Highly flexible Al-doped ZnO/Ag/Al-doped ZnO multilayer films deposited on PET substrates at room temperature

Jun Ho Kim\textsuperscript{a}, Da-Som Kim\textsuperscript{b}, Sun-Kyung Kim\textsuperscript{b}, Young-Zo Yoo\textsuperscript{c}, Jeong Hwan Lee\textsuperscript{d}, Sang-Woo Kim\textsuperscript{d}, Tae-Yeon Seong\textsuperscript{a,}\textsuperscript{*}

\textsuperscript{a}Department of Materials Science and Engineering, Korea University, Seoul 02841, Republic of Korea
\textsuperscript{b}Department of Applied Physics, Kyung Hee University, Gyeonggi-do, Republic of Korea
\textsuperscript{c}Dusun Hi-Metal Co. Ltd., Yeonam-dong, Buk-gu, Ulsan 44252, Republic of Korea
\textsuperscript{d}School of Advanced Materials Science and Engineering, Sungkyunkwan University, Suwon 16419, Republic of Korea

Received 25 August 2015; received in revised form 5 October 2015; accepted 27 October 2015
Available online 3 November 2015

Abstract

We investigated the effects of the Ag layer thickness on the electrical and optical properties of AZO (36 nm)/Ag/azo (36 nm) multilayer films that were deposited on polyethylene terephthalate (PET) substrates using a radio frequency magnetron sputtering method. The AZO/Ag/AZO films had transmittances over 74–89\% at 550 nm. The relationship between the transmittance and the Ag layer thickness was investigated with three-dimensional finite-difference time-domain (3D FDTD) simulations to understand high transmittance. As the Ag layer thickness increased from 15 to 23 nm, the carrier concentration increased from $5.84 \times 10^{21}$ to $9.66 \times 10^{21}$ cm$^{-3}$, while the sheet resistance decreased from 10.15 to 3.47 $\Omega \text{ sq}^{-1}$. The Haake figure of merit (FOM) was calculated for the samples with various Ag layer thicknesses; it was a maximum at 19 nm ($43.9 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$). The resistance change for the 100 nm-thick ITO only films was unstable even after 5 cycles, while that of the AZO (36 nm)/Ag (19 nm)/AZO (36 nm) film remained constant up to 1000 cycles.

\textsuperscript{c}Corresponding author. Tel.: +82 2 3290 3288; fax: +82 2 928 3584.
\textsuperscript{E-mail address}: tyseong@korea.ac.kr (T.-Y. Seong).

