances and how it affects the current voltage characteristics. It can be seen that for increased efficiencies the parallel resistance must head towards infinity and the series resistance must head to zero. They also show that output current is mainly affected by parallel resistance while output voltage is mainly affected by series resistance.

1.7 Present Day Solar Cells

Photovoltaic cells can be classed under different generations:

First generation solar cells are p-n junction and Schottky junction solar cells made from high purity single crystal semiconductor, so as a result were very expensive (20 % efficient at $300/m²)\textsuperscript{43}

Second generation solar cells use the first generation but reduce costs using by cheaper and abundant materials, cheaper manufacturing methods and increasing the cost efficiency (15 % efficient at $75/m²)\textsuperscript{43}

Third generation solar cell are designed to be more efficient and therefore lower the cost. This is achieved by having multiple junctions so they can absorb in multiple regions of the visible light spectrum (40 % efficient at $120/m²)\textsuperscript{43}

Most commercially available solar cells that are seen on house roofs are crystalline silicon. There are two main types of crystalline silicon cells they are single crystal and polycrystalline. Single crystal silicon is very expensive to produce due to the manufacturing process and the high purity materials that are required. Polycrystalline solar cells are cheaper to produce but still relatively high cost. This is due to the expense of high purity silicon as it is used in many applications including computers and other electrical devices.
1.7.1 Different Type of Solar Cells

Many different types of solar cells have been created over time increasing in efficiency as knowledge and technology evolve. Shown in figure 1.7.1a.

Figure 1.7.1a Efficiencies of different solar cells over time.
Table 1.7.1a shows the up to date efficiencies of different types of solar cell as well as open circuit voltages, short circuit currents and fill factors.  

<table>
<thead>
<tr>
<th>Type of solar cell</th>
<th>Solar cell</th>
<th>Efficiency (%)</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon</td>
<td>Crystalline Silicon</td>
<td>25.0 ± 0.5</td>
<td>0.706</td>
<td>42.7</td>
<td>82.8</td>
</tr>
<tr>
<td></td>
<td>Multicrystalline Silicon</td>
<td>20.4 ± 0.5</td>
<td>0.664</td>
<td>38.0</td>
<td>80.9</td>
</tr>
<tr>
<td>III-V</td>
<td>Multicrystalline GaAs</td>
<td>18.4 ± 0.5</td>
<td>0.994</td>
<td>23.2</td>
<td>79.7</td>
</tr>
<tr>
<td></td>
<td>Crystalline InP</td>
<td>22.1 ± 0.7</td>
<td>0.878</td>
<td>29.5</td>
<td>85.4</td>
</tr>
<tr>
<td>Thin film</td>
<td>Silicon</td>
<td>16.7 ± 0.4</td>
<td>0.645</td>
<td>33.0</td>
<td>78.2</td>
</tr>
<tr>
<td></td>
<td>GaAs</td>
<td>27.6 ± 0.8</td>
<td>1.107</td>
<td>29.6</td>
<td>84.1</td>
</tr>
<tr>
<td></td>
<td>CIGS</td>
<td>19.6 ± 0.6</td>
<td>0.713</td>
<td>34.8</td>
<td>79.2</td>
</tr>
<tr>
<td></td>
<td>CdTe</td>
<td>16.7 ± 0.5</td>
<td>0.845</td>
<td>26.1</td>
<td>75.5</td>
</tr>
<tr>
<td>Organic</td>
<td>Organic Polymer</td>
<td>8.3 ± 0.3</td>
<td>0.816</td>
<td>14.4</td>
<td>70.2</td>
</tr>
<tr>
<td></td>
<td>Organic submodule</td>
<td>3.5 ± 0.3</td>
<td>8.62</td>
<td>0.847</td>
<td>48.3</td>
</tr>
<tr>
<td>DSSC</td>
<td>Dye sensitised amorphous Si</td>
<td>10.4 ± 0.3</td>
<td>0.729</td>
<td>22</td>
<td>66.2</td>
</tr>
</tbody>
</table>

1.7.1.1 Silicon Solar Cells

Most commercially available solar cells that are seen on house roofs are crystalline silicon. These are normally polycrystalline silicon. This is due to single crystal silicon being very expensive to produce, whilst polycrystalline is cheaper to produce but still relatively high cost. High purity silicon required for solar cells is also required in many other applications including computers and other electrical devices. These are both classed as first generation and have been around since the early 1940's. They have been in development since having reached
efficiencies of 25 % which is close to the theoretical maximum according to the Schottky Queisser limit.\textsuperscript{43}

1.7.1.2 Thin Film Solar Cells

Thin film solar cells are second generation, these are cheaper to produce than highly crystalline solar cells and can be fabricated from different kinds of semiconductors. Due to the low cost they also have a shorter energy payback time compared to silicon solar cells. The films can be deposited in many different ways, which are normally chosen with cheaper manufacture processing methods than creating a single or multi-crystalline semiconductors.\textsuperscript{43}

1.7.1.3 Organic Solar Cells

Organic solar cells are second generation. As the name suggests they use conducting organic molecules and polymers like fullerenes, polyacetylene, polythiophene and polypyrrole. As described earlier when a photon is absorbed, excitons are generated and charges are separated when they reach a junction with a different work function. This is why organic solar cells use blends to maximise the junctions and minimise the distance the excitons have to travel.\textsuperscript{36, 46}

1.7.1.4 Dye Sensitised Solar Cells

Dye Sensitised solar cells (DSSC) are second generation, usually based on a porous n-type semiconductor, e.g. titanium dioxide that is treated with a dye that binds to the semiconductor. These dyes are tailored to absorb light. Most of the efficient dyes are Ruthenium based with organic ligands. The dye sensitised semiconductor is then placed in an electrolyte, usually triiodide/iodine in an organic solvent which transports holes to the contact.\textsuperscript{36}
1.7.1.5 Extremely Thin Absorber Solar Cells

Extremely Thin Absorber (ETA) solar cells are designed to keep costs low by using a reduced amount of materials. These are similar to DSSC but use a thin layer of inorganic light absorbing materials instead of the dye. They also can be made without electrolyte and use a different semiconductor as the other charge carrier instead.\textsuperscript{36, 43}

1.7.1.6 Perovskite-Based Solar Cells

Perovskite solar cells are a relatively new (first reported in 2009) and are reducing the use of rare and expensive elements such as tellurium, indium and gallium which prevent large scale applications. Perovskite cells typically use lead triiodide perovskite (CH$_3$NH$_3$PbI$_3$) due to its high charge mobility and long charge lifetimes, meaning the current collection from the photoelectrons is efficient and has relatively low recombination. This is one of the reasons why perovskite solar cells have managed to reach efficiencies over 15 % in a short time. Other benefits of using perovskites are their low temperature solution deposition methods.\textsuperscript{47}

1.8 Why Tandem Solar Cells

Tandem solar cell designs are made to absorb high-energy wavelengths at the first half cell, while the lower energy passes through the first half cell and then gets absorbed by the second absorber. This can be carried out multiple times to improve photon harvesting and reduce losses due to thermalisation. The tandem cell approach is a way of managing the light to gain a higher efficiency. This is done by increasing the number of absorbers in the cell, so increasing the number of band gaps available for electrons to be excited into. Tandem cells have less losses due to thermal excitation. The theoretical efficiencies can be improved by increasing the number of absorption layers with materials with suitable band gaps in the device. For one absorption layer the efficiency is 31.0 %, for 2 absorption layers the efficiency increases to 42.5 %, increasing to infinite absorption layers the efficiency is increased to 68.2 % for non-concentrated light.\textsuperscript{43} Having more
than one adsorbing band gap means more of the solar spectrum can be more effectively harnessed.

1.8.1 Tandem Solar Cell Structure

There are two types of tandem solar cell constructions, 4 terminal and 2 terminal configurations shown in figure 1.8.1a. Both these types absorb the high-energy photons first then the low-energy. The 4 terminal can have the cell independently optimised, while the 2 terminal have the cells optimised together. Tandem solar cell efficiencies are shown in table 1.8.1a.

![Figure 1.8.1a Schematic of 4 and 2 terminal tandem configurations.](image)

<table>
<thead>
<tr>
<th>Type of solar cell</th>
<th>Solar cell</th>
<th>Efficiency (% )</th>
<th>( V_{oc} ) (V)</th>
<th>( J_{sc} ) (mA cm(^{-2}))</th>
<th>FF (% )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Multi-junction</td>
<td>GaInP/GaAs/Ge</td>
<td>32.0 ± 1.5</td>
<td>2.622</td>
<td>14.37</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td>GaAs/CIS (thin film)</td>
<td>25.8 ± 1.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Organic (tandem)</td>
<td>8.3 ± 0.3</td>
<td>1.733</td>
<td>8.03</td>
<td>59.5</td>
</tr>
</tbody>
</table>

Tandem cells are made up of a photoanode and a photocathode. The anodic (n-type) side conducts the electrons whereas cathodic (p-type) side conducts holes through the semiconductor lattice. The advantage of having a 2 terminal tandem configuration is the ability to gain an increase in cell voltage, which is explained by the energy diagram shown in figure 1.8.1b. Simultaneous
absorption of photons by n-type and p-type quantum dots (Q-dots) leads to excitement of the electrons from their valence to conduction bands. The electrons in the conduction bands of n-type and p-type quantum dots inject into the conduction band of the n-type semiconductor and the energy level of the redox species in the electrolyte, respectively. The n-type and p-type quantum dots are regenerated by acquiring electrons from the electrolyte and p-type semiconductor valence band, respectively.

Figure 1.8.1b A diagram of the band energies for a low cost tandem solar cell with the voltage produced form each photo electrode giving the total voltage of the complete cell.

1.9 Previous Work of Cathodic Semiconductors in PV Context

p-type semiconductors transport positive charges through the lattice and also impede the movement of electrons making the majority charge carriers positive. These positive charges are called holes. Holes are a lack of an electron in valence band that moves through the lattice.
Wide band gap p-type semiconductors have a high demand due to their wide application such as LEDs, laser diodes, transistors and photovoltaic cells. Desirable properties for semiconductors for cell construction are high porosity, chemical stability, photo stability, suitable band energies positions and a suitable band gap. Examples of wide band gap p-types are copper(I) thiocyanate (CuSCN), copper aluminate (CuAlO$_2$), nickel oxide (NiO) and strontium copper(I) oxide (SrCu$_2$O$_2$). Of these nickel oxide (NiO) is a popular p-type semiconductor material due to its many useful properties. These include its large optical band gap which means it is transparent to visible light, its good hole carrying ability; multiple methods of fabrication and high stability. High porosity is desirable for this type of layer due to the higher internal surface area which helps scatter the light and eventually be absorbed by the absorber material. This also can reduce the thickness of the absorber, reducing the distance the charge has to travel in the absorber which in turn reduces some of the recombinations. This has to be optimised to gain these benefits and minimise problems associated with increasing porosity and recombination sites from defects and pinholes.

p-type absorber semiconductors are also necessary to construct a working tandem solar cell. Copper indium sulfide (CuInS$_2$), copper(I) oxide (Cu$_2$O), cadmium telluride (CdTe), copper indium gallium selenide (CuInGaSe$_2$), tin sulfide (SnS), iron sulfide (Fe$_2$S)$_2$, copper(I) sulfide (Cu$_2$S), copper bismuth sulfide (Cu$_3$BiS$_3$), copper zinc tin sulfide (Cu$_2$ZnSnS$_4$) and gallium nitride (GaN) are examples of p-type absorber semiconductor materials that have band gaps suitable for harnessing the solar spectrum.

1.10 Previous Work of Anodic Semiconductors in PV Context

n-type semiconductors are negative charge transporters. In this case electrons pass through the lattice while positive charges are impeded, making electrons the majority charge carriers. Common n-type semiconductors used in solar cells are titanium dioxide (TiO$_2$) and zinc oxide (ZnO), other semiconductors such as tin oxide (SnO$_2$), niobium(III) oxide (Nb$_2$O$_3$), tungsten trioxide (WO$_3$) and bismuth vanadate (BiVO$_4$) are also used as wide band gap semiconductors.
Chapter Two: Experimental

2.1 Aerosol Assisted Chemical Vapour Deposition

2.1.1 Theoretical background

A number of fabrication methods have been used to construct semiconductor photoelectrodes including electrodeposition,\textsuperscript{70-72} screen printing,\textsuperscript{51} successive ionic layer absorption reaction (SILAR),\textsuperscript{48} pulse laser deposition,\textsuperscript{73} RF sputtering,\textsuperscript{74} sol gel,\textsuperscript{75} spray pyrolysis,\textsuperscript{76, 77} vacuum evaporation,\textsuperscript{78} atomic layer deposition (ALD)\textsuperscript{79} and hydrothermal reactions.\textsuperscript{80, 81}

Of these methods, aerosol assisted chemical vapour deposition (AACVD) a type of chemical vapour deposition (CVD) is very attractive for a number of reasons. First, it complements the well-known techniques of spray pyrolysis and CVD. The recent surge of publications on the topic of AACVD demonstrates the increasing popularity of this method, primarily due to its low cost, simplicity, scalability and reproducibility. It allows the simple fabrication of thin, well adhered, multicomponent films from single source precursors without requiring the use of expensive scientific and technical apparatus. It also provides the flexibility of controlling the texture (and hence the internal surface area of the electrode) systematically by altering the solvents.\textsuperscript{82} Other benefits of AACVD include the removal of the stringent requirements of the use of conventional and expensive CVD apparatus (including compatible metal-organic precursor development), the ability to use precursors of relatively low volatility and the increased compactness of the apparatus and fast processing time compared to other CVD techniques.

The first step in AACVD is to choose a precursor to make the desired film when thermally decomposed. The precursor must also be dissolved or suspended in a solution which can be atomised into an aerosol. The precursor solution remains at ambient temperature and atmospheric pressure while the aerosol is generated by a piezoelectric transducer, the aerosol is then transported into the reaction chamber which is a heated zone by a carrier gas, as shown in the set up in figure 2.1.1a. The reaction chamber can be either vertical or horizontal (depending on the type of the precursor, the solvent used and the thin film deposited).
The AACVD process utilizes a vaporisable/combustible aerosol to deliver the precursors to the heated reaction zone. The formation of fine features at the nanoscale are governed by two main decomposition pathways as shown in figure 2.1.1b. The first is the heterogeneous process, which is similar to the concept of making thin films by spray pyrolysis. In a heterogeneous process, the aerosol cascades onto the heated substrate surface and the film is produced by gradual adsorption and decomposition of material on the substrate surface. The alternative pathway is the homogeneous process, in which the decomposition occurs in the vapour-phase. This process exploits the exothermic high-temperature oxidation of the reactive carrier aerosol to generate steep local temperature gradients for controlling the vapour-phase decomposition for particle formation and growth. Upon entering the high-temperature environment, the carrier aerosol droplets ignite and react exothermically. A series of processes then lead to the vaporisation and condensation of nanoscale particles within the thermal boundary region of the reacting droplets. The formation and growth of the nanoscale particles occur entirely within the thermal boundary region of individual droplets, making each carrier aerosol droplet effectively a micro-reactor. As a result, nanoscale particles from the gaseous state plummet on the substrate surface to produce films. AACVD is thus a relatively simple and versatile technique for nanostructure and texture controlled deposition of thin film electrodes.
The changes made in the deposition solution composition and its influence on the decomposition pathways can be evaluated by understanding the effect on certain fundamental properties. Two key parameters that are influenced by these compositional changes are the aerosol droplet size and the enthalpy of the combustion. The aerosol droplets size depends upon the density and surface tension of the deposition solution at a constant frequency. Estimates of the aerosol droplet size using the equation:

\[ d = \left( \frac{\pi \sigma}{\rho f^2} \right)^{1/3} \]  

(eq. 2.1.1a)

where \( d \) is the aerosol droplet diameter, \( \sigma \) is surface tension of the solvent, \( \rho \) is the solvent density and \( f \) is the frequency of the piezoelectric transducer.

Figure 2.1.1b Different paths of decomposition using AACVD to create thin films
2.1.2 Substrate preparation

Commercially available fluorine doped tin oxide coated transparent conducting glass (FTO) substrates (Pilkington Group Ltd) were used as a substrate. Typical sheet resistance of FTO glass substrates was 8 Ω/□ (TEC 8). The substrate slides were cut into appropriate sizes (i.e. rectangle size of 1 x 2 cm). These were then cleaned and stored in ethanol. In some cases, selected areas of FTO substrates were etched, cleaned and then stored in ethanol.

2.1.2.1 Etching FTO Substrates

First, the selected areas of FTO glass substrates were masked with Kapton tape (DuPont™ Kapton® polyimide films, HN film with Silicone adhesive) in order to protect the conducting oxide coating. In most cases, a 0.6 cm by 1.2 cm area of FTO coating was protected by masking with Kapton tape. The masked FTO substrates were then placed in a shallow petri dish and the exposed area was dusted with zinc powder. 1 M Hydrochloric acid (HCl) was gently poured onto the petri dish and left for 15 min. The samples were then removed from the acid solution and the conductivity of the exposed area was checked with a multi-meter. The etching process was repeated, until the FTO layer had been removed from the glass.

2.1.2.2 Cleaning FTO Substrates

The FTO substrates were washed with cold water and sonicated in propan-2-ol, acetone, ethanol and deionised water (resistivity = 18.2 MΩ) and stored in absolute ethanol until use. This method has been adopted for FTO cleaning as it removes most of the dirt/dust and fatty depositions from the FTO surface.85
2.1.3 Nickel Oxide Thin Film preparation

Porous nickel oxide (NiO) films were prepared for use as a cathodic photo semiconductor which can then be sensitised for use in the construction of solar cells.

A schematic diagram of the two chamber configuration AACVD apparatus is shown in figure 2.1.1a. Each FTO coated glass substrate was heated to 600 °C on a temperature controlled hot plate surface. For the preparation of the NiO films, nickel (II) acetylacetonate (0.05 mol dm\(^{-3}\)) was used as the precursor material. Precursor solution was prepared by heating and stirring nickel (II) acetylacetonate and 1 cm\(^2\) of N,N-dimethylaminoethanol (used to improve the solubility of the nickel(II) complex and to enhance volatility) in toluene for 30 min. The solution was then allowed to cool to room temperature. The precursor solution was placed above the piezoelectric modulator of an ultrasonic humidifier to atomize the solution into fine aerosol droplets. Using air as a carrier gas, the aerosol droplets were first transferred at a flow rate of 0.21 dm\(^3\) min\(^{-1}\) into the first chamber where any large particles were separated and held. A second carrier gas (air) at a flow rate of 2.34 dm\(^3\) min\(^{-1}\) was then used to direct the small particles towards the heated substrate, where they underwent evaporation, decomposition and chemical reaction to synthesise the desired NiO film.\(^{86}\)

\[
2\text{Ni(C}_5\text{H}_8\text{O}_2\text{)}_2\text{(C}_4\text{H}_{11}\text{NO}) + 37\frac{1}{2}\text{O}_2(\text{g}) \rightarrow 2\text{NiO(s)} + 28\text{CO}_2(\text{g}) \uparrow + 27\text{H}_2\text{O}(\text{g}) \uparrow + \text{N}_2(\text{g}) \uparrow
\]

(eq. 2.1.3a)

2.1.4 Copper (II) and Copper (I) Oxide Thin Film preparation

Copper oxide (CuO and Cu\(_2\)O) films were prepared as a cathodic photo absorber and sensitiser for use in the construction of solar cells.

The deposition apparatus was set up as shown in the schematic diagram of the two chamber AACVD configuration in figure 2.1.1a. FTO glass substrates were kept face up on the surface of a temperature controllable hot plate surface and were heated to 600 °C. Copper (II) acetylacetonate (0.0075 mol dm\(^{-3}\)) was used as the precursor material for the preparation of CuO and Cu\(_2\)O films. The precursor solution was prepared by heating and stirring copper (II) acetylacetonate in HPLC grade methanol until a clear blue solution was achieved. The solution
was then allowed to cool to room temperature. The precursor solution was placed above the piezoelectric modulator of an ultrasonic humidifier to atomize the solution into fine aerosol droplets. Using argon as a carrier gas, the aerosol droplets were transferred at a flow rate of 0.21 dm$^3$ min$^{-1}$ into the first chamber where any large particles were separated and held. A second carrier gas (argon) at a flow rate of 2.34 dm$^3$ min$^{-1}$ was then used to direct the small particles toward the heated substrate, where they underwent evaporation, decomposition and chemical reaction to synthesize the copper metal film. This was followed by an annealing step to obtain the desired CuO and Cu$_2$O. The Cu samples were then allowed to cool down to room temperature under argon. Cu samples were also converted to Cu$_2$O or CuO by annealing under argon as described in the chemical equations below.\textsuperscript{87, 88}

\[
\text{Cu(C}_5\text{H}_8\text{O}_2\text{)}_2 \rightarrow \text{Cu(s)} + 6\text{C(s)} + 4\text{CO(g)}↑ + 8\text{H}_2\text{(g)}↑ \quad (\text{eq. 2.1.4a})
\]

\[
4\text{Cu(s)} + 2\text{O}_2\text{(g)} \rightarrow 2\text{Cu}_2\text{O(s)} + \text{O}_2\text{(g)} \rightarrow 4\text{CuO(s)} \quad (\text{eq. 2.1.4b})^{87}
\]

\subsection*{2.1.5 Copper (II) Ferrite Thin Film Preparation}

Copper (II) ferrite (CuFe$_2$O$_4$) films were prepared as a cathodic photo absorber and sensitisier for use in the construction of solar cells.

Copper (II) ferrite (CuFe$_2$O$_4$) precursor was prepared by adding trifluoroacetic acid (0.084 mol dm$^{-3}$ TFA) and N,N-dimethylaminoethanol (0.06 mol dm$^{-3}$ dmaeH) to a stirring solution of iron (III) acetylacetonate (0.06 mol dm$^{-3}$ Fe(acac)$_3$) in methanol at room temperature. After stirring the solution for 20 min, anhydrous copper (II) chloride (0.03 mol dm$^{-3}$ CuCl$_2$) was added to the above mixture and stirred for a further 2 hrs. The reaction mixture was then stirred and gently heated to dryness. The resulting solid residue was redissolved in a solution of 2:3 methanol/ethanol.\textsuperscript{89}

Each FTO glass substrate was heated to 600 °C on the surface of a temperature controlled hot plate. The precursor solution was then placed above the piezoelectric modulator of an ultrasonic humidifier to atomize the solution into fine aerosol droplets. Using air as a carrier gas, the aerosol droplets were initially transferred at a flow rate of 0.21 dm$^3$ min$^{-1}$ into the first chamber where any large
particles were separated and held. A second carrier gas (air) at a flow rate of 2.34 \text{dm}^3 \text{min}^{-1} was then used to direct the small particles towards the heated substrate, where they underwent evaporation, decomposition and chemical reaction to synthesize the desired CuFe$_2$O$_4$ film. Please refer to the figure 2.1.1a for further details of the apparatus.

\[
[\text{Fe}_2(\text{C}_5\text{H}_8\text{O}_2)_4(\text{C}_4\text{H}_{11}\text{NO})_2][\text{CuCl}_4] + 40\frac{1}{2}\text{O}_2^{(g)} \rightarrow \text{CuFe}_2\text{O}_4^{(s)} + 28\text{CO}_2^{(g)} \uparrow + 27\text{H}_2\text{O}_2^{(g)} \uparrow + 2\text{Cl}_2^{(g)} \uparrow + 2\text{NO}_2^{(g)} \uparrow \quad (\text{eq. 2.1.4})^{89}
\]

### 2.1.6 Bismuth Vanadate Thin Film preparation

Bismuth vanadate (BiVO$_4$) films were prepared to make compact anodic photo semiconductor for use as the anode in the construction of solid state solar cells.

For the preparation of the BiVO$_4$ films, bismuth (III) nitrate pentahydrate (0.02 mol dm$^{-3}$) and vanadyl (IV) acetylacetonate (0.02 mol dm$^{-3}$) were used as the source materials. The precursor solution was prepared by heating and stirring bismuth (III) nitrate pentahydrate in methanol. Acetylacetone (0.39 mol dm$^{-3}$) was added to improve the solubility of the bismuth (III) complex and to enhance volatility, Vanadyl (IV) acetylacetonate in methanol was then added until the solution became clear and the resulting mixture was cooled to room temperature. The two chamber configuration AACVD apparatus was used for the BiVO$_4$ film deposition as indicated in figure 2.1.1a. An FTO coated glass substrate was heated to 600 °C on a temperature controlled hot plate. The precursor solution was then placed above the piezoelectric modulator of an ultrasonic humidifier to atomize the solution into fine aerosol droplets. Using air as a carrier gas, the aerosol droplets were transferred at a flow rate of 0.21 \text{dm}^3 \text{min}^{-1} into the first chamber where any large particles were separated and held. A second carrier gas (air) at a flow rate of 2.34 \text{dm}^3 \text{min}^{-1} was then used to direct the small particles toward the heated substrate, where they underwent evaporation, decomposition and chemical reaction (see below) to deposit the BiVO$_4$ films.

\[
2\text{Bi}(\text{C}_5\text{H}_6\text{O}_2)_3 + 2\text{VO}(\text{C}_5\text{H}_6\text{O}_2)_2 + 63\text{O}_2^{(g)} \rightarrow 2\text{BiVO}_4 + 50\text{CO}_2^{(g)} \uparrow + 40\text{H}_2\text{O}_2^{(g)} \uparrow \quad (\text{eq.2.1.6a})
\]
2.1.7 Zinc Oxide Thin Film Preparation

Zinc oxide (ZnO) films were prepared to make compact seed layer films to be used as a base to a porous film for an anodic photo semiconductor which can then be sensitised for use in the construction of solar cells.

