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Characteristics of indium-free ZTO/Ag/ZTO multilayer electrode grown on glass substrate at room temperature

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Transparent conducting films having a hybrid structure of ZTO/Ag/ZTO were prepared on glass substrates by sequential deposition using RF/DC magnetron sputtering at room temperature. The electrical and optical properties of hybrid transparent conducting films were investigated with varying the thickness of Ag and ZTO layers. In order to estimate and compare with the experimental results, the simulation program, EMP (Essential Macleod Program) was adopted. With increasing the Ag thickness, hybrid films showed a noticeable improvement of the electrical conductivity, which is mainly dependent on the electrical characteristic of the Ag layer. ZTO (40 nm) / Ag (12 nm) / ZTO (40 nm) film exhibits a sheet resistance of 5.39 Ω/sq. with an optical transmittance of 89%. This indicates that indium - free ZTO/Ag/ZTO multi layer electrodes are a promising low-cost and low-temperature processing electrode scheme.

Key words: TCO, ZTO, ZTO/Ag/ZTO, EMP, Multilayer.

Introduction

Transparent conducting oxide (TCO) thin film are used as transparent electrodes for flat panel displays, solar cells and various optical devices. Among many TCO materials, indium tin oxide (ITO) has been paid much attention because it is widely used for transparent conductive electrodes in optical devices [1-7]. However, ITO film is sputtered at a fairly high substrate temperature of more than 300 °C [8]. In addition, the high cost of indium, which is the main component in ITO, is critical problem for the application using ITO electrodes. For this reason, various indium free TCOs thin films such as Ga - ZnO, Al - ZnO, ZnO - SnO_2 have been extensively investigated as replacements for the ITO electrode [9-10]. Recently, TCO/metal/TCO multilayer structures have been designed to achieve both high conductivity and high transmittance [11]. Furthermore, TCO/metal/TCO multilayer structures have better bending performance when deposited on flexible substrates, which indicates that such structures are a potential candidate to apply in the flexible electronics [12].

In this work, ZTO / Ag / ZTO multilayer on glass substrates was prepared by RF and DC magnetron sputtering at room temperature. The structural, electrical, optical properties of indium-free ZTO / Ag / ZTO multilayer film were systematically evaluated at different thickness of the Ag and ZTO layers. In order to estimate and compare with the experimental results, the simulation program, the Essential Macleod program (EMP), was adopted.

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Experimental

The ZTO/Ag/ZTO multilayer electrodes were deposited by RF magnetron and DC magnetron sputtering at room temperature on glass substrates. The ZTO target was fabricated using high purity ZnO (99.99%) and SnO_2 (99.99%) powders with an weight ratio of ZnO: SnO_2 of 65 : 35. More details about the sputtering conditions are given in Table 1. Deposition conditions were maintained carefully stable during the growth of ZTO/Ag/ZTO multilayer films.

For optical characterization, the EMP was adopted and the calculated results were compared with measured optical properties [12]. The simulation with variable parameters such as wavelength (400-700 nm) and thickness

Table 1. Deposition parameters and sputtering condition of ZTO/Ag/ZTO multilayer film.

Deposition parameter	Sputtering condition	
Target	ZTO ($ZnO : SnO_2$ = 65 : 35 wt%)	Ag (99.99%)
Base pressure	5×10^{-5} torr	
Working pressure	2.5×10^{-2} torr	
Substrate	Glass	
Substrate temperature	Room Temperature	
Deposition rate	2.5 nm/min.	0.7 nm/sec.
RF/DC Power	RF 100 W	DC 100 W
Working gas	Ar 50 sccm	

of layers [Glass / ZTO / Ag / ZTO] was designed.

The thickness of the ZTO layer was varied between 20-60 nm and Ag layer was varied between 6 and 18 nm. Film thickness was determined by the Alpha-step. The electrical resistivity of the films was obtained using a four-point probe method. The optical transmission spectra were measured in the wavelength ranging from 400-700 nm by a spectrophotometer. The crystal structure of the films was analyzed by X-ray diffraction. In addition, the interfacial properties of the optimized ZTO (40 nm) / Ag (12 nm) / ZTO (40 nm) electrodes were analyzed using AES depth profiling.

