International Journal of Technology (2016) 8: 1335-1343
ISSN 2086-9614

THE INFLUENCE OF DEPOSITION TIME AND SUBSTRATE TEMPERATURE DURING THE SPRAY PYROLYSIS PROCESS ON THE ELECTRICAL RESISTIVITY AND OPTICAL TRANSMITTANCE OF 2 WT% FLUORINE-DOPED TIN OXIDE CONDUCTING GLASS

Tri Arini[1], Akhmad Herman Yuwono[1,2*], Latifa Hanum Lalasari[3], Nofrijon Sofyan[1,2], Ghiska Ramahdita[1,2], F. Firdiyono[3], Achmad Subhan[4], Chairul Hudaya[5]

[1]*Department of Metallurgy and Materials Engineering, Faculty of Engineering, Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia*
[2]*Tropical Renewable Energy Center (TREC), Faculty of Engineering, Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia*
[3]*Research Center for Metallurgy and Materials, LIPI Puspiptek Serpong, Cisauk-Banten 15314, Indonesia*
[4]*Research Center for Physics, LIPI Puspiptek Serpong, Cisauk-Banten 15314, Indonesia*
[5]*Department of Electrical Engineering, Faculty of Engineering, Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia*

(Received: November 2016 / Revised: December 2016 / Accepted: December 2016)

ABSTRACT

Transparent conducting oxide (TCO) glasses play an important role in various technology, including dye sensitized solar cells. One of the most commonly used glass is indium tin oxide (ITO) glass, which is expensive. Therefore, the main purpose of this research was to determine if ITO glass can be replaced with fluorine-doped tin oxide (FTO) glass, which is easier and more economic to manufacture. For this purpose, a tin chloride dehydrate ($SnCl_2.2H_2O$) precursor was doped with ammonium fluoride (NH_4F) using a sol-gel method and spray pyrolysis technique to investigate the fabrication process for conductive glass. NH_4F was doped at a ratio of 2 wt% in the $SnCl_2.2H_2O$ precursor at varying deposition times (10, 20, and 30 minutes) and substrate temperatures (250, 300, and 350°C). The results revealed that longer deposition times created thicker glass layers with reduced electrical resistivity. The highest optical transmittance was 75.5% and the lowest resistivity was 3.32×10^{-5} Ω.cm, obtained from FTO glass subjected to a 20-minute deposition time at deposition temperature of 300°C.

Keywords: Ammonium fluoride doping; Conductive glass; Electrical resistivity; Optical transmittance; Tin chloride dehydrate

1. INTRODUCTION

As the world population and industrial growth increases, the need for energy unavoidably raises. The primary energy source used globally is fossil fuels, including crude oil, natural gas, and coal. However, fossil fuel sources are not renewable and reservations will continue to decline over the next few years. One abundant alternative energy source that has not been maximized is sun light, which is converted by solar cells into photon energy and electricity. Sun light is one of the answers to global energy problems. More specifically, dye-sensitized solar cells (DSSC) are third-generation photovoltaic devices based on a photo-electrochemical

*Corresponding author's email: ahyuwono@eng.ui.ac.id, Tel. +62-21-7863510, Fax. +62-21-7872350
Permalink/DOI: https://doi.org/10.14716/ijtech.v7i8.7065

process involving interactions among photon absorption, sensitizing dye and semiconductor oxide. These cells are promising a simple and low-cost solution, and the sensitizing dye can be extracted from natural plant sources abundant in tropical regions.

One of the most important parts of DSSC is the transparent conductive oxide (TCO). The most commonly used TCO is indium tin oxide (ITO); however, ITO production costs are very high due to the scarcity of raw materials (i.e., the indium (In) element). Thus, an alternative material is needed, and one oxide with characteristics similar to ITO is tin oxide (SnO_2). Previous studies have examined how to obtain glass with excellent conductivity and high transparency using various chemical and physical approaches, such as evaporation (Muranaka et al., 1986), electron beam evaporation (Shamala et al., 2004), sputtering (Brousseau et al., 1997), spray pyrolysis (Paraskevi & Munkegade, 2008), sol-gel method (Ganz et al., 1997), and chemical vapour depostion (Ray et al., 1997). The current research used the sol-gel method by doping the tin chloride precursor with a fluorine source. The main focus of the work was to investigate the effect of deposition time and substrate temperature during spray pyrolysis process on TCO properties, including crystal structure, morphology, electrical resistivity, and optical transparency.

