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Effect of Oxygen Flux on FTO Thin Films Using DC and RF Sputtering

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Transparent conductive oxides (TCOs) are essential material in optoelectronics such as solar cells, touch screens and light emitting diodes. Particularly TCOs are attractive material for infrared cut off film due to their high transparency in the visible wavelength range and high infrared reflectivity. Among the TCO, Indium tin oxide has been widely used because of the high electrical conductivity and transparency in the visible wavelength region. But ITO has several limitations; expensive and low environmental stability. On the other hands, fluorine doped tin oxide (FTO) is well known for low cost, weather ability and stable in acidic and hydrogen. In this study, two different magnetron sputtering techniques with RF and DC modes at room temperature deposition of FTO thin film was conducted. The change of oxygen content is influence on the topography, transmittance and refractive index.

Keywords : FTO, sputtering

I. Introduction

As the increase of expectations for energy savings, various effect have been attempted to reduce the energy loss through a window. Among them alternative coatings with high/low/high refractive index has been widely utilized to control the incoming solar energy thereby reflecting the specific wavelengths. Transparent conducting oxides (TCOs) were promising material for low emissivity and infrared ray reflecting coatings due to the high infrared ray reflection caused by high free electron density [1]. Most of the previous researches about TCOs have been focused on indium tin oxide (ITO), but the depletion of the indium has encouraging various studies to find the alternatives of ITO. TCO films based on tin oxide (SnO_2) have been regarded as attractive material with excellent optical properties, chemical durability and good electrical conductivity [2]. But the stoichiometric un-doped SnO_2 has low electrical conductivity resulting from low intrinsic carrier concentration [3]. Therefore the challenge was preparing non-stoichiometric doped thin films. The conductivity of weakly non-stoichiometric tin oxide films is supposed to be due to doubly ionized vacancies serving as donors [4]. Antimony (Sb), Arsenic (As), bromine (Br) and fluorine (F) are generally mentioned as dopant of SnO_2 thin films to improve its electrical property. Fluorine can take place for the oxygen easily and acts as a donor which is cause by the similar ionic radius. Actually the ionic radius of F^- (1.36A) is smaller than O^{2-} (1.40A) [5]. Fluorine doped

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tin oxide (FTO) has many advantages such as low cost, chemical stability in acidic and basic solutions [6], thermal stability in oxidizing environments at high temperatures and mechanically strong [7,8]. Thin film of fluorine doped tin oxide (FTO) can be deposited by many techniques, such as sputtering, evaporation, chemical vapor deposition, spray pyrolysis, etc. From among these DC and RF magnetron sputtering systems are the most attractive techniques for industrial development because of good reproducibility, possibility of using commercially available large area and require low deposition temperature [9,10]. Recently, the development of a deposition process at a low temperature is very important for the application of film formation on a heat sensitive substrate [11]. The properties of deposited FTO thin films are found to be dependent on the several processing conditions.

In the present work, we investigated the influence of the sort of power source (RF generator and DC generator) and oxygen flux. The thickness and refractive index of deposited film were measured by ellipsometry system after than the surface roughness observed using atomic force microscope additionally transmittance of the FTO films was estimated by UV-Vis/NIR spectroscope.

II. Experiments and Discussion

FTO thin films were deposited by magnetron sputter on glass substrates. The sputtering target, 4 inch diameter, was made up with 90 wt.% SnO_2 and 10 wt.% SnF_2 with a purity of 99.99% (obtained from LTS research laboratories, Inc.) And the prepared glass substrates were cleaned by an ultra-sonic cleaner for 10 min in acetone and then ethyl alcohol.

During deposition, RF power generator was set at 250 W, Ar gas flow was fixed at 50 sccm which controlled by the mass flow controller, work pressure was set at 20 mTorr and the process was conducted at room temperature. When using DC power generator, the voltage was fixed at 425 V and the current was changed depending on process conditions. And the other conditions were maintained the same as before. In order to investigate the influence of the oxygen contents in process on the film properties, the introducing oxygen amount was varied from 0 to 5.

The thickness and refractive index of the coated FTO films were measured by ellisometer (Ellipso technology, Elli-SE-U). Based on deposition rate, the thickness of the film fixed to 100 nm by adjusting the time for comparing the accurate optical performance. Surface morphology of the formed film was observed by atomic force microscope (Park systems, XE-100). Finally the transmittance of the deposited FTO thin film was measured using UV-Vis/NIR spectrometer (Jasco, V-670). Many previous reports stated that the not annealed FTO thin film has amorphous structure for this reasons the electrical property was cannot measured.

