



Temperature dependence of Fluorine-doped tin oxide films produced by ultrasonic spray pyrolysis

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ABSTRACT

Fluorine-doped tin oxide (FTO) films were prepared at different substrate temperatures by ultrasonic spray pyrolysis technique on glass substrates. Among F-doped tin oxide films, the lowest resistivity was found to be $6.2 \times 10^{-4} \Omega\text{-cm}$ for a doping percentage of 50 mol% of fluorine in 0.5 M solution, deposited at 400 °C. Hall coefficient analyses and secondary ion mass spectrometry (SIMS) measured the electron carrier concentration that varies from $3.52 \times 10^{20} \text{ cm}^{-3}$ to $6.21 \times 10^{20} \text{ cm}^{-3}$ with increasing fluorine content from $4.6 \times 10^{20} \text{ cm}^{-3}$ to $7.2 \times 10^{20} \text{ cm}^{-3}$ in FTO films deposited on various temperatures. Deposition temperature on FTO films has been optimized for achieving a minimum resistivity and maximum optical transmittance.

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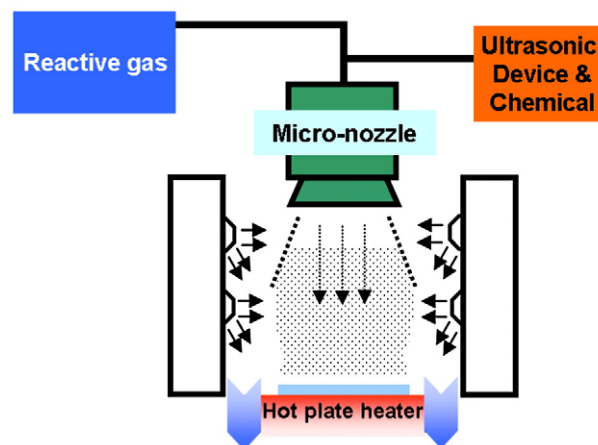
1. Introduction

An important application of thin film technology has been the development of transparent and conducting oxide (TCO) coatings that serve as window layers transparent to solar radiation and also as electrical contacts. Among these TCO's the fluorine-doped tin oxide (FTO), being an n-type, wide band gap semiconductor (≥ 3 eV) with special properties, high transmittance in the visible range and high reflectance in the infrared, excellent electrical conductivity, greater carrier mobility and good mechanical stability are used in different devices like solar cells as transparent, protective electrodes, [1] flat panel collectors as spectral selective windows, sensors for detection of gases, sodium lamps, gas sensors, and varistors [2–4]. FTO films have been prepared by various techniques, such as chemical vapour deposition, metalorganic deposition, rf sputtering, sol–gel, and spray pyrolysis [5–7]. Spray pyrolysis is used to prepare films because of its simplicity and commercial viability [8,9]. Moreover, the spray pyrolysis technique is well suited for the preparation of doped tin oxide thin films because of it is ease to adding various doping materials, controlling the texture via various deposition temperatures and mass production capability for uniform large area coatings. In this study, FTO films were deposited with different working temperatures in a controlled way and the study on the effect of deposition temperatures on structural and electrical properties.

2. Experimental details

Thin films of FTO on glass were prepared using a homemade ultrasonic vertical spray pyrolysis system with a hot plate heater, as

shown in Scheme 1. The initial solution is prepared from 0.5 mol hydrated stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in 1.0 L of deionized water and Corning glass (EAGLE 2000) was used as substrates. The sample size is around $7.0 \text{ cm} \times 7.0 \text{ cm}$. The fluorine doping was achieved by adding ammonium fluoride (NH_4F) to the starting solution. The percentage of fluorine doping was varied from 0 to 75 mol%. (The fluorine concentrations were 0–0.75 M in the starting solution.) The substrate temperature (working temperature) was varied from 360 °C to 500 °C and the deposition time was 5–10 min for all the depositions. The thickness of deposited films is around 550 nm. Air is used as carrier gas at a constant flow rate of 20 L/min. For each concentration, several sets of films were prepared and found to be reproducible. Crystal structure of the films was studied by X-ray diffraction (XRD)



Scheme 1. Illustration of ultrasonic spray pyrolysis deposition (SPD) apparatus.

