Structure effect on electrical properties of ITO films prepared by RF reactive magnetron sputtering

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Abstract

ITO films have been deposited onto glass substrates by rf reactive magnetron sputtering using an In–Sn (90–10) alloy target. After the deposition, the films were annealed in air at 500 °C for 30, 60, 90 and 180 min respectively. The film structure varies as the annealing time is changed. The films electrical properties show a strong dependence on the film structure. Although all the films show a preferred orientation along the (400) direction, the film which has a high (222) diffraction peak intensity has a high carrier mobility and a low resistivity.

Keywords: Electrical properties and measurements; Indium oxide; Sputtering; Structural properties

1. Introduction

Indium tin oxide (ITO) film as a transparent conductor layer is an important material in the field of optoelectronic devices such as solar cells, electroluminescence and liquid crystal displays [1–3]. Although the main present application of the ITO film is in transparent electrodes for liquid crystal displays, there are also several applications for architectural and automotive uses.

High quality ITO films have been prepared by various deposition methods such as vacuum evaporation, rf and dc sputtering, rf ion plating, spray pyrolysis, screen printing and CVD. Among these methods, the magnetron sputtering is widely used in making ITO films for display devices since the method is superior in its controllability and the film obtained by this method shows good uniformity over a wide area on large size substrates [4–12]. Some results have shown that it is necessary to anneal sputtered ITO films in order to decrease their resistivity [4,5,8], The films electrical property depends very much on its structure [5,11,12].

In this article, ITO films are prepared by rf reactive magnetron sputtering and annealed in air at 500 °C for different time (30–180 min). The structural influence on the films electrical properties are studied.

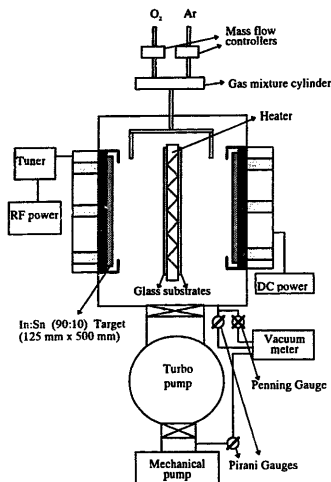[1] On leave from Changchun Institute of Physics, Chinese Academy of Sciences, Changchun 130021, P.R. China

2. Experiment

ITO films were deposited on glass substrates at ambient temperatures using rf reactive magnetron sputtering techniques. The schematic of the deposition system used in this work is shown in Fig. 1. The system is equipped with both rf and dc sputtering sources. In this work, only the rf source is used. The chamber is pumped with a turbomolecular pump (TPU510) backed by a rotary pump (EDWARDS E2M40). The pressure of the chamber is monited by a Pirani–Penning gauge combination and measured using a Balzers TPG 300 total pressure gauge controller. The substrates are microscopy glass slides. The target is In–Sn (90:10) alloy of 99.99% purity (125x500 mm^2 ALCATEL CIT). The distance between the target and substrate is about 40 mm. The cathode is cooled by running water. A RFX 13.56 MHz, 2500 W generator and an ATX tuner (Advanced Energy) are used as the rf power supply.

The vacuum chamber is evacuated down to a pressure of 3×10^{-5} mbar prior to deposition. The oxygen reactive gas is then introduced into the chamber and the required pressure (9×10^{-4} mbar) is set. Argon gas is introduced thereafter till the preset pressure is reached (4×10^{-3} mbar). After that, the oxygen reactive gas is shut off and the alloy target is presputtered (600 W rf power) in an argon atmosphere for about 10 min with a shuttle covering the substrate in order to remove the surface oxide layer formed during exposure to air. The oxygen reactive gas is then introduced again and the

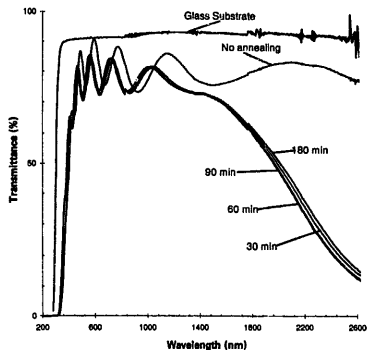Fig. 1. The magnetron planar sputtering system used in the experiments.

Fig. 2. Specular transmittance spectra of ITO films as-deposited and annealed at different time.

