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Author(s)	Wang, RX; Beling, CD; Fung, S; Djuriši, AB; Kwong, C; Li, S
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The effect of thermal annealing on the properties of indium tin oxide thin films

R. X. Wang*, C. D. Beling, S. Fung†, A. B. Djurišić, C. Kwong, and S. Li
Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China
*email: wangrx@hkususa.hku.hk
†email: sfung@hkucc.hku.hk
Tel: (852)-28592374, Fax: (852)-28557445

Abstract-**ITO thin films were deposited on glass substrates using e-beam evaporation. The influence of post-deposition annealing on the optical properties of the films was investigated in detail. It was found that the annealing conditions strongly affect the optical properties of the films. The transmittance of films annealed in forming gas (mixed 80% N_2 and H_2) at first increases dramatically with increasing annealing temperatures up to 300ºC but then drops for higher temperature anneals around 400ºC. An interesting phenomenon is that the transmittance of the darkened film can recover under further 400ºC annealing in air. Atomic force microscopy, X-ray diffraction and X-ray photoemission spectroscopy have been employed to obtain information on the chemical state and crystallization of the films. Analysis of this data suggests that incorporation and decomposition reactions of oxygen can be controlled to reversibly change the optical properties of the ITO thin film.**

Keyword: ITO, thin film, post-annealing

I. INTRODUCTION

Indium tin oxide (ITO) is usually considered as a most promising candidate for transparent electrode materials and high electrical conductance. It is often used as a transparent conducting material in many opto-electronic devices, such as the III-V compound devices [1], organic and inorganic light emitting devices, ultraviolet photodetectors. Several methods such as thermal evaporation [2,3], RF and DC sputtering [4-7], e-beam evaporation [1,8-10],and so on have been employed to deposit ITO films on different substrates. However, the electrical and optical characteristics of ITO films are quite sensitive to the preparation methods and conditions. A better understanding and study dependence of properties of the film on different fabrication conditions is still required for the applications of ITO thin film in opto-electronic devices.

With reference to vacuum deposition techniques, such as evaporation, laser ablation and sputtering, the important control parameters are deposition rate, substrate temperature, and oxygen partial pressure. An oxygen environment is necessary for films deposited by metallic sources alone. More generally the gaseous environment during any deposition involving metallic and oxide sources can have a large effect on the quality and opto-electrical properties of the film [11-15]. Moreover, many studies have shown that both the electrical conductivity and optical transmittance of ITO thin films can be improved by post-deposition annealing [16-18]. In the present work, we investigate the effect of post-deposition annealing in air and other gases on the transmittance of the e-beam evaporated ITO films deposited on glass. To aid the interpretation of post-deposition annealing effects atomic force microscopy (AFM), X-ray diffraction (XRD) and X-ray photoemission spectroscopy (XPS) measurements were performed. In general it is found that oxygen incorporation into the ITO film is beneficial for optical transmittance and that a major reason for this is the removal of metallic In to form both indium oxide phases.

II. EXPERIMENTAL

In_2O_3:SnO_2 (9:1) powder was used as the evaporation source. Before loading into the chamber, glass substrates were cleaned in an ultrasonic cleaner for 10 min with acetone, ethanol, and DI water and then dried with nitrogen gas. The background vacuum in the chamber was 2×10^{-5} Torr. After deposition, the films were annealed at temperatures of 200°C, 300°C and 400°C in air, N_2 :H_2 mixed forming gas, Ar and N_2.

The crystallization structures of the films were examined with a Philips PW1825 X-ray diffractometer at room temperature. The chemical compound information for oxygen, indium and tin was studied using a PHI 5600 XPS with monochromatic Al K_α X-ray source for superior energy resolution. The typical operation parameters were 350 W for the X-ray source and a tilted angle of 45 º for analyzer. All XPS experiments were carried out under ultra-high vacuum conditions at room temperature. The decomposition of the component peaks in the XPS spectra was carried out with a mixture of Gaussian and Lorentzian functions. The relative element ratio was calculated from the ratio of integrated areas of the corresponding component peaks and corrected with instrument response factor. The transmittance of the ITO films without a bare substrate as a reference was measured by a HP 8453 UV-visible spectrophotometer system with a measurement wavelength range from 190 nm to 1100 nm. The surface morphology of samples was observed using an Atomic Force Microscopy (AFM) system Digital Instrument Nanoscope III. The images were obtained in tapping mode under ambient environment at room temperature with a scanning area of 5 μm×5 μm.

III. RESULTS AND DISSCUSSIONS

Figure 1 shows the transmittance curves of e-beam evaporated ITO film in the as-deposited condition and after annealing in air and forming gas at 200ºC and 400ºC,

respectively. It can be seen that post-deposition annealing at 200ºC greatly improves the transmittance. Such phenomenon results from the film becoming polycrystalline [16] and further oxidized [10,16,17]. Moreover, the transmittance edge of the annealed films shifts to shorter wavelengths. This is the Burstein-Moss shift [17]. This observation is consistent with the electrical properties of the films as listed in Table 1, where the carrier concentration and the mobility of the annealed films becomes significantly higher than those of the as-deposited film. Similar variation of sheet resistance has also been observed in films prepared by other techniques after post-annealing in various gaseous atmospheres [18]. Figure 1 also shows that the transmittance of annealed samples depends on the annealing gas. The transmittance of ITO film annealed in air is higher than that of the films annealed in forming gas at the same temperature. It is interesting that a sharp reduction in transmission is seen when the film is annealed above 400°C where the transmittance drops to a low 24% which is even smaller than that obtained in as-deposited film. It is interesting to note, however, that the transmittance of the film can be recovered to 72 % if it is further annealed in air at 400°C.

