Transparent, conductive ZnO:Al thin film deposited on polymer substrates by RF magnetron sputtering


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Abstract

In this paper, we present the optical, electrical, structural and mechanical properties exhibited by aluminum-doped zinc oxide (ZnO:Al) thin films produced by RF magnetron sputtering on polymeric substrates (polyethylene terephthalate, PET; Mylar type D from Dupont) with a standard thickness of 100 μm. The influence of the uniaxial tensile strain on the electrical resistance of these films was evaluated in situ for the first time during tensile elongation. In addition, the role of the thickness on the mechanical behavior of the films was also evaluated. The preliminary results reveal that the increase in electrical resistance is related to the number of cracks, as well as the crack width, which also depends on the film thickness. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Transparent, conducting oxides have important uses for a variety of applications, including flat panel displays, touch screens, IR reflectors, solar cells and optical sensors [1]. Nowadays, there is great interest in replacing glass with polymer substrates, particularly in flat-panel display technology [2], where low volume, light weight and robustness are relevant. In flexible applications, there is a trade-off between using thick layers to reduce the resistivity and thin layers that can withstand greater strain in the substrate. In addition, the added flexibility of polymeric substrates opens new application fields that utilize curved surfaces, for example large-area, flexible position-sensitive detectors [3].

The transparent, conductive oxide used in this study was ZnO:Al, deposited at room temperature in a RF magnetron sputtering system. The substrate was polyester with a standard thickness of 100 μm. In order to correlate the influence of mechanical strain on the electrical properties, we measured electrical resistance as a function of the mechanical strain using special electrical probes attached to a miniature tensile-testing machine.

2. Experimental details

The polymeric substrate used in this work was polyethylene terephthalate (PET) with a standard thickness of 100 μm, from Dupont® (Mylar type D). Before depositing the ZnO thin films, the substrates were ultrasonically cleaned in a detergent bath, followed by isopropyl alcohol and dried in nitrogen. The substrates, with dimensions of 10×10 cm², were placed inside the chamber and then evacuated to a base pressure of 7×10⁻⁷ mbar. The ZnO:Al thin films were produced by RF magnetron sputtering from a commercially available, sintered ceramic ZnO:Al₂O₃ (98:2) target with 99.99% purity (Cerac) of 50 mm in diameter, placed at a distance of 20 cm from the substrate.

The flow rate of the sputtering gas (argon) was controlled by a mass flow controller to 10 sccm and the deposition pressure was fixed to 1.7×10⁻² mbar (optimized deposition conditions for this chamber in order to guarantee uniformity over 10×10 cm²; see [4]). In order to correlate the effect of the thickness on the film...
properties, a set of three samples of 100, 120 and 140 nm was produced.

The growth morphology was analyzed using a field-effect Hitachi S-1400 scanning electron microscope.

Optical transmittance measurements were performed with a Shimadzu UV/Vis 3100 PC double-beam spectrophotometer in the wavelength range from 300 to 1500 nm.

The thickness of the films was measured using a Sloan Dektak 3D profilometer. The resistivity, carrier density and Hall mobility were obtained from four-point probe (square configuration, 5-mm side with Cr contacts deposited by thermal evaporation assisted by an electron gun) measurements using a Biorad HL5500 system with a permanent magnet of 5 kG.

The electrical resistance as a function of uniaxial strain was measured in situ using special electrical probes. These measurements were performed with a tensile testing machine (Rheometric Scientific Minimat, Firmware 3.1), working at a constant speed of 2.5 mm/min at room temperature. Since the films were deposited on polymeric substrates, the samples were cut with a gauge length of 50 mm and a gauge width of 10 mm. For crack development during straining, the tensile tester was mounted on an Olympus BH-2 optical microscope stage, and the images were recorded via a digital Olympus Camedia C-2020 camera connected to the microscope.

3. Results and discussion

The films prepared were physically stable and presented very good adherence to the polymer substrates.
No cracking or peel-off of the films was observed after deposition. Fig. 1 shows a set of three SEM micrographs of ZnO:Al of different thickness. As the thickness increases from 100 (Fig. 1a) to 140 nm (Fig. 1c), we observe an increase in the grain size. In addition, for the thicker film, the surface of the polymer is completely covered by the ZnO:Al, since the induced roughness of the pre-treated surface of the polymer disappears [5].

