Oil thermal annealed nano-structured indium tin oxide thin films for display applications

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Abstract — Indium tin oxide-coated thin films (200 nm) are deposited on glass substrates by using R.f. sputtering technique. Here, we investigate the influence of new technique of treatment, which is called as "oil thermal annealing" on the nano-structured indium tin oxide thin films at fixed temperature (150 °C) which improves adhesion strength, electrical conductivity and optical properties (transmittance) of the films. Oil thermal annealing is used to reduce inherent defects that may be introduced during the prepared thin film and cooling processes. Proposed technique is highly suitable for liquid crystal displays, solar cells and organic light emitting diodes, and many other display-related applications.

Keywords *— oil thermal annealing, ITO thin film, surface morphology, nano layered, displays.*

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1 Introduction

Indium tin oxide (ITO) or tin-doped indium oxide is an n-type band-gap (3.3–4.3 eV) semiconductor, which shows high transmission in the visible and near-IR regions of the spectrum.[1] It is widely used as a transparent electrode in various optoelectronic devices such as liquid crystal displays, organic light emitting diodes, solar cells and other flat panel displays, and liquid crystal light shutters.[2] Typically, ITO is produced by deposition of a mixture of In_2O_3 (~90–95%) and SnO_2 (~5–10%), and its high conductivity is due the oxygen vacancies in In_2O_3 and the presence of tin doped, which has a higher valance than indium.[3] Depending on the deposition method used, ITO films can have different conductivity, transparency, and surface morphological structures. However, it is evident that surface roughness of ITO films is an important feature in many applications and has a significant influence on device performance. Main concern in using ITO includes high material costs, mechanical instability, and uniform film adhesion on the glass substrate. ITO films can be prepared by various techniques, such as chemical vapor deposition, thermal evaporation, DC sputtering and radio-frequency (RF) magnetron sputtering techniques, spray coatings, pulsed laser deposition, and sol–gel method.[4] The magnetron sputtering techniques are most compatible with the integrated circuit processing, which can continuously produce large area ITO techniques, the precise controls of oxygen flow and target composition ratio are very important to the deposition of ITO films due to the oxidation state and the amount of Sn doping.[5] Moreover, carrier density may also be modified by the post-annealing process by means of changes in the Sn-activation state.[6] Many studies aimed at improving the electrical and optical properties by optimizing the aforementioned deposition and annealing conditions are frequently reported.[7] However, studies concerning to reduce the inherent defects from simple thermal annealing in the oil is not studied well so far.

In this research, we report on the characteristics of ITO film have been deposited on glass substrates by a RF sputtering system and then followed by new annealing method, which we named it as oil thermal annealing (OTA). Presented study shows that oil thermal annealing method provide evidence that the annealing greatly affect the final surface morphology of ITO thin films.

2 Experimental

2.1 Deposition of indium tin oxide layer

Glass substrates containing indium tin oxide thin films were prepared by RF sputtering technique. The ITO target (99.9% purity) was a commercially available hot-pressed pallet composed of 90 wt.% In_2O_3 with 10 wt.% SnO_2. The ITO films with a thickness of 200 nm were deposited by using RF sputtering device with temperature 200 °C at pressure, with basic vacuum 3×10^{-5} Torr, after the plasma by Ar gas 6×10^{-3} Torr.

2.2 Post-deposition oil thermal annealing treatments

The OTA device consists of a simple container filled with the oil (DOWTHERM™ A Oil is used for oil thermal annealing since it is high performance heat transfer fluid at the temperature: 15–400 °C (60–750 °F)). Substrates were dipped inside the oil at different temperatures at different time interval.

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FIGURE 1 — Shows oil thermal annealing set-up used in this study.

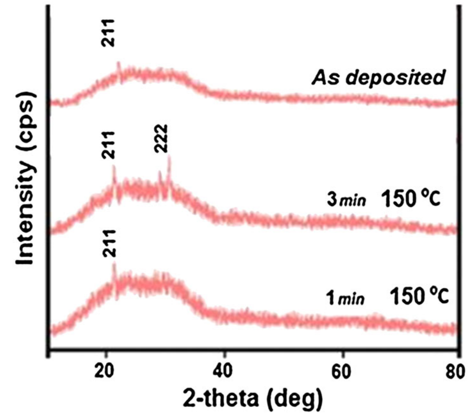

FIGURE 2 — X-ray diffraction patterns of samples annealed in indium tin oxide thin films by used thermal oil annealing at 150 °C in 1 and 3 min. For the sake of comparison "as deposited" films X-ray diffraction pattern is also given.

