Preparation of Indium Tin Oxide Thin Film by Rapid Thermal Annealing Treatment

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ABSTRACT: Indium Tin Oxide (ITO) thin films were deposited at room temperature and then annealed by a rapid thermal annealing under different different temperature from 400°C to 700 °C for 5min in the atmosphere of 98% nitrogen + 2% hydrogen ambient gas. In order to know the rapid thermal annealing effect, we investigated for their structural, optical and electrical properties by using x-ray diffraction and scanning electron microscopy while optical properties were studied by the UV transmittance equipment. It is observed that the ITO thin film annealed at 500°C reveals the strong Intensity and narrowest full with at half maximum among the temperature ranges studied. The uniformity of the electronic properties and the optical properties was also improved.

KEYWORDS: ITO, rapid thermal annealing, RF magnetron sputtering.

I. INTRODUCTION

The transparent conducting oxide (TCO) thin film have been extensively studied recently, because it contain low electrical resistivity and high transmittance in the visible region. For this reason, ITO thin films are widely used in optoelectronic device such as organic light-emitting material, solar cell, electromagnetic wave shielding film, liquid crystal display and electroluminescence and so on [1-3]. Indium tin oxide (ITO) films can be produced by various techniques including DC and RF magnetron sputtering [4], electron beam evaporation [5], chemical vapor deposition [6], pulse laser deposition [7], and reactive thermal evaporation [8]. However, among the various techniques, from the view point of commercialized production, the RF magnetron sputtering method is a suitable technique.

In addition, in case of the sputtering method, it can be control about deposition parameters and it make it possible to mass the production. In order to optimize about the electrical and optical properties, ITO Thin film is carried on the substrate temperatures between 200°C to 500 °C during the deposition, or post deposition annealing [9-10].

Recently, in case of the applying for substrate about the color filter of liquid crystal display and the organic luminescent devices, flexible display, flexible solar cell, it cannot be applied to high temperature deposition. Most of all, in this research, one of the important technical issues is research about the development of a low temperature deposition technique.

We report the effects of rapid thermal annealing (RTA) temperature and atmosphere of ITO thin films grown on glass substrates by radio-frequency (RF) reactive magnetron sputtering. The outstanding merit of RTA is in the simplicity of the process, and the annealing time is an only a few seconds or a few minute. [11] The RTA process offers the short cycle time, reduced thermal exposure, and changed the crystal linny in the thin film.

In this study, we made a change about the structural, optical properties, electrical properties of ITO thin film by controlling the RTA treatment conditions during the few minute under the 98% nitrogen + 2% hydrogen gas ambient at different selected temperatures. And we investigated about the relationship between ITO thin film and the RTA Temperatures, and then we used these ITO thin films as the transparent conducting oxide film substrates, TiO₂ based dye-sensitized solar cells were fabricated, it was also analyzed by a variety of equipment and at the same time, the solar
energy conversion properties were investigated.

II. EXPERIMENTS

ITO films were prepared on glass substrates by RF magnetron sputtering with an ITO target with the purity, In$_2$O$_3$ : SnO$_2 = 90$: 10 wt.% at room temperature. Prior to deposition, the glass substrates were ultrasonically cleaned with acetone, methanol and DI water for 5 minutes. And it dried before loading in the sputtering system.

The sputtering chamber was evacuated to a base pressure of 1.5x10$^{-4}$ Pa using the rotary pump, diffusion pump and turbo molecular pump combination. Prior to the deposition, the target were pre-sputtered for 20min under an RF power of 150W in order to remove any contamination on the target surface.

The Sputtering chamber was operated in the ambient Ar gas, at a constant sputtering pressure 1.21N/m$^2$ and sputtering power of 100 W and substrate was not heated with the a target to substrate distance of 7cm, and Thickness was controlled at 100nm by controlling deposition time.

After the deposition, the ITO thin films were annealed at different selected temperature (400, 500, 600, 700$^\circ$C respectively in the98% nitrogen + 2% hydrogen ambient for 5min by RTA chamber equipment (ultechKorea).

To analyze the grown ITO thin film, The X-ray diffraction experiment (XRD, JEOL JDK-3500K) as conducted using the Cu-Kα radiation (wavelength 1.54 Å), and the microstructure shape of ITO the thin film was observed by using FE-SEM (FE-SEM: Jeol, JSM-6700F). The resistivity of the film was measured by a four-point-probe method (CMT-ST 1000), and all transmittance spectra were taken at room temperature in air, with the average transmittance from 200 to 800 nm (UV-1800, Shimadzu).
III. RESULTS AND DISCUSSION

Fig 2. Shows the XRD pattern of as-deposited and RTA treated ITO thin films in the 2θ (degree) range of 20° - 80° at different RTA Temperatures. The as-deposited ITO thin film is prepared at room temperature, which limits the ad atom mobility. It could be seen that X-ray diffraction pattern of as-deposited ITO thin film did not show any peak, it is an amorphous layer. However, After RTA in 98% nitrogen + 2% hydrogen ambient, the ITO films showed an obvious conversion from an amorphous to polycrystalline structure. ITO thin films became crystalline by annealing effect.

