

## Annealing Effects on Opto-electronic Properties of Thermally-evaporated ITO/Ag/ITO Multilayered Films for Use in Color Filter Electrodes

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**Abstract:** The effects of post-deposition annealing on optical and electrical properties of thermally-evaporated ITO/Ag/ITO films have been investigated. The thickness of ITO, Ag and ITO films in the multilayered structure was constant at 50, 10 and 40 nm. The multilayered films were deposited on glass substrate without intentional substrate heating. A significant variation in resistivity and transparency was observed after thermal treatment from 300 to 540°C for 1 h. The high-quality films with resistivity as low as  $3.5 \times 10^{-3}$  Ohm-cm and transmittance more than 70% have been obtained by using suitably-controlled deposition parameters. The films grain structures and the surface morphology were illustrated using the X-ray Diffraction Patterns (XRD) and Scanning Electron Microscopy (SEM) respectively. The allowed direct band gap at the annealing temperature ranging from 300-540°C was estimated to be in the range of 3.62-3.78 eV. A band gap widening with an increase in annealing temperature was observed.

**Key words:** Indium Tin Oxide (ITO) . Annealing . Transparent conducting oxide . Multilayered films . Thermal evaporation

### INTRODUCTION

Indium Tin Oxide (ITO) is a highly degenerate n-type semiconductor with low electrical resistivity. ITO is a wide band gap semiconductor [1-6], which shows high transmittance in the visible and near-IR regions of the electromagnetic spectrum. ITO thin films are used in transparent electrodes in flat panel displays and solar cells, surface heaters for automobile windows [7], camera lenses and mirrors as well as transparent heat reflecting window materials for buildings, lamps and solar collectors [1]. There are several deposition techniques to grow ITO thin films including chemical vapor deposition, magnetron sputtering, evaporation [7-9], spray pyrolysis and pulsed laser ablation. The sputtering is widely used for ITO but it sometimes causes surface damage in device contact regions [8, 9]. These techniques normally require either a high substrate temperature (300-500°C) during deposition or a post deposition annealing treatment of the films at high temperature (300-700°C) [17-21]. The high temperature treatments generally damage the substrate and film surfaces [2]. An alternative way to improve the STN-LCDs (super twisted nematic liquid crystal displays) for application in color filter electrodes is to use the ITO/Metal/ITO (IMI) layered films [1, 2, 4, 10, 11], which represent lower resistivity than single layer ITO films of the same thickness. In recent years,

several IMI structures with Ag as an inter-layer have been reported [1, 10, 11].

It has been reported that the ITO/Ag/ITO multilayered film has a much lower sheet resistance than a single layer ITO film with the same thickness [1, 12-15]. Therefore, IMI evaporated film is the best way to produce high-quality ITO films with smooth surface, low resistivity, high transparency and high work function for the application of OLED at low substrate temperature [2, 11]. In this study, ITO/Ag/ITO multilayered films were deposited on glass substrates by thermal evaporation [7-9, 16]. The influence of post-deposition annealing on the optoelectrical properties of the IMI structure was studied. Finally, the X-ray diffraction (XRD) and UV-vis spectrometry were used for characterization.

### MATERIALS AND METHODS

The deposition of ITO and Ag thin films were performed by a thermal evaporation system from two tungsten crucibles in the presence of oxygen using a high-vacuum coating system (Model: JDM250). The ITO pellet (In<sub>2</sub>O<sub>3</sub>, 90 wt% and SnO<sub>2</sub>, 10 wt%) and Ag (of 99.99% purity) was used to prepare ITO/Ag/ITO thin films, which was deposited on a glass substrate without intentional substrate heating. The oxygen partial pressure in the chamber was kept at about

$10^{-4}$  mbar during the evaporation [16]. The distance between the deposition source (tungsten boat) and the rotating substrate holder was constant at 30 cm. The thicknesses of ITO/Ag/ITO multilayered films were kept constant to 50/10/40 nm, respectively. Although the deposition rate in evaporation method can be controlled by the source current [16], we used a fixed current for the evaporation boat and kept the evaporation rate around 1 Å/s during the film deposition. The thickness of deposited films was controlled using a 6MHz quartz crystal thickness monitor. The substrates were previously cleaned in both propanol and methanol solutions in an ultrasonic bath for 15 min and then dried in a high-purity  $N_2$  gas stream just before loading into the system for film deposition.

