Flexible and Transparent Conducting ZZO/Ag/ZZO Multilayer Grown by Sputtering at Room Temperature

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We studied the optical, electrical, and structural properties of indium-free Zr-doped ZnO (ZZO)/Ag/ZZO multilayers prepared on poly(ether sulfone) (PES) substrates by RF magnetron sputtering at room temperature. The optical and electrical characteristics of the crystalline ZZO/Ag/ZZO multilayer electrodes can be improved by the insertion of a nano-sized Ag interlayer with an optimized thickness between top and bottom ZZO films, owing to the very low resistivity. The ZZO/Ag (12 nm)/ZZO/PES exhibited high transmittance of ~85.6% in the wavelength range from 450 to 600 nm and a low resistivity of ~$5 \times 10^{-5}$Ω·cm. Additionally, X-ray photoelectron spectroscopy (XPS) investigations for the ZZO/Ag/ZZO multilayers confirmed no interfacial reaction between the ZZO and Ag films. The performances indicate that the indium-free ZZO/Ag/ZZO multilayers are promising as transparent conducting films for low-cost flexible optoelectronics applications.

Keywords: transparent conducting oxides, zirconium-doped ZnO, flexible, resistivity, transparency

1. Introduction

Recently, highly-flexible and transparent conducting oxide (TCO) components have been investigated for various optoelectronics applications.1–4) Amorphous ITO films fabricated on flexible polyethylene naphthalate, poly(ethylene terephthalate) (PET), and poly(ether sulfone) (PES) substrates at low substrate temperatures have been adopted for flexible TCO applications.5–7) However, the amorphous ITO films with high resistivities, brittle properties and high costs are not practical. Thin Ag layer inserted amorphous ITO sandwich structures with superior flexibility are potential candidates.8–10) Particularly, ZnO-based flexible oxide-metal-oxide multilayers with low costs are getting important attention. Indium-free ZnO/Ag/ZnO, AZO/Ag/AZO, and ZnO/Cu/ZnO multilayers prepared on plastic substrates have been reported.11–13) Recently, an indium-free TCO material, Zr-doped ZnO (ZZO) fabricated at room temperature has received particular attention owing to its high visible transparency of ~90%.14–17)

In this work, we report on the optical transparency- and sheet resistance-tunable ZZO/Ag/ZZO multilayers fabricated on PES substrates. Owing to the metallic resistivity of the nano-sized Ag film inserted between the ZZO films at an optimized Ag thickness, we obtain a low sheet resistance of 6.5 Ω/sq and an average optical transmittance of ~85.6% in the wavelength range from 450 to 600 nm. The flexible ZZO/Ag/ZZO multilayer is a promising indium-free TCO film for low-cost flexible optoelectronics applications due to the high transparency, low sheet resistance, and low process temperature.

2. Experimental

ZZO/Ag/ZZO multilayer films with various Ag thicknesses were fabricated on flexible PES substrates using a dual-target RF magnetron sputtering system at room temperature. The surface cleaning of the PES substrate was pretreated by Ar+ ion bombardment. First, the bottom ZZO film with a thickness of 40 nm was deposited at room temperature in the sputtering system using a ZZO target (5 mass% ZrO2-doped ZnO). Subsequently, an Ag layer with varying Ag thicknesses was continuously sputtered using an Ag target for investigating the effects of different Ag thicknesses on the properties of the sandwich structures. A low deposition rate was obtained by adjusting an argon (Ar) pressure and a sputtering power for depositing the ultrathin films.18,19)

Finally, the top ZZO film with a thickness of 40 nm was sputtered onto the Ag film under the process conditions identical to those of the bottom ZZO film. The physical thicknesses of ZZO films and complete multilayers were measured by a surface profilometer. The Ag thickness was obtained by X-ray photoelectron spectroscopy (XPS) depth profiling. The electrical properties of the multilayer were studied by Hall effect measurement. Optical-transmittance measurement was performed by a spectrophotometer in the wavelength range of 200–800 nm. Crystalline structures were examined by X-ray diffraction (XRD) analysis. The interfacial properties of the optimized ZZO/Ag (12 nm)/ZZO electrode were analyzed using XPS depth profiling. The cross-section of the film was analyzed by using a high-resolution transmission electron microscope (HR-TEM) to confirm the Ag layer thickness.

