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OPTICAL TRANSMITTANCE, ELECTRICAL RESISTIVITY AND MICROSTRUCTURAL CHARACTERISTICS OF UNDOPED AND FLUORINE-DOPED TIN OXIDE CONDUCTIVE GLASS FABRICATED BY SPRAY PYROLYSIS TECHNIQUE WITH MODIFIED ULTRASONIC NEBULIZER

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ABSTRACT

Fluorine-doped tin oxide (FTO) is one of the conductive glasses that have strategic functions in various important applications, including dye-sensitized solar cell (DSSC). In the current work, the effects of deposition time (5, 10, 20, 30, and 40 minutes) upon the fabrication process of FTO thin film using spray pyrolysis technique with modified ultrasonic nebulizer has been studied in regard to its microstructural, optical, crystallinity, and resistivity characteristics. The variation was also performed by comparing the pure tin chloride precursor and the solution that was doped with fluor (F) at 2 wt% in order to see the doping effect on the properties of thin film. The thin films were characterized using x-ray diffraction (XRD), scanning electron microscope (SEM), ultraviolet-visible (UV-Vis) spectroscopy, and digital multimeter. On the basis of current investigation, it has been found that the best FTO was obtained through the pyrolysis technique of 20-minute deposition time, providing optical transmittance of 74%, a band gap energy (E_g) of 3.85 eV and sheet resistance (R_s) of 7.99 Ω/sq. The fabricated FTO in the present work is promising for further development as conducting glass for dye-sensitized solar cell (DSSC).

Keywords: Conductive glass; Deposition time; Fluorine-doped Tin Oxide; Spray pyrolysis; Transparent

2. INTRODUCTION

Transparent conductive oxide (TCO) has been used for various applications, such as window layers in heterojunction photovoltaic cells, gas sensors, substrates for electrodeposition, transparent contacts in photovoltaic and optoelectronic devices, and special coatings (Yadav et al., 2009). The most common conducting glass that has been commercialized by the manufacturing industry is indium based TCO, or indium tin oxide (ITO). ITO is widely used due to its high transmittance of ~80% and good sheet resistance of ~18 Ω/sq. However, indium is one of the rare metal elements, making its stock in the future limited while demand for this essential material keeps increasing, and thus its very expensive price. This has brought into

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scientific and technological consideration the need for a substitute for TCO other than ITO. One promising material is tin oxide (SnO_2) based conducting glass. Although tin oxide has low resistance, if added with another doping ion, such as antimony (Sb) or fluorine (F), its resistivity is reduced (Hammad et al., 2011). Suhaimi et al. (2015), upon their investigation, have achieved the best transmittance of 75% and sheet resistance of 8.5 Ω/sq. In the case of Indonesia, the main raw mineral containing tin (Sn) can be found in Bangka Island as the world biggest source for tin. It is therefore a huge advantage if the tin oxide based TCO can be manufactured from the abundant mineral source in Indonesia (Inonu, 2013).

For application with photovoltaic cells, TCO thin film must be attached to a transparent substrate. The commonly used substrate material is glass (Rozati, 2006). Glass became the primary choice owing to its ability to withstand high heat and its good transparency (>90%). TCO must have good transparency in order to absorb as much photon radiation from UV light from the sun as possible. In addition, to facilitate electron transfer from the photovoltaic circuit, TCO must have a minimum value of obstacles. Unfortunately, to get good transparency, the structure of materials must be amorphous, while the value of crystallinity is directly proportional to the conductivity. Therefore, there exists compensation, or trade-off, between these two values to achieve optimal conductivity (Morris & McElnea, 1996).

The TCO thin film deposition process can be realized through various methods. One of the most promising is a spray pyrolysis, where the thickness of the layer formed in the thin layer deposition process must be considered (Patil et al., 2007). Several previous researchers reported that they obtained an optimum result at a thickness of ~520 nm (Shaaban et al., 2012). Using this pyrolysis technique, the resulting TCO layer is determined by how many particles fight and form a bond to the substrate. A typical deposition method uses a spray pyrolysis such as ultrasonic nebulizer which functions as an atomizer, an air compressor, a chamber, and a nozzle (Kumara et al., 2014). An ultrasonic nebulizer is a high-frequency tool commonly used in medical devices to dissolve drugs to pass into the oral cavity to the trachea (White, 2014). For thin film manufacturing process purposes, however it needs several modifications so it can be used. The aim of this work is therefore to study the feasibility of using an ultrasonic nebulizer as an atomizer for the spray pyrolysis process to fabricate transparent tin oxide conducting glass. This study also purposely investigates the effect of un-doping and fluorine doping (2 wt%) as well as deposition time (5, 10, 20, 30, and 40 minutes) under fixed heating temperature of 300^{o}C on the optical transmittance and electrical resistivity of TCO glass.

