Properties of Indium Tin Oxide Transparent Conductive Thin Films at Various Substrate and Annealing Temperature

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ITO thin films with thickness of 3000 Å were fabricated by rf magnetron sputtering system with a 10 mol % SnO_2 - 90 mol % In_2O_3 target at various substrate temperature and annealing temperature in air. And we investigated structural, electrical and optical characteristics of them. It's resistivity, carrier concentration and Hall mobility was 2×10^{-4} Ωcm, $7\times10^{20}\sim9\times10^{20}\,cm^{-3}$ and 21～23 $cm^2/V\cdot sec$ respectively. And it's optical transmittance and energy band gap was above 85 % in the visible range and 3.53 eV respectively.

Keywords : Indium Tin Oxide (ITO), Transparent conducting oxide (TCO), RF magnetron sputtering, Electrical resistivity, Optical transmittance

1. INTRODUCTION

Interest in TCO (Transparent Conductive Oxide) thin films of nonstoichiometric has increased markedly in recent years, because of their high conductivity and transparency in the visible region. They find wide applications in modern optoelectronic and photovoltaic devices[1-3]. Among TCO thin films, ITO (Indium Tin Oxide) is prominent material because of low resistivity and wide energy band gap. ITO thin film has useful application as a heat mirror that transmits visible light and reflects infrared and as a transparent electrode of Ⅰ-Ⅲ-$Ⅵ_2$ solar cells with more wider energy band gap. Also, ITO can be used as the window layer in n^+-p hetero-junctions as like degenerate n-type semiconductor. However the properties of ITO thin films are strongly dependent on various preparation conditions and fabrication apparatuses. So, it is necessary to accept the accurate properties of ITO thin films for effective applications of advanced devices[4-8].

Reactive ion plating, dc sputtering, rf sputtering, reactive evaporation, chemical vapor deposition, and spray pyrolysis, have all been used successfully to produce transparent conducting coatings of ITO on glass. However, films with the highest degree of transmission and the lower resistivity are prepared by magnetron sputtering.

In this study, ITO thin films with thickness of 3000 Å were fabricated by rf magnetron sputtering system with a 10 mol % SnO_2 - 90 mol % In_2O_3 target at various substrate and annealing temperature in air. And we investigated structural, electrical and optical characteristics of them.

2. EXPERIMENTAL PROCEDURE

The ITO thin films were fabricated by rf planar magnetron sputtering under the magnetic field of 3,000 Gauss, and the target were prepared by sintering the mixture of In_2O_3 powder with a purity of 99.9% and SnO_2 powder with a purity of 99.99%.

Sputtering was carried out at substrate temperature (T_S) of 100℃ ~500℃ with a rf power of 100W and annealing temperature(T_A) of 300℃ ~500℃. The films were deposited onto Corning 7059 glass, and the substrate was placed parallel to the target surface with a 5 cm distance. And the shutter was placed between target and substrate in order to prevent undesirable sputtering.

And we investigated electrical and optical characteristics of them. The electrical resistivity, carrier concentration and Hall mobility were measured by 4-point probe system (SR1000, Chang Min Tech.) and Hall-effect measurement system (Keithly 300). The optical transmission was measured by UV-visible spectrophotometer (UV-3501, Hitachi). Film thickness was measured by surface profile measuring system (Dektak3, USA).

3. RESULTS AND DISCUSSION

3.1 Electrical and structural characteristics of ITO thin films by substrate temperature (T_S)

Figure 1 shows the dependence of resistivity, carrier concentration and mobility on T_S. The ITO thin films were deposited under conditions of 3,000~4,000Å thickness and 11 mTorr gas pressure. At non-annealing condition, the lowest resistivity was obtained by T_S above 400℃. The decrease in resistivity with increasing T_S could be attributed to the improved crystalline nature of these films. And the increase in T_S may have led to oxygen-deficient films, resulting in an increase in carrier density. In order to analyze the conduction mechanism, Hall mobility and carrier concentration was measured. In Fig. 1, the resistivity tends to decrease with increase of Hall mobility and carrier concentration. Conduction mechanism of TCO investigated by many scholars classified into two large groups, one was the occurrence of intrinsic carrier by oxygen vacancy and the other was the introduction of extrinsic carrier by impurity doping. As a result of this research, the occurrence of carrier caused to development of resistivity was greatly affected by impurity doping and oxygen vacancy. However, the knowledge of conduction mechanism of ITO films is still limited and further investigations are needed to understand the characteristics of these films. ITO samples were further analyzed in order to identify the mechanisms in these films. The X-ray Diffraction (XRD) measurements, obtained for 2θ scans between 20° and 60°, has been made on ITO thin films in order to obtain their structure. The XRD patterns of the ITO thin films deposited on glass at different T_S are shown in Fig. 4(a).