3. Results and Discussions

3.1 Resistivity

Figure 1 shows the resistivity and sheet resistance of ZZO (40 nm)/Ag/ZZO (40 nm) multilayers as functions of Ag thicknesses. As compared to the single ZZO film with the resistivity of 9.1 $\times 10^{-4}$Ω·cm reported previously,14) the Ag-inserted multilayers show significantly decreased resistivity while the Ag thickness is higher than 8 nm. The ZZO/Ag/ZZO multilayer displays decreased resistivity and sheet resistance with increasing Ag thickness since the Ag film acts as the main carrier transfer channel of the multilayer. Although the ZZO/Ag/ZZO multilayer with a 16-nm-thick...
3.2 Transmittance and figure of merit value

Figure 2 shows optical transmittances of ZZO (40 nm)/Ag/ZZO (40 nm) multilayers as functions of Ag thicknesses. The transmittance of the multilayers is critically dependent on the Ag thickness. The ZZO/Ag/ZZO with a Ag thickness of 6 nm shows a low transparency, which may be due to the light scattering by randomly distributed Ag islands. The insertion of a 6–12 nm Ag layer caused a remarkable increase in the transmittance at wavelengths between 400 and 800 nm. For Ag thicknesses of 6 and 8 nm, relatively low transmittance were measured. Probably because of the surface plasmon resonance (SPR) effect of the Ag layer at the optimized thicknesses (10–12 nm), continuous increase in the Ag thickness causes an improvement of the transmittance. At an Ag thickness of 12 nm, the highest transmittance of ~85.6% was obtained in the wavelength range from 450 to 600 nm. However, further increase in the Ag thickness above 12 nm leads to a decrease in the transmittance, even though the multilayer with 16-nm-thick Ag possesses the lowest resistivity.

Figure 3 shows the average transmittance (T) in the wavelength range from 450 to 600 nm and the calculated figure of merit value (FOM, T^10/Rsheet) of the multilayers from the T value and sheet resistance (Rsheet). The ZZO/Ag (6 nm)/ZZO multilayer shows a very low FOM value owing to the low transmittance and high sheet resistance. The maximum FOM value (32.3 × 10⁻³ Ω⁻¹) of the ZZO/Ag (12 nm)/ZZO sample was obtained. However, further increase in the Ag thickness lowers the FOM value since the transmittances of the multilayers decrease significantly.

3.3 Microstructures and interface structures

3.3.1 XRD spectroscopy

Figure 4 shows XRD spectra obtained from ZZO (40 nm)/Ag/ZZO (40 nm) multilayers as functions of Ag thicknesses. Regardless of the Ag thickness, all of the XRD spectra display microcrystalline structures. The Ag (111) peak at ~38.3° starts to appear at an Ag thickness of 8 nm, there is no peak related to crystalline Ag. A crystalline Ag (111) peak at ~38.3° starts to appear at an Ag thickness of 10 nm. Increasing the Ag thickness from 10 to 16 nm results in the intensity of the Ag (111) peak. Despite the low room temperature during the Ag and ZZO sputtering process, the ZZO/Ag/ZZO multilayer is composed of microcrystalline structures.

3.3.2 XPS examinations

Figure 5(a) shows the XPS depth profiles of the optimized ZZO/Ag (12 nm)/ZZO multilayer on the PES substrate. The individual bottom ZZO, Ag, and top ZZO layers are well defined without interfacial reaction. The constant atomic concentration of Zn, O, Zr, and Ag atoms reveals that both bottom and top ZZO films were uniformly deposited onto the
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In this work, we proposed an indium-free ZZO/Ag/ZZO multilayer processed by continuous RF magnetron sputtering at room temperature. We obtained the optimized ZZO/Ag/ZZO multilayer with high-transmittance and a low sheet resistance by controlling the Ag thickness. This indicates that this new structure is a promising candidate for advanced optoelectronics applications due to the high transmittance, very low resistivity, low-cost elements, and low process temperature.

4. Conclusion

In this work, we proposed an indium-free ZZO/Ag/ZZO multilayer processed by continuous RF magnetron sputtering at room temperature. We obtained the optimized ZZO/Ag/ZZO multilayer with high-transmittance and a low sheet resistance by controlling the Ag thickness. This indicates that this new structure is a promising candidate for advanced optoelectronics applications due to the high transmittance, very low resistivity, low-cost elements, and low process temperature.

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REFERENCES