# Structure and Optical Properties of Low Cost FTO Thin Films on Various Substrate Temperature Using Tap Water Solvent

Win Nilar Thaw [a], Manato Takeuchi [a], Kenji Yoshino [b]

## Abstract

Tin-doped $SnO_2$ (FTO) thin films were successfully grown on glass substrate with the temperature from 200 to 450˚C by spray pyrolysis method. All FTO thin films were characterized by XRD, SEM, AFM, optical transmittance and four-point probe measurements to know the structure and optical properties of the films. In the results, from the XRD, compared with ICDD of $SnO_2$, all the FTO thin films had the tetragonal structure except at 200 ˚C. In addition, it was confirmed that the sheet resistivity decreased with increasing the substrate temperature. The lowest sheet resistivity was $4.33\times10^5$ Ω/cm$^2$ at 450 ˚C.

*Keywords*: FTO, TCO, XRD, SEM, AFM

## 1. Introduction

Transparent conductive oxides (TCOs) films are very useful for electronic devices because of their optical properties (above 80%) and electrical properties ($10^{-3}$ Ωcm) and their wide band gap energy (3.8 eV). They are important component in a number of the electronic devices including liquid crystal displays, organic light emitting diode, touchscreens and photovoltaics[1)]. In polycrystalline thin film solar cells, the dominant materials are copper indium gallium diselenide (CIGS)[2)] and cadmium telluride (CdTe)[3)]. In addition, single Si solar cells depend on the TCO transparent electrode properties. The implication of the distinctions properties is that the TCO is either deposited directly onto the glass substrate before the absorber layers are deposited, or it is deposited on the top of the semiconductor after all of the layers have been deposited. There are many methods making TCOs films: metalorganic chemical vapor deposition (MOCVD), chemical vapor deposition (CVD)[4)], Atomic pressure chemical vapor deposition, magnetron sputtering[5)], DC and RF sputtering, sol gel method[6)], spin coating[7)], dip coating[8)] and spray pyrolysis methods. The oxides are often extrinsically doped to render high conductivity. The most important n-type TCOs are $In_2O_3$, ZnO and $SnO_2$.

Spray pyrolysis method is the deposited thin film when the precursor solution is sprayed onto the heated substrate, where the constituents react to form a chemical compound. When a precursor solution is sprayed onto a heated substrate, the evaporation of the solvent in the air and deposit as thin film. In addition, spray pyrolysis method can be making in the atmosphere, it is very simple and the equipment is not expensive than the sputtering, CVD methods etc. and it is easy to making without much time. Even multilayer thin film can be making by spray pyrolysis. These films were used in various applications such as solar cells, sensors, energy storage devices and biomedical applications.

In spray pyrolysis, the most important parameter is the surface substrate temperature. The higher the substrate temperature, the rougher and more porous films. If the temperature is too low the films are cracked. In between the higher and lower temperature, dense smooth films can be obtained. The crystallinity, texture and other physical properties of the deposited films is depended onto the substrate temperature. The precursor solution is the other important parameter which affects the morphology and the properties of the deposited films. In addition, the film morphology and properties can be changed by using various supplement in the precursor solution[9)].

Tin-doped indium oxide (ITO) is mostly favored due to its combination of important properties such as low electrical resistivity, high optical transmittance, high infrared reflectance, hardness and excellent substrate adherence[10-13)]. Indium is used as a main raw material, but the conductivity and optical transmission of ITO thin films is deteriorated at high temperature of the 300˚C. In addition, the indium is a rare metal so the price of indium increases and the requirement is not stable.

Therefore, the attraction material is changed to the tin chloride ($SnO_2$). $SnO_2$ has the wide band gap structure (3.8 eV and more) at room temperature and condenses in the rutile tetragonal structure. $SnO_2$ is doped with fluorine, chlorine and antimony[14-16)] etc., for low sheet resistivity[17)]. And $SnO_2$ based transparent conductive films have excellent chemicals stability and can be used in high temperature oxidizing atmosphere. In addition, $SnO_2$ is slightly more transparent than indium oxide because it is stable and texture structure can be formed on the film surface[18)].

