Fabrication of fluorine-doped tin oxide by using Indonesian local stannic chloride precursors with spin coating method

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Abstract. Fluorine-doped tin oxide is a thin layer of transparent conductive oxide, which has a function as a semiconductor. Fabrication of fluorine tin oxide from this research was expected to replace indium-doped tin oxide. Indium-doped tin oxide function as a commercial transparent conductive oxide. The raw material of indium was limited, so the price of indium is higher than fluorine. The material used are Indonesia local tin (IV) Chloride, ammonium fluoride, and methanol. Conductive liquids has made by the sol - gel method. Sol gel liquids doped with ammonium fluoride to make a high conductivity. The transmittance value at the 1, 2, 3, 4, and 5 minutes deposition time were respectively 69.7; 43.6; 14.4; 14.1 and 34.7%. In this research, spin coating method under 3000 RPM on fix substrate temperature of 300°C. The results of the experiment shows, increased deposition time, make the thickness of the layer increased while resistivity and transmittance decreased. The optimum parameter for glass conductivity fabrication were obtained at 4 minutes time deposition, substrate temperature at 300°C has a resistivity of 125 kΩ, transmittance 14.1% and band gap energy 2.48 eV.

1. Introduction
Indonesia as a country that has the potential to use large solar energy is still not optimal in utilizing this type of energy. Based on data from the Ministry of Energy and Mineral Resources, solar radiation in Indonesia in the western region can reach 4.5 kWh/m²/day, while in the eastern region it is even greater around 5.1 kWh/m²/day [1]. A device that can convert solar heat radiation into energy is Dye Sensitize Solar Cell (DSSC). This research develops Transparent Conductive Oxide (TCO) with Fluorine Tin Oxide (FTO) type for fabrication DSSC. FTO was developed compared to Indium Tin Oxide (ITO) because indium as a coating material from thin films was relatively rare, the price of indium was also very expensive. This can be seen from the comparison of Indium and Fluorine reserves and production. Indium has a reserve of 6000 tons and production reaches only 475
tons/year while fluorine having reserves of 120 million tons and production reached 4 million tons/year [1].

Fabrication an FTO thin film in this research using the spin coating method. Spin coating method is one of the coating techniques for FTO using a spinning process [2]. Factors that influence the results of the spin coating method are rotation speed, temperature of substrate, and time of deposition.

2. Materials and Methods
The material used in this research was soda lime microscope glass substrate, stannic chloride (SnCl₄) from PT. Timah Industry Cilegon, NH₄F (98%, Merck), and methanol. Glass substrate was cleaned using commercial glass cleaning fluid. Cleans using an ultrasonic cleaner for 15 minutes. At first dissolve 8.1 ml of SnCl₄ with 91.82 ml of methanol. Furthermore, the addition of NH₄F doping was 0.2 grams. The solution was stirred for 30 minutes becomes homogeneous. Deposition using a simple spin coating machine as figure 1, with the distance of the solution from the glass substrate to the tip of the pipette were 2 cm. Conductive solutions are dropped vertically above the substrate surface, where the spin coating machine's rotating at 3000 RPM

![Figure 1. Scheme of the spin coating process](image)

The repositioning is carried out in 2 repetitions. After the deposition process was completed. Spin spinning machine with a predetermined time variation of 1, 2, 3, 4, and 5 minutes. The coating process was carried out as many as 3 repetitions where each process pause was dried for 10 minutes in an oven with a temperature of 110°C. After the spin coating process was done, the coated glass substrate was fed into a muffle furnace at 300°C. Conductive Glass testing uses a multimeter (Sanwa), 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 Points Probe (FPP5000).

3. Results and Discussion
3.1 Identification of FTO Conductive Glass Resistivity
Testing to determine the resistivity value of the FTO conductive glass using a multimeter. Table 1 shows the resistivity of FTO at 300°C with deposition time variation. Based on Table 1, the largest resistivity was owned by 1 minute deposition time and the smallest was owned by 4 minutes. This is because drying done on spin coating does not coincide with the deposition process so it must be moved first to the top of the hotplate and requires a longer transition time. This caused premature clumping of the solution to the substrate. The factor caused high resistivity was increasing in layer thickness, so it can be increased of particle size and granular densification [3].
Table 1. The resistivity of FTO at 300°C with deposition time variation

| Deposition time (min) | Resistivity (Ω) |
|-----------------------|-----------------|
| 1                     | 12000 k         |
| 2                     | 10071 k         |
| 3                     | 8700 k          |
| 4                     | 125 k           |
| 5                     | 303 k           |

3.2 Identification of Morphological and Semi Quantitative Analysis of FTO
Figure 2 shows the results of SEM image of FTO with a magnification of 50,000 X in deposition time variation.

