Cranfield University

Clair Atterbury.

Investigation into the manipulation of the properties of Indium Tin Oxide (ITO) coatings.

School of Applied Science.

MSc. Ultra Precision Technologies.

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MSc Thesis. Ultra Precision Technologies

2007 - 2008

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Investigation into the manipulation of the properties of Indium Tin Oxide (ITO) coatings.

### Supervisors: Prof John Nicholls and Mr Phil Hatchett

Academic Year 2007 to 2008

This thesis is submitted in partial fulfilment of the requirements for the degree of MSc Ultra Precision Technologies.

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### ABSTRACT

This thesis investigates the manipulation of the properties of Indium Tin Oxide (ITO) coatings. This is carried out with a combination of Experimental and Theoretical work. The coating of ITO onto a glass substrate was both theoretically modelled and the practical work analysed to observe the effects. Observation of the effects on the output parameters when depositing a single layer of ITO via Electron beam evaporation onto a glass substrate multiple times with varying conditions was carried out. The amount of ITO required to produce optimum % transmission and the deposition conditions required to provide <20  $\Omega$ / $\Box$  and <100  $\Omega$ / $\Box$  were investigated.

This study then considered the addition of a single layer of an additional coating both theoretically and practically to maximise the %T for the wavelength ranges under consideration. From this, the ideal refractive index for the additional coating to maximise the %T for the ranges was deduced. Progression was then made to consider multiple layers. Theoretical work carried out on the addition of extra layers and the deduction of the optimal refractive index implied that overall, Cryolite would produce the best average %T across the ranges considered.

In addition to this, the results of ITO deposition via Evaporation and sputtering were examined to determine the difference the technique used has upon the coating produced.

### DEDICATION

I would like to dedicate this work to my parents who have supported me through this MSc and throughout my life. I would also like to dedicate this work to the memory of Leah Bushell who has also supported me through the important times in my life and my memory of her will always be with me throughout my MSc and life.

Without their kind support, I would not have got as far as I have.

### ACKNOWLEDGMENTS

I would like to thank the following people for their kind help during my project:

- Dr Chris Sansom and all of the Precision Engineering department at Cranfield
- Mr Phil Hatchett and Mrs Gail Hatchett
- Prof John Nicholls
- Ms Sharon Mcguire
- Dr John Mitchell and UPSII generally
- Ms Christine Kimpton
- Mr Andrew Dyer
- Diamond Coatings

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### 1 Introduction

### 1.1 The project

This project involves the investigation of Indium Tin Oxide (ITO) coatings and the manipulation of their % Transmission (over the visible and the immediately neighbouring ranges) and Sheet Resistivity. The main deposition method considered will be Ion Assisted Vapour Deposition. Sputtering will also be considered for comparative purposes.

Chapter 1 introduces the project and considers the project aims and objectives.

Chapter 2 investigates prevalent literature available on this subject.

The Experimental and Theoretical work carried out is reported and discussed in chapters 3 & 4.

Chapter 5 discusses the results obtained in chapters 3 and 4.

Chapter 6 then moves on to form Conclusions and make Recommendations for future work.

Unfortunately, the application of this work can not be discussed for commercial reasons.

### 1.2 Aims and Objectives

The aims and objectives of this project are as follows:

• To review theoretical model of the effects of adding a layer of ITO onto a glass substrate

- Observation of the effects on the output parameters when depositing a single layer of ITO via Electron beam evaporation onto a glass substrate multiple times with varying conditions
- Determination of the ITO deposition conditions required to provide <20  $\ensuremath{\Omega/\Box}$
- Determination of the ITO deposition conditions required to provide <100  $\ensuremath{\Omega/\Box}$
- Determination of the effects of adding coatings to maximise %T by theoretical modelling
- Observation of the results of depositing coatings onto the ITO to maximise %T by Evaporation
- Examination of the results of ITO deposition via IAD and sputtering to determine the difference the technique used has upon the coating produced
- The primary %T values to be considered in this project are the values it takes over the visible range

### 2 Literature Review

### 2.1 Indium Tin Oxide (ITO)

A Transparent Conducting Oxide (TCO) can be defined as a thin film that is transparent to visible light and conducts electricity (Subrahmanyam, 2002).

Indium Oxide is a transparent ceramic material with the following structure:

Figure 1 Indium Oxide



(Source Zhou, 2005)

Indium Oxide maintains its transparency when it is doped with Tin. The addition of tin has the desirable effect of making the material conductive by increasing a number of free electrons present (Eite *et al*, 2004). Indium Oxide doped with Tin, commonly known as Indium Tin Oxide (ITO) is a TCO. Depending upon the temperatures involved, ITO can take the following forms (Lawson, 2008):

- Room temperature deposition results in an amorphous ITO coating (a-ITO).
- At temperatures above about 150°C, ion bombardment results in the nucleation of small crystal sites. The overall result being the production of Polycrystalline ITO films (p-ITO). Heating to about 200°c also produces a polycrystalline structure. p-ITO has a very smooth surface profile.

There are numerous techniques for depositing ITO. This will be reviewed below.

### 2.2 Review of commonly employed ITO coating techniques

A review of the prevalent ITO literature reveals that the following techniques have been used to apply ITO coatings:

Physical processes e.g. Dip Coating (Piao et al, 2006, Chen et al, 2005, Agerter et al, 2003, Al-Dahoudi et al, 2003, Goebbet et al, 1999, TakÅhashi et al, 1997, Nishio et al, 1996), Spin Coating (Psuja et al, 2007, Al-Dahoudi et al, 2006, Han et al, 2005, Hong et al, 2004), Spray Coating (Goebbet et al, 1999, Bisht et al, 1999), Direct gravure printing (Puetz et al, 2005)

- 2. Laser based processes e.g. Pulsed laser deposition (Viespe et al, 2007, Teghil et al, 2007, Ngaffo et al, 2007)
- 3. Arc Discharge deposition (Chen et al, 2004, Niino et al, 2002)
- Chemical Vapour Deposition (Goebbet *et al*, 1999), Chemical Solution Deposition (Yun *et al*, 2005)
- 5. Physical Vapour Deposition:
  - a) Sputtering e.g. RF (Boycheva et al, 2007, Bertran et al, 2003), DC (Shen et al, 2006, Boehme et al, 2005), Magnetron (Lee et al, 2007, De Bosscher et al, 2005, Gao et al, 2001, Strumpfel et al, 2000, Kusano et al, 1998, Lippens et al, 1998, Wu et al, 1997, Baouchi, 1996), High Vacuum Sputter roll coating (Mayr, 1986), Pulse package sputtering (Gnehr et al, 2005), Cyclotron resonance plasma sputtering (Yasui et al, 2001)
  - b) Evaporation techniques e.g. Electron Beam deposition (Raoufi et al, 2008, Fallah et al, 2006), Ion Assisted Deposition (Wang et al, 1999, Yu et al, 2008, Lee et al, 1999)

The references given in each case illustrate examples where the application of the technique has been discussed. This thesis will be focussing on the Physical Vapour deposition route of Electron Beam Evaporation (with Ion Assisted Vapour Deposition). Sputtering of ITO will also be considered. Sputtering and Evaporation with Ion Assisted Vapour Deposition are the most common techniques applied today (AtoZ of materials, Cerac technical publications). These techniques are therefore considered in more detail below.

### 2.2.1 Electron Beam Evaporation

According to Bashir (1998), the process of evaporation involves heating a solid to a sufficiently high temperature that vaporisation occurs. This process is followed by the solid recondensing onto a cooler substrate. Evaporation is a physical vapour deposition process that can be achieved via various heating mechanisms such as radiation, eddy currents, electron beam bombardment, a laser beam or electrical discharge (Bunshah, 1980). The Electron beam bombardment heating method will be focussed upon in this section as this is the technique used in this work.

The process of electron beam evaporation is illustrated in Figure 2. According to Smith (1995), the process of Electron beam evaporation is as follows. Electrons are emitted from a hot filament and their acceleration is induced via the high voltage applied as is illustrated in Figure 3. The electron beam is deflected by a magnetic field. The filament is hidden and the beam is deflected to make it take the desired path to ensure that the filament does not sit in the path of the evaporant. The crucible is typically water cooled to minimise outgassing or melting complications. The accelerated electrons impact the evaporant with a power that is sufficient to heat most materials to greater than 1000°C (Traub, 2008). Pellicori (2002) feels that heating of over 1200°C can commonly be achieved. The use of a suitable evaporant would thus result in vaporisation of that evaporant and recondensation onto the substrate.

Pellicori (2002) states that this method is the most common method used to deposit ITO due to the suitability of the temperatures involved.

Figure 4 illustrates an electron beam evaporation gun in operation.



Figure 2 Process of Electron Beam Evaporation





High Voltage (approx 8 to 10 kV) accelerates the electrons

Permanent magnets and coils used to deflect the electron beam 270°

(Source Hatchett, 2008)

Figure 4 Electron beam Evaporation Gun in operation



(Source Hatchett, 2008)

### 2.2.2 Ion Assisted vapour Deposition

Ion assisted Vapour deposition is used to assist Physical Vapour Deposition processes such as Sputtering or Evaporation (Hirvonen, 2004). In this section, the Physical Vapour Deposition process considered is Electron beam evaporation (as discussed in the previous section). In conjunction with Electron Beam Evaporation, ions are used to assist the process. A typical ion assisted vapour deposition chamber where this is carried out is illustrated in Figure 5. It can be seen that in addition to the electron beam gun discussed in the previous section, there is also an ion source present that typically produces a low energy broad ion beam (Hirvonen, 2004). Other important features are the substrate heaters that are used to heat the substrate to the desired temperature and the thickness monitor that in conjunction with the IC/5 determines the thickness of coating that has been deposited on the substrate. The substrate dome is the housing for the substrates and is rotated at the desired speed by the substrate drive.



