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Remote plasma sputtering of indium tin oxide thin films for large area flexible electronics

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ABSTRACT

Indium tin oxide (ITO) thin films with a specific resistivity of $3.5\times10^{-4}\,\Omega$ cm and average visible light transmission (VLT) of 90% have been reactively sputtered onto A4 Polyethylene terephthalate (PET), glass and silicon substrates using a remote plasma sputtering system.

This system offers independent control of the plasma density and the target power enabling the effect of the plasma on ITO properties to be studied. Characterization of ITO on glass and silicon has shown that increasing the plasma density gives rise to a decrease in the specific resistivity and an increase in the optical band gap of the ITO films. Samples deposited at plasma powers of 1.5 kW, 2.0 kW and 2.5 kW and optimized oxygen flow rates exhibited specific resistivity values of $3.8\times10^{-4}\,\Omega$ cm, $3.7\times10^{-4}\,\Omega$ cm and $3.5\times10^{-4}\,\Omega$ cm and optical gaps of 3.48 eV, 3.51 eV and 3.78 eV respectively.

The increase in plasma density also influenced the crystalline texture and the VLT increased from 70 to 95%, indicating that more oxygen is being incorporated into the growing film. It has been shown that the remote plasma sputter technique can be used in an in-line process to produce uniform ITO coatings on PET with specific resistivities of between 3.5×10^{-4} and $4.5\times10^{-4}\,\Omega$ cm and optical transmission of greater than 85% over substrate widths of up to 30 cm.

1. Introduction

Indium tin oxide (ITO) is a commonly used transparent conducting oxide (TCO) with applications as a transparent electrode for flat panel displays [1], photovoltaic devices [2] and as an infrared mirror in energy saving windows [3]. ITO offers the best combination of electrical conductivity and visible light transmission with excellent environmental stability, reproducibility and surface morphology [1,3].

ITO is based on indium oxide (In_2O_3), a wide optical gap ($\approx$3.6 eV [4]) semiconductor material which, as a result of being n-type degenerate, is electrically conducting. Two explanations given in the literature for the source of the free carriers in indium oxide are (a) oxygen vacancies [5] and (b) a hydrogen doping mechanism [6–8]. In ITO, the free charge carrier (electron) concentration is further increased by substitutionally doping In^{3+} sites with Sn^{4+} [9]. The doping efficiency is related to the energy delivered to the growing film during deposition. To effectively dope the ITO, commercial films are deposited at high temperature [10,11].

The recent interest in flexible electronic devices has increased demand for processes offering low temperature deposition of high quality ITO films onto large area polymeric substrates [12]. The move to polymeric substrates is driven by their relatively low cost, mechanical flexibility, and light weight [2]. These properties not only make flexible devices attractive to the end customer, but also enable efficient mass manufacturing using 'roll to roll' processes [10]. However, due to the thermal sensitivity of polymers, sputter deposition of high quality ITO remains an area of intense research [11].

To meet the requirements of flexible displays, research has focused on methods of depositing materials at low temperature, ideally less than 78 °C (the glass transition temperature of PET) [10]. Wakeham et al. [11] deposited ITO with a specific resistivity of $3.8\times10^{-4}\,\Omega$ cm and average visible (400–750 nm) light transmission (VLT) greater than 90%, on to a range of flexible substrates (<15 mm diameter bend radius) using a remote plasma system. The high quality of the ITO was attributed to the increased energy at the substrate surface as a result of the high density plasma (10^{13} ions cm^{-3}), used in this sputtering process.

The remote plasma system benefits from independent plasma generation and target biasing, resulting in control of the flux of ions and their energies. The ability to generate a high flux of low energy ions has been shown to be beneficial for most thin film deposition processes [13]. This investigation extends the original work of Wakeham et al. [11] with the aim of developing a large area ITO process for use on polymeric substrates. After initial optimization of the deposition parameters, two sets of ITO films were deposited onto glass and silicon to explore the

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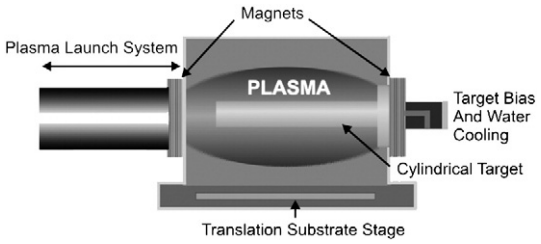

Fig. 1. A schematic diagram of the remote plasma system fitted with a 50 cm cylindrical target. The plasma is generated in the plasma launch system (PLS) and a magnetic field is used to form a plasma envelope around the target. In this diagram, the substrate travels in plane.

effects of varying the plasma power for films deposited under optimized and oxygen depleted conditions. Firstly, at a depleted oxygen flow rate of 18 sccm a set of films was deposited using plasma powers in the range of 2.0–3.5 kW. Then a second set of films was deposited at the optimum oxygen flow rate of 25 sccm employing plasma powers in the range of 1.5–2.5 kW. For comparison, a sample radiatively heated to 200 °C was deposited at this same optimum oxygen flow rate. Finally, the optimized process was used to deposit ITO onto A4 PET substrates to demonstrate the compatibility of the process with polymeric substrates.

