

## Structural, Optical and Electrical Properties of Fluorine Doped Tin Oxide Thin Films Deposited Using Inkjet Printing Technique

(Struktur, Sifat Optik dan Elektrik Filem Nipis Timah Oksida Terdop Florin  
Dimendapkan Mengguna Teknik Cetakan Inkjet)

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### ABSTRACT

*This paper reports on structural, optical transmittance and electrical properties of fluorine-doped tin oxide (FTO) thin films deposited using an inkjet printer. The FTO ink was synthesized from a mixture of tin chloride pentahydrate ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ) and ammonium fluoride ( $\text{NH}_4\text{F}$ ) solutions. The thin films were deposited on glass substrates at ambient temperature or heated at  $40^\circ\text{C}$  and  $60^\circ\text{C}$ . The surface electronic state and the elemental composition of the thin films were analyzed using XPS spectroscopy. The spectra of the FTO thin films revealed that tin, oxygen, fluoride and carbon were present in the samples. The signals corresponding to  $\text{Sn } 3d_{5/2}$ ,  $\text{O } 1s$ , and  $\text{F } 1s$  were found at 486.6 eV, 530.5 eV and 684.5 eV, respectively. XRD analysis showed that the FTO films were in the form of crystalline with cassiterite shape. The optical and electrical properties of the films were affected by the deposition temperatures. It was observed the film deposited at  $40^\circ\text{C}$  has the optimum optical transmittance and sheet resistivity which were 91%T and  $16 \Omega/\square$ , respectively.*

*Keywords: Fluorine-doped tin oxide; inkjet printing; transparent conducting oxide*

### ABSTRAK

*Kertas ini melaporkan sifat struktur, transmisi optikal dan kerintangan bahan timah oksida dop fluorin (FTO) yang disalut menggunakan teknik cetakan inkjet. Dakwat FTO dihasilkan melalui kaedah percampuran antara bahan timah klorida pentahidrat ( $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ ) dengan ammonium florida ( $\text{NH}_4\text{F}$ ). Penyalutan filem lapisan nipis FTO di atas substrat kaca telah dijalankan pada suhu bilik,  $40^\circ\text{C}$ , dan  $60^\circ\text{C}$ . Analisis permukaan dan komposisi kimia telah dijalankan menggunakan XPS. Analisis XPS menunjukkan kewujudan unsur penting seperti Sn, oksigen, fluorin dan juga karbon. Unsur tersebut wujud dengan puncak isyarat  $\text{Sn } 3d_{5/2}$ ,  $\text{O } 1s$ , and  $\text{F } 1s$  pada tenaga ikatan 486.6 eV, 530.5 eV dan 684.4 eV. Pencirian menggunakan XRD pula menunjukkan bahawa sampel FTO yang terhasil bersifat hablur dan mempunyai bentuk hablur kasiterit. Didapati, sifat optik dan elektrik filem nipis yang dihasilkan adalah dipengaruhi oleh suhu semasa penyalutan. Kerintangan elektrik yang optimum pada  $16 \Omega/\square$  dengan ciri optik pada 91%T telah diperolehi bagi filem nipis yang disalut pada suhu  $40^\circ\text{C}$ .*

*Kata kunci: Cetakan inkjet; oksida lutsinar mengkonduksi; timah oksida terdop fluorin*

### INTRODUCTION

Inkjet printing technique is a new developed thin films deposition technique method as an alternative to the current conventional deposition methods such as spin coating, chemical vapour deposition, sol-gel technique, and spray pyrolysis (Banerjee et al. 2003). There are some advantages in using inkjet printer, such as ability on nanoscale printing, easy and quick process and various printing design for electronic circuits. This technology has become a special deposition technique for ceramic (Ding et al. 2004) and followed by conductive polymer. Lately, the inkjet printing technology has been rapidly developed for metal oxide substances (Chabinye et al. 2005). In OLED and electronic devices industries, inkjet printing technology is making

rapid developments towards commercial productions (Chabinye et al. 2005).

