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The Effect of deposition times on preparation of SnO₂:F conductive glass by Indonesian local stannic chloride precursors

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Abstract. The performance of fluorine-doped tin oxide (FTO) as an alternative semiconductor besides indium tin oxide (ITO) has been investigated. Currently, the precursors often used in the manufacture of fluorine-doped tin oxide (FTO) are commercial precursors on the market. In the present work, a thin film FTO will be fabricated using a pyrolysis spray technique with an ultrasonic nebulizer using Indonesian local precursors of stannic chloride with the variation of deposition times (5, 10, 15, 20 and 25 minus). Thin films were characterized by using x-ray diffraction (XRD), scanning electron microscope (SEM), ultraviolet-visible (UV-Vis) spectroscopy, and four-point probes. The optimum result obtained by pyrolysis technique with a deposition time of 20 minutes and substrate temperature at 300 °C has a resistivity of $1.059 \times 10^{-4} \Omega \cdot \text{cm}$ and transmittance 89.614%. Fluorine-doped tin oxide (FTO) fabricated by using these local Indonesian precursors promise for further development as a glass of dye-sensitized solar cells (DSSC).

1. Introduction

The current energy crisis is beginning to remind people to find or even create new energy sources that can be utilized globally. Renewable energy sources are needed in large quantities and could be used for a long time. Sunlight is an energy source that suitable for human because it is environmentally friendly and can be obtained in large quantities. There are tools that can store sunlight and convert into electrical energy such as Direct Sensitized Solar Cell (DSSC) [1].

Currently, most solar cells still use Indium Tin Oxide (ITO) as Transparent Conductive Oxide (TCO). The reserves of indium mineral is small found in the world so the price is very expensive to be used as a doping ingredient. Therefore, the role of indium as doping for Tin Oxide is replaced by fluorine which has conductive properties that are not inferior to indium. The reserves of fluorine mineral is also founded



greater than indium. In addition, FTO coated glass substrates can reduce about 40% of material costs [2]. Fabrication of FTO by using many different methods such as thermal evaporation [3] [4], sputtering [5], spray pyrolysis [6], spin coating [7].

A. H. Yuwono et al. [8] have successfully conducted researches in the manufacture of fluorine-doped tin oxide (FTO) by comparing the precursors and solvents. The precursors used are tin (II) chloride dihydrate ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) and anhydrous tin (IV) chloride (SnCl_4) pro analysis (p.a). Precursor pro analysis (p.a) is a commercial precursor that has a fairly expensive price and limited availability. Indonesia is one of the countries that have a large potential for producing tin.

In this study, a thin glass conductor coating was made by ultrasonic spray pyrolysis nebulizer method using stannic chloride (SnCl_4) local Indonesia as a precursor in the manufacture of fluorine-doped tin oxide (FTO) conductive glass.

2. Experimental Method

The materials used in this research were glass substrate microscopes of soda lime, stannic chloride (SnCl_4) local Indonesia, NH_4F (98%, Merck Ltd., Germany) and methanol (Merck Ltd., Germany). The research began with the substrate glass cleaning by using commercial detergent, then the substrate glass was soaked with acetone then ultrasonication for 15 minutes.

The preparation of the solution was carried out by mixing 8.18 grams of SnCl_4 with 9.82 ml of methanol. The solution was stirred thoroughly with a magnetic stirrer at a moderate rate for 30 minutes. The next step was an addition of doping as much as 0.2 gram NH_4F then the solution was stirred homogeneous for 30 minutes.

The deposition was performed by ultrasonic spray pyrolysis nebulizer method (GEA Medical 402A1) with 10 cm distance and velocity ± 30 ml / 10 min and substrate glass placed on hot plate with varying deposition times of 5, 10, 15, 20 and 25 minutes at a fixed substrate temperature of 300 °C. The characterizations of the fabricated FTO glass were performed by scanning electron microscope-energy dispersive spectroscopy (JEOL-JSM 6390A), x-ray diffraction/XRD (Shimadzu XRD-7000), UV-Vis spectroscopy (Thermo UV-Vis Genesys 10s) and four-point probe (FPP5000).

3. Results and Discussion

The x-ray diffraction pattern of SnO_2 thin film that grows on a glass substrate with a variation of deposition times of 5, 10, 15, 20, 25 minutes is shown in Figure 1. The XRD measurement results show that the peaks show the SnO_2 material phase with the plane crystals (110), (101), (200), (211), (310), (301) and tetragonal crystal structures according to the SnO_2 rutile pattern [5].

