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Development of ZnO-based transparent conductive coatings

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ABSTRACT

We have developed a range of single and multilayer transparent conducting coatings consisting of three to five alternating layers of Al-doped ZnO (AZO) and metals using E-beam evaporation method. The prepared optimized coatings show excellent optical and electrical properties, improved thermal and long-term stability. Optimum thickness of metal and AZO layers was determined for high optical transmittance and good electrical conductivity. X-ray diffraction, spectrophotometer, atomic-force microscopy, scanning electron microscopy and four-point probe were used to explore the possible changes in electrical and optical properties. It was found that the multilayer coatings consisting of Al-doped ZnO and Ag metal show satisfactory properties of low resistance of 5 Ω/sq, high transmittance of 90% and thermal stability up to 500 °C.

1. Introduction

Transparent conductive oxide (TCO) thin films and coatings are an important and integral part of a number of electro-optical devices because of their technological applications. Depending on the conductivity and transmittance, these coatings are used in flat-panel displays, solar cells, etc [1–3]. Typical TCOs are impurity-doped indium oxides, tin oxides and zinc oxides that offer commercially acceptable performance in terms of conductivity, transmittance, environmental stability, reproducibility and surface morphology [4–7]. These doped ZnO thin-film coatings such as Al-doped ZnO (AZO) [8], In-doped ZnO (IZO) [9], Ga-doped ZnO (GZO) [10], and Mg-doped ZnO (MZO) [11] are developed swiftly into commercial products due to their easy manufacturing and excellent properties. To obtain desired electrical and optical properties, TCOs are normally deposited at elevated temperatures or subjected to post-deposition heat treatment. Among those AZO coating possesses low electrical resistivity and high optical transmittance [12,13]. However, their resistivity is rather high in some cases to adapt as a transparent electrode for improved practical application. In order to improve the properties of transparent conductors, development of multilayer coatings consisting of three to five alternative layers of metal and semiconductor or dielectrics is investigated [14,15]. However, simultaneous optimization of conductivity and transparency presents a considerable challenge in film deposition. Earlier works [16–18] reported that ITO/Ag/ITO can be used to surpass ITO for higher conductivity and lower cost. For ITO/Ag/ITO trilayer films, ITO lacks the high refraction required to reduce the strong reflection from the Ag layer [19]. Because of the high refraction of ZnO, ZnO/metal/ZnO trilayer films with high transmittance and conductivity have been studied [20–23]. However, there are few reports on multilayer transparent conducting film having superior properties for the application point of view. In order to obtain good TCO, E-beam evaporation method was used to deposit a multilayer, a single-layer AZO and Ag films. The deposition process was optimized for the preparation of the TCO film.

Our previous study on the AZO/Ag/AZO multilayer indicated that it is possible to obtain good-quality TCO [24]. However, the coatings are not so durable against moisture for long time though the coated glasses have to be packed with desiccants during transport and storage in order to avoid moisture-induced degradation. Further, the properties of the multilayer are not stable above 500 °C. It is reported that the durability of the coating in humid environment can be improved by depositing the top oxide layer at a higher pressure in order to reduce the internal stress of the layer [25,26]. Again thermal stability and the durability of the multilayer can be improved by the insertion of a metal interlayer between Ag and oxide layer [27]. In order to investigate this problem and to develop a high-quality multilayer film, different multilayer structures of four and five layers with other metal interlayers such as Al, Cu are reported in this work. We also focus on the determination of the optical constants and thicknesses of AZO using spectroscopic ellipsometry. This also allows the prediction of layer thickness for higher optical transmittance.

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2. Experimental

Thin films of AZO single layer, AZO and Ag multilayer such as AZO/Ag/AZO, AZO/Ag/AZO/Ag/AZO structures were deposited on glass substrates (corning eagle 2000 glass) in an E-beam evaporation system. The multilayer films were formed without vacuum break using an Al-doped zinc oxide sintered target [ZnO, (OSAKA, 99% purity) doped with 2 wt% Al_2O_3 (Alcoa, 99.7% purity), pressed and sintered at 1400 °C for 2 h)] and metal Ag chips (99.999% purity). The electron beam was focused on the sintered target with a diameter of 11 mm and a thickness of 4 mm. The substrate (15 mm long, 10 mm wide and 0.7 mm thick) was placed parallel to the target surface at a distance of 130 cm. The AZO target was mounted on a water-cooled holder and the temperature of the substrate was changed from 50 to 250 °C with an accuracy of ±5 °C. Heating of the substrate was done using a resistance heater. Hot filament was fixed in a holder on the back side of the substrate holder, which was formed in a semicircular way to enhance heat transfer by radiation. The heating rate was maintained at 5 °C/min. The substrate was heated for a definite period to ensure warming of the complete substrate. A thermocouple (K-type Chromel–Alumel) placed in contact with the substrate holder was used to monitor the substrate temperature. After deposition, the substrate was cooled normally to room temperature without maintaining any rate. The E-beam chamber was pumped down to 9×10^{-7} Torr prior to deposition. AZO films were deposited at 4 kV and 20–50 mA at a substrate temperature of 200 °C. Ag films were deposited at 8 kV and 20 mA at a substrate temperature of 30 °C. Deposition of AZO and Ag films was performed at a pressure of 2×10^{-5} Torr, which is due to the rise of the residual pressure during operation. Specimens with different thickness are fabricated and characterized.

