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UTILIZATION OF INDONESIAN LOCAL STANNIC CHLORIDE ($SnCl_4$) PRECURSOR IN THE PROCESS OF MAKING FLUORINE-DOPED TIN OXIDE (FTO) CONDUCTIVE GLASS

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ABSTRACT

UTILIZATION OF INDONESIAN LOCAL STANNIC CHLORIDE ($SnCl_4$) PRECURSOR IN THE PROCESS OF MAKING FLUORINE-DOPED TIN OXIDE (FTO) CONDUCTIVE GLASS. Thin layer of fluorine-doped tin oxide (FTO) conductive glass has been deposited on a glass substrate heated at a temperature of 350°C using the ultrasonic spray pyrolysis nebulizer method with variations in fluorine doping and substrate temperatures. This experiment uses the raw material of Indonesian local stannic chloride ($SnCl_4$) (PT Timah Industri) as a precursor with a temperature variation of 250, 300, 350, 400°C. The structure and morphology of the optical and electrical properties of all the thin layers have been examined. XRD results show that all thin layers have a tetragonal crystal structure. In this experiment, there is a significant influence on the role of fluorine doping on resistivity and transmittance values. With the addition of 2% wt doping, the resistivity and transmittance values decrease. The optimum value is obtained by doping 2 wt%, substrate temperature of 350°C with a resistivity value of $9.28.10^{-5}$ Ω.cm and transmittance value of 88%.

Keyword: FTO conductive glass, Indonesian local precursor, ultrasonic spray pyrolysis nebulizer, deposition temperature, tetragonal

ABSTRAK

PEMANFAATAN PREKURSOR STANNIC CHLORIDE ($SnCl_4$)LOKAL INDONESIA PADA PROSES PEMBUATAN KACA KONDUKTIF *FLUORINE-DOPED TIN OXIDE* (FTO).Lapisan tipis kaca konduktif *fluorine-doped tin oxide* (FTO) telah di deposisi di atas substrat kaca yang dipanaskan dengan temperatur 350 °C menggunakan metode *ultrasonic spray pyrolisis nebulizer* dengan variasi doping *flourine* dan temperatur substrat.Percobaan ini menggunakan bahan baku *stannic chloride* ($SnCl_4$) lokal Indonesia (PT Timah Industri) sebagai prekursor dengan variasi temperatur 250, 300, 350, 400 °C. Struktur, morfologi sifat optik dan listrik dari semua lapisan tipis telah di teliti. Hasil XRD memperlihatkan bahwa semua lapisan tipis mempunyai struktur kristal tetragonal. Pada percobaan ini memperlihatkan adanya pengaruh yang besar atas peran doping *flourine* terhadap nilai resistivitas dan transmitansi. Dengan adanya penambahan doping 2% wt, nilai resistivitas dan transmitansi mengalami penurunan. Nilai optimum diperoleh pada doping 2 wt%, temperatur substrat 350 °C dengan nilai resitivitas $9,28.10^{-5}$ Ω.cm dan nilai transmitansi 88%.

Kata kunci: kaca konduktif FTO, prekursor lokal Indonesia, *ultrasonic spray pyrolisis nebulizer*, temperatur deposisi, tetragonal

INTRODUCTION

Along with the increasing population growth and industrial growth in the world, the world's need for energy will increase. The availability of energy in the earth is also limited. For this reason, it is necessary to develop safe and renewable energy resources. One of the biggest potential energy sources is sunlight. One method for converting sun-light is dye sensitized solar cell (DSSC). In the fabrication of dye sensitized solar cell, several components are needed. These components consist of transparent conductive oxide (TCO), semiconductor oxide material, dye sensitizer, electrolyte, and counter electrode [1]. One of the oxides used in making TCO other than ITO is fluorine-doped tin oxide (FTO) [2].

Various methods have been employed to grow SnO2 films both physically and chemically. Latifa, et al. [3] have succeeded in conducting research in the making of fluorine-doped tin oxide (FTO) by ultrasonic spray pyrolysis nebulizer method with optimum resistivity values of $4.01x10^{-5}$ Ω.cm and transmittance value of 84.808% using pro analysis (p.a.) stannic chloride ($SnCl_4$) precursor with fluorine doping. Pro analysis (p.a.) stannic chloride ($SnCl_4$) is a commercial pre-cursor that has a fairly expensive price and limited availability.

Indonesia is one of the countries that have a large potential tin producer. One of the tin companies in Indonesia which is engaged in tin exploration is PT. Timah Industri. This company has produced stannic chloride ($SnCl_4$), but it has not been commercially marketed as it still requires deeper assessment of material specifications and their use. Table 1 is an analysis of the elements contained in pro analyst (p.a, 98%, Merck Ltd., Germany) stannic chloride ($SnCl_4$) and stannic chloride ($SnCl_4$) produced by PT Timah Industri by testing using ICP-OES.