Transparent conducting oxide (TCO) semiconductors are widely used as transparent films in electronic devices such as thin film solar cells, displays devices, electrochromic displays, defogging aircraft and automobile windows, gas sensors and other areas (Elangovan & Ramamurthi 2005). Currently, Sn doped  $\text{In}_2\text{O}_3$  (ITO) is the most extensively used electrodes for such applications due to its excellent properties such as low resistivity ( $\sim 10^{-4} \Omega \text{ cm}$ ) and high optical transmittance (80-90%T) (Li et al. 2005). However, the abundant use of ITO as TCO thin films has several drawbacks such as scarcity, highly toxic, and expensive source of indium itself. Numerous efforts

to develop alternative electrode materials are in progress (Kim et al. 2008). Fluorine doped tin oxide (FTO) is a possible alternative to ITO because FTO is inexpensive as well as chemically and thermally stable (Kim et al. 2008). Fluoro-doped tin oxide was reported to behave as n-type semiconductor with wide band gap within 3.0 to 3.6 eV (Han et al. 2007). FTO were found to be nanostructure (Khonsari et al. 2003), can strongly adhere to the substrate and resistance to the physical etching. The fluorine doping to the SnO<sub>2</sub> framework, can promote more numbers of charge carriers and therefore enhanced the electrical conductivity (Russo et al. 2008).

In this study, we prepared FTO films by inkjet printing technique with variation in deposition temperatures. The variation of the deposition conditions may affect the nanostructure grains size and surface morphology of the thin films, hence on the electrical and optical properties.

## EXPERIMENTALS DETAILS

### FTO SOLUTION SYNTHESIS

The dissolution method was employed to synthesize FTO solution. FTO solution was prepared based on previous method by Elangovan & Ramamurthi (2005) and Han et al. (2007) with minor modifications. About 10.0 g of SnCl<sub>4</sub>·5H<sub>2</sub>O was dissolved in 100 mL ethanol in a sealed container. The solution was stirred continuously for at least 5 h until all the tin chloride pentahydrate completely dissolved. At this point the solution was almost a clear solution with a slight turbidity and labeled as mixture A.

Mixture B was prepared by dissolving 2.0 g of NH<sub>4</sub>F in 4 mL deionized water in a sealed container. After both mixtures A and B fully dissolved, mixture A were placed in a water bath and heated up to 40°C. Then, the mixture B was added to mixture A. The water bath temperature was raised to 60°C. The mixed solution was allowed to stir overnight to ensure complete mixing, and turned into a clear solution. Finally, the mixed solution was filtered using 0.45 µm cartridge and ready to be used for thin film deposition.

### DEPOSITION OF THE FILMS

The FTO thin films were deposited on microscopic glass (2.0 × 2.5 cm<sup>2</sup>) substrates using a commercial inkjet printer (Dimatix Inkjet Fujifilm Materials printer model DMP-2800 series). The ejection of ink from the nozzle of this printer is controlled by application of a voltage pulse. This voltage may control volume, form and velocity of the ink droplet. The optimum printing parameters such as voltage and droplet shape have been selected to deposit high quality thin films. The FTO ink was deposited on glass substrates at ambient temperature or heated at 40 and 60°C. Finally, FTO thin film was annealed at 450°C for 1 h before surface characterizations.

## CHARACTERIZATIONS

The phase of fluorine doped tin oxide materials were characterized by X-ray diffraction (XRD) (Bruker AXS D8 Advance) and the diffraction angle were measured with the x-ray radiation of Cu Kα (40 kV, 40 mA). X-ray photoelectron spectroscopy (XPS) (AXIS Ultra 'DLD' by using second edition of Kratos software) measurements were carried out to evaluate the surface electronic state and to analyze the elemental composition of FTO. Variable pressure scanning electron microscope (VP-SEM, LEO model 1450VP) and transmission electron microscope (TEM, CM12 Philips) were used in order to measure the surface morphology and the nanostructure particles size. Meanwhile, the optical transmittance and the sheet resistivity of the deposited thin films were measured using UV-VIS spectrophotometer and the four-point probe method, respectively.

