Optimization of Fabricating Fluorine-doped Tin Oxide by Using Spray Pyrolysis Methods

S Saehana¹ Darsikin¹, Z Arifin², and Nasar¹

¹ Department of Physics Education, Tadulako University, Jln. Soekarno-Hatta km. 09 Kel. Tondo, Palu, Indonesia
² Mechanical Engineering Departement, Sebelas Maret University, Jl. Ir. Sutami 36A Kentingan Surakarta 57126, Solo, Indonesia

*Corresponding author: sahulasahana@gmail.com

Abstract. In this study, Fluorine-doped Tin Oxide (FTO) was fabricated and synthesized by using spray pyrolysis methods for solar cells applications through the variation of the concentration and deposition time of precursor solution of SnCl₂:F. The glass substrate furthermore was heated at a temperature of 450°C prior to deposition and the sheet resistance was about 56 to 137.25 Ω/cm². X-Ray Diffraction, Scanning Electron Microscopy, UV-Vis Spectroscopy, and four-point probe were employed to investigate the characteristic of the FTO. This product was further applied as an electrode in the dye-sensitized solar cell (DSSC) and a photovoltaic effect was observed.

Keywords: FTO, spray pyrolysis, DSSC application.

1. Introduction

Fluorine-doped Tin Oxide (FTO), as a type of Transparent Conducting Oxide (TCO), is widely applied in the photovoltaic area and some of its advantages include stability under atmospheric conditions, chemically inert, mechanically hard, high-temperature resistant, high tolerance to physical abrasion, and less expensive than indium tin oxide [1-3].

Fluorine-doped Tin Oxide (FTO) with high performance (low resistance and high transmittance) is required in many application [4-8]. There is a possibility of producing this compound through the use of different methods such as spray pyrolysis [7-9], sol-gel [10,11], chemical vapor deposition [12] and DC magnetron sputtering [13]. However, some of these methods are complicated and, as a result, the spray pyrolysis method was used due to its requirement of low-cost materials and effectiveness at low temperature [8].

In the previous study [14], several parameters were reported to be affecting the performance of the FTO, and they include the concentration of the solution and the time of deposition. In this paper, FTO was produced by using the spray pyrolysis method and an investigation was conducted on the effect of the concentration and deposition time on its performance. The combination of these parameters in
producing high-performance FTO was chosen as optimum because of their usefulness in producing DSSC solar cells.

Furthermore, in this study, Dye-Sensitized Solar Cells (DSSC) was produced through the application of the FTO as an electrode. A comparison was made between this approach and the use of commercial FTO and the performance for both was calculated under solar lighting.

2. Materials and methods

The materials used for the fabrication of the FTO glass include the solution of Tin(II) Chloride (SnCl$_2$.2H$_2$O, Merck, Germany), Ammonium Fluoride (NH$_4$F, Merck, Germany), and Ethanol (96%, Merck, Germany). 1 gram each of SnCl$_2$ and NH$_4$F materials were fed into the ethanol solvent and stirred till it became homogeneous. Furthermore, spray pyrolysis method through the application of OMRON NE-C28 Nebulizer was used to deposit the solution on a glass substrate with a wide scale of about 1cm x 1cm and thickness of 2mm. The concentration of the solution and time deposition of nanoparticle were investigated to obtain the optimum resistance. Furthermore, the sample was heated at 450ºC for 30 minutes and a conductive transparent thin layer was formed. The sheet resistance and transmittance were measured by using a four-point probe (PROHEX digital multimeter) and UV-vis spectroscopy (8452 UV-Visible spectrophotometer - Agilent). Scanning Electron Microscopy (JEOL JSM-6360LA) was used to investigate the morphology of the FTO film and XRD diffraction (XRD, PW1710) applied to characterize its crystallization. However, in the optimization process, the solution concentration and deposition time were varied to obtain the optimum performance of FTO and after the production, it was used as an electrode in the DSSC solar cell. It is important to point out that the Ruthenium complex was used as a dye, Titanium Dioxide as a photo electrode, Tri-Iodide solution as an electrolyte, and platinum as a catalyst.

3. Results and discussion

FTO was fabricated by spray pyrolysis method as shown in Figure 1 [14,15]. This involves the production of nanoparticles by spraying droplets from the solution onto the heated surface (Fig 1). When a droplet contacts the hot surface, it vaporized and the lagging oxide particles became attached to the surface [9]. However, several parameters were observed to be affecting FTO resistance and they include solution concentration, deposition time, temperature, and distance between the nebulizer and the substrate [14].