All diffraction peaks were shifted to larger angles afterannealing, which implies that there was a change in the residual strain between the lattice planes [12] The intensities of the four major peaks, (222), (400), (440), and (622) of ITO thin film, were significantly by annealing condition. (Card number ASTM 6-0416). [13] All the peaks in the patterns can be indexed to In$_2$O$_3$ with cubic structure. No impure phase phases corresponding to other tin compounds such as Sn, SnO, SnO$_2$ were detected which means that the tin atoms were probably doped substitutionally into the In$_2$O$_3$ lattice [14].

In particular, the line at 2θ at 31.56° which corresponds to reflection from the (222) plane is close to the position of the strongest line of reference indium oxide. As the annealing temperature increases to 400 °C, 500 °C, The intensity of (222) peak increases rapidly more than The other samples. This situation means that adatoms had an enough mobility to migrate on the substrate with transferred kinetic energy by rapid thermal annealing effect. Fejimura et al. suggested that, in the crystal structure, the surface energy density of the main orientation is the lowest (Fujimura et al., 2003). [15] Grains with the lowest surface energy become larger in the film, and develops the lower orientation growth at the crystallographic direction. This means that (222) textured film must form in an effective equilibrium state where enough surface mobility is given to impinging atoms by RTA condition [16].

It can be concluded that the RTA processing improve the crystallinity of the ITO films at the 500°C condition.

However, when the annealing temperature increased over the 500°C, the peak intensity was reduced. D. Izumi Group reported a similar situation and they observed a similar peak split in the ITO film. In addition, they proposed the residual stress model [17] Although there are many reasons, the reduction of crystal growth was occurred by the penetration of oxygen into the ITO thin film. This phenomenon is suppressed by the diffusion of oxygen atoms due to the adsorption on the ITO thin film. Finally it was obtained at the poor crystal linity in the ITO thin film. In this study, the development of the intrinsic stress could be caused by the overstacking at the high temperature condition (over 500°C). We investigated the full width at half height (FWHM) to understand about the crystallizability of the ITO thin film, as the annealing temperature increase, the full width at half height (FWHM) changed from 0.43° to 0.48°. Particularly, the FWHM decreased significantly to 0.43 for the sample annealed at 500°C. Perhaps, this result is connected with the grain growth and particle growth and so on.
Fig. 2. XRD patterns of ITO films before and after rapid thermally annealed at different temperatures.
Fig. 3. FWHM of ITO films as a function of different annealing temperature

Figure 4(a) shows a sample of non-RTA treated and Fig. 4. (c), (e), (g) show samples of RTA treated at different selected temperatures. In case of the sample of non-RTA ITO thin film, its particle size is not almost observed. Because of the amorphous structure and it have only small ITO particles size with the 20 nm grain size. The particle size is too small to observe in the X-ray diffraction analysis. As the annealing temperature increase, the particle size change and increase the crystal growth because of the decrease of defects, and this result is coincided with the XRD result. At the annealing temperature 400°C, ITO thin film contained fine grains, and the grains agglomerated, so the grain boundaries could not be easily distinguished. For ITO thin films annealed at high temperature (>500°C), the grain size clearly increased. According to the Lin et al. result, he suggested that a temperature can stimulate the migration of grain boundaries and cause the coalescence of more grain during annealing processes [18]. However, with the increasing temperature, the small microstructure was obtained in ITO thin film because the microstructure is denser in the ITO thin film. Fig 4. (B) Showed the cross-section SEM image about ITO thin film with RTA treatment at 500°C and 700°C. In case of the ITO Thin film treated by RTA at 500°C for 5min, had the greatest film thickness. In this condition, it can lead to greater residual stress, and it have effect on film thickness by increasing the internal stress. So ITO thin film showed the feature of columnar shape on the substrate and its film thickness is increased. However, the ITO Thin film treated by RTA at 700°C it had the lowest thickness by the damage effect in the high temperature. Its effect can develop a crack situation and so on. These results are good agreement with the XRD data.
Fig. 4. (A). The SEM surface images of the ITO thin films deposited at various annealing temperatures of (a) as-deposited, (b) 400°C, (c) 500°C and (d) 700°C respectively.