Moreover, the next attention TCO films are zinc oxide (ZnO) thin films. ZnO has a wide bandgap (3.4 eV) and a large exciton binding energy (60 meV) at room temperature. The most important is ZnO have the ability to grow single crystal substrates[19)]. Zinc Oxide has the good conductivity[20)], high optical transparency[21)] and low deposition temperature. But

a) Master Student, Dept. of Electronic and Applied Physics Engineering.
b) Professor, Dept. of Electronic and Applied Physics Engineering.

the zinc oxide thin film can get the low resistivity at the vacuum process[22].

In this process, the major aim is to make the low cost fluorine doped tin oxide (FTO) thin films. Therefore, the spray pyrolysis method (no vacuum process) and the tap water is used. And then, the films are examined by XRD, SEM, four point probe and optical transmission measurements to know the structure and optical properties of thin films.

## 2. Experiment

In this procedure, tin (IV) chloride pentahydrate and 17 mol% of ammonium fluorides was mixed with 100 ml of the tap water. Second, the solution was stirred to dissolve all constituents. After that the precursor solution was sprayed onto the heated substrate by adding the 50˚C from 200 to 450˚C substrate temperature. Spray time was 100 times. And FTO thin film was formed after annealing for 5 minutes. And then FTO thin films were characterized by XRD, SEM, AFM, four-point probe and optical transmittance measurements.

## 3. Results and Discussion

### 3.1 FTO Thin Films

Tin (IV) chloride pentahydrate was used as a precursor with the solvent of tap water. Ammonium fluoride (17%) was used as the dopant by the spray pyrolysis methods. The temperature was changed from 200 to 450 ˚C by 50˚C. Fig. 1 showed the pictures of prepared samples. In all sample with solvent of tap water, the films showed the tendency of white[23].

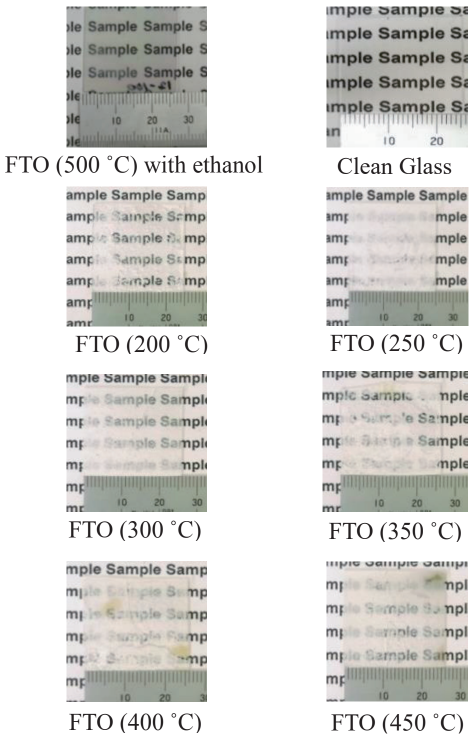


Fig. 1 FTO thin Films

### 3.2 XRD Results

The crystal structure of the films was characterized by XRD measurement. Fig. 2 shows the X-ray diffraction spectrum on various substrate temperature. When all films were compared with the ICDD of $SnO_2$[24], the films were clearly observed the intensity of the plane (110), (101) and (211) except for 200˚C. Therefore, they were identified as the thin film of $SnO_2$. Although there was no peak at 200 ˚C, it showed the tendency of amorphous structure but the other peaks of (311), (400) and (420) (ICDD of $(NH_4)\ SnCl_6$)[24] were also observed.

