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Annealing Effects of Indium Tin Oxide films grown on glass by radio frequency magnetron sputtering technique

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Abstract

Indium tin oxide (ITO) films were deposited on a glass slide at a thickness of 280 nm by radio frequency(rf) magnetron sputtering from a ceramic target composed of In_2O_3 (90%) + SnO_2 (10%). We investigated the effects of the annealing temperature (T_a) between 200 and 350 ℃ for 30 min in air on such properties as thermal stability, surface morphology, and crystal structure of the films.

X-ray diffraction spectra revealed that all the films were oriented preferably with [222] direction and [440] direction and the peak intensity increased with increasing annealing temperature. X-ray photoelectron spectroscopy (XPS) showed that the sodium was out-diffused from the glass substrate at the annealing temperature of 350℃. The sodium composition of the ITO film annealed at 350℃ for 30 min was 2.5% at the surface. Also the sodium peak almost disappeared after 3 keV Ar^+ sputtering for 6 min. The visible transmittance of all ITO films was over 77%.

Key Words : ITO, glass, rf magnetron sputtering, annealing, sodium

1. Introduction

Indium tin oxide films have been attracting increasing interest because of their importance in a wide range of applications such as solar cells, liquid crystal displays, photodetectors, etc [1-5]. Indium tin oxide, in particular, is the most extensively studied and commonly used material for these device. Most of these films were deposited on glasses or on different crystals' surfaces at a relatively high substrate temperature (over 150℃). But on alkali-rich substrates (soda-lime glass), considerable amounts of sodium and potassium diffuse across the glass surface into the deposited layer when the temperature exceeds 200℃ [6]. The diffusion of sodium is crucial for the formation and crystallization of the TiO_2 layer because the changes in structure and composition depend on the temperature and the duration of the heat treatment [7-8].

The diffusion of alkali from glass substances into the films such as TiO_2 or SiO_2 was reported by a secondary ion mass spectroscopy (SIMS) depth profile with annealing temperature [6]. The out-diffusion of alkali from glass substances into the glass surface was reported by an XPS depth profile with annealing temperature [9]. However, to date the diffusion of alkali into the ITO film from glass substrates with annealing temperature has not been well investigated. Therefore, the

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purpose of this study is to obtain the atomic diffusion of alkali metal into the ITO films as a function of annealing temperature.

In the present work, we investigate the effect of the thermal annealing of the ITO films grown on a glass substrate prepared by rf magnetron sputter at the annealing temperature range from 200, 250, 300, and 350 ℃. The effects of thermal annealing on such properties as crystallinity, surface roughness, and thermal stability of the ITO films have been investigated by x-ray diffracotmeter (XRD), atomic force microscope (AFM) and x-ray photoelectron spectroscopy (XPS).

2. Experiment

Commercial glass slide (Halfwhite glass, Superior Co.) were used for this experiment. The plate was cut into 12 mm × 12 mm samples. The weight composition of glass samples used in this study was SiO_2 (72.8%-73.0%), Na_2O (14.6%-14.8%), K_2O (0.70%-0.80%), CaO (5.80%-6.00%), MgO (3.9%-4.1%), Al_2O_3 (1.35%-1.40%), and Fe_2O_3 (0.045%-0.047%). Indium tin oxide films were grown on bare glass at room temperature with a thickness of 280 nm by rf magnetron sputter. Base pressure of the chamber was 5×10^{-7} torr. For reactive sputter deposition, oxygen reactive gas was introduced into the chamber up to 2×10^{-5} torr and argon gas (99.99% purity) was added through a highly sensitive piezoelectric valve controller until chamber pressure reached 3.2×10^{-3} torr. A water-cooled substrate table was insulated to the ground and connected with a direct current (dc) source as the bias supply. The sputtering power was continuously adjustable from 0 to 300 W. An ITO target, supplied by Cera, was used in this work. This target, 2 in. in diameter and mounted on the magnetron, was composed of 90% In_2O_3, 10% SnO_2 by weight. Before being introduced into the chamber, substrates were ultrasonically cleaned in a neutral detergent solution and rinsed in deionized water to eliminate possible contamination. The substrates were loaded from the loadlock with an adjustable target-to-substrate distance. This distance was kept constant at about 40 mm. The rf power was kept at 100 W. The substrate temperature was maintained at room temperature during the deposition. The thickness of ITO films grown in this experiment was 280 nm.

Four films were prepared with annealing treatments in air for 30 min. To compare with annealing samples one sample was not annealed. Annealing under four different temperature conditions were studied: 200 ℃, 250 ℃, 300 ℃, and 350 ℃.