As for the AACVD deposition of ZnO thin films, a single chamber configuration AACVD apparatus was used as shown in figure 2.1.7a.

![Figure 2.1.7a A diagram of the two chamber configuration AACVD apparatus set up.](image)

FTO glass substrates were heated to 420 °C on the surface of a temperature controllable hot plate. For preparation of the ZnO films, zinc acetate (0.1 mol dm\(^{-3}\)) was used as the source material. The precursor solution was prepared by heating and stirring zinc acetate in methanol until a clear solution was obtained and then allowing the solution to cool down to room temperature. The precursor solution was then placed above the piezoelectric modulator of an ultrasonic humidifier to atomize the solution into fine aerosol droplets. By using air as a carrier gas, the aerosol droplets were first transferred at a flow rate of 0.25 dm\(^3\) min\(^{-1}\) toward the heated zone. On the heated FTO substrate, the precursor aerosols underwent evaporation, decomposition and chemical reaction and finally deposit the desired ZnO film. The samples where then annealed in air for further 1 hour at 400 °C in a tube furnace.

\[
\text{Zn(C}_2\text{H}_3\text{O}_2\text{)}_2 + 4\text{O}_2(g) \rightarrow \text{ZnO}(s) + 4\text{CO}_2(g)\uparrow + 3\text{H}_2\text{O}(g)\uparrow \quad (\text{eq. 2.1.7a})
\]
2.1.8 Tungsten Oxide Thin Film Preparation

Tungsten oxide (WO₃) films were prepared to make compact seed layer films to be used as a base to a porous film for an anodic photo semiconductor which can then be sensitisitised for use in the construction of solar cells.

As for the AACVD deposition of WO₃ thin films, a single chamber configuration AACVD apparatus was used as shown in figure 2.1.7a. FTO glass substrates were heated to 600 °C on the surface of a temperature controllable hot plate. For the preparation of WO₃ films, ammonium (meta) tungstate hydrate suspension (0.0083 mol dm⁻³) was used as the precursor. The precursor solution was prepared by heating and stirring ammonium (meta) tungstate hydrate in ethanol until a clear solution was obtained and then allowing the solution to cool to room temperature. The precursor solution was then placed above the piezoelectric modulator of an ultrasonic humidifier to atomize the solution into fine aerosol droplets. By using air as a carrier gas, the aerosol droplets were first transferred at a flow rate of 0.25 dm³ min⁻¹ towards the heated zone. On the heated FTO substrate, the precursor aerosols underwent evaporation, decomposition and chemical reaction to deposit the desired WO₃ film.

\[
H_{26}N_6O_{40}W_{12} + 4\frac{1}{2}O_2(g) \rightarrow 12WO_{3(s)} + 6N_2(g)↑ + 13H_2O(g)↑ \quad (eq. 2.1.8a)
\]

2.2 Electrodeposition

2.2.1 Theoretical background

Electrodeposition (ED) has been well-established as a thin film deposition method over a period of several decades.⁹⁰ ED is a vast area of research and development, technological, environmental and wider applications. Therefore, it is impossible to provide a thorough account of the theoretical background of ED.⁹⁰ For the benefit of the work presented in this thesis; a brief description of ED is given below.

Electrodeposition from a solution works on the basis that the movement of ions in an electrolyte solution can be perturbed by an applied electric field (or an applied pulsed electric field), and that nucleation and deposition of desired
materials (or nucleation and precipitation of desired materials, in the case of indirect electrodeposition) as thin films can be facilitated under that circumstance. ED can be generally divided into two systems, namely anodic and cathodic electrodepositions. Typically, at the cathode positively charged ions (usually metal) are attracted and migrate through the solution as the ions get closer to the electrode surface. Its surrounding solution molecules now align with the electric field rather than surrounding the ion. The target ion may get close enough to the surface to be adsorbed. Moreover, it is now close enough for the ions to accept electrons and undergo charge transfer and nucleation to occur on the electrode surface. Further growth of nucleation results in the deposition of desired films on the surface as shown in figure 2.2.1b. The counter electrochemical reaction takes place on the anode surface. By conveniently selecting the anodic and cathodic substrates, films of the desired materials can be obtained by this route. The parameters that affect ED film growth and properties are as follows: current density, agitation, solution temperature, diffusion velocity of ions, concentration of ions, substrates/electrodes shape, substrates/electrodes texture and topography or chemical defects. The films can be single crystal or polycrystalline depending on the solvent type and parameters mentioned above.\textsuperscript{91}

![Diagram of Electrodeposition setup.](image-url)
2.2.2 Nickel (II) Oxide Thin Film Preparation

The substrate was prepared as described in section 2.1.2. Nickel oxide (NiO) films were prepared to make compact films to be used as a base and buffer layer for a porous film for a cathodic photo semiconductor which can then be sensitised for constructing solar cells.

Initially, Ni(OH)\textsubscript{2} thin films were deposited by ED and then converted to NiO. The reference electrode was Ag/AgCl/KCl whereas the counter electrode was Pt. The working electrode was a FTO glass substrate. By using a 0.01 M nickel nitrate (Ni(NO\textsubscript{3})\textsubscript{2}) solution, nickel hydroxide (Ni(OH)\textsubscript{2}) was deposited on to the FTO glass by holding the substrate electrode at 0.6 mA with about 1.5 cm\textsuperscript{3} submerged in the electrolyte for a defined period of time. This period was set for 5 and 10 minutes to achieve the desired film thickness of final NiO layer. The ED reaction is given in equation 2.2.3a and b.\textsuperscript{92-94} These samples were then placed in a tube furnace and heated to 400 °C for 30 min in air, then removed and cooled in air. This is similar to a method followed by K-W Nam et al.\textsuperscript{92} The annealing step in air converted the
nickel hydroxide to NiO by driving off water. This occurs at temperatures above 250 °C to 300 °C as shown in equation 2.2.3c.\(^{92,93}\)

\[
\text{NO}_3^- + 7\text{H}_2\text{O} + 8\text{e}^- \rightarrow \text{NH}_4^+ + 10\text{OH}^- \\
\text{Ni}^{2+} + 2\text{OH}^- \rightarrow \text{Ni(OH)}_2 \\
\text{Ni(OH)}_2 \rightarrow \text{NiO} + \text{H}_2\text{O}
\]

(\text{eq.2.2.3a})^{94}\]

(\text{eq. 2.2.3b})^{94}\]

(\text{eq.2.2.3c})

2.2.3 Zinc Oxide Thin Film Preparation

Zinc oxide (ZnO) films were prepared to make compact seed layer films to be used as a base to a porous film or a porous film for an anodic photo semiconductor which can then be sensitised for use in the construction of solar cells.

Three precursor materials/solutions were used to obtain ED ZnO seed layers on FTO glass substrates for ZnO nano-rod deposition, namely zinc acetate, zinc nitrate and zinc chloride. Each seed layer deposition procedure is given below.

2.2.3.1 Electrodeposition from zinc acetate precursor

First, an aqueous solution of 0.05 M zinc acetate and 0.1 M potassium chloride (KCl) was prepared.\(^{95,96}\) Initially, a potential of -0.54 V was applied to the FTO substrate using a Thurlby power pack. FTO glass was the working electrode in a two electrode set up with Pt gauze as the counter electrode. The solution was mixed with a magnetic flea throughout the deposition (for a period of 1 hour). The ZnO films deposited by this method were not uniform and patchy. The films deposited by this method were not reproducible. Therefore, it was decided to look for alternative methods for ZnO film deposition.

As an alternative method, a solution of 0.05 M zinc acetate and 0.1 M KCl was prepared and maintained at pH 10.56 by using disodium EDTA and KOH. ZnO thin films were electrodeposited by applying a potential of -0.508 V\(^{95}\) (vs. Ag/AgCl reference electrode) using chronoamperometry to a FTO glass substrate
in a three electrode mode. The counter electrode was Pt gauze. Depositions were carried out for a period of 30 or 45 min with a flea stirring throughout the deposition time. Unfortunately, the ZnO seed layers made by this route were also patchy. Hence, it was decided to search for alternative methods of making ZnO seed layers.

2.2.3.2 Electrodeposition from zinc chloride precursor

An aqueous solution of $5 \times 10^{-4}$ M zinc chloride and 0.1 M potassium chloride was prepared. The solution was then oxygenated using compressed gas which was bubbled through the solution for ~2 hours. The solution was heated to ~80 °C using a water bath. Using a chronoamperometry a potential of -1.0 V vs. Ag/AgCl reference electrode was applied to FTO glass in a three electrode system with Pt gauze as the counter. This was carried out with a magnetic flea stirring throughout the deposition time and deposition was carried out for 20 min between 79 - 83 °C. After the completion of the deposition, all samples were dried using a hot air gun, then rinsed with water and dried again with a hot air gun. Unfortunately, the film seed layers made by this route were also patchy. Hence, it was decided to search for alternative methods of making ZnO seed layers.

2.2.3.3 Electrodeposition from zinc nitrate precursor

An aqueous solution of 0.1 M zinc nitrate and 0.1 M potassium nitrate was prepared. Nitrogen was bubbled through the solution for 15 min then the solution was slowly heated to ~70 °C using a water bath. The solution was stirred with a magnetic flea. Using chronoamperometry a potential of -1.0 V vs. Ag/AgCl was applied to the working electrode (FTO glass substrate) in a three electrode system with Pt gauze as the counter. Before the deposition was begun, the FTO surface was pre-coated with ZnO by applying a potential of -1.3 V for 2 min. Then the ED was conducted at -1 V (vs. Ag/AgCl) for 20 min at a temperature between 68 - 75 °C while stirring the ED solution. After the completion of the deposition, all samples were dried using a hot air gun, then rinsed with water and dried again with a hot air gun. Unfortunately, the films were not compact as expected but did
give a uniform film. Because of the uniformity of the film, this was used as a method to fabricate seed layer of ZnO for the ZnO nano-rod growth.

2.2.4 Copper (II) Oxide Thin Film Preparation

Copper (II) oxide (CuO) films were prepared as a cathodic photo absorber and sensitiser for use in the construction of solar cells.

An aqueous solution of 0.01 M copper sulfate (CuSO₄), 0.01 M sodium ethylenediaminetetraacetic (Na₂EDTA) and sodium thiosulfate (Na₂S₂O₃) was prepared. Argon was bubbled through the solution for 15 min then the deposition was also carried out under argon. Using chronoamperometry a potential of -0.6 V vs. Ag/AgCl reference electrode was applied to the working electrode (FTO glass substrate) in a three electrode system with Pt gauze as the counter. The deposition was carried out at room temperature for 30 min. The samples were then annealed at 500 °C for 30 min using a ramp rate of 20 °C/min before being allowed to cool to room temperature.

2.3 Chemical Bath Deposition

2.3.1 Theoretical background

Chemical bath deposition (CBD) is a deposition process that is suited to large area thin film fabrication as it is a low cost, simple and low temperature method (normally below 100 °C). Chemical bath deposition requires substrates to be immersed into a dilute solution of soluble salts. The reactions are designed to precipitate the desired material onto the substrate.

\[ \text{M}_x\text{X}_y + y\text{NaY} \rightarrow x\text{MY}(s)\downarrow + y\text{NaX} \]  

(eq.2.3.1a)

MY is the material that is desired to be deposited which is in soluble in the solvent of choice so as to allow precipitation, MₓXᵧ is the soluble metal salt (X represents a halide, nitrate or other soluble anion) and NaY is any soluble salt with the appropriate cation required for the desired material.
The reaction is sometimes carried out at elevated temperatures to decrease the deposition time or to provide enough energy to pass the energy barrier of the reaction. When the precipitate is formed, it coats all the surfaces that are immersed in the solution. This is due to the pH of the solution creating a surface charge which is determined by the zero point charge (pz0) of the substrate surface and causes deposition onto the substrate.\(^9\)

![Diagram of CBD setup](image)

**Figure 2.3.1a shows a diagram of CBD setup.**

Chemical bath deposited films can occur through ion by ion growth and cluster by cluster growth mechanisms.\(^{10}\) The ion by ion growth mechanism takes place on the substrate at a surface nucleation site by successive anion / cation adsorption and the crystal growth by successive adsorption on the crystal. The cluster by cluster growth mechanism occurs when the anion / cations nucleate in the solution to form colloids. These colloids increase in size and also combine with smaller colloids through Ostwald ripening until they can no longer be suspended in solution and precipitate. These colloids can be made of the insoluble material which is desired or a hydroxide which later undergoes decomposition to the desired material.

![Schematic of CBD deposition main mechanisms](image)

**Figure 2.3.1b Schematic of CBD deposition main mechanisms.**
The use of different precursors, additives and temperatures can affect the mechanism and structure of the deposited film.\textsuperscript{101, 102} Zinc oxide is a very well studied material and many morphologies have been created using chemical bath deposition including rods, sheets, spindle, snowflakes, tubes, belts and ellipses.\textsuperscript{101}

2.3.2 Zinc Oxide Seed layer

The substrate preparation is already described in section 2.1.2. Zinc oxide (ZnO) seed layers were found to be essential for the growth of nano-rods on FTO substrates by CBD. Deposition of rods was not observed without a ZnO seed layer. Zinc oxide seed layers were prepared using AACVD (as discussed in section 2.1.7) and electrodeposition (as discussed in section 2.2.4).

2.3.3 Zinc Oxide nano-rod and nano-tube Thin Film Preparation

ZnO films were prepared to make porous films on top of a compact seed layer for an anodic photo semiconductor which can then be sensitised for use in the construction of solar cells.

2.3.3.1 Chemical Bath deposition of Zinc Oxide nano-rods

ZnO nano-rods were grown on the ZnO seed layer previously prepared on FTO substrates (sections 2.1.7 and 2.2.4). ZnO compact seed layer containing FTO glass substrates were mounted back to back using double sided tape. These were then attached to a stand by a rig with crocodile clips protected with PTFE tape.

First, 75 ml of 0.02 M Zn(NO$_3$)$_2$ aqueous solution was added to 75 ml of 0.8 M NaOH aqueous solution while stirring in a 250 ml 3 necked round bottom flask. Then, the solution was carefully heated up to 80 °C. As soon as the solution temperature reached 80 °C, the stirring was stopped and the seeded FTO samples were lowered into the solution and left for 50 min.\textsuperscript{103} The temperature of
the CBD solution was maintained at 80 °C by using a heating block and an external temperature probe (IKATRON ETS D3) in feedback loop control. After the 50 min period, the samples were removed and dried with cool air before rinsing with distilled water and dried with cool air again.

2.3.3.2 Chemical Bath etching/conversion of Zinc Oxide nano-rods to nano-tubes

In order to achieve high surface area of textured ZnO electrodes, ZnO nano-rods samples were converted to ZnO nano-tubes by chemical bath etching/conversion. As in the previous case, ZnO nano-rod electrodes were mounted back to back using double sided tape. These were then attached to a stand by a rig with crocodile clips protected with PTFE tape. A 150 ml of 3.5 M KCl solution was placed in a 250 ml 3-necked round bottom flask. The solution was carefully heated to 85 °C and the temperature maintained by using a heating blocks and an external temperature probe (IKATRON ETS D3). When the solution was at 85 °C, the samples with ZnO rods were lowered into the solution with gentle stirring and left for ~24 hours. After etching was completed, the samples were removed and dried with cool air. Then the samples were rinsed with distilled water and dried with cool air again.

2.3.4 Copper Indium Sulfide Thin Film Preparation

Copper indium sulfide (CulnS₂) films were prepared as a cathodic photo absorber and sensitisfer for use in the construction of solar cells.

A 10 ml of 1.2 M thioacetamide \((C_2H_5NS)\) aqueous solution was added to 10 ml of aqueous 0.8 M InCl₃, 10 ml of an aqueous solution of 0.3 M CuSO₄ and 10 ml of distilled water was added while stirring in a 50 ml beaker. Then, the solution was carefully heated up to 80 °C. As soon as the solution temperature reached 70 °C, the samples were lowered into the solution and left for 30 min. The temperature of the CBD solution was maintained at 80 °C by using a heating block and an external temperature probe (IKATRON ETS D3) in feedback loop control. After the 30 min period, the samples were removed and dried with cool air before
rinsing with distilled water and dried with cool air again. The depositions were repeated with each sample. The samples were annealed under Ar to 300 °C for 30 min using a ramp rate of 15 °C/min then allowed to cool to room temperature under Ar.

2.4 Doctor Blade Technique

2.4.1 Theoretical background

Doctor blade technique is a physical coating method. The blade or applicator is set a certain distance from the substrate surface. This applies a paste or slurry made for the desired film linearly spread cross the substrate surface leaving a thin wet film which requires drying through evaporation.\(^\text{105}\) The wet films prepared by this method sometimes require post-heating depending on the solvent and binder type used in the paste.

![Diagram of doctor blade setup](image)

**Figure 2.4.1a shows a diagram of doctor blade setup.**

Film thickness can be calculated by the thickness formula.

\[
d = \frac{1}{2} \left( g \frac{c}{\rho} \right)
\]

(eq. 2.4.1a)

\(d\) is film thickness, \(g\) is the gap between the blade and the substrate, \(c\) is the solid content \(\text{g/cm}^3\) and \(\rho\) is the final density of the film \(\text{g/cm}^3\).
2.4.2 Nickel (II) Oxide Thin Film Preparation

2.4.2.1 NiO paste preparation

The substrate preparation is already described in section 2.1.2. 1.5 g of nickel oxide (nano-powder 30 nm MTI Corporation); 5 ml of 10 % ethanol cellulose in ethanol; and 10 ml of α-terpinol was placed into a ball mill machine (Fritsch, pulveriště 6) and ball milled for 2 hours at 230 rpm. After the ball milling process the resultant paste was then allowed to settle so that large particles sunk to the bottom. Only the top of the paste was used for doctor blading. This is the same procedure as that reported by A. Nattestad et al.50

2.4.2.2 Doctor blading of the paste

Nickel oxide (NiO) paste was spread on top of the FTO coated glass substrate by the doctor blade technique. One layer of Scotch tape was used as a spacer and the wet paste was also spread only once. As soon as the wet coating was obtained on the substrates, they were subjected to a heating cycle in order to increase the adherence of the coating onto the FTO substrate. To obtain the adherence, the samples were placed on a hot plate and gently heated to 80 °C for 10 min, then to 120 °C for 10 min, then to 200 °C for 5 min and finally to 250 °C for 10 min and then the samples were allowed to cool at room temperature. The heating cycle is described in the figure 2.4.3a below. Next, they were placed in a gas evacuated tube furnace and heated at 350 °C for 30 min with a ramp rate of 15 °C per min. Finally, the samples were allowed to cool to room temperature under vacuum. The resulting NiO films were pale green in colour.
2.5 Electrodeposition and doctor-blade combined technique

A disadvantage of the doctor blade technique is the creation of pinholes which means the electrolyte can directly contact with the FTO. This contact can lead to recombination which greatly reduces cell efficiency. Electrodeposition gives good coverage but has the problem that the films do not have as high porosity as doctor bladed NiO so have lower surface area.

A combination of electrodeposition and doctor blade techniques were used to gain the benefits of each technique and eliminate some of the flaws to which these techniques are prone. Electrodeposition methods allow good coverage of coating material with minimal pinholes whereas the doctor blade technique gives a film with a well-controlled porous textured morphology. By combining these two techniques, films with desired texture were achieved. The blocking layer helped to minimise the interface between the back contact with the electrolyte therefore reducing paths for recombination. Electrodeposition can also be performed after the doctor blade technique has been used to obtain thin films. This causes deposition deep within the porous layer close to the back contact due to less resistance and therefore blocking the FTO surface first\textsuperscript{106} as well as improving electrical contact between the doctor bladed NiO particles.
2.5.1 Nickel (II) Oxide Thin Film Preparation

Nickel (II) oxide thin films were prepared using this combined ED and doctor blade technique. First the electrodeposition was used to achieve a compact NiO film (refer to the section 2.2.3). Then, the doctor blade route was followed to deposit a textured NiO layer on top of the compact NiO film (section 2.4.3).

2.6 Construction of Cathodic Photoelectrochemical Cells

2.6.1 Cathodic Photosensitised NiO Cells using CuInS$_2$ as the Sensitiser

Nickel Oxide (NiO) films were prepared for use as a cathodic photosemiconductor which can be used and sensitised to fabricate photocathodes. Copper indium sulfide was chosen as the sensitizer due to its p-type behaviour and its optical band gap which is $\sim 1.5$ eV.$^{107}$ This band gap is desirable for terrestrial solar absorption. This can then be used as a photocathode in construction of solar cells.
The photocathodes were fabricated by two successive steps; NiO was firstly deposited onto FTO using ED for 5 min (as described in section 2.2.3). Then CuInS$_2$ was deposited onto the porous NiO using CBD (as described in section 2.3.5).

Unfortunately CuInS$_2$ proved to be unstable in several electrolytes and was difficult to reproduce as it could be clearly seen that the film on the samples were not uniformly distributed leading to different current voltage curves for the same parameters.

### 2.6.2 Cathodic Photosensitised NiO Cells using CuO as the Sensitiser

Porous nickel oxide (NiO) films were prepared for use as a cathodic photosemiconductor which can then be sensitised. Copper Oxide was chosen as the sensitisier due to its p-type behaviour and its optical band gap which is ~1.6 eV.$^{108}$ This band gap is desirable for terrestrial solar absorption. CuO can be used as a sensitiser in photocathodes to construct a solar cell. CuO was also chosen over Cu$_2$O. CuO is more stable compared to Cu$_2$O, and also exhibits a greater $J_{sc}$ performance, as found from the experiment carried out in section 2.1.4.

NiO was deposited onto FTO coated glass substrates using electrodeposition and doctor blade combination as described in section 2.5.1. CuO thin films were deposited onto the porous NiO using AACVD as described in section 2.1.4 using air as the carrier gas.

NiO was successfully sensitised with CuO and this was carried forward to make solid state solar cells.

### 2.7 Construction of Fully Solid-State Cathodic Photosensitised Solar Cells

Various semiconductor materials, (NiO, CuO, CuFe$_2$O$_4$, ZnO, WO$_3$ and BiVO$_4$) were used in different solid state cell combinations to construct a range of fully solid-state cathodic photosensitised solar cells. The figure 2.7 shows the layered deposition structure of the materials to construction of such devices.
2.7.1 Cathodic Photosensitised NiO Cells using CuO as the Sensitiser and ZnO as the Anode Semiconductor Phase

Nickel oxide (NiO) films were prepared to make a porous film to be sensitised. Copper oxide (CuO) was chosen as the sensitisier due to its success in experiment in section 2.6.2. In this instance however, CuO was deposited using electrodeposition to maximise contact between the NiO and CuO. It was also hoped that this approach would give deeper penetration of the pores and fill nearer the back contact, leading to less resistance as well as minimising the distance and therefore shorting the hole diffusion length and reducing recombination. Zinc oxide (ZnO) was chosen for the anodic photo-semiconductor which would act as the electron transporter in the construction of a solid state solar cell. ZnO has a high flatband potential and a wide band gap of $\sim 3.2$ eV. The schematic of the layers is shown in figure 2.7a.

NiO was deposited onto FTO using electrodeposition and doctor blade combination as described in section 2.5.1. On top of the NiO sample, CuO was deposited using ED as described in section 2.2.5. On top of this, NiO, CuO samples, ZnO was deposited using AACVD at 600 °C as described in section 2.1.7. These samples were then annealed at 600 °C for 30 min.
Solar cells constructed this way only showed ohmic and photoconductivity behaviour with no $J_{sc}$ or $V_{oc}$. So this line of investigation was terminated and the knowledge gained was carried forward to different solar cells.

