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Highly flexible ZnO/Ag/ZnO conducting electrode for organic photonic devices

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Abstract

We investigated the electrical, optical and bending characteristics of ZnO (40 nm)/Ag (18.8 nm)/ZnO (40 nm) multilayer film deposited on polyethylene terephthalate (PET) substrate and compared them with those of indium-tin-oxide (ITO) (100 nm thick). The ITO single and ZnO/Ag/ZnO multilayer films gave maximum transmittance of 92.9% and ~95% at ~530 nm, respectively. For the ITO single and ZnO/Ag/ZnO multilayer films, the carrier concentration was measured to be 1.19×10^{20} and 6.68×10^{21} cm^{-3}, respectively and the mobility was 32.06 and 21.06 cm^2/V s, respectively. The sheet resistance was 175.99 and 4.98 Ω/sq for the ITO single and ZnO/Ag/ZnO multilayer films, respectively. Haacke's figure of merit (FOM) of the ITO single and ZnO/Ag/ZnO multilayer films was calculated to be 2.36×10^{-3} and 104.5×10^{-3} Ω^{-1}. The ZnO/Ag/ZnO multilayer films showed dramatically improved mechanical stability when subjected to bending test.

Keywords: D. ZnO; Ag; Multilayer; Flexibility; Transparent conducting electrode

1. Introduction

Flexible transparent conductive oxides (TCOs) are technologically very important for their applications in optoelectronic, photovoltaic devices, and displays [1–3]. Sn-doped indium oxide (ITO) is most commonly used because of its superior optical and electrical properties [4,5]. However, indium is a rare and expensive metal, which will result in a rapid increase in the fabrication costs in future applications. Thus, a variety of oxides with high transmittance, viz. SnO_2 [6], ZnO [7], TiO_2 [8], and Nb_2O_5 [9], have been widely studied to develop cost-effective TCO. In addition, for flexible organic light emitting diode (OLEDs) applications [10], transparent conducting electrodes (TCEs) must have bending stability together with reliable electrical and optical properties. The mechanical flexibility is essential for the realization of low cost roll-to-roll process for organic optoelectronic devices [11]. To meet the requirements, transparent oxides sandwiching a thin metal film, i.e., dielectric/metal/dielectric (D/M/D) multilayers have been extensively investigated, including SnO_2/Ag/SnO_2 [12], Nb_2O_5/Ag/Nb_2O_5 [13], Al_2O_3/Ag/Al_2O_3 [14], WO_3/Ag/WO_3 [15], ZnSnO/Ag/ZnSnO [16], MoO_3/Ag/MoO_3 [17], TiInZnO/Ag/TiInZnO [18], ZrON/Ag/ZrON [19] TiO_2/Ag/TiO_2 [20], and ZnO/Ag/ZnO [21,22]. Ag is commonly used as the middle layer for D/M/D multilayers, since Ag thin films (less than 20 nm thick) show low resistance and high transmittance in the visible spectrum. For instance, Yu et al. [12], investigating the effects of Ag layer thickness and SnO_2 layer thickness on the electrical and optical properties of SnO_2/Ag/SnO_2 tri-layer films prepared on quartz glass substrates, reported that the SnO_2/Ag/SnO_2 multilayer film (50 nm/5 nm/50 nm) exhibited the maximum FOM of 6.0×10^{-2} Ω^{-1} with a sheet resistance of 9.67 Ω/sq, a resistivity of 1.0×10^{-4} Ω cm and an average transmittance of 94.8% in the visible region. In addition, Fan and Bachner [20] showed that a

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TiO_2/Ag/TiO_2 multilayer (18 nm/18 nm/18 nm) prepared with RF sputtering gave a reflectivity of 98% at 10 μm and a transmission of ~80% in the 500–600 nm region. Sahu et al. [21] investigated the optical and electrical properties of ZnO/Ag/ZnO multilayer electrodes as functions of ZnO and Ag thicknesses and reported that the optimum thickness of Ag films was 6 nm for high optical transmittance and good electrical conductivity, e.g., a sheet resistance of 3 Ω/sq and a transmittance of 90% at 580 nm. Hajj et al. [22], investigating the electrical and optical properties of ZnO/Ag/ZnO multilayer electrodes prepared by ion beam sputtering for flexible optoelectronic devices, showed that the introduction of a Ag layer between two ZnO layers decreased the sheet resistance and widened the transmittance window in the visible region. The ZnO/Ag/ZnO (35 nm/10 nm/20 nm) multilayer electrode had a sheet resistance of 6 Ω/sq, a transmittance of ≥80% in the visible region, and figure of merit (FOM) of $16.5\times10^{-3}\ \Omega^{-1}$. In this study, the optical and electrical properties of ZnO/Ag/ZnO multilayer were also investigated and compared with those of ITO single film, that were deposited with a radio frequency (RF) sputtering system at room temperature. FOM was also calculated to characterize the performance of the multilayer. The samples were subjected to bending test to investigate their mechanical flexibility.