![Figure 1. FTO fabrication process using spray pyrolysis method [14].](image1)

![Figure 2. XRD pattern of FTO films after annealing at temperature 400 °C (fabricated in 0.3 M for 10 minutes)](image2)

In order to understand the crystallization and morphology of the FTO film, it was fabricated using 0.3 M concentration, deposited for 10 minutes, and later characterized by using X-Ray Diffraction
Spectroscopy (XRD). Moreover, Scanning Electron Microscopy (SEM) was conducted for two different FTOs fabricated from different concentration and deposition time.

Figure 2 shows the XRD pattern in the films after annealing at 450 °C for 30 min. The crystalline structure was found to be tetragonal SnO₂ (JCPDS no. 770451 and space group: F42/mmm(136)). However, the density and size of the FTO nanoparticle grain were found to be increasing with the concentration of the solution as shown in Figure 3.

![Figure 3: Scanning Electron Microscopy of FTO fabricated in different conditions: (a) 0.3 M of solution concentration and deposition for 40 minutes and (b) 0.7 M of solution concentration and deposition for 40 minutes.](image)

The transmittance of FTO at visible wavelength was observed by using UV-vis spectroscopy (8452, UV-Visible spectrophotometer - Agilent) as shown in Figure 4. The transmittance of two FTOs with different concentration and deposition were compared and was discovered to be reducing with increased value. This is associated with the increase in particle size due to the high value of these parameters as depicted in Figure 3. Therefore, to fabricate high performing FTO, the combination of solution concentration and deposition time was required.

Figure 4 shows the transmittance values decreasing with increase in concentration and time deposition. This is associated with the increasing amount of fluorine administered which caused an increment in the concentration. This makes several F atoms enter the SnO₂ crystal structure either by filling in the O atomic vacancy or by occupying the position of the Sn atom through substitution. This, consequently, led to the increment in the number of free electrons and the concentration of the charge carrier and a reduction in the amount of light passed on by the glass FTO [20]. Therefore, the reduction in transmittance may be attached to the increasing concentration.

![Figure 4: The optical transmittance of FTO fabricated from: (a) 0.1 M of solution concentration for 20 minutes; (b) 0.7 M of solution concentration for 40 minutes.](image)
In this study, to obtain a high performing FTO, optimization was conducted through the testing of a few solution concentration and deposition time. However, the effect of both parameters on sheet resistance and transmittance are shown in Tables 1 and 2. The sheet resistance was determined by employing a 4-point probe method with PROHEX digital multi tester. It was, therefore, predicted that high solution concentration containing a high amount of fluorine and more F⁻ anions substituted with O²⁻ anions created more free electrons and decreased the resistance value [20].

Table 1. FTO performance in 20 minutes of deposition time.

| No | Solution Concentration (M) | Sheet Resistance (Ω/cm²) | Transmittance (%) |
|----|---------------------------|--------------------------|-------------------|
| 1  | 0.1                       | 1,000                    | 91.91             |
| 2  | 0.3                       | 630.50                   | 83.20             |
| 3  | 0.5                       | 181.25                   | 90.24             |
| 4  | 0.7                       | 56.00                    | 80.77             |

Table 1 shows the value of solution concentration was varied and deposition time kept constant at about 20 minutes. For 0.7 M, the sheet resistance and transmittance were found to be about 56 Ω/cm² and 89.77, respectively. In Table 2, the deposition time less than 20 minutes produced high resistance while those above produced low resistance with transmittance value below 80%.

From the results obtained, as shown in Table 1 and 2, both parameters (solution concentration and deposition time) affect the resulting sheet resistance of FTO. Through the combination of the two parameters, a value between 56 to 137.25 Ω/cm² was obtained with the lowest found at a concentration of 0.7 M and 20-minute deposition time. This was predicted to be related to the loading level of nanoparticle formation on the substrate [16].