The lattice constant is shown in Fig. 3. All substrates temperatures were agreement with the lattice constant of $SnO_2$ (*a* axis is 4.7381Å)[25]. Therefore, it can be obtained that FTO thin films have tetragonal structure. Fig. 4 shows the full width at a half maximum of the substrate temperature of (211), (101) and (110). As the substrate temperature increases, it was confirmed that the value of full width at half maximum becomes small. It is considered that the state of more perfect crystallinity and an increase in crystallite size are observed as the substrate temperature increases[26].

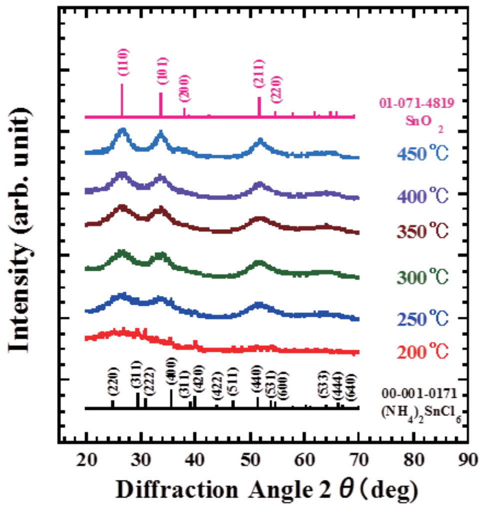


Fig. 2 XRD patterns of FTO thin films
on various substrate temperature

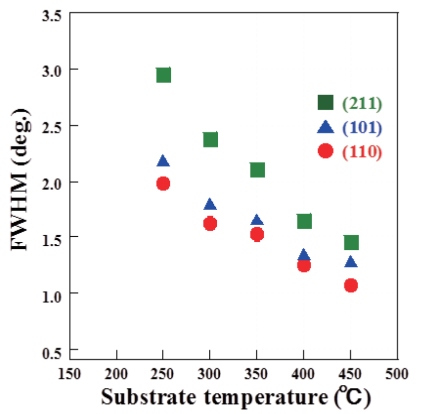


Fig. 3 The lattice parameter of the FTO films
on various substrate temperature

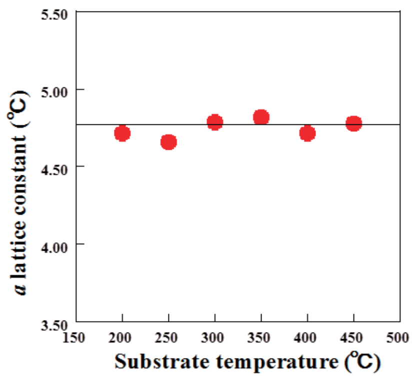


Fig. 4 The full width at half maximum of the peak at various substrate temperature

### 3.3 SEM and AFM Results

The surface and cross-sectional state of the FTO thin films were characterized by SEM. Figs. 5 and 6 shows the surface images, respectivity the cross-sectional image of the FTO thin films. The thickness of the films were from 0.6 to 4.2 µm. The 3D images of the FTO by AFM are shown in Fig. 7 and the values of the RMS are shown in Fig. 8. Unevenness of the films was observed at the temperature of 350 ˚C. this is assumed that the grain size increases as increasing the substrate temperature [27]. And when the temperature increased to 450 ˚C, the distribution of grains was uniformly on the surface. In addition, the RMS value was the highest at the temperature of 350 ˚C and then decreased from 400 ˚C.

