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The Influence of Ag Thickness on the Electrical and Optical Properties of ZnO/Ag/SnO_2 Tri-layer Films

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ABSTRACT

Transparent and conductive ZnO/Ag/SnO_2 (ZAS) tri-layer films were deposited onto glass substrates at room temperature by using radio frequency (RF) and direct current (DC) magnetron sputtering. The thickness values of the ZnO and SnO_2 thin films were kept constant at 50 nm and the value for Ag interlayer was varied as 5, 10, 15, and 20 nm. In the XRD pattern the diffraction peaks were identified as the (002) and (103) planes of ZnO, while the (111), (200), (220), and (311) planes could be attributed to the Ag interlayer. The optical transmittance and electrical resistivity were dependent on the thickness of the Ag interlayer. The ZAS films with a 10 nm thick Ag interlayer exhibited a higher figure of merit than the other ZAS films prepared in this study. From the observed results, a ZAS film with a 10 nm thick Ag interlayer was believed to be an alternative transparent electrode candidate for various opto-electrical devices.

Keywords: ZnO/Ag/SnO_2, Optical and electrical properties, Figure of merit, XRD, AFM.

1. Introduction

The increased usage of transparent and conductive oxide (TCO) films such as Sn doped In_2O_3 (ITO) for liquid crystal displays and solar cells has stimulated the development of an economical and efficient TCO film possessing a desirable high visible transmittance and low electrical resistivity. Thus, Ga doped ZnO (GZO) film was developed as a prospective substitute for conventional ITO films due to its high visible transmittance (≥80%) and relatively low electrical resistivity (≤1×10^{-2} Ωcm) [1,2]. However, it is known that relatively high post-deposition annealing temperatures are required to yield GZO films with adequate visible transmittance and low electrical resistivity for display applications. W. T. Yen reported that the electrical resistivity of GZO thin films deposited via pulsed DC magnetron sputtering decreased to values as low as 1.3×10^{-4} Ωcm at a post-annealing temperature of 300°C [3]. Although a high annealing temperature of 300°C could ensure GZO films with resistivity values comparable to ITO thin films, the process cannot be applied to the deposition of TCO film onto polymer substrates for flexible display devices. Recently, S. Heo reported that the influence of a Ni interlayer on the opto-electrical properties of GZO films and GZO 50 nm/Ni 2 nm/GZO 50 nm films deposited onto glass substrates yielded opto-electrical performance values higher than that of single layer GZO films [4]. In this study, new transparent and conducting ZnO/Ag/SnO_2 (ZAS) tri-layer films were prepared onto glass substrates to investigate the opto-electrical properties of the films as a function of Ag interlayer thickness. A 50 nm thick ZnO thin film is selected as a bottom layer due to room-temperature crystallization effect [4].

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Table 1. Experimental conditions for SnO_2 and ZnO/Ag/SnO_2 thin films.

Parameters	Condition
Base pressure (Torr)	6.0×10^{-7}
Deposition pressure (Torr)	1.0×10^{-3}
RF sputtering power (W/cm²)	ZnO : 6.0, SnO_2 : 2.5
DC sputtering power (W/cm²)	Ag : 1.6
Ar gas flow rate (sccm)	10
Film thickness (nm) SnO_2 single layer ZnO/Ag/SnO_2 tri-layer	100 50 / 5, 10, 15, 20 / 50
Deposition rate (nm/min) ZnO/Ag/SnO_2	10.0 / 25.5 / 10.0

2. Experimental Part

ZnO/Ag/SnO_2 tri-layer films and SnO_2 single layer films were deposited with RF and DC magnetron sputtering onto glass substrates (2×2 cm^2) at room temperature using ZnO (99.99% purity, 3 inch diameter), SnO_2 (99.99% purity, 3 inch diameter) and Ag targets (99.95% purity, 3 inch diameter), respectively. The substrates were cleaned via ultrasonication in acetone and ethanol for 10 min, respectively, followed by rinsing in deionized water. The glass substrates were dried under a flow of nitrogen gas. Prior to sputtering, the chamber was evacuated to 1×10^{-7} Torr and the sputtering of ZnO, Ag, and SnO_2 targets was performed under a pure Ar gas atmosphere. Table 1 shows the used target and sputtering conditions in this study.

After deposition, the thickness and crystallinity of the films was measured using a surface profiler (Dektak 150, Veeco), scanning electron microscope (SEM, JSM-6500, JEOL) and X-ray diffractometer at Korea Basic Science Institute (KBSI), Daegu center (XRD, Cu-Kα radiation, X'pert Pro MPD, PANalytical), respectively. Variations in surface morphology and root mean square (RMS) roughness as a function of Ag thickness were evaluated using an atomic force microscope over a 3×3 μm^2 scan area (AFM, XE-100, Park system). The electrical properties and optical transmittance over a wavelength range of 380–780 nm were measured using a Hall effect measurement system (HMS-3000, Ecopia) and a UV-visible spectrophotometer (Cary 100 Cone, Varian), respectively. Bare glass substrates yielded an optical transmittance of 93.1% within the visible wavelength range.

