Indian J. Phys. **84** (**5**) 539-546 (2010)

The effect of Ag intermediate layer on crystalline, optical and electrical properties of nano-structured thin film

D Kalhor[1*], R Zahiri[2], S A Ketabi[1] and A Ebrahimzad[1]
[1]School of Physics, Damghan University of Basic Sciences, Damghan, Iran
[2]School of Geology, Damghan University of Basic Sciences, Damghan, Iran

E-mail : Kalhor@dubs.ac.ir

Received 06 October 2009, accepted 19 November 2009

Abstract : ITO thin films and ITO/Ag/ITO multilayered films were prepared on glass substrate by reactive thermal evaporation technique without intentionally heating the substrate. After deposition the films were annealed in air at three different temperatures (300°C, 420°C and 540°C). The thickness of each layer in the ITO/Ag/ITO films was kept constant at 50 nm/10 nm/40 nm. The opto-electrical and structural properties of ITO/Ag/ITO multilayered films were compared with conventional ITO single-layer films. Although both films had identical thickness, 100 nm, the ITO/Ag/ITO films showed a lower resistivity. XRD spectra showed that Ag intermediate layer had a small effect on crystalline properties of ITO/Ag/ITO films.

Keywords : Indium-tin-oxide, multilayered films, thermal evaporation, annealing.

PACS No. : 73.61.-R

1. Introduction

Indium tin oxide (ITO) has attracted intensive interest because of its unique characteristics of good conductivity and high optical transmittance over the visible wavelength region. The thin films of ITO have found many applications as liquid crystal displays [1], anti-static coatings [2], heat mirrors [3], solar cells [4], flat panel displays [5] and organic light emitting diodes (OLED) [6].

There are several deposition techniques to grow ITO thin films including chemical vapor deposition [7], evaporation [8,9], sputtering [10], spray pyrolysis [4] and pulsed laser ablation [2,5]. But most of these techniques require either a high substrate temperature (300–500°C) during deposition or a post deposition annealing treatment of the films at high temperature (above 300°C) [10,11].

*Corresponding Author

Most of the investigations of ITO reported in the literature have been carried out on sputter deposited films [12]. Fewer studies have been reported on thermally deposited ITO films [8]. However, the knowledge of structure and electrical as well as the optical properties of ITO films is still limited and further investigations are needed to understand the physical characteristics of these films. The thermal evaporation technique has an advantage over the other methods because it does not cause radiation damage to the substrate [13].

In recent years 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 [11,12]. In this study, single-layer ITO films and a sandwich structure of ITO/Ag/ITO multilayer films were deposited on glass substrates by reactive thermal evaporation method. The influence of an intermediate Ag layer on the optoelectrical properties of the ITO/Ag/ITO films was investigated after annealing at different temperatures. The X-ray diffraction (XRD) and UV-Vis spectrometry were used for characterization of the films.

2. Experimental details

ITO thin films and ITO/Ag/ITO multilayered films were deposited by a reactive thermal evaporation method on glass substrates at room temperature. The deposition was performed using a high-vacuum coating system (Model : JDM250). The target material used in this study for deposition of ITO layers was an ITO pellet (Merck Co.) with nominal 99.9% purity In_2O_3 : SnO_2 (90 wt% and 10 wt%, respectively). For deposition of silver layer Ag metals with high purity (purity : 99.95%) was used.

Tungsten boat was chosen as a resistively heated source for the evaporation. Generally, the vacuum chamber was evacuated down to pressure 6.0×10^{-5} mbar prior to deposition. After evacuation, oxygen gas was introduced into the chamber and the required pressure of 1.0×10^{-4} mbar was set. The deposition rate was 0.1 nm/s and the thickness of deposited films was controlled using a 6 MHz quartz crystal thickness monitor. The thickness of ITO and ITO/Ag/ITO multilayered films were kept constant at 100 nm and 50/10/40 nm, respectively. After deposition the films were annealed in air atmosphere for 1 h at three different temperatures (300°C, 420°C and 540°C). The conventional $\theta - 2\theta$ X-ray diffraction (XRD) study on samples was carried out in a D8 Advanced Bruker X-ray diffractometer at room temperature, with monochromatic Cu$K\alpha$ ($\lambda = 1.54$ Å) in the scan range of 2θ between 15° and 65° with a step size of 0.02 (2θ/s). The measurements were undertaken with beam-acceleration conditions of 35 kV/35 mA. Transmission spectra of the samples were recorded using a UV-Vis spectrophotometer (UNICO SQ4802) in the spectral range of 300–1100 nm and the sheet resistance of the films was measured by using a four-point probe (Model : FPP5000).