Fig. 3. Diffuse transmittance spectra of ITO films as-deposited and annealed at different time.

shutter is removed and the film deposition process starts. Both the argon inert gas flow and the oxygen reactive gas flow are controlled by a mass flow controller (Datametrics, controller 1605). The rf forward and reflected powers during the film deposition are 1200 and 12.3 W respectively. The deposition time is about 25 min. After the deposition, the films are annealed in a tube furnace at 500 °C in air for 30, 60, 90 and 180 min respectively. The annealing processes are as follows: preparing some samples in the same sputtering conditions and then dividing them into five groups, one group remains without annealing and the other four groups are annealed for four different times. The samples in the same group give similar results.

The film thickness is about 610 nm measured by an SLOAN DEKTAK IID. The film resistivity is measured using a Veeco FPP-5000 four-point probe. The Hall effect is measured by the Van der Pauw method. The magnetic intensity is about 0.4 T. The film transmittance is measured using a Shimadzu double-beam spectrophotometer UV-3101PC. The film diffuse transmittance and reflectance are measured using the integrating sphere attachment which has been installed in the sample compartment of the UV-3101PC. The film X-ray diffractions (XRDs) were made using a Philips geiger counter PW1710 computer-controlled diffractometer. Cu Kα radiation from an X-ray tube with normal focus was used.

3. Results and discussion

The transmittance of the ITO films as-deposited and annealed at different time are shown in Fig. 2. It is clear that

the annealing process results in the decrease of the transmittance in the visible region. This is because of the variation in the sample surface roughness. It has been found that the annealing increases the film surface roughness [13]. The rough surface scatters light and reduces the transmittance. Figs. 3 and 4 show the diffuse transmittance and reflectance of the films as-deposited and annealed at different times. It can be seen that annealing will increase the film diffuse transmittance and reflectance. However, an increase in the annealing time does not have a great effect on them. In fact, the diffuse transmittance and reflectance are the forward and backward scattering light. This is proof that annealing will result in an increase of the light scattering.

In the near infre-red region, free electrons play an important role in the ITO films transmittance. The decrease in the transmittance of the ITO films in the IR region is because of the free-carrier (in ITO films, it is an electron) absorption. The higher the electron concentration, the lower the trans-
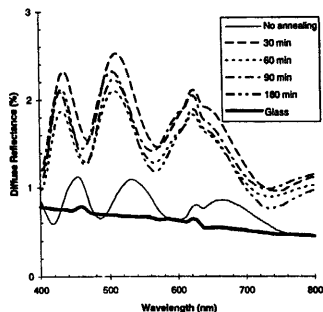
Fig. 4. Diffuse reflectance spectra of ITO films as-deposited and annealed at different time.
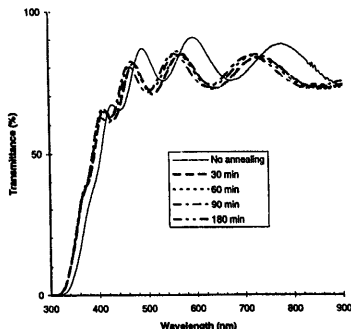

Fig. 5. Specular transmittance in the visible region of ITO films as-deposited and annealed at different time.

Fig. 6. X-ray diffraction patterns of ITO films as-deposited and annealed at different time.

mittance in the IR region. Therefore, the results of Fig. 2 show that the annealing process will increase the electron concentration. However, it is only the annealing temperature that has a great effect on the electron concentration, the annealing time has no clear effect on it.

In order to clearly see the variations in the optical band gap, the transmittance in the UV and visible region of the ITO films as-deposited and annealed at different times are shown in Fig. 5. The optical band gap shifts to the high enegy direction as the films are annealed. This shift is called the Brustein–Moss shift. It is related to the electron concentration, the higher the electron concentration, the larger the shift. From Fig. 5 it can been seen that the shift does not depend upon the annealing time. This is more evidence that the annealing time has no clearly effect on the electron concentration.

Fig. 6 shows the X-ray diffraction (XRD) patterns of the ITO films as deposited and annealed at different times. All the films show the In_2O_3 crystal structure [14]. The films
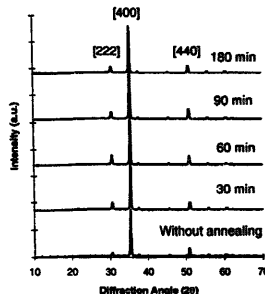
have a preferred orientation along the (400) crystal plane, indicating that the grains in the films are mainly aligned in the [100] direction and are perpendicular to the surface of the glass substrates. However, it can be seen that the (222) peak intensity increases first and then decreases as the annealing time is increased. Later we will see that this variation results in the change in the carrier mobility of the ITO films.

