Highly conductive and transparent aluminum-doped zinc oxide thin films deposited on polyethylene terephthalate substrates by pulsed laser deposition

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ABSTRACT

Highly transparent and conductive aluminum-doped zinc oxide thin films were deposited on low-cost flexible polyethylene terephthalate substrates at room temperature using pulsed laser deposition and the effects of oxygen pressure and film thickness on film properties were investigated. It was found that grain sizes play a greater role only at smaller film thicknesses in affecting carrier mobility. Resistivity changes at larger film thickness can be caused by near surface/interface depletion that affected both mobility and carrier concentration. The inherent film transparency did not change and any reduction in the film transmittance is likely related to a thickness dependent attenuation effect. This means that different transparent conducting oxides should each possess an optimum film thickness, whereby optimized zinc oxide is typically about 100 nm. A low resistivity of ~6.6×10^{-4} Ω cm with a high normalized transparency index of >0.9 for a 110 ± 10 nm thick room-temperature deposited film was obtained, representing one of the best results obtained to date.

1. Introduction

Transparent conducting oxides (TCOs) deposited on polymeric substrates are subjects of extensive research efforts to enable the development of electronic devices for applications in photovoltaics, displays, transistors and electrochromics on flexible substrates [1–5]. The TCOs generally have to exhibit a resistivity not exceeding the order of 10^{-3} Ω cm and have an average transmittance of above 80% in the visible region to be considered suitable for application as a transparent electrode [6]. Indium tin oxide (ITO) is currently the most commonly used TCO in many applications of electronic and optical devices [7–11]. However, ITO is not only considered to be toxic and expensive, it typically requires a heat treatment of over 300 °C to achieve the desired high transparency and low resistivity, making it difficult for applications using polymer based materials [12–14]. Therefore, there is an urgent need to seek alternative materials that can effectively substitute the use of ITO at lower process temperature to advance the development of electronic or optical devices on plastic substrates [15–20]. A lower process temperature also allows for potential usage of TCOs as top electrode in polymer based devices without possible device degradation due to heat treatment [1,21]. Zinc oxide (ZnO), with a wide direct band gap of 3.34 eV, is one potential candidate that is non-toxic,

abundant and inexpensive. ZnO exhibits high transparency in the visible region and can possibly be doped with group III elements such as aluminum or gallium to improve its electrical properties [22–24].

The development of applications on polymer substrates has many advantages. A typical glass substrate suffers from being brittle and excessively heavy. Development of transparent electrodes on flexible plastic substrates provides realistic solutions for a flexible, lightweight, robust and cost-effective starting substrate that can be of great importance to portable, large area or niche devices [25–27].

In the design of a transparent electrode on polymer substrates using thin film technology, the film thickness of the TCO is of great importance since it is directly related to the strain that it can withstand. Hence, a thinner TCO results in greater flexibility since the critical radius of a thin film is proportional to the film thickness [28]. Unfortunately, it is generally reported that thinner TCOs result in films of lower conductivity [29]. Thus far, it is a challenge to produce thin oxide layers with suitably low resistivity. For example, the lowest resistivity reported for gallium-doped zinc oxide deposited on polyethylene terephthalate (PET) substrates at room temperature is ~7.8×10^{-4} Ω cm but this is for a relatively thick 800 nm film [18]. However, for TCO in the range of about 100 nm, the lowest resistivity is reported by Gadre and Alford with a value of ~4×10^{-3} Ω cm for a 85 nm thick indium gallium zinc oxide film on polyethylene naphthalate substrates, and this is only achievable after a 150 °C post-deposition anneal [30]. The nature of the dependence of resistivity, or even transparency, on film thickness

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is not widely reported and it is therefore important to conduct more investigations to understand the dependency. In this study, we deposited aluminum doped zinc oxide (AZO) thin films at room temperature on PET substrates using pulsed laser deposition (PLD) without any post-deposition annealing. We first examine the crystallographic structure, optical and electrical properties of these films as a function of oxygen pressure to optimize the deposited film properties. At the optimized growth condition, we varied the thickness of the deposited AZO film on PET substrates and discuss the effects on resistivity and transparency.

2. Experimental procedures

AZO thin films were deposited on 125 μm thick polymeric PET substrates using the PLD technique with a ZnO:Al (1.5 wt.% Al$_2$O$_3$) ceramic target of purity 99.999%. The PLD uses a KrF excimer laser (wavelength of 248 nm and 25 ns pulse width) operating at a repetition rate of 20 Hz with a total energy of 300 mJ. The deposition chamber was evacuated to a base pressure of 1.3×10^{-6} Pa. The target–substrate distance was maintained at 6 cm during the deposition while the oxygen pressure was varied from 2.6×10^{-3} to 1.3 Pa. The entire deposition process was performed at room temperature and typical thickness of the films was about 110 ± 10 nm. In the second part of the experiments, at a chosen oxygen pressure (which gives optimum results), we repeated the deposition process for different duration to achieve different film thicknesses. All the film thicknesses were measured using the Veeco multi-mode atomic force microscope (AFM) nanoscope IV Tapping Mode. Optical measurements were performed using a Shimadzu double beam UV-3600 UV–vis–NIR spectrophotometer and electrical characterization was carried out using the HL5500PC Hall effect measurement system via the Van der Pauw method at room temperature using indium as contacts. Crystallinity of the films was measured using an X-ray-diffraction (XRD) system, equipped with Cu Kα radiation with graphite monochromator and a HI-STAR General Area Detector which is configured in horizontal theta/2theta Bragg–Brentano geometry.