3. Results and discussion

3.1. Crystalline properties :

The film design of the investigated ITO/Ag/ITO multilayer was (50 nm ITO/10 nm Ag/40 nm ITO). Figure 1 shows the XRD spectra of ITO single-layer films after annealing at different temperatures and Figure 2 shows the XRD spectra of ITO/Ag/ITO multilayer films for comparison. It is seen that the films have amorphous structure before annealing. It was commonly observed that the as-deposited ITO films comprised only of amorphous phase when the substrate was maintained at room temperature during deposition. Park *et al*. reported the same result [14]. This was generally interpreted as due to the lack of energy for deposited atoms on the substrate surface for which it was difficult for them to rearrange and form crystalline structures [1]. Kloppel *et al*. reported that the ITO crystallinity in IMI films is influenced by the

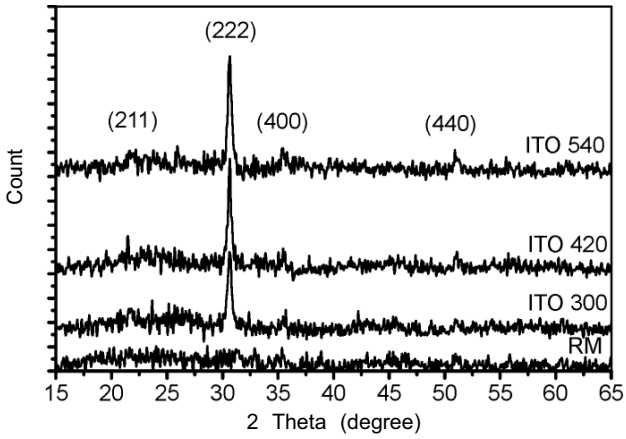

Figure 1. XRD spectra of ITO thin films annealed at different temperatures.

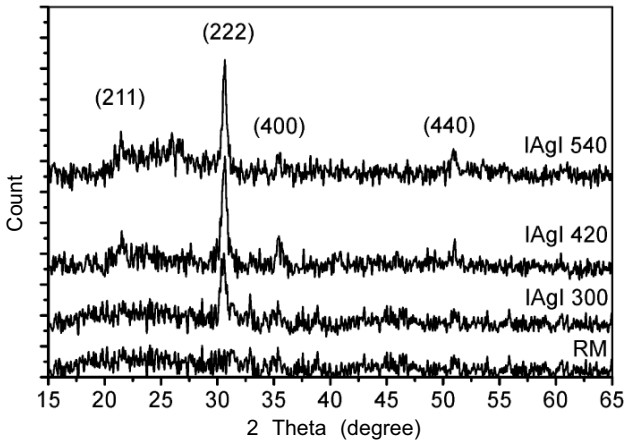

Figure 2. XRD spectra of ITO/Ag/ITO multilayered films annealed at different temperatures.

microstructure and purity of an intermediate Ag film [15].

Figures 1 and 2 show that the film structures have been changed from amorphous to crystalline after one-hour annealing at 300°C to 540°C in air. Preferred orientation of both ITO and ITO/Ag/ITO films was (2 2 2), corresponding to the indium tin oxide bixbyite structure.

The lattice constant "*a*" was calculated from the (2 2 2) peaks of the XRD spectra with the following equation [16] :

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}.$$

Here *d* is the distance of the two adjacent (2 2 2) planes and "*a*" is lattice constant. The results are shown in Figure 3. The inter-planer distance, *d*, for (2 2 2) crystal planes changes systematically with increment of temperature to 420°C and gets closer to the unstained lattice parameter which is 10.118 Å. This is probably due to the lattice

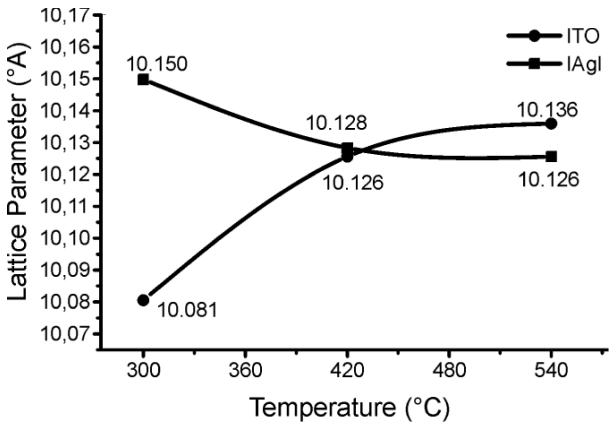

Figure 3. Calculated lattice parameter of the films annealed at different tempearature.

relaxation and crystallization of the film and it means that film favors to release its stress along [1 1 1] direction during annealing and at 420°C it has minimum value of stress. The same result was reported by Kavei *et al.* for annealing at 400°C [17].