At 5 minutes deposition time (Figure 1.a), the crystalline structure looks amorphous, this is probably due to the short deposition time so that the droplet of solution is not able to be dispersed evenly to all parts of the glass surface [9]. With a crystal structure that is still amorphous, its conductivity is small. The grain boundary consists of an amorphous phase where the amorphous phase will absorb the energy that is passed so that the material conductivity will decrease.

Crystal growth begins to occur at 10 minutes of deposition time. Increasing deposition time from 10 to 25 minutes causes a change in intensity on the crystal plane. The crystal field (200) has the most dominant structure compared to the intensity of other structures. The research conducted by G. Gordilo, et.al [10] explained that the most dominant crystal plane (200) indicates that the quality of the crystal is getting better and also if the size of the crystal is getting larger. The increase of deposition time will cause an optimal balance between electrical resistance and optical transmittance.

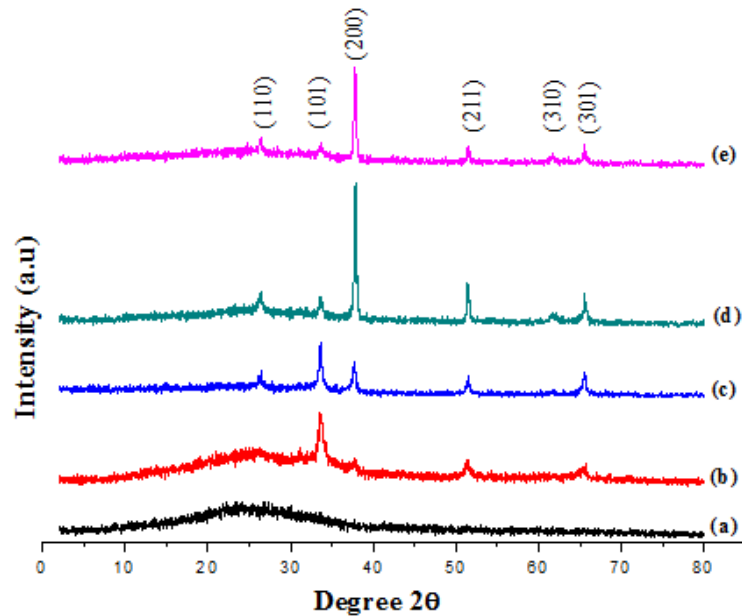


Figure 1. XRD patterns of FTO thin layers heated at 300 °C during the pyrolysis process with a variation of deposition times : (a) 5; (b) 10; (c)15; (d) 20 and (e) 25 minutes.

The longer deposition time causes the crystallite size to expand because the longer the deposition time, the SnO_2 particles grow denser thus reducing porosity and electron transfer becomes easier and thus decreases the reactivity value [3]. This is supported by research conducted by D. Tatar, et. al [11] which said that the higher crystallinity values will make the lower resistivity value.

Table 1. Semi-quantitative EDS-SEM analysis of FTO at 300 °C with a variation of deposition times.

Element	% mass				
	5 min	10 min	15 min	20 min	25 min
O	22.34	19.86	17.47	16.20	15.44
Na	3.75	1.43	-	-	-
Mg	1.53	-	-	-	-
Si	28.59	15.12	13.21	3.49	1.60
Ca	6.74	5.02	3.66	2.01	1.19
Sn	37.05	58.57	65.66	78.30	81.77

The results of semi quantitative analysis of SnO_2 thin layers with variations of deposition times are shown in Table 1. From the results of semiquantitative analysis of EDS, it can be seen that the chemical composition of the thin layer shows major elements, namely O and Sn derived from precursor solutions of Indonesian local precursors of stannic chloride whereas Na, Mg, Si, and Ca are obtained from soda glass [12]. Lalasari et.al [13] in the previous research using pro-analytic precursors indicated Sn and O elements without any other impurities.