2. EXPERIMENTAL SETUP

The precursors used in this experiment were $SnCl_2.2H_2O$ (*Merck*®) and NH_4F (*Merck*®) as the tin and fluorine sources, respectively. Ethanol was used as a solvent for dissolving $SnCl_2.2H_2O$, and distilled water was used to dissolve NH_4F. The coating method was carried out by using the spray pyrolysis technique with a modified ultrasonic nebulizer *(GEA® series 402AI)* as the atomizer.

2.1. Precursor Mixing

This works involved two types of solutions. The first solution (undoped) is a mixture of 12 grams $SnCl_2.2H_2O$ with 100 ml of ethanol. The solution was thoroughly stirred with magnetic stirrer at medium speed for 30 minutes. The second solution (doped) uses the initial composition of the first solution with the added doping of as much as 2 wt% fluor (F) by dissolving 0.24 grams of NH_4F with 0.56 ml of distilled water. This solution was dropped carefully by using a pipette to prevent solution turbid (Memarian & Rozati, 2012).

2.2. Thin Film Deposition Process

2.2.1. Substrate preparation

The substrates were soda lime (Na_2O-MgO-CaO-SiO_2) glasses with a dimension of 25×19×1 mm. They were washed with soap to remove dirt and grease, and furthermore put in a beaker containing ethanol solvent under ultrasonic cleaner for 30 minutes. The clean substrates were subsequently dried and stored in sealed containers.

2.2.2. Modification of ultrasonic nebulizer

An ultrasonic nebulizer is a medical tool usually used to dissolve drugs for patients with respiratory disease. This tool was selected for thin film fabrication with spray pyrolysis method due to its ability to break down the liquid particles into aerosol form. Based on the manufacturer specifications, ultrasonic nebulizer 402AI GEA © series has the frequency of 1.7 MHz ± 10, atomizing rate of 3 ml/min, tank capacity of 300 ml, and a sound output of 50 dB. To create a funnel for the aerosol to be sprayed onto substrate surface, an Erlenmeyer pyrex flask (Iwaki®) was cut to provide a height of 10 cm. The ultrasonic nebulizer modification scheme is depicted in Figure 1.

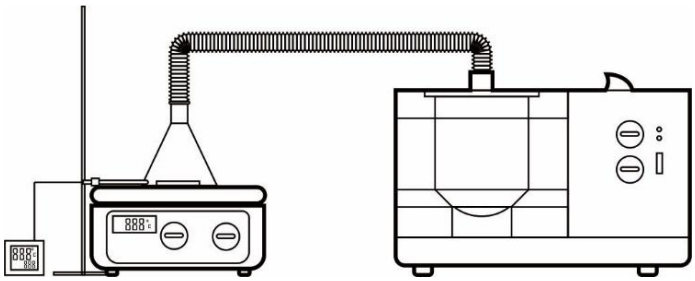

Figure 1 Modification of ultrasonic nebulizer

2.2.3. Hot plate

In this work, a hot plate was used for the heating the glass substrates placed on it at a fixed temperature of 300°C, as controlled by a thermocouple. For preventing the contamination of fluorine on the tool, the experiment was firstly started with the undoped solution. We performed variations by adjusting the deposition times to 5, 10, 20, 30 and 40 minutes. Once this work was completed, we performed the same deposition time variation with the doped solution. The sample code under those variations (undoped-doped and deposition time) is outlined in Table 1.

Table 1 Sample code of undoped and doped TCO glasses with different deposition time

Solution	Temperature (^oC)	Deposition time (minutes)	Sample Code
Undoped $SnCl_2.2H_2O$ + C_2H_5OH	300	5	0%-300-5’
		10	0%-300-10’
		20	0%-300-20’
		30	0%-300-30’
		40	0%-300-40’
Doped $SnCl_2.2H_2O$ + C_2H_5OH + (NH_4F+H_2O)		5	2%-300-5’
		10	2%-300-10’
		20	2%-300-20’
		30	2%-300-30’
		40	2%-300-40’

The resulting FTO glasses were characterized by using optical microscope (GENESYS® 10s

UV-Vis Spectroscopy), crystal (X-Ray Diffraction Cu-Kα), microstructure (Scanning Electron Microscopy JEOL® JSM-6390A), and resistivity (Sanwa® CD800a digital multimeter).