2. EXPERIMENTAL METHOD

The materials used in this experiment included tin chloride dihydrate ($SnCl_2.2H_2O$), ammonium fluoride (NH_4F), distilled water, and ethanol (Et-OH). All chemical reagents had analytical grade purity and were purchased from Merck.

The FTO fabrication process began with cleaning the glass substrates using commercial detergent, followed by immersion in ethanol in a glass beaker. To complete the cleaning process, both the glass substrates and beaker were ultra-sonicated for 15 minutes. The substrates were dried in an oven overnight before being used, while the tin precursor solution was prepared by dissolving 12 grams of $SnCl_2.2H_2O$ in 100 ml of ethanol and stirring this combination for 30 minutes. The fluorine doping solution was made by dissolving NH_4F in distilled water, followed by rigorous stirring until a homogeneous solution was obtained. This doping solution was added with a dropper to the tin precursor solution, and the mixture was stirred for 30 minutes. The ratio between NH_4F and $SnCl_2.2H_2O$ was fixed at 2 wt%.

The deposition process for the solution mixture on soda lime substrate was carried out using the spray pyrolysis method and an ultrasonic nebulizer (GEA Medical 402A1) at a distance of 10 cm and a speed of ± 30 ml/10 min. One variation in the fabrication stage was the varying deposition times of 10, 20, and 30 minutes at a fixed heating temperature of 300°C. Another synthesis variation was the varying temperature of 250, 300, and 350°C at a fixed deposition time of 20 minutes.The characterizations of the fabricated FTO glasses were performed with scanning electron microscope-energy dispersive spectroscopy (SEM-EDS; JEOL-JSM 6390A), x-ray diffraction (XRD; Shimadzu XRD-7000), ultra violet- visible spectroscopy (Thermo UV-Vis Genesys 10s), and a four-point probe (FPP5000).

3. RESULTS AND DISCUSSION

3.1. Deposition Time Variation

The first investigation was carried out by varying the deposition time during the spray pyrolysis process to 10, 20, and 30 minutes at a fixed heating temperature of 300°C. For study purposes, SEM-EDS observations were taken of the fabricated glasses at these variables.

