

# Fabrication of High-Performance Silver-Based Transparent-Electrode Films on ITO Multilayer Structures

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## ABSTRACT

A high-performance transparent-electrode film with a silver-based (Ag) sandwich structure in between an ITO (tin-doped indium oxide) multilayer was deposited on a glass substrate by DC magnetron sputtering at room temperature. The optical and electrical properties of single layers of Ag and of ITO and multilayer structures of ITO/Ag/ITO (S1), ITO/Ag/ITO/Ag/ITO (S2) and ITO/Ag/ITO/Ag/ITO/Ag/ITO (S3) were investigated by spectrophotometer and four-point probe, respectively. These properties were studied as-deposited and after annealing in a vacuum. It was found that the optical transmittance and the sheet resistance of the Ag film decreased when the film thickness increased. However, the optical transmittance of the Ag film could be enhanced by a sandwich structure composed of ITO/Ag/ITO. The average optical transmittance in the visible and near infrared range of S1 and S2 decreased when the film systems were annealed in a vacuum. The sheet resistance of S2 was lower than that of S1 and S3 for the as-deposited process, while the sheet resistance of S1 was lower than that of S2 and S3 after annealing in a vacuum. These results depended on the characteristics of the multilayer electrodes and on structural improvements of the Ag and ITO components after annealing the films.

**Key words:** indium tin oxide, silver, annealing, multilayer, DC magnetron sputtering

## INTRODUCTION

Tin-doped indium oxide (ITO) thin film belongs to the class of wide-gap n-type semiconductors ( $E_g \approx 4$  eV), with good conductivity and high optical transmittance across the visible spectrum; it is widely used as a transparent, conductive electrode in flat panel displays, electrochromic devices or photovoltaic solar cells (Betz *et al.*, 2006; Granqvist, 2007; Lungenschmied *et al.*, 2007). However, the ITO

films prepared at room temperature using conventional magnetron sputtering have a relatively high electrical resistivity ( $\geq 1 \times 10^{-3} \Omega \cdot \text{cm}$ ) (Fahland *et al.*, 2001; Aiempanakit *et al.*, 2008). High-quality ITO films are commonly obtained by annealing at high temperature ( $>300^\circ\text{C}$ ) in a vacuum during or after the deposition process. The annealing can lead to material crystallization, reducing the crystalline structure defect, and increasing oxygen vacancies in ITO films, resulting in high transparent and conductive films

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(El Hichou *et al.*, 2004; Lee and Park, 2004; Guillén and Herrero, 2006, 2007). After annealing, the electrical resistivity of ITO as low as  $2\text{-}3 \times 10^{-4} \Omega\cdot\text{cm}$  and optical transmittance in the visible spectrum above 90% have been reported for thicknesses around 300 nm (El Hichou *et al.*, 2004; Lee *et al.*, 2004; Guillén and Herrero, 2006). On the other hand, improving the properties of ITO films for flexible optoelectrical applications has used ITO/metal/ITO (IMI) multilayer structures, which have a lower resistivity than single-layer ITO films of the same thickness. Silver (Ag) is a first choice because it has the lowest resistivity of all materials (below  $2 \times 10^{-6} \Omega\cdot\text{cm}$  at room temperature) for the bulk of the material (Lide, 1995).

In the current study, single-layer Ag and ITO films, and multilayer structures of ITO/Ag/ITO (S1), ITO/Ag/ITO/Ag/ITO (S2), and ITO/Ag/ITO/Ag/ITO/Ag/ITO (S3) were deposited on glass substrate by DC magnetron sputtering at room temperature. The optical and electrical properties of films have been analyzed and compared between as-deposited and annealing in vacuum. The objective was to determine the interdependence between optical and electrical parameters for each multilayer structure before and after annealing.

## MATERIALS AND METHODS

The Ag and ITO films were prepared by

DC magnetron sputtering on glass substrate at room temperature using an Ag target (99.9% in purity, 3 inch in diameter, and 0.25 inch thick) and an ITO target composite mixture of 90wt%  $\text{In}_2\text{O}_3$  and 10wt%  $\text{SnO}_2$  (99.99% in purity, 3 inch in diameter and 0.25 inch thick). The glass substrates were ultrasonically cleaned in acetone and deionized water before deposition.