3. RESULTS AND DISCUSSION

3.1. Crystallinity

The crystallinity of the resulting conducting glasses was determined by XRD with scanning range 2Θ of 10-80^o as depicted in Figure 2. The diffraction peaks appear for (100) (101) (200) (211) (310) (301) crystal planes to confirm that SnO_2 phase in TCO has a tetrahedral crystal structure. According to ICDD 00-046-1088 reference, the TCO samples 2%-300-20' and 2%-300-40' had more distinct peaks compared to those of by undoped (0%-300-20') and doped 2%-300-5'. This confirms the former ones are more crystalline than the other two. In addition, it can be found that the intensity of (301) peak in sample 2%-300-40' is higher than that of (100) but it is accompanied with the decrease in the intensity of (100) when compared to sample 2%-300-20'. This gave an indication that the crystal grains underwent crystal growth in the direction of *l* axis by lowering the value on the *h* axis upon the increase in the deposition time of 20 to 40 minutes. The most noticeable difference was found in the samples 2%-300-5', which shows the dominant amorphous phase where only the onset of (200) crystal plane peak was observed. This confirms again that the deposition time of 5 minutes was too short for the crystal growth on TCO substrates by spray pyrolysis technique with ultrasonic nebulizer to occur. In general, it can be seen that the preferred orientation of fluorine doped (FTO) conducting glass in this study was shown by (200) crystal plane. This is different for the case of undoped one (0%-300-20') where the highest peak was demonstrated by (100) crystal plane.

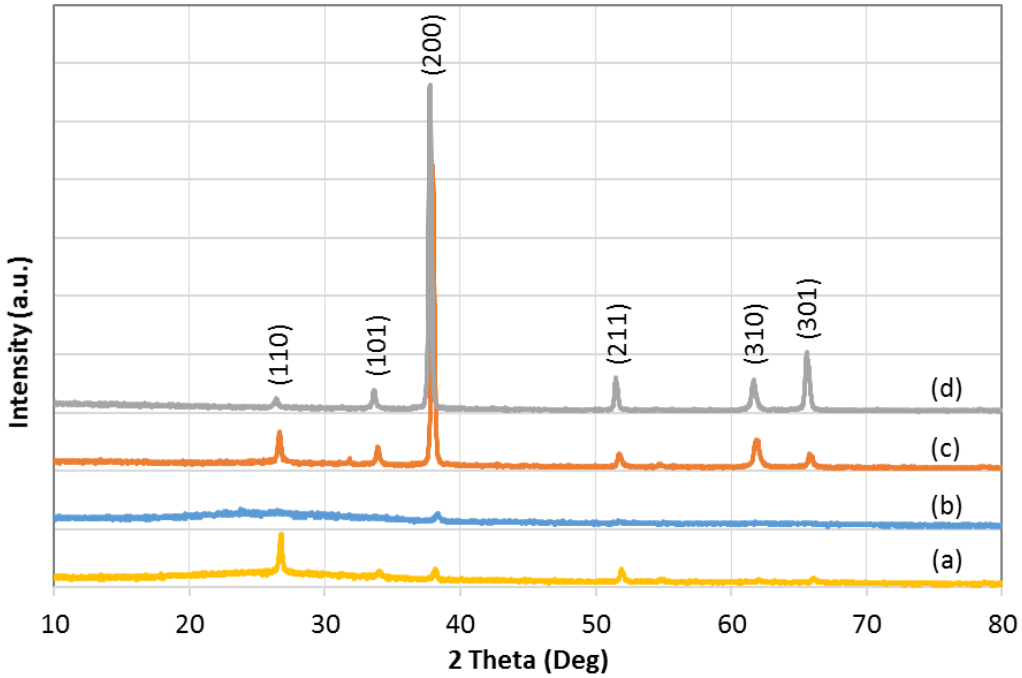

Figure 2 Diffractogram of TCO glasses under condition of: (a) undoped (0%-300-20'); (b) doped (2%-300-5'); (c) doped (2%-300-20'); (d) doped (2%-300-40')

This shows the addition of doping elements F will affect the shape of the SnO_2 crystals produced. In addition, the graph results show a considerable increase in the value of crystallinity between the doped and undoped samples. This proves the influence of F doping will improve the crystallinity of the SnO_2 crystal structure thin film. The higher the crystalline phase is formed, the smaller the generated grain boundary will be. Banyamin et al. (2014)

showed that the grain boundary material consists of an amorphous phase which absorbs the electron energy passed through it. It can cause conductivity properties to decrease. In addition, since the value of the dopped element is very small (2% wt), there will be no reaction between Sn compound formation with F. Fluorine only has a role as catalyst to increase the value of tin oxide crystallinity.