### 2.7.2 Cathodic Photosensitised NiO Cells using CuFe$_2$O$_4$ as the Sensitiser and ZnO as the Anode Semiconductor Phase

Porous nickel oxide (NiO) films were prepared for use as a cathodic photo semiconductor which can then be sensitised. NiO was deposited using AACVD to maximise the contacts between the NiO and FTO as well as forming larger pores for the absorber to penetrate. This would maximise contact and minimise resistance by reducing the distance the holes would have to travel, and therefore reduce recombination. Copper (II) ferrite (CuFe$_2$O$_4$) was chosen as the sensitiser due to its p-type behaviour and direct optical band gap which is $\sim1.42$ eV.$^{112}$ This band gap is desirable for terrestrial solar absorption. AACVD was used to deposit a compact layer and improve contact. Zinc oxide (ZnO) was chosen for the anodic photo-semiconductor which would act as the electron transporter in constructing solid state solar cells. AACVD was used to deposit a compact layer to fill the pores and make good contact with CuFe$_2$O$_4$. Annealing was used to improve the contact between each layer. The schematic of the layers is shown in figure 2.7b.

NiO was deposited on FTO using AACVD as described in section 2.1.3. On top of the NiO sample CuFe$_2$O$_4$ was deposited using AACVD as described in section 2.1.5. On top of the NiO, CuFe$_2$O$_4$ samples, ZnO was deposited using AACVD at 600 °C as described in section 2.1.7. These were then annealed at 600 °C for 30 min.

These solar cells showed an improvement on the previous and they were photo active. Unfortunately the photo activity was very low with a $J_{sc}$ that was barely measurable.
2.7.3 Cathodic Photosensitised NiO Cells using CuFe$_2$O$_4$ and CuO as Sensitisers and ZnO as the Anode Semiconductor Phase

Nickel oxide (NiO) films were prepared to make a porous film to be sensitised. Copper (II) ferrite (CuFe$_2$O$_4$) and copper oxide (CuO) were chosen as the sensitiser due to their p-type behaviour and direct optical band gaps. The combination of CuFe$_2$O$_4$ and CuO lead to improved performance. AACVD was used to deposit these layers to provide good contact and compact layers. Zinc Oxide (ZnO) was chosen for the anodic photo-semiconductor which would act as the electron transporter in the solid state solar cell. AACVD was used to deposit a compact layer to fill the pores and make good contact with CuO. Annealing was used to try and improve the contact between each layer. The schematic of the layers is shown in figure 2.7c.

NiO was deposited on FTO using AACVD as described in section 2.1.3. On top of the NiO sample CuFe$_2$O$_4$ was deposited using AACVD as described in section 2.1.5. On top of the NiO, CuFe$_2$O$_4$ sample CuO was deposited using AACVD as described in section 2.1.4. On top of this the NiO, CuFe$_2$O$_4$, CuO samples, ZnO was deposited using AACVD at 600 °C as described in section 2.1.7. These were then annealed at 600 °C for 30 min.

Unfortunately, these solar cells also showed very low photo activity with a $J_{sc}$ that was barely measurable and also an increase in series resistance.

2.7.4 Cathodic Photosensitised NiO Cells using CuO as the Sensitiser and WO$_3$ as the Anode Semiconductor Phase

Porous nickel oxide (NiO) films were prepared to be sensitised. Copper oxide (CuO) was chosen as the sensitiser due to its p-type behaviour and direct optical band gap. AACVD was used to deposit a compact layers and also to improve layer to layer contact. Tungsten oxide (WO$_3$) was chosen as the anodic photo semiconductor which would act as the electron transporter in constructing a solid state solar cell. WO$_3$ has good transmission above 80 % at wavelengths greater than 300 nm and a wide band gap of ~2.7 eV.$^{110,113}$ AACVD was used to deposit a compact layer to make good contact with CuO. Annealing was used to
improve the contact between each layer. The schematic of the layers is shown in figure 2.7d.

NiO was deposited onto FTO using AACVD as described in section 2.1.3. On top of the NiO sample CuO was deposited using AACVD as described in section 2.1.4. On top of the NiO, CuO sample WO₃ was deposited using AACVD as described in section 2.1.8. These were then annealed at 600 °C for 30 min.

Solar cells fabricated by this method showed very low photo activity with a $J_{sc}$ that was barely measurable. This poor result was due to bleaching of the CuO layer when depositing WO₃. This bleaching could be the result of the conversion of CuO to CuWO₄, similar to that discovered by J.Y. Zheng et al. The equations below show how this could occur.

$$\begin{align*}
H_2W_2O_{11} + 2CuO &\rightarrow 2CuWO_6 + H_2O(g)↑ \\
CuWO_6 &\rightarrow CuWO_4 + O_2(g)↑
\end{align*}$$

(eq. 2.7.4a)\(^{108}\) (eq. 2.7.4b)\(^{108}\)

### 2.7.5 Cathodic Photosensitised NiO Cells using CuFe₂O₄ as the Sensitiser and WO₃ as the Anode Semiconductor Phase

Porous nickel oxide (NiO) films were prepared to be sensitised. Copper (II) ferrite (CuFe₂O₄) was chosen as the sensitiser due to its p-type behaviour and direct optical band gap. CuFe₂O₄ was also chosen to try and stop the bleaching that occurred when using CuO. AACVD was used to deposit a compact layer and also provide good layer contact. Tungsten Oxide (WO₃) was chosen for the anodic photo semiconductor to act as the electron transporter in the construction of a solid state solar cell. AACVD was used to deposit a compact layer to fill the pores and make good contact with CuFe₂O₄. Annealing was used to try and improve the contact between each layer. The schematic of the layers is shown in figure 2.7e.

NiO was deposited onto FTO using AACVD as described in section 2.1.3. On top of the NiO sample CuFe₂O₄ was deposited using AACVD as described in section 2.1.5. WO₃ was deposited on top of this using AACVD as described in section 2.1.8. These were then annealed at 600 °C for 30 minutes.
These solar cells showed very low photo activity with a $J_{sc}$ that was just visible above the noise but did demonstrate that the concept was possible.

### 2.7.6 Cathodic Photosensitised NiO Cells using CuFe$_2$O$_4$ and CuO as Sensitisers and BiVO$_4$ as the Anode Semiconductor Phase

Nickel oxide (NiO) films were prepared to make a porous film that was sensitised. Copper (II) ferrite (CuFe$_2$O$_4$) and Copper oxide (CuO) were chosen as the sensitisers due to their p-type behaviour and direct optical band gaps. The combination of CuFe$_2$O$_4$ and CuO lead to improved performance. AACVD was used to deposit compact layers with good layer to layer contact. Bismuth vanadate (BiVO$_4$) was chosen for the anodic photo semiconductor which would act as the electron transporter in the construction of a solid state solar cell. BiVO$_4$ has a direct optical band gap of ~2.4 eV and good n-type behaviour. AACVD was used to deposit a compact layer to fill the pores and make good contact with CuO. Annealing was used to try and improve contacts between each layer. The schematic of the layers is shown in figure 2.7f.

NiO was deposited onto FTO using AACVD as described in section 2.1.3. On top of the NiO sample CuFe$_2$O$_4$ was deposited using AACVD as described in section 2.1.5. On top of the NiO, CuFe$_2$O$_4$ sample CuO was deposited using AACVD as described in section 2.1.4. On top of this the NiO, CuFe$_2$O$_4$, CuO sample BiVO$_4$ was deposited using AACVD as described in section 2.1.6. These were then annealed at 600 °C for 30 minutes.

Cathodic photosensitised NiO cells constructed using CuFe$_2$O$_4$ and CuO as the sensitisers and BiVO$_4$ as the anodic semiconductor phase were shown to demonstrate promising results. Thus further examination was performed and a comprehensive study was conducted on this particular device configuration to optimise the performance. Individual device components (i.e. individual layers) were also subjected to further studies.
Chapter Three: Material Characterisation Techniques

3.1 X-ray Diffraction

X-ray Diffraction (XRD) is a useful analytical technique for solids as it is non-destructive and can be used to determine the material fabricated by the position of atoms in the crystal lattice. X-rays are scattered by the electron clouds around atoms. The interatomic distances have the correct intervals to cause interference of X-rays.\(^{115}\) The X-rays are scattered by the atoms in the material on different planes. These planes are described by the Miller indices with the descriptions \(h, k\) and \(l\), these have values of zero, positive or negative integers. The separation of these planes can be described using the lattice spacing \(d\) and the Miller indices \(hkl\) normally denoted as \(d_{hkl}\).\(^{116}\)

![Diagram](image)

**Figure 3.1a The reflections of X-rays by atoms in the lattice planes.**\(^{117}\)

For a reflection in the XRD pattern to occur, the reflected X-rays by angle \(\theta\) must all be in phase. When the primary X-ray beam has the same angle, \(\theta\) with the atomic planes then the angle of incidence (90° – \(\theta\)), is the same for the reflected X-ray beam (Figure 3.1a). Therefore the wave fronts A’ and B’, must
have path lengths that vary by an exact integer \((n)\), for the reflected X-rays to be all in phase. Hence the path difference \((\delta)\) is a product of the integer and wavelength \((\delta = n \lambda)\). As CD and CC’ are wave fronts of the primary and reflected X-rays, respectively, for constructive interference the path difference can be written as\(^{116}\)

\[
\delta = DE + EC' = 2d_{hkl}\sin\theta = n\lambda \quad \text{(eq.3.1a)}
\]

Lattice spacing and incident angle of the X-ray is described by the Bragg equation 3.1a. The Bragg equation can be used to calculate the lattice spacing using the constructive interference and the angle\(^{118}\)

\[
n\lambda = 2d_{hkl}\sin\theta \quad \text{(eq. 3.1b)}
\]

Powder samples have a large number of small crystallites that are randomly aligned, meaning the X-rays are diffracted in all directions simultaneously as described by the Bragg equations, therefore producing continuous cones of diffraction. Measuring the angle positioning of the cones by photographic film or a radiation detector can be used to determine the diffraction pattern that is like a fingerprint for the crystalline material\(^{116}\). Therefore, these can be used to determine the material, the lattice parameters, crystallinity and phase of a crystallite material. These materials can be matched with other spectra from JCPDS (Joint Committee on Powder Diffraction Standards) of which there are thousands of standards available. All of this can be carried out without causing damage to the sample. However XRD cannot characterise amorphous materials\(^{118}\).

Since each crystalline material is unique (due to the organisation, distance and positioning of each atom) constructive and destructive interference of the scattered X-rays are also unique for each material like a fingerprint. NiO, for example has a cubic rocksalt crystal structure which is a face centred cubic lattice as shown in figure 3.1b.
Chapter 3 Characterisation Techniques

Figure 3.1b Schematic of NiO face centred cubic crystal lattice.

The XRD diffraction pattern contains specific reflections at different degrees which correspond to different planes that reflect the X-rays causing interference. The figure 3.1c shows the discrete reflections of crystalline NiO.

Figure 3.1c A typical XRD diffraction pattern for NiO with each reflection labelled with the plane causing the reflection.
Chapter 3 Characterisation Techniques

The phase and crystallinity of samples were analysed using X-ray Diffraction (XRD). The samples were prepared by placing them in holders using blue tac so the glass was flush with the top of the sample holder. The samples were then placed in the X-ray diffractometer (Bruker D8) in the grazing incidence mode (scanning angle between 15° and 70°), and operating with monochromatic high density Cu Kα1 (wavelength, \( \lambda = 0.154 \) nm) radiation using a PSD detector as shown in figure 3.1d. Each sample was run for 1 or 2 hours.

Figure 3.1d A photo of D8 X-ray diffractometer that was used.

An important feature of XRD analysis is its ability to estimate the crystallite size in the material. The crystallite size \((t)\) is obtained from Scherrer equation (equation 3.1c)

\[
t = \frac{K \lambda}{B \cos \theta} \quad \text{(eq. 3.1c)}
\]
Where $\lambda$ is the wavelength of the incident X-ray (in nm), $K$ is a constant (here assumed to be $0.94^{119}$), $B$ is the full-width-half-maximum (FWHM) value of the specific diffraction peak (in radians), and $\theta$ is the angle at which the peak is observed. The width of the peak is strongly affected by instrumental effects and stress in the film.$^{120}$ As shown in equation 3.1c, in highly crystalline materials where crystallite size are large, $B$ must be small thus sharp reflections are observed. So the less crystalline materials have broader reflections.

### 3.2 Raman Spectroscopy

Raman Spectroscopy is another non-destructive characterisation method which relies on an inelastic light scattering by elementary excitations from lattice vibrations.$^{121}$ The incident photons are generated by a non-ionising laser which can be absorbed, scattered or pass through the sample without interaction. The scattering occurs due to the incident photon being distorted by the electron clouds.

With visible and near-infrared radiation two types of scattering; Rayleigh and Raman can occur. Raman scattering occurs when the vibrational state of the molecule changes and there is an energy transfer from the photon to the molecule or the other way around. This is an inelastic process and in general is weak with approximately one in every $10^6$ - $10^8$ of scattered photons being Raman.$^{122, 123}$ Interaction of a molecule with an electromagnetic field would lead to the transfer of energy from the field to the molecule only if the Bohr frequency condition is met (Equation 3.2a)

\[
\Delta E = h\nu = h\frac{c}{\lambda} = h\bar{\nu}
\]  

(eq. 3.2a)

$\bar{\nu}$ is a wavenumber and $\Delta E$ is the energy difference between two quantised states.$^{124}$
Figure 3.2a A description of the vibrational Raman effects based on energy level approach.

The energy difference between the incident and emitted radiation equals one quantum of vibrational energy and the emitted photons are called Stokes photons. However, if the molecule loses vibrational energy and upon re-emission the obtained photons possess higher energies than the excitation energy, these photons are called anti-Stokes photons. The scattered irradiation involves two parts. Firstly, Rayleigh scattering where the frequency remains the same as the incident beam and secondly, Raman scattering at which frequency is shifted by the value of the vibrational frequency of the molecule. This Raman shift in the energy of the laser photons leads to the formation of Raman spectrum for the specific material, hence enabling Raman spectroscopy to be used as a method to identify different compounds. Raman also has the advantage of being able to study amorphous samples as it relies on the whole molecule interaction rather than the lattice structure. The vibrational interaction with the molecule can also be used to help analyse functional group and other chemical bonds by their vibrational modes at different wavenumbers. These specific vibrational modes can be used to identify the material being analysed. Figure 3.2b shows an example of Raman spectroscopy for NiO.
Figure 3.2b Typical Raman spectrum of NiO with each peak labelled with the wavenumber.¹²⁷

Raman spectroscopy was performed using a HORIBA Jobin Yvon LabRAM HR (with 632.8 nm He-Ne laser) Raman spectrophotometer (HORIBA Jobin Yvon Ltd., Middlesex, UK). The spectra were obtained in the range of 100 to 1600 cm⁻¹.

3.3 Field Emission Gun Scanning Electron Microscopy

Secondary electrons are generated when the primary beam of electrons (from the field emission gun) interacts with the electrons in the analyte. This electron transfers enough energy to the analyte electron to be ionised out of the sample at characteristic energies. These secondary electrons provide surface information, as secondary electrons are generated near the surface. Secondary electrons generated near the surface are likely to leave the sample while secondary electrons generated deep in the sample will likely be reabsorbed before they can escape, as shown in figure 3.3a.
Field Emission Gun Scanning Electron Microscope (FEG-SEM) is a topographical technique that can also be used to show the cross sectional film thickness if samples are specially prepared. FEG-SEM uses a large stable current with low voltage in a small beam under high vacuum. The system works by scanning the surface of the sample with a focused beam of electrons, which frees electrons from the atoms at the surface (from a depth of a few nm), as well as being reflected back from the sample. These freed electrons are called secondary electrons, and have energies of less than 50 eV. Secondary electrons are collected by an Everhard-Thornley detector and are converted in to a signal which is processed in to an image of the surface. Reflected electrons have energies of greater than 50 eV and can be collected by a second detector. These electrons are commonly referred to as backscattered electrons and provide elemental analysis as elements with large atomic numbers generate a higher number of back scattered electrons than those with lower atomic numbers.
The surface morphology and cross section of samples were investigated using FEG-SEM. The sample is required to be clean, vacuum compatible and electrically conductive.\(^\text{131}\) Samples were cut and fixed to aluminium studs with conducting carbon tabs. Silver paint was used to make good contact with the stud and the sample. While the electrodes fulfil the first two criteria, the third is not achieved, as the samples are constructed from a wide band gap semiconductor. Therefore samples were placed in a gold evaporator and a thin film of gold was deposited. These were then placed in the Leo 1530 VP FEG-SEM equipment for imaging using a 5 kV accelerating voltage and a 30 \(\mu\text{m}\) aperture in a high vacuum.\(^\text{132}\)
3.4 Ultraviolet-Visible Spectroscopy

Ultraviolet-Visible spectroscopy is used to study the optical properties of materials. These are important for understanding components in a solar cell. The outer energy levels of electrons consists of optical transition energies in a range of about 1–6 eV, 200 nm to 3000 nm wavelength range. This wavelength range is known as the optical range and covers ultraviolet (UV), visible and infrared regions. When solid materials are illuminated by a light beam of intensity $I_0$, and the light beam crosses the sample, as a result of absorption, reflection and scattering of the beam by the sample, the intensity of the transmitted beam is reduced to $I$. The beam intensity attenuation $dl$, after passing through the differential thickness $dx$, of a material is formulated using Equation 3.4a.

$$dl = -\alpha I \, dx$$  \hspace{1cm} (eq. 3.4a)

Where $I$ is the beam intensity at a distance $x$ into the material and $\alpha$ is the absorption coefficient of the material. Upon integration of Equation 3.4a, the Beer-Lambert law is obtained (Equation 3.4b) which relates the incoming light intensity to the thickness.

$$I = I_0 e^{-\alpha x}$$  \hspace{1cm} (eq. 3.4b)
Experimental optical spectra are usually plotted showing the intensity of (absorbed, emitted, reflected, or scattered) radiation as a function of the photon energy (in eV), wavelength (in nm), or the wavenumber (in cm$^{-1}$).  

$$E = \frac{hc}{\lambda} = \frac{1240}{\lambda} = 1.24 \times 10^{-4} \tilde{\nu}$$  

(eq. 3.4c)

Optical spectrophotometers function at different modes to measure different optical properties of materials, such as optical density (OD), absorbance (A), or transmittance (T). These parameters are calculated using the following equation, providing that the thickness of the sample is known.

$$A = OD = \log \frac{l_0}{I}$$  

(eq. 3.4d)

$$\alpha = \frac{(OD)}{x \log e} = \frac{2303 (OD)}{x}$$  

(eq. 3.4e)

$$T = \frac{I}{I_0} = 10^{-OD}$$  

(eq. 3.4f)

$$A = -\log_{10} T = -\log_{10} 10^{-OD} = OD$$  

(eq. 3.4g)

As can be understood by the above equations, for low optical densities, absorbance will be very close to optical density ($A \approx OD$) so that the absorbance spectrum displays the same shape as the optical density.

Optical absorption measurements were performed using a Perkin-Elmer Lambda 35 UV-vis spectrophotometer. A bare FTO substrate was used as reference. The films were scanned in the range of 300-800 nm with a slit size of 2 nm. Absorbance, transmittance and Tauc plots of different samples were plotted to study the optical transitions and band gap energies of deposited films. The light passes through a series of slits and gratings before it is split into two equal beams (i.e. the dual beams). Consequently the light that passes to the samples travels in one direction and little scattering occurs. As the light travels through the sample, some of the light is absorbed by the various layers in the electrode. Light that is transmitted is detected by the photodiode, which generates an electrical current proportional to the amount of light absorbed at different wavelengths, resulting in an absorbance vs. wavelength spectrum. To get around the scattered light
problem, an integrating sphere can be used to collect the scattered light by redirecting to the detector.

Figure 3.4b shows a schematic of a dual beam setup.\textsuperscript{134}

Figure 3.4c shows a schematic of an integrated sphere.\textsuperscript{135}

3.5 Current Density Voltage Curves

PEC performance was measured using current density–voltage $(J-V)$ measurements. $J-V$ measurements were used to analyse the photocurrent generation of the electrodes. This was then used to calculate the photovoltage onset and photocurrent density at 0 V for electrodes and for complete cells to calculate the open circuit voltage $V_{oc}$ and short circuit current density $J_{sc}$. 

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J-V measurement were carried out using either a three-electrode configuration, where the sample acted as the working electrode, Ag/AgCl/KCl as reference electrode and a platinum wire as a counter electrode or two-electrode configuration where the sample acted as the working electrode and platinum wire or platinum glass was the counter and reference combined. The potential of the photoelectrode was controlled by a potentiostat (Eco Chemie μ-AutoLab-type III) or (Eco Chemie Autolab PGSTAT-12) both by computer controlled GPES software. In the electrochemical cell light enters through a quartz window and travels about 5 mm path length in the electrolyte before illuminating the photoelectrode. Either a halogen lamp (Prior CL150) at 1000 Wm\(^{-2}\) or AM 1.5 Class A solar simulator (Solar Light 16S – 300 solar simulator), at 1000 Wm\(^{-2}\) light intensity, sources were used. Light intensity was calibrated by a solar pyranometer (Solar Light Co., PMA2144 Class II) traceable to NPL standard. In both configurations steady-state and chopped J-V curves were measured. For the chopped measurements, the light was manually chopped at regular intervals of time to record dark and photocurrent simultaneously. The potential ranges selected depended on the open circuit voltage of the cell. The cell was studied under dark and illuminated conditions.

Figure 3.5a shows a photo of the instrumentation used for J-V measurements.
3.6 Incident Photon to Electron Conversion Efficiency

Incident Photon to Electron Conversion Efficiency (IPCE) measurements were used to analyse the photon conversion efficiency of the electrodes at different wavelengths. The population of electrons generated at a given wavelength of light are then transferred to an external circuit. This is divided by the population of incident photons at that wavelength which is equivalent to the maximum number of electrons that could be produced, assuming a 1:1 ratio.  

\[ IPCE(\%) = \frac{n_{\text{electron}(\lambda)}}{n_{\text{photon}(\lambda)}} \times 100 \]  

(eq. 3.6a)

The population of electrons generated at a given wavelength of light is measured as the current density \(J\) at the set wavelength. The population of photons is measured by the optical power of the light source illuminating the system

\[ IPCE(\%) = \frac{J(\lambda)}{P(\lambda)} \times 100 \]  

(eq. 3.6a)

Where \(J(\lambda)\) corresponds to the measured current density in \(\mu\text{Acm}^{-2}\) per wavelength, \(P_{in}(\lambda)\) is the output optical power in \(\text{Wm}^{-2}\), and \(\lambda\) is the wavelength of the incident irradiation in nm. In general, the IPCE is measured under short-circuit conditions and is graphically displayed versus the corresponding wavelength. The IPCE corresponds to the photoresponse or external quantum efficiency.

IPCE measurements were carried out using a 75 W Xenon lamp connected to a monochromator (Bentham, TMc300) and the system was calibrated using a silicon diode (Bentham). The samples were measured in either 2-electrode mode or 3-electrode mode. In 3-electrode mode platinum is used as the counter electrode, the sample is used as the working electrode and Ag/AgCl is used as the reference electrode.

3.7 Capacitance Studies

Capacitance studies measure the interaction of electrodes with the electrolyte where by double layer capacitance occurs as described in figure 1.4.3a.
This causes a charge build up near the surface of the electrode. By altering the voltage with different frequencies a change in the double layer will be seen. This change can be measured as double layer doesn't respond instantly. This delay is caused by a combination of double layer capacitance and pseudo capacitance. Pseudo capacitance is where a reversible redox reaction has occurred.

![Diagram](image)

**Figure 3.7a** A typical current-potential plot for a general electrochemical system illustrating the applied AC sinusoidal potential.

Both Mott-Schottky and the scan rate method are used to calculate the flat band potential \((V_{fb})\) of the electrodes. Capacitance-voltage measurements were carried out on electrodes in photoelectrochemical set up in 3-electrode mode. Both Mott-Schottky and scan rate measurement methods were carried out in dark conditions.