## RESULTS AND DISCUSSION

The measurement of surface tension or interfacial tension of the ink used was determined using high performance tensiometer. The range of 23.21 to 23.38 mN/m surface tension was observed by standard mode of DuNouy (Huh-Mason) ring method. The surface tension is related to the contact angle of the ink drop where by the lower surface tension will result in lower contact angle. The lower contact angle leads to the reduction of puddle depth of the coating on the substrate. A good ink droplet with suitable voltage can make a good contact attachment of the coating. Figure 1 shows how the voltage of the droplets can affect the ink firing process. Figure 1(a) shows the required droplets without any satellite effect and Figure 1(b) shows the droplets with the satellite effect. Smooth and single droplets without satellite effect were required to produce less crack coating on the substrate and to ensure the ink will adhere strongly to the surface.

### STRUCTURAL CHARACTERIZATION AND COMPOSITIONAL ANALYSIS

Figure 2 shows the XRD patterns of FTO thin films deposited at various deposition temperatures. The results show that the films were observed to be of cassiterite type with the tetragonal rutile structure. The calculated values of the lattice parameters were found at 4.74 and 3.19 Å for *a* and *c* lattice, respectively. The diffractogram were found to be in good agreement with the previous work (Banerjee et al. 2003; Ding et al. 2004; Purushothaman et al. 2008) and with the standard JCPD data number (01-072-1147). The diffraction peaks can be indexed to the SnO<sub>2</sub> phase framework (Bisht et al. 1999). The peaks are identified at the orientation of (110), (101), (200) and (211) and they fit well with the previous work by Banerjee et al (2003). There are two peaks labelled (1) and (2) which attributed to the impurities phase. The crystallite sizes were calculated from the Scherrer's equation given by:

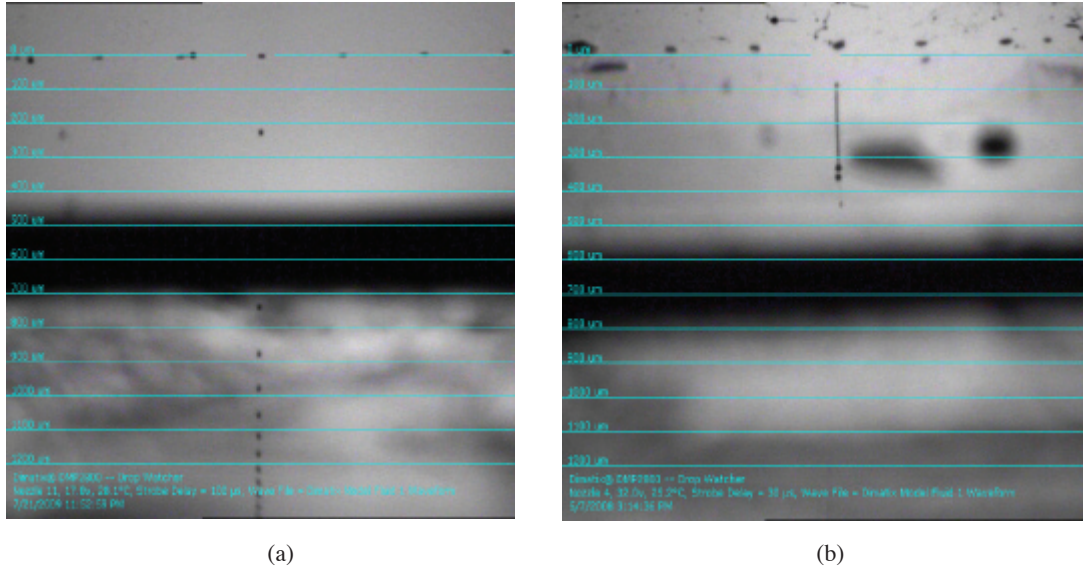


FIGURE 1. The photograph of inkjet printing droplets from the drop watcher  
(a) droplets at 17 volt and (b) droplets at 32 volt