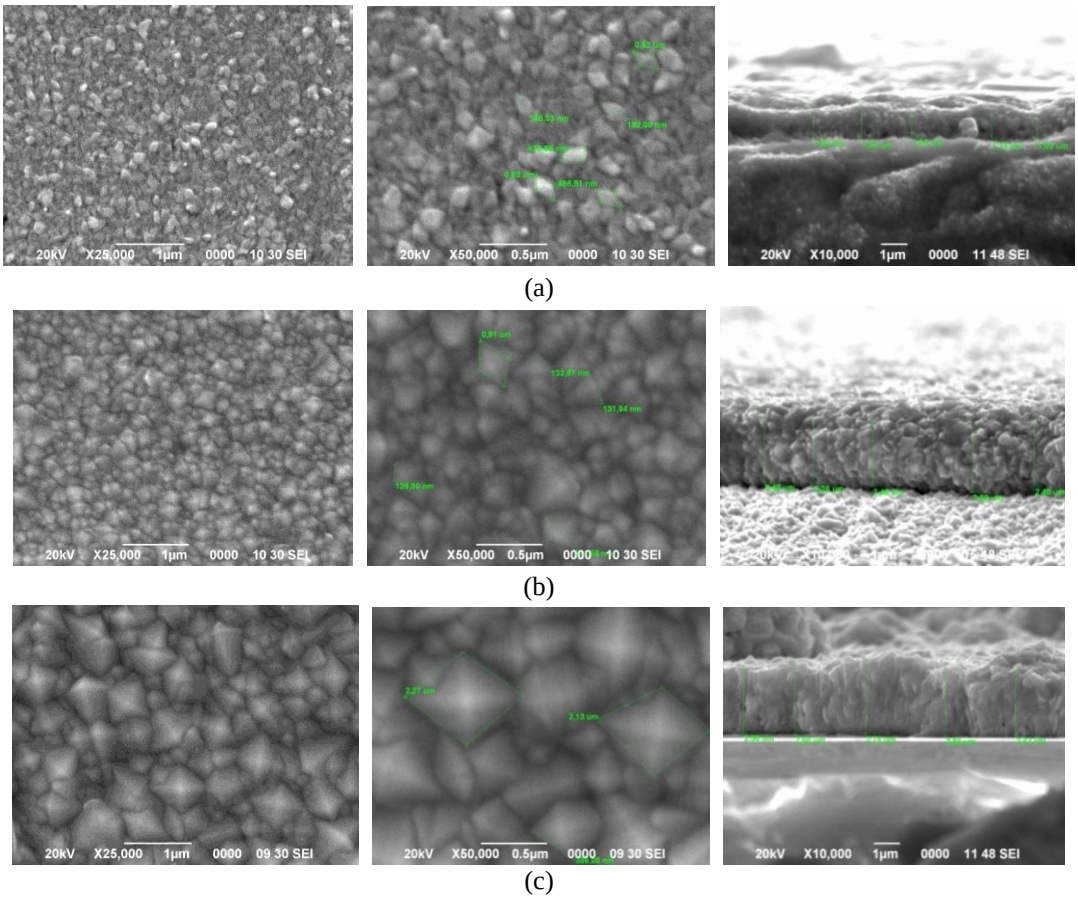

Figure 1 Top view (left) and cross section (right) SEM images of 2 wt% FTO thin layers heated to 300°C during the pyrolysis process with deposition time variation of: (a) 10; (b) 20; and (c) 30 minutes

Figures 1a–c show the top view and cross section SEM images of FTO thin layers heated to 300°C during pyrolysis with deposition time variations of 10, 20, and 30 minutes. At 10 minutes (Figure 1a), the resulting FTO thin film appeared as a layer consisting of individual and separated small particles with an average size of 0.52 μm. As a consequence, several porosity voids were observed among the particles. Increasing the deposition time to 20 minutes resulted in larger particle sizes, averaging 0.91 μm (Figure 1b). The particles became more compact and interconnected when the porosity was reduced significantly. A deposition time of 30 minutes produced much larger particles averaging 2.13 μm, and the FTO layer formed trapezium-shaped grains (Moholkar et al., 2008) scattered with smaller particles. The cross sectional images in Figures 1a–c also reveal that the thickness of the FTO layer was 1.00, 2.38, and 2.42 μm for deposition times of 10, 20, and 30 minutes, respectively. Longer deposition times increased the thickness of the FTO layers; however, this had an adverse effect on optical transmittance, which was studied further using UV-Vis spectroscopy.

Figure 2 shows a diffractogram of FTO glasses at deposition time variations of 10, 20, and 30 minutes, heated to 300^{o}C. Several peaks appear at 2θ degrees of 26.511, 33.766, 37.843, 51.610, 61.690, and 65.750^{o} confirming the (110), (101), (200), (211), (310), and (301) crystal planes and the tetragonal rutile structures of the cassiterite SnO_2 phase. The full-width at half maximum (FWHM) values of these diffraction peaks decreased significantly from 0.262° at 10 minutes to 0.229° and 0.205° at 20 and 30 minutes, respectively. This is consistent with the

results from the crystallite size estimation, which increased from 12.16 nm at 10 minutes to 73.61 and 124.60 nm at 20 and 30 minutes, respectively.

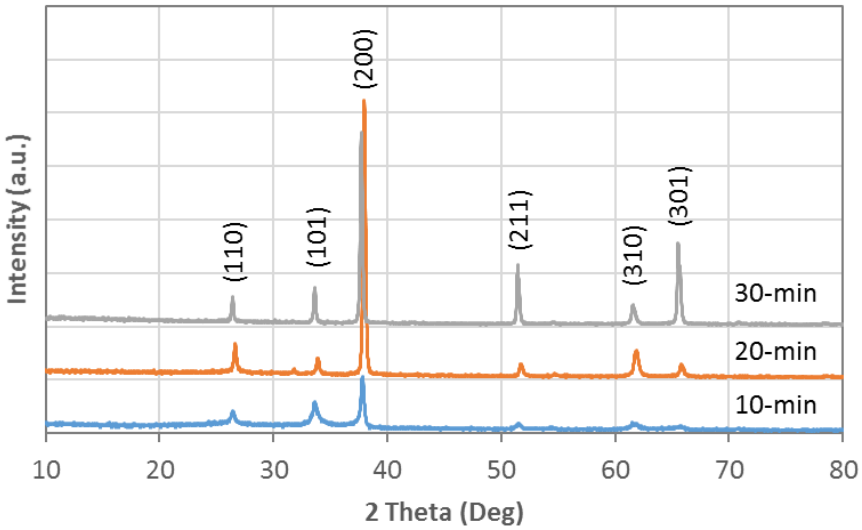

Figure 2 XRD pattern of 2 wt% FTO thin layers with deposition time variations of 10, 20, and 30 minutes at a constant deposition temperature of 300°C