Result and discussion

Fig. 1 shows the sheet resistance and resistivity of ZTO / Ag / ZTO multilayer film grown on a glass substrate with 40 nm thickness of the bottom and top ZTO films as a function of the Ag thickness. The sheet resistance of single ZTO layer film with a thickness of 80 nm was about 5.7×10^5 ohm/sq. due to the low substrate temperature. However, after Ag layer between the ZTO layers was placed, the sheet resistance reduced rapidly without any post annealing process. The sheet resistance and resistivity of the ZTO/Ag/ZTO multilayer film decreased systematically with increasing Ag thickness.

Fig. 2(a) shows the simulation results of optical transmittance on the ZTO / Ag / ZTO multilayer film as a function of Ag thickness. The optical simulation was carried out by means of an EMP. It was shown that the insertion of the Ag layer from 6 to 12 nm between ZTO layers led to an increase in the optical transmittance, especially in the wavelength range 400-700 nm. However the thickness of the Ag layer increases more than 12 nm, the transmittance of the ZTO / Ag / ZTO multilayer film became decreased.

Fig. 2(b) shows the measured optical transmittance of the ZTO/Ag/ZTO multilayer films as function of the Ag thickness. As shown in the result of simulated optical transmittance, the transmittance of ZTO / Ag / ZTO multilayer films is sensitive to the thickness of the Ag layer. It is shown that the transmittance was systematically increased with increasing the Ag layer thickness from 6 to 12 nm. The transmittance of multilayer films with Ag thickness of 6 nm and 12 nm at exhibited 84 and 89% a 550 nm wavelength respectively. However, a further increase of Ag thickness resulted in a decrease of transmittance, due to higher light reflectance.

Fig. 3 shows the calculated figure of merit (ϕ_{TC}). In

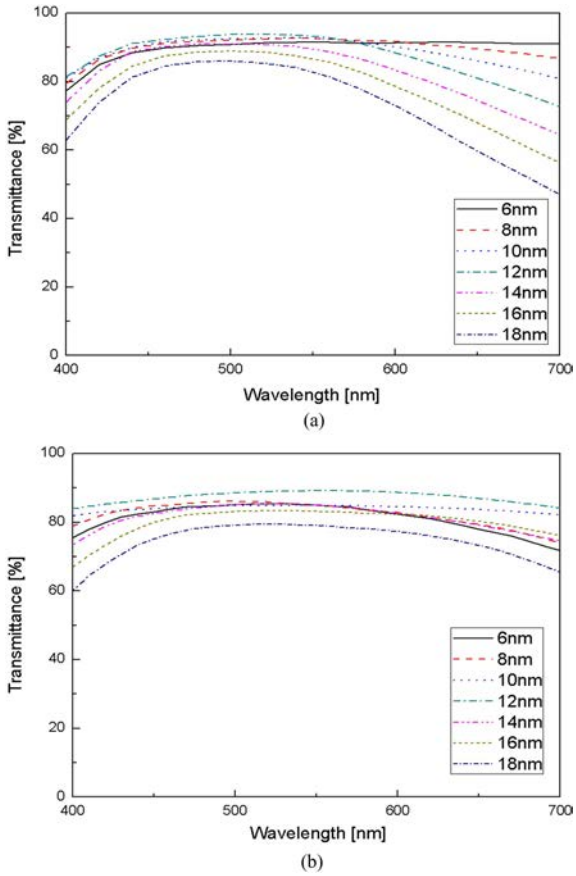

Fig. 2. (a) Simulated optical transmittance of the ZTO/Ag/ZTO multilayer film using EMP program as a function of Ag Thickness and (b) Measured optical transmittance of the ZTO/Ag/ZTO multilayer as a function of the Ag thickness.

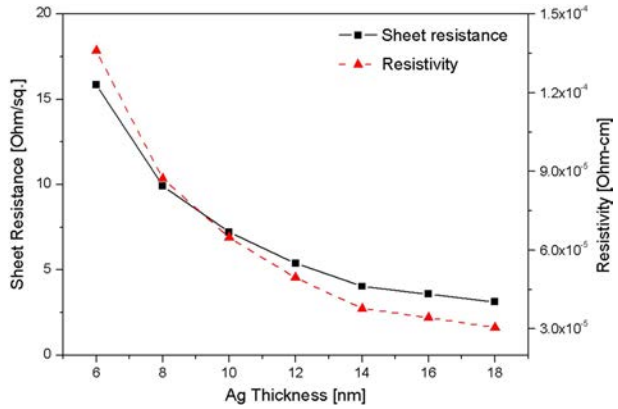

Fig. 1. Sheet resistance and resistivity of the ZTO/Ag/ZTO multilayer film as a function of Ag thickness in the range of 6 -18 nm.