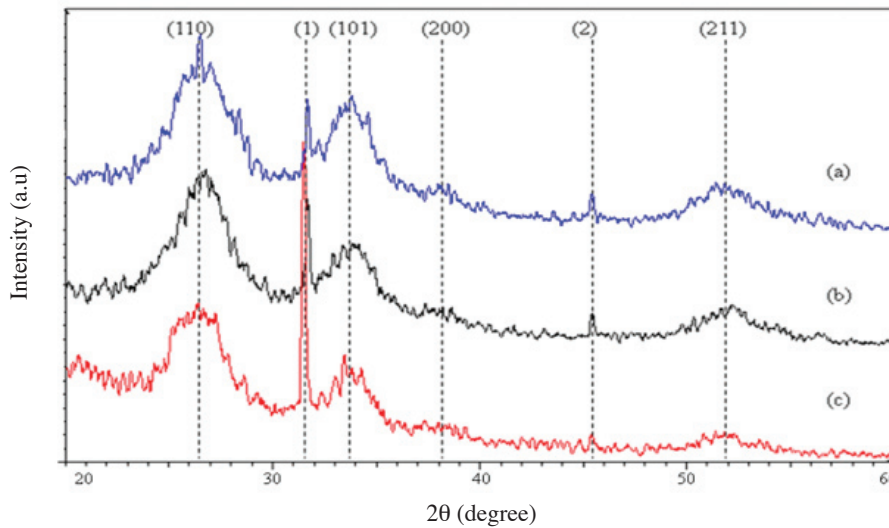


FIGURE 2. XRD diffractogram of FTO films for different deposition temperature:  
(a) ambient temperature at 25°C, (b) 40°C and (c) 60°C

$$L = k\lambda / \beta \cos \theta \quad (1)$$

The extent of broadening, ' $\beta$ ' is the value of the full width at half maximum (FWHM) intensity of the peak and after the value in radians is corrected for the instrumental contribution it can be substituted into Scherrer's equation. ' $\lambda$ ' as a lambda represent the wavelength of X-ray, and the theta, ' $\theta$ ' is the angle corresponding to the peak. The  $k$  constant varies from 0.8 to 0.98 depends on the crystalline shape. From the calculation, the crystallite size was found to be in the range of 75 to 96 Å. From the peaks observed, the fluorine phase was not visible in the diffractogram and it was assumed to be overlapped with the SnO peaks. This is reasonable considering that the fluorine doping level is

relatively small for the system. However, the existence of fluorine was successfully determined by using XPS characterization analysis.

Figure 3 shows the XPS peaks of as-deposited FTO thin film which was fabricated with inkjet printing technique. The spectra of the FTO thin film revealed that tin, oxygen, fluoride and carbon were present in the samples. The signals corresponding to Sn  $3d_{5/2}$ , O  $1s$ , and F  $1s$  were found at 486.6 eV, 530.5 eV and 684.4 eV, respectively and these signals match very well with those reported by Martinez et al. (2006). The XPS spectra in Figure 3 shows that the FTO samples in the form of thin film consist of Sn=65.82, O=32.86 and F=1.32 (wt/wt%) and shows the Sn element oxidation state as Sn<sup>4+</sup>. Amanullah et al. (1998) have

attributed the peaks for Sn  $3d_{5/2}$ , and  $O_{1s}$ , around 486.4 eV and 530.3 eV by using the XPS technique, but they did not report the fluorine peak of FTO thin film. The fluorine peak was only observed for FTO films prepared by chemical vapour deposition (Khonsari et al. 2003) and DC reactive sputtering (Martel et al. 2001). However, the  $F_{1s}$  signals for these both technique were assigned to C-F bonds which comes from the precursors used (Bisht et al. 1999).

In this study, we have observed the fluorine peak at the binding energy of 684.4 eV, the same value as reported earlier by Martinez et al. (2006). In this work,  $F_{1s}$  signal can be assigned to the formation of Sn-F bonding. Fluorine signals showed in this XPS studies is the first time reported for FTO films prepared by inkjet printing technique. Besides that, FTO films prepared by spray pyrolysis done by Singh et al. (1985); Moholkar et al. (2007) and Thangaraju et al.

