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The Influence of Metallic Inter-layer on the Structural, Optical and Electrical Properties of ITO Thin Films Annealed at Different Temperatures

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Abstract: In this work new transparent conductive films that had a sandwich structure composed of ITO/metal/ITO multilayer films were prepared by reactive thermal evaporation technique on glass substrates without intentional substrate heating. Ag, Au and Cu thin films have been used as intermediate metal layer. The thickness of each layer in the ITO/metal/ITO films was kept constant at 50nm/10nm/40nm. The films were annealed in air at different temperatures ranging from 300 to 540°C for 1 h. The structural and optoelectrical properties of the films were compared with conventional ITO single-layer films with 100 nm thickness. XRD pattern showed that both inserting an intermediate layer and increasing annealing temperature have profound influence on the crystallinity and the electrical properties of thin films. It was found from SEM images that IMI films are composed of small nanoparticles The UV-Visible transmittance spectra were also confirmed that the annealing temperature has significant effect on the transparency of multilayered films.

Key words: Indium Tin Oxide (ITO) . annealing . multilayered film . thermal evaporation

INTRODUCTION

A combination of transparency and conduction can be achieved in two different types of materials. One of these comprises extremely thin films of metals, especially of Ag, Au or Cu. Their luminous transmittance can be up to 50% for a single film, but much larger if the film is embedded between non-absorbing layers serving essentially so as to anti-reflect the metal [1, 2]. Second, the wide-band gap oxide semiconductor is also possible, where Indium Tin Oxide (ITO) is the most used and widely studied transparent semiconductor among the various oxides [1, 3, 4]. ITO is a highly degenerate n-type semiconductor which has a low electrical resistivity [5]. This material has attracted intensive interest because of its unique characteristics of good conductivity, high optical transmittance over the visible wavelength region, excellent adhesion to the substrates and stable chemical property [3, 6].

However, although it has been found for about 40 years that ITO has both the excellent electrical and optical properties, the theoretical understanding of ITO has been limited, especially because of the complex crystal structure of ITO thin film, which exhibits a bixbyite structure with a unit cell containing 40 atoms and two non-equivalent cation sites [1, 2].

Due to its unique properties, ITO has been used in a wide range of applications including heat-reflecting mirrors [5], antireflection coatings [7] and gas sensors [8, 9] and as transparent electrodes in solar cells [10], various kinds of displays [1] and (organic) light emitting diodes [4, 11].

There are several deposition techniques to grow ITO thin films including chemical vapor deposition [12], magnetron sputtering [13, 14], evaporation [7, 15], spray pyrolysis [16] sol-gel [17] and pulsed laser ablation [3, 11]. All these studies have shown that physical properties of ITO thin films depend greatly on the method and conditions of elaboration. 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) [5, 12, 18]. Heating promotes material crystallization and reduces the crystalline structure defects; allow achieving more transparent and conductive films [19]. Nevertheless the resistivity is rather high in some cases for improved practical applications. Thus methods to enhance the conductivity of transparent electrodes are being investigated. In this sense, inclusion of a thin metal film in combination with ITO or other metal oxides has been shown effective to obtain transparent and conductive electrodes more adjusted to the required specifications [19]. In recent years, several

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advantageous ITO/Metal/ITO (IMI) structures using a metallic film as an inter-layer to improve the properties of the films have been reported [18-22].

In this study, single-layer ITO films and a sandwich structure of ITO/Metal/ITO multilayer films were deposited on glass substrates by reactive thermal evaporation method. The influence of an intermediate metal layer on the optoelectrical properties of the IMI films was investigated and also the effect of annealing at different temperatures on these properties was discussed.

MATERIALS AND METHODS

ITO thin films and ITO/Metal/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 material used in this study for deposition of ITO layers was an ITO pellet with nominal 99.9% purity In_2O_3:SnO_2 (90 wt% and 10 wt%, respectively). For deposition of metallic layers Ag, Au and Cu 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 6MHz quartz crystal thickness monitor. The thickness of ITO and ITO/Metal/ITO multilayered films were kept constant to 100 nm and 50/10/40 nm, respectively. After deposition the films were annealed in air for 1h at different temperatures ranging from 300°C to 540°C (with 60°C temperature interval). The conventional θ-2θ, X-ray diffraction (XRD) study on samples was carried out in a D8 Advanced Bruker X-ray diffractometer at room temperature, with monochromatic CuK_a (λ=1.54 Å) in the scan range of 2θ between 15° and 55° 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 290-1100 nm and the sheet resistance of the films were measured by using a four-point probe (Model: FPP5000).