Figure 5 Typical Ion Assisted Vapour Deposition Chamber

<sup>(</sup>Source – Hatchett, 2008)

Hirvonen (2004) feels that the energetic ions used in ion assisted deposition play various beneficial roles in thin film coating processes. These benefits can be divided into two main categories. These categories are generic effects of thin film growth and Chemical effects on growth. The Generic effects of ion assistance on thin film growth are as follows:

- o Enhanced adhesion
- Texture modification
- $\circ$  Nucleation
- o Stress control
- $\circ$  Densification
- Surface morphology and patterning

The Chemical effects of ion assistance on thin film growth are:

• Stoichiometry and synthesis control.

### 2.2.3Sputtering

Sputtering is again a physical vapour deposition process. The basic process of sputtering is illustrated in Figure 6.





<sup>(</sup>Source Bunshah, 1980)

The basic process of sputtering consists of positively charged ions (typically created from a working gas (usually Argon) and a glow discharge) striking a target resulting in the dislodging of target atoms which then condense onto the substrate (Bunshah, 1980). Magnetic fields produced from magnets can be used to enhance the process by localising the plasma to provide optimum performance (Traub, 2008).

### 2.2.4 Comparison of Evaporation and Sputtering

Traub (2008) performed a comparative study between Evaporation and Sputtering. In this study, the technique which conformed to the features in each case was identified. The results of this were as follows:

### Table 1 Comparison of Evaporation and Sputtering Techniques

Feature considered	Evaporation	Sputtering
Highest rate	Ø	
Highest film density		Ø
Highest purity films produced		
Best Adhesion		Ø
Lowest film stress	Ŋ	
Best Step coverage		Ŋ
Highest film thickness uniformity		
Lowest material consumption		Ø
Lowest material investments		
Lowest x-ray emissions		Ø
Best thickness control		
Best Compound deposition control		N

### 2.3 Single Layer ITO deposition and analysis of factors that effect the properties of the ITO layer reported in the literature

The literature demonstrates that people have considered the effect of limited variables in their deposition process and the effect that they have on the single layer ITO coating produced.

Liu, Mihara, Matsutani, Asanuma, Kiuchi (2003), Liu, Matsutani, Asanuma, Kiuchi (2003), Liu *et al* (2002), Pokaipisit and Morton *et al* (1999) have all utilised Ion assisted Deposition to deposit a single layer of ITO and considered the effect on certain variables on the results produced.

Liu, Mihara, Matsutani, Asanuma, Kiuchi (2003) considered the effects that Evaporation rate, Substrate Temperature, Oxygen Ion beam energy and density had on the results observed over the wavelength range of 200 and 1000nm.

Liu, Matsutani, Asanuma, Kiuchi (2003) investigated the effects of the varying the acceleration voltage and current densities of the oxygen ions produced using an electron cyclotron resonance source. The differences that occur when the deposition was carried out at room temperature and 200°C were also observed.

Liu *et al* (2002) reported the effects that variables such as thickness and growth rate had on the results achieved.

Pokaipisit (undated) looked at the variables of ion beam energy density, oxygen flow rate and substrate temperature.

Morton *et al* (1999) considered variables such as deposition rate, oxygen flow, and drive current on the sheet resistivity produced.

The effect of certain variables has also been considered for other deposition techniques:

Amirishahbazi *et al* (2005) and Bashar (1998) considered the effect of certain variables on the resulting single layer of ITO produced via Sputtering. Bashar

(1998) performed a more comprehensive study encompassing a wider range of variables.

Kim *et al* (2005) reported the effect of certain variables on the deposition of a single layer of ITO via pulsed laser deposition.

Regarding the analysis of variables, it can be seen from the literature that different variables have been studied in isolation for various specific deposition systems and methods. It is for this reason that the author has decided in this thesis to perform a more comprehensive study considering all of the major variables that can be altered and observed on the LAB600 and their effects on the results rather than just considering the variables that are assumed to have a greater dependence.

Unfortunately, with all of the studies reported in the literature, the authors had either different or undisclosed sheet resistivity requirements (and thus thicknesses). Unless the required sheet resistivity matches the sheet resistivity requirements of this thesis, a direct comparison of the Transmission and Resistivity results can not be successfully performed as is demonstrated by all of studies mentioned above that demonstrate that the variables chosen have an effect on the results obtained. To do more work with this, the conditions given in the literature would need to be replicated to enable direct comparisons to be performed. This was not possible with the constraints placed on this work and it is for this reason that the results from the papers are not shown.

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### 2.4 Layers reported to have been employed with ITO in an attempt to maximise the %T observed in the visible region

Dobrowolski *et al* (1987) and SPO (2000) both report the deposition of a single layer of SiO<sub>2</sub> on top of an existing layer of ITO in an attempt to improve the %T observed in the visible region.

Morton *et al* (1999) again looked at the results of a single layer of  $SiO_2$ . However, in this case, a layer of  $Al_2O_3$  was also introduced between the substrate and the ITO in an attempt to further improve the results.

Gilo *et al* (1999) on the other hand considered the addition of a single layer of  $MgF_2$  whose thickness ranged between 50 to 250 nm to the existing ITO layer again in an attempt to maximise the %T.

Dever *et al* (1998) takes this work a step further and considered the codeposition of ITO and  $MgF_2$ .

Stetson (2006) on the other hand proposed a more complex multilayer stack arrangement consisting of both  $TiO_2$  and  $SiO_2$  again with the aim of maximisation of %T across the visible range.

It can be seen from this section that the most commonly reported coating materials to have been applied in an attempt to maximise the %T of ITO in the visible region are SiO<sub>2</sub>, TiO<sub>2</sub> and MgF<sub>2</sub>. It is for this reason that this thesis will initially consider the addition of these layers to the ITO as a starting point in the quest to maximise the %T.

# 2.5 Data used in theoretical section

All the plots in this section were produced with Essential Macleod.

# 2.5.1 ITO Data Sources

The four main sources of ITO that were used in the theoretical section were obtained from Essential Macleod. The data and the original source for each set of data is given below:

# 2.5.1.1 ITO DATA 1

The data referred to as ITO data 1 was obtained from Essential Macleod. It was originally sourced from: http://windows.lbl.gov/materials/chromogenics/default.htm.

The values it provided for refractive indices and Extinction coefficients are illustrated on the following page:



Material: ITO



# 2.5.2.2 ITO DATA 2

Extinction Coefficient

Refractive Index

The values it provided for refractive indices and Extinction coefficients are illustrated on the following page: The data referred to as ITO data 2 was obtained from Essential Macleod. No original source was listed.







## 2.5.2.3 ITO DATA 3

The data referred to as ITO data 3 was obtained from Essential Macleod. It was originally sourced from the SOPRA Database The values it provided for refractive indices and Extinction coefficients are illustrated on the following page: Figure 9 Plot of Refractive index and Extinction Coefficient for ITO data 3

Material: ITO (1)



Refractive Index Extinction Coefficient

## 2.5.2.4 ITO DATA 4

The data referred to as ITO data 4 was obtained from Essential Macleod. It was originally sourced from Hoppe, H, N S Saricittci, and D Meissner, Optical constants of conjugated polymer/fullerene based bulk-heterojunction organic solar cells. Molecular Crystals & Liquid Crystals, 2002. 385: p. [233]/113-[239]/119.

The values it provided for refractive indices and Extinction coefficients are illustrated below:

Figure 10 Plot of Refractive index and Extinction Coefficient for ITO data 4



It can be seen from the four sources of ITO data here that there are discrepancies between the different sets of data. Each set of data was therefore used for each consideration in the theoretical work to enable a comparison to be made.
2.5.2 Other data used in the theoretical section
2.5.3.1 SiO <sub>2</sub>
The refractive index and extinction coefficient data used for SiO <sub>2</sub> was sourced from Essential Macleod. The original source of the data was from Palik, Edward D. Handbook of the Optical Constants of Solids I. Academic Press, 1985 and p 12. Palik, Edward D. Handbook of the Solids II. Academic Press, 1985 and p 12. Palik,
2.5.3.2 TiO <sub>2</sub>
The refractive index and extinction coefficient data used for TiO <sub>2</sub> was sourced from Essential Macleod.
2.5.3.3 MgF <sub>2</sub>
The refractive index and extinction coefficient data used for $MgF_2$ was sourced from Essential Macleod. The original source of the data was from the SOPRA database.

### 2.5.3.4 Cryolite

The refractive index and extinction coefficient data used for MgF2 was sourced from Essential Macleod. NPL (2008) concurred with Essential Macleod that the refractive index values were accurate.