The as-deposited films by thermal evaporation were pale grey. Then the films were annealed in air for 1h, ranging from 300 to 540°C (with 60°C temperature interval). The phase composition of ITO/Ag/ITO films was characterized using XRD technique with a D8 Advanced Bruker X-ray diffractometer at room temperature, with monochromatic CuK $\alpha$  ( $\lambda = 1.54$  Å) in the scan range of  $2\theta$  between 10 and 70° with a step size of 0.02 (2 $\theta$ /s). The measurements were undertaken with beam-acceleration conditions of 35 kV/35 mA. The UV-visible optical transmission spectra of films were recorded by a double-beam spectrophotometer (UNICO SQ4802) in the spectral range of 300-1100 nm, a four-point probe (Model: FPP5000) was used to measure the resistivity of the films. The X-ray

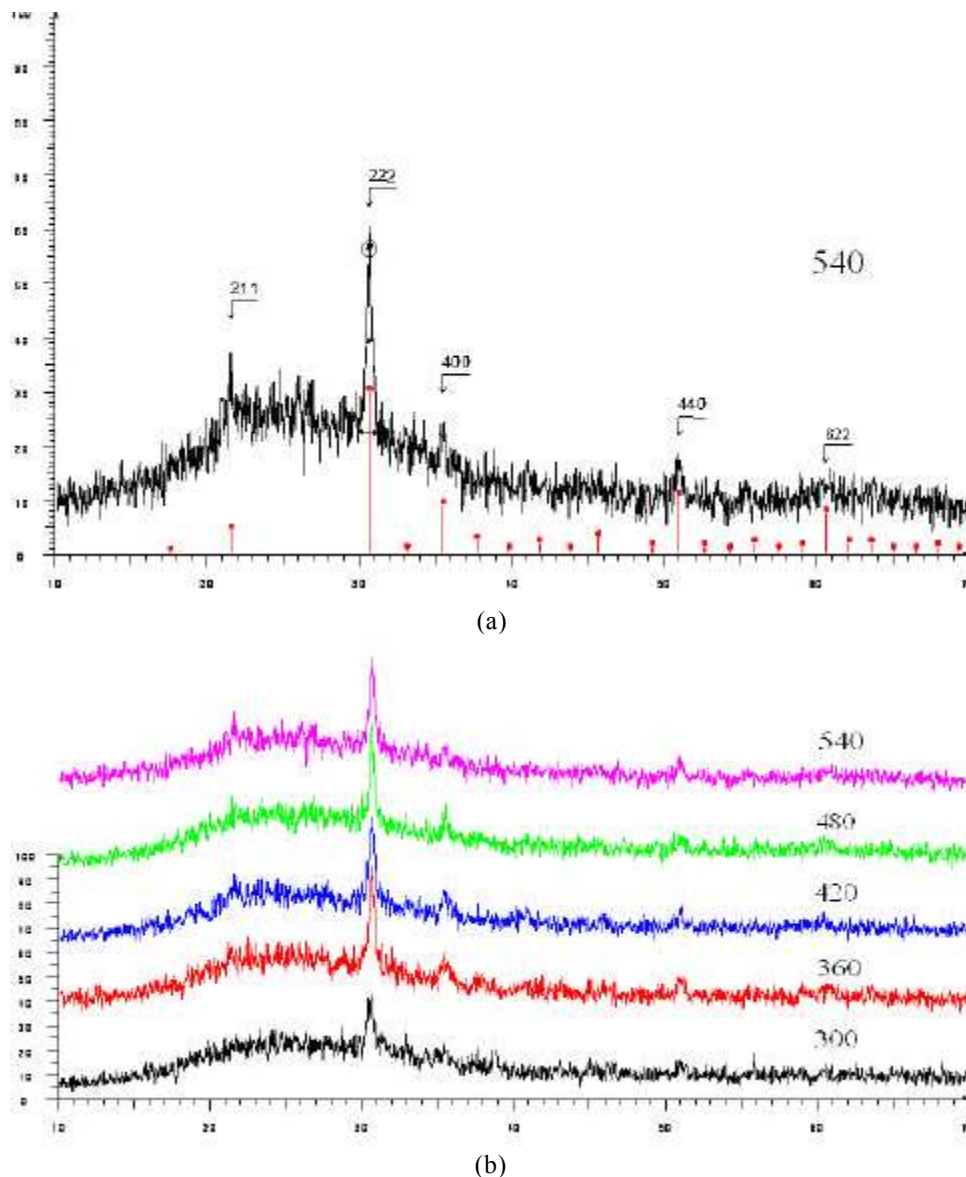


Fig. 1: XRD spectra of ITO/Ag/ITO multilayered films annealing at 540°C (a) comparing 300-540°C (b)

Table 1: The physical properties change due to annealing

Temperature (°C)	Transmission % (nm)		$E_g$ (eV)	$\rho$ ( $\Omega$ -m) *E-3	Grain Size in(222) (nm)
	550	1100			
300	25	30	3.60	1.6	18.3
360	35	35	3.62	3.2	20.3
420	40	40	3.68	3.7	20.0
480	55	60	3.70	4.9	25.5
540	70	80	3.72	5.5	25.6

diffraction pattern indicated that the multilayered films were oriented similar to the ITO bixbite structure. The films exhibited the maximum intensity peak corresponding to the predominant orientations (222).