Table 2 is the result of calculation for interplanar (*d*) spacing and lattice parameters *a* and *c* using Bragg equation. The TCO samples have lengths of *a* and *c* in the range of 0.4707 to 0.4759 and 0.3187 to 0.3209 nm, respectively. This value corresponds to the reference results of SnO_2 ICDD 00-046-1088. Furthermore, the calculation of crystallite size (*t)* using the Scherrer's equation provided the value for the undoped (0%-300-20') sample as 5.8 nm, while the *d* value for the doped (2%-300-20') was 6.6 nm. This result proves the effects of ion fluor (F) in enlarging the size of the crystal SnO_2. Meanwhile, the increased deposition time (20 to 40 minutes) also showed the growth of the crystal size up to 7.9 nm. This suggests the addition of period deposition for 20 minutes can cause the crystals to grow ~1 nm larger.

Table 2 Lattice parameter and crystal size of undoped and fluorine doped TCO glasses

Sample	2Θ (°)	*d* (nm)	FWHM (°)	Miller Indices (*hkl*)	Lattice Parameter		*t* (nm)	t_{avg} (nm)
					a_{avg} (nm)	c_{avg} (nm)		
0%-300-20'	26.7641	0.3328	0.1380	110	0.4707	0.3209	10.3243	5.803
	34.0410	0.2631	0.4720	101			3.0709	
	38.1913	0.2354	0.2360	200			6.2153	
	51.8922	0.1760	0.2360	211			6.5312	
	66.0860	0.1412	0.5760	301			2.8707	
2%-300-5'	26.5327	0.3357	0.6300	110	0.4747	-	2.2604	3.041
	38.2935	0.2348	0.3840	200			3.8211	
2%-300-20'	26.7072	0.3335	0.1770	110	0.4727	0.3187	8.0486	6.65
	33.9181	0.2641	0.1970	101			7.3555	
	37.9519	0.2369	0.2560	200			5.7255	
	51.7267	0.1765	0.1970	211			7.8190	
	61.7932	0.1500	0.3940	310			4.1000	
	65.7838	0.1418	0.2400	301			6.8783	
2%-300-40'	26.4487	0.3367	0.1970	110	0.4759	0.3205	7.2278	7.899
	33.6464	0.2661	0.1570	101			9.2228	
	37.7491	0.2381	0.2360	200			6.2068	
	51.4839	0.1773	0.1570	211			9.8013	
	61.6125	0.1504	0.3150	310			5.1228	
	65.5746	0.1422	0.1680	301			9.8144	

3.2. Electrical Properties

The electrical resistivity of the resulting TCO glasses in this study was measured by using a digital multimeter (Sanwa® CD800a). In Figure 3, a downward trend of the sheet resistance by addition of deposition time from 5 to 40 minutes can be clearly seen for both undoped and doped conditions. These results confirm that the longer deposition time resulted in better TCO conductivity. As has been investigated by XRD study, this can be attributed to the crystallinity of SnO_2 phase where the higher crystallinity is directly proportional to the easier electron transfer, and thus higher conductivity. This is in agreement with previous work done by Tatar and Duzgun (2012). In our present work, it is also confirmed that the addition of fluorine doping has resulted in the decrease in electrical resistivity significantly.