In this study, an experiment will be conducted to make a thin layer of fluorine-doped tin oxide (FTO) conductive glass using stannic chloride ($SnCl_4$) produced by PT Timah Industri as a precursor in the making of thin layer of fluorine-doped tin oxide (FTO) conductive glass using an ultra-sonic spray pyrolysis nebulizer method.

Table 1. Characterization Results of stannic chloride ($SnCl_4$) with ICP-OES

Element	*Pro analyst* (p.a) (ppm)	PT Timah Industri (ppm)
Al	0,183590	0,028548
B	-0,014869uv	-0,058768uv
Ca	0,896188	0,357120
Fe	0,276722	0,531371
K	-0,757319uv	-0,738114uv
Li	-0,016001uv	-0,018576uv
Mg	0,055139	0,052942
Na	0,295840	0,286162
Ni	-0,017752uv	0,00391uv
Si	0,592301	0,239495
Sn	15779,7x	18150,7x

Note :

- (-) and (uv) : the elements obtained are very low
- (x) : the element obtained is very high

EXPERIMENTAL METHOD

The materials used in this study were soda lime micro-scope slide glass substrate, Indonesian local stannic chloride ($SnCl_4$) (PT Timah Industri), NH4F (98%, Merck Ltd., Ger-many) and methanol.
This research was initiated by cleaning the substrate glass using commercial detergent, then the substrate glass was soaked in acetone and then ultrasonified for 15 minutes.

The solution making was done into two types of solution. The first solution (undoped) was a mixture of 8.18 grams of stannic chloride ($SnCl_4$) with 9.82 ml of methanol. The solution was thoroughly stirred with a magnetic stirrer at medium speed for 30 minutes. The second solution (doped) uses the initial composition of the first solution by adding doping as much as 0.2 grams of NH4F. This solution is stirred again for 30 minutes again to make it homogeneous.

Deposition was carried out using the ultrasonic spray pyrolysis nebulizer method with ultrasonic nebulizer of GEA Medical 402A1 with a distance of 10 cm and a speed of ± 30 ml/10 minutes and the substrate glass was placed on the hot plate with varying substrate temperatures of 250, 300, 350 and 400°C at the fixed time of deposition for 20 minutes.

The crystal structure of the thin layer formed was analyzed using x-ray diffraction (Shimadzu XRD Cu-Kα, -7000), while the morphological structure of the thin layer was seen using a scanning electron microscope-energy dispersive spectroscopy (JEOL® JSM-6390A). Optical transparency of the thin layer was analyzed using UV-Vis spectrophotometer (GENESYS® 10s). The four point probe (FPP5000) is used to find out the resistivity value and thickness of the formed layer.

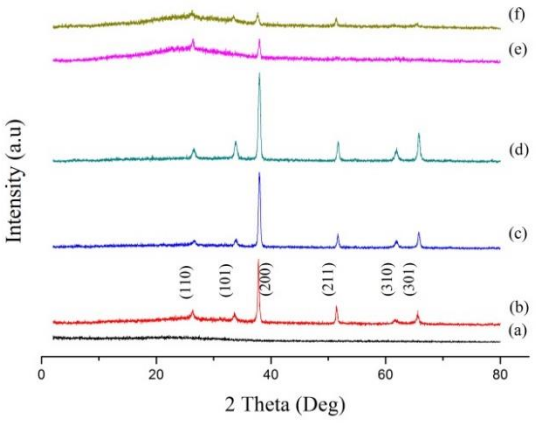

Figure 1. The x-ray diffraction pattern of SnO_2 thin layer with substrate temperature variations, fixed deposition time of 20 minutes; (a) Doping 2% wt, 250°C; (b) Doping 2% wt, 300°C; (c) Doping 2% wt, 350°C; (d) Doping 2% wt, 400°C (e) Undoped, 300°C; (f) Undoped, 350°C

RESULTS AND DISCUSSION

The X-ray diffraction pattern of SnO_2 thin layer that grows on the glass substrate with substrate temperature variations is shown in Figure 1. The XRD measurement results indicate that the peaks show the SnO2 material phase with the crystal planes of (110), (101), (200), (211), (310), (301) with tetragonal crystal structures according to the SnO_2 pattern [4].

The increase in the substrate temperatures of 250, 300, 350 and 400°C in SnO_2 thin layers which have been given doping for minutes causes a change in intensity in the crystal plane. At a substrate temperature of 250°C it still looks amorphous, this shows that the SnO2 crystalline phase cannot yet form properly at a substrate temperature of 250°C. This is because the behavior at low substrate temperatures is not enough to complete the chemical reaction, the solvent evaporates on the substrate surface then melts and the vapor diffuses into the substrate [5].