### 2.6 Review of Coating analysis techniques employed in this project and the reasoning for applying them to the ITO coatings

With all the available coating analysis techniques that can be employed, the choice of which techniques to use is numerous. This section addresses the techniques employed in this thesis and explains the reasoning behind the decision to use them.

### 2.6.1 Atomic Force Microscopy (AFM)

According to Whitehouse (2002), the AFM can be used to investigate the topography of various surfaces by means of a very small stylus and cantilever and a means of measuring the deflection of the tip of the cantilever as is illustrated in the figure below:

### Figure 11 Typical Atomic Force probe



(Source Whitehouse, 2002)

Yun *et al* (2004) reports that Surface roughness deteriorates the conductivity and homogeneity of ITO thin films. It is for this reason that Yun *et al* (2004) etched their ITO coating surface to make it smoother in an attempt to minimise this effect. This work implies that average surface roughness is therefore an important parameter to consider. The unetched sample reported in the work of Yun *et al* (2004) had an average surface roughness of approximately 4.8Å, whereas optimum etching produced an average roughness of approximately 3Å.

In this thesis, the author therefore decided to use the AFM on a selection of samples to determine the average roughness in each case so that a comparison could be made between the different coating techniques and different sample thicknesses.

### 2.6.2 Scanning Electron Microscopy (SEM)

Whitehouse (2002) reports that the SEM is essentially a microscope that utilises electrons rather than light. Whitehouse (2002) feels that the advantages of electrons are that the electron beams have a comparatively small spread meaning that the SEM has a smaller numerical aperture and a very good depth of field.

The SEM was chosen as an analysis technique in this thesis as it is useful to know the actual thickness of the coatings produced rather than just assuming the thickness entered into the IC/5 controller unit is accurate. The SEM is a very versatile tool that can show much more than this, but this report focuses on this small aspect of the SEM as this was the aspect of interest here.

### **3** Application

ITO finds very wide and varied applications in various market sectors. Applications of ITO are wide and varied. The applications can range from L-3 Wescam Imaging systems right the way across the spectrum to novel applications such as the production of Star Wars style light sabres (Azo Nano, 2005) like the one illustrated below:





(Source Sagecroft Technologies, 2008)

The application of this work is the coating of certain windows of the L-3 Wescam stabilized multi-spectral airborne imaging systems. The source of the information in this section is L-3 Wescam (2008).

L-3 Wescam produces a variety of these imaging systems. An example of a typical L-3 Wescam imaging system is shown on the following page:

Figure 13 MX-15



(Source: L-3 Wescam, 2008)

The example shown above is the MX15. It incorporates the following features:

• Colour daylight camera with zoom capabilities. Below are examples of images produced with the 'day spotter'.

Figure 14 Day spotter images



(Source L-3 Wescam, 2008)

• Monochromatic night camera. The pictures on the following page illustrate the benefits of images produced with the night spotter:

Figure 15 Comparison of Day Spotter and night spotter



Night time: Using Day Spotter



Night time: Using Night Spotter

(Source: L-3 Wescam, 2008)

• Laser illumination

Figure 16 Benefits of combining the night spotter and laser illumination



No light: using spotter only



No light: using laser illuminated night spotter

(Source L-3 Wescam, 2008)

- Laser range finding capabilities
- The enhanced range local area processing (ELAP) haze penetration capabilities are illustrated on the following page:
Figure 17 ELAP Haze penetration capabilities

Before: With haze



After: With ELAP Processing



(Source L-3 Wescam, 2008)

The applications of L-3 Wescam imaging systems are wide and varied. Examples of applications are listed below:

- Defence Imaging systems are used for the collection, analysis and dissemination of visual intelligence providing a faster, more accurate stream of dynamic visual information, thus making them an invaluable tool for the following defence sectors:
  - o Army
  - o Navy
  - $\circ$  Air force
  - Marines
  - Coast Guard
- Homeland security Apart from the obvious application of Maritime security here, there is also the opportunity to facilitate search and rescue operations.
- Airborne law enforcement The imaging system enhances the ability to carry out law enforcement and perimeter security. In addition to this, the

imaging system can be used by emergency medical services and other civil applications.

- Space The imaging systems are in use at the International Space Station Alpha where they provide real-time images. Another space related application is the use of miniaturised Camera and transmission systems that provide information directly from astronauts' helmets.
- Sports These imaging systems have provided unique coverage from numerous major sporting events including the Winter and Summer Olympic Games, Gymnastics, Cycling, Racing, Football, Golf, Hockey, Yachting, Swimming, Skiing and Baseball.

The requirements for the coatings under consideration in this project are high % transmission in the visible spectrum and neighbouring IR region and <20 and <100 ohms per square sheet resistivity. The project primarily focuses on the visible region but also considers the neighbouring region out of interest. Other relevant requirements are laid down by the use of the coating and the conditions it has to withstand (More detailed specifications can not be specified in this thesis due to their highly sensitive nature).

### **4 Experimental work**

### 4.1 Methodology

This section focuses on the analysis of coatings produced at PJ Coatings with various conditions via Electron Beam Evaporation both with and with out Ion Assisted Vapour Deposition in a Leybold LAB600 (a photograph of the LAB600 is shown below):

Figure 18 Leybold LAB600



(Details of this technique are illustrated in section 2). The samples analysed in this section were produced in a clean room facility at PJ Coatings. The parameters entered into the IC/5 controller unit set to deposit these coatings are listed in Appendix A. This section also considers sputtered ITO samples (supplied by Diamond Coatings) for comparative purposes in section 4.5. Diamond Coatings did not supply the conditions that they used to sputter their samples for commercial reasons.

Transmission measurements (%T) were taken with a Cary Spectrophotometer. Measurements were taken to enable the study of the visible region and the adjacent area, as is laid out in the aims and objectives. The analysis looked at the average %T over the ranges 400-700nm, 450-900nm, 400-800nm and 700-

3000nm (the neighbouring infrared range is considered in addition out of interest as noticeable differences have been observed in %T measurements over this range).

The standard method used to determine sheet resistivity is to measure the resistance by placing the DVM probes on a 2"x1" test piece. The result of this is then divided by two to obtain a value for the ohms per square.

### 4.2 Results

This section presents the results from the Experimental work. The observations made from these results and resulting discussions are located in section 6.

### 4.2.1 Effects of deposition parameters on the output parameters when depositing a single layer of ITO via Electron beam evaporation onto a glass substrate multiple times with varying conditions

The ITO samples considered are shown in the photograph below:



Figure 19 The ITO samples

The reproducibility of the deposition conditions was evaluated statistically using the "Analysis of Variance" (ANOVA). ANOVA is a tool supplied by Microsoft

Excel that analyses the variance of data used to analyse the significance of variables on a result by returning an 'F value' and an 'F<sub>crit</sub> value' for the rows and columns considered<sup>1</sup>. ANOVA two factor without replication was applied to the data in this thesis as no replication was present in the data analysed in each case. With the data in this thesis, two columns were considered for each ANOVA analysis procedure, one containing one of the variable types and the other containing one of the result types. This process was carried out for every variable and every result obtained in turn to individually assess the contribution of each variable to each result. The values of F were observed in each case and compared to  $F_{crit}$  for the columns. F >  $F_{crit}$  means that the Variable column under consideration is significant to the selected result column. The bigger the value of F in relation to  $F_{crit}$ , the more significant the variable is to the result. Conversely, if  $F < F_{crit}$ , this means that the variable column considered is not significant to the result column considered (Note F and  $F_{crit}$  are referring to the F value and critical value of the F value respectively used in F tests for the equality of two standard deviations).

Table 2 summarises the values of F and  $F_{crit}$  for each variable and result considered in the ANOVA analysis. The highest and lowest value for each row in the table is shown in bold text.

The Results considered in this ANOVA analysis are Inner Resistivity, Outer Resistivity and Average %T for 400-700nm, 450-900nm, 400-800nm and 700-3000nm respectively. Even though the aims are to just consider the visible and near surrounding area, 700 – 3000nm was also considered here out of interest.

<sup>&</sup>lt;sup>1</sup> Microsoft Excel 2007 Help Files

Variables ► Results	Ar Flow	Pressure	02 flow	Anode Voltage	Anode Current	lon Assisted Deposition	Temp	ITO % Composition	Deposition rate	Thickness
Inner Resistivity	115	114	67	a	120	122	380	124	112	119
Outer Resistivity	113	111	65	ω	117	120	413	121	110	116
Average %T (400 - 700nm)	7460	9368	920	ω	9003	9759	10565	9938	7115	9656
Average %T (450 – 900nm)	9991	12237	955	10	12187	13070	10251	13218	9675	12816
Average %T (400 – 800nm)	8473	10447	931	თ	10270	11021	10200	11217	8106	10903
Average %T (700 – 3000nm)	513	403	57	Ω	514	504	4388	505	493	460

Table 2 Table summarising the values of F obtained in the ANOVA analysis ( $F_{crit}$  = 4 for all calculations (to 0 dp))

It can be seen that each result is affected by all of the variables considered to a greater or lesser extent. This implies that it is not very likely that any simple patterns will be present between the individual variables and their results. The next obvious step to this analysis would be to determine relationships between the variables that have the largest effect and the corresponding results (e.g. Temperature) to observe the effects because if any simple relationships between one variable and the results were present, they would most likely to be observed here. To perform this, each variable would have to be altered while all the other variables were held constant in a methodical manner for numerous runs. This unfortunately was not possible in this work as the number of practical hours where the equipment was available for use was severely limited.