Mott-Schottky measurements were carried out using Eco Chemie Autolab PGSTAT-12 and computer controlled FRA software. AC frequency was varied at different applied DC bias close to zero bias. This varies the capacitance values of the solid/electrolyte interface. This data is then analysed using Mott-Schottky plots. The slope of the plots can be used to calculate the flat band potential of the solid electrolyte interface.
Scan rate measurements were carried out using Eco Chemie Autolab PGSTAT-12 and computer controlled GPES software. This method involves varying the voltage and measuring the current at different scan rates. The different scan rate slopes were then used to calculate another plot. The slope of this plot provides another method to calculate the flat band potential of the solid electrolyte interface.\textsuperscript{138}
Chapter Four: Results and Discussion of the Semiconductors/Electrolyte Interfaces and Solar Cells

4.1 Wide Band gap Cathodic Semiconductor

4.1.1 Nickel Oxide Thin Films

Nickel oxide (NiO) is a desirable material for solar cells which is abundant, inexpensive and high stability as it occurs naturally in the form of bunsenite.\(^\text{139, 140}\) Stoichiometric NiO forms face-centred cubic lattice, with slight triangular distortions at low temperatures.\(^\text{141}\) High purity crystalline NiO can be characterized as an insulator, with reported band gaps between 3.5 and 4.0 eV and reported resistivity as high as \(10^{13} \Omega \text{cm}\). The conductivity of NiO is altered dramatically by the presence of defects and/or nonstoichiometry.\(^\text{141}\) Excess oxygen in NiO crystallites results in nonstoichiometric NiO\(_x\), \(^\text{142}\) in which the average oxidation state of nickel is greater than the \(2^+\) value found in the stoichiometric material. The inferred population of Ni\(^{3+}\) ions acts as acceptor centres, and the NiO\(_x\) exhibits transport properties of a p-type semiconductor \(^\text{143}\) with resistivity as low as \(10^{-1} \Omega \text{cm}\).\(^\text{141}\) Highly conductive p-type behaviour has also been reported for lithium-doped nickel oxide prepared by powder sintering.\(^\text{141}\) Due to NiO films having many desirable properties of high p-type conductivity, high stability and optical transparency they have been used in many applications, such as gas and chemical sensors,\(^\text{144}\) electrochromic ‘smart windows’,\(^\text{145}\) transparent conducting layers,\(^\text{143}\) catalysts and fuel cells. This is due to its excellent chemical and thermal stability,\(^\text{142}\) its wide band gap of 3.6 eV \(^\text{146}\) and its ease of processability. For example, many NiO thin film fabrication methods have been reported using physical and chemical techniques some of which include sputtering,\(^\text{147}\) doctor blade,\(^\text{148}\) hydrothermal,\(^\text{149}\) thermal evaporation,\(^\text{78}\) thermolysis,\(^\text{150}\) spray pyrolysis,\(^\text{76}\) sol-gel,\(^\text{151}\) chemical bath deposition \(^\text{152}\) as well as many others. It is for these reasons that NiO was used as the wide band gap cathodic semiconductor layer for the present study.

In this study, NiO thin films were prepared using the doctor blade (DB) method, electrodeposition (ED) and aerosol-assisted chemical vapour deposition (AACVD), or combinations thereof. The following sections describe the material,
chemical and electrical characteristics of the NiO thin films, fabricated by each method, in order to assess and optimise its performance in tandem cells.

4.1.2 Doctor bladed Nickel Oxide Thin Films

4.1.2.1 SEM Characterisation

The surface morphology of NiO thin films prepared by the DB method is shown in figures 4.1.2.1a. This resulted in a NiO thin film with good porosity and particle size of approximately 30 nm. This was expected as 30 nm NiO nanoparticles were used to make the paste for doctor blading. SEM analysis also shows evidence of coalescing of the NiO nanoparticles, which indicate good inter-particle connections; therefore, this should give good electrical conduction. The NiO also has good mechanical strength when tested using the ‘scotch tape’ method.

![SEM Image](image.png)

Figure 4.1.2.1a SEM of doctor bladed NiO at 200 kX zoom.
4.1.2.2 J-V Characterisation

Figure 4.1.2.2a shows NiO electrode by doctor blade in 2 electrode mode in a triiodide electrolyte. The manually chopped photo current shows a photo current density of about 30 µA cm$^{-2}$ at 0 V and an onset potential of about 0.075 V. The chopped current also shows a dark current density of about 15 µA cm$^{-2}$ at 0 V. As this also shows a large dark current and resistive behaviour it was not a suitable electrode for the use in solar cells. One of the reasons for the large dark current and resistive behaviour is recombination and current is able to flow in either direction. In this case it was thought that is due to the I$^-$/I$_3^-$ electrolyte reaching the back contact.

![J-V curve of NiO thin film prepared by the DB method in a two electrode configuration with Pt as the counter electrode in an I$^-$/I$_3^-$ electrolyte.](image)

Figure 4.1.2.2a J-V curve of NiO thin film prepared by the DB method in a two electrode configuration with Pt as the counter electrode in an I$^-$/I$_3^-$ electrolyte.
4.1.3 Electrodeposition of Nickel Oxide Thin Films

4.1.3.1 SEM Characterisation

Topographical information was used to study the morphology and coverage of the electrochemically deposited NiO blocking layer without annealing. This study was carried out using SEM.

Figure 4.1.3.1a shows the surface morphology of electrochemically deposited Ni(OH)₂ on top of FTO glass using an aqueous Ni(NO₃)₂ solution at a magnification of 200 kX. It can be seen that Ni(OH)₂ has been compacted when being prepared for SEM. It shows good coverage of the FTO and where the surface is not damaged, worm-like structures can be seen which are approximately 15 nm thick and 100 – 150 nm in length. The solution of Ni(NO₃)₂ was electrochemically deposited to form Ni(OH)₂ according to the reaction scheme shown in equations 4.1.3.1a and b. The Ni(OH)₂ is not soluble in water at pH 7, so when the local pH at the working electrode (FTO) changes, this causes precipitation and nucleation at the electrode surface, which results in a thin film.

\[
\text{NO}_3^- + 7\text{H}_2\text{O} + 8e^- \rightarrow \text{NH}_4^+ + 10\text{OH}^- \quad \text{(eq. 4.1.3.1a)}^{94}
\]

\[
\text{Ni}^{2+} + 2\text{OH}^- \rightarrow \text{Ni(OH)}_2 \quad \text{(eq. 4.1.3.1b)}^{94}
\]

The good coverage of the electrodes means that there are few pinholes leading to the FTO surface. This should mean that the electrode has high shunt resistance which is desirable so the current is forced to travel in one direction. The worm like structures that can be seen in figure 4.1.3.1a. This is desirable as they increase the porosity of the electrode therefore increasing the surface area where charge generation and separation can occur.
Chapter 4 Results and Analysis of the devices

Figure 4.1.3.1a SEM of electrochemically deposited Ni(OH)\textsubscript{2} without annealing at 200 kX magnification.

The morphology and coverage of the electrochemically deposited NiO blocking layer after being annealed is shown in figure 4.1.3.1b. Annealing, the Ni(OH)\textsubscript{2} drives off water in the presence of air to form NiO. SEM comparison of figure 4.1.3.1a and b shows that some of the porosity is lost due to coalescence of the particles which occurs through Oswald ripening and loss of water. The film has cracked due to the loss of water, exposing some of the FTO which could lead to a decrease in shunt resistance. This would reduce the efficiency of the completed solar cell. The particles of the NiO are granular and are approximately 20 nm so the worm like structures have converted due to the annealing. The coalescence of the particles should improve physical and electrical connectivity. The SEMs show that the coalescing of the particles has improved the mechanical strength of the structure compared to that of the Ni(OH)\textsubscript{2} as there is no damage to the NiO film when preparing for SEM. The Ni(OH)\textsubscript{2} is annealed to NiO as shown in equation 4.1.3.1b. This takes place at temperatures above 250 °C - 300 °C so the water is driven off as gas.
Chapter 4 Results and Analysis of the devices

\[ \text{Ni(OH)}_2(s) \rightarrow \text{NiO}(s) + \text{H}_2\text{O}(g) \uparrow \quad (\text{eq. 4.1.3.1b}) \]

Figure 4.1.3.1b SEM of electrochemically deposited Ni(OH)_2 after annealing to form NiO at 200 kX magnification.

4.1.3.2 \( J-V \) Characterisation

Figure 4.1.3.2a shows the \( J-V \) characteristics of the NiO electrode prepared by electrodeposition for 90 min then annealed at 450 °C, measured in a two electrode configuration in a \( \text{I}^-/\text{I}_3^- \) electrolyte. The \( J-V \) plot shows a photo current density of about 28 \( \mu \text{A cm}^{-2} \) at 0 V and an onset potential of about 0.080 V. The chopped current also shows a dark current density of about 1 \( \mu \text{A cm}^{-2} \) at 0 V. This is slightly lower than achieved for the DB NiO but has a significantly lower dark current of 15 \( \mu \text{A cm}^{-2} \). Electrodeposited films have shown good promise as a base for solar cells due to its strong photo activity but the films have low porosity which needs to be enhanced to maximise the photo current when later used with other layers.
Chapter 4 Results and Analysis of the devices

Figure 4.1.3.2a  $J$-$V$ curve of NiO thin film prepared by the ED method after annealing at 450 °C in a two electrode configuration with Pt as the counter electrode in an $I^+I^-_3$ electrolyte.

Using the advantages of electrodeposited NiO for its good sample coverage and doctor blade for its high porosity. Therefore, combination of these two techniques was used for device construction to try and combine the advantages.

4.1.4 Electrodeposition and doctor blade combination Nickel Oxide Thin Films

4.1.4.1 Preparation of Porous NiO Electrodes

In this section, NiO electrodes were prepared using a combination of electrochemical deposition and doctor blade method to explore the film characteristics. Clean FTO glass was used as a substrate to deposit NiO electrochemically. Then NiO paste was applied using the doctor blade method and annealed to give a highly porous structure. Selected films then had another
electrochemical deposited NiO layer on top to minimise pinholes and increase particle connectivity.

4.1.5 Material/Structural Properties

The NiO electrodes’ structural properties were analysed using XRD. The NiO electrodes were deposited using a combination of electrochemically deposited and doctor bladed methods.

4.1.5.1 XRD Characterisation

The figure 4.1.5.1a shows X-ray diffraction patterns of the samples as prepared in table 4.1.5.1a. Reflections at 37.2°, 43.2° and 62.9° correspond to cubic NiO (JCPDS 00-047-1049). Reflections at 26.6°, 33.8°, 37.8°, 51.8°, 61.7°, and 65.7° correspond to cubic SnO$_2$ (JCPDS 00-046-1088) which is from the FTO substrate. For sT1 and sT2, only FTO shows up on XRD due to the electrodeposited NiO being too thin to show up through the background of FTO. The peak at 43.2° is dominant which shows the NiO film is organised to the (200) plane. This confirms the results reported by H-L Chen et al.$^{153}$ The XRD also show that the doctor blade NiO layer gives the strongest diffraction pattern which means there is little difference observed in the diffraction patterns with a DB NiO layer.
Chapter 4 Results and Analysis of the devices

Figure 4.1.5.1a XRD diffraction patterns of samples sT1 to sT8 and sT17, sT18 as prepared in table 4.1.2.1a.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ED1 300 s</th>
<th>Annealed in Air</th>
<th>DB</th>
<th>Annealed under Vac</th>
<th>ED2 120 s</th>
<th>Annealed in Air</th>
<th>Annealed under Vac</th>
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<tr>
<td>1</td>
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<td>X</td>
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<td></td>
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<td>X</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>3</td>
<td>sT3</td>
<td>X</td>
<td>X</td>
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</tr>
</tbody>
</table>

Samples were also fabricated with longer electrodeposition times, using 600 s under the DB layer and 300 s over the top, to fill more of the pores and increase electrical connectivity.
Chapter 4 Results and Analysis of the devices

Fig. 4.1.5.1b shows diffraction patterns as prepared in table 4.1.5.1b. Reflections at 37.2°, 43.2° and 62.9° correspond to cubic NiO (JCPDS 00-047-1049). Reflections at 26.6°, 33.8°, 37.8°, 51.8°, 61.7°, and 65.7° correspond to cubic SnO₂ (JCPDS 00-046-1088) which is from the FTO substrate. The peak again appearing at 43.2° show the same preferential orientation of NiO. Increasing the thickness of the electrochemically deposited layer has not changed the orientation of the cubic NiO (JCPDS 00-047-1049). For sT9 and sT10, only FTO shows up on XRD due to the electrodeposited NiO being too thin to show up through the background of FTO. The increase of electrochemically deposited layers of NiO does not affect the orientation of the film.

Figure 4.1.5.1b XRD diffraction patterns of samples sT9 to sT16 and sT19, sT20 as prepared in table 4.1.5.1b.
Table 4.1.5.1b Sample Preparation of NiO on FTO glass

<table>
<thead>
<tr>
<th>Sample</th>
<th>ED1 600 s</th>
<th>Annealed in Air</th>
<th>DB</th>
<th>Annealed under Vac</th>
<th>ED2 300 s</th>
<th>Annealed in Air</th>
<th>Annealed under Vac</th>
</tr>
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</table>

Figure 4.1.5.1c shows XRD diffraction patterns of NiO on FTO prepared by doctor blade method with the optimum J-V curve. The diffraction patterns have been used to using 26.6°. The cubic NiO reflections at 37.2°, 43.2° and 62.9° correspond to the NiO diffraction pattern (JCPDS 00-047-1049). Reflections at 26.6°, 33.8°, 37.8°, 51.8°, 61.7°, and 65.7° correspond to cubic SnO2 (JCPDS 00-046-1088) which is from the FTO substrate. The cubic NiO reflection at 37.2° (111) is dominant this shows that the NiO has a preferred orientation of (111). This is as reported by H-L Chen et al.153 The reflection at 62.9° corresponds to (220). All these reflections match to NiO diffraction pattern (JCPDS 00-047-1049). This also shows that doctor blading gives reproducible results with regards to XRD analysis.
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Figure 4.1.5.1c XRD diffraction patterns of samples with the optimum photoelectrochemical performance which was deposited by electrodeposition and doctor blade NiO.

4.1.6 Optical Properties

The optical properties of the NiO electrodes were analysed using absorbance measurements, transmission measurements and band gap calculations. The NiO electrodes were deposited using a combination of electrochemically deposited and doctor bladed methods.

4.1.6.1 UV-Vis Characterisation

4.1.6.1.1 Absorbance

Figure 4.1.6.1.1.a shows the absorption spectrum for NiO sample sX5 prepared by a combination of doctor blade and electrodeposition. The absorption measurements were repeated in order to establish that the data is the same at different locations on the samples. It can be seen that they all show a sharp
absorbance edge onset at approximately 360 nm (3.44 eV). There is a small peak observable at 380 nm (3.26 eV), in all three graphs is due to d-d transitions of the Ni^{2+} ion which is within the band gap. This has also been reported by Y. Qi et al.\textsuperscript{154}

![Graph showing UV-Vis spectra for sample sX5 at different locations.]

**Figure 4.1.6.1.1a UV-Vis spectra for sample sX5 at different locations.**

### 4.1.6.1.2 Transmittance

Figure 4.1.6.1.2a shows multiple transmittances spectrum for NiO sample sX5 prepared by a combination of doctor blade and electrodeposition. The absorption measurements were repeated in order to establish that the data is correct at different locations on the sample. All three transmission spectra for the NiO films have low intensity of transmission with a maximum transmission being between 30 % and 35 % at 800 nm. The transmission intensity decreases with decreasing wavelength. Faint troughs at 380 nm (3.26 eV), 430 nm (2.88 eV) and 720 nm (1.72 eV) can be seen. These are due to d-d transitions of the Ni^{2+} ions within the band gap as reported by Y. Qi et al.\textsuperscript{154}
Figure 4.1.6.1.2a transmittance spectra for sample optimal sample produced by electrodeposition and doctor blade deposition.

The transmittance for the NiO electrodes is low (less than 35 %) over the visible region. This may impede the construction of an efficient completed cell as if the light has to travel through the NiO layer before reaching the absorber layer, the effectiveness of the absorber will be reduced. As shown by the structural properties, the electrodes have proven to be porous in nature. This may lead to the transmission being higher through the NiO than measured due to the scattering effects of the small particle size and thickness of the layer causing reduced transmission.
4.1.6.1.3 **Tauc plots (Band gap) Calculations**

The Tauc plot shown in Figure 4.1.6.1.3a shows a direct optical band gap of just above 3.5 eV for the NiO film. This value is consistent with the literature.\textsuperscript{110, 155}

![Tauc Plot](image)

*Figure 4.1.6.1.3a Tauc Plot to estimate the direct band gap.*

4.1.7 **PEC Properties**

The NiO electrodes’ photoelectrochemical (PEC) properties were analysed using J-V characterisation and IPCE measurements. The NiO electrodes were deposited using a combination of electrochemical deposition and doctor bladed methods.

4.1.7.1 **J-V Characterisation**

Figure 4.1.7.1a shows a J-V plot of NiO electrode sample sX5 which is the optimum sample. This graph shows the sample in 2 electrode mode using triiodide as the electrolyte (0.04M I\textsubscript{2}, 0.4M LiI, 0.4M TBAI (Tetrabutylammonium iodide) and 0.3 M NMB (N-Methylbenzimidazole) in AN/MPN (1:1 Acetonitrile/3-Methoxypropionitrile)). The manually chopped photo current shows a photocurrent density 24 µA cm\textsuperscript{-2} at 0 V and an onset potential of 0.1 V. The chopped
photocurrent also shows a dark current density of 7 μA cm\(^{-2}\) at 0 V. The photocurrent density is slightly lower than both DB or ED 30 μA cm\(^{-2}\) and 28 μA cm\(^{-2}\) respectively. The dark current is between NiO deposited by DB of 15 μA cm\(^{-2}\) and ED 1 μA cm\(^{-2}\). The onset potential is higher than both DB or ED which are 0.075 V and 0.080 V respectively. This shows a much larger voltage but a smaller photocurrent compared to that of \(J_{sc}\) 40 μA cm\(^{-2}\), \(V_{oc}\) 0.005 V as reported for porous NiO electrodes in I\(_3\) by L. Lepleux et al.\(^\text{80}\) The photoelectrochemical properties of the NiO electrodes show that they have good p-type semiconductor behaviour and good rectifying behaviour.

![J-V plot for sample NiO sX5 in two electrode mode showing p-type behaviour.](image)

### 4.1.7.2 IPCE Characterisation

Figure 4.1.7.2.a shows IPCE spectra for NiO electrodes samples sX7. The band gap of the NiO electrode is 3.4 eV, with an efficiency approximately 2.0 % at 350 nm with a sharp drop at 360 nm as the spectrum plateaus to around 0.3 % at larger wavelengths. This is higher than IPCE value of 1.0 % reported by J.H. Rhee et al.,\(^\text{156}\) but lower than the IPCE value reported by H. Zhu et al. at approximately
4.5 %. The IPCE shows that most of the photocurrent is generated at high energy wavelengths which are consistent with the optical experiments’ findings that also show high absorbance at higher than 350 nm. This means NiO is a relatively good base for p-type solar cells.

Figure 4.1.7.2a IPCE spectra for NiO electrode.

4.1.8 Electrical Properties

The NiO electrodes’ electrical properties were analysed to gain information about the materials conduction, valence bands and the Fermi level using two capacitance measurements: Mott-Schottky and the scan rate method to estimate the flat band potential of the electrode. The NiO electrodes were deposited using a combination of electrochemically deposited and doctor bladed methods.
4.1.8.1 Capacitance Characterisation

4.1.8.1.1 Mott-Schottky Plots

Figure 4.1.5.1.1a shows a Nyquist plot for NiO electrode sample SX7 in 0.1M LiClO₄ in Acetonitrile over a range of voltages from 0.05 V to 1.00 V. The capacitance values were determined by fitting the data to an equivalent circuit Rs-Cs. These capacitance values were then used to construct a Mott-Schottky plot.

![Nyquist plot for NiO electrode sample SX7 in 0.1M LiClO₄ in Acetonitrile.](image)

Figure 4.1.8.1.1.a Nyquist plot for NiO electrode sample SX7 in 0.1M LiClO₄ in Acetonitrile.

Figure 4.1.8.1.1b shows a Mott Schottky plot for NiO electrode sample SX7 this can be used to estimate the flat band potential when the gradient crosses the x-axis. The flat band potential of estimated to be approximately 0.37 V vs NHE reference electrode. This is similar to the reported value by X-H Chan et al. The donor density was estimated to be $1.27 \times 10^{22}$ cm$^{-3}$ using equation 4.1.8.1.1a and the relative permittivity for NiO ($\varepsilon_{\text{NiO}} = 11$).
\[
\frac{1}{C^2} = \frac{2}{q \varepsilon_0 \varepsilon_r N_d} \left( |V - V_{fb}| - \frac{kT}{q} \right) 
\]  
(eq. 4.1.8.1.1a)

$C$ is capacitance, $q$ is electronic charge, $A$ is surface area of electrode, $N_d$ is donor density, $k$ is the Boltzmann constant, $T$ is temperature, $\varepsilon_0$ is permittivity of vacuum, $\varepsilon_r$ is relative permittivity of the semiconductor, $V$ is applied potential and $V_{fb}$ is the flat band potential.

**Fig. 4.1.8.1.1b** Mott Schottky plots for NiO electrode sample SX7.

### 4.1.8.1.2  Scan rate measurements

Figure 4.1.8.1.2.a shows the voltammetry of NiO electrode SX7 in tri-iodide electrolyte (as prepared in 3.1) at different scan rates. This data is then used to calculate the capacitance which is used to construct the Mott-Schottky plot, as shown in figure 4.1.4.1.2.b.
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Figure 4.1.8.1.2a cyclic voltammetry of NiO electrode SX7 in tri-iodide electrolyte at different scan rates.

Figure 4.1.8.1.2b shows that the flat band potential (\(V_{fb}\)) is approximately 0.39 V vs. NHE in a tri-iodide electrolyte (as prepared in 3.1). This is close to the value calculated by the impedance methods which is close to the literature reported value by X-H Chan et al.\textsuperscript{157} The donor density was estimated to be \(1.10 \times 10^{24} \text{ cm}^{-3}\) using equation 4.1.8.1.1a and the relative permittivity for NiO (\(\varepsilon_{\text{NiO}} = 11\)).

Figure 4.1.8.1.2b Mott-Schottky of sample SX7 in triiodide electrolyte.

\[
y = -1.168E+07x + 2.233E+06 \\
R^2 = 9.905E-01
\]
4.1.9 AACVD Nickel Oxide Thin Films

4.1.9.1 SEM Characterisation

Aerosol-assisted chemical vapour deposition (AACVD) was used to fabricate a NiO thin films. The surface morphology of a NiO thin film prepared by this method is shown in figure 4.1.9.1a. The SEM image shows that the NiO film exhibits good porosity with its column like structures which widths ranging from 300 nm to 600 nm with pores of about 200 nm. SEM also shows that the column like structures are roughly perpendicular to the FTO surface, this should mean the columns have good connectivity so theoretically, this should also give good electrical conduction. The structural properties of the NiO electrodes show good coverage and good porosity when AACVD is employed. The NiO also has good mechanical strength as tested by the ‘scotch tape’ method.

Figure 4.1.9.1a SEM of AACVD NiO at 50 kX zoom.
4.1.9.2 J-V Characterisation

Figure 4.1.9.2a shows the J-V plot for a NiO electrode prepared by AACVD for 20 min measured in a two electrode configuration with a I/I$_3^-$ electrolyte. The manually chopped photo current shows a photo current density of 7.6 µA cm$^{-2}$ at 0 V and an onset potential of about 0.1 V. The chopped current also shows a dark current density of 0.3 µA cm$^{-2}$ at 0 V. AACVD deposited films have shown good promise as a base for solar cells due to its high porosity and very low dark current but does have lower photoactivity than the combination method.

![Figure 4.1.9.2a J-V plot for NiO deposited by AACVD in tri-iodide electrolyte.](image)

4.1.10 Conclusions

In this section NiO thin films have been prepared by doctor blade (DB), electrodeposition (ED), aerosol assisted chemical vapour deposition (AACVD) or a combination of these techniques, for use as a wide band gap p-type semiconductor in tandem and solid-state solar cells. The NiO films were studied to
assess the surface morphology, porosity, mechanical strength, electrical and photochemical properties for each of the deposition methods.

NiO deposited by the DB method show high porosity made of particles of with a diameter of about 30 nm. These also show good mechanical strength and a photocurrent of 30 µA cm\(^{-2}\) at 0 V and an onset potential of about 0.075 V but has a dark current 15 µA cm\(^{-2}\) at 0 V. These samples show promise but the dark current is too high and needs to be lower for construction of a useful solar cell.

NiO deposited by ED show lower porosity than DB NiO made of particles of about 20 nm. These also show good mechanical strength and a photocurrent 28 µA cm\(^{-2}\) at 0 V and an onset potential of about 0.080 V but has a dark current 1 µA cm\(^{-2}\) at 0 V. These samples show promise but increased porosity for construction of a solar cell would be desirable.

NiO deposited by a combination of ED and DB show high porosity made of particles of about 30 nm. These also show good mechanical strength and a photocurrent 24 µA cm\(^{-2}\) at 0 V and an onset potential of about 0.10 V but has a dark current 7 µA cm\(^{-2}\) at 0 V. These samples have high porosity, slightly lower photocurrent and lower dark current than DB NiO and so will be used in construction of solar cells.