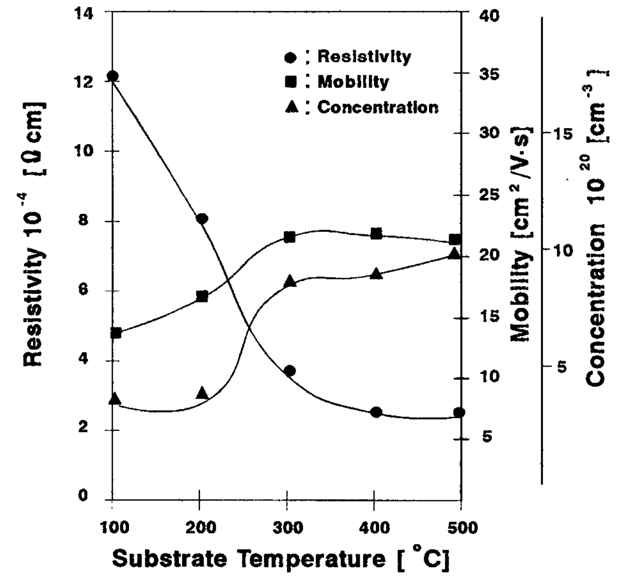

Fig. 1. Dependence of resistivity, carrier concentration and Hall mobility of ITO thin films on substrate temperature.

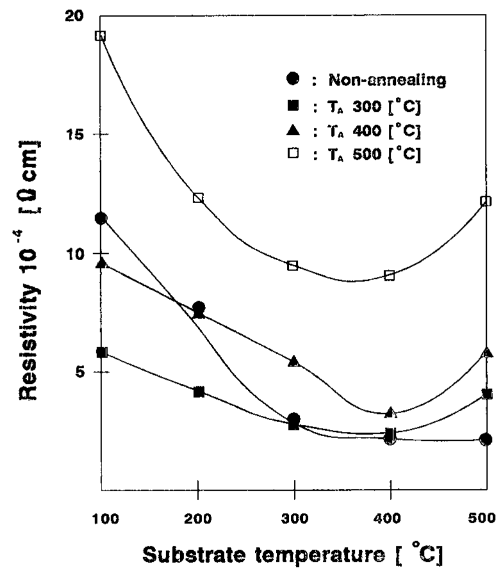

Fig. 2. Variations of resistivities of ITO thin films at different annealing temperature.

The films show the maximum intensity peak corresponding to the (222) pre-dominant orientation. All other peaks observed are (211), (400), (332), (440) and (622). With increasing substrate temperature the diffraction peaks don't change significantly, but they become more intense at T_S above 300℃. This means that the crystallinity of the resulting films is improved and the grain size becomes larger with elevating substrate temperatures. The grain size has been estimated using Scherrer formula and they are in the range of 100~350Å.

3.2 Electrical and structural characteristics of ITO thin films by annealing temperature (T_A)

Figure 2 shows the resistivity variation of ITO thin films applied annealing temperature (T_A) of 300~500℃ in air. The resistivity of ITO thin films after annealing at 400~500℃ almost increases for each T_S. But the resistivity of samples with T_A of 300℃ decreases gradually until T_S of 400℃ and increases again above T_S of 400℃. Further analysis carried out in order to investigate conduction mechanism for these phenomena in Fig. 2. And Fig. 3 shows the variation of resistivity, carrier concentration and Hall mobility in case of ITO thin film applied T_A of 300℃. The resistivity tends to decrease with increase of carrier concentration and Hall mobility in films with T_S until 400℃, and the minimum value are 2×10^{-4} Ωcm. And then, carrier concentration and Hall mobility was about $7\times10^{20}\sim9\times10^{20}$ cm^{-3} and $21\sim23$ cm^2/V·sec, respectively.

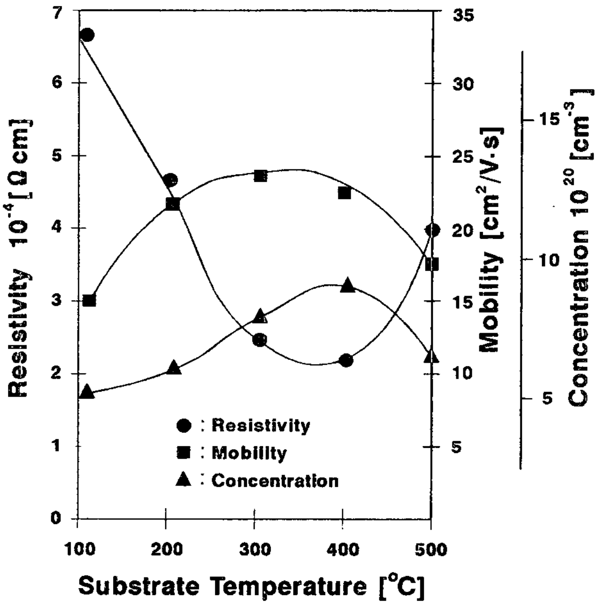

Fig. 3. Dependence of resistivity, carrier concentration and Hall mobility on T_A of 300℃.