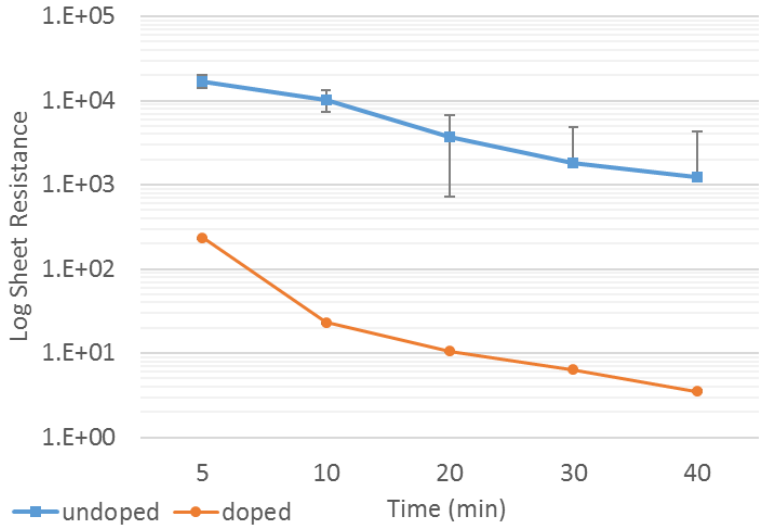

Figure 3 The electrical resistivity of the undoped and fluorine doped TCO glasses

3.3. Electrical Properties

Figure 4 shows the observation results on the optical transparency of fluorine doped and undoped TCO glasses. It can be seen that the deposited samples have changes in the composition of colors with increased deposition time. Figure 4 shows the doped sample glass remained visibly transparent up to 20 minutes, while the undoped sample remained transparent longer up to 40 minutes. For the doped samples, the 30 and 40 minute-deposition time resulted dark appearance of the TCO glasses.

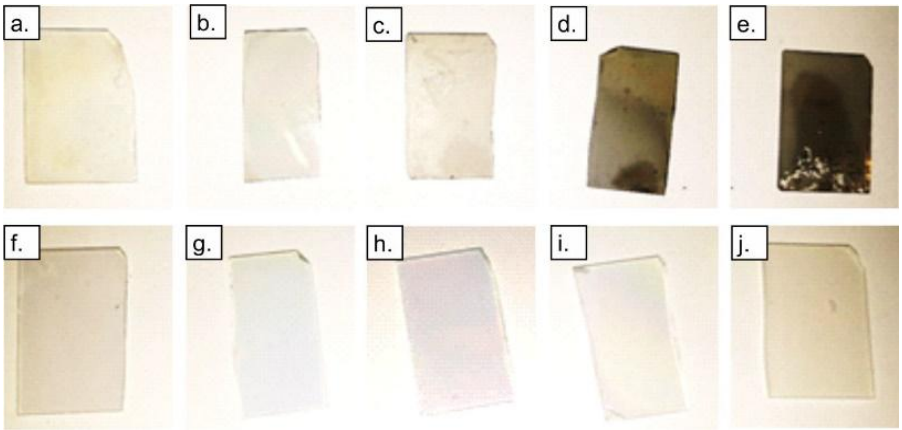

Figure 4 Visual transparency of FTO glasses: (a.) 2%-300-5'; (b.) 2%-300-10'; (c.) 2%-300-20'; (d.) 2%-300-30'; (e.) 2%-300-40'; (f.) 0%-300-5'; (g.) 0%-300-10'; (h.) 0%-300-20'; (i.) 0%-300-30'; (j.) 0%-300-40'

Further optical properties observation with UV-Vis spectroscopy on the TCO glasses has been performed with the results presented in Figure 5. It shows the different values of optical transmittance of the fluorine doped samples related to various deposition times of 5, 20 and 40 minutes. The TCO glass with 2%-300-5' condition has the highest transmittance value at 92%; while that of 2%-300-20' obtain a transmittance of 74%, and the last sample of 2%-300-40' became the most turbid sample with an optical transmittance of only 28%. These results showed that longer deposition time, the film will be thicker and this resulted in less light can pass through.

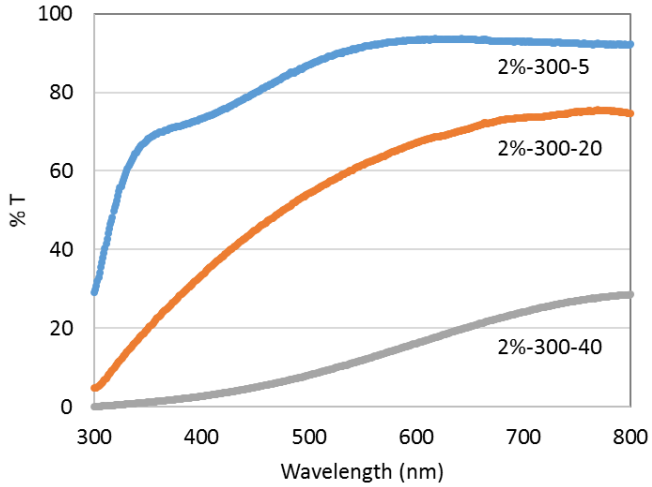

Figure 5 Optical transmittance of the fluorine doped samples with 5, 20, and 40 minute deposition times