The thickness of the ITO films was measured by α-step (Tencor, alpha step 500). X-ray diffraction measurements were carried out with a Rigaku Geigerflex computer-controlled diffractometer with Cu Kα radiation. The geometry of the diffractometer was the same for all the studied samples (grazing incidence diffraction = 5°, V = 40 kV, I = 30 mA). An AFM (PSI Co.) was used to study the surface morphology of the ITO films and to measure the root-mean-square (rms) surface roughness. Optical characteristics of the ITO films were deduced from the transmission spectra measured with a UV-3100 (Shimadzu Co.) to investigate relative transmittance of the films.

XPS was used to investigate the composition of the ITO surface and depth profile of the ITO films. The XPS data were obtained with a Physical Electronics PHI 5700 ESCA spectrometer using Mg Kα(hν = 1253.6 eV) x-ray source with an energy resolution of 0.86 eV. The x-ray source setting was always 300 W, 15 kV, and 20 mA.

Depth profiles were obtained by rastering a 3 keV Ar^+ beam over a 2 mm × 2 mm surface. At a base pressure of 1 × 10^{-10} torr, we have taken the XPS core level lines of In *3d*, Sn *3d*, O *1s*, Na *2p*, and Ca *2p* to obtain chemical information of the surface of the films. The transmission spectra of the films were recorded on a Hitachi UV-VIS-NIR double-beam spectrophotometer with a blank glass substrate in the reference beam.

3. Results and Discussion

α-step measurement show that the thickness of all ITO films is 280 nm. Annealing does not affect the thickness of the ITO films. The XRD spectra of the ITO films grown on bare glass as a function of T_a are shown in Fig. 1. The XRD measurements revealed that the ITO films deposited at room temperature (RT) and annealed at a temperature range from 200 ℃ to 350 ℃ were polycrystalline and retained a cubic bixbyite structure of the Mn_2O_3 (I) type, having lattice parameters corresponding to those of crystal In_2O_3. In these ITO films, no SnO_2 phase was detected from the x-ray patterns, which implies that tin replaces indium substitutionally in the bcc lattice. This is in accordance with the observations of some studies on ITO films prepared with different methods [10-12]. These XRD patterns (Fig. 1) show very strong two peaks at 2Θ = 30.46° and 51.02° and five small peaks, which could be attributes to the diffraction from crystal planes with orientations of (222), (440), (211), (400), (431), (541), and (622), respectively.

Incidentally, the hump between 2Θ = 20° and 30° is owing to the background of the glass substrates.

The ITO films grown on glass have a preferred orientation along the [222] and [440] direction regardless of annealing temperature. And (220) and (440) peak intensities in Fig. 1 increase with increasing of annealing temperature.

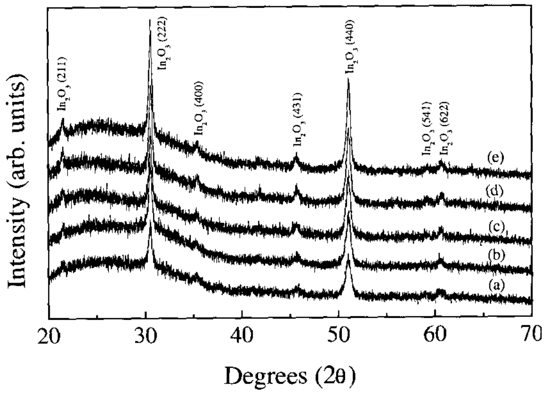


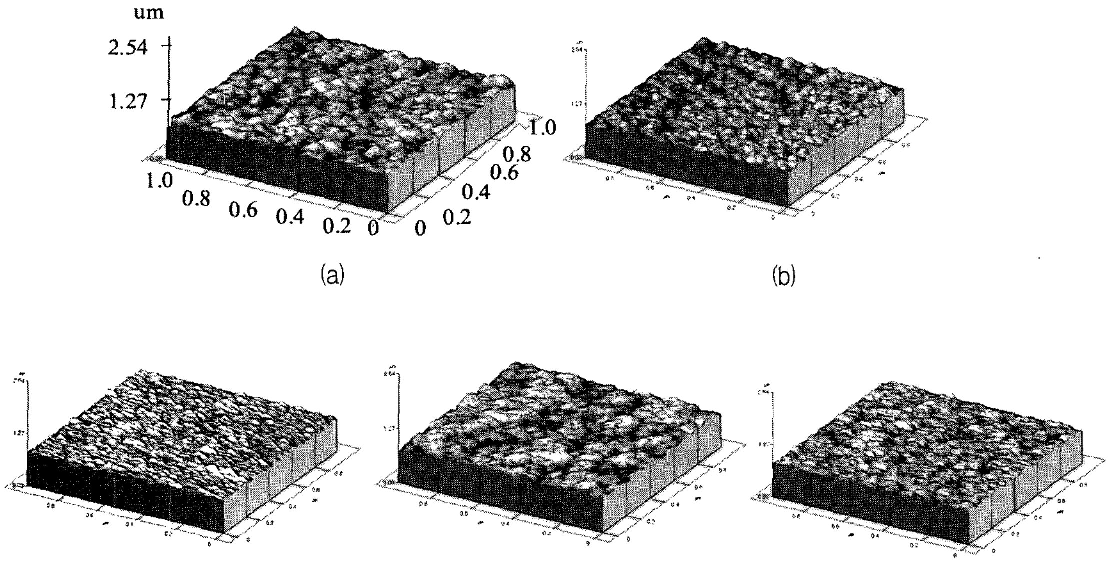
Fig. 1 XRD spectra of the ITO films grown on bare glass as a function of annealing temperature: (a) as-grown, (b) 200, (c) 250, (d) 300, and (e) 350℃ for 30 min in air.