Table 2. Performance optimization of FTO in 0.7 M of concentration.

| No | Deposition Time (Minute) | Sheet Resistance (Ω/cm²) | Transmittance (%) |
|----|--------------------------|--------------------------|-------------------|
| 1  | 5                        | 10.000                   | 79.38             |
| 2  | 7                        | 1.382                    | 85.87             |
| 3  | 10                       | 578                      | 84.21             |
| 4  | 15                       | 129                      | 79.99             |
| 5  | 20                       | 56                       | 80.77             |
| 6  | 25                       | 26                       | 72.17             |
| 7  | 30                       | 29                       | 77.65             |
| 8  | 35                       | 31                       | 78.89             |
| 9  | 40                       | 15                       | 64.50             |

From the results obtained, as shown in Table 1 and 2, both parameters (solution concentration and deposition time) affect the resulting sheet resistance of FTO. Through the combination of the two parameters, a value between 56 to 137.25 Ω/cm² was obtained with the lowest found at a concentration of 0.7 M and 20-minute deposition time. This was predicted to be related to the loading level of nanoparticle formation on the substrate [16].
Figure 5. (a) DSSC solar cell with optimized FTO; (b) I-V Characteristics of DSSC applying synthesis FTO (blue square) and its comparison with commercial FTO (red circle).

4. Conclusion
In this study, the conductive thin layer of FTO produced using the spray pyrolysis method has a low sheet resistance between 56 to 137.25 Ω/cm² and transmittance over 80%. In the fabrication process, the varied solution concentration and deposition time were tested to get the optimum value of 0.7 M and 20 minutes, respectively. The FTO obtained was used as a DSSC component and the phenomenon of photovoltaics was observed.

Acknowledgement
This work was supported by the Riset Terapan Unggulan Perguruan Tinggi Decentralization Research Grant from the Research, Technology and Higher Education of the Ministry of the Republic of Indonesia for 2018 fiscal year. The researcher also appreciates Dr. Eng. Agus Purwanto, M.Si for supplying materials needed for the research.
References

[1] Chiba, Y., et. al. 2006 Japan. J. Appl. Phys. 45(25) L638–L640.
[2] Dai, S., et. al. 2005 J. Sol. Energy Mat. Sol. Cells 85 447–455.
[3] Gratzel, M., 2001 J. Sol-Gel Sci. Tech. 22 pp. 7–13.
[4] Noh E., et. al. 2013 Sci. World J. 2013 pp. 1-8.
[5] Chuang S-H, Tsung C-S, Chen C-H, Ou S-L, Horng R-H, Lin C-Y, and Wu D-S 2015 ACS Appl. Mater. Interfaces 7 (4) pp 2546–2553.
[6] Chou, T.P., et. al. 2008 J. Nanophotonics 2 pp. 023511.
[7] Purwanto A, Widiyandari H, and Jumari A 2012 Thin Solid Films 520 (6) pp. 2092–2095.
[8] Russo B, and Cao G.Z 2008 Appl. Phys. A 90 pp. 311–315.
[9] Suyitno, Arifin Z, Santoso A.A, Setyaji A.T, and Ubaidillah 2014 Appl. Mech. Mat. 575 689-695.
[10] Senthilkumar V, Vickraman P, and Ravikumar R 2010 J. Sol-Gel Sci. Tech. 53(2) 316–321.
[11] Shi, X.H. and K.J. Xu 2017 Mat. Sci. Semiconductor Process. 58 1–7.
[12] Chavarría-Castillo K.A et. al. 2016 Mat. Research 19 pp. 97-102.
[13] Banyamin Z.Y, Kelly PJ, West G, and Boardman J 2014 Coatings 4 732-746.
[14] Darsikin, Z Arifin, Nasar and Saehana S 2018 Mat. Sci. Eng. 395 1-5.
[15] Montero, Chialvo, M.R.G and Chialvo, A.C 2009 J. Mater. Chem. 19 3276–3280.
[16] Supriyono, Surahmana H, Krisnandia Y.K, and Gunlazuardia 2015 J. Procedia Environ. Sci. 28 242–251
[17] Saehana S, Darsikin, Yuliza E, Khairurrijal and Abdulah M 2012 J. Sol. Energy Eng. 136 044504-1.
[18] Saehana S, Muslimin, and Abdulah M 2014 J. Renew. Sustain. Energy. 6 023109.
[19] Saehana S, Arifin A, Khairurrijal, Abdulah M 2012 J. Appl. Phys. 111 123109.
[20] Widhiyanuriyawan D, Maksum I.M, Bintarto R, and Arifin Z 2019 Mat. Sci. Eng. 494 012066.