No other phases, except the tin oxide phase, were detected in the fabricated glasses based on XRD characterization, including tin chloride hydrate ($SnCl_2.2H_2O$) and ammonium fluoride (NH_4F) precursor phases. This confirms that conversion from these precursors to tin oxide doped with fluorine was successful during the spray pyrolysis process. This result is also in agreement with that proposed by Ren et al. (2011), in which the O atom was replaced by F atoms in SnO_2. Further study of the XRD results also revealed that the intensity of the diffraction peaks increased as deposition times increased from 10 to 30 minutes. In addition, the (200) crystal plane was the preferred orientation of the FTO thin layer on the glass substrate. Previously, Gordillo et al. (1994) showed that (200) is the desired crystal plane for optimal balance between electrical resistance and optical transmittance.

Table 1 Resistivity of 2 wt% FTO thin layers with deposition time variations of 10, 20, and 30 minutes at 300°C during the pyrolysis process

Deposition Time	Resistivity (Ω.cm)
10 min	6.19×10^{-4}
20 min	3.32×10^{-5}
30 min	2.63×10^{-5}

Table 1 presents the electrical resistivity test results for the FTO thin layers under the aforementioned conditions. The values decrease significantly up to one order higher (i.e., from 6.19×10^{-4} to 3.32×10^{-5} Ω.cm) when the deposition time was prolonged from 10 to 20 minutes. At 30 minutes, the resistivity was slightly reduced to 2.63×10^{-5} (Ω.cm). This electrical conductivity result is related to the particle and crystal structure growth of the SnO_2 phase, which was observed by SEM (Figure 1) and XRD (Figure 2). At 10 minutes (Figure 1a), the spray pyrolysis process resulted in small particles accompanied by pores or voids as a consequence of incomplete connections among these particles. These pores acted as a sink for electronic charges, resulting in the resistivity of the film being higher. As the deposition time

increased to 20 minutes, the SnO_2 crystallites grew larger, and interconnection was well established. Additionally, the thickness of the film increased to 2.38 μm. As demonstrated visually by the compacted particles and reduced porosity in Figure 1b, the electronic transfer among particles became easier, and resistivity reduced significantly (Zhao et al., 2008). At a deposition time of 30 minutes, the particles were significantly larger with less pores, as shown in Figure 1c, and reduced resistivity was obtained, although the order of its value was the same as that at 20 minutes. This could be related to the thickness of the thin film, which slightly increased to 2.42 μm.

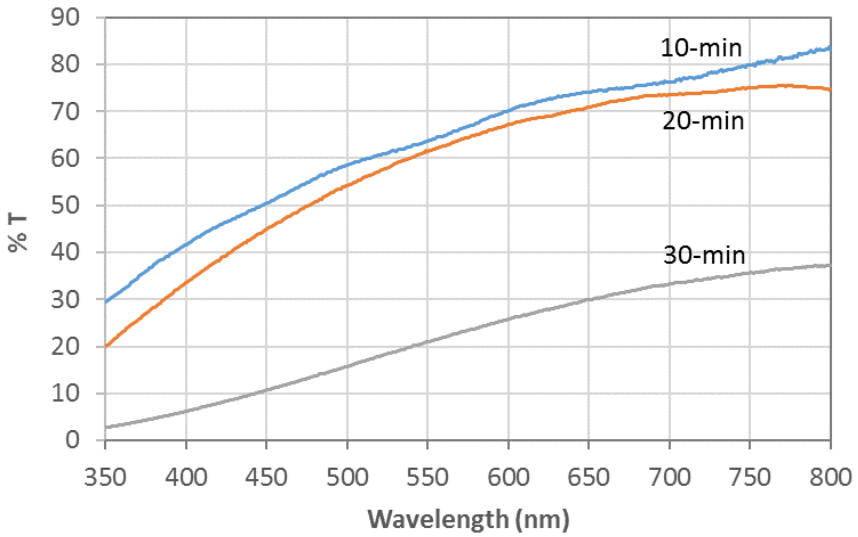

Figure 3 The optical transmittance of 2 wt% FTO thin layers with deposition time variations of 10, 20, and 30 minutes at a constant deposition temperature of 300°C