NiO deposited by AACVD show higher porosity than DB NiO made of particles of about 300 to 600 nm with pores of about 200 nm. These also show good mechanical strength and a photocurrent 7.6 µA cm\(^{-2}\) at 0 V and an onset potential of about 0.10 V but has a dark current 0.3 µA cm\(^{-2}\) at 0 V. These samples have with very high porosity, low dark current so will be used in construction of solar cells.

NiO films deposited by AACVD or a combination of ED and DB will be used to fabricate sensitised photocathodes. AACVD was chosen for the very high porosity and very low dark current. The combination of ED and DB was chosen for their high porosity and moderate photocurrent and low dark current.
4.2 Narrow Band gap Light Absorber Cathodic Semiconductor

4.2.1 Copper (II) and (I) Oxide Thin Films

Copper(II) oxide (CuO) is a desirable material for solar cells due to stability as it occurs naturally as tenorite. CuO crystallises with a monoclinic crystalline lattice. CuO is readily available, inexpensive and nontoxic and this makes it even more attractive for different applications. CuO is appealing for use in solar cells due to its high absorptivity and a low thermal emittance. Furthermore, it is a promising semiconductor for solar cell fabrication due to its suitable optical properties. Due to the existence of copper vacancies in the structure, CuO exhibits native $p$-type conductivity. Its band gap is reported to be between 0.7 and 1.7 eV. These bands are associated with charge transfer of the form $O_{2p}$ to $Cu_{3d}$. CuO has valence and conduction band edges at $-5.00$ eV and $-3.66$ eV respectively to the vacuum level reference. CuO has potential applications in solar energy devices, gas sensor applications, high-Tc superconductors, nanowires, nanoscale quantum dots and some materials with giant magnetoresistance. In this study CuO was used as the light absorber cathodic semiconductor layer due to their characteristic properties.

In this study, CuO and Cu$_2$O thin films were prepared using AACVD. The following sections describe the material, chemical and photochemical characteristics of the CuO and Cu$_2$O thin films, fabricated in order to assess and optimise its performance in tandem cells.

4.2.1.1 Preparation of CuO and Cu$_2$O Electrodes

AACVD 0.0075 M Cu(acac)$_2$ for 50 min at 500 °C under argon and annealed under argon at different temperatures ranging from 150 to 325 °C.
4.2.2 Material/Structural Properties

4.2.2.1 XRD Characterisation

XRD shows that for annealing at temperatures below about 200 °C, copper metal has dominant crystallite signal, at annealing temperatures between 200 °C and 300 °C Cu₂O is the dominant crystallite signal and above 300 °C CuO is the dominant crystallite signal.

![XRD diffraction pattern](image)

**Figure 4.2.2.1a XRD diffraction pattern of copper films annealed at different temperatures.**

From the XRD data, a graph can be plotted from taking the intensity of reflections at about 35.7, 36.5 and 43.7 which correspond to most intense reflections for CuO, Cu₂O and Cu respectively to give a rough estimate of which is dominant as each temperature. At annealing temperatures below about 200 °C copper metal has dominant crystallite signal between 200 °C and 300 °C Cu₂O is the dominant crystallite signal and above 300 °C CuO is the dominant crystallite signal.
4.2.3 PEC Properties

4.2.3.1 J-V Characterisation

The J-V characteristics of the CuO/Cu$_2$O electrodes were evaluated in a three electrode configuration using a 3 M KCl Ag/AgCl reference electrode and Pt mesh counter electrode in an aqueous 1 M Na$_2$SO$_4$ electrodes adjusted to pH 4.9 by adding an appropriate amount of 0.1 M H$_2$KPO$_4$. The chopped J-V curves are shown in figure 4.3.2.1a. The electrodes annealed at low temperatures showed no or poor photo-activity due to incomplete oxidation of the copper. The chopped J-V plots show sharp negative current spikes when the light is incident on the sample, then the current decays to a steady state current. The presence of these current spikes show evidence of high recombination in the photoelectrodes. The current spikes seem vary in height due to an artefact from digital signal sampling.\textsuperscript{163}
Figure 4.2.3.1a  J-V curves of copper films annealed at different temperatures.

J-V curve was used to find the photocurrent density, which was calculated by subtracting the dark current from the overall current. This was used to construct a plot of photocurrent density (at 0 V vs. Ag/AgCl) vs. annealing temperature in order to assess the dependence of photocurrent at each temperature, as shown in figure 4.3.2.1b. The plot shows an increase in photocurrent with an increase in annealing temperature. At temperatures below 200 °C the film is Cu metal according to XRD and as expected this gives a poor photocurrent. Between 200 °C and 300 °C this corresponds to Cu$_2$O but the current increase even more above 300 °C where CuO is the dominant so this suggests that it would be better to use CuO over Cu$_2$O as the absorber.
4.2.4 Conclusions

In this section copper metal thin films have been prepared by AACVD then annealed to form Cu$_2$O or CuO, for use as a narrow band gap p-type semiconductor as an absorber in photocathodes and solid-state solar cells. The Cu$_2$O and CuO films were studied to assess the chemical and photochemical properties for each of the films. Cu$_2$O and CuO were successfully fabricated by this method but it was proved that CuO annealed at 325 °C provided the highest photocurrent density. Due to this CuO will be fabricated directly using air as the carrier gas for AACVD rather than a post annealing process. This method will then be used to sensitise the porous NiO electrodes.
4.3 Wide Band gap Anodic Semiconductor

4.3.1 Zinc Oxide Thin Films

Zinc oxide (ZnO) is a desirable material for solar cells as it occurs in nature as zincite and therefore it shows that it is highly stable, as well as zinc being relatively inexpensive and abundant.\textsuperscript{139} ZnO has a hexagonal wurtzite crystal structure and exhibits partial polar characteristics on the crystal surface.\textsuperscript{101} ZnO is a very well-studied group II–VI n-type semiconductor. Due to its unique properties such as transparency in the visible region and high infrared reflectivity, acoustic characteristics, high electrochemical stability and excellent electronic properties. It has been widely used in chemical sensors, surface acoustic wave devices, photonic crystals, photoanodes in thin film solar cells.\textsuperscript{164} So far, several kinds of techniques have been utilized to fabricate ZnO nanoscale materials, such as molecular beam epitaxy, sputtering, chemical vapour deposition (CVD), spray pyrolysis, pulsed laser deposition (PLD), anodic alumina oxide (AAO) template, electrochemical deposition, and aqueous solution deposition methods. Many studies have focused on the synthesis of large scale well-aligned high-quality ZnO nano-rod arrays.\textsuperscript{165, 166} It is for these reasons that ZnO was used as the wide band gap anodic semiconductor layer for the present study.

In this study, ZnO thin films were prepared using electrodeposition (ED) and chemical bath deposition (CBD). The following sections describe the material, chemical and electrical characteristics of the ZnO thin films, fabricated by each method, in order to assess and optimise its performance in tandem cells.

4.3.1.1 Preparation of Porous ZnO Electrodes

ZnO electrodes were prepared by a multiple methods of electrochemical deposition (ED), aerosol assisted chemical vapour deposition (AACVD) and chemical bath deposition (CBD). Clean FTO glass was used as a substrate to deposit thin, compact layers of ZnO electrochemically or by AACVD - this layer acted as a seed layer for growth of hierarchical ZnO nano-rods by chemical bath deposition. ZnO nano-rods and nano-tubes where then grown using chemical bath deposition on different seed layers with the aim to give a high porosity structure.
4.3.2 Electrochemical deposition of ZnO

4.3.2.1 XRD Characterisation

This experiment was carried out to grow nanostructured zinc oxide for solar cell applications, using electrochemical methods to make sure that the structures have good electrical contact to the FTO glass, to find if, using different zinc oxide precursors would affect the zinc oxide film.\textsuperscript{101,167}

![XRD diffraction pattern of electrodeposited zinc oxide on FTO substrate.](image)

Fig. 4.3.2.1a The XRD reflections show crystalline zinc oxide and tin oxide are present. ZnO shows preferred orientation at the (002) reflection showing preferential alignment of the ZnO film.

4.3.2.2 SEM Characterisation

The annealing the Zn(OH)\textsubscript{2} seed layer to convert it to ZnO, the film was characterised by SEM to determine the surface morphology as shown in figure
4.3.2.2a. From image (a) it can be seen that the electrodeposited film has poorer surface coverage which is undesirable for application in solar cells. From images (b) and (c), it can be seen that the ZnO films adopt an open structure with low porosity, and from image (d) it can be seen that the film thickness is approximately 500 nm at its maximum thickness. This compact irregular diffused grain ZnO is similar to that found by A. I. Inamdar et al. 26

Figure 4.3.2.2a SEM images of zinc oxide film on FTO glass substrate deposited electrochemically using zinc acetate as the precursor.

Figure 4.3.2.2b shows the surface morphology of ZnO films prepared by electrodeposition of a different precursor – zinc nitrate. By comparing the SEM image for zinc nitrate and zinc acetate, it can be seen that morphology is significantly different. Images (a), (b) and (c) shows a porous structure which consists of randomly orientated thin plate/petal like structures, which are similar to those reported by T. Yoshida et al. 98 Due to the morphology, it is undesirable for use as a seed layer for ZnO nano-rods due to its non-uniformity.
Next, zinc chloride was used as the precursor for fabrication of ZnO by electrodeposition. The XRD is shown in figure 4.3.2.2c and the surface morphology is shown in figure 4.3.2.2d. Images (a), (b) and (c) show that the ZnO films have hexagonal nano-rod like structures and the film uniform and consistent along the sample. All the rods are of a similar length and diameter but have poor alignment. If orientation and rod length can be enhanced this would prove promising for solar cell applications. Image (d) shows the cross-section of the film. From this it was estimated that the film thickness was 200 - 400 nm but damage to the film makes it difficult to give an accurate answer.
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Figure 4.3.2.2c XRD diffraction pattern of zinc oxide film on FTO glass substrate deposited electrochemically using zinc chloride as the precursor.

Fig 4.3.2.2c XRD diffraction pattern of zinc oxide films produced by zinc chloride precursor. The XRD reflections show that crystalline zinc oxide and tin oxide are present. The sample has tin oxide due to the glass substrate which has a thin layer of fluorine doped tin oxide to make it conductive.
SEM Characterisation of ZnO films using a zinc nitrate precursor.

Figure 4.3.2.2d SEM images of zinc oxide film on FTO glass substrate deposited electrochemically using zinc chloride as the precursor.

Fig 4.3.2.2d SEM images of zinc oxide films using zinc chloride as the precursor deposited on an FTO glass substrate using electrochemical deposition.

Comparison of precursors

Zinc chloride was shown to be the most promising as it was the only zinc oxide film with a good porous structure. But unfortunately the film did not uniformly cover the whole electrode surface. The zinc acetate precursor films were very poor as they were not uniform and had low porosity. Zinc nitrate gave a porous film with poor structure but show good coverage which make it the best option for producing a seed layer.
4.3.3 ZnO CBD with different seed layers

This experiment was carried out to try and get good uniform deposition of nanostructure zinc oxide rods, to increase nano-rods orientation, to maximise the surface area available so it can be used for solar cell application. Fig 4.3.3a shows the XRD diffraction patterns of zinc oxide nano-rods. The reflections show that crystalline zinc oxide and tin oxide are present. The large reflection related to the ZnO (002) plane shows preferred orientation for the crystal structure.

![XRD diffraction pattern](image)

Figure 4.3.3a XRD diffraction pattern of zinc oxide nano-rods deposited using CBD on a seed layer of zinc oxide on FTO substrate.
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Figure 4.3.3b SEM of zinc oxide nano-rods deposited using CBD on different seed layers of zinc oxide on FTO substrate.

Table 4.3.3a deposition method and time for seed layer and nano-rods

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<td>AACVD</td>
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Fig 4.3.3b shows the SEM images of ZnO hexagonal nano-rods grown by CBD on different seed layers as listed in table 4.3.3a. Sample (a) has diameters in the region of 50 to 200 nm. The rods have quite good alignment which suggests good contact to the FTO and also has good porosity. Sample (b) show films with good porosity and has a range of rod diameters in the region of 50 to 100 nm and these have quite poor orientation which suggests there will be reduced electrical contact to the FTO as the charges have to travel further to be collected. Sample (c) show films with good porosity and has a range of rod diameters in the region of 50 to 100 nm but most are ~50 nm. The rods have poor alignment which suggests there will be reduced electrical contact to the FTO as the charges have to travel further to be collected. Sample (d) show films with good porosity and has a range of rod diameters of approximately 50 to 75 nm but the small diameters may lead to high series resistance. The rods have good alignment which suggests there will be good electrical contact to the FTO as the charges can travel directly to be collected. Sample (e) show films with good porosity and has a range of rod diameters of approximately 50 to 100 nm. The rods appear moderately aligned which suggests there will be a slight reduction in electrical contact to the FTO as the charges have to travel further to be collected. Sample (f) has a range of diameters of approximately 50 to 250 nm the wide rods could give a lower series resistance, as the cross section area is greater. The rods are compact, some have merged together which may lead to higher recombination rates. This would be due to lattice imperfections allowing the electron and the hole to recombine. The rods have good orientation which suggest there will be good electrical contact with the FTO as the charges have to travel further to be collected and but the film has moderate porosity.

This shows that the diameter of the nano-rods varies with seed layer method and time. Most samples have rods in the 50 - 100 nm range. Some have larger ranges of 50 - 250 nm this is due to particles of a given size being deposited on the surface. The crystals prefer to nucleate on crystals that are already there, these undergo Ostwald ripening and therefore the diameter of the rods is set by the initial crystal which is deposited by the buffer layer. The (0001) face has higher energy than the other faces. The crystal grows on this surface so little change to
the diameter occurs. This shows that the seed layer controls the diameter and orientation of the nano-rods.

Figure 4.3.3c SEM cross section of zinc oxide nano-rods deposited using CBD on different seed layers of zinc oxide on FTO substrate.

Fig 4.3.3c shows the SEM images of cross sections. Shows good control over rod length as they are all about 1 μm. They are all within a very close tolerance in all samples which suggest it is controlled by the time and
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concentration of the chemical bath deposition. The (0001) face is higher energy and polar than the other faces so the crystal grows on this surface. This causes little change to the diameter while the length of the crystal increases during CBD, as deposition of alternate stacking of Zn\(^{2+}\) and O\(^{2-}\) ions are attracted to the polar surface. These methods give higher orientated rods than the electrochemical method used previously.

4.3.4 PEC Properties

4.3.4.1 J-V Characterisation

![Graph showing J-V characteristics](image)

Figure 4.3.4.1a J-V curve for zinc oxide nano-rods in 0.1 M LiClO\(_4\) in propylene carbonate.

Figure 4.3.4.1a shows the current voltage characteristics of the zinc oxide nano-rods. The J-V characteristics of zinc oxide rods in a PEC cell shows the photocurrent onset is at -0.27 V in 0.1 M lithium perchlorate dissolved in propylene carbonate. This shows that the flat band potential is roughly in this area. The
experiment was carried out in an organic solvent as when it was carried out in aqueous solutions the current changed and shifted due to the ZnO being dissolved into the solution because of a localised pH change occurring at different voltages.

4.3.5 Optical Properties

4.3.5.1 UV-Vis Characterisation

4.3.5.1.1 Absorbance

Figure 4.3.5.1.1a shows absorbance over the visible region of ZnO nano-rods.

Fig. 4.3.5.1.1a shows the light absorption properties of the zinc oxide nano-rods. The absorbance spectrum shows that the intercept of the two linear tangents is at 398 nm which gives a band gap threshold\textsuperscript{109} for the zinc oxide nano-rods of approximately 3.1 eV, which correlates to the known band gap of zinc oxide.\textsuperscript{109}
This also shows there is little adsorption of visible light (380 nm - 740 nm) which is desirable for a semiconductor for use in a photovoltaic device.

4.3.6 ZnO Nano-rods to Nano-tubes

In this section, the conversion of ZnO nano-rods to nano-tubes was attempted in order to increase the surface area of the nano-rods and hence increase their photocurrent. Conversion to nano-tubes was carried out by selectively etching the centres of the nano-rods to make them hollow using KCl as the etching agent.

4.3.6.1 Material/Structural Properties

4.3.6.1.1 SEM Characterisation

The etching time of the ZnO nano-rods in the KCl etching agent was systematically varied to form nano-tubes\textsuperscript{,31,32} and the SEM images in figure 4.3.6.1.1 show the surface morphology of the electrodes. From image (a) to (k) it can be seen that the nano-rod centres are gradually being etched away.
Figure 4.3.6.1.1 SEM of zinc oxide nano-rods after different etching times from 0 to 240 min in potassium chloride solution in CBD setup.
Table 4.3.6.1.1 Times and description of nano-rod etching

<table>
<thead>
<tr>
<th>Image</th>
<th>AACVD buffer deposition time/min</th>
<th>CBD to form rods time/min</th>
<th>CBD to convert rods into tubes time/min</th>
<th>Descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>3</td>
<td>50</td>
<td>0</td>
<td>Shows hexagonal rods</td>
</tr>
<tr>
<td>b</td>
<td>3</td>
<td>50</td>
<td>30</td>
<td>Shows no sign of dissolving</td>
</tr>
<tr>
<td>c</td>
<td>3</td>
<td>50</td>
<td>60</td>
<td>Shows no sign of dissolving</td>
</tr>
<tr>
<td>d</td>
<td>3</td>
<td>50</td>
<td>90</td>
<td>Shows that the rods started dissolve</td>
</tr>
<tr>
<td>e</td>
<td>3</td>
<td>50</td>
<td>120</td>
<td>Shows that the rods started dissolve</td>
</tr>
<tr>
<td>f</td>
<td>3</td>
<td>50</td>
<td>150</td>
<td>Shows that the rods started dissolve</td>
</tr>
<tr>
<td>g</td>
<td>3</td>
<td>50</td>
<td>180</td>
<td>Shows that the rods started dissolve</td>
</tr>
<tr>
<td>h</td>
<td>3</td>
<td>50</td>
<td>210</td>
<td>Shows that the rods started dissolve</td>
</tr>
<tr>
<td>i</td>
<td>3</td>
<td>50</td>
<td>240</td>
<td>Shows that the rods started dissolve</td>
</tr>
<tr>
<td>j</td>
<td>3</td>
<td>50</td>
<td>180</td>
<td>Magnified view of g shows that the centre of the rod is being dissolved</td>
</tr>
<tr>
<td>k</td>
<td>3</td>
<td>50</td>
<td>210</td>
<td>Magnified view of h shows that the centre of the rod is being dissolved</td>
</tr>
</tbody>
</table>

Fig 4.3.6.1.1 shows the SEM images from a vertical perspective from the substrate view of rods exposed to potassium chloride CBD for different durations of time. Figure j) to k) shows that the KCl has started to dissolve the hexagonal face of the zinc oxide nano-rods and has started to turn them into nano-tubes. But the process is not 100% complete. This shows that it is possible to dissolve the rods into tubes the etching also occurs at any defects in the crystal lattice preferentially. The KCl then goes onto dissolve the rods. This is due to the higher concentration of defects at the centre of the rod and the higher energy (0001) hexagonal surface being more vulnerable to attack. In this way the rods are converted to tubes. The SEMs shows that dissolving the hexagonal face using the current method will take a lot longer than 4 h to turn the nano-rods into nano-tubes but it does show it is possible.
4.3.6.1.2 XRD Characterisation

Figure 4.3.6.1.2a XRD diffraction pattern of zinc oxide nano-tubes formed from etched nano-rods.

Figure 4.3.6.1.2a shows XRD after the rods have been turned into tubes. The XRD reflections show that only crystalline zinc oxide and tin oxide are present.
4.3.6.1.3 SEM Characterisation

The sample was made first with a seed layer which was deposited with AACVD for 3 min using 0.1 M zinc acetate. Nano-rods were then grown using CBD at 80 °C for 50 min with 0.01 M zinc nitrate and 0.4 M NaOH. The nano-rods were converted into nano-tubes using CBD at 80 °C for 24 h with 3.5 M KCl. The surface morphology is shown in figure 4.3.6.1.3. It can be seen from image (b) that nano-rods have been fully converted to nano-tubes by etching of the hexagonal face, however, in some cases the etching has progressed too far and this has resulted in etching of the walls where defect occur.

4.3.6.1.4 XRD Characterisation

The XRD shows that ZnO will not deposit without a seed layer. Seed layers deposited using AACVD shows strong reflections for ZnO with the most dominant reflection corresponding to (100) orientation. While seed layers deposited using electrodeposition hardly show any ZnO related reflections this is due to the layer is very thin as it was deposited for 5 min.
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Figure 4.3.6.1.3 XRD diffraction pattern of zinc oxide nano-rods produced using different buffer layers.

4.3.7 Conclusions

In this section ZnO seed layers have been prepared by ED and AACVD, for use as a seed layer for ZnO nano-rods. ZnO nano-rods and nano-tubes were successfully fabricated on different seed layers using CBD, for use as a wide band gap n-type semiconductor in solid-state solar cells. Different precursors for ED proved to have a great effect on the morphologies of the films. From the precursors used zinc nitrate gave a porous film but poor structure, however good coverage was achieved which makes it the best option for producing a seed layer using ED. AACVD also proved to provide a seed layer that gives better rod alignment than the ED seed layer. Nano-tubes have been successfully fabricated by etching nano-rods using KCl. ZnO nano-rods and nano-tubes could be used as a porous n-type semiconductor for use as a photoanode. AACVD provided a good seed layer so will also be used as an n-type semiconductor in solid-state solar cells.
4.4 Liquid Based Photoelectrochemical Cells

4.4.1 Cathodic Photosensitised NiO Cells using CuInS₂ as the Sensitiser

In this section, NiO was deposited by electrodeposition and the CuInS₂ sensitiser was deposited on top using chemical bath deposition.

4.4.1.1 XRD Characterisation

XRD show reflections for CuInS₂ and FTO. Any reflections related to NiO are very low due to the layer being a very thin due to it being electrodeposited for 5 min.

Figure 4.4.1.1 XRD diffraction pattern of photoelectrode NiO sensitised with CuInS₂ fabricated on FTO substrate.
4.4.1.2 J-V Characterisation

Photoelectrochemical cell was set up in three electrode mode with 0.1 M K$_2$SO$_4$ as the electrolyte. The J-V curve shows a photocurrent at 0 V is 10 µA cm$^{-2}$ and a dark current 20 µA cm$^{-2}$ with a photocurrent onset of 0.15 V as shown by figure 4.4.1.2a.

![J-V Curve](image)

Figure 4.4.1.2a J-V curve of photoelectrode NiO sensitised with CuInS$_2$ fabricated on FTO substrate in 0.1 M K$_2$SO$_4$.

Unfortunately these samples proved to be unstable in the many electrolytes, they were most stable in K$_2$SO$_4$ but these were still unstable. The samples also proved to be difficult to reproduce as even on the same sample the CuInS$_2$ film were not uniform. This led to different performance even without changing any parameters. As seen by figure 4.4.1.2b J-V curve shows a photocurrent at 0 V is 7 µA cm$^{-2}$ and a dark current 38 µA cm$^{-2}$ with a photocurrent onset of 0.15 V.
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Figure 4.4.1.2b J-V curve of photoelectrode NiO sensitised with CuInS$_2$ fabricated on FTO substrate in 0.1 M K$_2$SO$_4$.

4.4.2 Cathodic Photosensitised NiO Cells using CuO as the Sensitiser

The NiO electrodes were deposited using a combination of electrochemically deposited and doctor bladed methods. CuO was deposited on top using AACVD.

<table>
<thead>
<tr>
<th>Sample</th>
<th>NiO deposited</th>
<th>CuO deposited</th>
<th>Electrode structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>M40</td>
<td>DB-ED</td>
<td>AACVD</td>
<td>FTO/NiO/CuO</td>
</tr>
<tr>
<td>M41</td>
<td>DB-ED</td>
<td>AACVD</td>
<td>FTO/NiO/CuO</td>
</tr>
</tbody>
</table>

4.4.3 Structural Properties

The NiO/CuO electrodes’ structural properties were analysed using XRD and SEM. The NiO electrodes were deposited using a combination of electrochemically deposited and doctor bladed methods.
4.4.3.1 XRD Characterisation

Figure 4.4.3.1a shows the diffraction pattern for photoelectrode NiO sensitised with CuO fabricated on FTO substrate. The cubic NiO shows preferred growth corresponding to the reflection at 43.2° (200) this is as reported by H-L Chen et al 153 when the samples are annealed. The reflections at 37.2° and 62.9° correspond to (111) and (220) respectively. All these reflections match to NiO diffraction pattern (JCPDS 00-047-1049). CuO shows reflections at 32.8°, 35.6°, 38.9° and 49.0°. All these reflections correspond to CuO diffraction pattern (JCPDS 03-065-2309).