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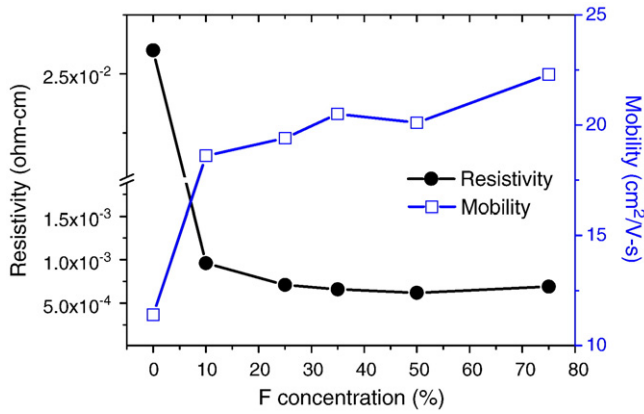


Fig. 1. Variation of resistivity and Hall mobility of FTO films with different fluorine doping. The deposited temperature is 400 °C and thickness of deposited films is around 550 nm.

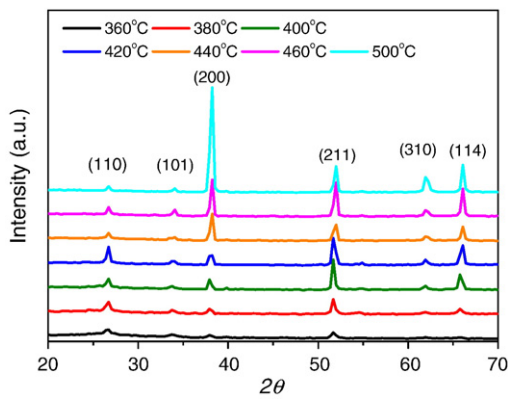


Fig. 2. XRD patterns of FTO films (fluorine concentration at 50 mol%) for different deposition temperature.

system using Cu-K α radiation. The surface morphology of the films, crystallites size and distribution were examined by JEOL 6500 scanning electron microscopy (SEM). The fluorine concentration of the films was examined by secondary ion mass spectrometry (SIMS). The electrical studies were carried out by Hall measurements in van der Pauw configuration. The visible transmission spectra of FTO films were measured using UV–Vis spectrometer with 190–1100 nm wavelength range using non-polarized light.

3. Results and discussion

The variation of sheet electrical resistivity (ρ) and mobility of the FTO films is shown in Fig. 1 as a function of fluorine concentration. It is found that the resistivity of the pure tin oxide thin films ($3.0 \times 10^{-2} \Omega\text{-cm}$) decreases with increasing fluorine concentration initially and then reaches a saturate value ($6.2 \times 10^{-4} \Omega\text{-cm}$ at 50 mol% F). However, the property of Hall mobility of FTO films is opposite to resistivity. The Hall mobility of FTO films was found to increase from 11 to $18 \text{ cm}^2/\text{V-s}$ for the increase in fluorine concentration from 0 to 10% and then saturated. Thus, it indicates that optimum doping concentration of fluorine could be around 50% in tin oxide films.

Fig. 2 shows the XRD patterns of FTO films grown with different working temperature. All the patterns correspond to the SnO₂ in the rutile structure and contain the characteristic SnO₂ peaks only. The films are polycrystalline in nature even though these films were deposited under various temperatures. The film has no preferred orientation as the growth temperature at 360 °C, whereas with progressive increase in deposition temperature, films tend to grow in specific crystallographic direction. This shows that the preferred orientation of the films depends on the working temperature. For films deposited on more than 400 °C, this slight preference changes from (211) to (200). It may be seen that, while the (211) and (110) texture in the films at low deposition temperature noticeable, the (200) texture is stronger in the films with higher working temperature. The high intensity of (200) reflection is observed for the films deposited on more than 440 °C. This increase in intensity leads to