The crystal grain size *D* was calculated from the (2 2 2) peaks of the XRD spectra by using the Debye–Scherrer formula [18] :

$$D = \frac{0.9\lambda}{B\cos\theta_B}.$$

Here λ = 0.154 nm and *B* is the full width at half maximum (FWHM) of the (2 2 2) peaks at the diffraction angle of $2\theta_B$. The results are shown in Figure 4.

3.2. Optical properties :

The as-deposited ITO films and ITO/Ag/ITO multilayer films looked pale grey in colour.

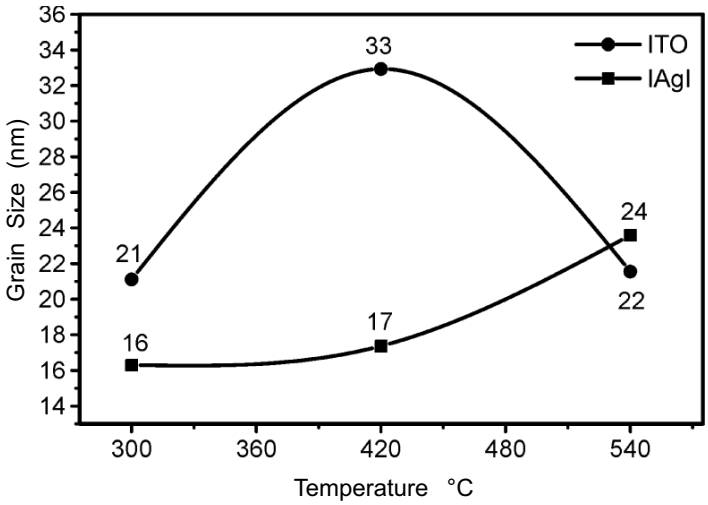

Figure 4. Calculated grain size of the films annealed at different temperature.

Salehi suggested that the low transparency of as-deposited ITO films was probably attributed to the amorphous structure and smaller grains existing in these films [13]. Zhu *et al.* suggested that the low transparency of an as-deposited ITO film was mainly caused by diffusing species which probably consisted of reduced metallic indium particles and defects in the film formed during the preparation [3].

The optical transmittance in the wavelength range of 300–1100 nm was measured. Figures 5 and 6 respectively show the optical transmittance change for ITO and ITO/Ag/ITO films due to the annealing in air for 1 h at different temperatures. The bare glass substrates used in this work had a ~95% optical transmittance. The ITO and ITO/Ag/ITO films had a maximum transmittance of 85% and 70% at 550 nm respectively. It can be seen that post deposition annealing greatly improves the

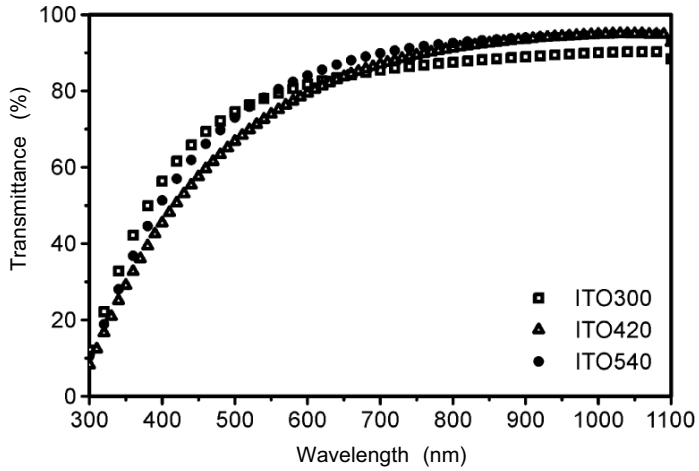

Figure 5. Optical transmittance of ITO films after annealing at different temperatures.