The deposition rate, defined as film thickness divided by deposition time, is important variable to controlling the film thickness, especially for optical coatings. In Fig. 1, the deposition rate of the RF

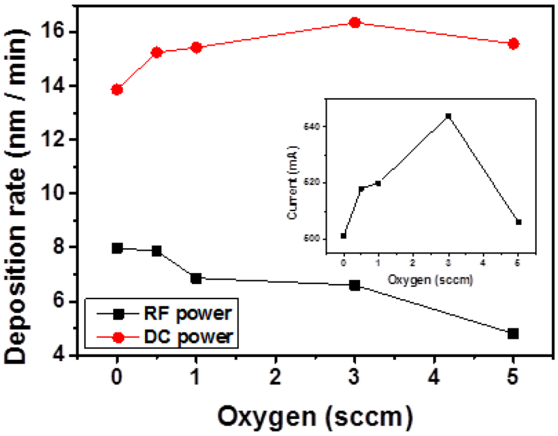

Figure 1. Changes of deposition rate according to oxygen contents. (Insert; Changes of the current versus the applied voltage by DC generator).

magnetron sputtering was lower than the DC magnetron sputtering at all conditions. Without oxygen atmosphere, the power density of both generators was same but the deposition rate was difference in the 7.98 nm and 13.87 nm each. Because using DC generator the positive current is continuously flow, while using the RF generator the positive and negative current is repeated flow. Appling the RF power, the increase of the oxygen flux was the cause of the decrease of deposition rate because that lots of oxygen in chamber was trapping on the target and prevent the deposition [12]. However using DC power stands for applying constant voltage so the current and current density versus the atmosphere in chamber were shown in the inserted figure. While injection of mixture gas ($Ar+O_2$)