3. Results and Discussion

It is well known that the optical and electrical properties of TCO films are dependent on their crystal structure and surface roughness [4]. Thus, structural characterization is important to evaluate the opto-electrical performance of the ZAS films. Figure 1 shows a cross-sectional SEM image of a ZAS film with a 10 nm thick Ag interlayer and figure 2 shows the thickness profile of ZAS films with 5, 15, and 20 nm thick Ag interlayers.

Figure 3 shows XRD patterns of the ZAS films which possess varying Ag interlayer thicknesses. The ZnO bottom films revealed a strong (002) plane peak and a weak (103) plane peak, respectively. The full width at half maximum (FWHM) of the ZnO (002) peak remained constant at 0.6° regardless of Ag interlayer thickness. The Ag interlayer films revealed several diffraction peaks corresponding to (111),

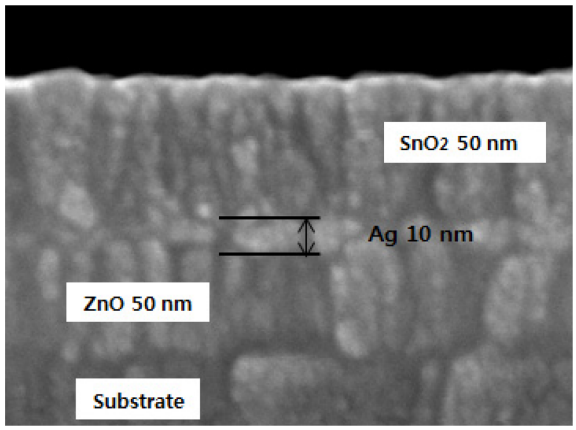

Fig. 1. SEM image of a ZAS film with a 10 nm thick Ag interlayer.

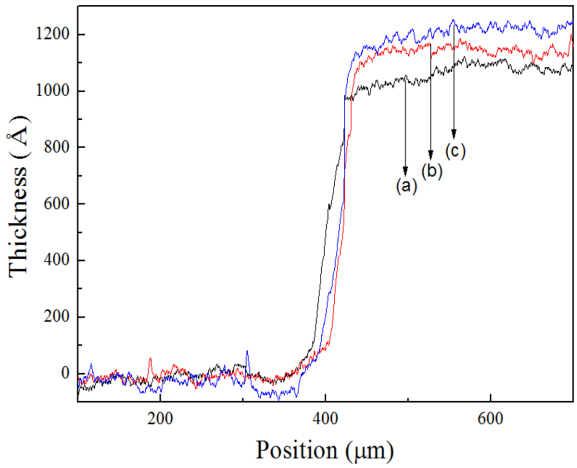

Fig. 2. The thickness profile of ZnO/Ag/SnO_2 tri-layer films. (a) ZnO 50 nm/Ag 5 nm/SnO_2 50 nm, (b) ZnO 50 nm/Ag 15 nm/SnO_2 50 nm, (c) ZnO 50 nm/Ag 20 nm/SnO_2 50 nm.

(200), (220), and (311) planes. As the Ag interlayer thicknesses increased from 5 to 20 nm, the FWHM of the Ag (111) peak decreased to as low as 0.59°. While both the ZnO and Ag interlayer exhibited characteristic diffraction peaks, the SnO_2 thin films did not exhibit any XRD peaks regardless of Ag interlayer thickness. Table 2 shows the crystallite size (D) of the Ag (111) plane evaluated by the Scherer formula for each film:

$$D = 0.9\ \lambda\ /\ B\ \mathrm{Cos}\ \theta, \quad (1)$$

where D is the crystallite size, λ is the X-ray radiation wavelength (Cu-Kα, 1.548 Å), B is the full width at half maximum (FWHM) of the characteristic diffraction peak, and θ is the Bragg angle of the diffraction peak [5]. As shown in Table 2, the crystallite size of the Ag interlayer increased proportionally with the thickness of the Ag thin film. In a previous study, J. Jeon reported that the crystallinity of the GZO film was enhanced by the Ni buffer layer [6]. However, it was concluded that the Ag interlayer may not enhance the crystallinity of the SnO_2 upper films deposited at room temperature.

