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Preparation of SnO2:F thin films-based transparent heaters by spray pyrolysis deposition technique

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Abstract

This paper presents the preparation of SnO_2:F thin films used as transparent heaters deposited on glass substrate by using spray pyrolysis deposition technique. Precursor solution for spraying was prepared by mixing $SnCl_4 \cdot 5H_2O$ and NH_4F in C_2H_5OH/De-ionized water. Glass substrate temperature for spraying was varied from 250°C to 400°C. The optical, structural, morphological and electrical properties of as-deposited films were characterized by using UV-Vis spectrophotometer, X-ray diffraction technique (XRD), Scanning Electron Microscope (SEM), and four-point probe technique, respectively. The maximum value of transmittance was increased with increasing substrate temperature, over 85% in visible region for substrate temperature of 350°C. XRD results showed tetragonal structure, predominantly with (110), (101), (200), and (211) orientation. Thermal performance is shown by temperature profiles under constant voltage driven from DC power supply. It is found that heating capability of the heaters is highly dependent on glass substrate temperature.

Keywords: Transparent heater, Spray pyrolysis deposition, Temperature profile

1. Introduction

Transparent heater is generally heater plate or sheet that can convert electrical energy into thermal energy. It is typically made from an optically transparent substrate which is coated with electrically conductive as well as visually transparent elements. In the present, indium tin oxide (ITO) is the most suitable material to make transparent heater because of its high transparency greater than 95% and its low sheet resistance (R_s) lower than 50 Ω/sq [1]. The optical and electrical properties of ITO is readily controlled [2-3]. The optimum coating and patterning methods of ITO films offer excellent heating performance with high transparency. However, ITO film heaters have some disadvantage, such as poor chemical stability (can be easily etched by strong acid), brittleness, and very high cost. Various efforts have been undertaken to develop the other transparent conducting films that can overcome these ITO disadvantages.

Fluorine-doped tin oxide (FTO) or SnO_2:F films is one of the transparent conducting films that can replace ITO material due to its high transparency in visible region (T>85%), high thermal, mechanical and chemical stabilities, high electrical conductivity, and cost-effectiveness compared to ITO material. In the recent years, FTO has been widely utilized in many applications such as solar cells, heat reflectors, and gas sensors [4].

FTO thin films can be prepared by various techniques including sputtering [5], sol-gel dip coating [6], and spray pyrolysis deposition [7]. Among various deposition techniques, spray pyrolysis is considered as one of the most suitable method for deposition of FTO thin films

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because of its simplicity, cheapness, high growth rate, and mass production capability for large area deposition [8].

In this work, FTO thin films were prepared by spray pyrolysis deposition technique at substrate temperatures of 250°C, 300°C, 350°C, and 400°C because these temperature are suitable for FTO crystal forming process [9]. Stannic chloride pentahydrate ($SnCl_4 \cdot 5H_2O$) and ammonium fluoride (NH_4F) were used as starting precursors. The aim of this work is also to study the optical, structural, morphological and electrical properties of as-deposited FTO thin films and heat-generating performance of FTO films used as transparent heaters.

2. Procedure

In this study, the FTO thin films were prepared by using homemade spray pyrolysis deposition system. Microscope slide (3.5 x 2.5 x 0.1 cm^3) was used as substrate. 4.908 g of stannic chloride pentahydrate ($SnCl_4 \cdot 5H_2O$) was dissolved in 10 ml of C_2H_5OH (absolute ethanol) and 10 ml of DI water for making SnO_2 starting precursor solution with 0.7 M concentration and stirred under room temperature until homogeneous solution was achieved. NH_4F was added into SnO_2 starting precursor solution by 0.2 grams for fluorine doping content of 6 wt. % and stirred under room temperature to obtain homogeneously mixed precursor. Glass substrates (microscope slides) were cleaned by sonication in de-ionized water, acetone, methanol, and isopropyl alcohol (IPA) for each 5 min, successively. 8 ml precursor solution was loaded to spray gun (airbrush model HKX HB-3G) and was then sprayed onto glass substrates heated at 250°C, 300°C, 350°C, and 400°C for 10 min. The distance between spray nozzle and glass substrate was fixed at 60 cm vertically. Air pressure from air pump was used as carrier gas to spray at starting pressure of 100 lbf/sq in (psi). Schematic diagram of spray pyrolysis system that used in this work is shown in Fig. 1. After deposition, the as-deposited FTO films were allowed to cool down naturally to room temperature.