To evaluate the effects of deposition time and resulting layer thickness on the transparency of FTO glass, UV-Vis spectroscopy was performed, and the results are presented in Figure 3. The highest optical transmittance of ~ 83.8% was obtained by the FTO glass at the 10-minute deposition time, while at 20 and 30 minutes, the optical transmittance decreased to 75.5% and 37%, respectively. Such decreases could be related to the increases in thickness of the FTO film, revealed by the SEM cross-sections of the samples (Figures 1a–c, right side).

3.2. Substrate Temperature Variation

Further investigation was carried out by varying the substrate temperature during the spray pyrolysis process to 250, 300, and 350°C at a fixed deposition time of 20 minutes. SEM-EDS observations were performed on the fabricated glasses under these conditions.

Figures 4a–c show top view and sectional SEM images of the FTO thin layers deposited for 20 minutes during pyrolysis at temperature variations of 250, 300, and 350°C. At 250°C, several voids are distributed over the substrate surface with an average grain size of 82.46 nm (Figure 4a). The visible presence of void porosity between groups occurred because the temperature was too low, causing the atoms to be absorbed by the substrate.

Figure 4b shows that the increase in substrate temperature to 300°C on a thin layer of FTO affects the surface morphology of the grains, causing the formation of larger grains averaging 128 nm. In addition, the particles became more compact and well connected, which reduced the porosity significantly, because the treatment temperature caused the grain layer to cluster, expand, and acquire additional energy to recover crystal structure.

Increasing the substrate temperature to 350°C resulted in larger particle sizes averaging 612.22 nm. Cross sectional images in Figures 4a–c reveal that the thickness of the FTO layer was 540 nm and 2.38 and 3.52 μm for substrate temperature of 250, 300, and 350°C, respectively. Thus, increasing the substrate temperature increased the thickness of the FTO layer. According to Lazi et al. (2004) high solution temperatures used to decrease solution viscosity cause the rate of movement of particles to increase, resulting in faster coating formation rates and thicker layers.