The observed optical transmittance difference between films deposited is a complex phenomenon with many contributing factors. Here the effect of chemical composition ratio on the transmittance is investigated by XPS. Figure 2 shows the O 1s

TABLE I. Properties of the ITO films deposited at 3.3Å/s: as-deposited, annealed at 200ºC in forming gas and air

	As-deposited	Air	Forming gas
Transmittance (500nm)	32%	74%	61%
ρ ($\times 10^{-4}$ Ω-cm)	555.4	9.3	5.8
μ (cm^2/Vs)	0.3	4.7	8.9
n ($\times 10^{21} cm^{-3}$)	0.3	1.4	1.1
O/In+Sn	2.1	2.3	1.5

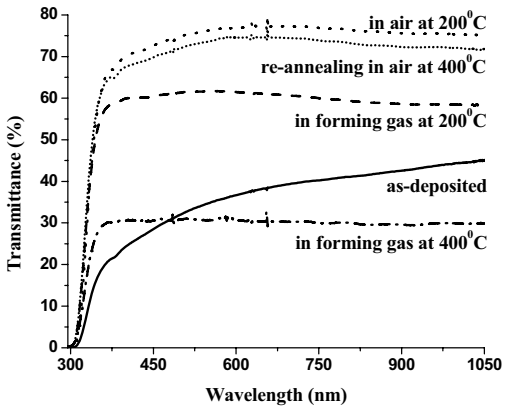

Fig. 1. Transmittance of the ITO films as-deposited and annealed in air and forming at 200ºC as well as at 400ºC

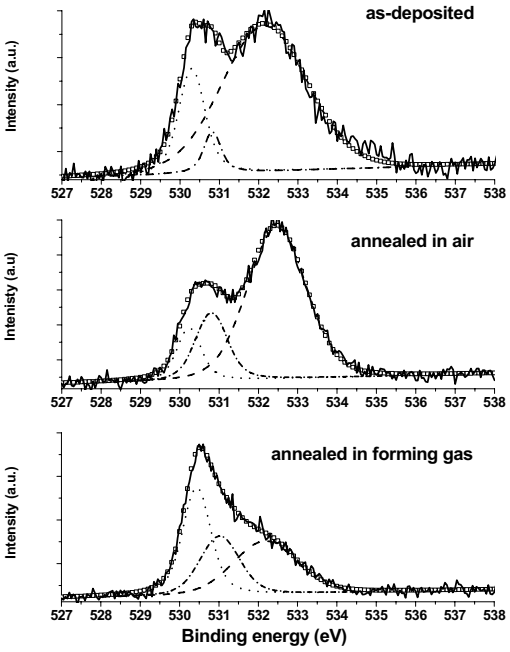

Fig. 2. O 1s XPS curves of the ITO films as-deposited and annealed in air and forming gas at 200°C

peak for the as-deposited film and the films annealed in air and forming gas at 200ºC. This data indicates significant differences in both the chemical states and the oxygen concentration for films annealed in different gases. Compared with the as-deposited film, the relative intensity of the surface oxygen $O_{\sim 532}$ peak increases for the film annealed in air. The opposite behavior is observed, however, for the film annealed in forming gas, i.e the relative intensity of $O_{\sim 532}$ peak is found to decrease with respect to that in the as-deposited film. The open squares in Fig. 2 are the best fit curves to the experimental spectra (solid lines). It can be observed that the relative intensity ratios between these three decomposed peaks vary with the annealing gas used showing that the chemical state of the oxygen is different for ITO films annealed under different ambient gases.

The integrated intensity ratios of O/(In+Sn) and the ratio $O_{530.3}/O_{530.8}$ are given in Table I, and are seen to vary according to the different post-deposition annealing gas. They can readily be explained in terms of the oxygen incorporation and decomposition reactions in the films that occur during the annealing process. Firstly, the oxygen incorporation reaction by oxygen diffusion is discussed. When an In_2O_3 source is evaporated by an e-beam, the as-deposited film generally contains metal phase indium. During annealing, residual oxygen atoms inside the film, on the top surface, and at the

interface between the film and substrate diffuse and interact with In atoms to form In_2O_{3-x} and In_2O_3 phases.