Fig. 2 shows the AFM surface images of the ITO films grown on bare glass as a function of T_a. A small difference is observed in their surface roughness. In order to get reliable surface roughness data, five different areas of each film were scanned. The rms surface roughness of the ITO films grown on glass annealed at RT, 200, 250, 300, and 350℃ was 4.0, 4.6, 4.7, 5.6, and 4.4 nm, respectively (refer to Fig. 3). A small increase in rms surface roughness of the ITO films occurred with T_a up to T_a = 300℃, but a decrease occurred with T_a = 350℃. The increase of rms surface roughness annealed at T_a = 300℃ may be caused by grain growth but the decrease of rms surface roughness annealed at T_a = 350℃ may be caused by out-diffusion of sodium atoms into the ITO film (refer to Fig. 2(e)).

XPS measurements have been carried out using an incident x-ray beam (hv= 1253.6 eV) irradiation a surface area of 2 × 2 mm^2.

For the XPS measurements of the films that had been removed, the native oxide layer and carbon contamination corresponds to the fact that the samples are exposed to air before the XPS measurements.

Thus the high resolution XPS spectra for the films were obtained after a sputter cleaning using



(a) (b)

(c) (d) (e)

Fig. 2 AFM surface images of the ITO films grown on bare glass as a function of annealing temperature : (a) as-grown, (b) 200, (c) 250, (d) 300, and (e) 350℃ for 30 min in air.

3 keV Ar^+ ion beam for 30 sec in order to remove surface contamination.

The atomic composition in the films are estimated from the XPS peak areas using relative sensitivity factors[13]. The depth profiles of the ITO film annealed at RT, 300 and 350℃ are shown in Figs. 4(a) - 4(c).

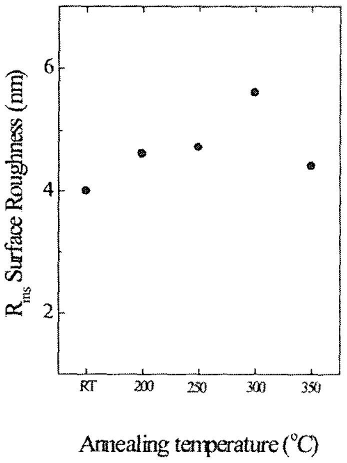
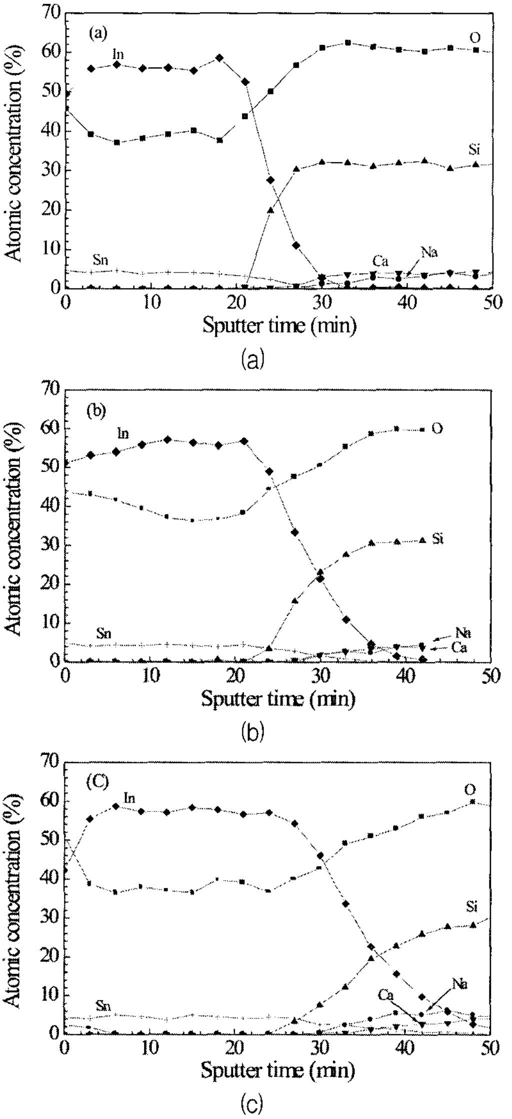


Fig. 3 Rrms surface roughness of the ITO films as a function of annealing temperature.