3. Results and discussion

3.1. Effect of oxygen pressure: Optical and electrical properties

A summary of the optical properties, together with the measured resistivity of AZO films deposited at room temperature, is shown in Fig. 1. The plot shows the measured resistivity and normalized transparency indices at different oxygen pressures. The resistivities of the films at the respective conditions are obtained from Hall effect measurements. The normalized transparency indices represent the fraction of transmission at various indicated spectral ranges after accounting for variations in
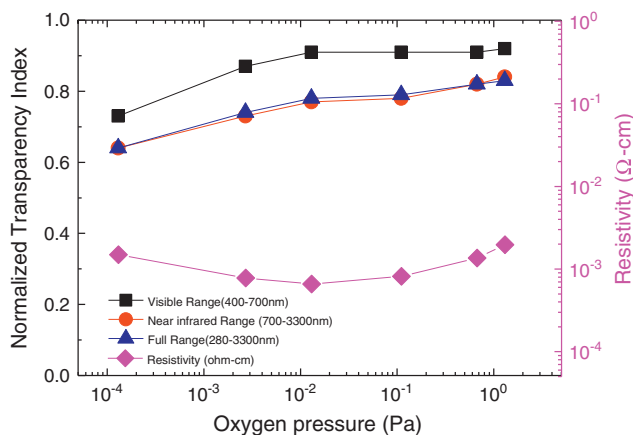
film thickness. From our previous publication [31], the normalized index T$_x$ is shown in Eq. (1) as follows:

$$T_x = \frac{\sum_{n=280}^{1700} \Gamma_n \times e^{-\alpha_n(x-d)} \times I_n}{\sum_{n=280}^{1700} I_n} \tag{1}$$

where Γ_n (%) is the measured transmittance at the wavelength n (nm), I_n is the intensity of the spectrum with a unit of W m^{-2} nm^{-1}, x is an arbitrary choice of normalization film thickness suitable for the specific application (e.g. $x = 110$ nm), d is the actual thickness of the film in the transmittance measurement and α_n is the absorption coefficient at the particular wavelength. In this work, although our thicknesses do not vary greatly, we have used Eq. (1) to give a more accurate transparency index. We use a normalization thickness of 110 nm and obtain the absorption coefficient from the transmittance at different wavelengths [31]. Thickness normalization in this aspect is critical to understand the optical properties of the film itself. Different thicknesses give variations in transmittance and this should be corrected in order to understand the film properties at each deposition condition. The use of the normalized index can also be useful for applications in different devices and separation into different wavelength regions can help in the understanding of film properties [31]. Fig. 1 shows that for the visible wavelength range, an oxygen pressure of above 1.3×10^{-3} Pa will be sufficient to result in a film with transmittance of greater than 80%, with the transmittance saturating at higher oxygen pressure. The overall normalized transparency appears to gradually increase with oxygen pressure, with a high transmittance of ~90% at oxygen pressures of 1×10^{-2} Pa or larger. The corresponding resistivity, however, shows optimum values in the mid-oxygen pressure regime, with higher resistivities measured at both lower and higher oxygen pressures.

The XRD spectra for all the AZO films grown on PET substrates obtained under various oxygen pressures show a peak at 34.4°, which is consistent with the ZnO (002) diffraction peak (Fig. 2(a)). This shows that all the films have a polycrystalline hexagonal wurtzite structure that is highly oriented along the c-axis [32,33]. Using Scherrer's formula, we note that there are slight variations in the calculated grain sizes that range from (14.6–17.6) ± 1 nm for the various oxygen pressures. A plot of the mobility and overall resistivity for the different calculated grain sizes in Fig. 2(b) showed no clear trends. This shows that such small changes in grain sizes may not be significant in affecting the transport properties, and other scattering mechanism (besides grain size) is affecting the mobility.

The electrical property of the AZO film is shown in Fig. 3 where the mobility, carrier concentration and resistivity are plotted against the different oxygen pressures during deposition. The improvement in resistivity for lower oxygen partial pressure can be observed to be due to the significant increase in carrier mobility. This can be due to a reduction in deep-level defects that can improve the carrier mobility by reducing scattering. This agrees with the concomitant improvements in transparency since a reduction of these defects will improve transmittance in the visible range and this is similarly observed in Fig. 1. This also means that, while defect scattering is dominant, grain boundary scattering may play a less significant role as was discussed. The increase in resistivity at higher oxygen partial pressures shown in Fig. 3 can be attributed to both a decrease in carrier concentration and in mobility. The large decrease in carrier concentration should increase the infrared transmittance and our transparency index in the infrared range, shown in Fig. 1, agrees with this interpretation. The smaller increase, or similar overall transparency, can be explained by the accompanying reduction of transmittance in the ultra-violet region by variation of the band gap through the Burstein–Moss effect. This competing factor can be shown by examination of our measured band gap variations. The band gap (E_g) of the AZO film on PET substrate is found by computing the

Fig. 1. Normalized transparency index of AZO films at different indicated wavelength ranges as a function of oxygen pressure during deposition at room temperature. The corresponding measured resistivities of the films are also included.