### 4.2.2 Determination of the ITO deposition conditions required to provide <20 $\Omega/\square$

Out of all of the ITO coatings carried out with electron beam evaporation, the following parameters were found to provide an ITO coating with a sheet resistivity <20  $\Omega$ / $\Box$ :

Table 3 Deposition conditions required to provide <20  $\Omega/$ 

The corresponding results obtained from these parameters from these were as follows:

## Table 4 Results obtained when <20 $\Omega$ / $\Box$ a was achieved

Duter Resistivity ohms/sq	17.5	19	19.35	19	17.5	19
Inner Resistivity ohms/sq	15.5	17.5	16.7	19.3	16.3	19

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4.2.3 Determination of the ITO deposition conditions required to provide <100  $\Omega$ / $^{o}$ 

The corresponding results obtained from these parameters from these were as follows:

Table 6 Results obtained when <100  $\Omega/\Box\Box$  was achieved

Inner Resistivity ohms/sq Outer Resistivity ohms/sq

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The below table shows the results of the additional coatings that were deposited on the ITO coatings.

SiO<sub>2</sub>, TiO<sub>2</sub> and MgF<sub>2</sub> were used as they are the most commonly reported coating materials to have been applied in an attempt to enhance the %T of ITO in the visible region.

No effect on ITO Resistivity was observed from the addition of any of the extra coatings applied.

			ПО		AR	%T 400	%T 450	%T 400
			Thickness		Deposition	to 700	to 900	to 800
Date	Run	<b>AR</b> Coating	kА	AR Thickness kA	Rate A/s	mn	mn	nm
120208	•	MgF2	1.8	0.70	10	2.99.7	98.9	<u> 66.5</u>
250208	1	MgF2	0.5	1.00	10	100.5	100.6	100.3
40308	1	MgF2	0.5	1.00	10	100.4	100.5	100.2
40308	3	MgF2	0.5	1.10	10	98.5	2.99.7	98.7
80208	1	MgF2	0.75	1.03	10	91.0	88.6	88.1
120508	2	SiO2	2	1.00	2	97.8	97.8	97.8
130508	2	TiO2	2	2.00	3.5	102.6	103.1	102.7
140508	<b>~</b>	TiO2	2	60.0	2.5	103.0	102.7	102.9
		SiO2		0.46	5			
		TiO2		0.28	3.5			
		SiO2		0.18	5			
		TiO2		0.80	3.5			
		SiO2		0.16	5			
		TiO2		0.26	3.5			
		MgF2		1.02	10			

Table 7 Additional coatings

NB. The values shown to be over 100 in the last 3 columns reflects the effects that limitations and approximations of the method used to obtain the data have on the accuracy of the result obtained. Obviously they are not really over 100. The data is shown merely for comparative purposes to determine the AR coating that does the best job out of what was considered.

In each case, enhanced values of average %T were obtained for all of the wavelength ranges under consideration.

### 4.2.5 Examination of the results of ITO deposition via IAD and sputtering to determine the difference the technique used has upon the coating produced

Three ITO samples were sent to Cranfield University for Analysis via AFM and SEM. The samples chosen were one sputtered ITO sample and a 'thick' and 'thin' Evaporation sample (one with approx 200nm coating thickness and the other with approx 75nm coating thickness). These samples were chosen to get comparative information on the effects of the deposition method used and thickness of the ITO coatings. Ideally, more samples should have been investigated firstly to ensure that consistent results were obtained and secondly to determine the effect of other parameters. The intention of this section was however just a preliminary investigation that could lead to more detailed studies from the results of this where these factors would be taken into account.

### 4.2.5.1 Atomic Force Microscopy

Atomic Force Microscopy was used to look at the surface roughness of the three samples and to determine how this was affected by the method of deposition and to observe the variation with thickness of coating.

The results of this were as follows:



Peak Surface Area Summit Zero Crossing Stopband Execute Cursor



Roughness Analysis

### Figure 21 AFM results for the thin ITO Evaporation Sample

Peak Surface Area Summit Zero Crossing Stopband Execute Cursor



Roughness Analysis



Peak Surface Area Summit Zero Crossing Stopband Execute Cursor



As this was only a preliminary study, not enough samples were taken to make conclusive observations. The purpose of this study was purely to determine whether such a study was required in the future as limitations on this work prevented this from being done. It can be seen from these results that more investigation is warranted as there appears to be a difference in average roughness observed with samples produced with different conditions and it is therefore recommended that this be studied further to see if this pattern was repeatedly observed.

### 4.2.5.2 Scanning Electron Microscopy

SEM work was conducted to observe the actual thickness of the ITO coatings in comparison to the thickness that was specified on the IC/5 controller. The results from this analysis are illustrated in figures 17-19.



Figure 23 SEM Results for the Sputtered ITO sample

Unfortunately, Diamond coatings could not specify the thickness of the ITO coatings they set for commercial reasons so this could not be compared to the the achieved thickness of their coating.



Figure 24 SEM Results for the thin ITO evaporation sample

The thickness for this coating was set to 75nm on the IC/5 controller.



Figure 25 SEM Results for the thick ITO evaporation sample

The thickness for this coating was set to 200nm on the IC/5 controller.

It can be seen with both the evaporation samples that a variation in thickness was observed across the sample. Again, this was a preliminary study, but it points towards the need for future work to be carried out in this field to determine what causes the variation in thickness and trying to eliminate it

### 5 Modelling ITO coating performance

### 5.1 Methodology

All analysis was carried out using Essential Macleod software. Analysis was performed with the Simplex Optimisation method provided by Macleod. All the diagrams shown in this section are from this software. The data sources used in these calculations are discussed in the literature review.

Analysis in this section was only carried out for the 400-700nm, 450-900nm (for three of the four data sets) and 400-800nm ranges as there is only one set of data here that would have met the 700-3000nm range requirements. It can be seen from the data that there are discrepancies between the different sets of data. Each set of data was used for each consideration in this section to enable a comparison to be made. It is for this reason that 700-3000nm was not considered here. Each range was considered separately for each section so that optimisation could be performed over each range separately. Optimisation was carried out with targets set every 25nm throughout each range.

### 5.2 Modelling Results

This section presents the modelling results. The observations made from these results and the resulting discussions are located in section 6.

### 5.2.1 Optimising the thickness of a single layer of ITO for %T

This section examines what thickness of ITO is required to give the optimum average %T for the wavelength ranges considered. The ITO on the substrate is illustrated in the figure below.

### Figure 26 Illustration of the ITO on the Substrate



The results of this are shown in Table 8:

Wavelength range /nm	ITO Data	Average %T across	Optimum ITO Thickness
		wavelength range	/nm
400–700nm	-	88.4	117.02
400-700nm	2	84.6	114.43
400-700nm	8	29.62	105.73
400-700nm	4	91.5	120.68
450-900nm	7	88.8	132.41
450-900nm	2	76.3	137.78
450-900nm	4	92.0	136.79
400-800nm	1	88.1	116.74
400-800nm	2	83.9	119.59
400-800nm	3	79.0	102.15
400-800nm	4	91.3	120.03

Table 8 Optimisation of %T by alteration of ITO thickness

# 5.2.2 Increasing the thickness to 2kÅ (200nm) to achieve the desired surface resistivity values

Even though the results in the previous section give thicknesses that exhibit the optimum average %T, unfortunately, these thicknesses do not meet the sheet resistivity requirements. To meet the sheet resistivity requirements, the ITO layer needs to be thickened. The effects of increasing the thickness of the ITO to 2kÅ is examined in this section.

Wavelength range /nm	ITO Data	ITO Thickness	Average %T across wavelength
		IkÅ	range
400–700nm	-	2	85.2
400-700nm	2	2	77.8
400-700nm	e	2	70.5
400-700nm	4	2	89.5
450-900nm	L	2	86.1
450-900nm	2	2	84.0
450-900nm	4	2	89.8
400-800nm	L	2	86.1
400-800nm	2	2	81.0

Table 9 Effects of increasing the thickness of ITO to 2kÅ

# 5.2.3 Increasing the % Transmission through the addition of other layers to the ITO layer

and an increase in cost (incurred via material costs and machine times). From the findings of Eite (2004), it therefore makes sense to primarily consider increasing the %T for the 20 Ohms/square samples as these samples are thicker and thus According to Eite (2004), increasing the thickness of an ITO coating results in an increase in conductivity, a fall in transmission experience a lower % transmission. It is for this reason that all of the work carried out on maximising the %T in the remainder of this section has therefore focussed on an ITO thickness of 2kÅ (required for 20 Ohms/square).

### 5.2.3.1 Addition of a single layer

This section considers increasing the average % Transmission of ITO by adding an additional single layer. This situation is illustrated in Figure 27. The addition of a single layer of SiO<sub>2</sub>, TiO<sub>2</sub> and MgF<sub>2</sub> is considered in turn (in tables 10-12). SiO<sub>2</sub>, TiO<sub>2</sub> and MgF2 were used as they are the most commonly reported coating materials to have been applied in an attempt to enhance the %T of ITO in the visible region (see section 2.4). It is for this reason that this thesis will initially consider the addition of these layers as a starting point in the quest to maximise the %T. These materials have refractive indices both above and below the refractive index of ITO. For each material, the optimum thickness was deduced through Simplex analysis.