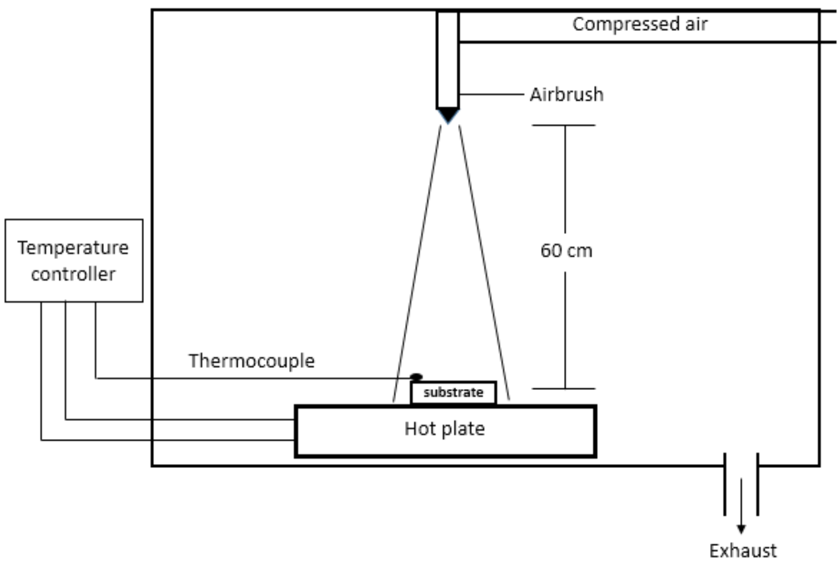

Fig. 1 Schematic diagram of spray pyrolysis deposition system in this work.

The optical characterization of as-deposited FTO thin films was carried out by UV-Vis spectrophotometer using a PG instruments T92^{+} in wavelength ranging from 250 to 800 nm. Structural characterization was carried out by X-ray diffractometer (XRD) using a Bruker D8 Discover with CuK_{α} radiation (wavelength = 0.15418 nm) operated at 40 kV and 40 mA. Morphological properties and thickness of as-deposited FTO films were characterized by using Hitachi S-4700 FESEM (Field Emission Scanning Electron Microscope). Electrical characterization of as-deposited FTO thin films was carried out by four-point probe technique using QUATEK QTI-5601TSR.

3. Results and Discussion

In the spray pyrolysis deposition technique, substrate temperature is a very important parameter. It can influence to crucial properties of the as-deposited FTO thin films. First characterization for this work is optical property. Fig. 2 shows the transmission spectra of as-deposited FTO thin films prepared at different substrate temperatures. The maximum transmittance in visible region increases with increasing substrate temperature that may contribute to the process of crystal forming dependence on substrate temperature that can be confirmed by XRD results in the next paragraph. The maximum transmittance in visible region is over 85% when using substrate temperature of 350°C. As substrate temperature rises up to 400 °C, the maximum transmittance in visible region lightly decreases due to more pore defects in its structure.

XRD patterns were used to confirm the crystal structure of as-deposited FTO thin films. Fig. 3 exhibits the XRD patterns of as-deposited FTO thin films prepared at different substrate temperatures. SnO_2 rutile tetragonal structure (JCPDS 41-1445) was formed when substrate temperature increased. The predominant planes of this thin films are ascribed to (110), (101), (200), and (211) orientation. It is evident that the crystallization can be initiated when the substrate temperature is elevated to 350°C.