Figure 2. SEM image of FTO thin layers with variation deposition times (a) 1, (b) 2, (c) 3, (d) 4, (e) 5 minutes
Conductive glass results at 300°C in variation deposition times 1, 2, 3, 4, and 5 minutes have not uniform surface morphology. This can occur because the conductive solution that was deposited does not spread during the rotation. Conductive solutions stored in the same area were not evenly distributed. Factors that influence the results of spin coating are conductive solutions have high viscosity making it difficult to spread and tend to agglomerate in certain regions. The surface morphology of glass substrate on a spin coating method does have a rough texture because of the continuous agglomeration of the glass substrate [4]. Figure 2. Shows the formation of fine grains from deposition times 3 to 5 minutes. It is known that increased of deposition times, caused the size of fine grains becomes larger.

Table 2 is the result of conductive glass EDS with a variation of deposition time 1, 2, 3, 4, 5 minutes at 300°C.

Table 2. The result of semi quantitative EDS of FTO with deposition time variation.

| Element | 1 min | 2 min | 3 min | 4 min | 5 min |
|---------|-------|-------|-------|-------|-------|
| O       | 23.86 | 29.37 | 23.53 | 27.93 | 22.44 |
| Na      | 3.98  | 2.19  | 2.16  | 1.29  | -     |
| Mg      | 1.38  | 0.83  | -     | -     | -     |
| Si      | 28.65 | 18.28 | 20.09 | 12.56 | 3.22  |
| Ca      | 7.66  | 4.17  | 5.18  | 3.28  | 1.09  |
| Sn      | 34.46 | 45.06 | 49.04 | 54.94 | 73.26 |

Table 2 shows, that the increasing wt % of Sn is related to the increasing of time deposition. As long as addition of wt% Sn element cause decrease of wt% of Na and Mg elements. At 5 minutes deposition time, Na was dissolved. For Mg, it starts to disappear in 3 minutes deposition times. The elements of Na and Mg were the composition of the glass substrate itself [5].

3.3 Identification of Diffraction Pattern on FTO Conductive Glass

Figure 3. The XRD pattern of FTO at 300°C with 4 minutes deposition time
Based on Figure 3, the XRD characterization results showed that the FTO with the spin coating method did not detect the sharp peak, the peak intensity indicates that the structure of FTO still amorphous.

3.4 Identification of FTO Transmittance
Transmittance is the relative amount of light entering and exiting through the substrate. Figure 4 shows a graph of the comparison between deposition time and FTO transmittance.

Figure 4. The graph of comparison between FTO transmittance and variation of deposition times (a) 1, (b) 2, (c) 3, (d) 4, (e) 5 minutes

Figure 4 shows that increasing variation of deposition times 1, 2, 3, 4, and 5 minutes, caused transmittance decreased respectively 69.7; 43.6; 14.4; 14.1 and 34.7%. This occurs because of the thickening of layer that attached to the substrate. Spin coating speed can also affect the thickness of the coating. Substrate spreading speed affects the centrifugal force in conductive solution and caused air turbulence during the rotation [6].

3.5 Identification of Band Gap Energy on FTO
Energy tape is a collection of lines at the same energy level, which will coincide and form a band [7]. Making this energy band gap graph uses the UV-VIS transmittance results which were included in the calculation using the Tauc Plot method. Figure 5 shows, the transmittance of FTO at 300°C during the spin coating process with deposition time variation.

The lowest energy band gap was achieved in 4 minutes deposition time. Energy band gap acts as a way to flow electricity more quickly. The longer the deposition time causes the band gap energy decreased. This indicates that the longer deposition time the energy band density decreases causing decreasing conductivity. The cause of the low band gap energy results can be caused by an increase in the thickness of the thin layer, the density of the layer and the homogeneity of the solution which is deposited on the substrate surface [8].
4. Conclusions
The results of the experiment shows, increased deposition time, make the thickness of the layer increased while resistivity and transmittance decreased. The optimum parameter for glass conductivity fabrication were obtained at 4 minutes time deposition, substrate temperature at 300°C has a resistivity of 125 kΩ, transmittance 14.1% and band gap energy 2.48 eV.

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