2. Experimental procedure

ZnO/Ag/ZnO multilayer thin films were sequentially deposited on polyethylene terephthalate (PET) substrates by an RF magnetron sputtering system. Ceramic ZnO target (99.99% purity) and pure Ag target (99.99% purity) were used at room temperature under a base pressure of less than 1×10^{-6} Torr. Before being loaded into the sputtering chamber, the PET substrates ($1.5\times1.5\ cm^2$) were cleaned with methanol and deionized water for 15 min per cleaning agent in an ultrasonic bath, and finally dried in a N_2 stream. Prior to deposition, the ITO, ZnO and Ag targets were pre-sputtered for 30 min to remove contaminants. ZnO and Ag were deposited using RF powers of 90 W and 30 W at Ar flow rates of 30 sccm and 13 sccm, respectively, under a working pressure of 10 mTorr. During sputtering, the PET substrate was constantly rotated at a speed of 12 rpm for ZnO and 23 rpm for Ag. The ZnO thickness of 40 nm and Ag thickness of 18.8 were selected based on the dependence of ZnO thickness on the optical and electrical properties [23]. For comparison, 100 nm-thick ITO thin films were also prepared using pure ITO target (99.99% purity). The thickness of the multilayer films was determined with high resolution transmission electron microscopy (HR-TEM, JEM-ARM, 200 F, JEOL). For instance, Fig. 1 shows a cross-section HR-TEM image of a ZnO/Ag/ZnO (40 nm/18.8 nm/40 nm) multilayer grown on the PET substrate. It can be seen that the individual layers are well defined. Hall measurements by the van der Pauw technique were carried out with a magnetic field of 0.55 T (HMS 3000, Ecopia). The four-point-probe technique was used for sheet resistance measurements. Transmittance of the multilayers was measured with a UV/visible spectrometer (UV-1800, Shimadzu). The crystal structure of the multilayers was determined with X-ray diffraction (XRD, ATX-G, Rigaku). The mechanical flexibility of the samples was analyzed using a bending test system (ZBT-200, Z-tec). The samples were clamped between two parallel semicircular-plates. One plate was mounted to the shaft of a motor, while the other was fixed to a supporter. The distance of the stretched mode was 80 mm and that of the bent position was 35 mm. The bending radius was approximately 9 mm and the bending frequency was 1 Hz. Finally, the resistance of the samples during the bending was measured using a multimeter.

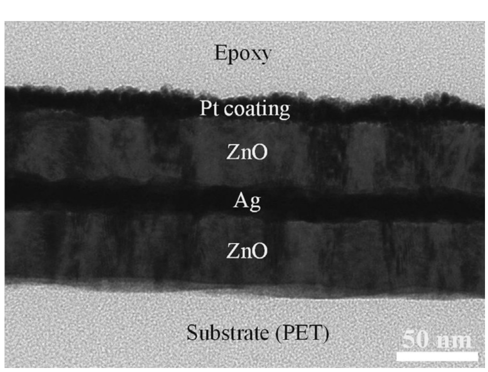

Fig. 1. A cross-section TEM image of ZnO/Ag/ZnO (40 nm/18.8 nm/40 nm) multilayer film grown on PET substrate.

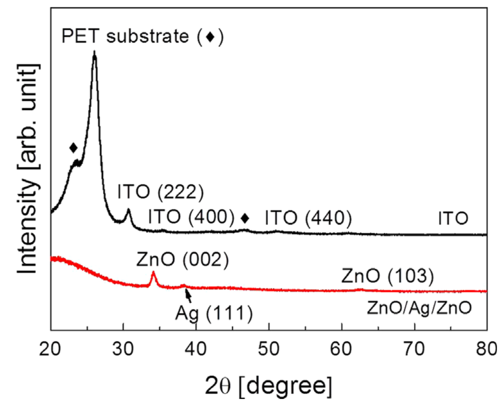

Fig. 2. XRD patterns obtained from reference 100 nm-thick ITO film and optimized ZnO/Ag/ZnO (40 nm/18.8 nm/40 nm) multilayer film deposited on PET substrates.

3. Results and discussion

Fig. 2 shows the XRD patterns from the reference 100 nm-thick ITO film and optimized ZnO/Ag/ZnO (40 nm/18.8 nm/40 nm) multilayer film deposited on the PET substrates. The ZnO/Ag/ZnO sample has peaks at $2\theta=34.2^\circ$ and 64.6° that correspond to the (002) and (103) planes of ZnO, respectively. In addition there is a peak at $2\theta=38.2^\circ$, corresponding to the (111) plane of Ag (JCPDS no. 65-3411 and 87-0720). On the one hand, the ITO sample have peaks at $2\theta=30.5^\circ$, 35.4°, and 51°, corresponding to the (222), (400), and (440) planes (JCPDS card no. 76-0152).

Fig. 3 shows the transmittance spectra obtained from the ITO single film and the ZnO/Ag/ZnO multilayer film. The transmittance of the multilayer film reaches an overall maximum and then gradually decreases with increasing wavelength, while that of ITO reaches an overall maximum and then slightly decreases. The