Figure 27 Illustration of the ITO and an additional layer

Medium - Air



Table 10 Results of the addition of SiO<sub>2</sub>

Wavelength range /nm	ITO Data	ITO /kÅ	Thickness	Average %T across wavelength range	Optimum Thickness /nm	SiO <sub>2</sub>
400–700nm	-	7		92.2	86.60	
400-700nm	2	7		87.8	88.67	
400-700nm	3	7		77.1	87.31	

80.75	89.83	93.73	88.34	87.20	89.86	88.28	82.05
95.5	91.8	91.7	94.3	92.1	88.9	77.1	94.9
2	2	2	2	2	2	2	2
4	£	2	4	£	2	3	4
400-700nm	450-900nm	450-900nm	450-900nm	400-800nm	400-800nm	400-800nm	400-800nm

Table 11 Results of the addition of  $TiO_2$ 

Wavelength range /nm	ITO Data	ITO Thicknes /kÅ	s Average %T across wavelength range	Optimum Thickness /nm	TiO <sub>2</sub>
400–700nm	-	2	80.3	108.93	
400-700nm	2	2	77.3	95.59	
400-700nm	e	2	67.1	123.96	

107.52	148.86	129.31	151.66	157.06	150.59	155.13	158.79
83.2	80.2	79.3	83.1	80.8	78.4	67.5	83.4
7	2	7	7	2	2	2	2
4	-	ы	4	-	ъ	e	4
400-700nm	450-900nm	450-900nm	450-900nm	400-800nm	400-800nm	400-800nm	400-800nm

Table 12 Results of the addition of  $MgF_2$ 

Wavelength range /nm	ITO Thickness /kÅ	ITO Data	Average %T across wavelength range	Optimum Thickness /nm	SLAR
400–700nm	2	-	92.6	91.46	
400-700nm	2	2	87.6	93.10	
400-700nm	2	3	77.4	92.28	

85.67	96.17	<b>99.07</b>	95.15	92.76	94.40	94.03	89.04
96.1	92.3	91.9	95.0	92.6	89.1	4.77	95.6
4	-	2	4	-	2	3	4
2	2	2	2	2	2	2	2
400-700nm	450-900nm	450-900nm	450-900nm	400-800nm	400-800nm	400-800nm	400-800nm

# 5.2.4 Optimisation of Refractive Index and Thickness for the addition of a Single Layer

Optimisation processes are good tools. It must however be remembered that they are only as good as their starting point. If the wrong starting point is chosen, optimisation can result in a local maximum instead of finding the true maximum. To through manipulation of Refractive index and thickness. It showed that the MgF2 gave the highest %T overall for all of the ranges out of all the single layers applied to the ITO. The Refractive index of MgF2 was therefore used as the starting point for this analysis. This starting point was used in conjunction with Simplex optimisation in Essential Macleod to determine an minimise the chance of this, the above work was carried out to determine a good starting point for the optimisation of %T optimised Refractive index and thickness for each case considered. The results of this are shown in Table 13 below:

Wavelength range /nm	ITO Data	Optimum Refractive	Optimum SLAR	Average %T for
		Index for SLAR	Thickness /nm	wavelength range
400–700nm	~	1.35452	93.57	92.7
400-700nm	7	1.42840	90.54	87.8
400-700nm	e	1.37595	92.93	77.4
400-700nm	4	1.32215	90.01	96.3
450-900nm	~	1.33534	101.63	92.4
450-900nm	7	1.40263	98.03	91.9
450-900nm	4	1.30834	103.14	95.3
400-800nm	Ť	1.33967	96.24	92.7
400-800nm	7	1.40417	93.24	89.1
400-800nm	3	1.35570	96.36	77.4
400-800nm	4	1.30834	94.06	95.8

Table 13 Optimisation of the refractive index and thickness for the addition of a single layer

5.2.5 Prod	uction of S	symmetrical	periodic layers to simulate the optimum Refractive indices and thicknesses
Wang (200	6) feels the	at symmetrica	al periodic layers can offer equivalent indices that are unachievable with a single material.
The next o	bvious step	o after obtaini	ning optimised refractive indices and thicknesses is to find symmetrical periods made from
common m	aterials use	ed in the visit	ible region that can simulate the optimum refractive indices and thicknesses. The results of
this for 400	-700nm wit	th ITO data 1	are shown below as a typical example:
		Physical Thickness	
Layer	Material	(mn)	
Medium	Air		
L	SiO2	33.75	
2	TiO2	10.82	
3	SiO2	33.75	
4	ITO	200	
Substrate	Glass		
Unfortunate	ely, the ab	ove example	e of the results from this show that the physical thicknesses required for each layer are
exceedingly	y small mai	king accurate	e deposition of such thicknesses exceedingly difficult. This is illustrated in the Experimental
section, wh	ere it could	d be seen tha	at the actual thicknesses obtained compared to the thicknesses that were programmed got
progressive	ily less acc	urate when th	he thickness considered were smaller.

## 5.2.6 Finding a material that is closest to the optimum refractive index

The next step from this is to find a material with the closest refractive index to the optimum refractive indices calculated previously. This is carried out in Table 14.

Table 14 Materials with the nearest refractive index to the optimum refractive indices

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Refractive index	coating material	1.35	1.46180	1.38542	1.35	1.35
Nearest standard	coating material <sup>2</sup>	Na₃AIF₀ (Cryolite)	SiO <sub>2</sub>	MgF <sub>2</sub>	Na₃AIF₀ (Cryolite)	Na <sub>3</sub> AIF <sub>6</sub>
Optimum Refractive	Index	1.35452	1.42840	1.37595	1.32215	1.33534
ITO Data		1	2	8	4	-
Wavelength range /nm		400-700nm	400-700nm	400-700nm	400-700nm	450-900nm

<sup>2</sup> Materials considered are listed in Essential Macleod under standard coating materials

			(Cryolite)	
-900nm	5	1.40263	MgF <sub>2</sub>	1.38542
-900nm	4	1.30834	Na <sub>3</sub> AIF <sub>6</sub> (Cryolite)	1.35
-800nm	<del>~</del>	1.33967	Na <sub>3</sub> AIF <sub>6</sub> (Cryolite)	1.35
-800nm	5	1.40417	MgF <sub>2</sub>	1.38542
-800nm	ო	1.35570	Na <sub>3</sub> AIF <sub>6</sub> (Cryolite)	1.35
-800nm	4	1.30834	Na <sub>3</sub> AIF <sub>6</sub> (Cryolite)	1.35

It can be seen from the table that the data used in the theoretical studies plays a crucial role in determining the best course of action. This therefore reinforces the importance of examining the results from multiple sets of data to try to get a broader picture.

### 5.2.7 Cryolite studies

The most frequently occurring material in this table is Cryolite. The next step from here is therefore to model the use of a single layer of Cryolite for each wavelength range for each set of ITO data (see Figure 28). Figures 23 - 33 illustrate the

normal incidence are given. Even though normal incidence is the primary consideration here, 3D plots are also shown to give results for the different ITO data sets for the wavelength ranges under consideration. 2D plots of %T versus wavelength for more information for other angles. Circle diagrams (based at a design wavelength of 510nm) are also given to give a clearer picture of the effects the layers have. Table 15 then summarises these results.

Figure 28 Illustration of the addition of Cryolite to ITO

Medium - Air



Figure 29 Results for ITO data 1 for 400-700nm

**ITOsingleAR:** Transmittance



58







### Figure 30 Results for ITO data 2 for 400-700nm

### **ITOsingleAR:** Transmittance






## ITOsingleAR: Reflection Coefficient Im(Reflection Coefficient) 0.75

# Figure 31 Results for ITO data 3 for 400-700nm

#### **ITOsingleAR:** Transmittance









99

# Figure 32 Results for ITO data 4 for 400-700nm

#### ITOsingleAR: Transmittance









Figure 33 Results for ITO data 1 for 450-900nm

### **ITOsingleAR:** Transmittance







#### ITOsingleAR: Reflection Coefficient Im(Reflection Coefficient) h.000.750.750.750.75100 -0.75 100-0.75-0.25 0.50 0.75 100-0.75-0.75

# Figure 34 Results for ITO data 2 for 450-900nm

### **ITOsingleAR:** Transmittance









# Figure 35 Results for ITO data 4 for 450-900nm

#### ITOsingleAR: Transmittance



76





#### Im(Reflection Coefficient) -1.00 -0.75 -0.25 -0

# Figure 36 Results for ITO data 1 for 400-800nm

### ITOsingleAR: Transmittance







#### Im(Reflection Coefficient)



# Figure 37 Results for ITO data 2 for 400-800nm

### ITOsingleAR: Transmittance







ITOsingleAR: Transmittance



# Figure 38 Results for ITO data 3 for 400-800nm

#### ITOsingleAR: Transmittance









-0.50+

-0.75

# Figure 39 Results for ITO data 4 for 400-800nm

#### **ITOsingleAR:** Transmittance









Wavelength range /nm	ITO Thickness /kÅ	ITO Data	Cryolite layer thickness /nm	Average %T for Cryolite studies	Average %T fo refractive index	· optimum
400-700nm	2	<del>~</del>	93.96	92.7	92.7	
400-700nm	2	2	95.49	87.4	87.8	
400-700nm	7	ო	94.82	77.4	77.4	
400-700nm	7	4	88.16	96.2	96.3	
450-900nm	7	<del>, -</del>	100.00	92.4	92.4	
450-900nm	7	2	101.51	91.8	91.9	
450-900nm	7	4	98.77	95.2	95.3	
400-800nm	7	~	95.47	92.7	92.7	
400-800nm	7	7	96.83	89.0	89.1	
400-800nm	2	3	96.85	77.4	77.4	
400-800nm	2	4	90.83	95.7	95.8	