Keywords: Al-doped ZnO; Ag; Transparent conducting electrode; Flexible device

1. Introduction

Transparent conductive oxide (TCO) thin films play an important role in photoelectric devices such as organic photovoltaic cells (OPVs) and organic light-emitting diodes (OLEDs) [1–3]. Sn-doped indium oxide (ITO) is used widely as a transparent electrode material in display and optoelectric devices due to its high transparency and low resistivity [4]. For example, ITO is a common anode for OLEDs since it forms good energy-level alignment, thereby providing the efficient hole injection into the organic layers [5–7]. On the one hand, the development of flexible displays requires mechanically robust flexible TCOs. However, ITO fails under relatively lower mechanical stress as compared with other device components [8,9]. Furthermore, the rare and expensive element In will increase the production costs of device application [10,11]. Therefore, it is important to develop low-cost TCO fabricated at low temperatures, which can replace the expensive ITO. To realize such TCOs, oxide/metal/oxide (O/M/O) structures have been actively investigated [12–14]. The O/M/O structures normally consist of a thin Ag layer (7–20 nm thick) sandwiched between two oxides (20–70 nm thick) with high dielectric constants. For O/M/O structures, a visible transmittance of larger than 90\% can be realized due to a large difference in the refractive indices of Ag and oxide layers [15,16] and good conductivity can be also achieved due to conductive Ag [17–19]. In particular, Al-doped ZnO (AZO) films are of particular interest because of low cost, nontoxicity, and chemical stability against H plasma environments.
However, the realization of the desirable optoelectronic properties of AZO films requires high substrate temperatures and/or post-growth annealing [20,21], which hampers their applications for flexible polymer substrates. To solve the problem, AZO/Ag/AZO multilayer films have been widely investigated by many researchers [14,17,22–31]. For example, Miao et al. [24] investigated the electrical, optical and infrared reflectance properties of AZO/Ag/AZO films prepared on glass substrates as a function of Ag layer thickness and showed that AZO (30 nm)/Ag (10 nm)/AZO (30 nm) films had the highest average visible transmittance of 85.4%. However, AZO (30 nm)/Ag (15 nm)/AZO (30 nm) had the lowest sheet resistance of 3.2 Ω sq−1 and the highest infrared reflection rate of 97% in far infra-red region. Guillén et al. [17], investigating the electrical and optical properties of AZO/Ag/AZO films deposited on glass substrates as a function of Ag layer thickness, showed that AZO (40 nm)/Ag (10 nm)/AZO (40 nm) films had a sheet resistance of 6 Ω sq−1 and maximum transmittance around 85% near 600 nm. Crupi et al. [25], investigating the thermal stability and optical and electrical properties of AZO (20 nm)/Ag/AZO (30 nm) films as a function of Ag film thickness, reported that the AZO/Ag (19 nm)/AZO films had the lowest sheet resistance of about 2.5 Ω sq−1 whereas the AZO/Ag (6.3 nm)/AZO films had the highest transmittance of about 80%. In this study, the optical and electrical properties of AZO/Ag/AZO multilayer films were also investigated as a function of Ag layer thickness and compared with those of ITO films. The AZO/Ag/AZO films were deposited on polyethylene terephthalate (PET) substrates by an RF sputtering system at room temperature. Haacke figure of merit (FOM) was calculated to characterize the performance of the multilayers. The mechanical flexibility of the samples was investigated.

2. Experimental procedures

AZO/Ag/AZO multilayer thin films were deposited on PET substrates by an RF magnetron sputtering system. Ceramic AZO target (ZnO:Al2O3=98.2 wt%, 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 (2.0 × 2.0 cm2) were cleaned with methanol and deionized water for 15 min per cleaning agent in an ultrasonic bath, and finally dried in a N2 stream. Prior to deposition, both the AZO and Ag targets were presputtered for 30 min to remove contaminants. The AZO and Ag layers were deposited with RF powers of 90 and 30 W, respectively. During the sputter deposition, the PET substrates were constantly rotated at a speed of 12 and 24 rpm for the AZO and Ag layers, respectively. The thickness of the AZO layer (dAZO) was fixed constant at 36 nm, while the thickness of the Ag films (dAg) was varied from 15 to 23 nm. The thicknesses of the multilayer films were determined with high-resolution transmission electron microscopy (HR-TEM, JEM-ARM 200F, Jeol). For example, Fig. 1 shows a bright field TEM image obtained from a AZO/Ag (19 nm)/AZO multilayer film. It is noted that the thickness of the Ag layer is somewhat irregular. Hall measurements were performed with the van der Pauw method using a magnetic field of 0.55 T (HMS 3000, Ecopia). The four-point-probe technique was used to measure the sheet resistances of the samples. The transmittance of the multilayer films was measured with a UV/visible spectrometer (UV-1800, Shimadzu). A bare PET substrate was used as the reference when measuring the optical transmittance of the multilayer samples. The crystal structure of the multilayers was characterized with X-ray diffraction (XRD, ATX-G, Rigaku). The mechanical flexibility of the samples was analyzed with 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 45 mm. Finally, the resistance of the samples during the bending test was measured using a multimeter.