Figure 6 provides the UV-Vis spectroscopy results comparison between the undoped and 2 wt% fluorine doped TCO glasses. It can be shown that under the same deposition time the undoped sample (0%-300-20') has a much higher transmittance up to 93% in comparison to the doped one (2%-300-20') which only obtained a value of about 80%. This shows that the addition of fluorine doping results in a decreased transmittance, although on the other hand it has increased the electrical conductivity significantly.

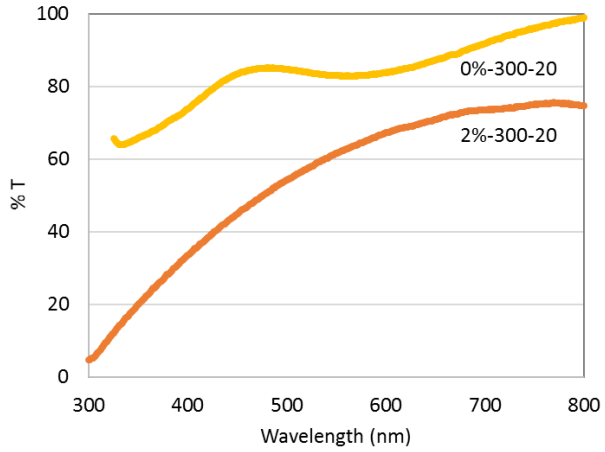

Figure 6 Transmittance *Vs* wavelength in undoped (0%-300-20') and doped (2%-300-20') samples

Figure 7 is the result of data processing on the UV-Vis spectra using the UV-Vis Tauc equation. It shows the value of the band gap (E_g) for four different samples, *i.e.* undoped (0%-300-20') and doped with various deposition time (5, 20 and 40 minutes). Increasing the deposition time from 5 to 20 minutes for the doped samples (2%-300-5' to 2%-300-20') has resulted in a change of E_g from 3.66 eV to 3.85 eV (+0.19 eV). However, with increased deposition time to 40 minute (sample 2%-300-40'), it has adversely decreased the E_g to 3.04 eV (-0.81 eV). This can be attributed to the Burnstein-Moss effect, explaining that the position of Fermi level (E_f) moves to the top of the minimum conduction band E_c, causing an energy absorption change: E_c-E_v = E_q becomes E_f-E_v> E_q (Rahal et al., 2013). The Burnstein-Moss effect can be resulted from the irregularity of crystal size, internal stress, or free carrier concentration (Banyamin et

al., 2014). Another considerable difference was demonstrated by the undoped sample (0%-300-20') when compared to the same deposition time, *i.e.* sample 2%-300-20'. The E_g value of 0%-300-20' sample achieved as low as 1.91 eV. These results are consistent with what has been obtained by Banyamin et al. (2014), which showed that the increase in carrier concentration can make the gap of the valence band and the lowest empty state in conduction band require more energy to charge the lowest level of energy, thus causing the value of the band gap to increase.