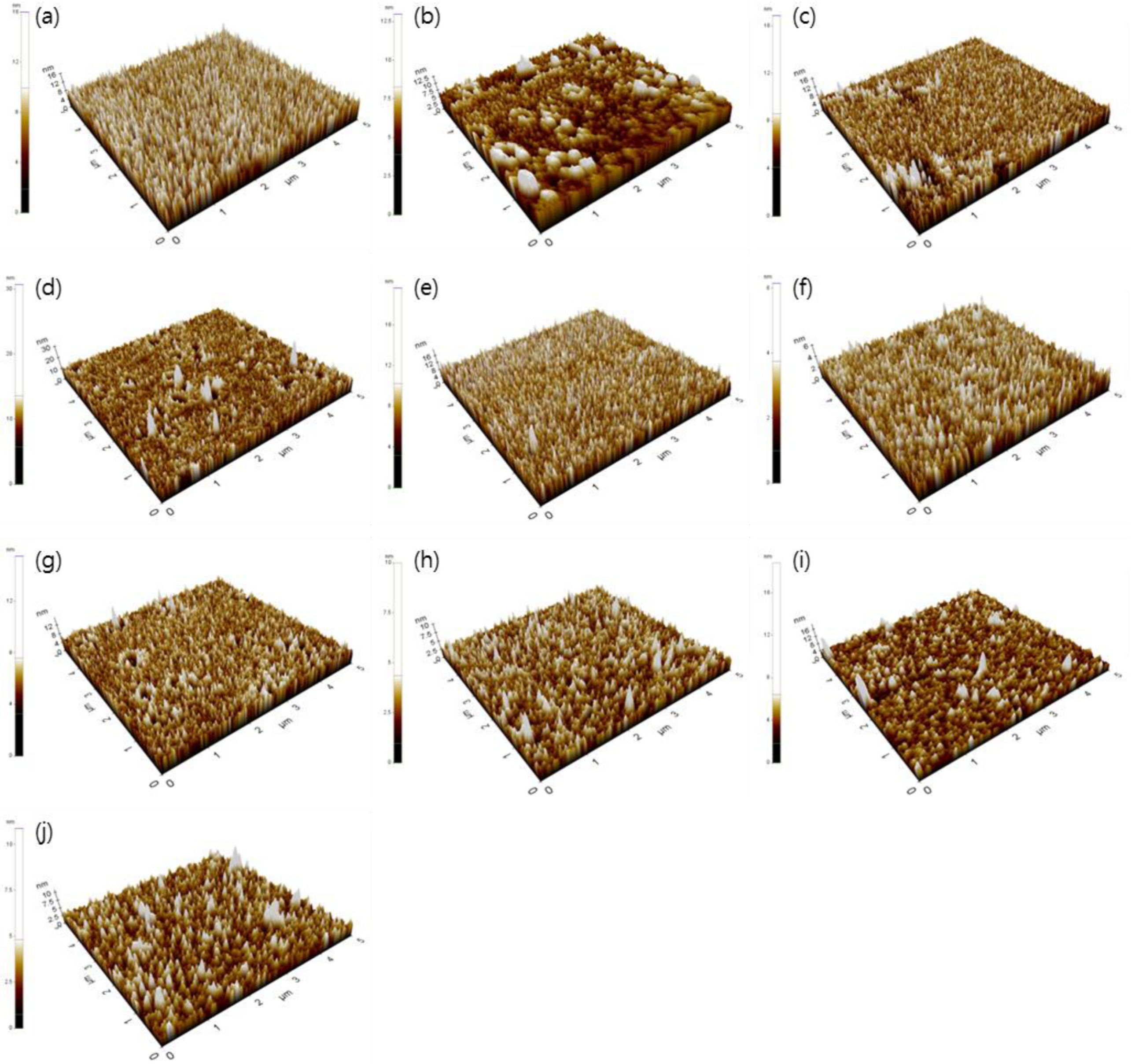

Figure 2. Three dimensional images of the surface topography observe by AFM. When using RF generator, increase of oxygen (a) 0 sccm, (b) 0.5 sccm, (c) 1 sccm, (d) 3 sccm, (e) 5 sccm,. And using DC generator, changes of the oxygen (f) 0 sccm. (g) 0.5 sccm, (h) 1 sccm, (i) 3 sccm, (j) 5 sccm.

attributed to the rise of the current density. As mentioned, the admixture gas was the factors for reducing the deposition rate on the contrary to this the increase of the current density driven to the faster.

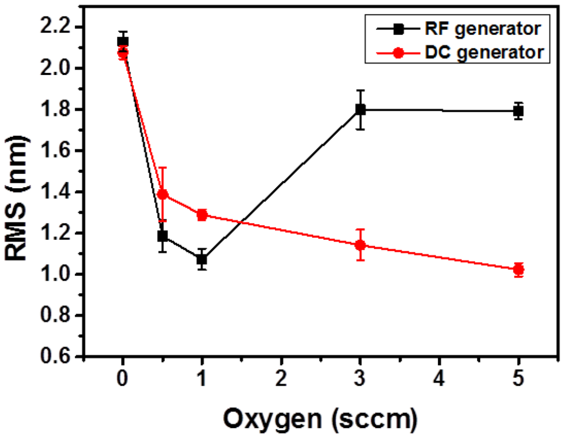

Figure 3. The changes of the surface roughness according to introduced oxygen contents.

The surface morphologies were characterized through the AFM using a non-contact mode. Observed area was 5*5 μm and the representative three dimensional surface images are presented in Fig. 2. In Fig. 2(a)~(e) and Fig. 2(f)~(j) are display the topography of the films deposited by RF and DC magnetron sputtering technique, respectively. In the initial condition without oxygen (Fig. 2(a), (f)) was very sharp columnar structure whereas introducing of oxygen was the result of forming smooth clusters in thin films. Because the oxygen ions had a high energy which assisted the aggradation of the materials and make the deposited films smoothly. In addition to this, surface roughness, root mean square (RMS), was compared and shown as the graph (Fig. 3). For accuracy, the RMS values were measured three times per a specimen and the error was displayed. Shown in the chart, the average RMS value that was not introduced oxygen in process higher as 2.1 nm than

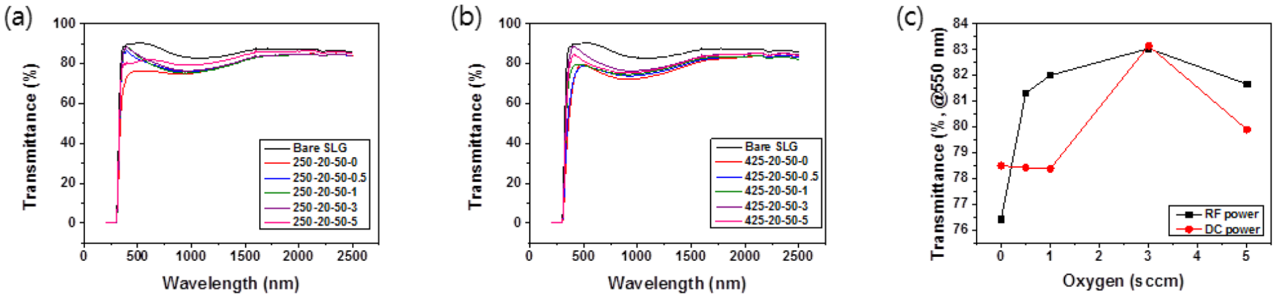

Figure 4. The variation of transmittance (a) using RF generator (b) using DC generator and (c) comparing the transmittance at 550 nm.