![Figure 4.4.3.1a XRD diffraction pattern for sample M41 photoelectrode NiO sensitised with CuO fabricated on FTO substrate.](image)

4.4.3.2 SEM Characterisation

SEM shows an image of plain doctor bladed NiO on the left and AACVD CuO on doctor bladed NiO on the right of figure 4.4.3.2a. Both are taken at the same magnification at 100 kX, as it can be seen the CuO has covered the NiO but also maintains the porous nanostructures.
4.4.3.2a SEMs of plain doctor bladed NiO on the left and AACVD CuO on doctor bladed NiO on the right at the same magnification.

4.4.4 Optical Properties

The CuO and NiO/CuO electrodes’ optical properties were analysed using absorbance measurements, transmission measurements and band gap calculations. The NiO electrodes were deposited using a combination of electrochemically deposited and doctor bladed methods. CuO was deposited on top of the NiO using AACVD.

4.4.4.1 UV-Vis Characterisation

4.4.4.1.1 Absorbance

Figure 4.4.4.1.1a shows the absorption spectrum of sample M41 of CuO on a NiO electrode prepared on FTO. It can be seen that they all show an absorbance edge onset at approximately 710 nm (1.75 eV), with an absorption peak at 435 nm (2.85 eV). This value is close to CuO as reported by K. K. Dey et al.\textsuperscript{170}
Figure 4.4.4.1.1a Absorption spectrum of sample M41 photoelectrode NiO sensitised with CuO fabricated on FTO substrate.

4.4.4.2 Band gap

Figure 4.4.4.2a shows a graph that is calculated from the absorption data for sample M41. This shows a direct optical band gap. The calculated direct optical band gap is approximately 1.8 eV. This value is close to the literature values of CuO (1.7 eV).¹¹⁰
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4.4.4.2a Graph to calculate direct optical band gap from absorption data for sample M41 photoelectrode NiO sensitised with CuO fabricated on FTO substrate.

4.4.5 Photoelectrochemical Properties

The NiO/CuO electrodes’ PEC properties were analysed using $J-V$ plots and IPCE.

4.4.5.1 $J-V$ Characterisation

Figure 4.4.5.1a shows the $J-V$ plots’ chopped and steady states photocurrent density of sample M41 ($\text{NiO}_{\text{db}}/\text{CuO}_{\text{aacvd}}$) in a 1 M NaOH set to pH 7.5 with HNO$_3$ electrolyte in three electrode mode with Ag/AgCl as reference and Pt as the counter electrode. The manually chopped photocurrent shows a photocurrent density of approximately 100 µA cm$^{-2}$ at 0 V and an onset potential of 0.3 V. The $J-V$ plots show current negative spikes when the light is incident on the film, which then decay to a steady state. These spike indicate recombination in the films. The current spikes seem to vary in height due to an artefact from digital signal sampling.$^{163}$
4.4.5.2 IPCE Characterisation

Figure 4.4.5.2.a shows IPCE spectra for NiO/CuO electrode sample M41. The IPCE shows a conversion efficiency of 4.5 % at 350 nm with a sharp drop at 470 nm (2.6 eV) and a second drop at 690 nm (1.8 eV). This second drop is consistent with the value calculated band gap by the previous methods. This value is close to the literature values of CuO (1.7 eV). This shows conclusive proof that that the NiO has been successfully be sensitised by the CuO.
Figure 4.4.5.2a IPCE spectra for sample M41 photoelectrode NiO sensitised with CuO fabricated on FTO substrate.

4.4.6 Conclusions

In this section porous NiO cathodes fabricated by a combination of ED and DB were sensitised using CuInS\textsubscript{2} and CuO. NiO was successfully sensitised with CuInS\textsubscript{2} deposited by CBD but these proved to be unstable and difficult to repeat due to the lack of uniformity of the films, so the study into CuInS\textsubscript{2} was stopped. CuO deposited by AACVD was successfully used to sensitise the porous NiO, this was confirmed by the IPCE spectrum. This showed a photocurrent density of approximately 100 µA cm\textsuperscript{-2} at 0 V and an onset potential of 0.3 V. This is a large improvement compared to plain NiO, which was 24 µA cm\textsuperscript{-2} at 0 V, which had an onset potential of 0.1 V. NiO sensitised by AACVD CuO provided a good photocathode for use in solid-state solar cells.
4.5 Solid State Solar Cells

4.5.1 Cathodic Photosensitised NiO Cells using CuO as the Sensitiser and ZnO as the Anode Semiconductor

Cells were prepared using NiO deposited by the combination of electrodeposition and doctor blade, CuO by electrodeposition and ZnO deposited by AACVD as discussed in section 2.7.1.

4.5.1.1 XRD Characterisation

Figure 4.5.1.1a shows XRD of photosensitised NiO cells using CuO as the sensitiser and ZnO as the anode semiconductor phase. This shows ZnO has been successfully deposited on the electrodes. CuO does not show up due to it being very thin as it was deposited using electrodeposition.

Figure 4.5.1.1a XRD diffraction pattern of sample M25 photovoltaic device NiO sensitised with CuO and ZnO as the anode fabricated on FTO substrate.
4.5.1.2 J-V Characterisation

Figure 4.5.1.2a shows the J-V curves for photosensitised NiO cells using CuO as the sensitizer and ZnO as the anode semiconductor phase. This shows ohmic and photoconductive behaviour with no photoactivity; this is very undesirable. With this cell construction the cells did not perform as expected and therefore the set up using CuO as the absorber and ZnO as the electron transporter has to be modified.

Figure 4.5.1.2a J-V plots of sample M25 photovoltaic device NiO sensitised with CuO and ZnO as the anode fabricated on FTO substrate.

4.5.2 Cathodic Photosensitised NiO Cells using CuFe$_2$O$_4$ as the Sensitiser and ZnO as the Anode Semiconductor Phase

Copper ferrite (CuFe$_2$O$_4$) has a spinel crystal structure that can exist as tetragonal and cubic structures.$^{171}$ It also shows p-type behaviour.$^{171}$ CuFe$_2$O$_4$ is expected to be a good sensitizer due to the high position of the conduction band which is also pH insensitive.$^{112}$ It also has a direct band gap 1.4 to 2.0 eV; this is desirable for absorption of the solar spectrum.$^{112}$ This band gap is due to two
charge transfers from $O_{2p}$ and the non direct transition from $Fe^{3+}_{3d}$ valence bands to the $Fe^{2+}_{3d}$ conduction band.\textsuperscript{172} CuFe$_2$O$_4$ has other desirable properties such as high thermal stability and good electrical conductivity.\textsuperscript{173} CuFe$_2$O$_4$ have been deposited by multiple methods sputtering, electrochemical deposition, sol-gel, hydrothermal, co-precipitation method and solid state reaction.\textsuperscript{173} It is for these reasons that CuFe$_2$O$_4$ was used as the light absorber cathodic semiconductor layer for the present study.

Cells were prepared using NiO deposited by AACVD, CuFe$_2$O$_4$ by AACVD and ZnO deposited by AACVD as discussed in section 2.7.2.

### 4.5.2.1 J-V Characterisation

Figure 4.5.2.1a shows the J-V curves for photosensitised NiO cells using CuFe$_2$O$_4$ as the sensitisier and ZnO as the anode semiconductor phase. This device shows photoactivity. The cells constructed using CuFe$_2$O$_4$ as the absorber and ZnO as the electron transporter show a lot more promise even though the values are very low and just above the detectible limits just above the noise.

![Figure 4.5.2.1a J-V plots of photovoltaic device NiO sensitised with CuFe$_2$O$_4$ and ZnO as the anode fabricated on FTO substrate.](image)
4.5.3 Cathodic Photosensitised NiO Cells using CuFe$_2$O$_4$ and CuO as Sensitisers and ZnO as the Anode Semiconductor Phase

Cells were prepared using NiO deposited by AACVD, CuFe$_2$O$_4$ by AACVD, CuO by AACVD and ZnO deposited by AACVD as discussed in section 2.7.3.

4.5.3.1 J-V Characterisation

Figure 4.5.3.1a shows the J-V curves for photosensitised NiO cells using CuFe$_2$O$_4$ and CuO as the sensitisers and ZnO as the anode semiconductor phase. Unfortunately, these solar cells showed very low photo activity with a $J_{sc}$ that was barely measurable with also an increase in series resistance.

![Figure 4.5.3.1a J-V plots of photovoltaic device NiO sensitised with CuFe$_2$O$_4$, CuO and ZnO as the anode fabricated on FTO substrate.](image)

4.5.4 Cathodic Photosensitised NiO Cells using CuO as the Sensitiser and WO$_3$ as the Anode Semiconductor Phase

Tungsten trioxide (WO$_3$) is a desirable material for solar cells as it occurs naturally as krasnogorite so it is highly stable.$^{139}$ According to the literature, WO$_3$ crystal structure is highly dependent on the fabrication temperature. The triclinic structure is formed at below 30 °C whereas monoclinic at below 330 °C. The
orthorhombic and tetragonal forms are formed at below 740 °C and above 740 °C respectively.\textsuperscript{174} WO\textsubscript{3} is a wide band gap semiconductor, varying from about 2.6 to 3.0 eV.\textsuperscript{175} These bands are associated with charge transfer of the form O\textsubscript{2p} to W\textsubscript{5d}.\textsuperscript{176} Thin films of amorphous WO\textsubscript{3} also show electrochromic behaviour that are blue when a negative potential is applied and become a very pale yellow (virtually colourless) when the potential is switched to positive values.\textsuperscript{177} WO\textsubscript{3} films have been deposited by a variety of methods, including physical and chemical deposition techniques. Chemical methods which have been used include spray pyrolysis, chemical vapour deposition and sol-gel.\textsuperscript{113} It is for these reasons that WO\textsubscript{3} was used as the wide band gap anodic semiconductor layer for the present study.

Cells were prepared using NiO deposited AACVD, CuO by AACVD and WO\textsubscript{3} deposited by AACVD as discussed in section 2.7.4.

\textbf{4.5.4.1 J-V Characterisation}

Figure 4.5.4.1a shows a current voltage plot for photosensitised NiO cells using CuO as the sensitiser and WO\textsubscript{3} as the anode semiconductor phase. Unfortunately, these solar cells showed very low photo activity with a J\textsubscript{sc} that was barely measurable. This poor result was also due to bleaching of the CuO layer when depositing WO\textsubscript{3}. This bleaching could be the result of the conversion of CuO to CuWO\textsubscript{4} similar to that discovered by J.Y.Zheng \textit{et al.}\textsuperscript{108} The equations below show how this could occur.\textsuperscript{108}

\begin{align}
\text{H}_2\text{W}_2\text{O}_{11} + \text{CuO} & \rightarrow 2\text{CuWO}_6 + \text{H}_2\text{O}_{(g)} \uparrow \quad (\text{eq 4.5.4.1a})^{108} \\
\text{CuWO}_6 & \rightarrow \text{CuWO}_4 + \text{O}_2(g) \uparrow \quad (\text{eq 4.5.4.1b})^{108}
\end{align}
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4.5.4.1a $J-V$ plots of photovoltaic device NiO sensitised with CuO and WO$_3$ as the anode fabricated on FTO substrate.

4.5.5 Cathodic Photosensitised NiO Cells using CuFe$_2$O$_4$ as the Sensitiser and WO$_3$ as the Anode

Cells were prepared using NiO deposited by AACVD, CuFe$_2$O$_4$ by AACVD and WO$_3$ deposited by AACVD as discussed in section 2.7.5.

4.5.5.1 $J-V$ Characterisation

Figure 4.5.5.1a shows a current voltage plot for photosensitised NiO cells using CuFe$_2$O$_4$ as the sensitisier and WO$_3$ as the anode semiconductor phase. Unfortunately, these solar cells showed very low but defiant photoactivity with a $J_{sc}$ that was just visible above the noise. The dark current is also very low so this means that this device set up could work but would require optimisation.
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Figure 4.5.5.1a J-V plots of photovoltaic device NiO sensitised with CuFe$_2$O$_4$ and WO$_3$ as the anode fabricated on FTO substrate.

4.5.6 Cathodic Photosensitised NiO Cells using CuFe$_2$O$_4$ and CuO as Sensitisers and BiVO$_4$ as the Anode Semiconductor

Bismuth vanadate (BiVO$_4$) is a desirable material for solar cells as it occurs naturally as clinobisvanite, dreyerite and pucherite which are highly stable. The main crystal forms of BiVO$_4$ are monoclinic (distorted sheelite structure, fergusonite structure), tetragonal (zircon type structure), and tetragonal (sheelite structure). The phase transition from tetragonal (zircon type structure) to monoclinic irreversibly occurs at 670−770 K. The phase transition is also observed at room temperature by crushing the powder. The transition, monoclinic to tetragonal (sheelite structure) can also occur reversibly at 528 K. BiVO$_4$ is an n-type semiconductor with a direct band gap of 2.4 eV. The charge transition is due to the movement of 2p electrons between vanadium and oxygen in VO$_4^{3-}$. The characteristic absorption band observed for the monoclinic BiVO$_4$ is assigned to the band transition from a 6s valence band of bismuth to a 3d conduction band of vanadium. The valence bands may be formed not only by Bi$_6$s but also from O$_{2p}$, namely a hybrid orbital of Bi$_6$s and O$_{2p}$. The tetragonal BiVO$_4$, only absorbs in the UV region due to the transition of 2p electrons between vanadium and oxygen in VO$_4^{3-}$. BiVO$_4$ has been recently studied for a photocatalyst for water splitting.
Several synthesis methods have been used to prepare monoclinic BiVO$_4$ such as sonochemical method, solid-state reaction, reflux, sol gel and hydrothermal method. It is for these reasons that BiVO$_4$ was used as the wide band gap anodic semiconductor layer for the present study.

4.5.6.1 Preparation of Porous NiO Electrodes

Cells were prepared using NiO deposited by AACVD, CuFe$_2$O$_4$ by AACVD, CuO by AACVD and BiVO$_4$ deposited by AACVD as discussed in section 2.7.6.

4.5.7 Material/Structural Properties

4.5.7.1 XRD Characterisation

Figure 4.5.7.1a shows the XRD reflections for each layer on FTO as well as layer combinations. This was done to check if any of the layers reacted and changed with the layers around them. The samples are also described in Table 4.5.7.1a. NCF corresponds to AACVD NiO with AACVD CuFe$_2$O$_4$ on top, this is shown in the diffraction pattern which the reflections match with the positions of the individual layers of NiO and CuFe$_2$O$_4$ so no measurable reaction is taking place between these layers using XRD, CFC corresponds to AACVD CuFe$_2$O$_4$ with AACVD CuO on top, the reflections match that of the individual layers so it can also be no measurable reaction occurring between the CuFe$_2$O$_4$ and CuO layers using XRD, CFB corresponds to AACVD CuFe$_2$O$_4$ with AACVD BiVO$_4$ on top, the reflections match that of the individual layers but a few of the reflections have different intensities which suggest no measurable reaction occurring between the CuFe$_2$O$_4$ and BiVO$_4$ layers using XRD but crystal orientation has changed and CBV corresponds to AACVD CuO with AACVD BiVO$_4$ on top, the reflections match that of the individual layers so it can also be no measurable reaction occurring between the CuO and BiVO$_4$ layers using XRD.
Chapter 4 Results and Analysis of the devices

Figure 4.5.7.1a show XRD diffraction patterns of each layer individually as well as layer combinations.

<table>
<thead>
<tr>
<th>Sample</th>
<th>AACVD NiO</th>
<th>AACVD CuFe₂O₄</th>
<th>AACVD CuO</th>
<th>AACVD BiVO₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 NiO</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 CuFe₂O₄</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 CuO</td>
<td></td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 BiVO₄</td>
<td></td>
<td></td>
<td></td>
<td>X</td>
</tr>
<tr>
<td>5 NCF</td>
<td>X</td>
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</tr>
<tr>
<td>6 CFC</td>
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</tr>
<tr>
<td>7 CFB</td>
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<td>X</td>
</tr>
<tr>
<td>8 CBV</td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>

4.5.7.2 SEM Characterisation

Figure 4.5.7.2a show AACVD NiO and AACVD CuFe₂O₄ on top of AACVD NiO as it can be seen the CuFe₂O₄ covers the NiO but still maintains the porosity.
4.5.7.3 Raman Characterisation

Samples as described in Table 4.5.7.1a. Figure 4.5.7.3a for each layer on FTO. The Raman spectrum of NiO show peaks at about 550 and 763 cm\(^{-1}\) corresponds to NiO as found by L. Mendoza et al.\(^{127}\) CuO spectra show peaks at about 300 and 345 cm\(^{-1}\) which correspond to CuO as found by J. F. Xu et al.\(^{180}\) CuFe\(_2\)O\(_4\) spectra shows peaks at 224, 292, 350, 409, 488 and 690 cm\(^{-1}\). Peaks at 488 and 690 cm\(^{-1}\) correspond to CuFe\(_2\)O\(_4\) octahedral and tetrahedral sites respectively as found by Valdés-Solís et al.\(^{181}\) While peaks at 224, 292, 350 and 409 cm\(^{-1}\) correspond to \(\alpha\)-Fe\(_2\)O\(_3\) as reported by J. A. Glasscock.\(^{182}\) which suggests that there is an impurity of \(\alpha\)-Fe\(_2\)O\(_3\). Raman of BiVO\(_4\) show peaks at 130, 215, 328, 370, 725 and 830 cm\(^{-1}\) this is corresponds with results found by Y. Liang et al.\(^{183}\)
Figure 4.5.7.3a shows the Raman spectrum for each of the layers deposited by AACVD onto FTO.

Figure 4.5.7.3b for layer combinations which are in direct contact with each other. The layer combinations were tested to check if any of the layers reacted and changed with the layers around them. NCF shows the same peaks as NiO and CuFe$_2$O$_4$ as expected. It is the same for CFC shows the peaks of CuFe$_2$O$_4$ and CuO. CBV shows that there is some reaction of the CuO and BiVO$_4$ layers as peak that do not occur in the individual spectra. CFB show the same peaks as CuFe$_2$O$_4$ and BiVO$_4$. 
Figure 4.5.7.3b shows the Raman spectrum for each of the layers deposited by AACVD onto FTO.

4.5.8 Optical Properties

4.5.8.1 UV-Vis Characterisation

4.5.8.1.1 Absorbance

Figure 4.5.8.1.1a shows UV-Vis absorption spectrum of individual AACVD layers deposited for 30 minutes on FTO glass (apart from BiVO₄ which had 50 minutes). FTO glass was used as the blank for this reason there is a sharp drop in absorption at about 310 nm. CuFe₂O₄ strong absorption over the whole of the visible region so will act as a good solar light absorber.
Figure 4.5.8.1.1a Absorbance spectrum over the visible region for each of the layers used to construct the solar cell.

4.5.8.1.2 Band gap Calculations

Figure 4.5.8.1.2a shows a Tauc plot for NiO which calculates the band gap of 3.4 eV for the AACVD NiO.
Figure 4.5.8.1.2a Tauc plot for NiO electrode deposited by AACVD.

Figure 4.5.8.1.2b shows a Tauc plot for CuFe$_2$O$_4$ which calculates the band gap of 1.95 eV for the AACVD CuFe$_2$O$_4$.

Figure 4.5.8.1.2b Tauc plot for CuFe$_2$O$_4$ electrode deposited by AACVD.
Figure 4.5.8.1.2c shows a Tauc plot for CuO which calculates the band gap of 1.76 eV for the AACVD CuO.

Figure 4.5.8.1.2c Tauc plot for CuO electrode deposited by AACVD.

Figure 4.5.8.1.2d shows a Tauc plot for BiVO$_4$ which calculates the band gap of 2.48 eV for the AACVD BiVO$_4$. This value is close to the calculated band gap by D. J. Payne et al.$^{184}$
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4.5.9 Photoelectrochemical Properties

4.5.9.1 J-V Characterisation

Figure 4.5.9.1a shows the $J$-$V$ curves for photosensitised NiO cells using CuFe$_2$O$_4$ and CuO as the sensitisers and BiVO$_4$ as the anode semiconductor phase. The $J$-$V$ curve of the best cell shows it has 0.541 μA cm$^{-2}$ (541nA) TX146 made up of NiO 20 min, CuFe$_2$O$_4$ 50 min, CuO 10 min, BiVO$_4$ 27 min, 30 min annealing and all deposited at 600 °C.
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Figure 4.5.9.1a $J$-$V$ curve of the best solid state cell.

4.5.9.2 IPCE Characterisation

Figure 4.5.9.1a shows the IPCE for photosensitised NiO cells using $\text{CuFe}_2\text{O}_4$ and CuO as the sensitisers and BiVO$_4$ as the anode semiconductor phase. IPCE (measured with an amplifier set at $10^7$) shows a peak at about 480 which corresponds closely to the $\text{CuFe}_2\text{O}_4$ absorption shown in figure 4.5.8.1.1a. This proves that the NiO has been successfully sensitised with $\text{CuFe}_2\text{O}_4$ and the electrons and holes generated in the $\text{CuFe}_2\text{O}_4$ are successfully transported to the FTO and Pt electrode respectively.
Figure 4.5.9.2a IPCE amplified with amplifier set at $10^7$ of the best sample.
4.5.10 Electrical Properties

4.5.10.1 Capacitance Characterisation

4.5.10.1.1 Mott-Schottky Plots

Mott-Schottky plot for the AACVD NiO prepared films show a flat band potential of 0.28 V in pH 5 vs. reference electrode Ag/AgCl. The slope moving in a negative correlation shows that this is a p-type material which is as expected. As this flat band potential is in a p-type material we know this is close to the valence band as described in chapter 2. The donor density was estimated to be $2.92 \times 10^{22}$ cm$^{-3}$ using equation 4.1.8.1.1a and the relative permittivity for NiO ($\varepsilon_{\text{NiO}} = 11$).

![Mott-Schottky plot](image.png)

Figure 4.5.10.1.1a Mott-Schottky plot of the AACVD NiO on FTO substrate at pH 5.
Mott-Schottky carried out on the AACVD CuFe$_2$O$_4$ prepared films show a flat band potential of -0.057 V in pH 5 vs. reference electrode Ag/AgCl. The slope moving in a negative correlation shows that this is a p-type material which is as expected. As this flat band potential is in a p-type material we know this is close to the valence band. The donor density was estimated to be 3.22x10$^{17}$ cm$^{-3}$ using equation 4.1.8.1.1a and the relative permittivity for CuFe$_2$O$_4$ ($\epsilon_{\text{CuFe}_2\text{O}_4} = 31$).

![Mott-Schottky plot of the AACVD CuFe$_2$O$_4$ on FTO substrate at pH 5.](image)

Figure 4.5.10.1.1b Mott-Schottky plot of the AACVD CuFe$_2$O$_4$ on FTO substrate at pH 5.
Mott-Schottky carried out on the AACVD CuO prepared films show a flat band potential of 0.181 V in pH 5 vs. reference electrode Ag/AgCl. The slope moving in a negative correlation shows that this is a p-type material which is as expected. As this flat band potential is in a p-type material we know this is close to the valence band. The donor density was estimated to be $9.09 \times 10^{17}$ cm$^{-3}$ using equation 4.1.8.1.1a and the relative permittivity for CuO ($\varepsilon_{CuO} = 18.1$).\textsuperscript{158}

![Mott-Schottky plot of the AACVD CuO on FTO substrate at pH 5.](image)

Figure 4.5.10.1.1c Mott-Schottky plot of the AACVD CuO on FTO substrate at pH 5.
Mott-Schottky carried out on the AACVD BiVO₄ prepared films show a flat band potential of 0.23 V in pH 5 vs. reference electrode Ag/AgCl. The slope moving in a positive correlation shows that this is a n-type material which is as expected.⁴⁰ As this flat band potential is in a n-type material we know this is close to the conduction band as described in chapter 2. The donor density was estimated to be 1.77x10^{18} cm⁻³ using equation 4.1.8.1.1a and the relative permittivity for BiVO₄ (ε_{BiVO₄} = 55).¹⁸⁶

Figure 4.5.10.1.1d Mott-Schottky plot of the AACVD BiVO₄ on FTO substrate at pH 5.
The band gap diagram is constructed from information from the Tauc plots and the Mott-Schottky measurements are shown in figure 4.5.10.1.1e. Table 4.5.10.1.1a shows the exact values used. Mott-Schottky measurements show the flat band potential which is the Fermi level, this was then assumed to be the valence band for p type semiconductors and conduction band for n type semiconductors. Due to in each case the Fermi level being very close to the respective band. The Tauc plot was used to calculate the band gap for each semiconductor, this was then used in conjunction with the estimated valence or conduction band to estimate the position of the unknown band.