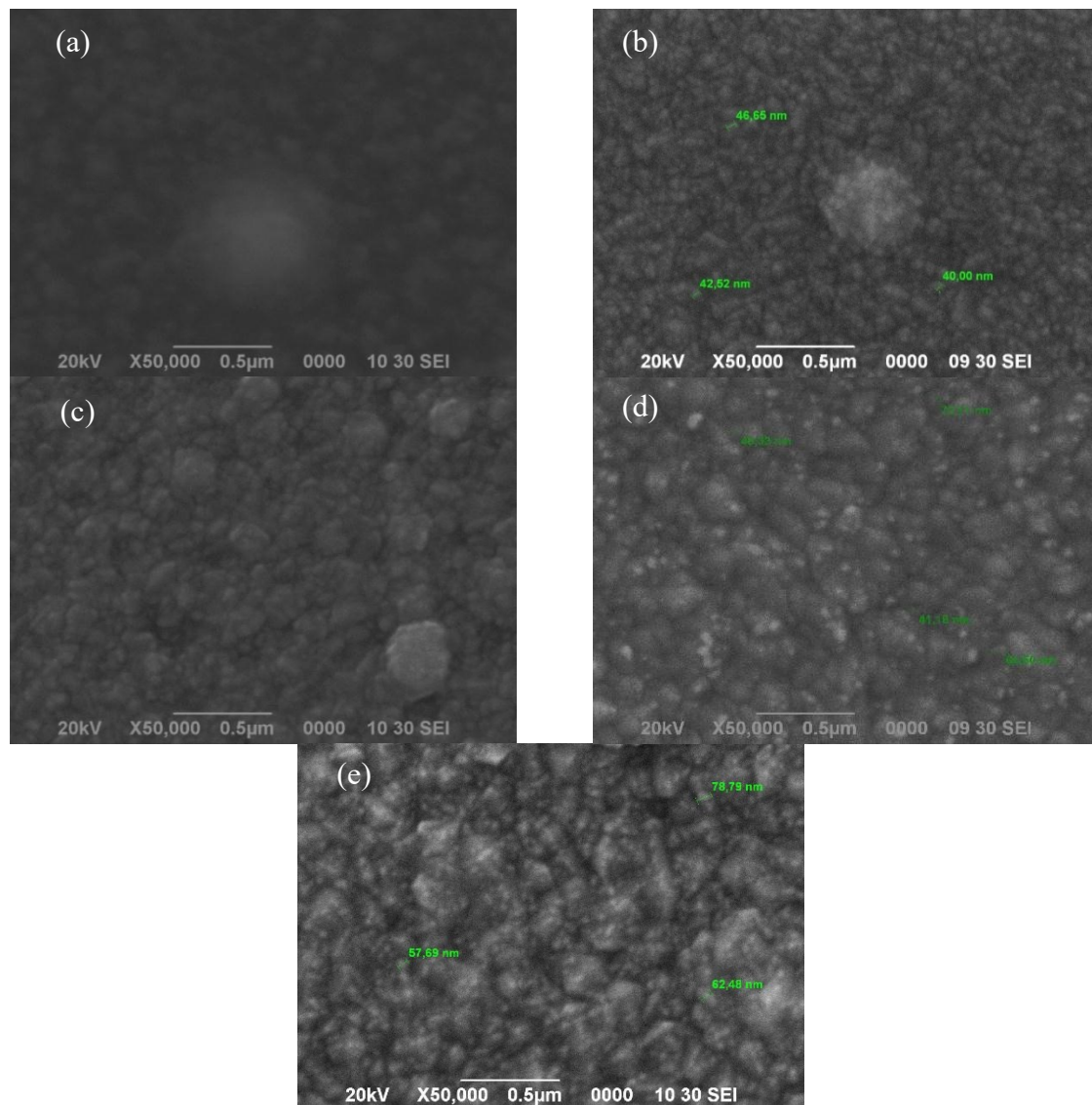


Figure 2. SEM images of FTO thin layers at a substrate temperature of 300°C and with variations of deposition times : (a) 5, (b) 10; (c)15; (d) 20 and (e) 25 minutes.

Figure 2 a-e shows grain growth trends with variations of deposition times. The particle morphology at 5 minutes deposition time is shown in Figure 2.a, thin films still show some void porosity between granules, this is probably due to the short deposition time, droplet solution is not able to be dispersed evenly to all parts of the glass surface[9]. With a magnification of 50,000x, at a deposition time of 10 minutes, the average grain size is approximately 43.56 nm. The average grain size for thin layers in a row for 20 and 25 minutes deposition time is 56.53 and 66.32 nm as shown in Figure 2 d-e.