Table 15 Cryolite Results in comparison to the results obtained for the optimum refractive index

The results in this table and the single layer studies show that Cryolite provides a very good solution. The next step from this is to consider more complex coatings to see if further improvement is observed.
5.2.8 Addition of a multi layer stack on ITO using needle synthesis
Another route to attempt to maximise %T is to investigate is the production of multi layer stacks applied on top of the ITO
utilising the needle synthesis technique. This is considered below. As such good results were achieved with the Cryolite in the
previous section, Cryolite will be used as one of the stack constituents. As the refractive index of Cryolite is less than that of

used AR material and will therefore has a more substantial contrast to Cryolite. An example of needle synthesis run in ITO, the other material used in the stack will be TiO2 as this has a refractive index greater than that of ITO, is a commonly progress is shown in Figure 40:

### Figure 40 Needle synthesis



veedle synthesis is carried out in Essential Macleod by firstly stating the layers that you wish to insert 'very tiny needles' containing the substances you wish to inject. In this case, the layers are Cryolite and TiO <sub>2</sub> that sit on top of the ITO. The next
step is to specify the materials that you want to 'inject' in these layers. Again, in this case, this is Cryolite and TiO2. Figure 40
shows Essential Macleod running the needle synthesis technique with these parameters.

The results from the needle analysis for 400-700nm ITO data 1 are shown in Table 16. The %T graphs and the circle diagrams that result from this analysis are shown in Figure 35.

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		Physical Thickness
Layer	Material	(nm)
Medium	Air	
-	Na3AIF6	173.23
2	Ti02	2.74
e	Na3AIF6	321.67
4	TiO2	0.65
5	Na3AIF6	216.48
6	Ti02	2.65
7	Na3AIF6	185.36
8	Ti02	1.05
6	Na3AIF6	335.26
10	TiO2	1.22
11	Na3AIF6	11.54
12	Ti02	3.08

13	Na3AIF6	434.53
14	Ti02	4.04
15	Na3AIF6	610.72
16	Ti02	0.52
17	Na3AIF6	437.15
18	Ti02	5.35
19	Na3AIF6	173.22
20	Ti02	5.31
21	Na3AIF6	396.61
22	Ti02	1.31
23	Na3AIF6	244.3
24	Ti02	3.27
25	Na3AIF6	189.88
26	Ti02	4.21
27	Na3AIF6	603.45
28	TiO2	4.54
29	Na3AIF6	177.38
30	TiO2	2.78
31	Na3AIF6	871.92
32	TiO2	4.93
33	Na3AIF6	7.31
34	TiO2	1.06
35	Na3AIF6	178.92
36	TiO2	1.48
37	Na3AIF6	294.37
38	TiO2	0.76
39	Na3AIF6	225.72

40	Ti02	2.55
41	Na3AIF6	500.11
42	TiO2	3.41
43	Na3AIF6	152.17
44	Ti02	0.17
45	Na3AIF6	134.8
46	TiO2	2.14
47	Na3AIF6	127.57
48	TiO2	5.34
49	Na3AIF6	188.89
50	TiO2	5.66
51	Na3AIF6	751.52
52	TiO2	6.4
53	Na3AIF6	33
54	ITO	200
Substrate	Glass	

Figure 41 Results from the TiO<sub>2</sub> and Cryolite multilayers

### ITOmultiAR: Transmittance






### ITOmultiAR: Reflection Coefficient



Average %T over 400-700nm for ITO data 1 = 82.2.

# 5.2.9 Addition of multilayer stacks using needle synthesis with ITO as one of the stack layers

The next logical step from this would be to consider having ITO and Cryolite as the stack layers to see the effects of this.

The results for 400-700nm ITO data 1 were as follows

Table 17 Multilayer stack consisting of Cryolite and ITO

		Physical Thickness
Layer	Material	(uu)
Medium	Air	
١	Na3AIF6	427.62
2	ITO	0.13
3	Na3AIF6	2039.36
4	ITO	0.19
5	Na3AIF6	2674.36
9	ITO	0.28
2	Na3AIF6	803.45
8	ITO	4.98
6	Na3AIF6	198.77
10	ITO	3.57
11	Na3AIF6	751.98
12	ITO	1.99
13	Na3AIF6	1383
14	ITO	4.49

	Na3AIF6	200.03
		1.07
	Na3AIF6	927.81
	ITO	3.12
	Na3AIF6	1177.65
	ITO	1.91
	Na3AIF6	180.44
	ITO	5.24
	Na3AIF6	1158.88
	ITO	0.17
	Na3AIF6	1187.34
	ITO	1.02
	Na3AIF6	961.57
	ITO	5.2
	Na3AIF6	30.18
	ITO	200
ostrate	Glass	

Figure 42 Results from the ITO Cryolite multilayers













Average %T for 400 to 700nm for this design = 89.9.

It can be seen from both of these results that there is a large variation in response over wavelength. This is clearly from the needle analysis, this would be a pointless exercise as some of the recommended layers are so thin that they are not unacceptable. The effect could be reduced by the addition of further layers, but as can be seen by the layer thicknesses given practically reproducible.

### 6 Observations and Discussion

### 6.1 Consideration of the Experimental results

This section makes observations and discusses the results of the analysis of coatings produced with various conditions via Electron Beam Evaporation with and without Ion Assisted Vapour Deposition in a Leybold LAB600 at PJ Coatings.

### 6.2.1 Observation of the effects of deposition parameters on the output parameters when depositing a single layer of ITO via Electron beam evaporation onto a glass substrate multiple times with varying conditions

The reproducibility of the deposition conditions was evaluated statistically using the "Analysis of Variance" (ANOVA).

Table 2 provided a summary of the values of F and  $F_{crit}$  for each variable and result considered in the ANOVA analysis.

The Results considered in this ANOVA analysis were Inner Resistivity, Outer Resistivity and %T for 400-700nm, 450-900nm, 400-800nm and 700-3000nm respectively. Even though the aims are to just consider the visible and near surrounding area, 700 – 3000nm was also considered here out of interest.

The main observations from these results were as follows:

 It can be seen that each result is affected by all of the variables considered to a greater or lesser extent. The next obvious step to this analysis would be to determine relationships between each result and each variable directly. Looking at the effects on variables such as Temperature on results produced would be interesting. To perform this, each variable would have to be altered while all the other variables were held constant in a methodical manner for numerous runs. This unfortunately was not possible in this project as the number of practical hours where the equipment was available for use was limited.

- Temperature and ITO % Composition were found to be the most significant variables overall that influenced average %T over the wavelength range 400-3000nm.
- Temperature was found to be the most significant factor influencing resistivity, although ITO % composition, Ion assistance, pressure, deposition rate, thickness and Argon flow also have considerable influence on resistivity.
- It is interesting to note that for each result considered (both transmission and resistivity), the variable that had the least significance to each result was the Anode Voltage. For the 700 to 3000nm region, this was the smallest observed difference between F and F<sub>crit</sub> in the ANOVA analysis. It is interesting than the presence or absence of Ion Assistance plays more of a role on the result that the value of the Anode Voltage in each case. This implies that the value of the Anode Voltage does not play an important part in Ion Assistance when considering these wavelength ranges and the Anode Current is the variable that plays the bigger role.
- When the %T was considered for each wavelength range, the values for F were larger than the values produced from the Resistivity analysis. This indicates that the %T is more sensitive to these variables than the resistivity.

### 6.2.2 Determination of the ITO deposition conditions required to provide $<20 \Omega/\Box$

Table 3 illustrates the parameters used to provide an ITO coating with <20  $\Omega$ /square. The results achieved are illustrated in Table 4.

The observations made from these results are as follows:

- It is Interesting to note that the desired resistivity has been obtained both with and without ion assisted deposition.
- In all of the cases considered, an ITO thickness of 2kÅ was required to obtain the required sheet resistivity.
- Without IAD, an O<sub>2</sub> flow of 40sccm and an Ar flow of 0sccm was required.
- With IAD, an O<sub>2</sub> flow of 12.8sccm and an Ar flow of 5sccm was required.

### 6.2.3 Determination of the ITO deposition conditions required to provide <100 $\Omega/\Box$

Table 5 illustrates the parameters used to provide an ITO coating with <100  $\Omega$ /square. The results achieved are illustrated in Table 6.

It can be seen that the thickness required to produce <100  $\Omega$ /square is considerably less than the thickness required to produce <20  $\Omega$ /square thus concurring with the observations of Eite (2004).

It can be seen that the relationship is not straight forward as an ITO thickness of 100kÅ is required to produce 83 ohms per square, whereas a 200kÅ layer produces a measured value of 17 ohms per square.