![Figure 4.5.10.1.1e Band diagram of structure of the solar cell constructed from Tauc plots and the Mott-Schottky measurements of each layer.](image)

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Band Gap (eV)</th>
<th>VB</th>
<th>CB</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>3.40</td>
<td>0.28</td>
<td>-3.12</td>
</tr>
<tr>
<td>CuFe₂O₄</td>
<td>1.95</td>
<td>-0.06</td>
<td>-2.01</td>
</tr>
<tr>
<td>CuO</td>
<td>1.76</td>
<td>0.18</td>
<td>-1.58</td>
</tr>
<tr>
<td>BiVO₄</td>
<td>2.48</td>
<td>2.71</td>
<td>0.23</td>
</tr>
</tbody>
</table>
Chapter 4 Results and Analysis of the devices

4.5.11 Optimisation

The photosensitised NiO using CuFe$_2$O$_4$ and CuO as sensitisers and BiVO$_4$ as the anode showed promise and was believed that the devices performance can be improved so an optimisation process was undertaken to achieve this.

The solar cells were then optimised by controlling the thickness of the AACVD deposited CuO to gain the maximum $J_{sc}$, this was done by controlling the deposition time. Keeping deposition times constant for the other layers, 20 min for NiO, 30 min for CuFe$_2$O$_4$, 21 min for BiVO$_4$ and annealed at 600 °C for 30 min. Figure 4.5.11a shows that at 10 min provided the highest $J_{sc}$. CuO deposition time was maintained at 10 min for the rest of the samples.

![Figure 4.5.11a](image)

*Figure 4.5.11a The $J_{sc}$ of the complete solar cells verses CuO deposition time.*

Optimisation was carried out by controlling the thickness of the AACVD deposited BiVO$_4$ layer. Keeping deposition times constant for the other layers, 20 min for NiO, 30 min for CuFe$_2$O$_4$, 10 min for CuO and annealed at 600 °C for 40 min. Figure 4.5.11b shows that at 27 min provided the highest $J_{sc}$. BiVO$_4$ deposition time was then maintained at 27 min for the rest of the samples.
Cells were optimised by controlling the thickness of the AACVD deposited CuFe$_2$O$_4$. Keeping deposition times constant for the other layers, 20 min for NiO, 10 min for CuO, 27 min for BiVO$_4$ and annealed at 600 °C for 40 min. Figure 4.5.11c shows that at 50 min provided the highest $J_{sc}$. So from then on the CuFe$_2$O$_4$ deposition time was maintained at 50 min.
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Figure 4.5.11c The Jsc of the complete solar cells versus CuFe$_2$O$_4$ deposition time.

Next to be optimised was the thickness of the AACVD deposited NiO this was done by controlling the deposition time. Keeping deposition times constant for the other layers, 50 min for CuFe$_2$O$_4$, 10 min for CuO, 27 min for BiVO$_4$ and annealed at 600 °C for 30 min. Figure 4.5.11d shows that at 20 to 30 min provided the highest and repeatable $J_{sc}$. NiO deposition time was maintained at 20 min for the rest of the samples.

Figure 4.5.11d The Jsc of the complete solar cells versus NiO deposition time.
Optimisation was then studied by varying the post annealing time. Keeping deposition times constant for the other layers, 20 min for NiO, 50 min for CuFe₂O₄, 10 min for CuO, 27 min for BiVO₄ and annealed at 600 °C. Figure 4.5.11e show that at 30 min provided the highest Jsc while 90 min provided the highest and most repeatable Jsc. 30 min was chosen over 90 min due to only a small increase in repeatability for a much longer annealing time was deemed unnecessary. From then on the annealing time was maintained at 30 min.

![Figure 4.5.11e The Jsc of the complete solar cells verses annealing time of the cell.](image)

AACVD deposition temperature for all layers were then optimised. Keeping deposition times constant for the layers, 20 min for NiO, 50 min for CuFe₂O₄, 10 min for CuO, 27 min for BiVO₄ and annealed at 600 °C for 30 min. Figure 4.5.11f show that at 600 °C provided the highest Jsc. From then on the deposition temperature was maintained at 600 °C for all the layers.
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Figure 4.5.11f The Jsc of the complete solar cells verses deposition temperature of all the layers.

AACVD deposition temperature for the CuFe$_2$O$_4$ was then varied. Keeping deposition temperatures at 600 °C for the other layers and deposition times constant for the layers, 20 min for NiO, 50 min for CuFe$_2$O$_4$, 10 min for CuO, 27 min for BiVO$_4$ and annealed at 600 °C for 30 min. Figure 4.5.11g show that 550 °C provided the highest J$_{sc}$. But 600 °C provided the highest and most repeatable J$_{sc}$ so it was decided to use 600 °C as it also greatly increased cell fabrication time due to waiting for the hotplate to heat up and cool down. The deposition temperature was maintained at 600 °C for the CuFe$_2$O$_4$ layers for the rest of the samples.
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4.5.11g Figure The Jsc of the complete solar cells verses deposition temperature of the CuFe$_2$O$_4$ layer.

4.5.12 Conclusions

In this section, sensitised photocathodes were used as a base for solid state solar cells. The photocathodes where made of porous NiO fabricated by using a combination of DB and ED and then were sensitised using AACVD CuO or AACVD NiO, sensitised using AACVD CuO. n-type semiconductors used to fabricate solid state cells are ZnO, WO$_3$ and BiVO$_4$. It was also found that CuFe$_2$O$_4$ also proved to be a good absorber especially when CuO is also used. ZnO proved to give poor performance while WO$_3$ and BiVO$_4$ both showed promise. BiVO$_4$ showed the highest performance. This was then studied layer by layer and optimised. After optimisation of NiO sensitised by CuFe$_2$O$_4$ and CuO with BiVO$_4$ as the anode, the best solid state solar cell had a J$_{sc}$ of 0.541 μA cm$^{-2}$ (541 nA) and a V$_{oc}$ of 0.14 V, TX146 made up of NiO 20 min, CuFe$_2$O$_4$ 50 min, CuO 10 min, BiVO$_4$ 27 min, using AACVD and then annealed for 30 min at 600 °C. This is less than photocurrent density that was achieved by the sensitised photocathode, 100 μA cm$^{-2}$ at 0 V and an onset potential of 0.3 V. IPCE shows that CuFe$_2$O$_4$ is the main sensitiser for this construction of solid state solar cells.
Chapter Five: Conclusions

5.1 Semiconductor Thin Films and Electrolyte Interface Conclusions

Different preparation techniques were used to fabricate porous nickel oxide films. NiO proved be a good wide band gap p-type semiconductor that provides a stable porous structure for solar cell applications. Aerosol assisted chemical vapour deposition and a combination of electrodeposition and doctor blade techniques gave highly porous films.

Copper(I) oxide and copper(II) oxide thin films were successfully produced from annealing copper metal films by controlling both the temperature and annealing time. Copper metal thin films were prepared by aerosol assisted chemical vapour deposition using argon as the carrier gas. Copper films were dominant when annealed under 200 °C, copper(I) oxide films were dominant when annealed between 200 °C and 300 °C and copper(II) oxide films were dominant above 300 °C. It was also shown that increased photoactivity and stability occurred with the increase in temperature, thus showing that copper(II) oxide was the best absorber. As copper(II) oxide was the desired film, it was able to be deposited directly using aerosol assisted chemical vapour deposition using air as the carrier gas.

Zinc oxide can form different structures depending on the deposition method and precursors used. Chemical bath deposition of zinc oxide produced a highly structured and porous structure when combined with a seed layer. The most effective seed layer was deposited using aerosol assisted chemical vapour deposition. This gives more uniform and better aligned rods compared to seed layer depositions with electrodeposition. It has also been shown that the rods can be preferentially etched to create tubes, therefore increasing the internal surface area even more.

5.2 Electrolyte Solar Cell Conclusions

Using the knowledge gained from the studies with single semiconductor photoelectrodes, efforts to fabricate sensitised photocathodes were undertaken.
Copper indium disulfide was chosen since it is a well known p-type semiconductor with a suitable band gap. This was used as a sensitisier for porous nickel oxide photocathodes using chemical bath deposition. Copper indium disulfide was successfully deposited on porous nickel oxide. It was found that using this deposition technique to produce bimetal semiconductor gave poor repeatability, thus making it difficult to optimise and this study was terminated at this point.

Copper(II) oxide was then chosen as the sensitisier due to it is a well known p-type semiconductor with suitable band gap and stability. Copper(II) oxide was able to successfully sensitise porous nickel oxide proven by the incident photon conversion efficiency. Current-voltage curves also proved that the electrodes were stable with repeatable photoactivity.

5.3 Solid State Solar Cell Conclusions

The knowledge gained from the experiments with single semiconductor photoelectrodes and sensitised photocathodes was used in studies with solid state solar cells. Multiple solid state photovoltaic devices were successfully fabricated using low cost materials and methods, using different semiconductors and configurations. Most of these showed poor or no photoactivity but did prove that the concept would work. One of the breakthrough was the construction of cathodic nickel oxide sensitised with copper ferrite and using tungsten trioxide as the anodic phase were successfully fabricated. These cells showed low photoactivity but did show that it could be successful. This then lead to the fabrication of cathodic nickel oxide sensitised with copper ferrite and copper(II) oxide with bismuth vanadate as the anodic phase. These solid state solar cells showed photoactivity with a $J_{sc}$ of 541 nA showing the concept works. The $J-V$ graph shows that there is a strong effect from parasitic resistance which needs to be minimised to improve cell performance. Incident photon conversion efficiency proves that the copper ferrite has successfully been used to sensitisise nickel oxide.
Chapter Six: Suggestions for Future Work

6.1 Future Prospective of a Semiconductor Thin Films and Photoelectrochemical Cells

Several different semiconductors were fabricated using multiple methods. In this study copper ferrite, a compound composed of cheap abundant elements was successfully used in a solar cell and deposited via cheap, scalable methods. Further exploration with more semiconductors in this field is required. The search for semiconductors should focus on ones that do not contain rare elements so that the cells could be easily scaled up.

Further studies are also required for improvement of these cells and into finding new p-type semiconductors with high hole mobility and charge lifetimes.

6.2 Future Prospective of Semiconductor Sensitised Cells

Research into photosensitised anodic based solar cells has increased greatly on the titanium dioxide dye sensitised cell by M. Grätzel and B. O'Regan in 1991. For anodic based solar cells it is now necessary to move away from liquid electrolytes to solid state cells, as these have an increased working life time compared to organic liquids, which over time tend to take on water.

During this study photocathodes were successfully fabricated but were not close to currents achieved by photoanodes. It is required to increase the photocurrent density of photocathodes to match that achieved by photoanodes to produce a working tandem solar cell. Improvements in the photocurrent density of photocathodes can be achieved by;

Increasing the hole mobility and life time. This could be done by doping or minimising the thickness of each of the layers.

Reducing the recombination will also improve the photocurrent density. This can be achieved by improving the layer to layer contact or reducing the charge diffusion length. This can be achieved by reducing film thickness or having a highly conducting and porous layered structure for the absorber.
Chapter 6 Suggestions for Future Work

Careful consideration of semiconductor band edges and their interactions with other layers is essential for maximising the current density.

6.3 Future Prospects of Semiconductor Sensitised Tandem Cells

Further work is required to combine the knowledge gained by the doctoral studies carried out at Loughborough University, Imperial College London and Bristol University to fabricate a working tandem solar cell with increased voltage. Work will be required to match the currents of the photoanode and photocathode. Efforts will also be required to manage the light so that the maximum amount of the light spectrum can be harnessed effectively. This will require careful consideration of the absorbed light as well as the absorbance of other components in the tandem cells.
Chapter Seven: Dissemination

During my doctoral study I have co-authored two peer-reviewed publications, made two oral presentations and fifteen poster presentations using my own project data. As a part of the Supergen Exitonic Solar Cells consortia activities I have attended five meetings and presented the output of my research project. I have also been involved in an outreach activity.

Publications (in peer-review journals) and a few selected posters were included at the end of this chapter.

7.1 Publications in peer-review journals


7.2 Oral presentations in conferences

(2). T. Smith and K.G.U.Wijayantha, Photocathodes for Tandem Solar Cells, Midlands Electrochemistry Group, University of Birmingham, 18th September 2013
7.3 Poster presentations in conferences


(9). **T. Smith** and K.G.U.Wijayantha, Towards Tandem Solar Cells, *Great Western Electrochemistry meeting*, University of Bath, 18th June 2012


### 7.4 List of Supergen Exitonic Solar Cells consortia Attended


7.5 List of Outreach Activities Participated

Effects of AACVD and Electrodeposited ZnO Seed Layer on the Growth and Alignment of ZnO Nanorods by Chemical Bath Deposition

Asif Ali Tahir, Thomas D. Smith, and K. G. Upul Wijayantha

Department of Chemistry, Loughborough University, Loughborough, Leics, LE11 3TU, UK

The effect of ZnO thin films as seed layers deposited by Aerosol Assisted Chemical Vapour Deposition (AACVD) and electrodeposition were systematically investigated on the growth and alignment behaviour of ZnO nanorods. A series of compact and uniform ZnO seed layers with different deposition times (1, 2 and 3 min) were deposited on FTO (Fritform-doped tin oxide) substrate using AACVD technique. For comparison, another series of ZnO seed layers were also deposited on FTO substrate by electrodeposition. The ZnO nanorods were grown on the seed layer coated FTO substrates by the chemical bath deposition (CBD). The XRD and SEM results show that vertically aligned ZnO nanorods are formed on seed layer deposited by AACVD as compared to the seed layer deposited by electrodeposition.

Keywords: Aerosol Assisted Chemical Vapour Deposition (AACVD), Seed Layer, ZnO Nanorods, Chemical Bath Deposition (CBD).

One-dimensional (1D) nanostructured semiconductor materials have attracted a significant interest because of their remarkable physical and chemical properties. Among one-dimensional (1D) semiconductor materials, ZnO have received widespread attention in recent years due to its wide optical band gap of 3.37 eV, large exciton binding energy (60 meV in bulk ZnO), piezoelectric properties and excellent mechanical and thermal stability. One-dimensional (1D) ZnO nanostructures are considered to be one of the most important semiconductor nanomaterials for fabricating nano-devices. The optical, electronic, and mechanical properties of nano-devices are highly dependent on shape, size, density, and alignment of nanostructures. This flexibility has enabled use of ZnO nanostructures in a wide range of applications like surface acoustic wave filters, photonic crystals, photodetectors, light emitting diodes, gas sensors, photo-catalysts, dye-sensitized solar cells and field emitters if the properties are conveniently altered. Hence, an enormous amount of effort have been devoted to develop fabrication methods which can provide better control over morphology and alignment of 1D ZnO nanostructures. Methods employed include vapor-phase transport (VPT), electrochemical deposition, pulsed laser deposition, metal-organic chemical vapor deposition (MOCVD), hydrothermal synthesis, atomic layer deposition and chemical bath deposition (CBD) techniques. Among wet chemical techniques, CBD is widely used because of its fast growth process, simple apparatus requirement, and scalability.21,22

Despite efforts on development alternative conducting substrates, F-SnO2 (FTO) is still widely preferred substrate for the growth of ZnO nanorods. However, the significant lattice mismatch between ZnO and FTO has detrimental effects on electronic and photodetector-chemical performance of ZnO nanorod electrodes prepared on FTO substrates. Typically, thin film seed layer is deposited onto the substrate to minimize this lattice mismatch problem. The seed layer also facilitates the nucleation and growth of ZnO nanorods. Hence, seed layer could provide a clean and smooth surface to further fabricate quantum well and superlattice devices with small lattice mismatch. Seed layers are usually introduced in the heteroepitaxial growth process of high quality semiconductor thin films. The growth of ZnO nanorods has been influenced by the crystallinity, orientation, surface roughness, and thickness of the ZnO seed layer. Seeded substrates have been prepared in a variety of ways including pulsed laser deposition, direct-current reactive magnetron sputtering, and radio frequency magnetron sputtering. Previous studies have shown that ZnO nanorod growth is...
sensitive to the substrate temperature, texture, and ZnO seed layer deposition technique. In this letter, we consider the complexity of the growth of ZnO seed layers by electrodeposition and AACVD and highlight the advantages of use of AACVD to deposit ZnO seed layers to obtain aligned growth of ZnO nanorods on the FTO substrate.

AACVD is a branch of the CVD which is simple to operate and very versatile. The advantages of AACVD are that a simple solution source can be used to fabricate high quality thin films ensuring the reproducibility. The thickness and architecture of the films can be easily controlled via experimental parameters, such as solution concentration, solvent, nature of carrier gas, carrier gas flow, deposition time, and substrate temperature etc., which indicates one of the prominent advantages of AACVD techniques. ZnO seed layer was deposited on FTO substrate (TEC 8 Pilington, 8 Ω/square) by AACVD as reported elsewhere. In a typical deposition, 10 ml of 1 M methanolic solution of zinc acetate was used to generate aerosol and air (from an air cylinder, provided by BOC) at 350 ml/min was used as carrier gas. Three FTO glass substrates were placed side by side in deposition chamber and aligned so that aerosol falls directly on to the middle of the substrate. The FTO substrate temperature was maintained at 420 °C and the depositions were carried out for 1, 2 and 3 minutes to obtain seed layers with different thickness. For comparison ZnO seed layers were also deposited using electrodeposition method reported earlier. ZnO nanorods were grown by chemical bath deposition (CBD) on seeded FTO substrate using method reported by Belaidi et al.

XRD is an ideal probe to characterize structure and orientation of thin film with respect to the substrate. The XRD pattern of AACVD grown ZnO seed layer is shown in Figure 1. Except diffractive peak from FTO (SnO₂) substrate are marked with asterisk (*). The seed layers deposited by AACVD showed a c-axis preferred orientation in which intensity of (002) ZnO diffraction peaks increase with the increase in deposition time were observed due to the preferred stacking along the (002) planes with the lowest surface free energy on the substrate surface. On the other hand, no ZnO diffraction peak was observed for the seed layers deposited by electrodeposition due to the scattered nature of films as shown in Figure 2(B).

The topographic SEM images of the ZnO seed layers deposited by AACVD and electrodeposition are shown Figures 2(A) and (B). The SEM analysis shows that the AACVD seed layer uniformly cover the FTO surface while the electrodeposited seed layer form a flower like structure scattered on the FTO surface. The density of the flower like structures increases with the increase of deposition time. For the electrodeposited seed layer for three minutes still the surface of FTO is not completely covered as shown by high resolution SEM image Figure 2(B). In contrast, the seed layer deposited by AACVD completely covers FTO and particles start growing along c-axis as evident by the preferred orientation (Fig. 1).

Figure 3(a) shows the XRD pattern of ZnO nanorods deposited by CBD when the ZnO seed layer was deposited using AACVD, while Figure 1(b) shows the XRD pattern of ZnO nanorods deposited by CBD when the ZnO seed layer was deposited by electrodeposition. A typical hexagonal c-axis (002) dominant orientation was found in both cases. However, the ZnO nanorods formed on the electrodeposited seed layer exhibits a polycrystalline structure and shows a weak c-axis-preferred growth orientation which is presumably due to the low coverage of electrodeposited seed layer used to deposit nanorods. Unfortunately, all our efforts on obtaining XRD diffraction pattern for electrodeposited seed layer were unsuccessful and we believe this is due to fact that the electrodeposited seed layer was patchy and discontinued (Fig. 2(B)). In contrast to that, the (002) orientation was much stronger when the seed layer was prepared by AACVD. The average nanorod length is 1.5 and 0.9 μm for the seed layer deposited by AACVD and electrodeposition respectively (Fig. 4). Furthermore, we observed that the growth rate of ZnO nanorods by CBD process is higher for the samples grown on AACVD seed layer compared to the samples grown on electrodeposited seed layer. The low growth rate of ZnO nanorods on electrodeposited seed layer may be due to the weak growth of it in the c-axis, which is a determining factor in the nucleation and subsequent growth of ZnO nanorods. This observation suggests that the vertical growth rate of the ZnO nanorods has a strong relationship with the orientation of the seed layer. The findings of this study are somewhat consistent with previous work which shows that the vertical alignment of the ZnO nanorods depends upon the preparative method and orientation of seed layer.
Figure 4 shows surface topography and cross-section (inset) images of the ZnO nanorods deposited on seed layers (a) deposited by AACVD and (b) by electrodeposition for the purpose of comparison. The sample without a seed layer was also deposited on FTO substrate using standard CBD conditions and their SEM morphology did not show any perpendicular alignment to the substrate surface (Fig. 5(b)). The surface morphology of the ZnO nanorods grown on electrodeposited seed layer shown in Fig. 4(b) composed of nanorods, approximately 50–100 nm in diameter, and their growth morphology did not show perfect perpendicular alignment to the substrate surface, as shown in the cross-section image (Fig. 4(b) inset). Nanorods grown on the electrodeposited seed layer have smaller diameters and larger densities than those of nanorods grown on AACVD seed layers. In marked contrast to the nanorods growth on electrodeposited seed layers, growth on AACVD seed layers as shown in Figure 4(a) shows improved alignment on the FTO substrate. In addition, coverage across the substrate was uniform, with a high density of nanorods with a uniform length. The rod diameter varies substantially from 50 nm to 250 nm and the length is about 1 µm. The dispersed rod diameter could be due to coalescence. Such dispersion of rod diameter is not evident for ZnO nanorods grown on electrodeposited seed layers, but occasionally shows smaller and thinner rods emerging from their tips. However, our results show that the seed layer fabrication methods have a strong influence on the morphology and alignment of ZnO nanorods.
The degree of vertical alignment of the ZnO nanorods increased with increasing the seed layer thickness. To investigate the effect of seed layer thickness on the density and alignment of the nanorods, we varied the deposition time of the seed layer while keeping the AACVD deposition conditions unchanged. Figure 5 shows the cross-sectional SEM images of the ZnO nanorods deposited on seed layers for 1, 2 and 3 minutes. Clearly, the degree of vertical alignment of the ZnO nanorods deposited on AACVD seed layer increased with increasing the seed layer deposition time. After a short deposition time (1 min), the films showed vertically aligned nanorods. But there is also some indication of rods coalescing into unified structures at random points. With the increase of the seed layer deposition time, the nanorods density increases and the degree of vertical alignment become better. Vertically well-aligned ZnO nanorod arrays were formed for the samples that had a seed layer deposited for three minutes. No significant rod density or alignment changes were found after further increase of seed layer thickness. In summary, our results show that deposition method and thickness of ZnO seed layer have a significant influence on the growth and alignment of vertically aligned ZnO nanorods. More importantly our results also proved that AACVD method can be used to deposit preferentially c-axis oriented ZnO seed layer with good crystallinity and smoother surfaces.

Fig. 5. Cross-section SEM images of ZnO nanorods grown by CBD on AACVD deposited seed layers for (a) 1 min (b) 2 mins, (c) 3 mins and (d) ZnO film deposited by CBD without seed layer.
in order to grow well-aligned ZnO nanorods on a range of substrates.

Acknowledgments: This work was supported by the EPSRC.

References and Notes


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Hierarchical ZnO nanorod electrodes: Effect of post annealing on structural and photoelectrochemical performance

Ijaz Ahmad Bhatti, T.A. Nirmal Peiris, Thomas D. Smith, K.G. Upul Wijayantha

1. Introduction

Synthesis of numerous ZnO nanostructures has recently attracted significant interest due to their promising applications in solar cells [1], transparent conducting films [2], ultraviolet-protection films [3], catalysis [4], and gas sensors [5]. In particular, ZnO nanorods have received extensive attention in photonic, electronic, optoelectronic and electrochemical devices due to ease of fabrication at ambient conditions [6].

Post-deposition heat treatment is one of the well-known processes that can be used to enhance electronic communication between substrate and electrode material by improving the adherence [7]. Conventional annealing using a furnace or hot plate is a common technique for the post-annealing of nanomaterials containing electrodes [8]. A great deal of interest has been received in recent years for irradiation with microwaves as an alternative advanced material processing technique and it was reported that this technique is capable of improving particle necking and crystallinity with a minimum thermal stress to the substrate and less effect on the electrode texture [9,10]. This is due to the fact that microwave irradiation generates completely different heating profile compared to that of conventional radiant heating. Microwave radiation interacts with lossy materials that result in rapid and uniform heating throughout the material which cannot be achieved by conventional radiant heating methods [11]. This, in turns minimizes the thermal gradient, particle diffusion and the processing time [12]. It has also been reported that the materials fabricated using low temperature techniques contains certain amorphous regions that can be converted to crystalline phases by microwave irradiation without affecting the film texture (i.e. micro and nanostructure) [13]. Processing materials under microwave irradiation is a relatively novel area of research hence there is a scarcity of information in the literature. Therefore, further research is essential to understand the effect of microwave irradiation on processing of various materials.