$$In \xrightarrow{O} In_2O_{3-x} \xrightarrow{O} In_2O_3 \quad \text{(i)}$$

Thus oxygen is incorporated mainly through the direct oxidation of the In metal phase [17]. These oxygen incorporation reactions are reflected by the observed variation of O/In+Sn intensity ratio, which as seen from Table 1, increases from 2.1 for the as-deposited film to 2.3 for the films annealed at 200°C in air. Oxygen in-diffusion and incorporation can thus explain the observed improvement in transmission under air annealing. In this case oxygen diffusion has enhanced film crystallization and the formation of the indium oxide phase during the annealing process. Fig. 3 shows the In 3d peak of the film annealed in air. The peak shifts to higher binding energy, as compared with films annealed in forming gas. This shift is explained through the increased binding energy of the In 3d peak produced when the In metal phase is converted into the indium-oxide phase through reaction with oxygen in the air. This supports the understanding that the high transmittance of the film annealed in air results from the removal of metallic In from the film. Moreover, we also find that the converse is also true, namely that metallic In can be produced by the decomposition of indium oxide causing a decrease in optical transmittance as discussed in the following.

The presence of oxygen decomposition reactions are reflected by the O/In+Sn ratio variations of the films annealed in forming gas. The oxygen loss of the film is indicated by a decrease of the ratio from 2.1 for the as-deposited film to 1.5 for the films annealed in forming gas. This means that the forming gas is likely to react with the top oxygen layer of the films to produce H_2O.

$$In_2O_3 \xrightarrow{H} In_2O_{3-x} + H_2O \quad \text{(ii)}$$

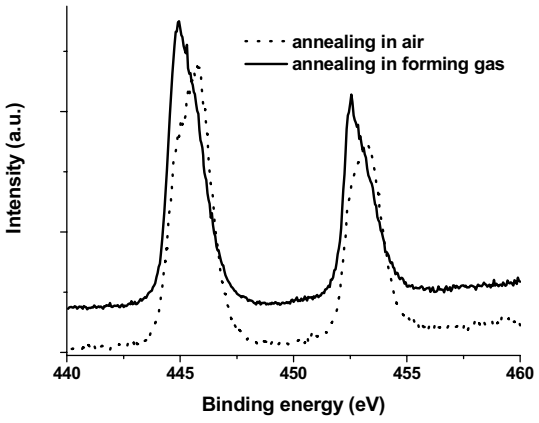

Fig. 3. In 3d XPS curves of the ITO films annealed in air and forming gas at 200ºC

These reaction products are then carried away by the flowing annealing gases during the annealing process leading to an oxygen deficient surface. Since oxygen diffuses continually out from bulk to the surface the oxidation reaction (i) is inhibited as the rate of In-O bond formation decreases and existing In_2O_3 can decompose to oxygen deficient phases and finally even to metallic In. These factors thus lead to a reduced transmittance for films annealed in forming gas. With further increasing annealing temperature above 400°C, the decomposition reaction

$$In_2O_{3-x} \xrightarrow{H} In + H_2O \quad \text{(iii)}$$

becomes important. From Fig.4, it can be seen that the morphology of the film annealed at 400°C with hundreds of nm sized clusters appearing on the surface is quite different from those of the film annealed at lower temperatures. Some metal precipitates on the surface of the ITO film annealed at 500°C in forming gas have also been observed using scanning electron microscopy [6]. It is thus suspected that the nm sized clusters are likely metallic indium. The evidence suggests that the oxygen decomposition reactions (iii) cause the observed dramatic drop of the film transmittance from 76 % to 24 % as a result of metallic In being present in the ultrathin film. As mentioned, the re-annealing of the darkened sample at 400°C in an atmosphere of air brings about a recovery of the transmittance, a fact that is readily explained with reference to the oxygen incorporation reactions (i).

IV. CONCLUSIONS

ITO thin films grown on glass substrates using the e-beam evaporation have been subject to different post-deposition annealing in different gaseous environments. From this study, it has been found that the concentration and chemical state of oxygen as seen using XPS strongly depends on the gaseous environment and the temperature of annealing. These different

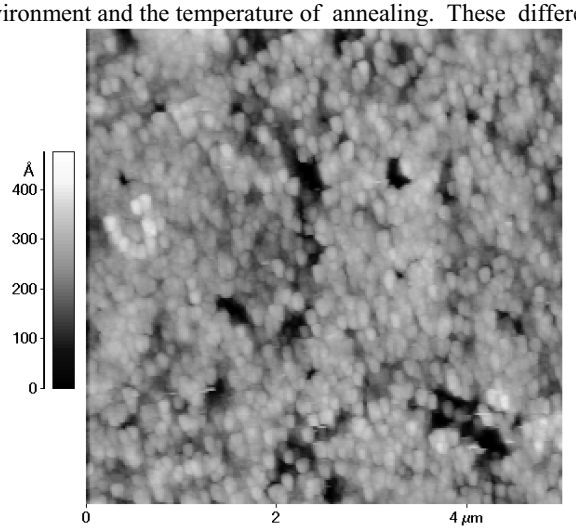

Fig. 4. AFM image of films as-deposited and annealing in forming gas at 400ºC

chemical states in turn produce notable variations in the optical transmission of the films. In conclusion the annealing temperature and gaseous atmosphere should be chosen carefully in order to optimize the incorporation of oxygen with respect to maximal electrical conductivity and optical transmittance of ITO films.

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