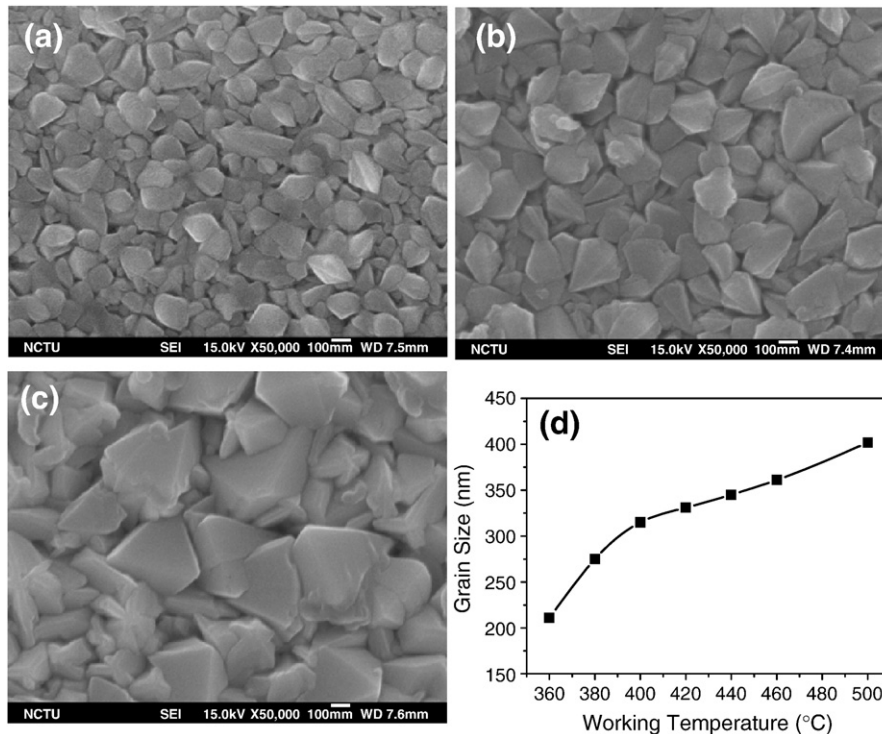


Fig. 3. SEM micrographs of FTO films (fluorine concentration at 50 mol%) obtained for different deposition temperature at (a) 360 °C, (b) 400 °C, and (c) 500 °C, respectively. (d) Grain size of various working temperature in FTO films.

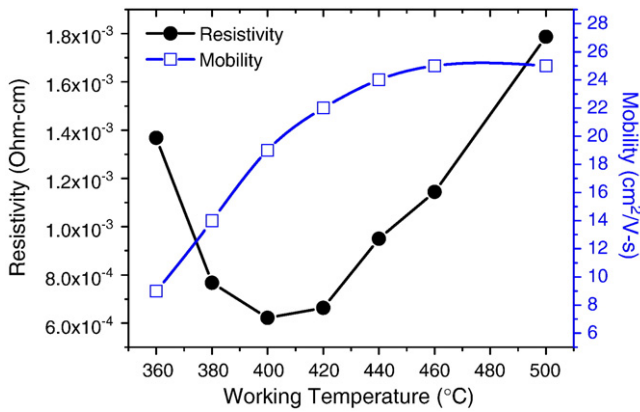


Fig. 4. Variation of resistivity and Hall mobility of FTO (fluorine concentration at 50 mol%) films with respect to deposition temperature.

better crystallinity of the films. Further, the XRD data could also corroborate the trend in microstructure development observed by SEM. The SEM micrographs displaying the surface morphology of FTO films are shown in Fig. 3 for the different working temperatures in this study. The FTO films are characterized by uniform-sized grains with cubical shape at the deposition temperature below 400 °C, which are on the average smaller than the grains in the high temperature region. The grain size of FTO films are rapidly increasing as working temperature increasing, and then the crystallite size would become saturate as the temperature reaches to 420 °C.

