Effect of Post-Deposition Annealing on the Structural, Optical and Electrical Properties of Ti-doped Indium Oxide Thin Films

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Abstract: Ti-doped In₂O₃ (TIO) thin films were deposited on glass substrates by RF magnetron sputtering. The films were then annealed at 100, 200 or 300 °C for 30 min to investigate the effects of the annealing temperature on the films' structural, electrical and optical properties. The films annealed at 200 °C and above were polycrystalline in phase, and their electrical resistivity decreased to as low as $7.5 \times 10^{-4} \Omega \text{ cm}$ at the annealing temperature of 300 °C. The films' optical transmittance in the visible wavelength region also improved from 77.7% to 81.2% when the annealing temperature was increased. The TIO films' figures of merit were evaluated, showing that the TIO films annealed at 300 °C had better optical and electrical performance than the other films prepared using lower temperature or no annealing.

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Keywords: thin film, sputtering, electrical properties, x-ray diffraction, figure of merit.

1. INTRODUCTION

Recently, Ti-doped In₂O₃ (TIO) films have attracted great attention for their potential application in various display devices due to their high stability in humid conditions and their low electrical resistivity [1]. In addition, TIO films have shown higher carrier mobility than conventional Sn-doped In₂O₃ (ITO) [2]. Various deposition methods have been used to obtain high-quality TIO films, including magnetron sputtering [3] and pulsed laser deposition [4].

Among the various deposition methods that are available, RF magnetron sputtering is the most widely used due to its ability to produce uniform films over large areas. However, it is well known that transparent conductive oxide films prepared at room temperature by RF magnetron sputtering have relatively low optical transmittance in the visible light range and high electrical resistivity [5,6]. Thus, the optical and electrical properties of conventional TIO films deposited at room temperature do not meet the typical demands of optoelectronic applications.

In a previous study, D. Kim investigated the effect of substrate temperature on the properties of 480 nm thick TIO

films deposited on glass substrate [7] and A. Chaoumead also reported on the influence of sputtering power and gas pressure on the structural and electrical properties of TIO films deposited by RF magnetron sputtering [8].

In this study, TIO thin films deposited by RF magnetron sputtering were annealed under vacuum, and the influence of different annealing conditions on the films' structural, electrical and optical properties were investigated by means of X-ray diffraction (XRD) analysis, UV-visible spectrophotometry, Hall Effect measurements, and atomic force microscopy (AFM).

2. EXPERIMENTAL PROCEDURES

TIO films were deposited at room temperature on glass substrates (30×30 mm²) by RF magnetron sputtering with a TIO target (Ti:In₂O₃ = 5:95 at%; 99.99% purity). Prior to each deposition, the chamber was evacuated to 6×10^{-7} Torr, and the distance between the target and the substrate was kept constant at 60 mm. Table 1 shows the experimental conditions used for this study.

After deposition, the films were annealed at 1×10^{-3} Torr for 30 min at various annealing temperatures; the maximum annealing temperature used was 300 °C to prevent thermal

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Table 1. The deposition conditions of TIO thin films.

Parameter	Conditions
Thickness (nm)	100
Base pressure (Torr)	6.0×10^{-7}
Deposition pressure (Torr)	1.0×10^{-3}
Target power (W/cm^2)	Pulsed DC, 2.2
Pulse frequency (kHz)	20
Ar gas flow rate (sccm)	20
Film thickness (nm)	100
Deposition rate (nm/min)	12
Annealing temperature ($^{\circ}\text{C}$)	100, 200, 300

Fig. 1. The XRD pattern of the TIO films annealed at different temperatures. (a) As deposition, (b) Annealed films at 100 $^{\circ}\text{C}$, (c) Annealed films at 200 $^{\circ}\text{C}$, (d) Annealed films at 300 $^{\circ}\text{C}$.

deformation of the glass substrate. The film thickness was confirmed using a surface profilometer and the root mean square (RMS) roughness of the films was analyzed by means of AFM (XE-100, Park Systems).