2. Experimental technique

2.1. Thin film deposition

ITO films were reactively sputtered from a metallic 90:10 wt.% In:Sn (purity 99.99%) target at different oxygen flow rates and plasma powers using an in-line large area remote plasma system (details of the technology are discussed elsewhere [11,14,15]) onto glass and silicon substrates. A schematic diagram of the system is shown in Fig. 1.

The remote plasma sputtering process uses a magnetically confined, remotely generated argon plasma to provide a uniform distribution of ions at the target surface. The process is resistant to target poisoning and is very stable as a result. The in-line system is fitted with a load lock and translating substrate holder (positioned 30 cm below the target) enabling a high sample throughput.

Prior to deposition the substrates were cleaned using an EcoClear® cleaning solution and dried with dry nitrogen gas. The chamber was evacuated to a base pressure of 6×10^{-4} Pa before being filled with argon to a process pressure of 0.3 Pa. The substrates were treated with a low power plasma (no DC bias was applied to the target/substrate) to desorb volatile surface contaminants such as hydrocarbon species and adsorbed water. The target was prepared for the coating process by pre-sputtering in Ar and then in the $Ar+O_2$ gas mixture required for the subsequent coating stage of the process.

After the initial process optimization (described in Section 3.1), two sample sets were used to investigate the effects of the plasma power at different oxygen flow rates. The process parameters used to deposit these samples are given in Table 1. The samples have been numbered using a system incorporating the O_2 flow rate as an identifier for the two different sample sets (i.e. samples 18-1 to 18-4 for the samples deposited at 18 sccm and 25-1 to 25-4 for the samples deposited at 25 sccm O_2). All samples were deposited onto unheated substrates except for sample 25-4 which was radiatively heated to 200 °C during thin film deposition. The samples were not annealed after deposition.

2.2. Characterization

Glass and silicon were initially employed as substrates for characterization purposes. ITO films deposited onto glass were examined using an AvaSpec UV–Vis–NIR spectrophotometer (spectral range 300–1100 nm) and a Jandel Engineering Ltd four point probe for their optical transmittance and specific resistivity respectively. The film thickness was measured using a Taylor Hobson Talystep profilometer.

Structural characterization was performed on ITO films deposited onto silicon using a Panalytical Xpert Pro X-ray Diffractometer using a Cu Kα (1.5418 Å) source running at a voltage of 40 kV and current of 30 mA. The 2θ range scanned was 10–65° with a 2θ step size of 0.017°. The average grain sizes were determined from the (222) peak employing the De Keijser single line method [16,17], which involves a least squares fitting of the XRD peaks using a pseudo-Voigt function and then applying the Scherrer equation [21] to the Lorentzian component of the peak.

To perform carrier concentration and mobility measurements, the films were etched into a cloverleaf shape and analyzed using the Van Der Pauw method on an Accent HL5500 Hall system [18].

3. Results

3.1. Initial process setup — influence of oxygen on optical and electrical properties

Before studying the effects of plasma launch power on the ITO properties, samples were deposited at oxygen flow rates from 0 to 25 sccm with increments of 5 sccm between depositions. The specific resistivity and optical transmission were measured to allow the optimum oxygen flow rate to be determined. A constant 2.0 kW plasma launch power and 1.0 kW target power were used throughout this initial optimization process.

Fig. 2 shows that with increasing O_2 flow rate, the ITO approaches full stoichiometry, resulting in an increase in visible light transmission (VLT) and 2 orders of magnitude decrease in specific resistivity between 15 and 25 sccm. At 25 sccm the ITO coating exhibits VLT of 92% and specific resistivity of $3.8\times10^{-4}\,\Omega$ cm. These results show that the process is stable and capable of producing high quality ITO.

3.2. Characterization of ITO samples deposited at flow rates of 18 and 25 sccm

All the ITO films deposited had thicknesses in the range 320–450 nm (Table 1). The effects of plasma power were investigated on films deposited under oxygen depleted conditions (oxygen flow rate of 18 sccm). The optical transmission data for ITO deposited at plasma powers from 2.0 to 3.5 kW (Fig. 3) shows that raising the plasma launch power results in an increase in the optical transmission. From Fig. 2, it can be seen that a similar effect is observed as the oxygen flow rate is increased.

Table 1
The deposition parameters for the two sets of ITO coatings deposited at oxygen flow rates of 25 sccm (sample numbers 25-1 to 25-4) and 18 sccm (sample numbers 18-1 to 18-4).

Sample	25-1	25-2	25-3	25-4	18-1	18-2	18-3	18-4
Argon (sccm)	70	70	70	70	70	70	70	70
RF plasma power (kW)	1.5	2.0	2.5	2.0	2.0	2.5	3.0	3.5
Deposition temperature (°C)	Ambient	Ambient	Ambient	200	Ambient	Ambient	Ambient	Ambient
Ion current (A)	3.4	4.4	5.4	4.2	4.2	5.3	6.1	6.9
DC bias (V)	294	230	185	240	240	189	160	147
Oxygen (sccm)	25	25	25	25	18	18	18	18
Thickness (nm)	350	380	450	320	400	400	400	400