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Characterization of Indium Tin Oxide Films after Annealing in Vacuum

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ABSTRACT

ITO thin films were deposited on glass substrate by dc magnetron sputtering without substrate heating. The effects of annealing in vacuum on the structural, optical and electrical properties were investigated. The samples of 120 nm ITO films were separately annealed at 200, 250, 300 and 350°C for 1 hour. The results showed that the increasing of the annealing temperatures improve the crystallinity of the films, increase the grain sizes and improve their optical and electrical properties. The optical transmission of films in the visible region increase while in the near infrared region decrease with increasing the annealing temperatures. The relative intensities $I_{(400)}/I_{(222)}$ of ITO films increase but the resistivity decrease with increasing the annealing temperature. The prepared ITO film as-deposited has a resistivity of 2.47×10^{-3} Ω.cm and decreases to 3.95×10^{-4} Ω.cm after annealing at 350°C for 1 hour and energy gap increases from 3.99 eV to 4.10 eV.

Key words: ITO film; annealing temperature; dc magnetron sputtering

INTRODUCTION

Indium tin oxide (ITO) films are transparent electrical conductor used for optoelectronic devices because they have low resistivity and high transmittance in the visible region with an n-type degenerated semiconductor and a wide energy band ($E_g \approx 4$ eV) (Laux *et al.*, 1998). Nowadays, the ITO films are widely used in many applications such as solar cell (Zhao, 2005; Hino, 2006), gas sensors (Vaishnav *et al.*, 2005), electrode in transparent organic light-emitting diode (OLED) (Chung *et al.*, 2005; Satoh *et al.*, 2005) and ferroelectric photoconductor storage device (Dimos *et al.*, 1994).

The ITO films have been prepared by various deposited techniques such as sol-gel (Kundu and Biswas, 2005), chemical vapor deposition (CVD) (Maruyama and Fukui, 1991), electron beam evaporation (Fallah *et al.*, 2006), radio frequency (rf) sputtering (Sreenivas *et al.*, 1985; Meng and dos Santos,1996; Park *et al.*, 2005), and direct current (dc) sputtering (Bender *et al.*, 1998; Jung and Lee, 2003), etc. The dc magnetron sputtering is one of the effective methods to deposit good film performance with high coating rate.

The optical and electrical properties of ITO films are interrelated and depend on their microstructure and stoichiometry which in turn depend on the substrate temperature or annealed temperature. The optical and electrical properties

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of ITO films were not satisfactory if they had been deposited without substrate heating or annealing afterward. In this paper we study the effect of annealing temperature treatment on the properties of ITO films deposited on glass substrate at room temperature by dc magnetron sputtering using an ITO target.

MATERIAL AND METHODS

The ITO films were prepared by dc magnetron sputtering on glass substrate at room temperature using an ITO target composite of mixture of 90wt% In_2O_3 and 10wt% SnO_2 (99.99% purity, 3 inch in diameter, and 0.25 inch thick). The glass substrates were ultrasonically cleaned in an acetone and deionized water before depositions.

The sputtering processes were performed in mixed Ar-O_2 (99.99% in purity) with separated by mass flow controller. The gases flow rate of argon and oxygen were fixed at 50 sccm (standard cubic centimeter) and 0.5 sccm, respectively. The distance between the ITO target and glass substrate was 8.6 cm, and the dc power was kept constant at 50 W. A turbo-molecular pump coupled with a rotary pump was used to achieve a base pressure of 6×10^{-4} Pa before introducing Ar-O_2 mixture and working pressure of about 5×10^{-1} Pa.

The film thickness was measured with a Dektek surface profiler. In this work, the measurements were performed on the films having the thickness about 120 nm with coating rate of 0.4 nm/s. The crystallinity and crystal orientation of ITO films were measured using X-ray diffraction (XRD, Rigaku, Japan) with a CuK_α source (λ = 1.54 Å) under an applied voltage of 30 kV and a current of 15 mA. The optical transmittance spectra of film in UV-Vis-NIR region were recorded by a spectrophotometer (UV-3100 Shimadzu Corporation, Japan). The film surface roughness of ITO films was investigated with atomic force microscope (AFM, SII SPA 400, Japan). The electrical properties were measured by four-point probe.