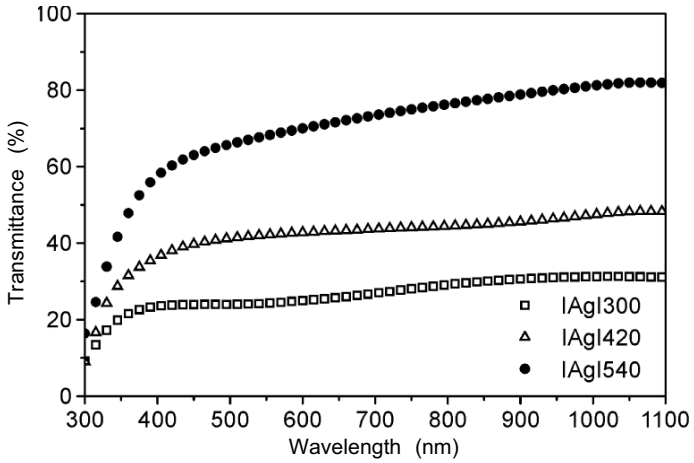

Figure 6. Optical transmittance of ITO/Ag/ITO multilayered films after annealing at different temperatures.

transmittance of the films. Such phenomenon results from the film becoming polycrystalline and further oxidized [19]. Also when the film was annealed in the ambient atmosphere, interstitial indium atoms and reduced metallic indium particles were gradually oxidized leading to its improved transparency [3]. The results are found to be in good agreement with those reported by Bertran *et al.* [20].

The transmittance data obtained for the films are used to calculate the absorption coefficients at different wavelengths using the following relation [21] :

$$T = \exp(-\alpha d)$$

where α is the absorption coefficient, d is the film thickness and T is the transmittance of the film. Furthermore, the optical band gap E_g can be determined using the relation :

$$\alpha h\upsilon = A(h\upsilon - E_g)^{1/2}$$

where $h\upsilon$ is the photon energy and A is a constant. We can find the optical band gap by extrapolating $(\alpha h\upsilon)^2$ diagram *vs.* $h\upsilon$ [22]. The results are shown in Table 1.

Table 1. The change of the physical properties of the films due to annealing temperature.

Sample	Temperature (°C)	Grain size in (2 2 2) (nm)	Lattice constant (Å)	Transmission % at 550 (nm)	Band gap E_g (eV)	Resistivity (10^{-3} Ωcm)
ITO	300	21	10.081	80	3.64	16.4
ITO	420	33	10.126	75	3.63	13.9
ITO	540	22	10.136	85	3.61	7.75
ITO/Ag/ITO	300	16	10.150	25	3.48	1.66
ITO/Ag/ITO	420	17	10.128	45	3.72	3.70
ITO/Ag/ITO	540	24	10.126	70	3.73	6.89

The band gap of the ITO/Ag/ITO films increased as the annealing temperature was increased from 300°C to 540°C. But the band gap of the ITO films was decreased

to some extent by increasing the annealing temperature. The increase in the band gap of ITO/Ag/ITO films is probably due to an increase in carrier concentration [23].

In degenerate *n*-type semi-conducting ITO thin films, the Fermi level overlaps the conduction band of In_2O_3. Therefore, the electrons could show the free-electron-like properties. The free electrons block the lowest states in the conduction band and consequently blue-shift or band gap widening is occurred. This phenomenon is known as the Burstein-Moss effect [23].

3.3. Electrical properties :

In general, the electrical conductivity of ITO films depends on carrier mobility and carrier density, which is mainly determined by oxygen vacancies or the concentration of substituted Sn^{+4} on In^{+3} sites [24,25]. In order to promote conductivity, the number of charge carriers could be increased [14,26]. Another possibility to enhance the conductivity is to increase the mobility. But the mobility is dependant on intrinsic scattering mechanisms and cannot be controlled directly [27].

As a result, higher annealing temperature led to the formation of lower resistance ITO thin films. The decrease in resistivity of ITO films with increasing annealing temperature could be attributed to the improved crystalline nature of the films [22]. This is basically due to the increase of the mobility and/or carrier density at higher annealing temperature. The decrease in resistivity in our ITO films is probably due to the increased charge mobility since the band gap widening due to increase of charge density is not seen in these samples. The decrease in resistivity in ITO/Ag/ITO films in comparison with ITO films was caused by an increment of electron density due to the Ag inter-layer in these films.

