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Pulsed laser deposition of indium tin oxide films on flexible polyethylene naphthalate display substrates at room temperature

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ABSTRACT

Pulsed laser deposition was used to deposit high-quality indium tin oxide (ITO) thin solid films on polyethylene napthalate (PEN) flexible display substrates. The electrical, optical, microstructural, mechanical and adhesive properties of the functional thin layer were investigated as a function of a narrow range of background oxygen gas pressure at room temperature, which is the most desirable thermal condition for growing transparent conducting oxides on flexible display polymer substrates. ITO films (240 ± 35 nm thick) deposited on PEN at room temperature in the range of 0.33 to 2.66 Pa background oxygen pressure are observed to exhibit low electrical resistivity (~10^{-4} Ω cm) and high optical transmission (~90%). Electromechanical uniaxial tensile testing, of the hybrid thin structures, results in crack onset nominal strains of around 2%. The ITO surface adhesion reaches a maximum at 1.33 Pa deposition pressure.

1. Introduction

Indium tin oxide (ITO) is the dominant transparent conducting oxide, used as a transparent electrode component, in the majority of display and optoelectronic applications [1,2]. There is an increased interest, of both fundamental and practical importance, in the deposition, and characterization, of ITO on thermally sensitive, flexible organic substrates at low temperatures [3].

Available flexible display substrates for depositing ITO at low temperatures (<100 °C) include polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) biaxially oriented thermoplastic semi-crystalline polyester films (125 µm thick). Other flexible substrate candidate materials include polycarbonate (PC), polyethersulfone and polyamide [4].

ITO deposition studies have been conducted using mostly PET and PC substrates including sputtering and pulsed laser deposition (PLD) techniques. As far as sputtering is concerned, Minami et al. [5] reported the preparation of very thin ITO layers on PET and glass substrates by direct current (DC) magnetron sputtering. The oxide films that were prepared at 60 °C were initially amorphous and became crystalline when annealed at a temperature of 150 °C for 25 h in air. The resistivity of the ITO on PET films is dependent on the SnO_2 content and is of the order of 10^{-3} Ω cm. An average transmittance above 97% in the visible wavelength range was measured. Shin et al. [6] investigated the properties of DC magnetron sputtered ITO on polymeric substrates at room temperature. The polymer substrates were PC, acrylic, and PET. Glass substrates were also used. The lowest resistivity value, for 0.133 Pa of oxygen pressure, is 9.3×10^{-4} Ω cm on the PC substrate. The optical transmittance at visible wavelength, 550 nm, is 85%. Kim [7] prepared ITO thin films on PET using DC magnetron sputtering, using a negative metal ion source, at low substrate temperature. By varying the partial pressure he found that at low pressures the resistivity reached a value as low as 6.2×10^{-4} Ω cm and optical transmittance of 87% at a wavelength of 550 nm. Atomic force microscopy (AFM) investigation of the ITO surfaces revealed a roughness range of values between 1.1 and 2.8 nm.

Considering PLD, Kim et al. [8] investigated the effect of substrate deposition temperature and oxygen partial pressure on the structural, electrical and optical properties of transparent conducting indium tin oxide thin films grown by PLD on flexible PET substrates. They concluded that ITO films, 200 nm thick, deposited on PET at room temperature and oxygen partial pressure of 6 Pa, exhibit low electrical resistivity, ~7×10^{-4} Ω cm, and high optical transmittance, ~87%, in the visible, 400–700 nm, range. Izumi et al. [9] have studied the electrical properties of crystalline ITO films prepared at room temperature by *in situ* laser irradiation PLD on PC substrates. They found that the PC substrates were coloured by *in situ* laser irradiation when the ITO layers were prepared on the substrates directly and therefore they pre-deposited a layer of Al_2O_3 and a layer of CeO_2 in order to prevent the colouring and achieve a low resistivity.

The desire for flexible substrates that will replace mechanically brittle substrates such as glass has to be considered in order to utilize

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roll-to-roll one-step processing of flexible display components [10]. During roll-to-roll manufacturing and in service conditions, the mechanical integrity of the ITO layer is an important parameter to consider. Cairns et al. [11] were the first to report the dependence of electrical resistance on applied uniaxial tensile strain for ITO deposited on polymer flexible display substrates. The increase in electrical resistance is due to cracking of the ITO layer with increasing strain. Cairns et al. [12] also reviewed various mechanical reliability issues regarding sputter-coated ITO polyester substrates, which are used in flexible display and touch-screen applications. They concluded that the mechanical properties of the ITO film are dominated by the properties of the substrate and that the deformation of the substrate is mapped by the crack patterns in the ITO.

PEN is attracting increased attention as a substrate material due to the fact that its properties, as a base flexible display substrate, are superior to PET [13]. PEN has a higher glass transition temperature, a higher hardness and higher degree of crystallinity than PET. These properties are attractive for fabricating flexible devices because of potential improvements in durability and the potential to use higher processing temperatures. Recently, Han et al. [14] reported the deposition of ITO films on PEN substrates by radio-frequency (RF) sputtering.

PLD is ideal for investigating the behaviour of thin oxide films on polymer substrates because it can yield high-quality ceramic films and allows for a fine degree of process control on composition and thickness. Experimental results on films deposited by PLD are broadly applicable to other physical vapour deposition techniques such as magnetron sputtering and RF sputtering.