The crystallization of the films was observed by means of high-resolution XRD (X'Pert Pro MRD, Philips), conducted at the Daegu Center of the Korea Basic Science Institute (KBSI). The optical transmittances and electrical properties of the films annealed at various temperatures were evaluated by means of UV-visible spectrophotometry (Cary100 Cone, Varian), and van der Pauw Hall effect measurements (HMS-3000 Ecopia) were acquired under a magnetic flux density of 0.5 T. The performance of the TIO films as transparent conducting films was quantified using the figure of merit (FOM) [9].

Table 2. Variation of the grain size as a function of annealing temperature.

Temperature ($^{\circ}\text{C}$)	FWHM ($^{\circ}$)	Grain size (nm)
As deposition	—	Amorphous
100	—	Amorphous
200	2.0	4.1
300	1.2	7.1

Fig. 2. Surface morphology (scan area; $2 \times 2 \mu\text{m}^2$) and RMS roughness of the TIO films annealed at different temperatures. (a) As deposition, RMS roughness; 0.87 nm, (b) Annealed films at 100 $^{\circ}\text{C}$, RMS roughness; 1.09 nm, (c) Annealed films at 200 $^{\circ}\text{C}$, RMS roughness; 1.90 nm, (d) Annealed films at 300 $^{\circ}\text{C}$ RMS roughness; 2.11 nm.

3. RESULTS AND DISCUSSION

XRD patterns were acquired from the as-deposited TIO films, and from the TIO films that were subjected to post-deposition annealing at 100, 200 and 300 $^{\circ}\text{C}$. In Fig.1, the films deposited at room temperature do not show any diffraction peaks, whereas those films annealed at 200 and 300 $^{\circ}\text{C}$ show diffraction peaks corresponding to the (211), (222), (400), (440) and (622) planes of In_2O_3 films. The full width at half maximum of the In_2O_3 (222) peak decreased with increasing annealing temperature, meaning that increasing the temperature enhanced the films' crystallization.

Table 2 lists the grain sizes of the films as evaluated using Scherer's formula [10]. The films annealed at 300 $^{\circ}\text{C}$ showed the largest grain size of 7.1 nm as measured on the In_2O_3 (222) plane.

Table 3. The dependence of the electrical properties of the films on annealing temperature.

Temperature (°C)	Carrier density ($\times 10^{20} \text{ cm}^{-3}$)	Mobility ($\text{cm}^2 \text{ V}^{-1} \text{ S}^{-1}$)	Resistivity ($\times 10^{-3} \Omega \text{ cm}$)
As deposition	6.59	8.32	1.14
100	6.78	8.45	1.09
200	7.28	9.43	0.90
300	8.19	10.11	0.75

Fig. 3. The optical transmittance spectra in the visible wavelength region for the as-deposited and the annealed TIO films. (a) As deposition, (b) Annealed films at 100 °C, (c) Annealed films at 200 °C, (d) Annealed films at 300 °C.

In Fig. 2, AFM images of the as-deposited and annealed TIO films show that the surface roughness increased with annealing temperature. The films annealed at 300 °C show the highest RMS roughness of 2.11 nm. This increasing surface roughness is attributed to the grain growth of the films, which had already been observed from the XRD patterns.

Fig. 3 shows the visible regions of the optical transmittance spectra collected for the as-deposited and the annealed TIO films. The bare glass substrates showed 90% optical transmittance. The average transmittance of the as-deposited films was about 77.7%, and the film annealed at 300 °C had a transmittance of 81.2%. This means that annealing increased the optical transmittance of visible light. In addition, it was observed that the absorption edges shifted towards shorter optical wavelengths with increasing annealing temperature. This hypsochromic shift of the absorption edge in the optical transmittance spectrum can be explained by the Burstein–

Fig. 4. Plots of $(\alpha h\nu)^2$ as a function of $h\nu$ for TIO films annealed at different temperatures. The extrapolation of the linear region to $h\nu = 0$ to determine optical band gap (E_g) values is as indicated with lines. (a) As deposition, (b) Annealed films at 100 °C, (c) Annealed films at 200 °C, (d) Annealed films at 300 °C.