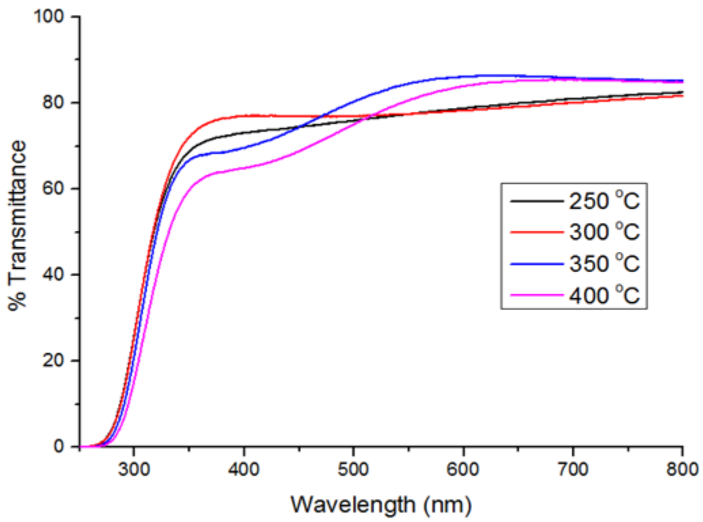

Fig. 2 Transmission spectra of as-deposited FTO thin films with different substrate temperature.

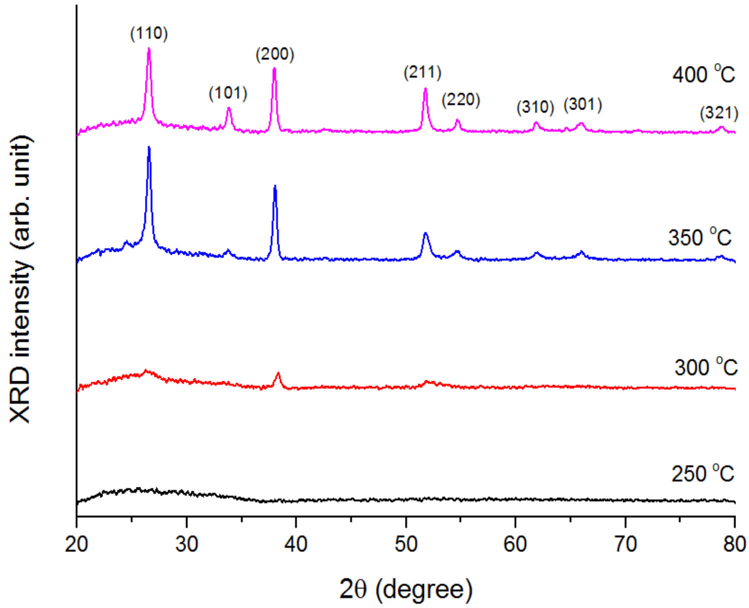

Fig. 3 XRD patterns of as-deposited FTO thin films with different substrate temperature.

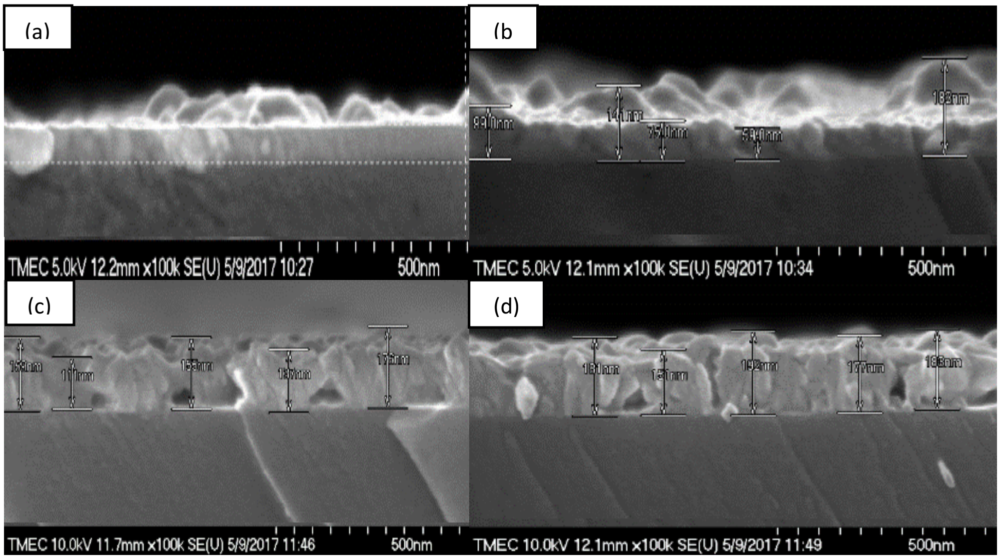

Fig. 4 Thickness of the as-deposited FTO thin films with different substrate temperature (a) 250°C, (b) 300°C, (c) 350°C, and (d) 400°C.