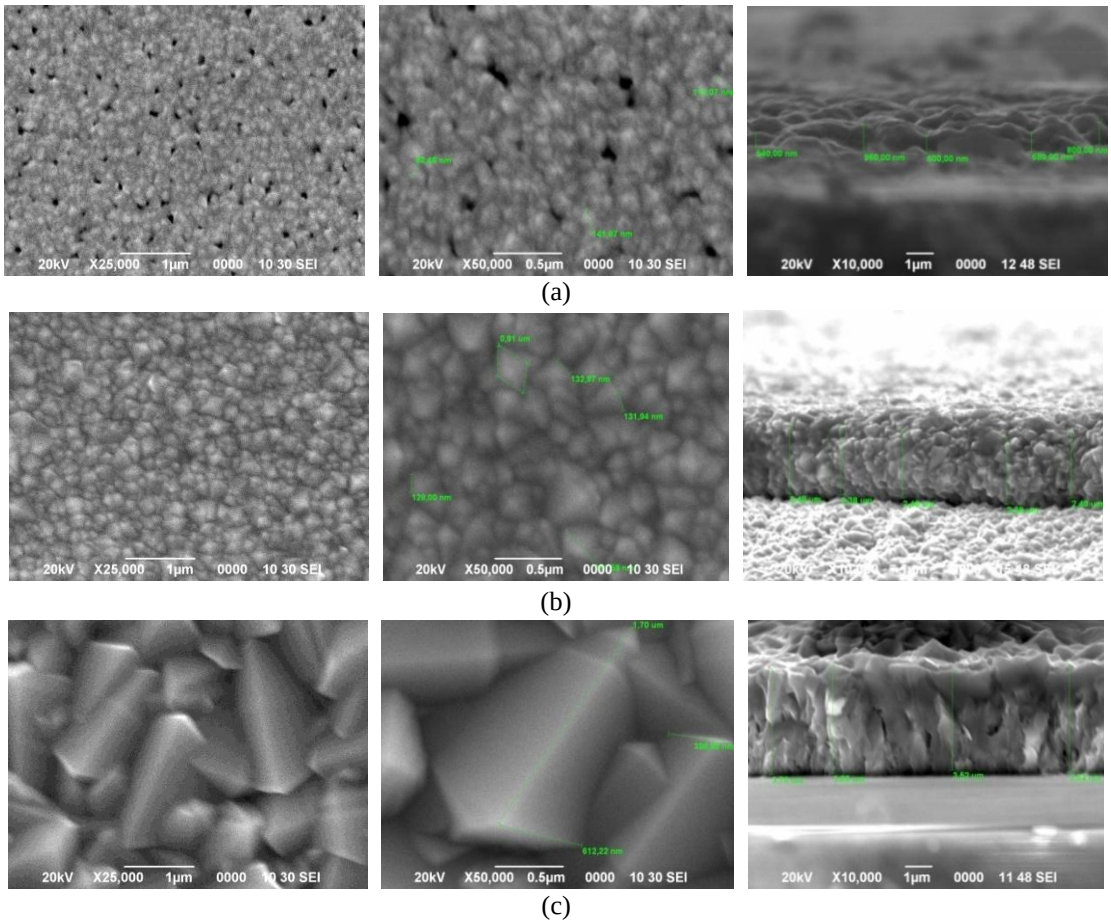

Figure 4 Top view (left) and cross section (right) SEM images of 2 wt% FTO thin layers deposited for 20 minutes during the pyrolysis process with substrate temperature variations of: (a) 250; (b) 300; and (c) 350°C

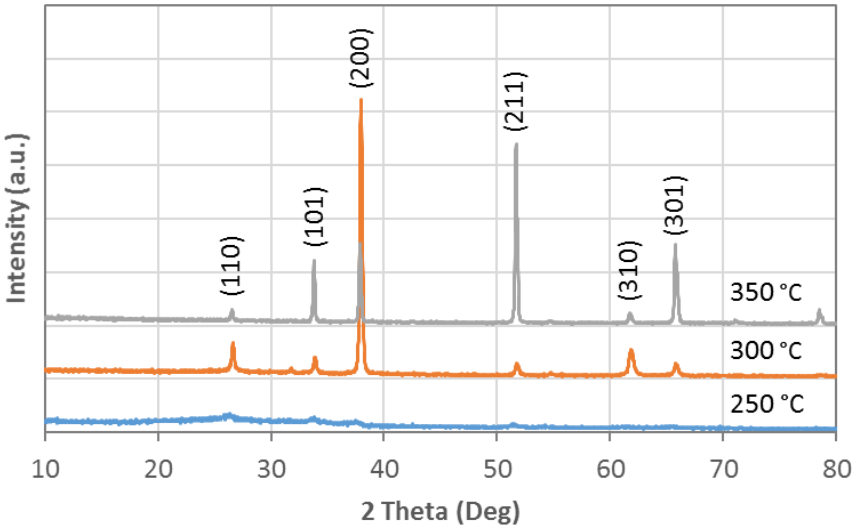

Figure 5 XRD patterns of the 2 wt% FTO thin layers with substrate temperature variations of 250, 300, and 350 °C at a constant deposition time of 20 minutes

Figure 5 shows the diffractogram of the FTO glasses at substrate temperature variations of 250, 300, and 350°C at 20 minutes. Several peaks appeared at 2θ degrees of 26.511, 33.766, 37.843, 51.610, 61.690, and 65.750^{o}, confirming the (110), (101), (200), (211), (310), and (301) crystal planes of the tetragonal rutile structures during the cassiterite SnO_2 phase. The value of the FWHM decreased significantly to 0.68, 0.229, and 0.165° for substrate temperature variation of 250, 300, and 350°C, respectively, which was consistent with the crystallite size increasing from 5.86 nm to 73.61 nm and 604.22 nm.

Figure 5 shows the XRD spectra of SnO_2 thin films deposited at different substrate temperatures, which indicate that the samples deposited at 250°C grew an amorphous structure. The crystal planes (110), (101), (200), as (211) were not as sharp, while the (310) and (301) crystal planes did not appear.

