Low temperature remote plasma sputtering of indium tin oxide for flexible display applications

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Abstract:
Tin doped indium oxide (ITO) has been directly deposited onto a variety of flexible materials by a reactive sputtering technique that utilises a remotely generated, high density plasma. This technique, known as high target utilisation sputtering (HiTUS), allows for the high rate deposition of good quality ITO films onto polymeric materials with no substrate heating or post deposition annealing. Coatings with a resistivity of 3.8×10^{-4} Ωcm and an average visible transmission of greater than 90% have been deposited onto PEN and PET substrate materials at a deposition rate of 70 nm/min. The electrical and optical properties are retained when the coatings are flexed through a 1.0 cm bend radius, making them of interest for flexible display applications.

Introduction

ITO is widely used as a transparent, conducting electrode in liquid crystal displays, LED's, solar cells and electrochromic devices [1]. Numerous publications have addressed the challenge of achieving increasingly low resistivity and high optical transmission in these films [2–7]. This is an unusual combination of properties since good optical transmission requires a material with a band gap of greater than approximately 3.0 eV whilst high electrical conductivity necessitates a high number of free charge carriers with high mobility. With the creation of oxygen vacancies and by substitutionally doping the In^{3+} sites in In2O3 with Sn^{4+}, the free carrier density can be increased sufficiently to move the Fermi level into the conduction band whilst the band gap remains similar to that of the host (In2O3). Thus, careful control of the deposition parameters during film growth results in coatings that are both electrically conducting and transparent to visible light.

With the growth of the flexible displays market comes a requirement for high quality ITO to be deposited onto polymeric substrates under ambient conditions. It is well established that films exhibiting a more crystalline structure have lower resistivity than those with an amorphous structure [8,9]. Crystalline growth can be promoted by heating the substrates [8,10,11] to temperatures in excess of approximately 180 °C. For growth onto flexible substrates however, this is not feasible due to the temperature sensitive nature of the organic material. Hence the deposition of good quality ITO onto polymeric materials without heating the substrates either during or post deposition still represents a significant challenge [10,12–14].

In this paper we describe a technique for the high rate deposition of highly transparent, conductive ITO films that could be of use in flexible, solid state light sources such as electroluminescent displays.

Experimental

The details of the coating technology have been described elsewhere [15]. A schematic showing the sputtering system is shown in Fig. 1. ITO films have been deposited by reactively sputtering from a 90:10 wt.% In:Sn target. Mass flow controllers regulate the flow of argon and O2 gases into the deposition chamber via distribution rings located at the target and substrate respectively. The coating process utilises a remote, high density plasma (10^{13} ions cm^{-3}) that is generated in a side arm adjacent to the deposition chamber. Thisside armisreferredtoasthe plasma launch system (PLS). Electromagnets at the exit of the PLS enhance and steer the plasma onto the target resulting in a high density plasma over the full surface area of the target. Under these conditions the argon ions have insufficient energy (approximately 30 eV) to sputter. With the application of asufficient negative DC bias to the target, the argon ions are accelerated across the target sheath. This yields high rate, uniform erosion of the target surface and hence the name given to this technique is high target utilisation sputtering (HiTUS). The HiTUS system used for this work accommodates four, 10.2 cm diameter, water cooled targets allowing for deposition of multilayer structures without needing to break the vacuum.
The substrates are securely mounted to a rotating platform 18 cm above the target. Throughout this work no substrate heating has been used either during or post deposition.

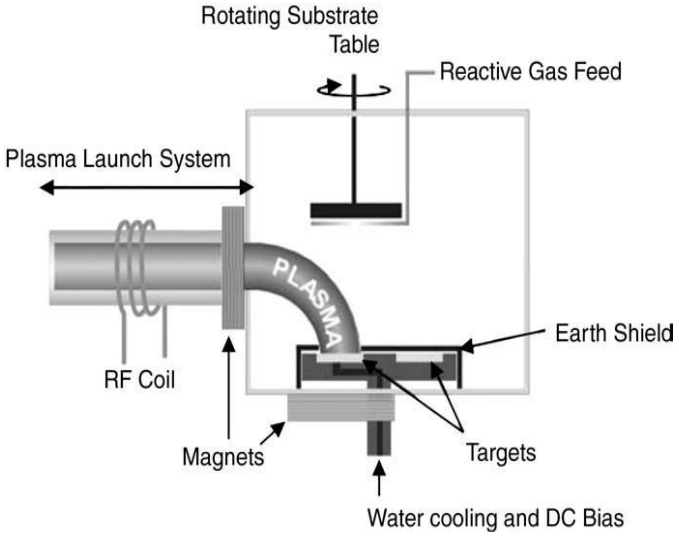

Fig.1.Schematic showing the HiTUS system. Electromagnets at the exit of the PLS enhance and steer the plasma onto the target.