Experimental set-up for the oil thermal annealing method is shown in Fig. 1 where temperature of the oil is measured by thermo couple. The first step is to increase the oil temperature to 150 °C then put the sample inside the oil at different time intervals from 1 and 3 min.

2.3 Thin-film characterization

The phase composition of ITO thin films annealed at different temperatures and also with different time scales were determined using X-ray diffraction (XRD) technique with a Rigaku Minitron X-ray diffractometer at room temperature, with monochromated Cu Kα (λ = 1.540562 A°) in the scan range of 2θ between 15° and 90°.

After OTA, each sample was taken out for atomic force microscopy (AFM) measurements to study the surface morphology of the films. Surface morphology of the AFM films was measured using Dimension Edge, Bruker instrument in tapping mode and nano-drive dimension-edge-tapping image-processing software were used to measure the surface roughness of the film.

Optical transmittance measurements were measured in the wavelength range of 300–1000 nm using an OCEAN OPTICS, HR 2000+ miniaturized spectrophotometer. Electrical properties of the films were measured using digital multimeter.

3 Results and discussion

3.1 Crystallographic properties of annealed indium tin oxide thin films.

In order to study the microstructure of the ITO thin films, the XRD measurements were performed. It was found that the film microstructure orientation is sensitive to the thermal annealing condition. + XRD patterns for ITO thin films (~200 nm thickness) at 150 °C for different annealed time (say 1 min, and 3 min).

For the sake of comparison, XRD pattern of as deposited films were also given (Fig. 2). At 150 °C, two diffraction peaks were observed in the spectra described as (211), (222). The average grain size was found to be 25 nm calculated using Debye–Scherer equation[8] as shown in Eq. 1.

$$D = K\lambda / \beta\cos\theta \qquad (1)$$

Where, λ = 1.540562 A°, K (=0.9) is Scherrer's constant, and β is the measured broadening of the diffraction line peak at an angle of 2θ, at half of its maximum intensity.

In particular, the strongest line at $2\theta = 30.5°$ [corresponding to the reflection from the (222) crystalline plane] is close to the position of the strongest line of the reference indium oxide.

The (222) plane has the strongest line for the annealed temperature 150 °C as well as annealed time durations. These results are in agreement with the earlier reported works.[9] Table 1 shows a measurement XRD results with respect to 150 °C (with different annealing time), which is almost comparable with standard pattern for pure indium oxide, In_2O_3.[10]

3.2 Roughness and micro-morphology characterization of indium tin oxide thin films

Figures 3 and 4 show the AFM images of ITO thin films deposited on a glass substrate after annealing at 150 °C at 1 min (Fig. 3) and 3 min (Fig. 4).

In addition, these granules also show irregular shapes, sizes, and separations. The second feature is that the evolution of the interface width w (or root mean square roughness, rms) at 150 °C where valleys, island structures, and mountains become more as duration of the film annealing increased (Fig. 4). These different cluster sizes influence the morphology of the films. The charge carriers traveling over a rougher

TABLE 1 — Measurement of X-ray diffraction results (2θ at orientation (hkl)) with different annealing time at 150 °C.

Annealing time	2θ at hkl <211>	2θ at hkl <222>
0	21.449	—
1	21.454	30.455
3	21.001	30.549

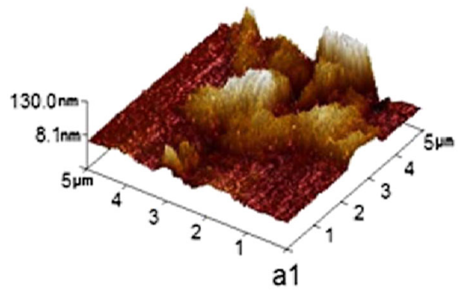

FIGURE 3 — Shows the atomic force microscopy surface images of the annealed indium tin oxide thin films by used oil thermal annealing technique at 150 °C, with time 1 min.

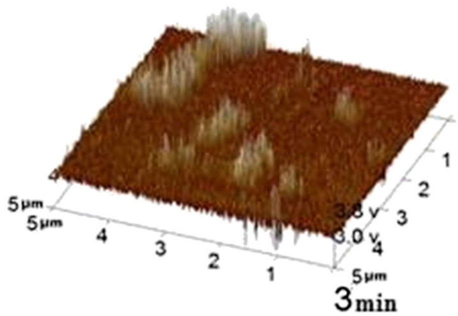

FIGURE 4 — Shows the atomic force microscopy surface images of the annealed indium tin oxide thin films by used oil thermal annealing technique at 150 °C, with time 3 min.

surface can be impeded more severely along their mean free path and, therefore, result in a decrease in mobility.