RESULTS AND DISCUSSION

Structural: In order to assess the contribution that crystallinity alone makes to the other film parameters, it is necessary to include and compare the XRD results from the annealing treatments. Figure 1(a-e) shows the XRD patterns of the ITO and IMI films annealed at different temperatures in air for 1 h. The as deposited films had amorphous structure which is not shown in the spectra. All the annealed films are polycrystalline. They crystallized in the cubic bixbyite structure of indium oxide [23] with the maximum intensity peak corresponding to the (222) predominant orientation [15].

The low intensity of peaks suggests that these thin films consist of a mixture of amorphous and crystalline phases [24]. The peaks of IMI structures in the XRD pattern are wider than the peaks of ITO single layer which indicate that the IMI films are composed of small nanoparticles [24]. But as it is seen in XRD spectra the metallic intermediate layer of the IMI structure have effectively provoked crystallization of the films, especially at lower annealing temperature. Kloppel *et al*. reported that the ITO crystallinity in IMI films is influenced by the microstructure and purity of an intermediate Ag layer [25] and Kim *et al* reported the same result about Au interlayer on ITO thin films [21]. Beside from that, with an increase in annealing temperature the intensity of the (2 2 2) peak increased which is in agreement with the literature [26].

Optical: Optical transmittance spectra of the samples are represented in Fig. 2. As can be seen the optical transmission of IMI films in the visible region improved with increasing annealing temperature [24].

The film deposited at room temperature revealed a black grey colour [6, 15]. Salehi suggested that the low transmittance of as-deposited ITO films was due to the amorphous structure and small grains in the films [15]. Zhua *et al*. attributed the low transmittance of an as-deposited ITO film to the presence of the point defects that were formed in the evaporated ITO film. The point defects could also act as diffusing species [6]. Annealing increases the optical transmittance of the films due to the improvement in the crystallinity of the films. The crystallinity probably affects the light scattering on the transparency of the IMI films. With the improvement of the crystallinity of the films, the light scattering decreases resulting in better transparency [24].

In a lot of studies the authors have shown that in ITO thin films and in the visible and UV regions, the reflectance is quite small and to a good approximation it can be neglected [27]. We have used this approximation in our analysis and the transmittance data obtained for the films were used to calculate the absorption coefficients at different wavelengths using the following relation [5]:

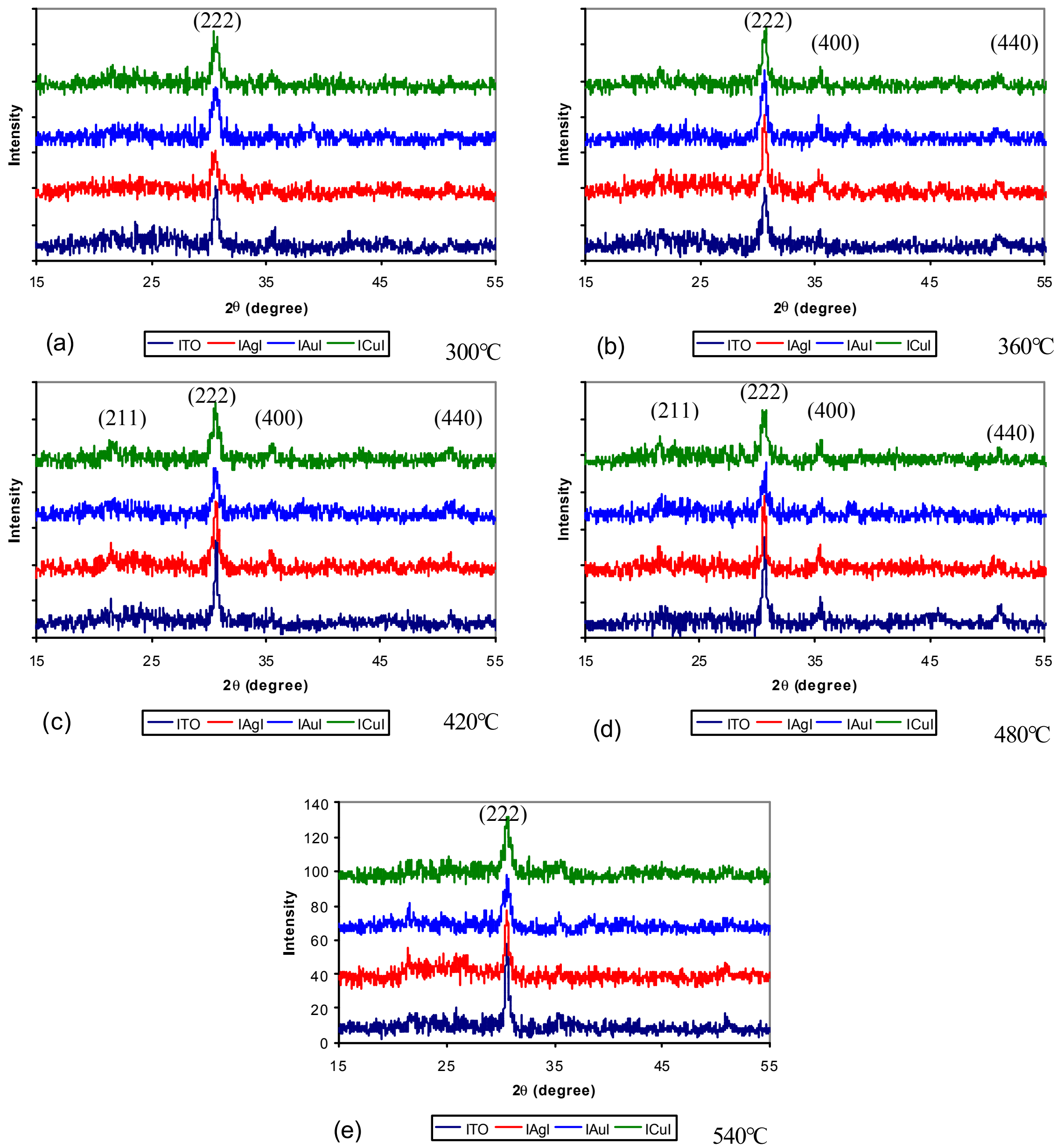

Fig. 1: XRD spectra of ITO and IMI films annealed at (a) 300°C, (b) 360°C, (c) 420°C, (d) 480°C and (e) 540°C

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

where d is the film thickness, α is the absorption coefficient and T is the transmittance of the film. The optical band gap E_g can be obtained from the following relation which is known as the Tauc plot [13]:

$$\alpha h\upsilon = A(h\upsilon - E_g)^2$$

where A is a constant, ν is the transition frequency and E_g is the band gap energy. The band gap of the films were determined from the plot of $(\alpha h\nu)^2$ vs hν by extrapolating the linear portion of the curve to $(\alpha h\nu)^2$ equal to zero [23]. The results are shown in Table 1.

Table 1: The optical band gap of the films annealed at different annealing temperature (eV)

Temperature	ITO	IAgI	IAuI	ICuI
300°C	3.70	3.58	3.61	3.70
360°C	3.70	3.77	3.72	3.73
420°C	3.70	3.80	3.72	3.72
480°C	3.70	3.79	3.73	3.74
540°C	3.66	3.78	3.74	3.76