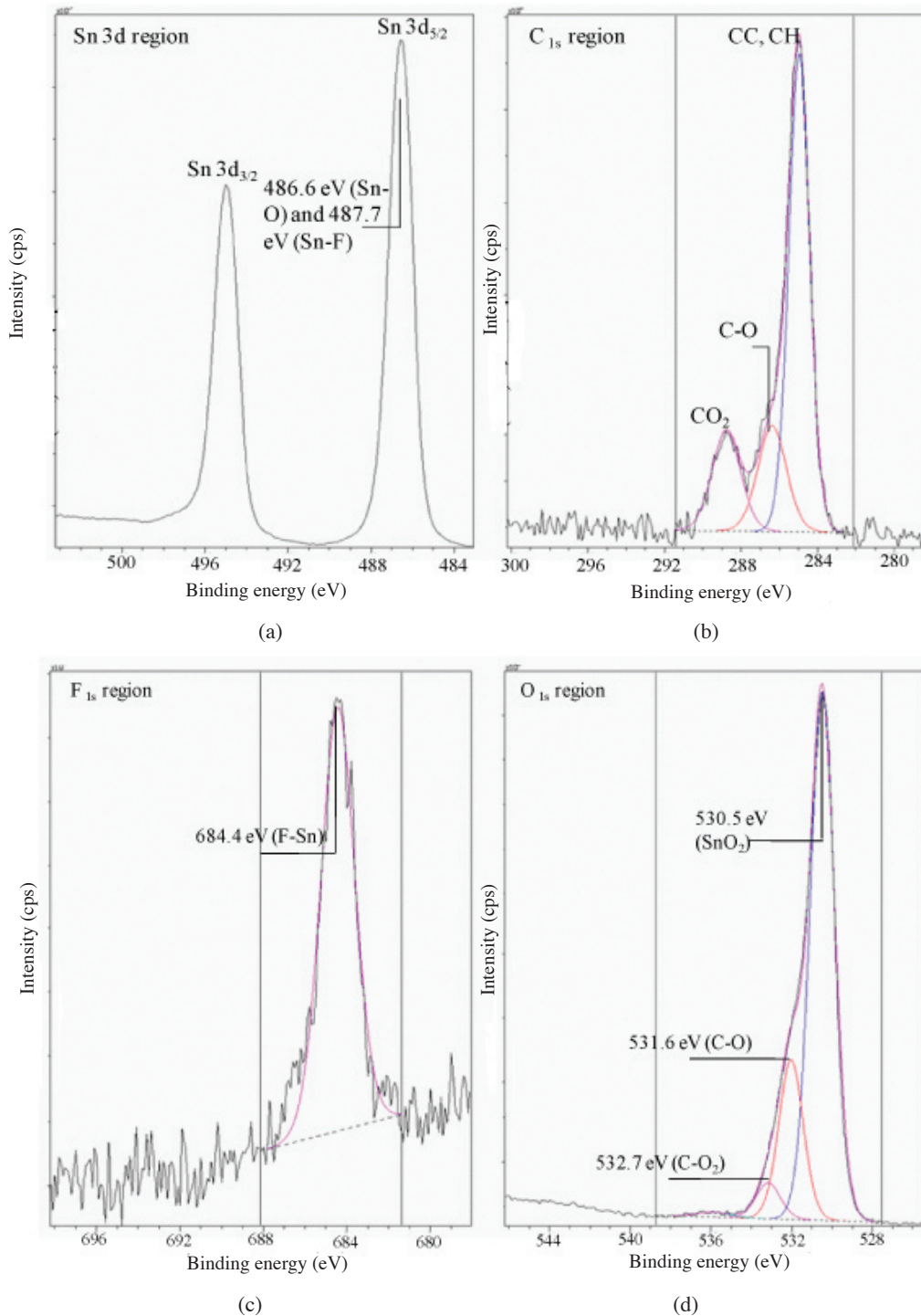


FIGURE 3. XPS pattern of FTO films (a) Sn  $3d_{5/2}$  and Sn  $3d_{3/2}$  region, (b) C  $1s$  region and (c) F  $1s$  region and (d) O  $1s$  region



(2002) did not notice or report for  $F_{1s}$  signals by XPS but the fluorine peaks only can be observed with scanning auger microscope (SAM). Table 1 shows the compositional analysis of FTO films.

