Effect of post-annealing in oxygen environment on ITO thin films deposited using RF magnetron sputtering

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Abstract. This work demonstrated the effect of post-annealing on electrical and optical characteristics of indium tin oxide (ITO) thin films. ITO with 100 nm thickness was successfully deposited using radio frequency (RF) magnetron sputtering in oxygen-free environment on soda-lime glass substrate without substrate heating. Post-annealing treatment was carried out on ITO thin films in oxygen environment. Different annealing temperatures were studied on the films from 300°C up to 600°C. The annealing time and oxygen flow rate were kept constant. As the annealing temperature increase, the structure of the thin film’s changes from amorphous to polycrystalline which lead to the effect of enhanced hall mobility. Annealing temperature strongly influence the optical transmission in visible region. It leads to higher transmittance of ITO thin films and is suitable for a blue light emitting diode (LED) application. In addition, higher annealing temperature also enhances film electrical performance. Further characterization of the deposited films was done using hall measurement, UV-Vis spectrophotometer and atomic force microscopic (AFM) to show the improvement on their electrical and optical characteristic. The optical and electrical characteristics of the films have been compared with each other.

1. Introduction

High electrical conductivity and optical transparency of transparent conducting oxide (TCO) thin films have been widely studied due to its exciting properties. Indium tin oxide (ITO) known as a typical TCO thin film displays superior performance as one of the n-type highly degenerate semi-conductor behaviour that having wide bandgap (~3.34 eV), low electrical resistivity, high optical transmittance and high electrical conductivity [1]. ITO thin films can be produced by variety number of technique such as electron beam evaporation, spray pyrolysis [2], direct current (DC) magnetron sputtering [3], radio frequency (RF) sputtering [4], thermal evaporation and pulsed laser deposition (PLD) [5]. ITO thin films are widely used in many applications such as solar cells [6], gas sensors [7], electrode in transparent organic light emitting diodes (OLEDs) [8] and ferroelectric photoconductor storage devices [3]. The high optical transmittance of ITO in the visible range of light spectrum with high work function and high conductivity [9] makes it suitable candidates for LED to emit light. This makes indium tin oxide (ITO) widely used in light emitting diodes (LEDs) as the transparent current spreading layer.

To obtain optimum ITO characteristic such as high transparency, low sheet resistivity and high electrical conductivity; parameters like deposition technique, deposition condition, the thickness must be optimal. As mentioned above, various methods have been employed to deposit ITO on the substrate.
To produce high quality thin films with superior crystalline quality, RF sputtering technique has been chosen in this present work because this technique have very low contamination and controllable deposition parameter [7]. This work represents the morphology and electro-optical characteristics of ITO grown on substrates by RF sputtering method at room temperature and followed by post-annealing in oxygen environment at a temperature of 300 °C, 400 °C, 500 °C and 600 °C for 1 hour.

2. Experimental Method
A sputtering system was used to deposit ITO films onto cleaned soda lime glass substrates at room temperature by RF-sputtering method. The ITO target consisted of 10:90 wt.% of SnO2:In2O3 with 99.99% purity with diameter 3 inch and thickness 3 mm. Before deposition, the substrates were cleaned through the following standard procedure including cleaning in ultrasonic cleaner for 10 min with ethanol and acetone. Then followed by cleaning with deionized water and dry using N2 gun. The base pressure of the sputtering chamber was evacuated to less than 2.02x10⁻5 mbar before deposition. Sputtering was carried out in high purity argon gas (99.999%) at rate of 10 sccm. Before deposition, the target was always pre-sputtered in the chosen sputtering condition to remove contaminants. During all the deposition process, no oxygen was added. The sputtering power of 50 W under room temperature and the working pressure was 6.46x10⁻3 mbar. All the ITO samples were with film thickness about 100 nm. For the present experiment, the deposited films were then annealed at temperature from 300 to 600 °C in oxygen environment. The samples have been placed in aluminium crucibles in the furnace. The desired temperature was reached in about 1 hour. Parameter and conditions used during deposition were listed in Table 1.

Atomic force microscopy (AFM) were used to measure the surface morphology. The optical transmission (7) and resistivity (Ω.cm) of the films were taken up by Cary500 UV–VIS–NIR spectrophotometer in the 300–800 nm wavelength range and conventional four-point probe technique respectively.

Table 1. Deposition parameters for ITO film by RF magnetron sputtering and post-annealing treatment.

| Conditions                | ITO film |
|---------------------------|----------|
| Thickness(nm)             | 100      |
| Sputtering power (W)      | 50       |
| Gas flow rate (sccm)      | 10       |
| Post -annealing temperature | 300 °C, 400 °C, 500 °C, 600 °C |

3. Result and discussion
3.1 Surface Morphology
AFM is a convenient method to analyse surface topography of a thin film and obtain information about the surface roughness. Impact of the annealing temperature on the surface morphology of the ITO thin films was investigated by AFM. Figure 1 shows the three-dimensional (3-D) AFM images of ITO thin films with varying annealing temperature respectively. As shown in Figure 1, the surface grain of the ITO thin films anneals from 300 °C to 600 °C become fine and more uniform. Table 2 show the surface profile parameters like root mean square roughness (Rq) and average surface roughness (Ra) on selected areas. Root mean square roughness (Rq) of the films annealed in the oxygen at a temperature of 300 °C, 400 °C, 500 °C and 600 °C was 4.92 nm, 4.45nm, 4.20 nm and 4.07 nm respectively. RMS average (Ra) values were 3.47nm, 3.20 nm, 3.24 nm and 3.15 nm. As the annealing temperature increase from 300 °C to 600 °C, the root mean square (RMS) surface roughness decrease from 4.92 nm to 4.07 nm. Uniformity, variation in oxygen vacancies, well orientation and regular size have affected the decreasing in RMS (Rq) [10]. Furthermore, it also due to the strong surface diffusion of absorbed molecules at higher temperatures leading to the enhanced deposition and diffusion controlled growth rate [11].
Table 2. Summary of the surface roughness of the ITO thin films annealed at different temperature in oxygen environment.