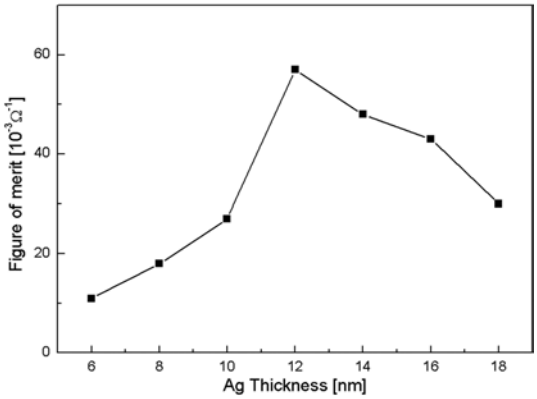

Fig. 3. Figure of merit of ZTO/Ag/ZTO multilayer film as a function of the Ag thickness in the range of 6 - 18 nm.

transparent conductor applications, optimization the coating parameter lays a key role on electric and optical characteristics. However, they are inversely correlated to each other. Hence the optimum value of these two parameters should be established using figure of merit. The most commonly used definition of figure of merit f_{TC} of a transparent conducting film was first given by Haacke [13] as:

$$\phi_{TC} = T^{10}/R_{sh} \quad (1)$$

Where T is the transmittance at a particular wavelength and R_{sh} is the sheet resistance of transparent conducting oxide. It was shown that the ϕ_{TC} value of the ZTO/Ag/ZTO multilayer film increases with increasing Ag thickness. Maximum ϕ_{TC} value ($57 \times 10^{-3}\Omega^{-1}$) of the ZTO/Ag/ZTO multilayer film could be obtained at an Ag thickness of 12 nm (T: 0.89 and R_{sh}: 5.39 Ω/sq.). However, as Ag thickness increased further, f_{TC} value became decrease due to transmittance decrease by the Ag metal layer.

Fig. 4 shows the sheet resistance and resistivity of ZTO/Ag/ZTO multilayer film as a function of the ZTO thickness at a constant 12 nm thickness of the Ag film. The sheet resistant of ZTO/Ag/ZTO multilayer film was maintained constantly without effect of ZTO layers thickness because the conductivity of the oxide/Ag/oxide multilayer is mainly affected by the Ag layer [9]. The thickness of the oxide layer in the oxide/Ag/oxide multilayer electrode is only of minor importance for the electrical properties of the multilayer electrode [14]. However, as the ZTO layer increased, the resistivity also increased continuously. The lowest resistivity of $2.87 \times 10^{-5}\Omega \cdot$ cm was obtained for the ZTO(20 nm) / Ag(12 nm) / ZTO(20 nm) multilayer. The increase in resistivity can be understood by Eq. (2).

$$R = 4.53V/I = \rho/d \quad (2)$$

The sheet resistance R and the resistivity ρ of the films were determined as a function of deposition parameters using four-point probe method. R was calculated by Eq. (2), which contains the calibration factor of the four-point system and the resistivity ρ was calculated using the optically derived thickness in the formula [15].

Fig. 5(a) shows the optical transmittance simulation result of the ZTO/Ag/ZTO multilayer film as a function of top and bottom ZTO thickness. The increase of the ZTO thickness from 20 to 40 nm, the peak transmittance also increased, because a ZTO thin film layer prevents Ag layer from being oxidized and plays role in the antireflection layer to block the reflected light. However, the ZTO layers thicker than 40nm resulted in a decrease of peak transmittance. Additionally the peak transmittance shifts towards the long wavelength regions when the thickness of the ZTO layers is further increased.