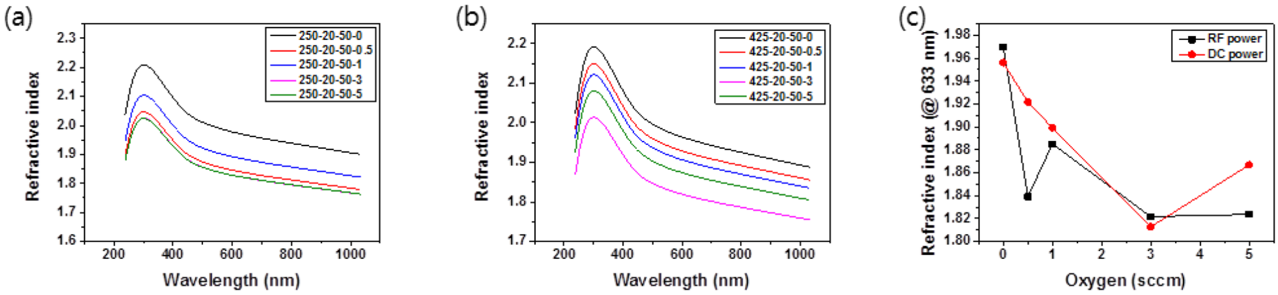

Figure 5. The trend of the refractive index (a) under RF sputtering system, (b) DC sputtering system and (c) comparison of the refractive index at specific wavelength.

other conditions and according to the increase of oxygen contents, the surface roughness was decreased. Following the previous research, the rough thin film formation in few oxygen inserted atmosphere is the result of the fewer oxygen diffuse and the shortage of the oxygen to fill up the oxygen vacancies [13]. Remaining oxygen ions existed in the sputtering gas, the oxygen vacancies are full filled with the oxygen and then the remainders are act as the surface impurities in the thin films [14].

Fig. 4 indicates that the variation of transmittance (T) with respect to the wavelength of deposited FTO thin films with diverse oxygen flux. In the all process conditions, the transmission exceeded 75% but lower than bare soda lime glass (90%) at 550 nm wavelength region. Deposited film by RF magnetron sputtering the transmittance was steadily increased until 83% before the oxygen introduced to 5 sccm. Deposited layer in only argon atmosphere was indicated low transmittance about 76% and steadily increase up to 83% at 3 sccm. Also applying DC magnetron sputtering the transmittance was slightly changed at 78% and then rapidly soaring to 83% at 3 sccm. Considering the transmittance, low oxygen flux than optimum condition leads to low performance and optimum oxygen flux was 3 sccm for the formation of non-stoichiometric later. It is stated that the decrease of the transmittance at lower oxygen flux, which is smaller than the optimum 3 sccm is due to the formation of non-stoichiometric [15]. When oxygen flux introduced over 3 sccm, the film formed a dense structure into a columnar or cluster structure with more defects [16].

The refractive index is an important parameter in the optical materials and its applications. The variations in the refractive index (n) spectra of the FTO films grown at diverse oxygen flux were presented in Fig. 5. According to increase of the wavelength, the refractive index was increased and then decreased due to the optical absorption of the thin films was increased in the wavelength range from 230 to 300 nm but decreases in the wavelength rage from 300 to 1000 nm. It can be attributed to the increase and decrease of optical absorption in the wavelength range from 230 to 300 nm and the wavelength range from 300 to 1000 nm, respectively [17].

Fig. 5(c) shows the refractive index at 633 nm as a variation of oxygen flux for FTO films. The refractive index of the FTO films decreased with increasing of oxygen flux. This decrease suggests that the density of the film deposited at high oxygen flux is less that that deposited at low oxygen flux. This indicates that there are more internal defects were existed in the FTO thin films growth with high oxygen flux than low oxygen flux [18].

III. Sumarry

In summary, the structural and optical properties of the deposited FTO thin films by various sputtering technique and oxygen contents were investigated at room temperature. Comparing the RF and DC magnetron sputtering systems, the deposition yield was significantly different but the other properties were similar. Using DC generator cause the higher deposition yield than RF generator because of the flow of current. On the other hand, the oxygen contents in the sputtering gas were significantly affects the all examined characteristics. The increase of the oxygen contents, the deposition rate, surface roughness and refractive index were decrease, but only the transmittance was increase. Known as increase of the oxygen in process chamber was served as the impurities in the deposited films. As this result simple controlling of the sputtering process conditions varying the property of the thin films and depending of the application can forming a thin film with desire characteristic.

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