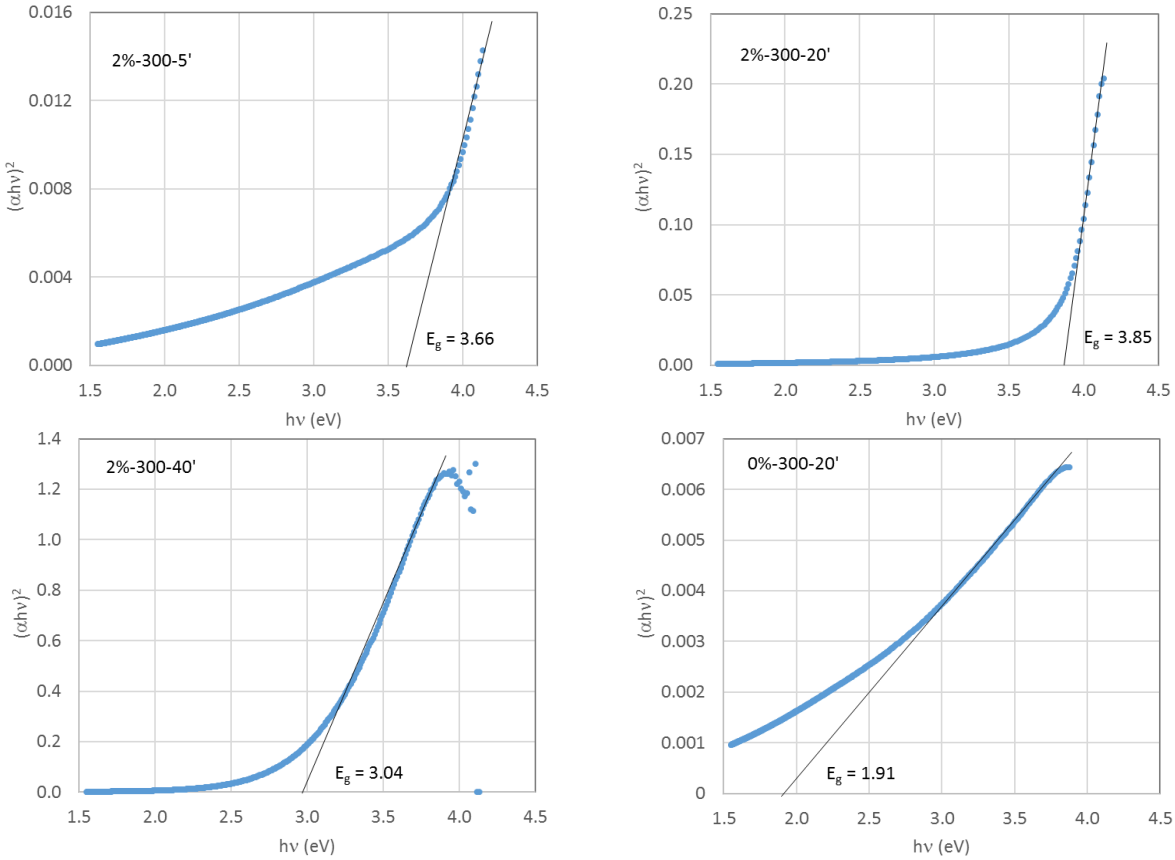

Figure 7 Optical band gap using Tauc equation

3.4. Microstructure

The SEM results in Figure 8 show the difference in grain size by each sample, both doped and undoped conditions. In Figures 7b-7e, there appears to be a grain growth trend with the addition of deposition time. It was found that at magnification 50,000×, sample 2%-300-10' exhibited a large average grain of about 392.6 nm., while for the samples 2%-300-20', 2%-300-30' and 2%-300-40'the average is 1.2, 2.2, and 7.54 µm, respectively. A totally different result on microstructures is shown by sample 2%-300-5' (Figure 7a) where huge aggregates were found throughout the substrate. This is highly possible due to the droplets of solution which were being unable to disperse evenly to all parts of the glass surface because of short deposition time. As a result, these droplets fall in the form of solid agglomeration upon solvent evaporation during concurrent heating process temperatures at 300 °C. On the other hand, a more significant microstructural difference was exhibited by undoped sample 0%-300-20' (Figure 7f) when compared to the same deposition time sample with doping (sample 2%-300-20', Figure 7c). For the undoped sample, the thin film microstructure looks homogeneous with small grain size but accompanied with quite number of voids (dark appearance). This is consistent with XRD test results in Figure 2 that confirm the amorphous phase is more dominant than the crystal grains Large grain boundaries will absorb more heat and resist moving electrons, thereby lowering conductivity properties of the material.