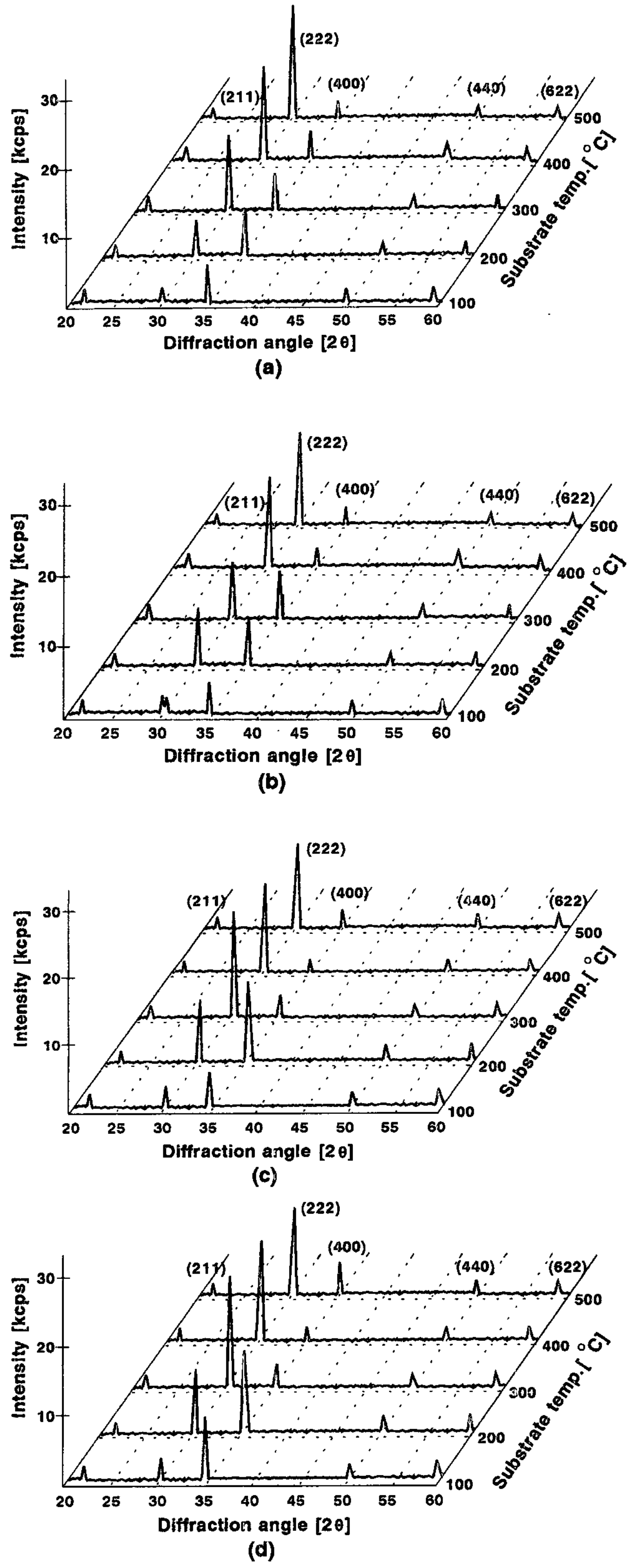

Fig. 4. XRD patterns of ITO thin films at various annealing temperature: (a) non-annealing, (b) 300℃, (c) 400℃, (d) 500℃.

On the other hand, it can be seen that the resistivity of ITO thin film deposited at T_S above 400℃ was increased after annealing. This is explained that the excessive amount of heat for ITO causes diffusion of oxygen into the film, thus reducing oxygen vacancies.

Figure 4 (b), (c), and (d) show the XRD patterns of these films with T_A of 300~500℃, indicating an improving crystallinity in films with increase of T_A. But these phenomena mean only the improvement of crystallinity of ITO thin films. It seems that the excellent crystallinity is not always proportional to the electrical conductivity for ITO thin films.

3.3 Optical characteristics of ITO thin films

A high transparency for the ITO thin film in the visible region is required in applications with transparent electrodes for optoelectronic devices. The optical transmission spectra corrected for the attenuation of the glass substrate from 200 to 900 nm for ITO thin films deposited at different T_S is shown in Fig. 5. And the thickness of films are about 3,000Å.