The ITO films were separately annealed in vacuum (2 Pa) for 1 hour at the temperature of 200, 250, 300 and 350°C, respectively. Then the films were investigated the effect of annealing treatment on structural, electrical and optical properties.

RESULTS AND DISCUSSION

The effect of annealing temperature at 200, 250, 300 and 350°C for 1 hour on crystal structure of the ITO films are shown in Figure 1. It could be seen that the XRD pattern of as-deposited ITO film is amorphous. After annealing at the temperature from 200°C to 350°C, the ITO films have shown the XRD peak with intensities of the four major peaks, (222), (400), (440) and (622). The crystallinity is increased as a function of annealing temperature. The results obtained are higher (400) peak intensity when the ITO film annealed in vacuum at higher temperature. Due to annealing processes, the structure of ITO film is rearranged by heating so amorphous ITO film is improving crystalline structure.

The effect of annealing temperature on the surface morphology of the ITO films was investigated by AFM. Figure 2 shows topological images by AFM of the ITO films (a) as-deposited and (b) to (e) after separately annealed in vacuum for 1 hour with various annealing temperature at 200, 250, 300 and 350°C, respectively. The increasing of annealing treatment affected to a larger grain size of ITO films, especially annealing at temperature of 350°C in Figure 2 (e), the grain size increase to the size larger than 100 nm. This result corresponds with increasing crystallinity in Figure 1 for which the ITO films showed higher crystal structure at higher annealing temperature.

Figure 3 shows the optical transmission of ITO/Glass for as-deposited and annealed in vacuum at annealing temperature of 200, 250, 300 and 350°C. The ITO films showed the optical transmission tend to increase in the visible region and tend to decrease in the near infrared region with increasing the annealing temperature. In fact,

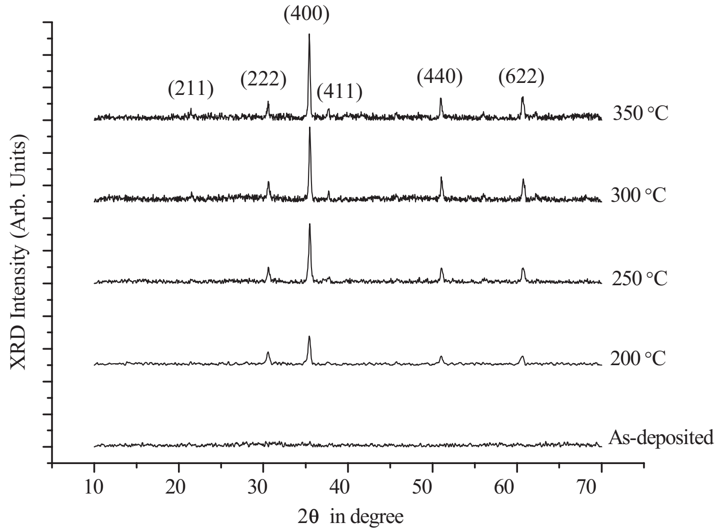

Figure 1 XRD pattern of ITO film for as-deposited and annealed at 200, 250, 300 and 350°C.