In this work, we find that the conductivity of ITO/Ag/ITO films declines with the annealing temperature increased above 300°C. Chen *et al.* reported that the conductivity of ITO/Ag/ITO films declines with the deposition temperature increased above 200°C because the surfaces of Ag layers become rough and scatter the conduction carriers [28].

4. Conclusion

Single-layer ITO and sandwich-structured ITO/Ag/ITO multilayer films were deposited on a glass substrate without intentional substrate heating by reactive thermal evaporation technique. ITO/Ag/ITO films showed a lower electrical resistivity and an optical transmittance of 70% at 550 nm. XRD spectra indicated that the 10-nm-thick Ag intermediate layers affect the crystallinity of the ITO film in IMI multilayers.

Also post annealing was shown to improve the optical quality due to oxidation of the indium particles and reduction in the number of defects.

References

[1] Chengyu, W Yongxing, Yuanliang, L X Tengcai, M Wang and W Paul *J. Non-Crystalline Solids* **353** 2244 (2007)

[2] H Kim, J Horwitz, S Kushto, G Piqué, A Kafafi, Z H Gilmore and C M Chrisey *J. Appl. Phys.* **88** 6021 (2000)

[3] F Zhu, C H A Huan, K Zhang and A T S Wee *Thin Solid Films* **359** 244 (2000)

[4] S Parthiban, V Gokulakrishnan, K Ramamurthi, E Elangovan, R Martins, E Fortunato and R Ganesan *Solar Energy Materials & Solar Cells* **93** 92 (2009)

[5] R K Gupta, K Ghosh, R Patel and P K Kahol *Appl. Surface Science* **255** 3046 (2008)

[6] G M Wu, H H Lin and H C Lu *Vacuum* **82** 1371 (2008)

[7] K Maknys, A G Ulyashin, H Stiebig, A Yu Kuznetsov and B G Svensson *Thin Solid Films* **511-512** 98 (2006)

[8] Belo, G S d Silva, B J P de Vasconcelos, E A de Azevedo and W M d Silva *Applied Surface Science* (in press) (2008)

[9] D C Paine, T Whitson, D Janiac, R Beresford, C O Yang and B Lewis *J. Appl. Phys.* **85** 8445 (1999)

[10] D Kim, Y Han, J S Cho and S K Koh *Thin Solid Films* **377-378** 81 (2000)

[11] Z Qi, X Chen, C Fan and W Chai *J. Materials Processing Technology* (in press) (2008)

[12] C Guillén and J Herrero *Solar Energy Materials & Solar Cells* **92** 938 (2008)

[13] A Salehi *Thin Solid Films* **324** 214 (1998)

[14] H J Park, J H Park, J I Choi, J Y Lee, J H Chae and D Kim *Vacuum* **83** 448 (2009)

[15] A Kloppel, W Riegseis, B Meyer, A Charmann, C Aube and J Stollenwerk *Thin Solid Films* **365** 139 (2000)

[16] L Hao, X Diao, H Xu, B Gu and T Wang *Appl. Surface Sci.* **254** 3504 (2008)

[17] G Kavei, A M Gheidari *J. Mat. Processing Tech.* (in press) (2008)

[18] L Hao, X Diao, H Xu, B Gu and T Wang *Appl. Surface Sci.* **254** 3504 (2008)

[19] R X Wang, C D Beling, S Fung, A B Djurisic, C Kwong and S li *IEEE* (2005)

[20] E Bertran, C Corbella, M Vives, A Pinyol, C Person and I Porqueras *Solid State Ionics* **165** 139 (2003)

[21] D Beena, K J Lethy, R Vinodkumar and V P M Pillai *Sol. Energy Mater. Sol. Cells* doi:10.1016/j.solmat.2007.05.009 (2007)

[22] H R Fallah, M Ghasemi and A Hassanzadeh *Physica* **E39** 69 (2007)

[23] H C Lee *Appl. Surface Sci.* **252** 2647 (2006)

[24] A Salehi *Thin Solid Films* **324** 214 (1998)

[25] M Nisha, S Anusha, A Antony, R Manoj and M K Jayaraj *Appl. Surface Sci.* **252** 1430 (2005)

[26] Y S Kim, J H Park, D H Choi, H S Jang, J H Lee, H J Park, J I Choi, D H Ju, J Y Lee and D Kim *Appl. Surface Sci.* **254** 1524 (2007)

[27] J M Dekkers *PhD Thesis,* University of Twente (Enschede : Netherlands) (2007)

[28] S W Chen and C H Koo *Mat. Letts.* **61** 4097 (2007)