The increase in the substrate temperatures of 300, 350 and 400°C causes a change in intensity in the crystal plane. At a substrate temperature of 300°C, the SnO_2 thin layer produces a polycrystalline structure, the intensity of the crystal plane (200) looks very dominant compared to the intensity of the other crystal planes which indicates that the crystal quality is better. An increase in the crystal plane (200) from a temperature of 300 to 350 and 400°C is due to the continued increase in film thickness [5].

Whereas in undoped SnO_2 thin layer (Figure 1e-f), the intensity of the crystal plane (200) is much lower with that of doped SnO_2 thin layer (Figure 1a-d). This shows that the addition of F doping element will affect the produced SnO_2 crystal shape [6]. In addition, it can also be seen from the results of the graph that the crystallinity value highly increases between the doped SnO_2 thin layer from the undoped one. This proves the effect of F doping will increase the crystallinity of the structure of SnO_2 thin layer. The higher the crystallinity phase formed, the smaller the grain boundary produced.

Figure 2 shows the SEM results of SnO_2 thin layer with substrate temperature variations, the fixed deposition time of 20 minutes. SEM photo results show the results of the grain size that looks different.

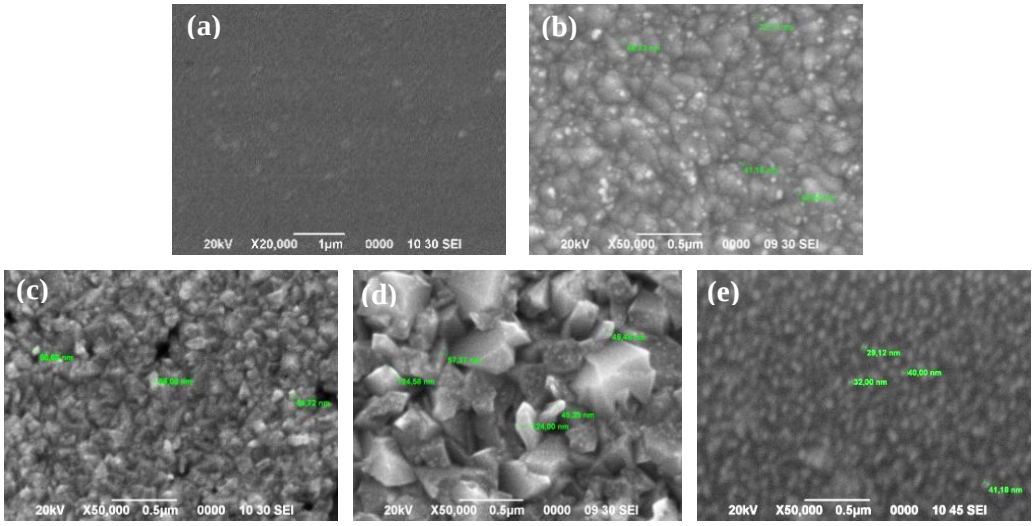

Figure 2. SEM photo results of SnO_2 thin layer with substrate temperature variations, the fixed deposition time of 20 minutes; (a) Doping 2% wt, 250°C; (b) Doping 2% wt, 300°C; (c) Doping 2% wt, 350°C; (d) Doping 2% wt, 400°C (e) Undoped, 300°C

Figure 2a-d shows the trend of grain growth by the addition of the substrate temperature to the doped SnO_2 thin layer. Figure 2a shows the absence of grain growth and large aggregates is found throughout the substrate, this is probably due to the deposition temperature that is still too low [7] so that the solution droplets are not able to be evenly dispersed to all parts of the glass surface.

At higher temperatures, i.e. 300, 350 and 400°C, heating takes place optimally so that the layer is denser [8]. These droplets fall in the form of droplets and are then ac-companied by evaporation of solvents when exposed to a high temperature of 300°C. This is what causes the appearance of microstructure to begin to appear at a substrate temperature of 300°C (Figure 2d). The grain size will increase as the substrate temperature increases in the doped SnO_2 thin layer (Figure 2a-d). The smallest grain size in the doped SnO_2 thin layer at 300°C is around 41.18 nm and increased to 44.72 and 45.25 nm at temperatures of 350 and 400°C. According to the experiment results by A. Kennedy et al. [9], in addition to being denser, an amalgamation process occurs on the substrate surface. Amalgamation is the buildup of nano-sized solid particles, so that the particles combine to form larger grains.