The sputtering processes were performed in mixed  $\text{Ar-O}_2$  (99.99% in purity) separately controlled by a mass flow controller. The gas flow rates of argon and oxygen were fixed at 50 sccm (standard cubic centimeter per minute) and 0.5 sccm, respectively for coating the ITO films, with only argon gas at a flow rate of 50 sccm for coating the Ag films. The distance between the target and glass substrate was 8.6 cm and the DC power was kept constant at 50 W and 100 W for coating the ITO and Ag films, respectively. A turbo-molecular pump coupled with a rotary pump was used to achieve a base pressure of  $6 \times 10^{-4}$  Pa before introducing the Ar or  $\text{Ar-O}_2$  mixture at a working pressure of about  $5 \times 10^{-1}$  Pa for sputtering in both cases. The film thicknesses of the ITO and Ag films were measured with a Dektak surface profiler. In this work, the coating rate of the Ag and ITO films was about 2.2 and 0.4 nm/s, respectively.

Three structures of film systems were prepared: ITO/Ag/ITO (S1), ITO/Ag/ITO/Ag/ITO (S2) and ITO/Ag/ITO/Ag/ITO/Ag/ITO (S3). The conditions of the film coatings are shown in Table 1. The thicknesses of the ITO and Ag films

**Table 1** Conditions of film coatings for single and multilayer structures.

Specimen	Ar:O <sub>2</sub> (sccm)	DC power (W)	Film thickness (nm)
Ag	50:0	100	7-15
ITO	50:0.5	50	120
(S1), ITO/Ag/ITO	(ITO) 50:0.5 (Ag) 50:0	(ITO) 50 (Ag) 100	(ITO) 60 (Ag) 15
(S2), ITO/Ag/ITO/Ag/ITO	(ITO) 50:0.5 (Ag) 50:0	(ITO) 50 (Ag) 100	(ITO) 40 (Ag) 7.5
(S3), ITO/Ag/ITO/Ag/ITO/Ag/ITO	(ITO) 50:0.5 (Ag) 50:0	(ITO) 50 (Ag) 100	(ITO) 30 (Ag) 5

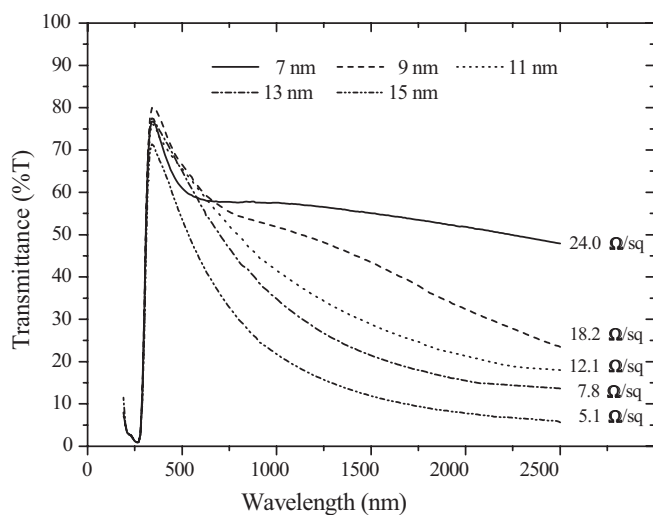
in the film systems were fixed at 120 and 15 nm, respectively. The optical transmittance spectra in the UV-Vis-NIR region and the electrical properties of film systems were investigated by a spectrophotometer (UV-3100 Shimadzu Corporation, Japan) in the wavelength range 200–2500 nm and a linear four-point probe (Jandel model RM3, England), respectively, before- and after annealing films in a vacuum (2 Pa) at 350°C for 1 h.