Moss effect [11], in which the absorption edge shifts toward shorter wavelengths in response to increasing carrier concentrations.

Table 3 shows the dependence of the films' electrical properties upon the annealing temperature. As the annealing temperature was increased from room temperature to 300 °C, resistivity decreased from 1.1×10^{-3} to $7.5 \times 10^{-4} \Omega \text{ cm}$ due to increases in both mobility and carrier concentration. Based on the XRD patterns and the results presented in Table 2, it is supposed that the observed decreases in resistivity with increasing annealing temperatures occurred because of grain growth, because grain growth reduces the density of grain boundaries, which act as traps for free carriers and as barriers to carrier movement.

Fig. 4 shows plots of $(\alpha h\nu)^2$ versus photon energy for the TIO films [12]. The optical absorption coefficient (α) can be calculated from the following relation [13]:

$$\alpha = \frac{1}{t} \ln \left(\frac{1}{T} \right) \quad (1)$$

where t is the film thickness and T is the optical transmittance. The relation between the optical absorption coefficient and the optical band gap (E_g) is given by the Tauc

Table 4. Variation of the optical band gap as a function of annealing temperature.

Temperature (°C)	Optical band gap (eV)	Reference
As deposition	4.04	This study
100	4.05	This study
200	4.07	This study
300	4.10	This study
GZO 100 nm	3.87	[15]

Table 5. The FOM values for TIO films annealed at different temperatures.

Temperature (°C)	Sheet resistance [$\Omega/\square$]	Transmittance [%]	Figure of merit [Ω^{-1}]
As deposition	114	77.7	7.0×10^{-4}
100	109	79.8	9.6×10^{-4}
200	90.9	80.4	1.2×10^{-3}
300	75.4	81.2	1.6×10^{-3}

formula [14]:

$$(\alpha h\nu)^2 = C(h\nu - E_g) \quad (2)$$

where $h\nu$ is the energy of the incident photons and C is the absorption edge width parameter.

Table 4 lists the optical band gaps of the TIO films annealed at various temperatures. All annealed films had wider optical band gaps than the as-deposited TIO films. The optical band gap of the TIO films shifted from 4.043 to 4.107 eV with increases in annealing temperature from 100 to 300 °C.

The FOM is an important index used to evaluate the performance of transparent conductive oxide films. The FOM is defined as

$$\text{FOM} = T^{10} / R_s \quad (3)$$

where T is the film's optical transmittance in the visible region, and R_s is the film's sheet resistance. Table 5 lists the FOMs of the TIO films annealed at various temperatures. The maximum FOM of $1.6 \times 10^{-3} \Omega^{-1}$ was observed for the films annealed at 300 °C. Since a higher FOM indicates better optical and electrical performance of the transparent conductive oxide film, it can be concluded that TIO films annealed at 300 °C would perform better than the films

annealed at lower temperatures in this study.

4. CONCLUSIONS

TIO thin films were deposited onto unheated glass substrates by RF magnetron sputtering and then vacuum annealed at 100, 200 and 300 °C for 30 min.

TIO films annealed at 200 °C and above showed diffraction peaks corresponding to the (211), (222), (400), (440) and (622) planes of In_2O_3 films. The full width at half maximum of the In_2O_3 (222) peak decreased with increasing annealing temperature, indicating that hotter annealing enhanced the films' crystallization. The films annealed at 300 °C showed a lower resistivity of $7.5 \times 10^{-4} \Omega \text{ cm}$, and showed a higher optical transmittance of 81.2% in the visible spectrum.

Based on the observed results, it can be concluded that post-deposition vacuum annealing at an optimized temperature enhances both the optical and electrical properties of the as-deposited TIO films.

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