### 6.2.4 Attempt to maximise the %T with the addition of extra layers

No effect on ITO Resistivity was observed from the addition of any of the extra coatings applied.

Table 7 illustrates the results of adding additional coatings to the ITO coating.

It can be seen that for 2kÅ of ITO, the coating applied on 140508 run 1 yielded the best practical %T results for the visible wavelength range and the immediate surrounding area.  $MgF_2$  also produced very high %T for 0.5kÅ of ITO and the wavelength ranges considered.

Additional coatings for ITO are further considered in the Theoretical Modelling section.

### 6.2.5 Examination of the results of ITO deposition via IAD and sputtering to determine the difference the technique used has upon the coating produced

### 6.2.5.1 Atomic Force Microscopy

Atomic Force Microscopy was used to look at the surface roughness of the three samples and to determine how this is affected by the method of deposition and to observe the variation with thickness of coating.

The results of this study are illustrated in Figures 14-16.

It is interesting to note that the Average roughness ( $R_A$ ) of the thick evaporation sample is over 3 times more than for the thin evaporation sample.

Yun *et al* (2004) report that Surface roughness deteriorates the conductivity and homogeneity of ITO thin films. It is for this reason that Yun *et al* (2004) etched the ITO coating surface to make it smoother. Their unetched sample had an average roughness of approximately 4.8Å, whereas the optimum etching resulted in a sample with an average roughness of approximately 3Å.

The study in this thesis reported the following average roughnesses for the samples considered:

Sputtered ITO Sample Average roughness = 11.1Å Thin ITO Sample Average roughness = 9.2Å Thick ITO Sample Average roughness =34.3Å.

It is interesting to note that the average roughness produced with the LAB600 and Diamond Coatings sputter sample was greater that the average roughness reported in the study of Yun *et al* (2004) where Chemical Solution Deposition was employed.

Another interesting observation that can be made from the thesis results is that the Average Roughness of the Thick ITO sample was about 3 times greater than the Average roughness of both the thin ITO sample and the sputtered ITO sample (which had similar Average roughness values). As this is a preliminary study, more work would need to be done to investigate this to see if this pattern was repeatedly observed.

Another interesting observation that has arisen from analysis of these results is that the ratio of Rq/Ra is fairly consistent for the evaporation samples and that this value is less than the value that this ratio takes for sputtering. Figures 17-19 illustrate the SEM results.

The purpose of this section was to examine the ITO coating thicknesses produced in comparison to the thicknesses that were set with the LAB600 deposition equipment.

It can be seen from the results that the sputtered ITO sample produced a fairly even coating whose thickness was 300nm. Unfortunately, for commercial reasons, Diamond Coatings could not provide the parameters used with this coating. Looking at the LAB600 samples, it can be seen that the thickness of the thinner sample showed variation between 92nm and 131nm compared to the specified 75nm. The thickness of the thicker sample however showed a thickness of 192nm compared to the specified 200nm. It can be seen that the thicker sample produced thicknesses that were comparable to the specified thickness, but as the required coating thickness became thinner, the accuracy of the coating thickness obtained diminished.

## **6.3 Consideration of the Theoretical Modelling results**

The table below provides a summary of the work carried out in the Theoretical modelling section.

Average %T			88.4	84.6	79.6	91.5	88.8	76.3	92.0
Optimum SLAR	coating thickness nm								
SLAR	Refractive	index							
ІТО	Thickness	mn	117.02	114.43	105.73	120.68	132.41	137.78	136.79
ΙТΟ	data		-	2	с	4	<del>.</del>	7	4
Wavelength	ange nm		400-700				450-900		
	<u> </u>								

Table 18 Summary of the thicknesses and the average %T from the theoretical studies

88.1	83.9	79.0	91.3	85.2	77.8	70.5	89.5	86.1	84.0	89.8	86.1	81.0
116.74	119.59	102.15	120.03	200	200	200	200	200	200	200	200	200
~	2	с	4	-	5	с	4	-	2	4	-	2
400-800				400-700				450-900			400-800	
				set at	kness to	effect on						

71.4	89.8	92.2	87.8	77.1	95.5	91.8	91.7	94.3	92.1	88.9	77.1	94.9
		86.60	88.67	87.31	80.75	89.83	93.73	88.34	87.20	89.86	88.28	82.05
		1.46180	1.46180	1.46180	1.46180	1.46180	1.46180	1.46180	1.46180	1.46180	1.46180	1.46180
200	200	200	200	200	200	200	200	200	200	200	200	200
с	4	~	5	e	4	<del>~</del>	7	4	~	7	с	4
		400-700				450-900			400-800			
		Single layer	2kÅ ITO									

80.3	77.3	67.1	83.2	80.2	79.3	83.1	80.8	78.4	67.5	83.4	92.6	87.6
108.93	95.59	123.96	107.52	148.86	129.31	151.66	157.06	150.59	155.13	158.79	91.46	93.10
2.34867	2.34867	2.34867	2.34867	2.34867	2.34867	2.34867	2.34867	2.34867	2.34867	2.34867	1.38542	1.38542
200	200	200	200	200	200	200	200	200	200	200	200	200
~	7	ю	4	~	5	4	~	2	e	4	<del>~</del>	5
400-700				450-900			400-800				400-700	
Single layer	of TiO <sub>2</sub> on 2kÅ ITO										Single layer	

2kÅ ITO		е	200	1.38542	92.28	77.4
		4	200	1.38542	85.67	96.1
	450-900	-	200	1.38542	96.17	92.3
		2	200	1.38542	99.07	91.9
		4	200	1.38542	95.15	95.0
	400-800	<del>.</del>	200	1.38542	92.76	92.6
		2	200	1.38542	94.40	89.1
		с	200	1.38542	94.03	77.4
		4	200	1.38542	89.04	95.6
Purely	400-700	-	200	1.35452	93.57	92.7
optimised		2	200	1.42840	90.54	87.8
Refractive indices of		с	200	1.37595	92.93	77.4
SLAR on 2kå		4	200	1.32215	90.01	96.3

92.4	91.9	95.3	92.7	89.1	77.4	95.8	92.7	87.4	77.4	96.2	92.4	91.8
101.63	98.03	103.14	96.24	93.24	96.36	94.06	93.96	95.49	94.82	88.16	100.00	101.51
1.33534	1.40263	1.30834	1.33967	1.40417	1.35570	1.30834	1.35	1.35	1.35	1.35	1.35	1.35
200	200	200	200	200	200	200	200	200	200	200	200	200
-	2	4	<del></del>	5	с	4	<del></del>	5	с	4	<del></del>	2
450-900			400-800				400-700				450-900	
ITO			1				Single layer	2kÅ ITO				

95.2	92.7	89.0	77.4	95.7
98.77	95.47	96.83	96.85	90.83
1.35	1.35	1.35	1.35	1.35
200	200	200	200	200
4	~	7	e	4
	400-800			

Given the discrepancies between the ITO data, it is exceedingly difficult to say which set of data provides the most accurate representation. It is for this reason that the results from all of the ITO data sets was examined.

The prevalent observations from the results displayed in this table are as follows:

- It can be seen from the results that increasing the thickness of the ITO layer to 2kÅ results in a decrease in transmission. This concurs with the results observed by Eite (2004).
- The addition of a single layer of SiO<sub>2</sub>, TiO<sub>2</sub> and MgF<sub>2</sub> respectively on top of 200nm of ITO in an attempt to maximise the average %T across all of the ranges considered produced some interesting results:
- The TiO<sub>2</sub> (with a refractive index greater than that of ITO) actually produced a decreased average %T in comparison to the plain layer of 200nm ITO
- The SiO<sub>2</sub> and MgF<sub>2</sub> (both with a refractive index less than that of ITO) on the other hand both enhanced the average %T observed for each range considered.
- Out of these three single layer coatings considered, MgF<sub>2</sub> created the best improvement of average %T overall on all of the wavelength ranges considered.
- The next step after considering the application of single layer coatings was to deduce the optimum coating thickness and optimum coating refractive index that could be used in a single layer. Optimisation processes are good tools. It must however be remembered that they are only as good as their starting point. If the wrong starting point is chosen, optimisation can result in a local maximum instead of finding the true

maximum. To minimise the chance of this, the Refractive index of  $MgF_2$  was therefore used as the starting point as it provided the highest enhancement of average %T across the wavelength ranges of interest. This starting point was used in conjunction with Simplex optimisation in Essential Macleod to determine an optimised Refractive index and thickness for each case considered. This point has been reemphasised here as it is important to bear in mind when considering the results obtained.

- Symmetrical layer periods were used in an attempt to simulate the optimum refractive indices and thicknesses deduced previously. Unfortunately, the results from this show that the physical thicknesses required for each layer are exceedingly small making accurate deposition of such thicknesses exceedingly difficult. (This was illustrated in the Experimental section, where it could be seen that the actual thicknesses obtained compared to the thicknesses that were programmed got progressively less accurate when the thickness considered were smaller).
- As symmetrical layer periods produced results that it was difficult to apply practically, the next step was to attempt to find a commonly used coating material that had a refractive index as close to the calculated optimum refractive indices as possible.
- Studying the optimum refractive indices illustrates that the majority of the data predicts that Cryolite produces the highest average %T for the wavelength ranges considered. Cryolite was therefore modelled for all of the ITO data for the wavelength ranges of interest. 2D plots of %T versus wavelength for normal incidence were produced. Even though normal incidence is the primary consideration here, 3D plots were also shown to give more information for other angles. Circle diagrams were also produced to give a clearer picture of the effects the layers were having.