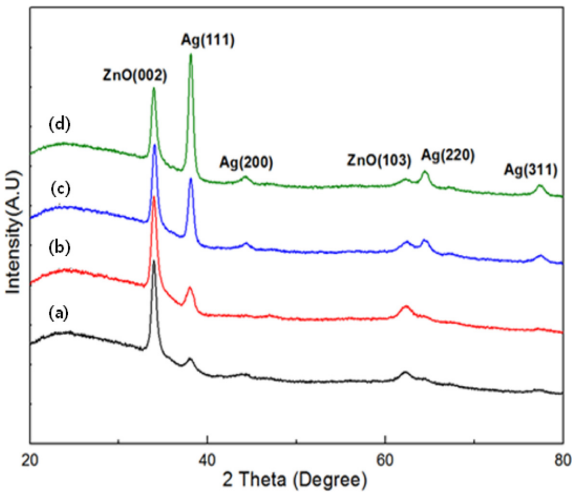

Fig. 3. XRD pattern of ZnO/Ag/SnO_2 tri-layer films. (a) ZnO 50 nm/Ag 5 nm/SnO_2 50 nm, (b) ZnO 50 nm/Ag 10 nm/SnO_2 50 nm, (c) ZnO 50 nm/Ag 15 nm/SnO_2 50 nm, (d) ZnO 50 nm/Ag 20 nm/SnO_2 50 nm.

Table 3 shows the electrical properties of a single 100 nm thick SnO_2 layer and ZAS tri-layer films. The SnO_2 thin films exhibited resistivity values 3.65×10^{-2} Ωcm higher than that of the ZAS tri-layer films. As the Ag interlayer thickness increased up to 20 nm, the electrical resistivity decreased to as low as 2.59×10^{-5} Ωcm with a carrier density of 1.48×10^{22} cm^{-3} and a mobility of 1.64 $cm^2\ V^{-1}s^{-1}$, respectively.

Figure 4 shows AFM images and the RMS roughness of the ZAS films. The films with 5 nm thick Ag films exhibited a RMS roughness of 1.41 nm and the films with 20 nm thick Ag films exhibited a higher RMS roughness of 1.88 nm. Thicker intermediate Ag thicknesses corresponded with a rougher surface morphology. From the XRD patterns, surface roughness was presumed to be affected by crystallization of the Ag interlayer. Y. Kim also reported a similar result that the crystallized Au buffer layer in ITO/Au bi-layer films increased the surface roughness of the ITO films [7].

Figure 5 shows the visible transmittance of the ZAS films. The films with 5, 15, and 20 nm thick Ag interlayers exhibited a decreased visible transmittance of 66.4, 69.2 and 63.0% due to increased reflection from the metal interlayer [8]. However, ZAS films with a 10 nm thick Ag interlayer exhibited a

Table 2. The crystallite size of Ag (111) plane in the ZnO/Ag/SnO_2 tri-layer films.

Film thickness (nm)	2 Theta (Degree)	FWHM (Degree)	Crystallite size (nm)
50 / 5 / 50	38.00	1.02	8.23
50 / 10 / 50	38.06	0.89	9.44
50 / 15 / 50	38.07	0.66	12.73
50 / 20 / 50	38.07	0.59	14.76

Table 3. Electrical properties of SnO_2 single layer and ZnO 50 nm/Ag 5-20 nm/SnO_2 50 nm tri-layer films.

Film thickness	Carrier density (cm^{-3})	Mobility ($cm^2\ V^{-1}S^{-1}$)	Resistivity (Ωcm)
SnO_2, 100 nm	5.49×10^{19}	3.11	3.65×10^{-2}
ZnO/Ag 5 nm/SnO_2	5.21×10^{21}	1.65	7.27×10^{-4}
ZnO/Ag 10 nm/SnO_2	7.09×10^{21}	7.30	1.21×10^{-4}
ZnO/Ag 15 nm/SnO_2	1.13×10^{22}	1.60	3.47×10^{-5}
ZnO/Ag 20 nm/SnO_2	1.48×10^{22}	1.64	2.59×10^{-5}

transmittance of 80.8%, which was higher than that of the other ZAS films. The visible transmittance was well known to be enhanced by 10-15 nm thick Ag interlayers on TCO/metal/TCO tri-layer films due to surface plasmon resonance (SPR) effects [9,10]. M. G. Varnamkhasti also reported similar optical properties in MoO_3/Ag/ITO tri-layer films [11]. In Table 3, although ZAS films with a 20 nm thick Ag interlayer exhibited the lowest resistivity of 2.59×10^{-5} Ωcm, a lower visible transmittance of 63.0% compared to the other films was a drawback that could deteriorate the optoelectrical performance of the ZAS films.