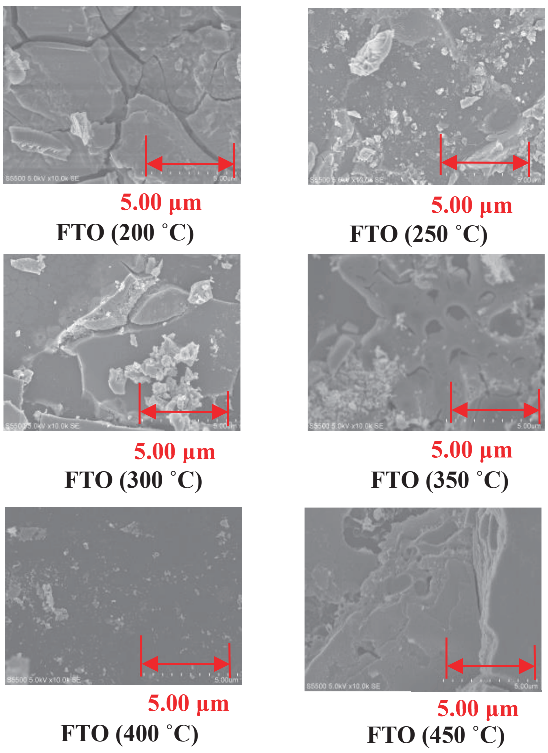


Fig. 5 The surface morphology of the FTO thin films on various substrate temperature by SEM

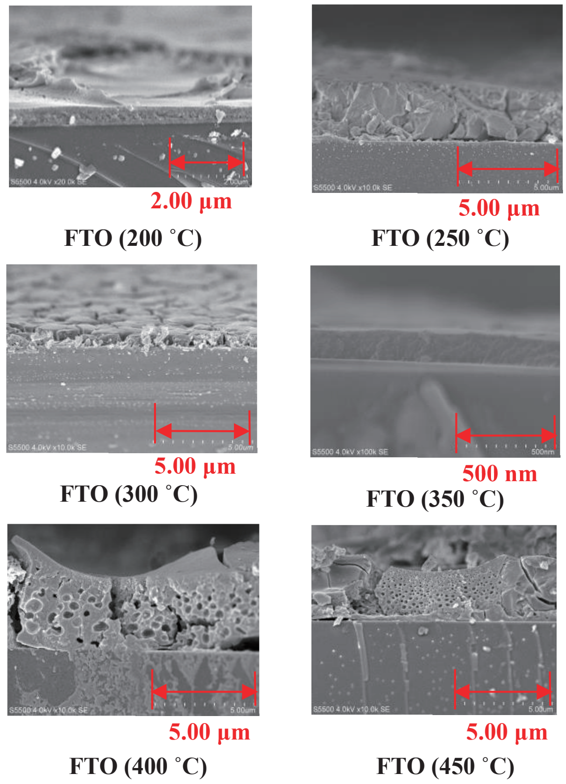


Fig. 6 The cross-section of the FTO films on various substrate temperature by SEM