The thickness of the film was measured using a surface profiler (Alpha-step 500, TENCOR) and confirmed by cross-sectional SEM observation. The α-step was used for measuring the thicker films; the ellipsometry has a sub-nanometer resolution and therefore was used for measuring the thinner films. The refractive indices of the films were also obtained from spectroscopic ellipsometry measurements. Conventional θ–2θ XRD studies were carried out by a Regaku (D/MAX 2500) diffractometer using CuK_α radiation to investigate crystallinity and crystal orientation of the films. Sheet resistance was measured using the four-point probe method. Optical transmittance was measured in the range 300–800 nm by a UV–VIS–IR spectrophotometer (Hewlett Packard 8452A, Palo Alto, CA).

3. Results and discussion

3.1. AZO thin film

XRD analysis shows that the AZO films exhibit a hexagonal structure having (0 0 2) preferred orientation [28]. The average grain size increases with film thickness. This leads to the increase in the surface roughness with thickness. From the ellipsometry measurements, the n/k values of AZO thin films were determined, where n is the refractive index and k is the extinction coefficient. Fig. 1 shows n/k values at a wavelength of 500 nm. The refractive index n increases with thickness from 1.68 and to a value closer to 2.1. The variation is explained by considering the packing density of the films. The packing density, q, is defined as $1-p$ where p is the volume fraction of the porosity [29]. The relationship between refractive index and packing density is given by the following equation [30]:

$$n_f^2 = [(1-q)n_v^4 + (1+q)n_v^2 n_s^2]/[(1+q)n_v^2 + (1-q)n_s^2] \quad (1)$$

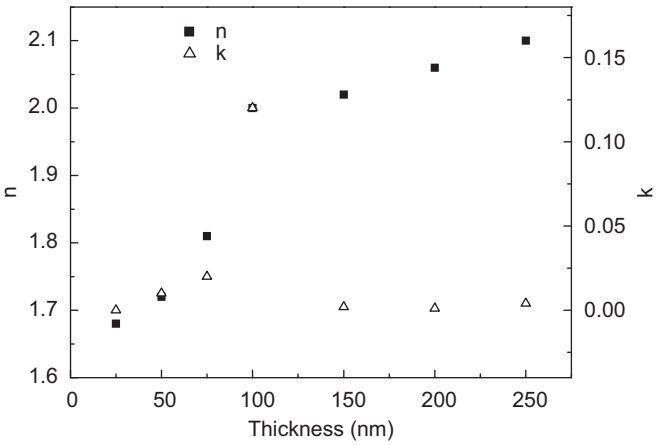

Fig. 1. Variations of n/k values (at 500 nm) of AZO thin films with thickness.

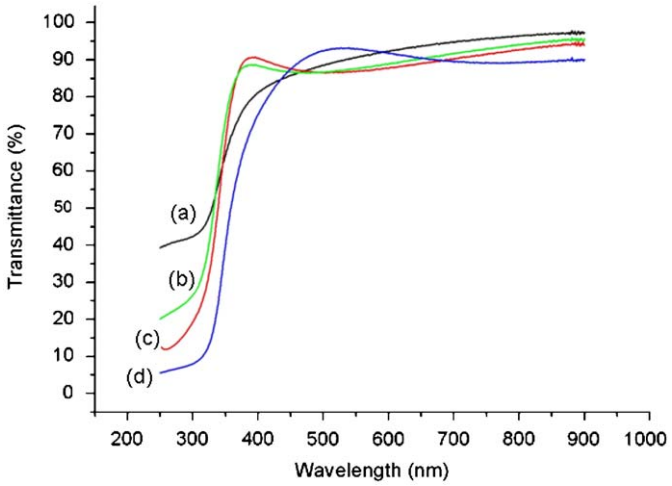

Fig. 2. The optical transmittance of AZO thin films with different thicknesses: (a) 25 nm, (b) 55 nm, (c) 70 nm and (d) 100 nm.

where n_f, n_v and n_s are the refractive indices of the film, of the pore in the film and of the solid material of the film, respectively. As n_v is normally taken to be that of the air, i.e., $n_v = 1$ and n_s is greater than 1, Eq. (1) predicts that n_f increases with packing density. On the other hand, packing density generally increases with grain size [29]. Surface roughness increases with film densities and forms larger crystals [30,31]. Since both grain size and surface roughness increase with film thickness, packing density increases with film thickness. As a result, the refractive index of the film increases with the film thickness as shown in Fig. 1.

Fig. 2 shows the optical transmittance of AZO thin films with different thicknesses between 300 and 800 nm. It is seen that the optical transmission in the visible region decreased substantially at short wavelengths near the ultraviolet range. The transmission in UV region decreased obviously with increase in film thickness [32]. Generally the visible transmission of film decreased with film thickness. However, the films exhibit optical transmittance greater than 80% in the visible range. By comparison, the absorption edge was observed at a slightly lower wavelength range for thinner AZO films. The shift of absorption edge may be attributed to the difference in grain size [33] and/or carrier concentration [34,35]. Resistivity of the AZO films increased with decrease of film thickness. The AZO film with thickness of 25 nm had the lowest resistivity of $2.5 \times 10^{-4}\,\Omega$ cm with maximum transmittance of 85% [28].