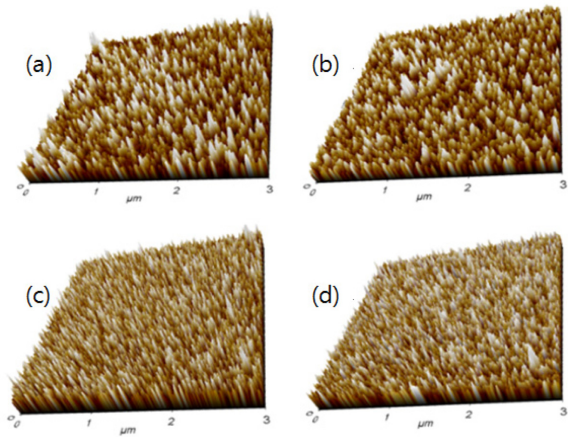

Fig. 4. Surface AFM images and RMS roughness of ZnO/Ag/SnO_2 tri-layer films (Scan area; 3×3 μm^2). (a) ZnO 50 nm/Ag 5 nm/SnO_2 50 nm RMS 1.41 nm, (b) ZnO 50 nm/Ag 10 nm/SnO_2 50 nm RMS 1.54 nm (c) ZnO 50 nm/Ag 15 nm/ SnO_2 50 nm RMS 1.68 nm, (d) ZnO 50 nm/Ag 20 nm/SnO_2 50 nm RMS 1.88 nm.

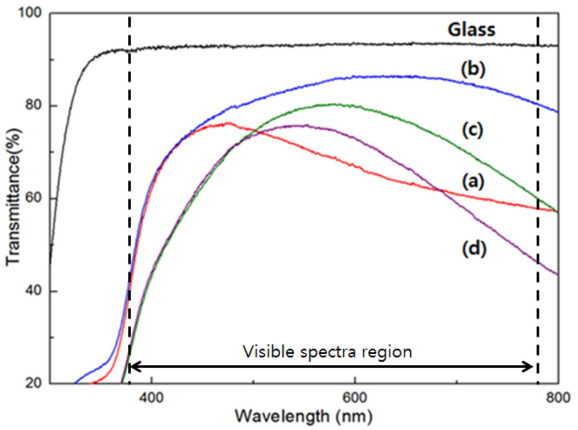

Fig. 5. The visible transmittance of ZnO/Ag/SnO_2 tri-layer films. (a) ZnO 50 nm/Ag 5 nm/SnO_2 50 nm, (b) ZnO 50 nm /Ag 10 nm/SnO_2 50 nm, (c) ZnO 50 nm/Ag 15 nm/SnO_2 50 nm, (d) ZnO 50 nm/Ag 20 nm /SnO_2 50 nm.

To consider the effects of the Ag interlayer on the optoelectrical performance of the ZAS thin films, figures of merit (FOM) of the SnO_2 and ZAS films were evaluated in Table 4. The FOM defined by G. Haacke [12] was:

$$FOM = T^{10} / Rs, \quad (2)$$

where T is the average visible transmittance and Rs is the sheet resistance [5]. The SnO_2 single layer films exhibited an Rs of 3650 Ω/□ and the ZAS films with a 5 nm thick Ag interlayer exhibited a decreased Rs of 69.2 Ω/□, respectively. As the Ag interlayer thickness increased up to 20 nm, the Rs value decreased to as low as 2.2 Ω/□. In Table 4, although ZAS films with a 20 nm thick Ag interlayer exhibited the lowest Rs values, ZAS films with a 10 nm thick Ag interlayer exhibited a higher FOM of 1.08×10^{-2} Ω^{-1} compared to the other films due to a low Rs of 11.0 Ω/□; a high visible transmittance of 80.8% was also observed in this study.

4. Conclusions

SnO_2 single layer and ZnO/Ag/SnO_2 (ZAS) tri-layer films with different Ag thickness values were deposited onto glass substrates via RF and DC magnetron sputtering. The electrical and optical properties of the films were found to depend on the thickness of the Ag interlayer. ZAS films with a 10 nm thick Ag interlayer exhibited a higher figure (1.08×10^{-2} Ω^{-1}) of merit than the other films.

From the observed figure of merit, it was concluded that ZAS tri-layer films with a 10 nm Ag

Table 4. Figure of merit of SnO_2 single layer and ZnO 50 nm/Ag 5-20 nm/SnO_2 50 nm tri-layer films.

Film Thickness	Visible transmittance [%]	Sheet resistance [Ω/□]	Figure of merit [Ω^{-1}]
SnO_2, 100 nm	81.8	3650	3.69×10^{-5}
ZnO/Ag 5 nm/SnO_2	66.4	69.2	2.42×10^{-4}
ZnO/Ag 10 nm/SnO_2	80.8	11.0	1.08×10^{-2}
ZnO/Ag 15 nm/SnO_2	69.2	3.0	8.36×10^{-3}
ZnO/Ag 20 nm/SnO_2	63.0	2.2	4.74×10^{-3}

inter-layer exhibited higher optoelectronic performance than the SnO_2 single layer and another ZAS films. Thus, ZnO 50 nm/Ag 10 nm/SnO_2 50 nm tri-layer films could be used as substitute TCO films in the place of conventional ITO thin films.

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