Fig. 5(b) shows the measured optical transmittance of ZTO/Ag/ZTO thickness. Like the simulated optical transmittance result, the increase of the ZTO thickness from 20 to 40 mn, the transmittance increased, also a further increase of ZTO thickness resulted in a decrease of transmittance.

Fig. 6 shows calculated figure of merit with increasing ZTO layers by Eq. (1). It was shown that the

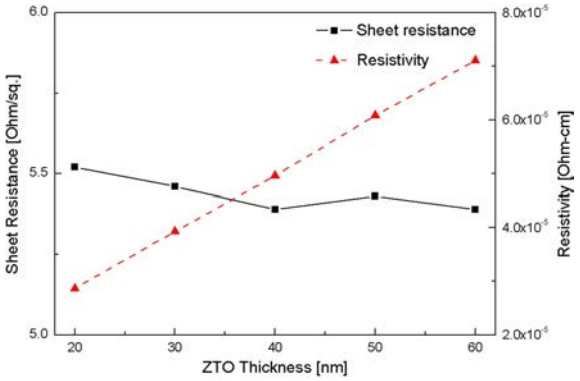

Fig. 4. The sheet resistance and resistivity of ZTO/Ag/ZTO multilayer film as a function of the ZTO thickness.

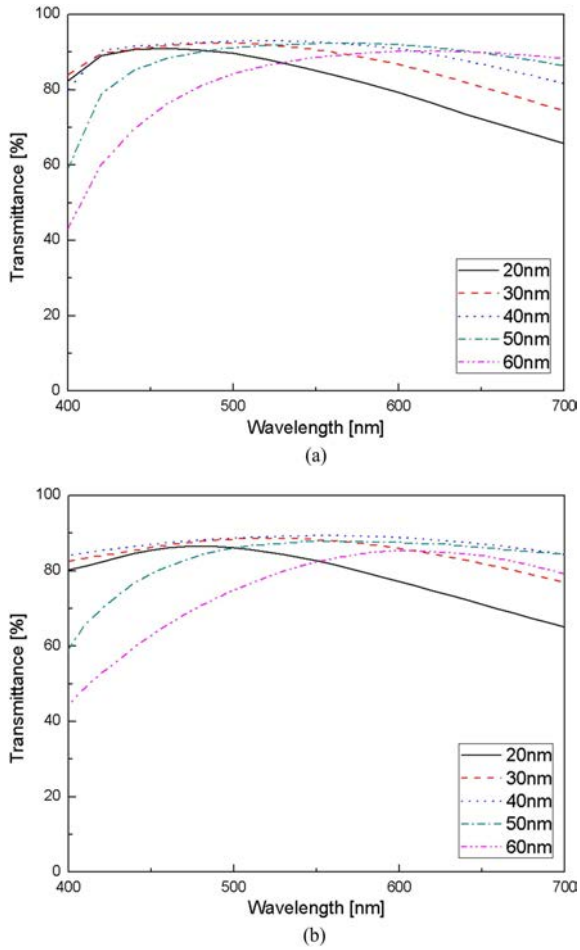

Fig. 5. The optical transmittance of the ZTO/Ag/ZTO multilayer film as a function of the ZTO thickness ; (a) the simulated by EMF and (b) measured by spectrophotometer.

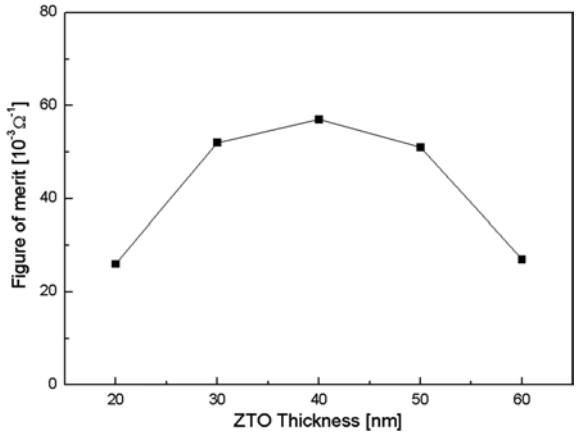

Fig. 6. Figure of merit of ZTO/Ag/ZTO multilayer film as a function of the ZTO thickness in the range of 20 - 60 nm.