The average amount of fluorine that exists in the thin film is  $[F]/[Sn] = 0.02$  which is much less than that taken in the starting solution which is  $[F]/[Sn] = 0.7$ . Similar results were also observed by other researchers (Tsud et al. 2001). The scenario is probably due to the remaining fluorine which escaped or disappeared into the surroundings. This is because, when the fluorine sources from the  $NH_4F$  were poured into the precursor solution, gases were released in the container.

#### MORPHOLOGICAL STUDIES

Figure 4 compares the VP-SEM micrographs of the FTO films deposited by inkjet printing technique at ambient temperature, 40, 60°C and a film deposited by spin coating technique. As can be seen from Figure 4, the films comprise of small grain size particles in the range of 20 to 30 nm with less crack on the surface. Besides that, there are some crystal shapes structures as shown in Figures 4(b) and 4(c). This situation was assumed to be caused by the excessive layer of coating on the films and temperature. The crystal forms were found only at the higher layers of coating and also when the temperature increased. Clearly, we found that the films deposited at higher temperature have developed

TABLE 1. The compositional analysis of as-synthesized and commercial FTO films

Sample	Element composition of the film (wt %)			[F]/[Sn]
	Sn	O	F	
FTO (ambient 25°C)	79.18	19.99	0.83	0.01
FTO (40°C)	65.82	32.86	1.32	0.02
FTO (60°C)	76.89	21.64	1.46	0.02
Commercial FTO	78.63	17.26	4.10	0.05

Average =  $[F]/[Sn] = 0.02$

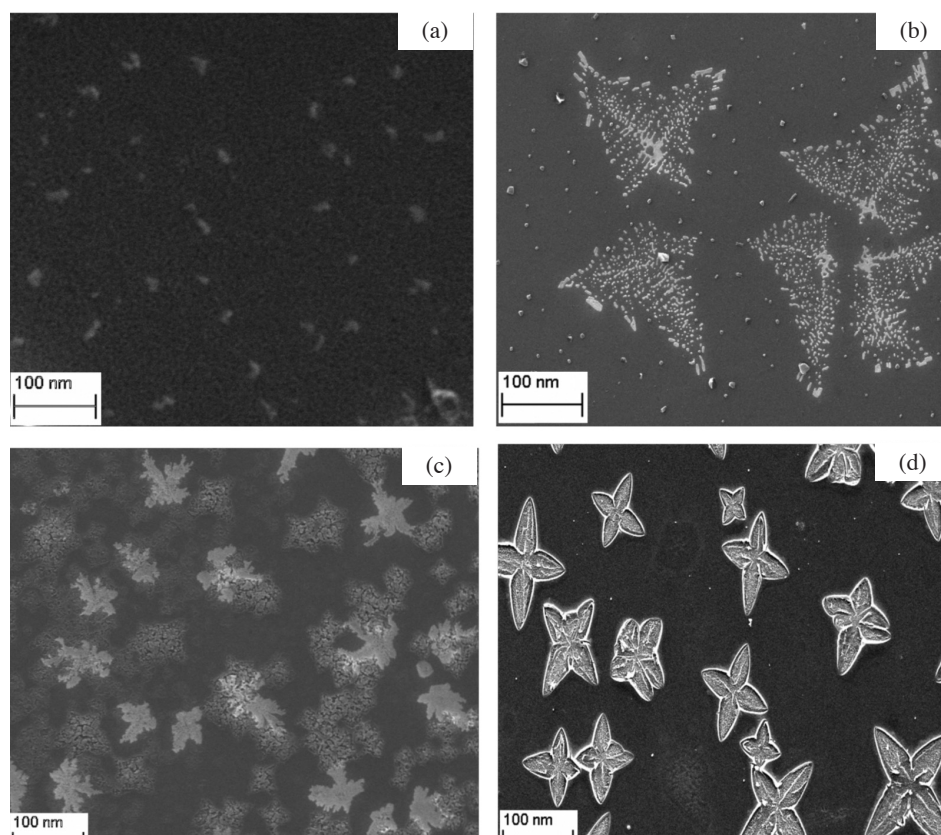


FIGURE 4. VP-SEM micrograph of FTO thin films grown by inkjet printing technique at (a) ambient temperature, (b) 40°C, (c) 60°C and (d) FTO films grown by using spin coating