Transmission measurements were performed using an Avaspec-2048 fibre optic spectrometer. All data has been taken with reference to the uncoated substrate and hence represents the transmission of the coating alone. Resistivity values were calculated from sheet resistance measurements using a four point probe and thickness measurements conducted using a Taylor Hobson Talystep profilometer.

Results

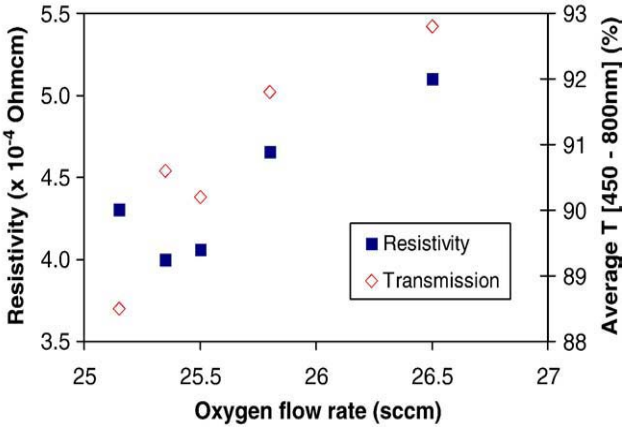

Fig. 2. The dependence of resistivity and transmission on oxygen flow rate.

All of the substrate materials used for this work underwent preconditioning in a diffuse, low intensity plasma prior to deposition. The substrates were not biased for this stage of the process and the impinging low energy Ar ions are seen to remove volatile species from the surface of the substrate resulting in excellent film adhesion. Following transmission measurements, no optical deterioration of the flexible substrates was noted after this pre treatment.

Influence of oxygen flow rate on optical and electrical properties of ITO Precise control over the partial pressure of oxygen during the deposition process is essential for high quality ITO film growth. High partial pressures of oxygen lead to fully stoichiometric films displaying excellent transparency but poor electrical conductivity due to the absence of oxygen vacancies and hence free charge carriers within the lattice. For ITO exhibiting good conductivity, it is necessary to reduce the flow rate of oxygen. Fig. 2 shows how the resistivity and average transmission (from 450 to 800 nm) vary for different flow rates of oxygen. It is clear that in order to obtain ITO with good electrical conductivity, the films should be slightly sub-stoichiometric [16].

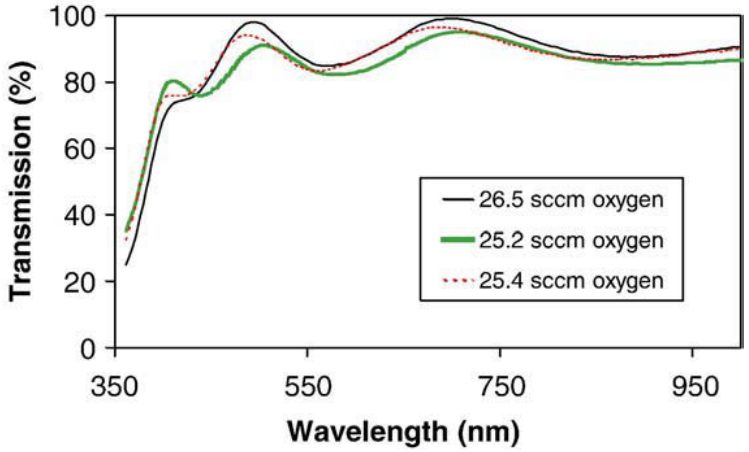

Fig.3.ITO transmission profiles for various flow rates of oxygen. The highest conductivity ITO occurs for films that are slightly under oxidized.

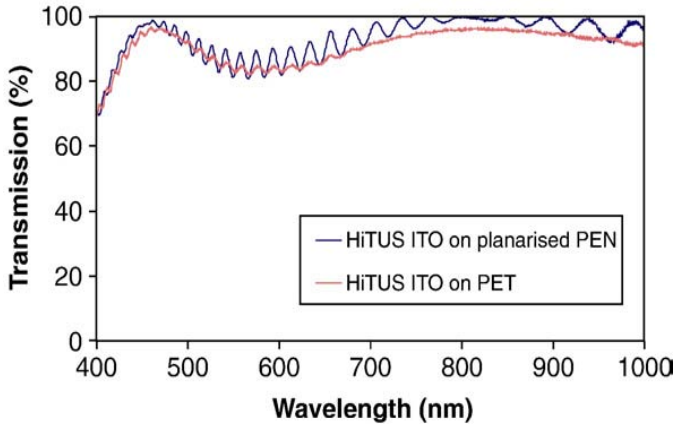

Fig. 4. Transmission profiles of ITO deposited onto PET and planarised PEN flexible substrates. The high frequency ripples are due to an adhesion layer that the manufacturers put in the reverse side of the substrate.