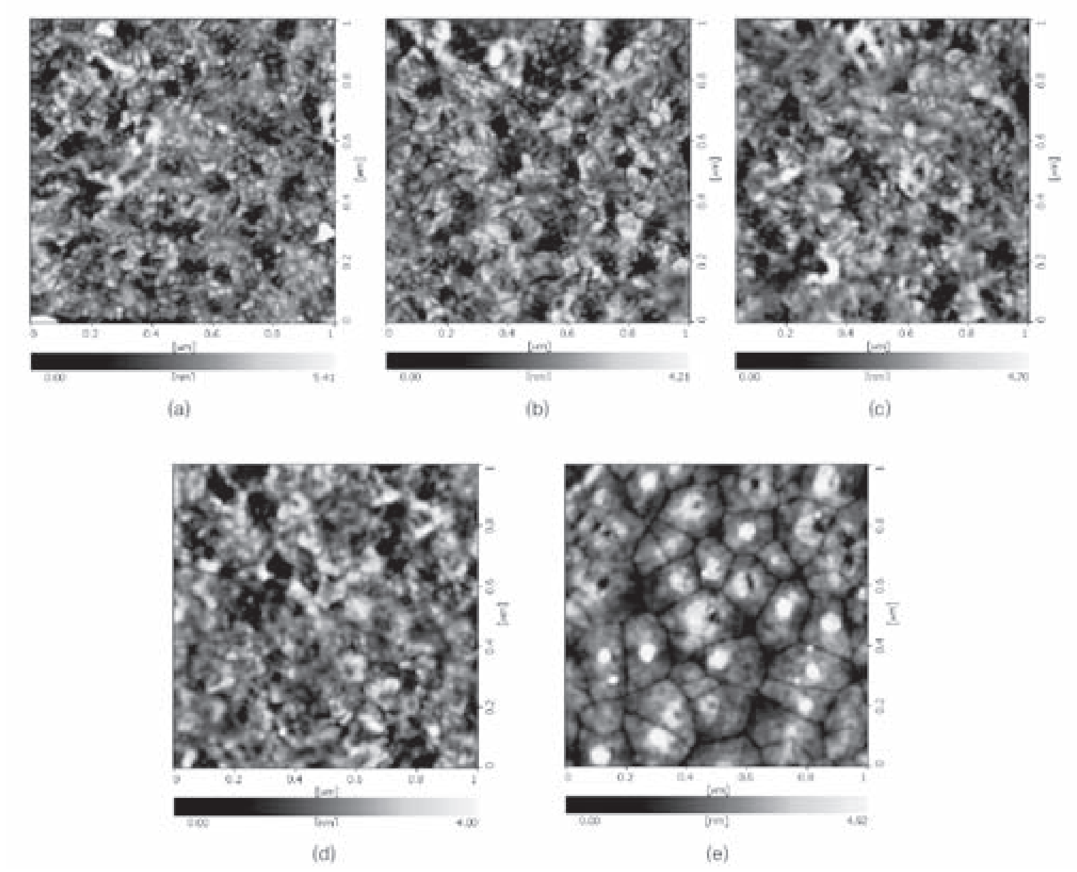

Figure 2 Top view of AFM images for the ITO films (a) as-deposited and annealed at (b) 200°C, (c) 250°C, (d) 300°C and (e) 350°C.

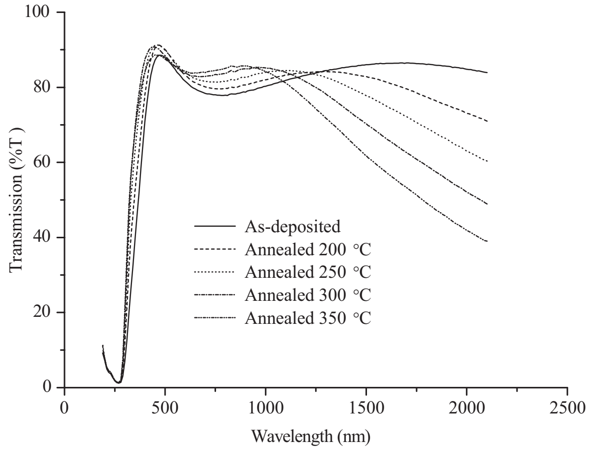

Figure 3 Optical transmissions of ITO/Glass for as-deposited and annealed at 200, 250, 300 and 350°C.

the mechanisms of transmission in the visible region of the ITO films depend on grain size and stoichiometry which affected to scattering mechanism in polycrystalline ITO films as grain boundary scattering (Hu *et al.*, 2004). From the result of structure in Figure 2, the larger grain size decreased grain boundaries scattering so ITO films were improved the optical transmission in the visible region. The decreasing of transmission in the near infrared depends on electrical property, which plasma frequencies of film increase with increasing carrier concentration resulted in higher reflection or lower transmission of infrared region and their property was explained with Drude theory (Bender *et al.*, 1998).

Considering at the edge of transmission in the range of 300 nm to 400 nm, the edge of transmission is shifted to lower wavelength as a function of increased annealing temperature. The optical transmission is able to calculate the energy of ITO according to the Taue relation by equation (1)

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

$$\alpha = \frac{\ln(1/T)}{d} \quad (2)$$

where E_g is the energy gap; α is the absorption coefficient calculated by equation (2); the constant A is different for different transitions; $h\upsilon$ is the photon energy; T is the film transmission and d is the thickness of films. The energy gap of ITO films as a function of annealing temperatures is shown in Table 1.