much more well defined facets than lower temperature and this indicates that higher temperatures can caused better crystallinity. This is consistent with previous work by Bisht et al. (1999); Banerjee et al. (2003); Han et al. (2007); Li et al. (2005) and Martinez et al. (2006) that report FTO substances is highly crystalline in nature. The film deposited by spin coating shows clear flowerlike crystal shapes on the surface as shown in Figure 4(d). The thickness of the films was observed to be at the range of 56 to 600 nm.

#### OPTICAL AND RESISTIVITY STUDIES

Figure 5 shows the optical transmittance of FTO thin film using UV-VIS spectroscopy. The film was deposited by inkjet printing technique at ambient temperature, 40 and 60°C. The transmission measured from wavelength 300 to 900 nm indicates that the films were transparent in the visible region. From the transmittance data it was found that the deposition temperature has improved the optical transmittance; 60%T at ambient to 80%T at 60°C. The optimum optical transmittance was 91%T for the thin film deposited at 40°C.

The films resistivity was measured with the four-point probe method and the sheet resistivity was calculated.

The sheet resistivity of the FTO thin films deposited at ambient temperature, 40 and 60°C were 21  $\Omega/\square$ , 16  $\Omega/\square$  and 23  $\Omega/\square$ , respectively. As in the case of the optical transmittance, the sheet resistivity of the film depends on the deposition temperature. Here the deposition temperature 40°C gave the optimum value of sheet resistivity and the optical transmittance. This result may be related to the structure of the film such as its uniformity.

#### CONCLUSION

The present work shows that FTO thin films can be prepared by using inkjet printing. The optical and electrical

properties of the films were affected by the deposition temperatures. It was observed the film deposited at 40°C has the optimum optical transmittance and sheet resistivity which were 91%T and 16  $\Omega/\square$ , respectively.

#### ACKNOWLEDGEMENTS

The first author would like to acknowledge the Malaysian Ministry of Science, Technology and Innovation for the NSF scholarship. This work was supported by the Malaysian Ministry of Higher Education under research university grant of UKM-GUP-BTT-07-26-178.

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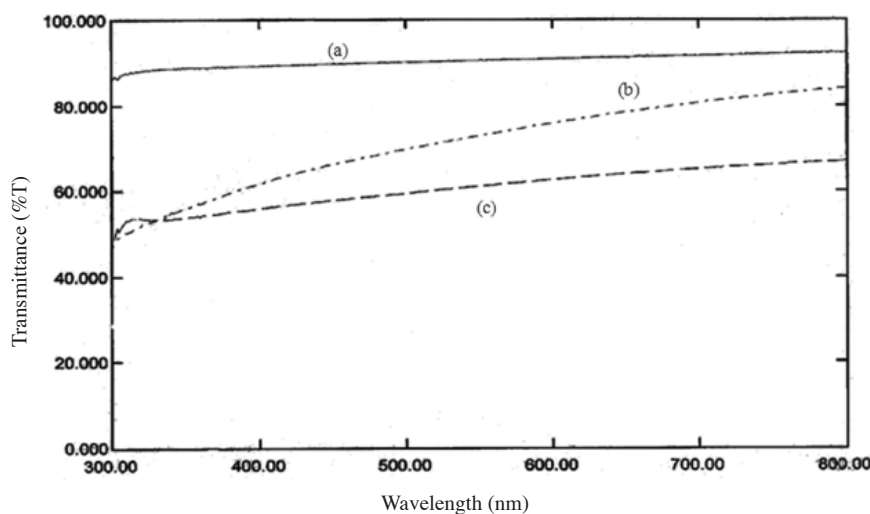


FIGURE 5. Optical transmittance of FTO films deposited by inkjet printing (a) 40°C, (b) 60°C and (c) ambient temperature

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Received: 21 July 2010

Accepted: 3 September 2010