Fig. 2 shows the transmittance vs. wavelength in the visible and near-infrared spectrum for three samples deposited on PET substrates. For comparison purposes, the spectrum of the PET substrate (solid line) is also presented. The average transmittance is 85% for all the films in the visible part of the spectrum.

From the transmittance data, it is possible to infer the optical gaps of the films by plotting $\alpha h^2$ vs. $h$ (where $\alpha$ is the absorption coefficient, and $h$ the photon energy) and by extrapolating the straight-line portion of this plot to the energy axis. These plots yield an optical gap of approximately 3.05 eV. The values obtained are not consistent with the optical gap of ZnO:Al thin films (the typical optical gap is 3.2 eV for films deposited on glass substrates [6,7]). This means that these values are due to the optical properties of the polymer substrate, which is partly absorbing in the high-energy range of the visible spectrum. Even with this disadvantage, but with its good thermal, electrical, mechanical and optical properties, the PET substrate is a powerful candidate for ZnO:Al transparent, conducting film deposition. A similar effect (absorption in the high-energy part of the visible spectrum) was reported in [8].

Fig. 3 shows the resistivity, Hall mobility and carrier density as a function of film thickness. In the thickness range studied (100–140 nm), the resistivity decreases with increasing thickness, accompanied by an increase in the Hall mobility, while the carrier density decreases. These results are consistent with the SEM photographs, since the highest value for the Hall mobility was obtained for the films with greater roughness.

The changes in the electrical resistance as a function of the uniaxial tensile elongation are presented in Fig. 4 for the three ZnO:Al films. For all samples, the resistance sharply increases at a certain threshold strain, which depends on film thickness. The resistance of the thinner ZnO:Al film increases at the highest threshold strain, while the resistance of the thick ZnO:Al film increases for the lowest strain. This is consistent with similar studies performed on silicon oxide deposited on PET substrates [9]. The increase in the resistance is due to the cracking of ZnO:Al with increasing strain. It was observed under the optical microscope during tensile elongation that the first cracks appeared for a nominal strain of 2% for the thinner sample. The cracks traverse the full width of the section, but the resistance is still finite. This suggests that something in the crack is responsible for the conduction [10]. Near a strain of 8%, a second type of crack (parallel to the straining direction and perpendicular to the first cracks) appears, due to lateral contraction of the sample. The fragments at the end of these cracks tend to overlap and enhance debonding. For values higher than 8% of nominal strain, the density of the first type of crack remains constant, while the density of the second cracks increases up to 10% nominal strain. For higher values, debonding within the secondary cracks is initiated and a deviation from linearity is observed. These results are consistent with the variation observed in the electrical resistance.

These observations are consistent with the SEM photographs presented in Fig. 5. The morphology of ZnO:Al of different thickness reveals that the thinner films exhibit the smallest cracks in width, at approximately 130 nm, while for the thickest film, the width of the crack is approximately 670 nm. It is also possible to observe that at this stage, the primary cracks parallel to
the tensile direction are largely open and leave wide PET areas visible underneath. The secondary cracks, initiated at 8% strain as a result of Poisson-ratio compression effects, also appear in the form of ‘tent-shaped buckles’ [11]. The oxide fragments are partially delaminated from the PET substrate, as observed in Fig. 6a. From the SEM observations, it was also possible to observe that the type of crack responsible for the fissures is an intergranular fracture path, as can be observed in Fig. 6b. This results in an interlocking of neighboring ZnO:Al fragments, and the area of contact is reduced as the strain in the substrate is increased.

4. Conclusions

ZnO:Al thin films produced by RF sputtering at room temperature were produced with high optical transmittance (85% in the visible spectrum) and low electrical resistivity ($\sim 10^{-2}$ $\Omega$ cm). The uniaxial tensile-strain test and its dependence on the electrical resistance were
reported. The results indicate that a finite resistance of the ZnO:Al film, even after cracks were observed to have propagated across the entire gauge length, was obtained. From the results, it is possible to conclude that the resistance is not directly related to the number of cracks, but to their width, which is dependent on the film thickness.

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