Fig. 3 shows the full transmission curves for three of the films shown in Fig. 2. The thickness of these coatings varies from about 330 to 350 nm and the deposition rate was 70 nm/min. Fig. 4 shows the transmission profile of approximately 210 nm of ITO deposited onto planarised polyethylene naphthalate (PEN) and polyethylene terephthalate (PET) flexible substrates supplied by Dupont Teijin Films™. The high frequency fringes are due to the adhesion layer used by the manufacturer on the reverse un-coated side of the substrate. The thickness of the PEN was 125 μm and that of the PET was 188 μm. Both films measured sheet resistances of 18 Ω/□ immediately after deposition corresponding to a resistivity of 3.8×10^{-4} Ωcm. After a period of 6 months, the samples were flexed through a bend radius of approximately 1.0 cm and re-measured. Sheet resistances were in the range 18 to 19 Ω/□.Further tests involved rolling a sample into a 1.5 cm bend radius and securing it in this position for a period of 1 week. Again, no notable change in sheet resistance was measured on unrolling the film demonstrating the potential of these coatings for use in flexible display applications. Further analysis of HiTUS deposited ITO on flexible substrates is to be performed in order to quantify the degree to

which these films can be flexed without showing degradation of electrical or optical properties.

ITO films with thicknesses of 425 nm were also deposited onto PEN and PET substrates with a sheet resistance of 9.0 Ω/□. The average transmission of these coatings was approximately 90% in the visible region.

Influence of process pressure on optical and electrical properties of ITO

Thequality of theITO films was found to be strongly related to the process pressure. This was controlled by variation of the argon flow rate. Initial experiments were performed for an argon flow rate of 50 sccm whichcorrespondedto approximately 3.2×10^{-3} mbar as this was seen to optimise the ion current to the target. Fig. 5 shows the results of a series of ITO films that were optimised for high transmission and low resistivity by varying the oxygen flow rate at a range of process pressures. The optimum films were taken to be those for which the resistivity was as low as possible, with average visible transmission of greater than approximately 88% (See for example Fig. 2).

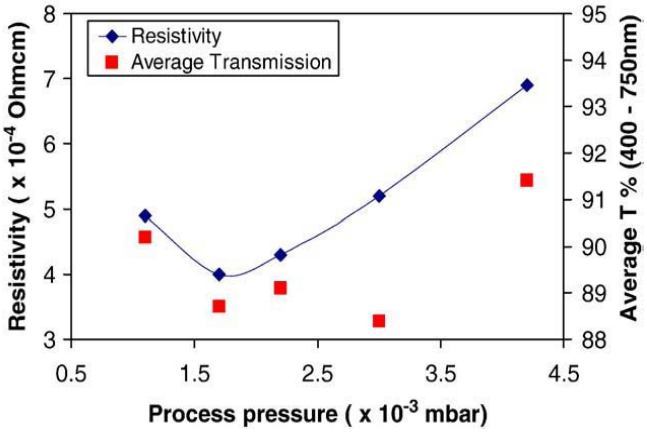

Fig.5.The effect of process pressure on the optical and electricalproperties of ITO.

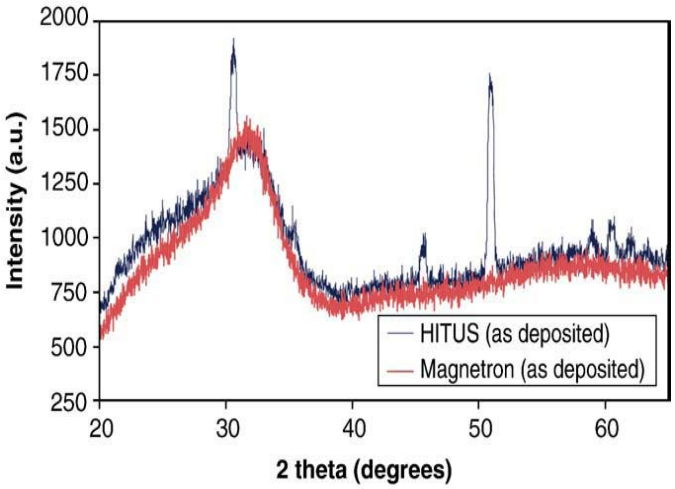

Fig.6.The effect of process pressure on the resistivity and deposition rate of ITO.