Fig. 7 shows the variations of the electron concentration, resistivity, Hall mobility and the ratio of the X-ray diffraction peak intensity of (222) to (400) with annealing time. The peak intensities were obtained by fitting the measured peak using two Gaussian curves with a height ratio of 2:1, width ratio of 1:1 and separated by a relevant $\Delta 2\theta$ (for (222) and (400) peaks of ITO films, $\Delta 2\theta$ are 0.078° and 0.090° respectively) because the Cu $K\alpha$ radiation contains two lines of wavelength 1.54060 and 1.54438 Å with an intensity ratio of 2:1 [16,17]. The related data are given in Table 1. As the annealing time is increased, the electron concentration does not change. However, the film resistivity and Hall mobility do change with the annealing time. It is well known that the resistivity is related with both the carrier concentration and the Hall mobility. Therefore, the variation of the films resistivity can be related with the variation of the Hall mobility. It can be seen that the film annealed at 500 °C for 60 min has the highest Hall mobility, and hence the lowest resistivity.

The variation in the Hall mobility can be related to the film structure. As shown in Figs. 6 and 7(d), the peak intensity ratio of (222) to (400) has the maximum value for films annealed at 500 °C for 60 min. Fig. 8 gives the relation between the X-ray peak intensity ratio of (222) to (400) and the Hall mobility. It is clear that the Hall mobility increases as the peak intensity ratio is increased. The mobility of the charge carriers in polycrystalline ITO is related to two scattering mechanism: ionized-impurity scattering and grain-boundary scattering. If we consider that the grain-boundary scattering is the dominant factor as discussed by Wu et al. [15], it can be suggested that the possibility of the carrier, which is scattered by grains oriented in the [222] direction, is smaller than that by grains oriented in the [400] direction.
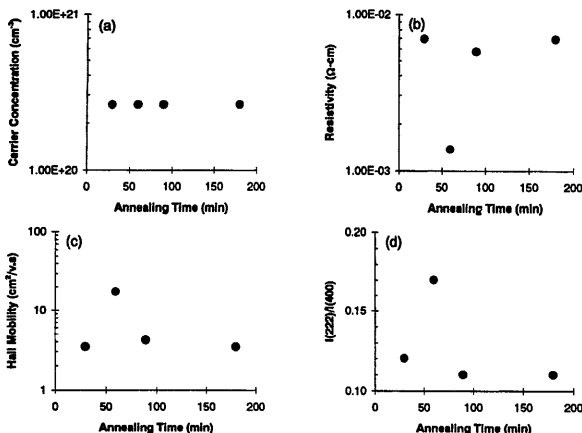
Fig. 7. The variations of the (a) carrier concentration, (b) film resistivity, (c) Hall mobility and (d) the peak intensity ratio of the X-ray diffraction, with annealing time.

Table 1
Electrical and structural properties of ITO films annealed at different times.

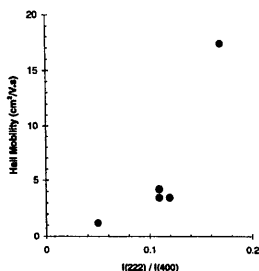| Annealing time (min)	n (cm^{-3})	ρ (Ω-cm)	μ_H (cm^2 V^{-1} s^{-1})	I(222)/I(400)
0	4.2×10^{19}	1.27×10^{-1}	1.18	0.05
30	2.6×10^{20}	6.93×10^{-1}	3.46	0.12
60	2.6×10^{20}	1.38×10^{-3}	17.39	0.17
90	2.6×10^{20}	5.71×10^{-3}	4.20	0.11
180	2.6×10^{20}	6.94×10^{-3}	3.46	0.11

Fig. 8. Hall mobility as a function of the peak intensity ratio of the X-ray diffraction.

4. Conclusions

ITO films prepared by rf magnetron sputtering have been annealed at 500 °C for varying times. The films have a preferred orientation along the [400] direction. Annealing does not change that preferred orientation, but changes the (222)

peak intensity. As the annealing time is varied, the X-ray peak intensity ratio of (222) to (400) varies. The films carrier concentration does not depend on the annealing time, but the Hall mobility does. The variation of the Hall mobility has been related to the changes in the film structure. The film which has a high X-ray peak intensity ratio (222) to (400) has a high Hall mobility and hence a low resistivity.

Acknowledgements

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