Fig. 4. (B). The SEM cross section images of the ITO thin film (e) 500°C (f) 700°C

Figure 5 show the AFM images of ITO films prepared after rapid thermal annealing at different temperature condition.
As a result of the experiment, in case of the Amorphous ITO thin film, it is obtained very low surface uniformity and the flat surface uniformity. The value of Rms is obtained about 0.73 nm. With the increasing of the RTA temperature, the value of root mean square (Rrms) are increased than an amorphous ITO thin film especially. In case of the annealed sample at 400 °C, 500 °C, It make it possible to apply for the optoelectronic device due to the low surface uniformity, it’s the value of Rms is obtained about 0.97 nm, 1.1 nm. At high temperature, the atoms have sufficient diffuse activation energy to occupy the correct site in the crystal lattice and the grain size will become larger in the film [19]. Its reason is connected with the grain growth after RTA annealing process. With the annealing temperature increases, the pitch of the film is changed between the surface morphology and the grain size. In case of the annealed sample at 600 °C, 700 °C, Its morphology were very increased the value of Rms is obtained about 1.59 nm, 2.4 nm. It cannot apply to the optoelectronic device such as OLED substrate. In the case of the high surface morphology, The High Voltage is focused on Top of the film. This symptom is caused by the dark spot in OLED device, it prevents to use the product and so on.

In general, the surface roughness and the microstructure, optical property have great effect on the transparent conducting oxide substrate. Most of all, if it apply for the substrate as the optoelectronic device, the surface morphology is very important than the other condition. If transparent conducting oxide substrate have a high surface roughness, at the same time, it apply for the optoelectronics device, there can be dark spots on the surface due to the concentration of the electric power, and it had a poor pixels [20]. As a result from the experiment we conclude that, ITO thin film has a very uniform surface to apply for the optoelectronic device.
Figures 6 show XPS data of the as-grown film and the Rapid thermal annealed thin films at different temperatures in 98% nitrogen + 2% hydrogen gases. No apparent chemical shift in the spectrum of Sn atoms under varying annealing conditions was observed, but there existed a noticeable difference in the oxygen and Indium spectra in different annealing ambient.

It was observed that, while the binding energy of Indium 2p in the ITO films Non RTA annealed did not change, However the binding energy was slightly shifted to a higher energy region, annealed with a 98% nitrogen + 2% hydrogen ambient in the ITO films Indicating the oxidation of metallic Indium atoms [21]. Furthermore, when the ITO film was annealed, the O1s peak was apparently decreased, which could be explained by the decrease of oxygen content in the films. By contrast, the O1s peak of the ITO films annealed in a 98% nitrogen + 2% Hydrogen ambient exhibited no detectable variation. As shown in Figures 5(a) and (b), two peaks for oxygen in the ITO and SnO, SnO$_2$ structure distinguished, because the binding energies for oxygen in this structure are 526 eV and 528 eV, respectively.

And XPS results also showed that Sn atoms segregated toward surface. [22] These differences are considered to correlate with the differences in carrier concentration and resistivity between as-deposited ITO sample and annealed ITO sample.
Figure 6. XPS spectra of ITO surface (o: RTA treated ITO Sample •: raw ITO Sample): 
(a) O1s; (b) In3d5/2 and In3d3/2; (c) Sn3d5/2 and Sn3d3/2.

Figure 7. Shows the transmittance of the ITO thin film, in accordance with the Rapid thermal annealing process, the samples were measured at the range of 200-800 nm by using the UV-spectroscopy meter, and the optical transmittance measured with respect to 550 nm.

The experiment shows that all annealed samples exhibited the optical transmittance higher than 80% at the visible light range (λ = 550 nm). It is known that the increase in optical transmittance can be attributed to the improvement of crystallinity and stoichiometry [23] The sample that was RTA treated for 5 min at 500 °C under the atmosphere of 98% nitrogen + 2% hydrogen gas ambient, exhibited the highest transmittance of 86%. The increase of transmittance is obtained by rapid thermal annealing the films. It may have been caused by a decrease in optical scattering effect [24].

And it can be attributed to increase of structural homogeneity and crystallinity. In addition, there was a shift in the absorption edge to shorter wavelength with increasing annealing temperature, which was due to the Burstein Moss shift. [25] However, if the annealing temperature increase over 500 °C, but the transmittance showed a decreasing trend than RTA annealed sample at 500 °C. In addition, ITO Thin film films annealed above 500 °C have effect on the surface roughness, and the microstructure and the small grains, the micro pores on the surface and the formation of SnO2 phase which occurred by intense thermal annealing over 500 °C. Although the correct reason cannot be known, it is considered that the replacement of In2O3 by SnO2 atoms occurred actively in the RTA process.
Fig. 7. Transmittance spectra for ITO films after RTA at the different temperature.