The effect of annealing temperature on the electrical property of ITO films was measured by four point probes. Figure 4 shows the resistivity as a function of annealing temperature. It could

Table 1 Relative intensity $I_{(400)}/I_{(222)}$, average transmission, energy gap and resistivity as a function of annealing temperature of ITO films.

Annealing temperature (°C)	Relative intensity $I_{(400)}/I_{(222)}$	%T (Visible)	%T (Near infrared)	E_g (eV)	Resistivity (Ω.cm)
-	-	82	82	3.99	2.47×10^{-3}
200	2.30	84	82	4.05	1.87×10^{-3}
250	3.67	85	81	4.07	1.39×10^{-3}
300	3.63	86	79	4.09	5.17×10^{-4}
350	4.58	85	76	4.10	3.95×10^{-4}

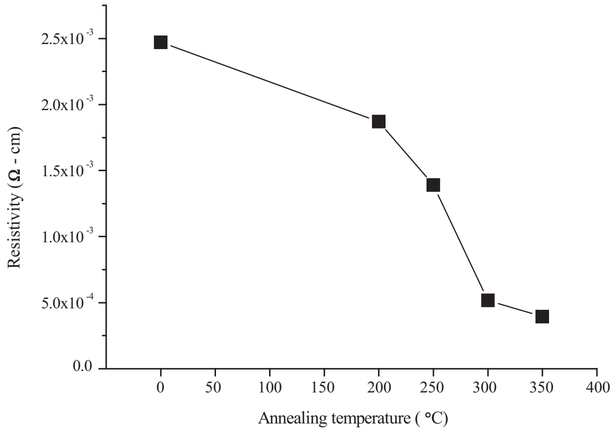

Figure 4 Resistivity of ITO films as a function of annealing temperature.

be seen that, the resistivity of ITO films decreases with the increasing of annealing temperature. Due to the annealing processes, the oxygen content in ITO films decreases with the effect of annealing temperature and it decreases the resistivity of ITO films and increases the carrier concentration as in equation (3).

$$\rho = \frac{1}{en\mu} \qquad (3)$$

where ρ is resistivity; e is electron charge; n is carrier concentration and μ is carrier mobility.

The values of relative intensity $I_{(400)}/I_{(222)}$ for crystal structure, average transmission and energy gap for optical property and resistivity for electrical property as a function of annealing temperature are shown in Table 1. The ratio of $I_{(400)}/I_{(222)}$ increases from 2.30 to 4.58 with the increasing of annealing temperature from 200°C to 350°C, respectively. This result showed that a favorable <100> texture for ITO films depended on the increasing of annealing temperature. In addition, the optical transmission of ITO films are related to annealing temperature which optical transmission in the visible region increases from 82% to 85% but optical transmission in the infrared region decreases from 82 to 76% when increasing annealing temperature from 0°C to 350°C. The energy gap of ITO films increases from 3.99 eV to 4.10 eV with the increasing of annealing temperature. This result can be explained with Moss-Burstein shift (Hamberg and Granqvist, 1986; Sernelius *et al.*, 1988) such that the increasing of energy gap depends on carrier concentration as equation (4), it corresponds with the decrease of resistivity.

$$E_g - E_{g0} = \frac{h}{2m^*}\left(3\pi^2 n_e\right)^{2/3} \qquad (4)$$

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

CONCLUSION

ITO films were deposited by dc magnetron sputtering at room temperature. The ITO films for as-deposited showed amorphous structure and high resistivity. After annealed in vacuum, the ITO films showed the better crystallinity with the increasing of the ratio of $I_{(400)}/I_{(222)}$ as a function of annealing temperature and improved the optical property with the increasing of the optical transmission in the visible region and the decreasing of the optical transmission in the near infrared region. The resistivity decreased and the energy gap of the ITO films increased with the increasing of annealing temperature. The properties of ITO films are improved after annealed in vacuum which are suitable for using in many application.

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