## RESULTS AND DISCUSSION

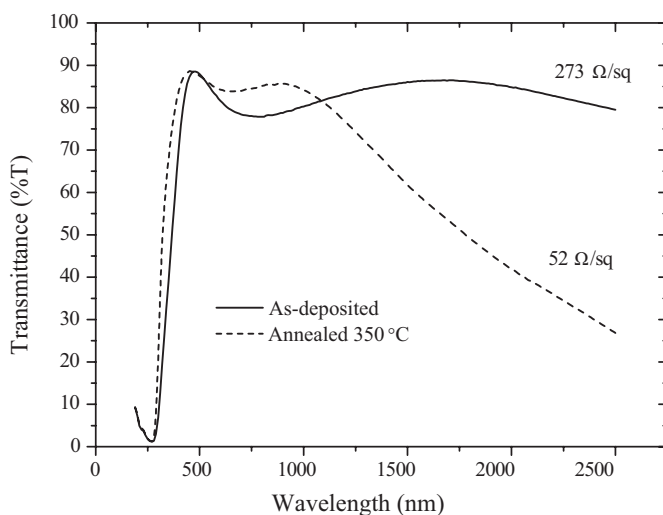
Figure 1 shows the optical transmittance spectra and the sheet resistance values of Ag films with different film thicknesses. The optical transmittance decreased with increasing film thickness; the variation may correspond with the growth of the Ag film. It has been shown that most metal films will be deposited from metallic islands that are initially isolated. They grow large enough to connect to each other until finally complete coverage of the whole area is achieved (Sun *et al.*, 2007). When the equivalent thickness is small, the metallic film consists of isolated metallic particles. Light passing through the film is attenuated by scattering, so the reflectance is low

and the transmittance is high corresponding to a minimum film thickness. The sheet resistance of the Ag film decreased with increasing film thickness because the higher thickness of Ag films produces electrical properties that are nearly as good as for Ag in bulk.

Figure 2 shows the optical transmittance spectra and sheet resistance values of ITO films of 120 nm thickness before- and after annealing the film in a vacuum at 350°C for 1 h. It shows that the annealing process enhanced the optical transmittance of ITO films, especially within the visible range (400–800 nm). For wavelengths above 1,000 nm, the optical transmittance of annealed ITO films was lower than the as-deposited film. The decrease in optical transmittance of annealed ITO films at long wavelengths is attributed to the increase in free carrier absorption. This effect can be explained by a Moss-Burstein shift. The absorption edge of the ITO film shifted to the lower wavelength after annealing the film in a vacuum (Hamberg and Granqvist, 1986), due to the increase in the energy gap, which depended on the carrier concentration (Equation 1), and it corresponded with the decrease in sheet resistance.



**Figure 1** Transmittance spectra of Ag for different film thicknesses.



**Figure 2** Transmittance spectra of ITO films for 120 nm thick before- and after annealing the film in a vacuum at 350°C for 1 h.

$$E_g - E_{g0} = \frac{h}{2m^*} (3\pi^2 n_e)^{2/3} \quad (1)$$

where,  $E_{g0}$  is the intrinsic band gap;  $m^*$  is the electron effective mass; and  $n_e$  is the electron concentration.

Based on Equations 2 and 3, the sheet resistance of the ITO film decreased, so the electron concentration increased after annealing the film in a vacuum, due to increased oxygen vacancies and activation of the  $\text{Sn}^{4+}$  in the ITO film (Morikawa and Fujita, 2000).

$$R_s = \frac{\rho}{d} \quad (2)$$

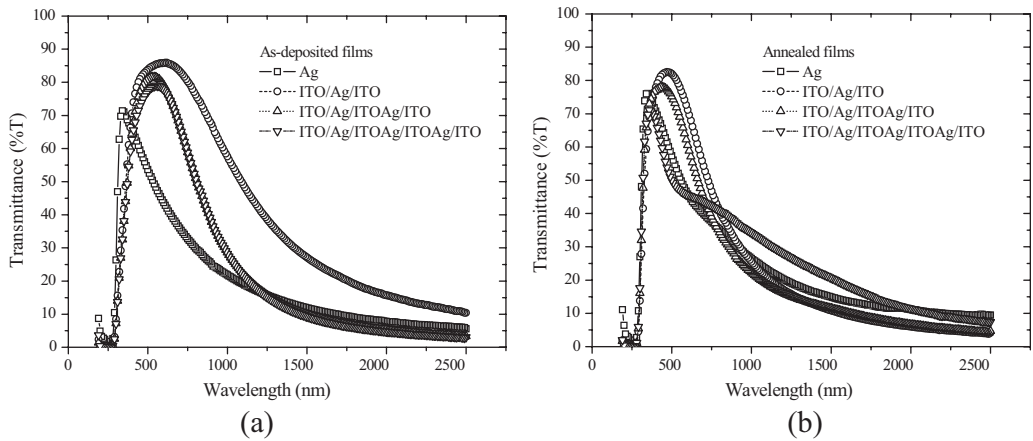
$$\rho = \frac{1}{en_e\mu} \quad (3)$$

where:  $R_s$  is sheet resistance;  $d$  is film thickness;  $\rho$  is resistivity;  $e$  is electron charge;  $n_e$  is electron concentration and  $\mu$  is carrier mobility.