The electrical resistivity (ρ) and Hall mobility (μ) of the FTO films with different deposition temperature are shown in Fig. 4. The resistivity is found to decrease with increasing working temperature initially but then increased for higher deposition temperature. The resistivity was found to decrease from 1.3×10^{-3} to 6.2×10^{-4} Ω -cm for the increase the FTO film deposition temperature from 360 °C to 400 °C. It is then increased to 1.8×10^{-3} Ω -cm for higher working temperature (500 °C). It is apparent from the figure that the Hall mobility is increasing with increasing deposition temperature till 420 °C and then saturates for the higher temperature. The Hall mobility of FTO films presents the similar trend in the result of grain size data (Fig. 3d). In general, the large grain of FTO films presents the high mobility property due to their less grain boundaries in the films to improve the electron mobility and resistivity. However, we found the FTO film deposited on high temperature shows the worst resistivity than others in this work. It is well known that the mobility and carrier concentration can both evidently influence the electrical property. The Hall coefficient measurement and secondary ion mass spectrometry (SIMS) were carried out on FTO films with various deposition temperatures to show the relation between electron carrier

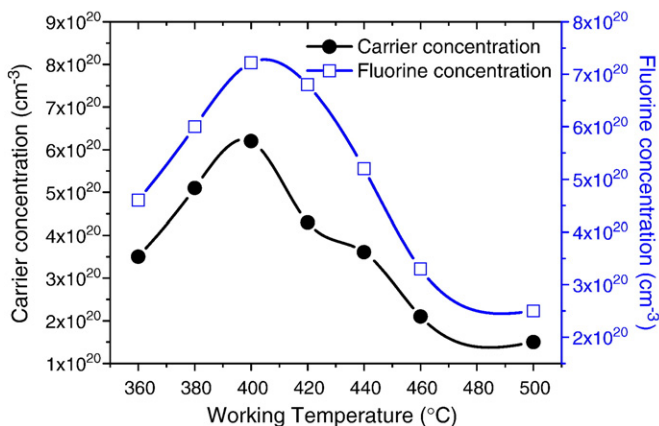


Fig. 5. Variation of carrier concentration and fluorine concentration of FTO (fluorine concentration at 50 mol%) films with different deposition temperature.

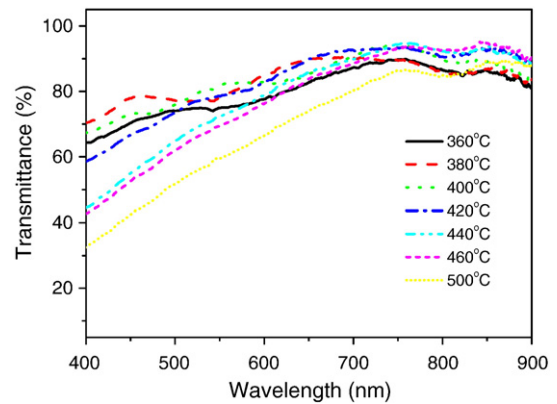


Fig. 6. Optical transmittance spectra of FTO (fluorine concentration at 50 mol%) thin films prepared at different deposition temperatures.

concentration and fluorine concentration as shown in Fig. 5. The figure clearly reveals that carrier concentration of FTO films is increasing with increase in working temperature firstly and reaches a peak value and then decreases with further increase the deposition temperature. The fluorine concentration of FTO films shows the similar trend to carrier concentration of the films. The increase in the value of fluorine concentration within a deposition temperature at 400 °C of FTO films probably represents a solubility limit of fluorine in tin oxide lattice. When deposition temperature was beyond 400 °C, the fluorine concentration would also increase again due to fluorine escaped from FTO films by high temperature deposition process. Hence, it implies that carrier concentration can be obviously controlled by the fluorine concentration in FTO films.

Optical transmission spectra of various deposition temperature FTO films in the range of 400–900 nm wavelength range are represented in Fig. 6. It was observed that visible transmittance would decrease with increasing the deposition temperature of FTO films. Highest transmittance (~77%) was obtained in FTO films on working temperature at 400 °C, whereas a lower transmittance (~60%) was observed in FTO films on working temperature at 500 °C. This important variation could be due to the optical scattering by surface morphology and grain boundaries of FTO films in this work.

4. Conclusions

Polycrystalline FTO films showed the preferential growth along (211) which has been found to changed to (200) on high deposition temperature. The grain size and surface morphology of FTO films would be increased by increasing deposition temperature. The carrier concentration of FTO films were clearly influenced by concentration of fluorine on variation working temperatures. The FTO film deposited on 400 °C revealed the minimum resistivity of about 6.2×10^{-4} Ω -cm and maximum transmittance of 77% in the visible band. This high conductivity and transparency of FTO films suggest that these films are likely to be useful as electrical contacts in various electronic and energy harvest applications.

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