To verify the measured transmittance spectra of the AZO/Ag/AZO multilayer films, three-dimensional finite-difference time-domain (3D FDTD) simulations were performed [32,33]. In the FDTD simulations, dAZO was fixed at 36 nm. On the one hand, dAg also varied from 15 to 23 nm with a step of 2 nm, which is the same as the measurement conditions. For accurate simulations, a spatial resolution of 1 nm was applied to all three orthogonal axes and dispersive optical constants were adapted for Ag [34] and AZO [35].

3. Results and discussion

Fig. 2 shows the XRD patterns obtained from the AZO/Ag/AZO multilayer films as a function of dAg. It is noted that apart from the PET, all of the peaks are fairly weak. All of the multilayer samples have weak peaks at 2θ=34.2° which correspond to the (002) plane of ZnO (JCPDS no. 36-1451). The multilayer samples also have weak peaks at 2θ=38.3°, corresponding to the (111) planes of Ag (JCPDS no. 04-0783). Apart from the characteristic peak of ZnO, no other phases, such as Al or any Al compounds, were observed. This finding indicates that there is no phase segregation or any secondary
phase and that Al was not incorporated into ZnO lattice [36]. The reference ITO film contains peaks at 2θ = 35.4°, corresponding to the (400) plane of In2O3 (JCPDS no. 06-0416). It is shown that the intensity of the Ag (111) peaks remains almost unchanged although its thickness increased from 15 to 23 nm, as shown in the inset. The reason for this behavior is not currently known. A similar feature was also observed by other researchers [37].

Fig. 3 shows the transmittance spectra of the ITO (100 nm thick) and AZO/Ag/AZO multilayer films with various dAg. Regardless of dAg, the transmittance reaches a global maximum over 480–505 nm and then it gradually decreases with increasing wavelength. For example, the AZO/Ag/AZO multilayers films with different Ag layer thicknesses have transmittances of 79–91% at 500 nm. The transmittance at 550 nm is measured to be 89%, 89%, 87%, 81%, and 74% for the samples with dAg = 15, 17, 19, 21, and 23 nm, respectively, while it is 88.7% for ITO. The transmission window narrows and the transmittance gradually decreases with increasing dAg. Consequently, the thicker samples show lower transmittance at the absorption edge and infra-red region.

Fig. 4 shows the carrier concentration and Hall mobility of the AZO/Ag/AZO multilayer films with various Ag layer thicknesses. The carrier concentration gradually increases with increasing dAg. As dAg increases from 15 to 23 nm, the concentration increases from 5.84 × 10^{21} to 9.66 × 10^{21} cm^{-3}, and the mobility also increases from 15.5 to 23.5 cm^2 V^{-1} s^{-1}.

Fig. 5 exhibits the resistivity and sheet resistance of the AZO/Ag/AZO multilayer films with various Ag layer thicknesses. The sheet resistance slowly decreases from 10.15 to 3.47 Ω sq^{-1} as dAg increases from 15 to 23 nm. It is noted that the as-deposited reference ITO has a sheet resistance of 145.5 Ω sq^{-1}. The resistivity also decreases from 6.87 × 10^{-5} to 2.74 × 10^{-5} Ω cm with increasing dAg. The resistivity is inversely proportional to the mobility and the carrier concentration [38]. This implies that the carrier concentrations play a dominant role in reducing the resistivity of the multilayer films.

The optical and electrical properties of TCOs are very important for their use in photonic and optoelectronic device applications. In other words, such applications require as high transmittance and low sheet resistance as possible. FOM is commonly used to investigate the relationship between optical and electrical properties of TCOs. A FOM, φTC was calculated for all samples using the equation defined by Haacke [39],

\[ \varphi_{TC} = \frac{T_{av}}{R_s} \]

where R_s is the sheet resistance and T_{av} is the average optical transmittance. T_{av} is defined as,

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

where T(\lambda) is the transmittance and V(\lambda) is the function of wavelength [39].
the photopic luminous efficiency function defining the standard observer for photometry [40,41]. \( T_{in} \) (over 450–750 nm) was estimated to be 88%, 88%, 85%, 79%, and 73% for the 15, 17, 19, 21, and 23 nm-thick AZO/Ag/AZO films, respectively, while ITO had 88%. As can be seen in Fig. 6, FOM reaches a maximum at 19 nm and then rapidly decreases with increasing \( d_{Ag} \). In particular, the multilayer sample with \( d_{Ag}=19 \) nm has the highest FOM (43.9 \( \times 10^{-3} \) \( \Omega^{-1} \)), which is much larger than that of ITO (2.01 \( \times 10^{-3} \) \( \Omega^{-1} \)).