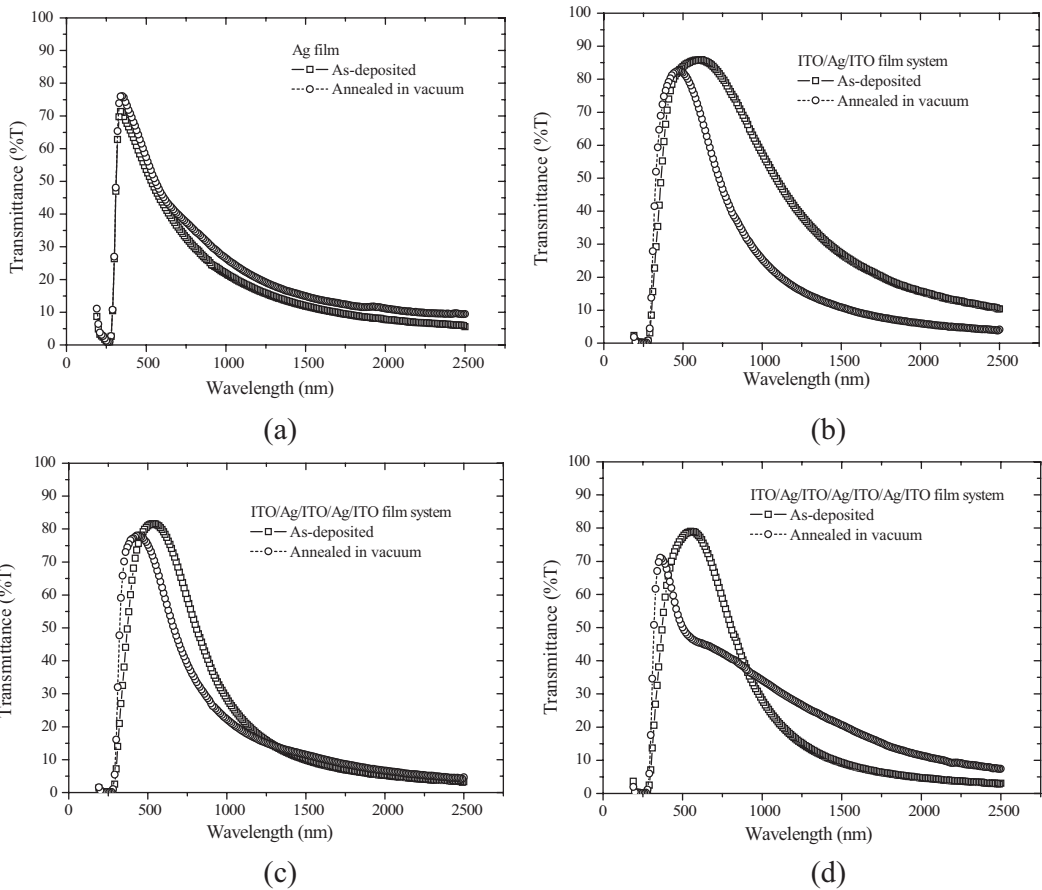
Figure 3 shows the optical transmittance spectra for as-deposited and annealing processes of the Ag film and film systems of S1, S2 and S3. The optical transmittance of the Ag film was enhanced by the sandwich structures, which were composed of ITO/Ag/ITO. However, increasing

the number of film layers increased the optical scattering at the boundary of each layer. Therefore, the optical transmittance of the film systems decreased with an increase in the number of film layers from S1 to S3 (Table 2).

Figure 4 shows the comparison of transmittance spectra for as-deposited and annealing film in a vacuum at 350°C for 1 h for the Ag film, S1, S2 and S3 film systems. The optical transmittance of the Ag film slightly increased, while the film systems decreased after annealing. The absorption edge of the pure Ag films was unaltered, while the film systems shifted towards a wider band gap because the band gap energy had increased and the carrier trap sites had decreased due to the reduction in structural defects. For the S3 system, the thickness of each Ag layer was 5 nm, which was less than the thickness of the Ag layer in the S1 and S2 systems. Therefore, oxygen atoms from the ITO films may have been able to diffuse into the Ag layers, which would have caused degradation of the Ag films after annealing and increased the optical transmittance in the near infrared range.