The average transmittances in the visible range exceed 85% for the films deposited at higher T_S. With increasing T_S, the structure of the films is improved gradually and the defect concentration decreases so that transmittance of the films is increased. Low deposition temperature results in an incomplete oxidation for the films and this leads to a relatively low transmittance. And it should be noted that ITO thin film provides an excellent UV shielding and IR shielding.

Absorption coefficients of the ITO thin films at different wavelengths were calculated from transmission and reflection data. The absorption coefficient α for the direct allowed transition can be written as

$$\alpha \propto (h\nu - E_g)^{1/2} \qquad (1)$$

where $h\nu$ is the photon energy and E_g the transition energy gap. Fig. 6 shows the photon energy dependence of α^2 for ITO thin films deposited at different T_S. Extrapolations[9] of the straight regions of the plots to $\alpha = 0$ give the energy gap E_g. There was a shift in the absorption edge to shorter wavelength with the T_S. This shift is known as Burstein-Moss shift and this shift energy can be written as[10,11]

$$E_g - E_{go} = \frac{\pi^2 h^2}{2m_r^*}\left(\frac{3N}{\pi}\right)^{2/3} \qquad (2)$$

where E_{go} is the intrinsic band gap and m_r^* the reduced effective mass. The E_g values obtained are about 3.3eV~3.7eV for films with each T_S. It is found that the carrier concentration N increases as T_S increases for the ITO thin film. Hence, a larger energy gap is obtained for higher T_S as predicted by Burstein-Moss equation (2).

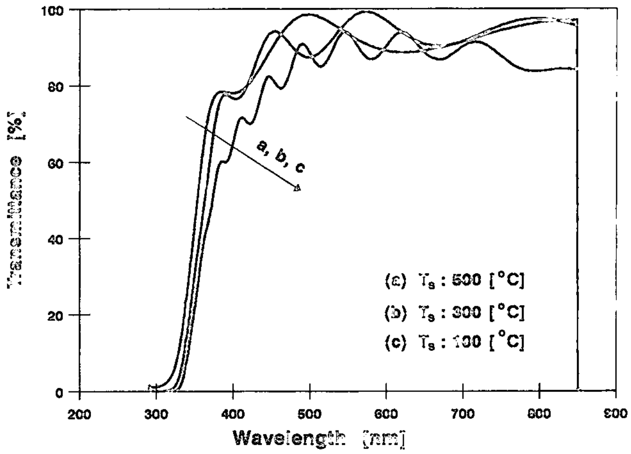

Fig. 5. Optical transmittance of ITO thin films annealed at 300℃.

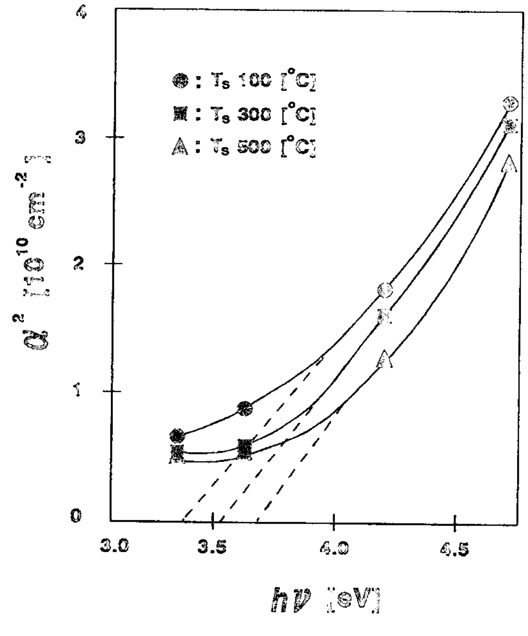

Fig. 6. Square of absorption coefficient as a function of photon energy.

4. CONCLUSION

ITO thin films with thickness of 3000Å were fabricated by rf magnetron sputtering system with a 10 mol% SnO_2-90 mol% In_2O_3 target at various substrate and annealing temperature in air. And we investigated structural, electrical and optical characteristics of them.

Single phase ITO thin film with the highest diffraction peak (222) at diffraction angle (2θ) of 29.8° was made well at the condition of T_S of 400℃ and T_A of 300℃. And it's resistivity, carrier concentration and hall mobility was $2\times10^{-4}\ \Omega$cm, $7\times10^{20}\sim9\times10^{20}$ cm^{-3} and 21 ~ 23 cm^2/V·sec, respectively. And it's optical transmittance and energy band gap was above 85 % in the visible range and 3.53 eV, respectively.

We concluded that ITO thin films were fabricated at these conditions had good transparent conductive oxide film's properties for $\mathrm{I\text{-}III\text{-}VI_2}$ solar cells with wide band gap from electrical and optical properties.

ACKNOWLEDGEMENTS

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