In quantitative analysis on AFM images, it is known that height roughness R_a has been used to describe the surface morphology. R_a is defined as the mean value of the surface height relative to the center plane. Surface roughness is calculated from Figs 3 and 4, is given in Table 2 for 150 °C with the comparison to as deposited films.

It can be seen from the table that surface roughness increases with increasing the annealing time. This behavior is due to the aggregation of the native grains into the larger clusters upon annealing.[11] This different cluster size influences the way of surface morphology looks like. The high temperature annealed (150 °C, 3 min) has larger clusters and becomes rougher, as expected with homogeneous surface. This study implies that surface roughness is having strong influence on degree of aggregation and cluster size of the films.

3.3 Electrical properties of indium tin oxide thin films

Conductivity as a function of annealing time at 150 °C is measured using previously coated ITO thin films (Fig. 5). One can

TABLE 2 — Measurement of atomic force microscopy surface roughness results with different annealing time at 150 °C.

Annealing temperature (°C)	Annealing time (min)	R_a(nm)
0	0	0.65
150	1	0.97
150	3	1.39

clearly see that substrates annealed at 150 °C with different time of annealing gives better conductivity values. More interestingly, 3 min annealed sample at 150 °C is having high conductivity value. The ITO thin film annealed at 150 °C (with 3 min) presented an electrical conductivity of $2.564 \times 10^3/\Omega$.cm, which is significantly higher than that of ITO film without an annealing (as deposited) having electrical conductivity $0.909 \times 10^3/\Omega$.cm.

3.4 Optical properties of indium tin oxide thin films

From the view point of device applications, it is important to have high light transmittance. Figure 6 shows the light transmittance characteristics of the oil thermal annealed ITO samples at 150 °C with 1 and 3 min annealing. It is noted that the transmittance of ITO film is improved with oil thermal annealing treatment even with as low as 150 °C temperature shows the capability of the layer to work in lower temperature scales.

It is seen that transmittance is ~70% for a sample annealed for 3 min at 150 °C whereas transmittance is more than 68% for a sample annealed for 1 min at 150 °C. Higher is the transmittance value, better is the device, so the reported oil thermal annealing definitely an bold step to increase the transmittance of the ITO coated films.

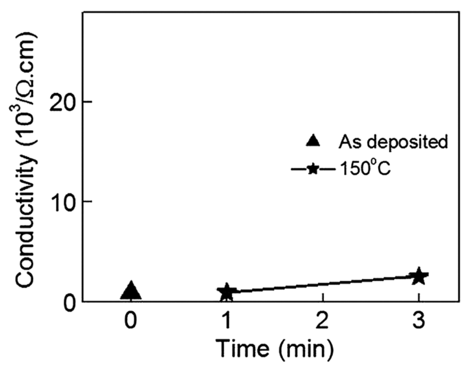

FIGURE 5 — Shows electrical properties where it emphasizes the relationship between the annealing times with conductivity.

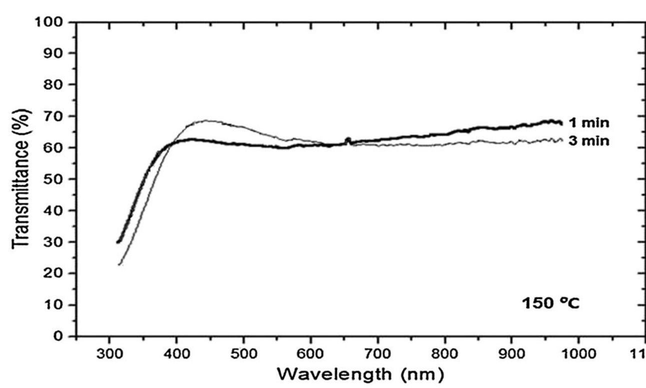

FIGURE 6 — Shows optical transmittance spectra of samples annealed in the thermal oil at 150 °C in 1 min, and 3 min.

It is indeed true that higher thermal annealing will improve the characteristic of the ITO films. More research on improving high transmittance up to 95% along with different temperature and also with different annealing time is in progress and will be reported in due course.

4 Conclusions

In conclusion, we studied the influence of new technique of treatment called as OTA for ITO thin films at fixed temperature 150 °C. Nano-structured ITO thin films improved adhesion strength, electrical conductivity, and optical properties (transmittance) of the films. Annealing is used to reduce inherent defects that may be introduced during the preparation of thin film and cooling processes. The annealed ITO thin films shows an electrical conductivity of $2.564 \times 10^3/\Omega$.cm, which is significantly higher than that of ITO film without an annealing having electrical conductivity $0.909 \times 10^3/\Omega$.cm. Proposed technique is highly suitable for photonics industry worth to mention liquid crystal displays, solar cells, and organic light emitting diodes.

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