Fig. 7 shows the dependence of resistance on bending cycle in the ITO only (100 nm thick) and optimal AZO (36 nm)/Ag (19 nm)/AZO (36 nm) multilayer films. The inset exhibits the bending tester used in this study. The resistance change can be defined as \( R-R/R_0 \), where \( R_0 \) is the initial resistance and \( R \) is the measured resistance after bending. The ITO only film shows very unstable feature even after five cycles, indicating the formation and propagation of cracks. On the contrary, the value of \( R-R/R_0 \) for the AZO/Ag/AZO multilayer film remains almost constant. This electrical stability (i.e. bending stability) is due to the presence of the ductile Ag layer with higher failure strain (4–50%) [42].

Fig. 8 exhibits the calculated transmittance spectra of AZO/Ag/AZO and Ag only films as a function of \( d_{Ag} \). The insets illustrate the stacking structures of the samples. As shown in Fig. 8(a), irrespective of \( d_{Ag} \), the transmittance reaches a global maximum over 475–495 nm and then it gradually decreases with increasing wavelength. The \( d_{Ag} \) dependence is in agreement with the experimental results (Fig. 3). Although the overall transmittance decreases monotonically with increasing \( d_{Ag} \), the transmittance is higher than 85% even with optically thick Ag layers (i.e. \( d_{Ag}=15–19 \) nm), particularly at blue-to-green wavelengths. Such high transmittance from O/M/O multilayer films is a direct consequence of the destructive interference between partial reflected waves [43–45], which can be illustrated by a complex phasor diagram [38]. The interference features from the AZO/Ag/AZO films are more evident when compared with Ag only films on PET substrates (Fig. 8(b)). For the Ag only films, the transmittance is less than 60% at \( \lambda \) of longer than 450 nm and decreases gradually with increasing wavelength. The high transmittance at near UV wavelengths (\( \lambda < 400 \) nm) is due to absence of the AZO layers because ZnO-based materials have large absorption at these wavelengths [45]. Taken together, the top and bottom dielectrics in the O/M/O films generate complex partial reflected waves, which enhance the transmittance. This indicates that the transmittance of O/M/O multilayer films can be further increased at specific wavelengths by tailoring the thickness and refractive index of dielectrics [43].

4. Summary and conclusions

The opto-electrical properties of AZO/Ag/AZO multilayer films deposited on PET substrates were investigated as a
function of the Ag layer thickness. The AZO/Ag (19 nm)/AZO multilayer films had the highest transmittance of 89.7% at 498 nm, which was attributed to the anti-reflection effect including complex optical media. As the Ag thickness increased, the carrier concentration gradually increased, while the sheet resistance slightly decreased. The AZO (36 nm)/Ag (19 nm)/AZO (36 nm) films had the highest Haacke's FOM much higher than that of ITO only samples. The optimal AZO/Ag/AZO electrode exhibited considerably improved mechanical flexibility compared to the ITO only film. These results show that AZO/Ag/AZO (36 nm/19 nm/36 nm) sample can be used as an important transparent multilayer electrode in flexible photovoltaic and photonic devices.

Acknowledgments

This work was supported by the Korea Evaluation Institute of Industrial Technology (Grant no. 10049601) and WC300 R&D (Grant no. S2317456) through Korea Institute for Advancement of Technology (KIAT) which is funded by the Small and Medium Business Administration, Korea. S.-K.K. was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF), which is funded by the Ministry of Science, ICT, and Future Planning (NRF-2013R1A1A01059423).

References