In this work we start by comparing the mechanical properties of uncoated PET and PEN polyester substrates. We then investigate the electrical, optical, microstructural, mechanical and adhesive properties of ITO layers deposited on PEN flexible display substrates at room temperature by PLD as a function of a narrow range of background oxygen gas pressure.

2. Experimental details

PEN biaxially oriented substrates were used. The thickness of all substrates is equal to 0.125 mm. Uniaxial tensile testing of PET and PEN bare substrates was performed using an Instron (model 5520) mechanical testing machine. Knoop hardness measurements, using a commercial nanoindenter (Micromaterials Nanotest platform), were conducted in order to compare the bare polyester substrates.

ITO films were prepared using a KrF excimer laser (Lambda Physik). The laser was operated at 10 Hz frequency and the energy density of the laser beam at the target surface was 3 J cm^{-1}. For the pre-ablation of the target 500 shots were fired and for the actual deposition 4000 shots were fired.

The PEN substrates were prepared by cutting a circular section, of 0.8 cm radius, from a biaxially oriented sheet of PEN. The substrates were cleaned, prior to deposition, for 15 min using acetone and 15 min using ethanol and then they were rinsed with distilled water and dried using compressed air. The cleaned substrate was attached to the unheated substrate holder using blue tack adhesive, which could be easily removed after deposition at room temperature.

The circular ceramic target was 90% In_2O_3 and 10% SnO_2 by weight (99.99% purity), with diameter 25 mm and thickness 5 mm. The vacuum created in the chamber was of the order of 1.33×10^{-7} Pa. The deposition pressures, PO_2, used were in the range of 0.33–2.66 Pa.

The film thickness, t_f, was measured by performing weight measurements before and after deposition and by using the density of the ceramic target, which is 7.1 g cm^{-2}. Typical film thicknesses were 240 ± 35 nm with no significant change or trend with oxygen background pressure. Also, film cross-sections were measured using scanning electron microscopy (SEM Jeol 7000F). Fig. 1 shows an ITO film cross-section observed using SEM. The operating voltage was equal to 10 kV. The weighing method and the SEM cross-sectional measurements were in agreement and within the resolution of the measurement technique.

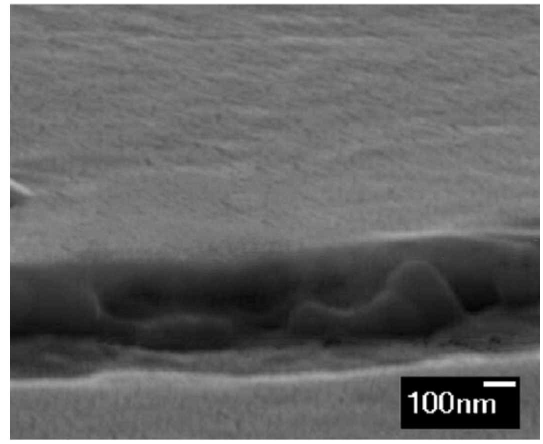

Fig. 1. SEM cross-sectional view of an ITO film deposited by PLD in the range of 0.33 to 2.66 Pa background O_2 pressure.

The average electrical resistance, *R*, of the films was measured, in eight different but symmetrical places on each sample, using a four-probe system with probe spacing of 1 mm.

The microstructure of ITO coatings was investigated using a Siemens X-ray diffractometer (Hilton Brookes). The θ–2θ technique was used (scanning range: 2θ from 20° to 70°) with Cu–Kα as the X-ray source. The operating step size was 0.05 and the counting time was 3 s. Measurements on bare and ITO-coated PEN samples were conducted and a comparison of the respective diffraction intensities was made. The sample plane and the sample holder plane must be parallel.

The surface of the films was studied using an AFM (Digital Instruments Dimension 3100) in contact-mode. The radius of the AFM tip was equal to 50 nm and the stiffness (*K*) of the silicon nitride cantilever was equal to 0.12 N/m. Optical transmittance measurements were conducted using a 638 nm laser diode and photocell system and the average of five measurements for each film are considered in this work.

The tensile electromechanical test is based on slight modifications of a commercial, mechanical test machine (Instron model 5520). These minor modifications were needed in order to incorporate *in situ* electrical resistance measurement capabilities for testing conductive coatings such as ITO on PEN composite films. First of all a thin PTFE sheet was placed between the machine compression base and the lower grip in order to create a closed electrical circuit between the two grips. Then, two copper wires were attached to each grip and connected to a multi-meter that monitors ITO electrical resistance changes. In order to ensure that the ITO coating will not be damaged when clamped, flat plate grips were used. The electrical resistance data, measured in Ω, was collected by a computer and can be combined with stress–strain data, in order to describe the electromechanical performance of flexible display components.

Also, ITO-coated samples were wrapped around polyvinyl chloride mandrels of several diameters, ITO coating in tension, and the film surfaces were observed *in situ* using an optical microscope (Leitz Laborlux 12HL Inspection Microscope).

After electromechanical testing, the resulting ITO surfaces were observed *ex situ* using SEM (Jeol 7000F). The SEM operating voltage was equal to 10 kV. The adhesive surface force properties of the produced films were also measured using contact-mode AFM and a mean value of six measurements at different symmetrical places, for each sample, is presented.

3. Results and discussion

We tested uncoated PET and PEN specimens in tension and found that the Young's modulus of PEN is 3.3 ± 0.4 GPa whereas that for PET