| Annealing Temperature (°C) | Root mean square roughness (Rq) | Average surface roughness (Ra) |
|----------------------------|---------------------------------|-------------------------------|
| 300                        | 4.92                            | 3.47                          |
| 400                        | 4.45                            | 3.20                          |
| 500                        | 4.20                            | 3.24                          |
| 600                        | 4.07                            | 3.15                          |

3.2 Electrical Studies

Benefiting from the excellent electrical conductivity, ITO thin films is promising for high-efficiency LED’s. To measure the electrical properties of ITO films, electrical measurements were obtained from Van der Pauw-style Hall measurements at room temperature. The variations in the electrical parameter, electrical resistivity and mobility, were quantified in Table 3 with different annealing temperature from 300 °C, 400 °C, 500 °C and 600 °C. As shown in the Figure 2, the resistivity of the ITO thin films slowly decreases as the annealing temperature increases. The changing on electrical characteristics affected by annealing temperature and annealing atmosphere due to the material ordering throughout crystallization and helped in smoothing the film surface by reducing the grain boundaries [12].

Carrier concentration and its mobility is well related to the resistivity. Meng et al report that the structure of films closely related to mobility. Figure 3 shows the abrupt point where the mobility of the ITO thin films decreases and increases again at 400 °C. The changes in mobility could be due to the alteration of the doping elements and network, grain boundary and ionized scattering. [13]. The increase in the carrier concentration caused the decrease in resistivity due to the oxygen content reduction. Post-

![Figure 1](image1.png)

Figure 1. Three dimensional (3-D) AFM images of (a) 300 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C.

![Image](image2.png)
annealing at temperature above 300°C is proven effective to improve crystallinity of the ITO thin films. It can be said that near the amorphous-crystalline transition has much impact on carrier mobility.

Table 3. Summary of the comparison of electrical data for different annealing temperature of deposited ITO thin films.

| Annealing temperature (°C) | Resistivity (Ω.cm) | Hall Mobility (cm²/ V.s) |
|---------------------------|-------------------|-------------------------|
| 300                       | 374               | 11.5                    |
| 400                       | 314               | 1.45                    |
| 500                       | 134               | 2.17                    |
| 600                       | 90.15             | 3.13                    |

3.3 Optical transmittance
Researches revealed that information about the optical performance of the films were influenced significantly by deposition parameters, roughness and film thickness. The optical studies were conducted by using a Cary500 UV–VIS–NIR spectrophotometer in the wavelength range of 300–800 nm. The transmittance spectra of the as deposited and post-annealed samples for temperature between 300 and 800 °C shown in Figure 4. The transmittance is gradually increasing to more than 85% as the ITO samples undergoes post annealing from 300 to 600°C. The transmittance of the ITO thin films improved significantly beyond 90% as the post-annealing temperature rises to 600 °C. Annealing process improves the transmittance of the film in visible light range. The transmittance increases from 78% to 82% at annealing temperature of 300°C at 450nm wavelength.

As discussed in previous AFM results, these indicate that optical transmittance through the ITO is increasing significantly as the surface morphological becomes smoother. Combined with the effect of annealing on crystallization, it is clearly shown that crystalline film transmission is much more than amorphous films [7]. Crystalline film transmittance is more higher as the grain size increase by decreasing grain boundaries the light is less scattered [14]. In order to improve the transmittance of the films in visible light range, post-annealing is the most likely method for oxidation of the compound with lower valance state [15]. It is concluded that the high transmittance of the ITO thin films has low resistivity which is consistent with the results obtained by four-point probe measurement as explained in the previous section.

Figure 2. Resistivity of the ITO thin films annealed at different temperature.
Figure 3. Hall mobility of the ITO thin films annealed at different temperature.

Table 4. Transmittance for as-deposited and ITO thin films annealed at different temperature.

| Annealing Temperature (°C) | Transmittance (%) |
|---------------------------|-------------------|
| As deposited              | 78 %              |
| 300 - 600                 | 80-82 %           |

Figure 4. UV-visible transmittance spectra of as-deposited ITO thin films and annealed at different temperature.
4. Conclusion
In this study, ITO thin films have been successfully deposited on soda lime glasses by RF magnetron sputtering technique at room temperature. The post-annealing was carried out from 300 °C to 600 °C in oxygen environment for 1 hour. Results indicate that annealing temperature has an impact on the microstructural, optical and electrical characteristics of ITO thin films. Increase of the annealing temperature enhances the crystallinity and further improves the optical and electrical characteristics of the films. The grain surface morphology of the ITO thin films become more consistent and the root mean square (Rq) decreases as the annealing temperature increases. The resistivity of the ITO thin films also decreases from 374 Ω.cm to 90.15 Ω.cm as the annealing temperature increase. The transmittance spectra of annealed ITO thin films are much higher compared to as-deposited at room temperature. The increment of the transmittance is promising in visible wavelength region specifically at 450 nm for nitride-based light emitting diode (LED).

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