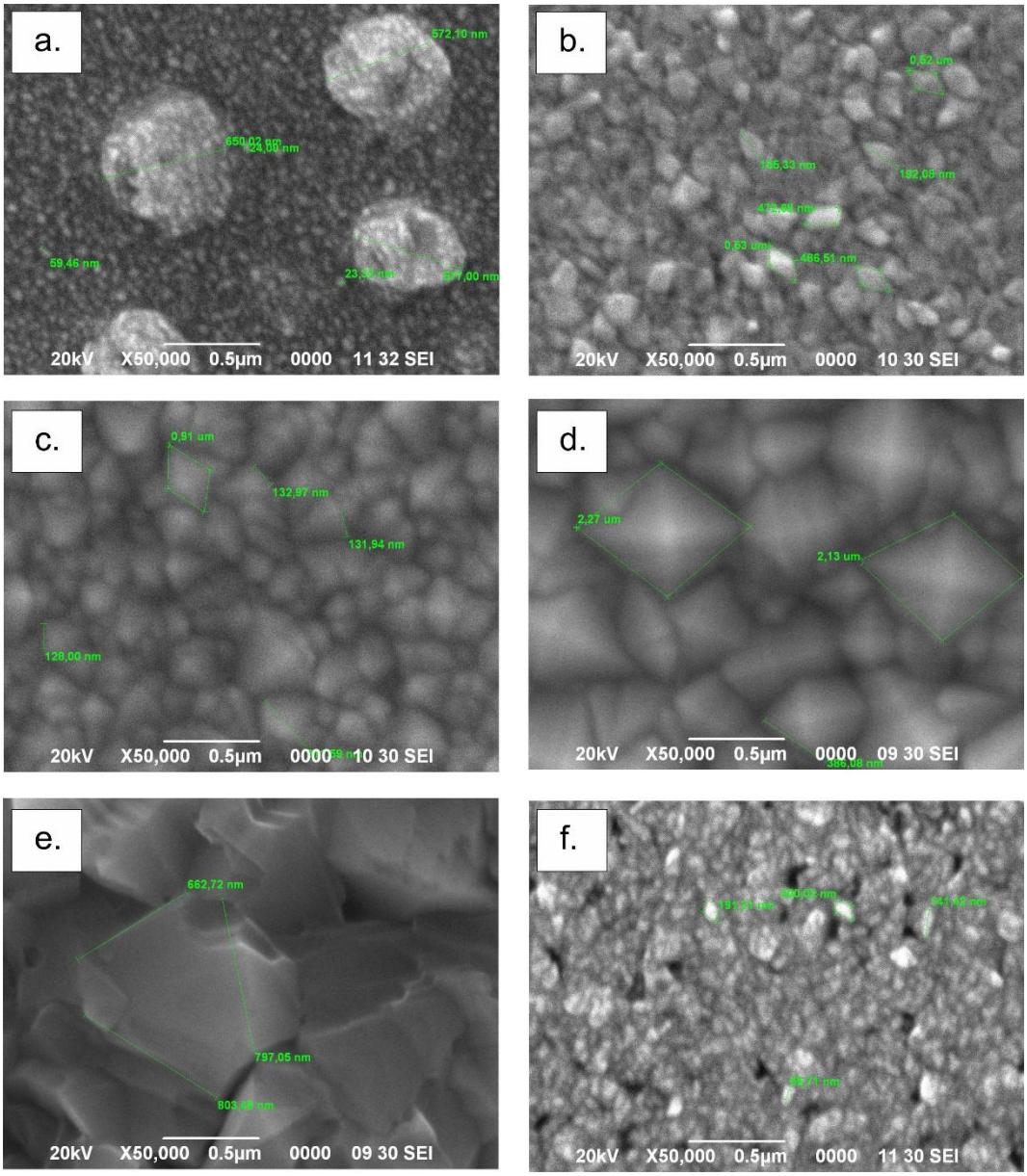

Figure 8 SEM microstructure of FTO thin film on 50,000× magnification: (a) 2%-300-5'; (b) 2%-300-10'; (c) 2%-300-20'; (d) 2%-300-30'; (e) 2%-300-40'; (f) 0%-300-20'

4. CONCLUSION

The ultrasonic nebulizer has been proven to be a suitable tool for fabricating a thin layer of FTO on a laboratory scale. It is also confirmed that the addition of fluorine ions into the Sn precursor has improve the properties of thin film performance by comparing undoped and doped samples at the same condition (temperature and deposition time, 20 minutes). These values were consistent in all characterizations carried out in this study including crystallinity, electrical resistivity, optical, and microstructure. Based on the characterization results obtained, the best value for FTO produced is at a deposition time of 20 minutes for doped samples. These samples had a transmittance of 74%, an energy band gap (E_q) of 3.85 eV, sheet resistance (R_s) of 7.99 Ω / sq, lattice parameter of a = 0.4727 nm and c = 0.3187 nm, crystallite size of 4.1–8.0 nm and particle size of 1.2 µm. Increasing the value of a thin layer deposition is shown to improve some properties of the film, such as crystallite and grain sizes.

5. ACKNOWLEDGEMENT

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