The as-deposited FTO film thickness was measured by using FESEM for 100,000x magnification that is shown in Fig. 4. The average thickness increases and roughness decreases with increasing substrate temperature contributing to the film formation process that is highly dependent on surface temperature. For the lower substrate temperature, FTO can be slowly formed causing thinner thickness. But for higher substrate temperature, FTO can be rapidly formed resulting in greater thickness. In this work, a cluster of large particles was also found on specific area of the films, especially at substrate temperature of 250°C and 300°C.

Surface morphology of as-deposited FTO thin films was also characterized by FESEM. Fig. 5 illustrates surface morphology of the samples deposited at different substrate temperatures. For substrate temperature of 250°C, particles were formed in small size with low density. As substrate temperature lifted to the range of 300-400°C, particles were formed into larger size due to the greater amount of heat provided to the system assisting the enhancement in crystallization. However, as-deposited FTO thin films prepared at 350°C and 400°C possessed significant voids with porous appearance. This feature may attribute to incompleteness of particle formation without post-annealing process.

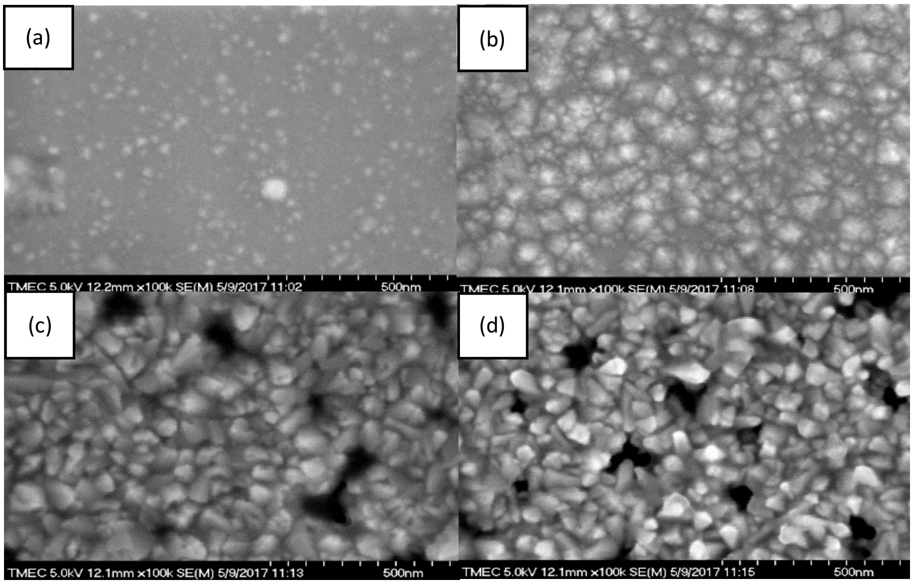

Fig. 5 Surface morphology of the as-deposited FTO thin films with different substrate temperature (a) 250°C, (b) 300°C, (c) 350°C, and (d) 400°C.

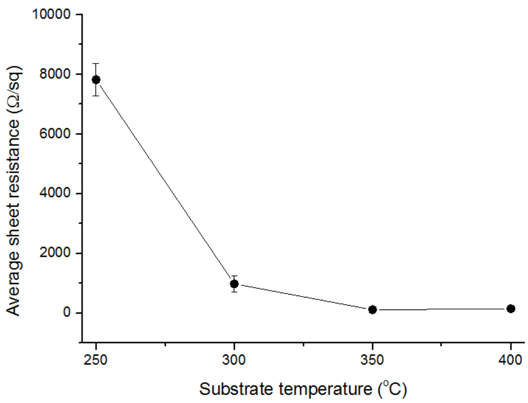

Fig. 6 Average sheet resistance (R_s) of as-deposited FTO thin films with different substrate temperatures.