Here, we have studied the post annealing effect of ZnO nanorods by conventional radiant and microwave heat treatments on the structural and photoelectrochemical (PEC) properties. The results demonstrate that although the hierarchical texture of ZnO is retained for some extent during the microwave treatment, it reduces the internal surface area. Further, it appears that there is no significant advantage the microwave treatment (i.e. improvements in contacts between rods and substrate by selective heating). As anticipated the conventional radiant heat treatment completely deforms the electrode texture thereby deteriorating the PEC performance.

2. Experimental

Fluorine doped tin oxide (FTO) glass substrates (TEC 8 Pilkington, 8Ω/□) were cleaned and sonicated in acetone, ethanol and deionized water and stored in absolute ethanol [13].
The effective area of the film was maintained at 1 cm². Aerosol assisted chemical vapor deposition (AACVD) technique was used to deposit a thin ZnO seed layer on FTO glass substrates at 400 °C using a precursor solution of 0.1 M zinc acetate (BDH Chemicals Ltd.) in methanol. The deposition was carried out for 4 min and the thickness of the seed layer was in the order of 50-100 nm [14]. After deposition of the seed layer, electrodes were placed in a tube furnace and annealed at 400 °C for 1 h. The ZnO nanorods were grown on ZnO seeded FTO by chemical bath deposition (CBD) method using a mixture of 0.8 M sodium hydroxide (Fisher Scientific) and 0.02 M zinc nitrate (Sigma Aldrich) solution maintained at 80 °C for 50 min. Dried ZnO nanorod films were subjected to 100% microwave irradiation and conventional radi- ant annealing for 30 min using a microwave furnace (MF-16/22, Carbolite Ltd., UK) operating at a frequency of 2.45 GHz and 2 kW power (during the heat treatments the temperature was maintained at 300 °C) [10,13]. The phase and crystallinity of as-deposited and annealed ZnO nanorod films were studied using Bruker D8 XRD, operating with monochromatic Cu Kα (λ=1.54 Å) radiation and PSD detector. Topographic images for the as-deposited, microwave treated and conventionally annealed ZnO nanorods were taken using Leo 1530 VP field emission gun scanning electron microscopy (FEG-SEM, at an accelerating voltage of 5 kV and a working distance of 6 mm). Surface areas of the films were investigated by conducting dye adsorption/desorption measurements [15]. The current–voltage characteristics of heat treated and untreated electrodes were studied using 0.1 M Na2SO4 aqueous electrolyte by potentiostat (Eco Chemi micro- AutoLab type III) through chopping the illumination from halogen lamp at 100 mW/cm² light intensity.

3. Results and discussion

X-ray diffraction patterns of zinc oxide nanorods grown on FTO glass substrates show the wurtzite crystallites of ZnO of (100), (002), (101), (102), (103), (200) and (110) orientations. Figure 1 shows that comparison of diffractograms correspond to as-deposited, microwave treated and conventional radiant annealed ZnO nanorod electrodes. The diffractograms reveal that there is a difference in the thin film crystallinity of as-deposited, microwave irradiated and conventional radiant annealed ZnO nanorods. The results indicate that as-deposited ZnO nanorods are highly crystalline in nature; therefore microwave and conventional annealing do not change the crystallinity any further. The grain size (along the (103) peak) is evaluated by using the Debye–Scherrer equation [16,17]. The calculated values for the grain size of as-deposited, microwave irradiated and conventional radiant annealed ZnO nanorods are 34±4, 67±9 and 110±10 nm respectively which are closely agreed with the estimated grain size using FEG-SEM images (Fig. 2).

FEG-SEM has been used for the topographic study of as-deposited, microwave and conventional radiant annealed ZnO nanorod electrodes and the images are given in Fig. 2(a), (b) and (c) respectively. Fig. 2(a) illustrates that as deposited ZnO nanorod image oriented almost perpendicular to the substrate. The topographical image of microwave irradiated ZnO nanorods indicates that microwave treatment of the films has caused sintering especially at the locations where the individual rods closed to each other, without significantly affecting the hierarchical structures (Fig. 2(b) and inset of it). This is due to the fact that, microwave heat generation take place within the material by an energy conversion rather than heat transfer, hence there is less room for coagulation of individual rods. The effect of conventional radiant annealing (at 300 °C) on the surface morphology of ZnO nanorods was clearly identifiable in Fig. 2(c). It appears that ZnO nanorods have sintered together and deformed the hierarchical structure. There is also evidence to show that necking and boundaries (between remaining-like features) have formed during the radiant annealing step. The internal surface area of each electrode was determined by conducting dye adsorption/desorption studies [15]. The projected surface area of ZnO electrodes of as deposited, microwave irradiated and conventionally annealed by radiant heat are 1.47 × 10⁸, 1.3 × 10⁸ and 0.96 × 10⁸ cm² (over 1 cm² of projected area) respectively. This indicates that the internal surface area of microwave irradiated and conventional radiant annealed ZnO nanorod electrodes have decreased compared to that of the as-deposited counterpart. This is due to the secondary growth and agglomeration of individual rods as evident from the SEM images. This effect is more pronounced in conventional radiant annealing than microwave treatment causing the destruction of the hierarchical structure. It has been reported elsewhere [18] that average grain size of the film increased with annealing, grain boundaries are developed between different crystalline phases which are responsible for specific properties of the materials. Comparison of the dielectric properties of ZnO and TiO₂ (Table 1) show their relative ability of heat generation by absorbing microwave radiation [19].

The photoelectrochemical (PEC) performance of ZnO electrodes has been studied by evaluating the current density–voltage (J–V) characteristics for as-deposited, microwave irradiated and conventional radiant annealed samples. The chopped J–V plots uncorrected for internal surface area differences are shown in Fig. 3. The plots illustrate that the charge transport of all electrodes are relatively poor and electrodes are resistive in nature. This is confirmed by the absence of characteristic rectifying shape in current-voltage curves. The current density of microwave irradiated electrode decreases compared to that of as-deposited electrode. The reduction of the photocurrent corresponding to conventional radiant annealed ZnO electrodes is more pronounced presumably due to deformation of rod structure. This appeared to be due to the poor charge transport within the electrode containing deformed features in nanoscale. It is well known that the charge transport within ZnO nanorods is more efficient compared to randomly oriented nanostructured electrodes [19]. The J–V plots indicate the same trend with the calculated projected surface areas of the electrodes. It is evident in the present work that the microwave treatment preserves the structure of nanorods better than in the case of conventional radiant annealing. Our previous study on TiO₂ showed that
microwave processing facilitates the growth of crystallites and inter-particles connections while preserving the electrode texture and improving the PEC properties appeared to be due to the enhanced charge collection [10]. It is clear from the present work that post annealing of ZnO nanorod has less effect on improving PEC performance as it leads to reduce the internal surface area of the electrodes. Furthermore, the conventional radiant heat treatment completely deforms the electrode texture thereby deteriorating the PEC performance.

4. Conclusions

Zinc oxide nanorods were grown on FTO-glass substrate by CVD method after depositing a seed layer by AACVD. The structural properties of as-deposited, microwave irradiated and conventional radiant annealed ZnO nanorods were studied by XRD. X-ray diffraction measurements show that ZnO nanorods grown in wurtzite crystal phase. There is a slight change of the crystallinity of as-deposited, microwave irradiated and the conventionally annealed electrodes. The SEM studies show that the microwave irradiation caused sintering of individual rods resulting in the growth of rod diameter whilst the conventional radiant annealing deformed the hierarchical ZnO structure. Contrary to our expectations, the post annealing of ZnO nanorods do not appear to have induced better connections between the rods and the substrate. The PEC studies indicate that all electrodes are resistive in nature. The current density of microwave irradiated electrode decreases compared to that of as-deposited electrode. The reduction of the photocurrent corresponding to conventional radiant annealed ZnO electrodes is more intense presumably due to deformation of rod structure. This appeared to be due to the poor charge transport in deformed electrodes.

Acknowledgments

I. A. Bhatti is very grateful to the Higher Education Commission in Pakistan for awarding post-doc fellowship to join the renewable energy research group, Loughborough University, UK. This work also partially supported by the Johnson Matthey Plc. and UK EPSRC.
References

**Electrochemically Grown ZnO Hierarchical Nanostructures for Solar Energy Conversion Applications**

Tom Smith, Alex Pollington, Upul Wijayantha

Department of Chemistry, Loughborough University, Loughborough, LE11 3TU

**Introduction**

The Sun bombards the earth with 1500 Btu/h of energy, and the present global energy demand is less than 0.01% of it. Unfortunately, the current methods of converting sunlight to useful forms of energy (i.e. photovoltaics) are not very efficient. One of key reasons for this is the lack of energy harvesting semiconducting materials with desired properties.

ZnO thin films are one type of semiconductor that show good promise for Extremely Thin Absorber (ETA) photovoltaics. This is due to their hierarchical structures, physical, optical and electronic properties. The hexagonal wurtzite crystals of ZnO show polar characteristics on top and bottom hexagonal faces due to the alternate stacking of O\(^2-\) and Zn\(^{2+}\). The hexagonal faces (0001) are quite stable and have high energy while the vertical faces (0110) and (2110) have lower energy and are non-polar. Here, we show the growth of ZnO can be controlled using electrochemistry to form nanorods/tubes by manipulating the surface energies and polarity.

**Experimental**

The ZnO films were deposited using electrodeposition. Sample A: a solution of 5x10\(^{-4}\) M ZnCl\(_2\) and 0.1M KCl was oxygenated with air. This was then heated to 80°C and stirred. ZnO was deposited on FTO with a buffer layer of ZnO by aerosol assisted chemical vapour deposition using chronoamperometry to apply ~1.0V vs. Ag/AgCl for 1800s.

Sample B: a solution of 1x10\(^{-4}\) M ZnCl\(_2\) and 0.1M KCl was made to pH 6.7. This was oxygenated throughout the deposition with oxygen and heated to 80°C and stirred. This time first applying ~1.3V vs. Ag/AgCl for 10s, then ~1.0V vs. Ag/AgCl for 7100s. The apparatus was set up as shown in Fig 2.

**Results & Discussion**

**Chroamperometry Sample A**

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<td>0.30</td>
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**SEM**

Sample A: The ZnO has formed hexagonal rods creating a very porous film.

Sample B: The rods are more compact and aligned. Some rods are so closely packed that they have come together and formed tube like structures.

**Conclusion and Further Work**

Chroamperometry has been shown to be a good tool to grow hierarchical structures of ZnO crystals.

Further work is currently underway to use these hierarchical structures as a foundation to make more efficient ETA solar cells (Fig 3).

**Acknowledgments**


**References**


Growth of Zinc Oxide Rods/Tubes Based Electrodes to be Utilised as Frameworks for the Development of Visible Light Harnessing Electrodes

Tom Smith, Upul Wijayantha

Department of Chemistry, Loughborough University, Loughborough, LE11 3TU

Introduction

The Earth receives 1500 EYln/a of Solar energy, and the present global energy demand is less than 0.01% of it. Unfortunately, the current methods of converting sunlight to useful forms of energy (i.e., photovoltaics) are not very efficient. One of the key reasons for this is the lack of energy harvesting semiconducting materials with desired properties.

Zinc Oxide (ZnO) thin films are one type of semiconductor that show good promise for light harnessing electrodes photovoltaics. This is due to their hierarchical structures, physical, optical and electronic properties. The hexagonal wurtzite crystals of ZnO show polar characteristics on the top and bottom hexagonal faces due to the alternate stacking of O^2- and Zn^2+ shown in Fig. 2. This Fig. also shows the unit cell in the bold dashed lines and the thin dashed lines show the hexagonal shape. The hexagonal faces (0002) are quite stable and have high energy while the vertical faces (1010) and (2110) have lower energy and are non-polar, this gives crystal orientated growth shown in Fig. 1. The reactions to grow the rods are shown in the following equations:

Zn(NO_3)_2 + 4NaOH → Na_2ZnO_2 + 2NaNO_3 + 2H_2O

Results & Discussion

A ZnO seeding layer was deposited using AACVD (Aerosol Assisted Chemical Vapour Deposition) onto FTO (Fluorine doped Tin Oxide) glass. ZnO rods were then grown on these buffer layers using CBD (Chemical Bath Deposition). ZnO rods could then be converted into tubulars by dissolving the rods using cBD. Aluminium doped Zinc Oxide (Al:ZnO) was also prepared by cBD.

XRD

Shows that both samples are only hexagonal ZnO crystals. The SnO_2 signatures originate from the FTO substrate. But there has been a change in reflection intensities which is the loss of the preferred orientation of the crystal being (002) in the samples.

SEM

A and B Shows the same sample, this has hexagonal nanorods with a range of diameters of approximately 50 to 75mm and the nanorods have a length of approximately 1pm. The rods have good orientation but the rods near the edge have been knocked over due to SEM preparation. This structure gives good porosity.

C Shows that the centre of the hexagonal faces have been dissolved forming tubes. ZnO tubes are not as neat or as uniform as the rods areas of the tubes have also been dissolved.

Conclusion

Aluminium doping improves the optical and electrochemical properties of the films for use as a framework for light harnessing applications.

Acknowledgments

EP5/RG SuperGen PV Consortium EP/G031088/1

Everyone in the Renewable Energy group, Chemistry Department, Loughborough University

References


Towards Tandem Solar Cells: Cathodic NiO electrode
Tom Smith & Upul Wijayantana
Department of Chemistry, Loughborough University, Loughborough, LE11 3TU

Introduction
The Sun bombards the earth with 1500 EW/h (E = 10^{-14}) of energy. The global energy consumption is about 0.49 EW/h in 2009. Hence, we only need to convert a fraction of available solar energy to meet our energy needs. Photovoltaics (PV) is one way of utilising the solar energy. In order to develop affordable PVs, there is a pressing need for novel, low-cost and efficient PV configurations today.

Generally, most PVs are constructed based on a single light harvesting semiconductor. The maximum achievable light to electricity conversion efficiency (ν/a) of such devices is given by the Shockley-Queisser limit. In order to move beyond the Shockley-Queisser limit while reducing the production cost to an affordable level, novel solar cell structures with new materials need to be explored. The objective of the present work is to develop semiconductor-sensitised anodic and cathodic half-cells and combine them to construct Tandem PV cells. It is estimated that such Tandem PV cells will substantially reduce the production and increase the light to electricity conversion efficiency. But it has been difficult to achieve that goal due to the poor performance of the available p-type semiconductors suitable for PV, NiO is a promising p-type semiconductor material to construct mesoporous photoelectrodes.

In fact, it has been proven that NiO electrodes can be employed in other device configurations such as gas sensors, electrochromic devices and fuel cells. The focus of this work is to construct porous NiO photocathodes on FTO glass substrates and characterise them for structural, optical and photoelectrochemical properties.

Experimental
First a thin compact layer of Ni(OH)₂, was deposited by using chronopotentiometry onto FTO glass (FTO) coated conducting glass at -0.6 mA for 30s and annealed at 450°C for 30 mins in air to obtain a thin NiO film. Then a wet NiO paste was painted on the compact layer using doctor blade method and annealed at 400°C under Argon for 30 mins. Finally, a thin layer of Ni(OH)₂, was deposited on top of it by chronopotentiometry at -0.6 mA for 30s and annealed 450°C in air for 30 mins.

Results & Discussion
Structural Properties
NiO has a cubic rocksalt crystal lattice as shown in the diagram on left. The lattice image has been angled particularly to highlight the (111) orientation which has a polar surface.

Formation of NiO was confirmed using XRD. Generally NiO prepared by this method preferentially oriented in the [111] direction.

Optical Properties
Absorption studies of the NiO thin film electrodes shows that there is a broad peak at about 550nm. Beyond that there is no light absorption. Please note that the absorption spectra has been distorted due to the light scattering properties of thick NiO electrode.

The direct optical bandgap of 3.3 eV has been estimated from the (αhν)² vs photon energy plot. This is in agreement with the literature values.

Photoelectrochemical Properties
The photoelectrochemical properties of NiO electrodes were studied by recording the photocurrent density against applied voltage as well as incident photon to electron conversion efficiency (IPCE).

The measurements were conducted in two-electrode mode in 0.04M I₂, 0.1M LiI, 0.4M TBAI and 0.3M NMB in AN/NMP electrolyte. According to J-V plot, the minimal dark current is observed compared to photocurrent and also shows good diode behaviour. The chopped response shows a slow response time (scan speed is 5 mV/s).

The band gap estimated from IPCE spectra (~3.4 eV) due to the band-to-band excitation agrees with the optical band gap calculated from the (αhν)² vs. photon energy plot.

Conclusions
Porous NiO electrodes have been prepared on FTO glass and structural, optical and photoelectrochemical properties were studied. NiO prepared in the present work is preferentially oriented in the [111] direction and has an optical band gap of 3.3 eV, hence transparent in visible region. The electrode has a porous microstructure with high internal surface area, NiO electrode prepared in this method shown to be very photoactive and easily scalable.

Acknowledgments
All members in the Renewable Energy group, Dept of Chemistry, Loughborough University.

References
Towards Tandem Solar Cells

Tom Smith & Upul Wijayantha
Department of Chemistry, Loughborough University, Loughborough, LE11 3TU

Introduction

The Sun bombards the earth with 1500 E/fm² (E = x10¹⁰) of energy. The global energy consumption was about 0.49 E/fm² in 2009. Hence, we only need to convert a fraction of available solar energy to meet our energy needs. Photovoltaics (PV) are one way of utilising the solar energy. In order to develop affordable PVs, there is a pressing need for novel, low-cost and efficient PV configurations today.

Generally, most PVs are constructed based on a single light harvesting semiconductor. The maximum achievable light to electricity conversion efficiency (η%) of such devices is given by the Shockley-Queisser limit, for a single junction this is about 31%.

In order to move beyond the Shockley-Queisser limit while reducing the production cost to an affordable level, novel solar cell structures with new materials need to be explored. The objective of the present work is to develop semiconductor-sensitised anodic and cathodic half-cells and combine them to construct tandem PV cells. It is estimated that such tandem PV cells will substantially reduce the production cost and increase the light to electricity conversion efficiency. But it has been difficult to achieve that goal due to the poor performance of the available p-type semiconductors suitable for PV. NIO is a promising p-type semiconductor material to construct mesoporous photoelectrodes.

In fact, it has been proven that NIO electrodes can be employed in other device configurations such as gas sensors, electrochromic devices and fuel cells. The focus of this work is to construct porous NIO photocathodes on FTO glass substrates and characterise them for structural, optical and photoelectrochemical properties.

Work to date

Structural Properties

Formation of thin film NIO and thin film CuO by aerosol assisted chemical vapour deposition (AACVD) was confirmed using XRD.

XRD was used to analyse the effect of the different annealing temperatures on controlling the formation of copper(i1) oxide or copper(i1) oxide. As shown Cu₂O is formed between 200°C and 250°C.

References


Acknowledgments

Towards Tandem Solar Cells

Tom Smith (2nd Year) & Upul Wijayantha
Department of Chemistry, Loughborough University, Loughborough, LE11 3TU

Introduction
The Sun bombards the earth with 1500 EWh/a (E = x10^18) of energy. The global energy consumption is about 0.49 EWh/a in 2009. Hence, we only need to convert a fraction of available solar energy to meet our energy needs. Photovoltaics (PV) is one way of utilising the solar energy. Today there is a pressing need for novel, low-cost and efficient PV configurations.

Semiconductors are the foundation of modern electronics, including radio, computers and telephones. They are distinguished from other materials because the valence band (VB) in them is nearly filled with electrons, while virtually no electrons are present in the conduction band (CB), the band immediately above the VB. Semiconductors play a central role in PV devices to harvest sunlight. Electrons can be promoted from the VB to the CB upon illumination and this phenomenon is conveniently exploited to harvest sunlight in PVs.

Work to date
Copper Oxide (CuO) was deposited using aerosol assisted chemical vapour deposition onto Nickel Oxide (NiO) cathodic semiconductor electrodes have been deposited by electrochemical and Dr. Blade techniques on transparent conducting oxide glass substrates (TCO). They were characterised for structural properties by XRD and scanning electron microscopy (SEM). The XRD confirmed the identity of NiO and CuO and SEM topography analysis showed the electrodes contain the desired textural properties. The photocurrent characterisation not only confirms that the photovoltaic is cathodic (i.e. majority carriers are electron vacancies), but also shows high photocurrent density. The optical characterisation also shows a good band gap of 1.8eV calculated from the UV-Vis spectra.

Semiconductor-sensitised Tandem PV cells
Generally, most PVs are constructed based on a single light harvesting semiconductor. The maximum achievable light to electricity conversion efficiency (η%) of such devices are given by the Shockley-Queisser limit.

In order to move beyond the Shockley-Queisser limit while reducing the production cost to an affordable level, novel solar cell structures with new materials need to be explored. The objective of the present work is to develop semiconductor-sensitised anodic and cathodic half-cells and combine them to construct Tandem PV cells. It is estimated that such Tandem PV cells will substantially reduce the production cost and increase the light to electricity conversion efficiency.

Conclusions
Cathodic semiconductor CuO/NiO electrodes have been successfully deposited onto TCO substrates. Their photocurrent density under simulated sunlight shows a good photocurrent, thereby bringing us a step closer to the construction of low-cost and highly efficient semiconductor-sensitised tandem solar cells.

Acknowledgements
EPSRC Supergen PV Consortium EP/I030884/1
Loughborough University Department of Chemistry

References
INTRODUCTION

The Sun bombards the earth with 5400 YJyr⁻¹ (Y = x10⁻²⁴) of energy. The global energy consumption is about 1.764 YJyr⁻¹ in 2009. Hence, we only need to convert a fraction of available solar energy to meet our energy needs. Photovoltaics (PV) is one way of utilising the solar energy. Today there is a pressing need for novel, low-cost and efficient PV configurations.

LIGHT CONVERSION

Semiconductors are the foundation of modern electronics, including radio, computers and telephones. They are distinguished from other materials because the valence band (VB) in them is nearly filled with electrons, while virtually no electrons are present in the conduction band (CB), the band immediately above the VB. Semiconductors play a central role in PV devices to harvest sunlight. Electrons can be promoted from the VB to the CB upon illumination and this phenomenon is conveniently exploited to harvest sunlight in PVs.

SEMICONDUCTOR-SENSITISED TANDEM PV CELLS

Generally, most PVs are constructed based on a single light harvesting semiconductor. The maximum achievable light to electricity conversion efficiency (η%) of such devices are given by the Shockley-Queisser limit. In order to move beyond the Shockley-Queisser limit while reducing the production cost to an affordable level, novel solar cell structures with new materials need to be explored. The objective of the present work is to develop semiconductor-sensitised anodic and cathodic half-cells and combine them to construct Tandem PV cells. It is estimated that such Tandem PV cells will substantially reduce the production cost and increase the light to electricity conversion efficiency.

WORK TO DATE

Copper Oxide (CuO) was deposited using aerosol assisted chemical vapour deposition onto Nickel Oxide (NiO) cathodic semiconductor electrodes have been deposited by electrochemical and Dr. Blade techniques on transparent conducting oxide glass substrates (TCO). They were characterised for structural properties by XRD and scanning electron microscopy (SEM). The XRD confirmed the identity of NiO and CuO and SEM topography analysis showed the electrodes contain the desired textural properties. The photoelectrochemical characterisation not only confirms that the photocurrent is cathodic (i.e. majority carriers are electron vacancies), but also shows high photocurrent density. The optical characterisation also shows a good band gap of 1.8eV calculated from the UV-Vis spectra.

CONCLUSIONS

Cathodic semiconductor CuO/NiO electrodes have been successfully deposited onto TCO substrates. Their photocurrent density under simulated sunlight shows a good photocurrent, thereby bringing us a step closer to the construction of low-cost and highly efficient semiconductor-sensitised tandem solar cells.

ACKNOWLEDGEMENTS

EPSRC Supergen PV Consortium EP/G031088/1
Loughborough University Department of Chemistry

REFERENCES

TOWARDS TANDEM SOLAR CELLS

TOM SMITH & UPUL WIJAYANTHA
Department of Chemistry, Loughborough University, Loughborough, LE11 3TU

INTRODUCTION
The Sun bombards the earth with 5400 $\text{Y.Jyr}^{-1}$ ($Y = 10^{24}$) of energy.\(^1\) The global energy consumption is about 1.764 $\text{Y.Jyr}^{-1}$ in 2009.\(^2\) Hence, we only need to convert a fraction of available solar energy to meet our energy needs. Photovoltaics (PV) is one way of utilising the solar energy. Today there is a pressing need for novel, low-cost and efficient PV configurations.

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LIGHT CONVERSION
Semiconductors are the foundation of modern electronics, including radio, computers and telephones. They are distinguished from other materials because the valence band (VB) in them is nearly filled with electrons, while virtually no electrons are present in the conduction band (CB), the band immediately above the VB. Semiconductors play an integral role in PV devices to harvest sunlight. Electrons can be promoted from the VB to the CB upon illumination and this phenomenon is conveniently exploited to harvest sunlight in PVs.

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