## RESULTS AND DISCUSSION

The film assembly of the investigated IMI multilayer was 50 nm ITO/ Ag 10 nm/ITO40 nm. Figure 1 shows the XRD spectra of ITO/Ag/ITO multilayered films. The ITO crystalline in IMI films is influenced by the microstructure and the purity of an intermediate Ag film [4]. These IMI films are prepared on glass substrate at room temperature by thermal evaporation [7-9]. However, the XRD spectra in Fig. 1 show that the IMI films structure have been changed from amorphous to crystalline after one-hour annealing at 300 to 540°C in air. The ITO grains of the ITO/Ag/ITO films were aligned (222), corresponding to the indium tin oxide bixbite structure [4]. To this end, the Ag intermediate layer of the IMI structure effectively provoked crystallization of the upper ITO films, even at low substrate temperature [4, 11]. The optical transmittance in the wavelength range of 300-1100 nm was also measured.

Figure 2 shows the optical transmittance change due to the annealing in air for 1h at temperature range of 300-540°C. The bare glass substrates used in this work had a  $\approx 92\%$  optical transmittance. The IMI films had 70% transmittance at 550 nm and 85% transmittance at 1100 nm [11]. Furthermore, we can find the optical absorption and also the optical band gap by extrapolating diagram  $(\alpha h\nu)^2$  vs.  $h\nu$  [6]. In addition, the results showed that a higher optical band gap could be obtained by increasing the annealing temperature. The average optical band gap,  $E_g$ , calculated in the present work is 3.715eV, the minimum band gap is 3.62eV and the maximum band gap is 3.76 for multilayered thin films annealed at 300°C, 540°C, respectively. We have also verified the surface morphology of the multilayered films by SEM instrument. Figure 3 shows the surface morphologies of post annealed samples for (a) 540°C, (b) 480°C, (c) 420°C. The surface morphology shows a small change after annealing above 360°C and some granules are

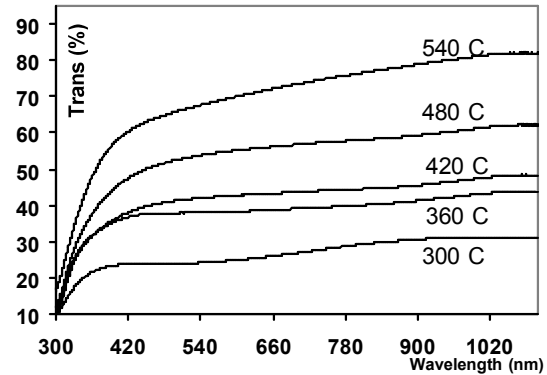


Fig. 2: Effect of annealing on transmittance of ITO/Ag/ITO Multilayered films in 300 to 540°C

seen on the surface. The granules sizes are estimated to be about 100 nm. Furong Zhu *et al.* [16], suggested that the granules observed on the surface of as-grown ITO films were mainly due to reduced indium metal agglomerations and associated structural defects. The metallic indium granules with different shapes and sizes were spread over the whole film and were responsible for the reduced transparency of the film. Figure 4 confirms the surface morphology of ITO/Ag/ITO film of this work is similar to the typical annealed ITO film [16]. The optical and electrical properties of ITO/Ag/ITO films are listed in Table 1. The decrease in the resistivity of ITO/Ag/ITO films was probably due to an increase of electron density caused by Ag inter-layer in the IMI films [1]. But in this research, we find that the sheet resistance increases after annealing above 360°C. The annealing process not only increases the optical transmittance of multilayered films due to the increased oxidation of indium and tin, but also can reduce the defects of the crystalline structure of ITO (i.e., vacancies and interstitial impurities) [11]. Table 1 shows that by increasing the annealing temperature up to 540°C,  $E_g$  was increased and it caused low optical absorption. Providing low absorption in the visible range is an essential feature of Metal Oxide Semiconductors, having a band gap of above 3 eV [21]. The average grain size was defined by the Scherrer equation [22].