- From the Cryolite modelling, it could be seen that on the whole, Cryolite generally produces an average %T slightly smaller than for the optimum refractive index. This is to be expected as the refractive index of Cryolite moves the situation away from the optimum configuration. It is however noted that the difference between the Average %T for Cryolite and the %T for the optimum refractive index is very small which implies that Cryolite is a very good approximation to the optimum refractive indices.
- The below table compares the Material that was found to be nearest to the calculated optimum refractive index and the material that actually gave the highest average %T for the wavelength range considered.

Table 19 Comparison of the material giving the highest %T and the material nearest to the optimal refractive index

Wavelength	ITO	Nearest	Material
range /nm	Data	standard	giving the
		coating material	highest %T on
			2KÅ ITO
400-700nm	1	Na <sub>3</sub> AIF <sub>6</sub>	Na <sub>3</sub> AIF <sub>6</sub>
		(Cryolite)	(Cryolite)
400-700nm	2	SiO <sub>2</sub>	SiO <sub>2</sub>
400-700nm	3	MaEa	MaEa
400 7001111			
400-700nm	4	Na <sub>3</sub> AlF <sub>6</sub>	Na <sub>3</sub> AIF <sub>6</sub>
		(Cryolite)	(Cryolite)
450-900nm	1	Na₃AIF <sub>6</sub>	Na <sub>3</sub> AIF <sub>6</sub>
		(Cryolite)	(Cryolite)

450-900nm	2	MgF <sub>2</sub>	MgF <sub>2</sub>
450-900nm	4	Na <sub>3</sub> AIF <sub>6</sub>	Na <sub>3</sub> AIF <sub>6</sub>
		(Cryolite)	(Cryolite)
400-800nm	1	Na <sub>3</sub> AIF <sub>6</sub>	Na <sub>3</sub> AIF <sub>6</sub>
		(Cryolite)	(Cryolite)
400-800nm	2	MgF <sub>2</sub>	MgF <sub>2</sub>
400-800nm	3	Na <sub>3</sub> AIF <sub>6</sub>	Na <sub>3</sub> AIF <sub>6</sub>
		(Cryolite)	(Cryolite)
400-800nm	4	Na <sub>3</sub> AIF <sub>6</sub>	Na <sub>3</sub> AIF <sub>6</sub>
		(Cryolite)	(Cryolite)

- It can be seen from this table that all of the predicted materials actually gave the highest average %T when considered. It can also be seen again that on the whole, Cryolite produces the highest average %T on the ranges considered on 2kÅ of ITO. Due to limited equipment access during this project, it was not possible to produce the ITO Cryolite coatings practically. This study would therefore be therefore a natural progression from this work.
- Another route taken in an attempt to maximise average %T was to investigate is the production of multi layer stacks on ITO using needle synthesis. As such good results were achieved with the Cryolite in the previous section, Cryolite was used as one of the stack constituents. As the refractive index of Cryolite is less than that of ITO, the other materials used in the stack was to be TiO<sub>2</sub> and Cryolite as this has a refractive index greater than that of ITO, is a commonly used AR material and therefore had a more substantial contrast to the Cryolite. The results from this however showed that some of the layers utilized in this are exceedingly thin. For reasons previously discussed, this can not

successfully be applied to Experimental TiO<sub>2</sub> and Cryolite work with any great accuracy. The average %T produced from this was found not to be as high as that produced with a single layer of Cryolite!!

- Another multilayer stack was modelled this time having ITO and Cryolite as the two materials in the stack to see the effects of this. Again, it could be seen from the results that some of the layers were exceedingly thin. Again, this can not successfully be applied to Experimental work with any great accuracy. The average %T is not as high as that produced with a single layer of Cryolite!!
- Cryolite seems to have produced some very encouraging results in the theoretical studies for the wavelength ranges considered. This is not the end of the story however, merely the beginning. Will Cryolite produce the results that they theory suggests? Is the next obvious question that needs to be addressed. If this hurdle is met, the next issue is that Cryolite is fairly soft (Chemical Land, 2008). This means that to make Cryolite a viable solution, a protective coating system would need to be developed to make it suitable.

### 6.4 Consideration of both the Experimental and Modelling results

The Experimental work carried out in this thesis shows that thick ITO layers are required to provide 20 ohms/square. The theoretical work carried out shows that the optimum transmission is obtained for lower ITO thicknesses, and the effect of increasing the thickness is to decrease the average %T across all of the wavelength ranges considered.

The Experimental work also shows that to obtain 100 ohms/square, the ITO layer required is thinner.

The results discussed above concur with the observations of Eite (2004) that increasing the thickness of an ITO coating results in an increase in conductivity.

Both the theoretical and experimental studies revealed that the average %T across the wavelength ranges considered could be increased by the addition of additional layer (s) of material.

### 6.5Comparison between the work reported in the literature and this thesis

This thesis has examined the work done with coatings added to ITO coatings in an attempt to maximise %T in the visible region and used it as a starting point for further investigation into the maximisation of %T in the visible region.

The numerous papers (considered in section 2) have shown that the deposition variables considered play an important role in the results that are obtained. This thesis has carried out a more comprehensive study with the lon Assisted Vapour Deposition parameters where more variables have been considered. The work carried out in this thesis concurs with the view that the variables used play a crucial role in the results obtained. It has been demonstrated by the results of this work that all of the variables considered effect the results obtained to a greater or lesser degree.

With all of the studies reported in the literature, the authors had either different or undisclosed sheet resistivity requirements (and thus thicknesses). Unless the required sheet resistivity matches the sheet resistivity requirements of this thesis, the work on variables illustrates that a direct comparison of the Transmission and Resistivity results can not be successfully performed as the result has been shown to be very variable dependent. It was for this reason that a direct comparison is not performed in this section. To do more work with this, the conditions given in the literature would need to be replicated to enable direct comparisons to be performed. Unfortunately, this was not possible due to the very limited practical time where the equipment was available.

### 6.6 More practical multilayer structures

A Multilayer structure that was applied in the Experimental section is illustrated in Table 20. This multilayer structure is more easily producible practically due to the more manageable thicknesses involved.

Table 20 Summary of the multilayers applied in the Experimental section

		Additional	ITO Thickness	AR Thickness	AR Deposition
Date	Run	Coating	kA	kA	Rate A/s
140508	1	TiO2	2	0.09	2.5
		SiO2		0.46	5
		TiO2		0.28	3.5
		SiO2		0.18	5
		TiO2		0.80	3.5
		SiO2		0.16	5
		TiO2		0.26	3.5
		MgF2		1.02	10

The results of this showed an enhancement of the average %T produced in the wavelength ranges of interest. Thicknesses of this magnitude would need to be applied to the theoretical work to make a more practically achievable coating.

### 7 Overall Conclusions and Recommendations

### 7.1 Consideration of the aims and objectives of the project

It can be concluded that all of topics in the aims and objectives have been worked upon in this thesis. Obviously, the time scale dictates the amount of work that can be carried out on each topic, but it can be seen that all aims and objectives have been examined in a detail commensurate to the timescale of this project.

### 7.2 General Conclusions

Unfortunately, ideal ITO thicknesses that produce maximum %T requirements do not produce 20 Ohms/square. To achieve this sheet resistivity requires a thicker ITO layer. The modelling work carried out demonstrated that making the ITO layer thicker diminishes the average %T observed over the wavelength ranges considered. Application of additional coatings enhances %T. Luckily, this is not at the expense of sheet resistivity.

Cryolite has produced some very encouraging results in the theoretical studies for the wavelength ranges considered. This is not the end of the story however, merely the beginning. Will Cryolite produce the results that they theory suggests? Is the next obvious question that needs to be addressed. If this hurdle is met, the next issue is that Cryolite is fairly soft (Chemical Land, 2008). This means that to make Cryolite a viable solution, a protective coating system would need to be developed to make it usable in the application considered. It is acknowledged that MgF<sub>2</sub> produces only a slightly lower result than Cryolite and that MgF<sub>2</sub> is more durable, but it is this author's opinion that instead of avoiding Cryolite for this reason, work should be done to discover how to make it more usable, for example, a coating of a material like diamond like carbon may be considered to enhance durability but minimizing the loss in transmission observed. It is this author's opinion that if you always do what you always did, you will always get what you have always got and it is therefore important to explore new options.

### 7.3 Recommendations for future work

It can be seen from this thesis that the main aims and objectives have all been worked upon in this thesis. This is not the end however, merely a foundation on the road of the quest for knowledge of ITO coatings. The author would therefore recommend the following as next steps as they naturally progress from this work:

- Practical implementation of Cryolite coating is it as good as the theory suggests?
- Research to devise a protective coating system to make Cryolite usable in the application considered
- Further investigation into multi layer coatings for 2kÅ ITO that would produce thicknesses that are more realistically producible in practice.
- The author wishes to leave reader with the following question Can Cryolite be beaten? – This is the ultimate question, but what is the answer......

### 8 Appendices

# Appendix A Parameters used with Electron beam evaporation

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