With the addition of deposition time, the grain becomes more compact and interconnected where porosity has been significantly reduced. The SnO₂ thin film with a deposition time of 25 minute looks denser and has a larger particle size compared to the deposition times of 10, 15 and 20 minutes (Figure 2 b-e) With increasing deposition time, the grain grows larger and the crystal interface decreases. Meeting the arrangement of particles causes lower electrical resistance. This is in line with previous studies that FTO with many grain boundaries causes a high value of electrical resistance [14][3].

Table 2. The resistivity of FTO thin layers with deposition time variations of 5, 10, 15, 20 and 25 minutes at 300 °C during the pyrolysis process.

Deposition time (min)	Resitivity ($\Omega\cdot\text{cm}$)
5	3.930×10^{-4}
10	3.020×10^{-4}
15	1.580×10^{-4}
20	1.059×10^{-4}
25	4.960×10^{-5}

From the results that can be seen in Table 2, it can be seen that the longer the deposition time the smaller the resistivity value. The resistivity values for thin layers for deposition times 5, 10, 15, 20 and 25 minutes are 3.930×10^{-4} ; 3.020×10^{-4} ; 1.580×10^{-4} ; 1.059×10^{-4} and $4.960 \times 10^{-5} \Omega\cdot\text{cm}$ as shown in Table 2.

Nafiseh Memarian, et. al said this scattering mechanism affects the electrical properties and increases the resistivity of the layer. In addition, the effect of grain boundaries also influence in quality of resistivity [16]. At 5 minutes deposition time, the granules in the glass appear small and there are inter-grain holes. The grain boundary appears when the particles are small and also because of incomplete bonds between atomic layers. Therefore, carrier mobility in thin films is low and resistance becomes high [17]. This is supported by the XRD results, at 5 minutes deposition time, the crystal structure formed is still amorphous so the conductivity is small [5].

With an increase in deposition time, the SnO_2 particles grow denser thus reducing porosity and interconnects are more connected, electronic transfer between grains becomes easier and resistivity has been significantly reduced [3]. From the results obtained from Table 3, it is found that the longer the time of deposit, the grain size has increased so that the sensitivity value becomes smaller, this is supported by research conducted by D. Tatar, et.al [11] which says that as high as the crystallinity value, the lower the resistivity value.

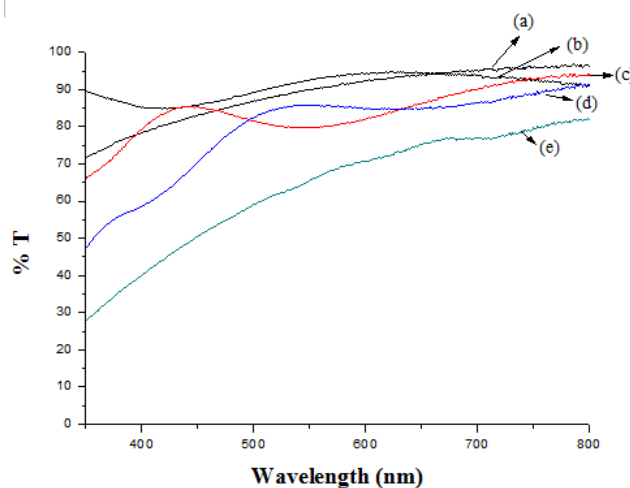


Figure 3. The optical transmittance of FTO thin layers at a constant deposition temperature of 300°C during the pyrolysis process with deposition time variation of (a) 5; (b) 10; (c)15; (d) 20 and (e) 25 minutes.

The observation result of SnO_2 thin layer transmittance spectrum with deposition time variation is shown in Figure 3. Transmittance values respectively at deposition times 5, 10, 15, 20 and 25 minutes were 96.881; 94.829; 94.294; 89.614 and 82.228%. This shows that the longer the coating time, the thicker the layer is formed so that the light passed is less and less [18]. Latifa, et al. [13] have carried out research using the same method but the precursor SnCl_4 pro analytic, in their research produced the best value for FTO produced a 15 minutes deposition time, which provides transmittance of 80,786%

and a resistivity of $4,01 \times 10^{-5} \Omega \cdot \text{cm}$. This is in line with the longer deposition time, the smaller the resistivity value and the less transmittance value [9][15].