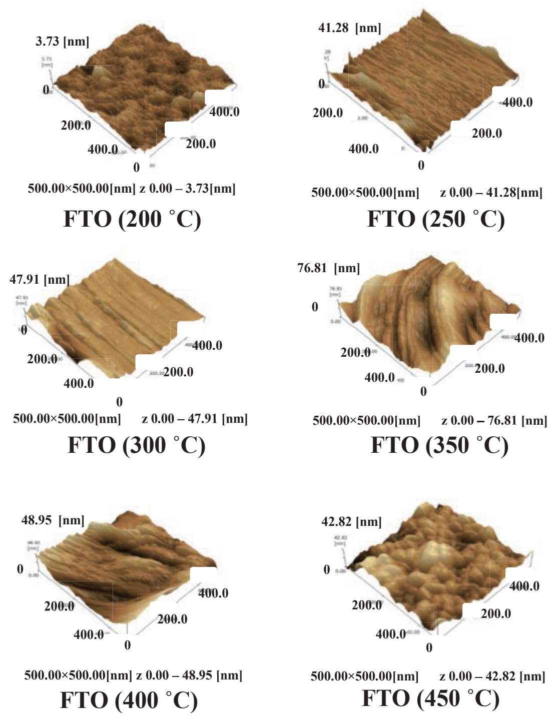


Fig. 7 The AFM (3D image) of the FTO films on various substrate temperature

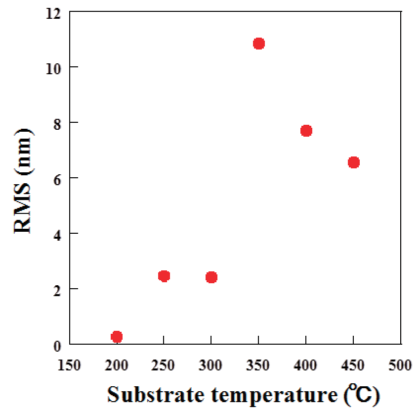


Fig. 8 The RMS values of the various temperature of the FTO films

### 3.4 Sheet Resistivity

The sheet resistivity of the FTO films on the different substrate temperature measured by four point probe measurement is shown in Fig. 9. The sheet resistivity was measured immediately after film making. The sheet resistivity at 200 ˚C was the highest value and the resistivity was dramatically decreased at 250˚C. This is because of the peak of the $SnO_2$ was observed from XRD and crystal growth occurred. The sheet resistivity decreased with the increasing substrate temperature. The smallest sheet resistivity is 4.33 x $10^5$ Ω/ $cm^2$.

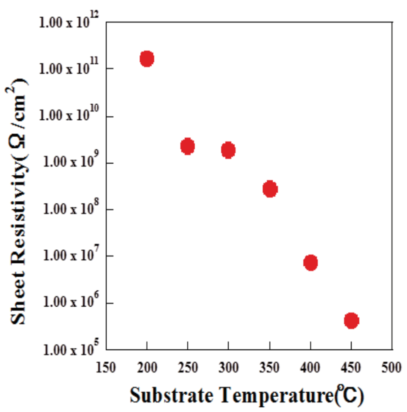


Fig. 9 The sheet resistivity of the FTO films

### 3.5 Optical Transmittance

The optical transmittance of the films from 200 to 800 nm at room temperature using a vertical detector is shown in Fig. 10. The crystallinity is improved and the impurity are reduced when the substrate temperature increases. Therefore, the transmittance can be high as impurities are reduced, but this result was not observed in this study. Furthermore, the best transmittance of the 30% is at 350˚C. It is lower than the transparent conductive film (80% or more transmittance in the visible range). This is assumed that the film surface shown in Fig. 1 is white, therefore an optical reflection and scattering occur and it causes low transmittance[28)].

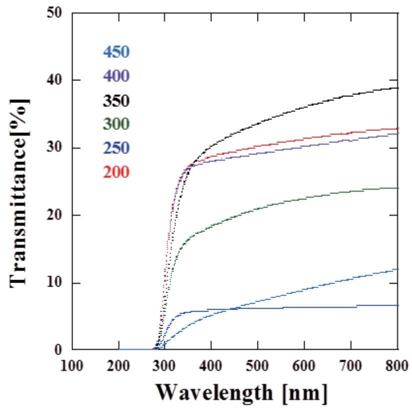


Fig. 10 The optical transmittance value of the FTO thin films

## 4. Conclusion

FTO thin films were prepared by spray pyrolysis method using tap water solvent. The 0.32 M of tin (IV) chloride penetrate was used as precursor and 17 mol% of ammonium fluorides were used doping agent on the various substrate temperature of 200 ˚C to 450 ˚C by changing 50˚C. The 100 times sprayed and annealed for 5 min. In the XRD, all films were observed the peaks (110), (101) and (211) of the ICDD of $SnO_2$ except at 200˚C substrate temperature and all films had the tetragonal structure of $SnO_2$. The full width at half maximum was small when the substrate temperature increased. It was assumed that the impurity decreased as the substrate temperature increased. In the SEM and AFM, the films thickness were from 0.6 to 4.2 μm. The unevenness was observed at the substrate temperature of 350 ˚C. The RMS value was large at 350 ˚C. In the four point probe measurement, the sheet resistivity decreased when the substrate temperature increased. It was considered that one of the reason was grain boundary decreased as the grain size increased and therefore, the influence of grain boundary scattering decreased. The lowest sheet resistivity was 4.33x $10^5$ Ω /$cm^2$. The optical transmission measurement showed the low transmittance. It was assumed that when the samples were white, the optical reflection and scattering were caused.

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