At temperatures greater than 250°C, the SnO_2 films presented polycrystalline structures, although some crystallographic characteristics changed depending on the substrate temperature. At 300°C, the intensity of the (200) crystal plan was dominant compared to the other planes, indicating that the crystal quality improved. A study by Gordillo et al. (1994) showed that the (200) plane was desirable for optimal balance between electrical resistance and optical transmittance. This is supported by the results of the current experiment, for which these factors were optimal at a substrate temperature of 300°C and a deposition time of 20 minutes, resulting in a resistivity value of 3.32×10^{-5} Ω.cm and transmittance value of 75.5%. At 350°C, changes in the intensity of crystal planes (110), (101), (200), (211), (310), and (301), especially in plane (211), increased. According to Gordillo et al. (1994), this increase in thickness of the SnO_2 films with a tendency to grow preferentially along the (101), (211) and (301) directions.

Table 2 presents the electrical resistivity test results for the FTO thin layers under the aforementioned conditions. The value decreased significantly, from 1.142×10^{-3} to 3.32×10^{-5} Ω.cm, when the substrate temperature was raised to 250–300°C. When the temperature was raised to 350°C, the value of resistivity reduced slightly to 2.15×10^{-5} Ω.cm. This can be attributed to the value of the measured crystallinity layer as shown in Figure 5. The crystallinity is directly proportional to the conductivity, which is supported by research conducted by Tatar and Duzgun (2012) stating that the higher the value of crystallinity, the lower the resistivity values. Thus, higher substrate temperatures result in lower resistivity values, producing conductive properties.

Table 2 Resistivity of 2 wt% FTO thin layers with substrate temperature variations of 250, 300, and 350°C at a constant deposition time of 20 minutes

Substrate Temperature	Resistivity (Ω.cm)
250°C	1.142×10^{-3}
300°C	3.32×10^{-5}
350°C	2.15×10^{-5}

The electrical conductivity results can also be associated with particles and crystal structure growth during the SnO_2 phase, as shown in the SEM images (Figure 4). The spray pyrolysis process at 250°C (Figure 4a) resulted in small particles with pores or voids caused by incomplete connections among these particles. These pores acted as a sink for electronic charges, and as a consequence, the resistivity of the film remained high. As the substrate temperature increased to 300°C, the SnO_2 crystallites grew larger, and interconnections were well established. As demonstrated visually by the compacted particles and reduced porosity in Figure 4b, electronic transfer among particles became easier, and resistivity was reduced significantly (Zhao et al., 2008). At 350°C, large particles had less pores, as shown in Figure 4c, and further decreases in resistivity were obtained (2.15×10^{-5} Ω.cm).

To evaluate the effect of substrate temperature on the thickness and transparency of FTO glass, UV-Vis spectroscopy was performed. The highest optical transmittance of ~90.7% was obtained by FTO glass at a substrate temperature of 250°C, while at 300 and 350°C, optical transmittance decreased to 75.5 and 55%, respectively due to the increased temperature of the substrate causing the layer to thicken (Figure 6). Thus, transmission of SnO_2:F thin films decrease as film thickness increases (Rahal et al., 2013).

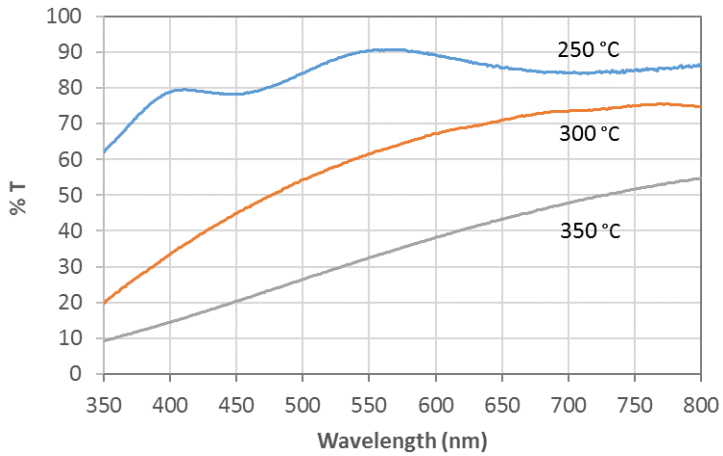

Figure 6 The optical transmittance of 2 wt% FTO thin layers with substrate temperature variations of 250, 300, and 350 °C at a constant deposition time of 20 minutes

4. CONCLUSION

It can be concluded that longer deposition times produce thicker FTO films and that increased substrate temperature also increases the thickness of thin films, resulting in decreased electrical resistivity. However, film that is too thick creates an adverse effect on optical transparency; therefore, there should be a balance between electrical resistivity and optical transparency, with the optimal trade-off being a TCO film deposited for 20 minutes, which provides transmittance

of 75.5% and a resistivity of 3.32×10^{-5} Ω.cm. The TCO film used in this study has potential for further development to enhance its functional properties.