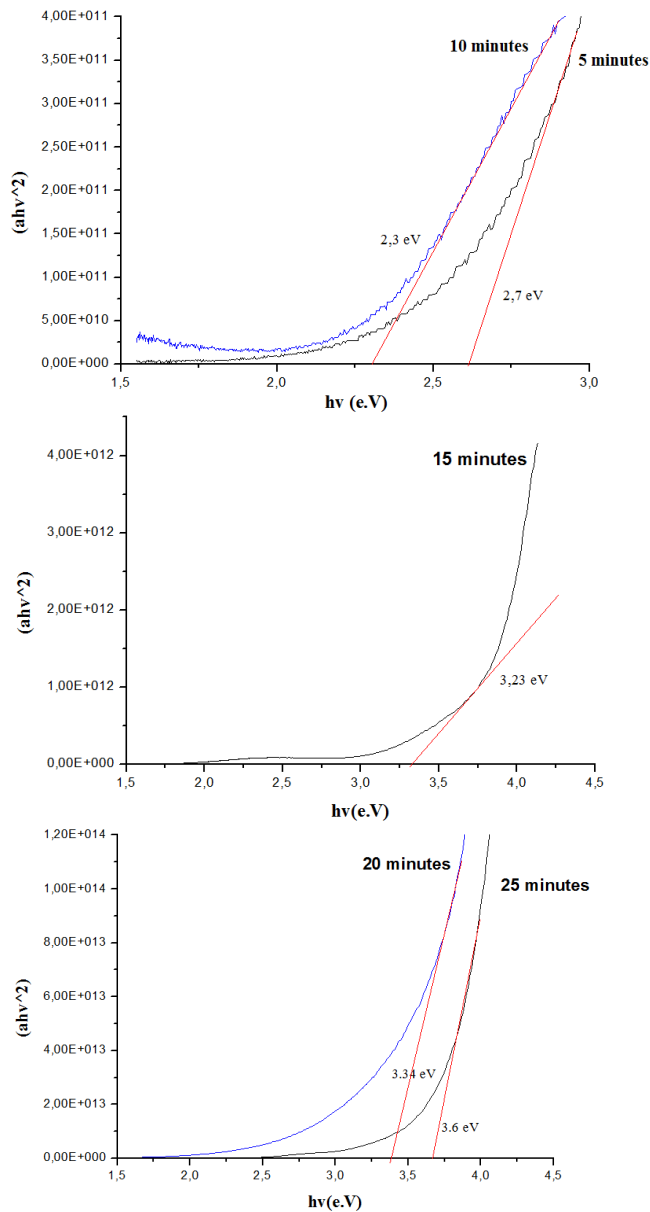


Figure 4. Energy band gap of FTO thin layers at a constant deposition temperature of 300 °C during the pyrolysis process with deposition time variation of (a) 5; (b) 10; (c) 15; (d) 20 and (e) 25 minutes.

An energy band is a collection of lines at the same energy level which will coincide and form a ribbon. Band gap energy can be known as the distance from the energy band that coincides with each other. The greater the value of the band gap energy obtained is expected to be slower in electron transfer due to the mobilization of electrons that are farther away. Figure 4 is a graph of band gap energy from the pyrolysis spray method at a temperature of 300°C.

Based on Figure 4, it is known that band gap energy from the pyrolysis spray method with the variation of deposition time 5, 10, 15, 20, 25 minutes obtained the band gap energy values are 2.7, 2.3, 3.23, 3.34, 3.6 eV, respectively. Bandgap results show a decrease in the deposition time of 10 minutes and then increase again from the deposition time of 15 minutes to 25 minutes. This result shows that the band gap energy is the smallest at 10 minutes deposition time so that it can be said that at 10 minutes deposition time has the highest energy density compared to other samples of deposition time.

4. Conclusion

Based on the investigation, it has been found that the use of Indonesian local stannic chloride (SnCl_4) can be used as an alternative precursor material in the manufacture of FTO thin films on a laboratory scale using pyrolysis spray technique using an ultrasonic nebulizer. The longer deposition time will increase the thickness of the FTO thin film so that electrical resistance decreases. However, layers that are too thick create an adverse effect on optical transparency. Therefore there must be a balance between electrical resistance and optical transparency. The optimum result obtained by pyrolysis technique with a deposition time of 20 minutes and substrate temperature 300°C has a resistivity of $1.059 \times 10^{-4} \Omega\cdot\text{cm}$ and transmittance 89.614%.

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