**Figure 3** Transmittance spectra of Ag, ITO/Ag/ITO (S1), ITO/Ag/ITO/Ag/ITO (S2) and ITO/Ag/ITO/Ag/ITO/Ag/ITO (S3) film systems for: (a) as-deposited; and (b) annealing films in a vacuum at 350°C for 1 h.



**Figure 4** Comparisons of transmittance spectra for as-deposited film and annealing film at 350°C for 1 h of: (a) Ag; (b) ITO/Ag/ITO (S1); (c) ITO/Ag/ITO/Ag/ITO (S2); and (d) ITO/Ag/ITO/Ag/ITO/Ag/ITO (S3) films.

**Table 2** Optical and electrical properties of Ag, ITO/Ag/ITO, ITO/Ag/ITO/Ag/ITO and ITO/Ag/ITO/Ag/ITO/Ag/ITO film systems for as-deposited and annealing films.

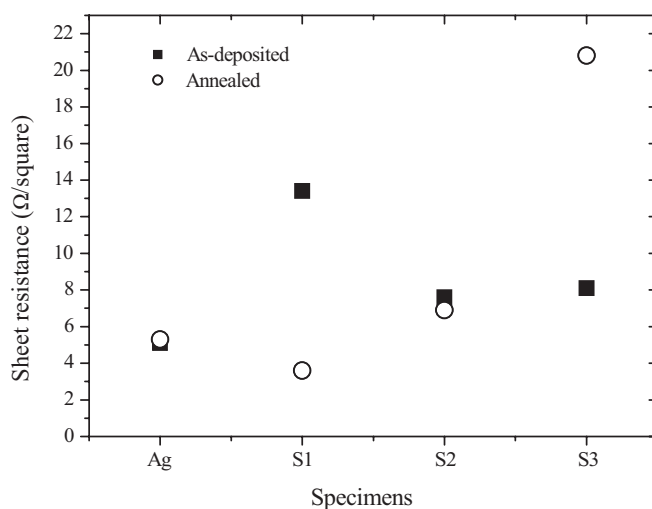
Specimen	Conditions	%T <sub>Vis</sub>	%T <sub>NIR</sub>	R <sub>s</sub> (Ω/sq)
Ag	As-deposited	47	20	5.1
	Annealed	50	24	5.3
(S1) ITO/Ag/ITO	As-deposited	82	51	13.4
	Annealed	69	24	3.6
(S2) ITO/Ag/ITO/Ag/ITO	As-deposited	73	27	7.6
	Annealed	61	21	6.9
(S3) ITO/Ag/ITO/Ag/ITO/Ag/ITO	As-deposited	71	26	8.1
	Annealed	49	31	20.8

Figure 5 shows the comparison of sheet resistance for the as-deposited and annealing film processes. After annealing the film, the sheet resistance of S1 was lower than that of S2 and S3, with the lowest value being 3.6 Ω/sq. The sheet resistance of S2 slightly decreased after annealing the film. However, the sheet resistances for both cases of S2 were lower than for S1 and S3 for the films as-deposited. The sheet resistance of S3 significantly increased after annealing the film, perhaps due to degradation of the Ag layers from diffused oxidation. Based on film resistance, the film system of S2 was better than that of S1 and

S3 for the film as-deposited, while the S1 system was better than S2 and S3 for the annealing film process.

## CONCLUSION

Ag and ITO films were deposited by DC magnetron sputtering at room temperature with single-layer Ag and ITO films and multilayer structures of ITO/Ag/ITO (S1), ITO/Ag/ITO/Ag/ITO (S2) and ITO/Ag/ITO/Ag/ITO/Ag/ITO (S3). The optical property of each film system depended on the multilayer structure of the film as-deposited

**Figure 5** Sheet resistances of Ag, ITO/Ag/ITO, ITO/Ag/ITO/Ag/ITO and ITO/Ag/ITO/Ag/ITO/Ag/ITO film systems for as-deposited and annealing films.

and structural improvement of the Ag and ITO films after annealing. For the as-deposited process, the S2 film system was better than the S1 and S3 systems, with the lowest sheet resistance being 7.6  $\Omega/\text{sq}$ . The S1 film system, with the lowest sheet resistance of 3.6  $\Omega/\text{sq}$ , was better than the S2 and S3 systems when compared after annealing. This resulted from improvement in the ITO films and the stability of the Ag film.

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