Significant differences are seen in Figure 2e, namely undoped SnO_2 thin layer. In undoped samples, the thin layer microstructure looks homogeneous with small grain size and is not dense so that it reduces sample conductivity [10].

Table 2. The effect of doping and substrate temperatures on SnO_2 thin layer with deposition time of 20 minutes

Substrate Temperatures (°C)	Resitivity (Ω.cm)	Thickness (μm)
Undoped, 300	$1.714x10^{-3}$	24.9
Undoped, 350	$1.029x10^{-3}$	48.6
Doping 2% wt, 250	∞	-
Doping 2% wt, 300	$1.059x10^{-4}$	483
Doping 2% wt, 350	$9.28x10^{-5}$	551
Doping 2% wt, 350	$8.55x10^{-5}$	598

The results of resistivity measurement of SnO_2 thin layer with variations of substrate temperatures are shown in Table 2. The resistivity of undoped SnO_2 thin layer at 300°C is 1.714×10^{-3} Ω.cm and decreases to 1.029×10^{-3} Ω.cm at a substrate temperature of 350°C. With the addition of doping 2% wt, the resistivity value decreases sharply. At a temperature of 250°C the resistivity value is undetectable due to the absence of a solution attached to the glass layer due to the low substrate temperature. Resistivity is detectable when the substrate temperature is increased to 300°C. The resistivity value decreased from $1.059x10^{-4}$ to $9.28x10^{-5}$ and $8.55x10^{-5}$ Ω.cm when the substrate temperature is increased from 300 to 350 and 400°C. With increasing substrate temperature, the grains grow larger and the interface-crystal decreases. The density of the particle structure leads to lower electrical resistance [11].

The thickness of undoped SnO_2 thin layer at temperatures of 300 and 350°C were 24.9 and 48.6μm. With the addition of doping 2% wt, the layer thickness increased at substrate temperatures 300, 350 and 400°C, which were 483, 551 and 598μm as shown in Table 2.

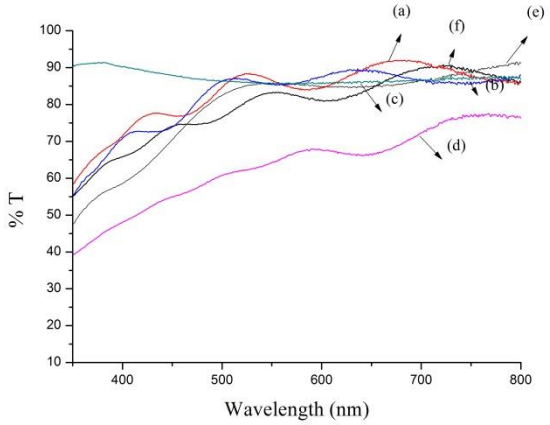

Figure 3. The transmittance spectrum of SnO_2 thin layer with variations of substrate temperatures, fixed deposition time of 20 minutes; (a) Doping 2% wt, 250°C; (b) Doping 2% wt, 300°C; (c) Doping 2% wt, 350°C; (d) Doping 2% wt, 400°C (e) Undoped, 300°C; (f) Undoped, 350°C

Based on the UV-Vis graph in Figure 3a-d, we can see the difference in the transmittance value of SnO_2 thin layer with variations of substrate temperatures. Transmittance values at substrate temperatures of 250, 300, 350 and 400°C were 92, 91, 88 and 78%, respectively. This shows that the higher the substrate temperature, the thicker the layer is formed so that the light passed is getting less [12]. Another difference is shown in Figure 3e-f, for the undoped SnO_2 thin layer has a higher transmittance values (92 and 91% for substrate temperatures of 300 and 350°C) compared to doped SnO_2 thin layer.

It can be shown that below the same substrate temperature the undoped sample (300, 350°C) has a much higher transmission up to 92 and 91% compared to the doped (300, 350°C) which transmittance values 91 and 88%. This shows that the addition of fluorine doping results in a decrease in transmission, although on the other hand it has significantly increased electrical conductivity.

CONCLUSION

From this study it can be concluded that Indonesian local stannic chloride ($SnCl_4$) produced by PT Timah Industri is proven to be a material that can be used as a precursor in making thin layers and can be recommended as a tool for making FTO thin layer on a laboratory scale. Giving doping fluorine has a great influence on the making of FTO thin layer. The higher substrate temperature will increase the thickness of FTO thin layer, so that the electrical resistance decreases. However, a too thick layer creates an adverse effect on optical transparency. Therefore, there must be a balance between electrical resistance and optical transparency. The optimal results in this experiment are the optimum value obtained at 2 wt% doping, 350°C substrate temperature with a resistivity value of $9.28x10^{-5}$ Ω.cm and transmittance value of 88%.

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