Fig. 8 shows that the resistivity of ITO thin film has close relation with the Rapid thermal Annealing temperature. This variation in resistivity may be due to different grain sizes.[26] Most of all, the ITO thin film is not clear about the mechanism of electrical conductivity in amorphous statue. However, with the increase of the Rapid thermal annealing Temperature, in the range of 400-500°C, the resistivity of ITO thin film was decreased. Obvious by the improvement of the crystallinity by activation of Sn dopant electron and Annealing effect. Especially, in figure 7. The resistivity of the ITO thin film was estimated about value of $4.1 \times 10^{-4} \Omega \cdot \text{cm}$ at 500°C condition for 5min.

In the case of the ITO thin film, when annealing temperature was in the 500°C for 5min in a hydrogen atmosphere, ITO thin film has a reduction of the oxygen near the surface by hydrogen ambient. And it is bring to increase of lattice defect. These results led to improve the electrical conductivity in the ITO thin film due to the increase of carrier density in the high temperature. [27] This result is in good agreement with the reported behavior in the article [28]. However, When the annealing temperature was higher than 500°C, ITO thin film showed the resistivity increased. It is well known that high conductivity of ITO thin films caused by dopant (Sn) and intrinsic defect (oxygen vacancy). This phenomena can be attributed to increase the resistivity by the more Sn atom. And it was segregated in the substrate by the high annealing effect.

The small grain and grain boundary have effect on bad electrical resistivity of the film. Which may be due to the decrease of carrier density and the limit of mobility at high Temperature. (>500°C)
Fig 8. Dependence of electrical properties (resistivity, hall mobility and carrier concentration) of ITO films after rapid thermal annealing for 5 minutes at different temperature (400°C, 500°C, 600°C, 700°C).

To identify the appearance of the crystal growth process in the above specimens, the cross-sectional TEM was observed. For the specimens without RTA treatment, it was confirmed that the small ITO crystals nucleated within the amorphous ITO in Fig 9 (a). And at the interface of the glass substrate. Due to the small size of the crystals, between 10 nm and 30 nm, they were unable to be observed in the X-ray diffraction pattern. For the specimens that were heat treated at 500°C for 5 minutes, the grain growth between the ITO particles had progressed considerably, and the formation of a crystalline structure ITO thin film composed of one particle was observed in the direction of the film thickness, as shown in Fig 9 (b). At this point, the particle size in the direction vertical to the thin film surface is the same as the film thickness, both 180 nm, and in the direction parallel to the thin film, it is about 200 nm. On the permeability front, maximum permeability is shown because no grain boundaries exist in the vertical direction, and when the conductivity was measured using the 4-point probe method, it was concluded that the number of grain boundaries influencing the conductivity is very small, resulting in superior electrical conductivity characteristics. For specimens that were heat treated a little longer, for 10 minutes in Fig 9 (c), particles grew further in the direction of the thin film, up to 300 nm.
However, simultaneous with the particle growth, small SnO2 particles form and grow at the interface of the ITO particles or at the interface between the glass substrate and ITO thin film, creating a negative influence on the permeability and conductivity. It is concluded that in the case of SnO2 particles that were observed to form and grow on the glass substrate, the growth is along the interface and hence has an especially negative influence on the permeability.

Fig. 9. Bright-field cross-section TEM images of (a) ITO thin film at room temperature and (b) after rapid annealing process at 500°C temperature for 5 minutes and (c) ITO thin film rapid annealing process at 500 °C over the temperature for 5 minutes.
V. CONCLUSION

It was demonstrated that RF magnetron sputtering technique combined with RTA process is observed that the ITO thin film annealed at 500°C for 5 min reveals more strong intensity and narrowest full width at half maximum than other samples. The condition is regard as a clear evidence about the crystal quality of improvement from the XRD data, the narrower FWHM.

From these investigations, the RTA method have the ability to reduced structural defects and enhance the UV transmittance at 550nm wavelength. The optical transmittance of ITO films deposited at an optimal condition was higher than 85% and its resistivity was obtained a low resistivity about 4.01 X 10^4 Ω cm by the rapid thermal annealing condition at 500°C for 5 min. However, with increasing the annealing temperature over the 500°C, its optical property was lower, and electrical properties of the films was higher than an optimal condition. Therefore ITO thin film electrode must have a low sheet resistance, a high transmittance in the ultraviolet-visible-infrared region and must have an excellent microstructure to apply in optoelectronics

REFERENCES