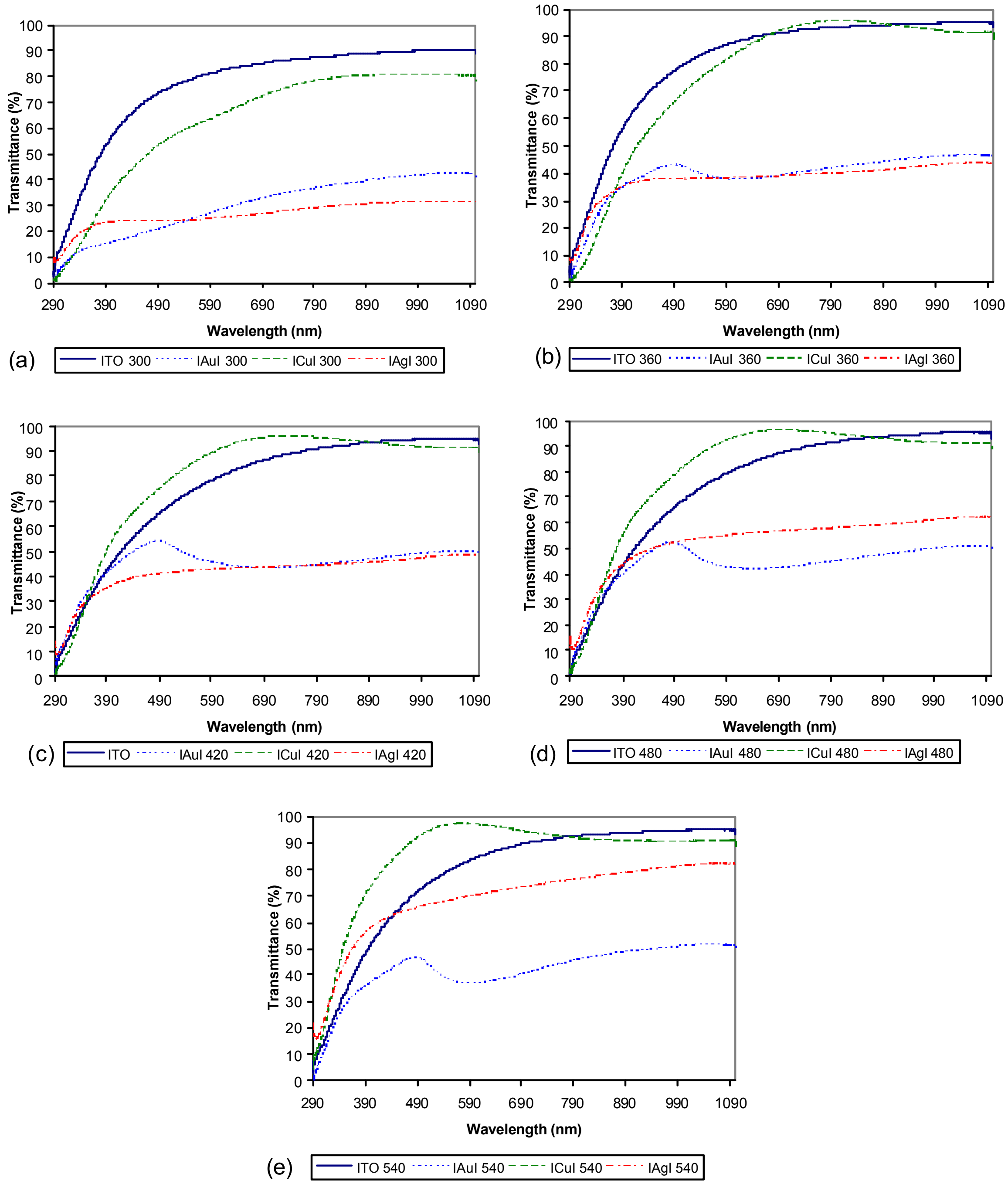

Fig. 2: Transmission spectra of ITO and IMI films annealed at (a) 300°C, (b) 360°C, (c) 420°C, (d) 480°C and (e) 540°C

It is seen that for IMI films a higher optical band gap could be obtained by increasing the annealing temperature.

Electrical: 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 [15, 20, 23, 24]. In order to promote conductivity, the number of charge carriers could be increased [20, 21]. Another possibility to enhance the conductivity is to increase the mobility. But the mobility is dependant on intrinsic scattering mechanisms and can not be controlled directly [28].

Table 2: The special resistivity of the ITO and IMI films annealed at different annealing temperatures (10^{-3} ohm-cm)

Temperature	ITO	IAgI	IAuI	ICuI
300°C	-	1.66	2.69	19.0
360°C	15.3	3.16	5.09	25.4
420°C	13.9	3.7	7.16	30.8
480°C	11.5	4.98	7.5	53.0
540°C	7.75	6.89	-	82.4

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 [24]. 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. Because the band gap widening which is due to increase of charge density is not seen in these samples. The decrease in resistivity in ITO/Ag/ITO and ITO/Au/ITO films in comparison with ITO films was caused by an increment of electron density due to the inter-layer in these films.

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 that scatter the conduction carriers [29].

CONCLUSIONS

Single-layer ITO and sandwich-structured ITO/metal/ITO multilayer films were deposited on glass substrates without intentional substrate heating by reactive thermal evaporation. From the results we may conclude that inserting an intermediate metal layer as well as increasing annealing temperature play major role in crystalinity and in controlling the electrical properties of the IMI films. Also post annealing was shown to improve the optical quality due to oxidation and reduction in the number of defects.

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