We have taken the XPS core-level lines of In *3d*, Sn *3d*, O *1s*, Na *1s*, and Ca *2p* to obtain measurements of the atomic concentration in the ITO films. The profiles were obtained by rastering a 3 keV Ar^+ beam over a 2 mm × 2 mm surface.

As shown in Figs. 4(a) and 4(c), the oxygen concentration at the surface of the ITO films at RT and T_a = 350 ℃ was found to be 46 and 51%, respectively, but the content of O has been reduced to 37 ~ 40% after sputtering of 3 min. And after sputtering of 3 min, the oxygen concentration in the ITO films was nearly constant with increasing sputter time. This higher oxygen concentration at the surface of the ITO films was due to the native oxide layer caused by air exposure and the removal of oxygen from the films caused by the preferential sputtering phenomenon[14]. This outdiffusion of sodium atoms was not found at the surface of ITO film annealed at T_a = 300 ℃(refer to Fig. 4(b)). But as shown in Fig. 4(c), the sodium atoms were greatly outdiffused to the surface of the ITO film annealed at T_a = 350 ℃

for 30 min in air. The sodium concentration at the surface of the ITO film was found to be 2.5%. And it was reduced to 1.8% after sputtering of 3 min. Next the sodium concentration was reduced to 0% after 6 min of sputtering. Sodium content on the interface increased with increasing T_a. The maximum sodium concentration at the interface of the ITO film as-grown was found to be 3.5%, but it has been increased to 6.5% at the ITO film annealed at T_a = 350 ℃ for 30 min in air. Also, the interdiffusion of oxygen, indium, and silicon between the ITO film and glass interface increased with increasing T_a.



(a)

(b)

(c)

Fig. 4 Depth profiles of the ITO films as a function of annealing temperature: (a) as-grown, (b) 300, and (c) 350 ℃ for 30 min in air.

The transmittance spectra of the ITO films were measured in the range between the 200 nm and 800 nm wavelength. Fig. 5 shows the transmission spectra of the ITO films as a function of annealing temperature.

It could be observed that the transmission in the visible region decreased substantially at short wavelengths near the ultraviolet range for all films

The average visible(400~800nm) transmission of ITO films annealed at various temperature is shown in Fig. 6. The transmission of ITO film has a minimum at T_a=200℃, then increases as the T_a changes from 250 to 350 ℃.

4. Conclusions

In this study, it was found that the ITO films grown on glass at a thickness of 280 nm annealed in air for 30 min as a function of annealing temperature have a polycrystalline ITO structure. All the films were oriented preferably with [222] direction and [440] direction and the peak

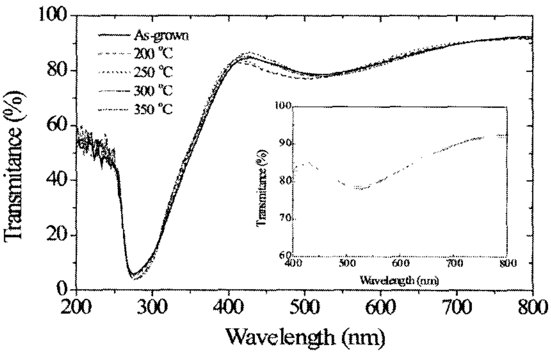


Fig. 5 Transmittance of the ITO films in the wavelength range of 200-800 nm. Inset shows the transmittance of the ITO films in the visible range.

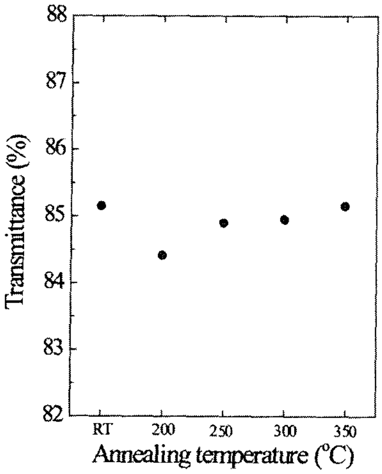


Fig. 6 The average visible transmission of the ITO films annealed at various temperature for 30 min.

intensity increased with increasing annealing temperature. The sodium was outdiffused from the glass substrate at the annealing temperature of 350 ℃. The sodium composition of the indium tin oxide (ITO) film annealed at 350 ℃ was 2.5% at the surface. Futhermore the sodium peak almost disappeared after 3 keV Ar^+ sputtering for 6 min.

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