5. ACKNOWLEDGEMENT

The authors are grateful for the financial support of the Thematic Grant from the Research Center for Metallurgy and Materials LIPI2016 and the 2015 Postgraduate Research Grant (Hibah Pasca Sarjana) from the Universitas Indonesia (contract No. 1725/UN2.R12/HKP.05.00/2015).

6. REFERENCES

Brousseau, J.-L., Bourque, H., Tessier, A., Leblanc, R.M., 1997. Electrical Properties and Topography of SnO_2 Thin Films Prepared by Reactive Sputtering. *Applied Surface Science*, Volume 108(3), pp. 351–358

Ganz, D., Reich, A., Aegerter, M.A., 1997. Coatings on GlassLaser Firing of Transparent Conducting SnO_2 Sol—gel Coatings. *Journal of Non-Crystalline Solids*, Volume 218, pp. 242–246

Gordillo, G., Moreno, L.C., de la Cruz, W., Teheran, P., 1994. Preparation and Characterization of SnO_2 Thin Films Deposited by Spray Pyrolysis from $SnCl_2$ and $SnCl_4$ Precursors. *Thin Solid Films*, Volume 252(1), pp. 61–66

Lazi, M.S., Simovi, K., Kovi, V.B.M.I., 2004. The Influence of the Deposition Parameters on the Porosity of Thin Alumina Films on Steel. *Serbian Chemistry Society Journal*, Volume 69(3), pp. 239–249

Moholkar, A.V., Pawar, S.M., Rajpure, K.Y., Almari, S.N., Patil, P.S., Bhosale, C.H., 2008. Solvent-dependent Growth of Sprayed FTO Thin Films with Mat-like Morphology. *Solar Energy Materials and Solar Cells*, Volume 92, pp. 1439–1444

Muranaka, S., Bando, Y., Takada, T., 1986. Preparation and Properties of Sb-doped SnO_2 Films by Reactive Evaporation. *Bulletin of the Institute for Chemical Research*, Kyoto University, Volume 64(4), pp. 227–234

Paraskevi, A., Munkegade, N., 2008. Structural and Sensing Properties of Nanocrystalline SnO_2 Films Deposited by Spray Pyrolysis from a $SnCl_2$ Precursor. *Applied Physics A Material Science and Processing*, Volume 91, pp. 667–670

Rahal, A., Benramache, S., Benhaoua, B., 2013. The Effect of the Film Thickness and Doping Content of SnO_2:F Thin Films Prepared by the Ultrasonic Spray Method. *Journal of Semiconductors*, Volume 34(9), pp. 093003(1–5)

Ray, S.C., Karanjai, M.K., Dasgupta, D., 1997. Preparation and Study of Doped and Undoped Tin Dioxide Films by the Open Air Chemical Vapour Deposition Technique. *Thin Solid Films*, Volume 307, pp. 221–227

Ren, Y., Zhao, G., Chen, Y., 2011. Fabrication of Textured SnO_2:F Thin Films by Spray Pyrolysis. *Applied Surface Science*, Volume 258(2), pp. 914–918

Shamala, K.S., Murthy, L.C.S., Rao, K.N., 2004. Studies on Tin Oxide Films Prepared by Electron Beam Evaporation and Spray Pyrolysis Methods. *Bulletin of Materials Science*, Volume 27(3), pp. 295–301

Tatar, D., Duzgun, B., 2012. The Relationship between the Doping Levels and Some Physical Properties of SnO_2:F Thin Films Spray-deposited on Optical Glass. *Journal of Physics*, Volume 79(1), pp. 137–150

Zhao, H., Liu, Q., Cai, Y., Zhang, F., 2008. Effects of Water on the Structure and Properties of F-doped SnO_2 films. *Materials Letters*, Volume 62, pp. 1294–1296