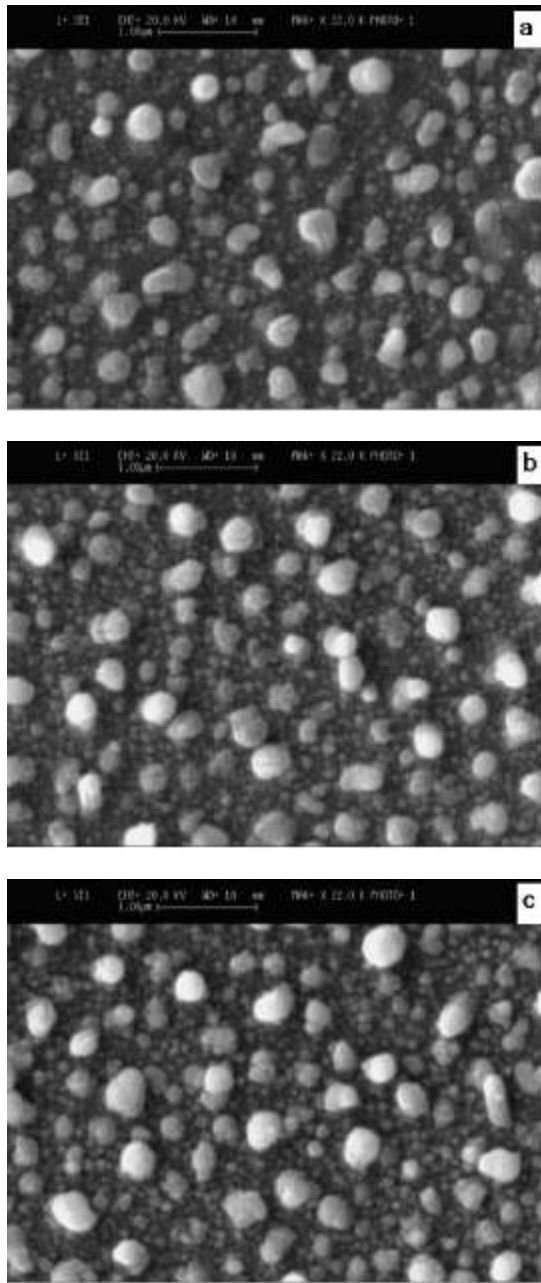


Fig. 3: SEM photographs of post annealing ITO/Ag/ITO for (a) 540°C, (b) 480°C, (c) 420°C

### CONCLUSIONS

The ITO /Ag/ITO multilayered film prepared by the thermal evaporation on glass substrate has an amorphous or nano grain structure. Having annealed at temperatures above 300°C, it crystallizes with a preferred (222) orientated plane. In order to promote conductivity, the number of charge carriers was increased by Ag doping [1, 4]. Another possibility to

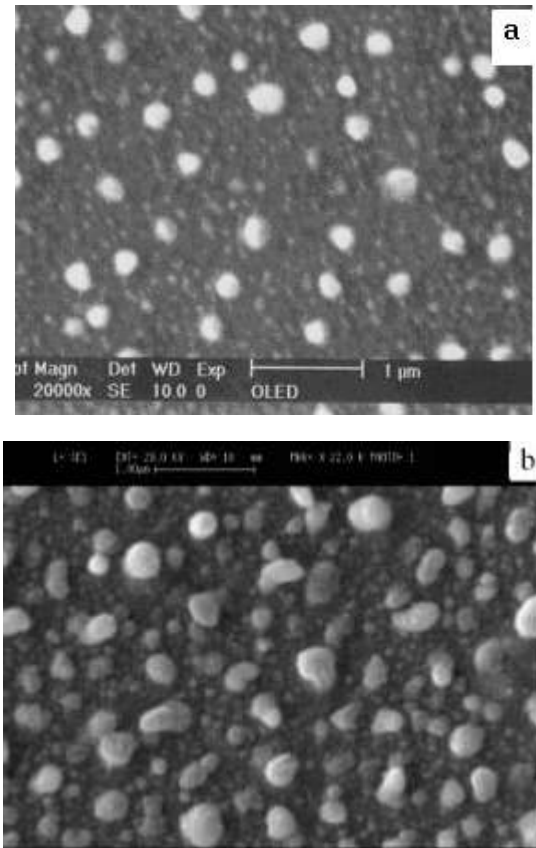


Fig. 4: SEM photographs of annealed samples (a) for ITO film of ref. [16], (b) for ITO/Ag/ITO multilayered films 540°C

enhance the conductivity is to increase the mobility. The mobility is dependant on intrinsic scattering mechanisms and can not be controlled directly [21]. The optical transmittance and the optical band gap are increased by annealing temperature up to 540°C (the results are shown in Table 1). The experimental results show that the magnitude of optical transmittance is roughly in the range 70-80% and the resistivity is about  $3.5 \times 10^{-3} \Omega\text{-cm}$  and it is increased by annealing in air for one hour.

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