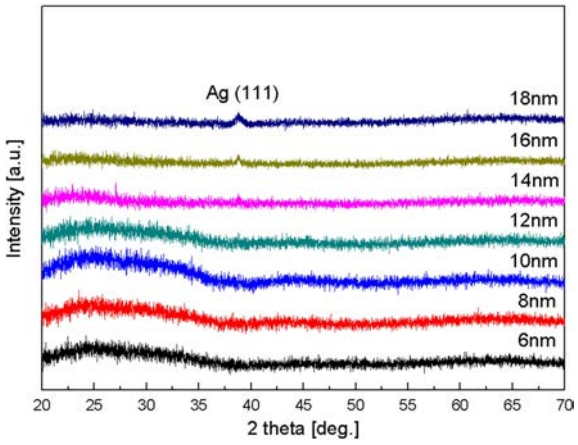

Fig. 7. The XRD diffraction patterns of the ZTO/Ag/ZTO multilayer films as a function of Ag thickness.

ϕ_{TC} value of the ZTO/Ag/ZTO multilayer film increases with increasing from 20 to 40 nm ZTO thickness. More than 40 nm of ZTO thickness resulted in a decrease of figure of merit decreased transmittance. The highest ϕ_{TC} value of ZTO/Ag/ZTO multilayer film was obtained at a ZTO thickness of 40 nm.

Fig. 7 shows the XRD patterns of the ZTO/Ag/ZTO multilayer films as a function of the Ag thickness from 6 to 18 nm. Up to a thickness of 12 nm, there was no peak related to crystalline of ZTO or Ag. As seen in Fig. 7, the XRD pattern of the ZTO/Ag/ZTO multilayer film exhibit the typical amorphous structure of the ZTO and Ag layers. At an Ag thickness of 14 nm, a crystalline Ag (111) peak appeared. In addition, it was found that the Ag (111) peak increased with increase the thickness of the Ag layer in the ZTO/Ag/ZTO multilayer film.

An AES depth profile result obtained optimized ZTO(40 nm) / Ag(12 nm) / ZTO(40 nm) multilayer film on a glass substrate is shown Fig. 8. The AES depth profile shows well-defined top ZTO, Ag and bottom ZTO layers. In addition, symmetrical features of the top and bottom ZTO films show the existence of identical ZTO layers with the same composition and

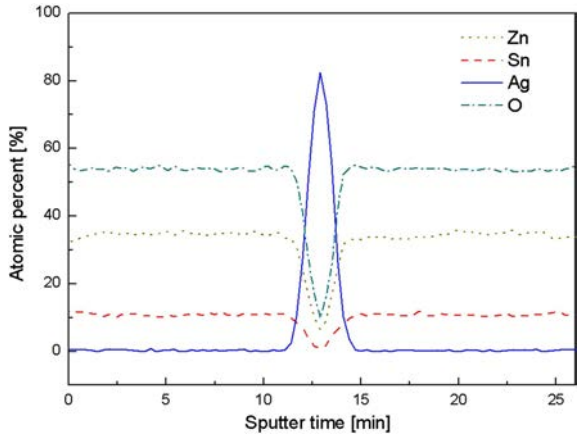

Fig. 8. AES depth profiles of ZTO/Ag/ZTO multilayer film grown on a glass substrate under optimized condition.

thickness. However, 82 atomic % was obtained in Ag layer due to the interfacial reactions between Ag and O in the the ZTO/Ag/ZTO miltilayers. It is noted that a blocking layer is needed to inhibit the oxidation of Ag layer in ZTO/Ag/ZTO multilayer.

Conclusion

ZTO/Ag/ZTO multilayer film was grown on glass substrate by RF/DC magnetron sputtering at room temperature. The structural, electrical and optical properties of the multilayer at different thickness of the Ag and ZTO layers were systematically studied. ZTO/Ag/ZTO multilayer film with a low sheet resistance and high transmittance was obtained by controlling the thickness of the Ag layers. The multilayer film with the thickness of ZTO(40 nm) / Ag(12 nm) / ZTO(40 nm) exhibits the maximum figure of merit of $57 \times 10^{-3}\,\Omega^{-1}$ with a sheet resistance 5.39 Ω/sq. and an transmittance of 89% at 550 nm wavelength, having satisfactory properties for applications such as transparent conducting electrodes.

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