The trend in the resistivity shown in Figs. 5 and 6 can be explained in terms of the energies of

the atoms and molecules arriving at the substrate. For process pressures lower than approximately 1.6×10^{-3} mbar, particle bombardment of the growing film is high enough to cause damage and re sputtering of certain crystallographic directions. The detrimental effect of excessive ion energy on the conductivity of ITO filmsisdescribed by Ishibashi et al. [17]. As the pressure increases, we enter a regime where the energy at the substrate surface is optimum for the promotion of crystalline film growth and hence the resistivities of the films decrease. Beyond this, it is speculated that scattering effects result in insufficient energy for crystalline growth and a structure with smaller grains is adopted with subsequent increases in grain boundary scattering and reduction of electrical conductivity. Fig. 6 shows the deposition rate as a function of process pressure. The trend in resistivity as a function of process pressure as described in Fig. 5 is also included for reference. This confirms that re-sputtering of the film is likely to occur for lower process pressures since for constant target power the deposition rate is seen to decrease. Similarly, an increase in scattering of the sputter yield at higher pressures also results in a reduction of the deposition rate. XRD analysis of these coatings could offer further evidence to support this argument since Kamei et al. [18] found that re-sputtering of the (440) plane orientation occurs preferentially over that of the (222) and (400) planes.

Discussion

It is well established that crystalline ITO films have lower resistivity than amorphous ITO films [19]. Numerous studies have shown that by increasing the energy at the substrate surface, thin films of ITO can be engineered to grow with a crystalline structure [10,20,21]. In the absence of substrate heating this must come from energetic particle bombardment of the growing film which ultimately is controlled by the energy within the plasma. With the high plasma densities [15] attainable using HiTUS (10^{13} ions cm^{-3}) it is therefore possible to impart significant energy to the growing film without the need for substrate heating. Whilst similar plasma densities can be achieved using magnetron sputtering this is a local effect immediately adjacent to the target. With the HiTUS system, a uniform plasma over a significantly larger area exists. Some analogy can perhaps be made with ion beam assisted deposition where a separate ion source directs a beam of ions at the film during growth [22]. Fig. 7 shows XRD results for as deposited HiTUS ITO compared with the results of magnetron sputtering [23]. Crystalline growth usually associated with elevated substrate temperatures is clearly visible despite the absence of substrate heating. The broad background peak at approximately 30° is due to the glass substrate.

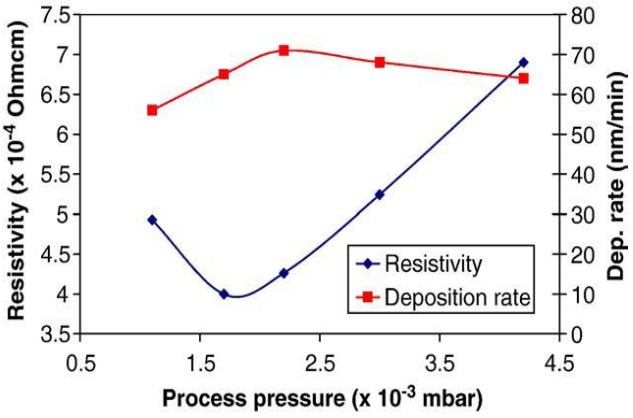

Fig.7.XRD results indicating that ITO films deposited using HiTUS show some crystallographic structure even at low substrate temperatures. A similar ITO film deposited using magnetron sputtering is included for comparison.

A distinguishing advantage of HiTUS over other sputtering techniques is that the plasma density is independent of the target power. This allows for high (or slow, if required) deposition

rates whilst maintaining close control over the plasma intensity. ITO deposition rates of up to 70 nm/min have been achieved using HiTUS. At sufficiently high pressure, the large separation of the target and substrates (18 cm) does not result in damage to film growth [17] since the energies of the impinging atoms and molecules are sufficiently reduced by the time they reach the substrate surface.

Due to declining indium supplies and hence its ever increasing cost, other materials are now being considered as possible TCO alternatives to ITO [24,25]. Particular interest is in doping of ZnO with either Ga (GZO) [26,27] or Al (AZO) [28]. T. Minami gives an excellent review of the current status of possible TCO alternatives to ITO [29]. For applications that require a TCO film thicker than 100 nm and allow a processing temperature of approximately 200 °C or higher, AZO and GZO could well offer a suitable alternative to ITO. However, this high substrate temperature would clearly not be suitable for applications on PET or PEN flexible substrate materials.

Conclusions

HiTUS technology has been used to deposit ITO films onto glass, PEN and PET substrate materials with a resistivity of 3.8×10^{-4} Ωcm and an average visible transmission of approximately 90%. XRD results have shown that our ITO films potentially grow with a crystalline structure without any external substrate heating and that deposition rates of up to 70 nm/min can be achieved without damage to film growth. Transmission and resistivity measurements 6 months after deposition show that the films are highly stable, retaining their optical
and electrical properties even after flexing. All of the attributes discussed here make ITO deposited by HiTUS ideal for applications in flexible electronics.

Acknowledgments

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