As- deposited FTO thin films were cut into 2 x 2.5 cm^2 to measure sheet resistance (R_s). The measurement was carried out at 16 different points and the average values were found to be 7800, 800, 112, and 141 Ω/sq for the samples prepared at temperature of 250°C, 300°C, 350°C, and 400°C, respectively. It is found that R_s drastically decreases with increasing substrate temperature from 250°C to 400°C with two order of magnitude that can be seen in Fig. 6.

The electrical electrodes were prepared by pasting silver paint at the edge of FTO thin films and used as a current collector then connected to DC power supply at operating voltage of 12 V. While supplying voltage, K-type thermocouple was used to measure a surface temperature at center of sample. Time versus temperature has been drawn in Figure 7 (a) and (c) to study the temperature profile. Surface temperature dramatically increased in a short duration and thereafter slowly increased until reached to saturated temperature of 72°C and 62°C for FTO prepared at substrate temperature of 350°C and 400°C, respectively. The saturated temperature corresponds to a sheet resistance of FTO thin films. High sheet resistance of the film results in low current passing through device and low thermal energy generated by Joule heating mechanism. Thermal imaging camera was used to observe temperature distribution at saturated temperature for each sample as can be seen in Fig. 7 (b) and (d).

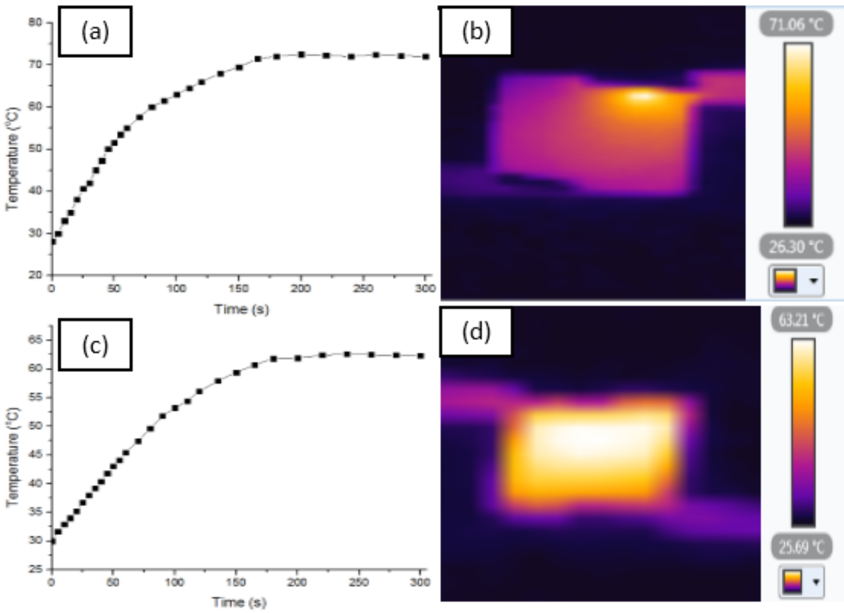

Fig. 7 Heat generating capability test of FTO thin films operated at 12 V DC (a) temperature profile of FTO thin films prepared at 350°C, (b) temperature distribution of FTO thin films prepared at 350°C while saturation, (c) temperature profile of FTO thin films prepared at 400°C, (d) temperature distribution of FTO thin films prepared at 400°C while saturation.

Power density of FTO thin films used as heater prepared at 350°C and 400°C is 3 kW/m^2 and 2.4 kW/m^2, corresponding to different saturated temperature. The power density and saturated temperature of these samples implies that power consumption is still too high.

4. Conclusion

This work presents the preparation of SnO_2:F or FTO thin films by spray pyrolysis deposition technique that can be applied as transparent heaters. As-deposited FTO thin films was characterized by many techniques. Transmittance in visible region, thickness of the films, particle size, and particle density increases with increasing substrate temperature meanwhile its sheet resistance rapidly decreases with increasing substrate temperature. DC power supply at operating voltage of 12 V was used to examine thermal performance of FTO thin films. Saturated temperature of samples prepared at 350°C and 400°C is 72°C and 62°C, respectively. The designing pattern of FTO thin films or make a composite with high transparent and high thermal conductivity materials can be helpful to decrease power consumption. It can be concluded that this process can be employed to prepare suitable transparent electrode for good transparent heater.

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