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

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Received 5 December 2014; accepted 5 February 2015
Available online 12 February 2015

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 × 10²² and 6.68 × 10²² cm⁻³, respectively and the mobility was 32.06 and 21.06 cm²/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.

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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. SnO₂ [6], ZnO [7], TiO₂ [8], and Nb₂O₅ [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 SnO₂/Ag/SnO₂ [12], Nb₂O₅/Ag/Nb₂O₅ [13], Al₂O₃/Ag/Al₂O₃ [14], WO₃/Ag/WO₃ [15], ZnSnO/Ag/ZnSnO [16], MoO₃/Ag/MoO₃ [17], TiInSnO/Ag/TiInSnO [18], ZrON/Ag/ZrON [19] TiO₂/Ag/TiO₂ [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 SnO₂ layer thickness on the electrical and optical properties of SnO₂/Ag/SnO₂ tri-layer films prepared on quartz glass substrates, reported that the SnO₂/Ag/SnO₂ 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 × 10⁻² Ω cm and an average transmittance of 94.8% in the visible region. In addition, Fan and Bachner [20] showed that a
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. Hajij 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 × 10$^{-3}$ Ω$^{-1}$. 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 × 1.5 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.

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 2θ=34.2° and 64.6° that correspond to the (002) and (103) planes of ZnO, respectively. In addition there is a peak at 2θ=38.2°, corresponding to the (111) plane of Ag (JCPDS no. 65-3411 and 87-0720). On the one hand, the ITO sample have peaks at 2θ=30.5°, 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
maximum transmittance is measured to be 92.9% and ~95% at about 530 nm for the ITO and ZnO/Ag/ZnO samples, respectively.

The carrier concentration and Hall mobility of the ITO single and ZnO/Ag/ZnO multilayer films were characterized, as shown in Table 1. The carrier concentration was determined to be $1.19 \times 10^{20}$ and $6.68 \times 10^{21}$ cm$^{-3}$ for the ITO single and ZnO/Ag/ZnO multilayer films, respectively. On the one hand, the mobility was 32.06 and 21.06 cm$^2$/V s for the ITO single and ZnO/Ag/ZnO multilayer films, respectively. Carrier mobility behavior is usually described in terms of scattering mechanisms such as phonon scattering, grain-boundary scattering, surface scattering, interface scattering, and ionized-impurity scattering [24]. Since the crystalline ZnO films are undoped, interface scattering may be dominant at the ZnO/Ag interfaces.

The resistivity and sheet resistance of the ITO single and ZnO/Ag/ZnO multilayer films were characterized, as shown in Table 1. The sheet resistance was measured to be 175.99 and $3 \times 10^3$ $\Omega$/sq for the ITO single and ZnO/Ag/ZnO multilayer films, respectively. Meanwhile, the resistivity was $1.62 \times 10^{-3}$ and $4.43 \times 10^{-5}$ $\Omega$ cm for the ITO single and ZnO/Ag/ZnO multilayer films, respectively. It is noted that the ITO single film shows higher sheet resistance and resistivity than the ZnO/Ag/ZnO multilayer film. The resistivity is inversely proportional to the mobility and the carrier concentration [25]. This implies that in our samples the resistivity is dominated by the carrier concentration, as shown in Table 1.

FOM ($\varphi_{TC}$) of the ITO single and ZnO/Ag/ZnO multilayer films was calculated using the equation defined by Haacke [26], as given below

$$\varphi_{TC} = \frac{T^{10}}{R_s}$$

where $R_s$ is the sheet resistance and $T_{av}$ is the average optical transmittance (in the range 450–780 nm). $T_{av}$ can be estimated using the relation shown below

$$T_{av} = \frac{\int V(\lambda)T(\lambda)d\lambda}{\int V(\lambda)d\lambda}$$

where $T(\lambda)$ is the transmittance and $V(\lambda)$ is the photopic luminous efficiency function defining the standard observer for photometry [12,27]. The ZnO/Ag/ZnO multilayer film gives FOM of 104.5 $\times 10^{-3}$ $\Omega^{-1}$. However, the FOM is significantly lower for the ITO single film, with a value of $2.36 \times 10^{-3}$ $\Omega^{-1}$. As both the samples show similar transmittance, the higher FOM for the ZnO/Ag/ZnO sample can be attributed to the dominant contribution of low sheet resistance.

Fig. 4 shows the change in resistance of the ITO single and ZnO/Ag/ZnO multilayer films on a PET substrate as a function of cycle. The insets of Fig. 4 exhibit the bending testers used. The change in resistance was defined as $R - R_0/R_0$, where $R_0$ is the initial resistance and $R$ is the measured resistance after bending. The value of $R - R_0/R_0$ for the ITO single film dramatically increases even after two cycles, Fig. 4(a). This is directly attributable to the generation and propagation of cracks. On the other hand, the value of $R - R_0/R_0$ for the ZnO/Ag/ZnO multilayer film remains almost constant, as can be seen in Fig. 4(b). This implies that the resistance of the ZnO/Ag/ZnO multilayer film remains almost unchanged during the bending test. This electrical stability is due to the presence of the ductile Ag middle layer [28]. Lewis et al. [28] investigated the optical, electrical, and bending properties of ITO/Ag/ITO multilayer electrodes for organic light-emitting diodes and reported that the ITO/Ag/ITO multilayer electrodes exhibited significantly lower sheet resistance and higher average transmittance (in the range 450–650 nm) than ITO only films. The significantly improved mechanical property of the ITO/Ag/ITO multilayer electrodes was attributed to the use of ductile Ag layer with higher failure strain (4–50%) [29].

It was shown that the ZnO/Ag/ZnO samples yielded rather high optical transmittance at 550 nm. It is known that a large difference between the refractive indices of Ag and the dielectric layer can cause efficient plasmon coupling, resulting in a visible transmittance higher than 80% [30]. Thus, the high transmittance of our ZnO/Ag/ZnO multilayers may also be attributed to surface plasmon resonance in the Ag layers when using an optimal ZnO thickness of 24–56 nm. Furthermore, the optical transmittance at wavelengths longer than 700 nm is higher in the ZnO/Ag/ZnO multilayers than in ITO. This may be caused by plasmon-absorption-dependent reflections due to the increasing carrier concentration [12].

### 4. Summary and conclusion

The opto-electrical and bending characteristics of ITO and ZnO(40 nm)/Ag(18.8 nm)/ZnO(40 nm) multilayer film deposited...
on polyethylene terephthalate (PET) substrate by RF sputtering were characterized. The ZnO/Ag/ZnO multilayer films had improved transmittance at 550 nm and significantly better electrical properties compared to the 100-nm-thick ITO single film. The ZnO/Ag/ZnO multilayer film exhibited much higher Haacke’s FOM than the ITO. The bending test results showed that the ZnO/Ag/ZnO multilayer electrode demonstrated dramatically improved mechanical stability than the ITO single film. The result shows that ZnO/Ag/ZnO multilayer film can be used as an important transparent multilayer electrode in flexible organic photovoltaic and photonic devices.

Acknowledgments

This work was supported by the Brain Korea 21 Plus Program funded by the Ministry of Science, ICT and Future Planning, Korea, and Ministry of Trade, Industry and Energy under Grant no. 10049601.

References


Fig. 4. Change in resistance of (a) ITO single and (b) ZnO/Ag/ZnO multilayer films on PET substrates as a function of cycle. The insets show a bending test system used in this work.


