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Effect of temperature and mass ratio \((\text{NH}_4\text{F}:\text{SnCl}_2.2\text{H}_2\text{O})\) to conductive glass fluorine doped tin oxide (FTO) performance

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Abstract. One of the most important components that influences the performance of dye sensitized solar cell (DSSC) is conductive glass. Conductive glass is required to have high optical transmittance and low electrical resistance. One of the conductive glass that is being researched at this time is fluorine-doped tin oxide (FTO) which has a cheaper price than conductive glass from other materials. FTO requires further research in order to have a transmittance above 80% and electrical resistance below 30 \(\Omega/\text{sq}\). Parameters that can affect the characteristic value of FTO are the deposition temperature and mass ratio \((\text{NH}_4\text{F}:\text{SnCl}_2.2\text{H}_2\text{O})\). This research varied the mass ratio of ammonium fluoride \((\text{NH}_4\text{F})\) at the 2, 4, 6, 8, and 10 wt% with a fixed sintering temperature of 400 °C. In addition, the variation of sintering temperature at 300, 350, 400, 450, and 500 °C in a fixed mass ratio of 4 wt% \(\text{NH}_4\text{F}\) were also studied. FTO was made by spray pyrolysis deposition method using the OMRON NE-C28 Nebulizer. This method was chosen because the easy installation and uniform layer thickness. The best results were obtained at the sintering temperature of 400 °C and mass ratio of 8 wt% with the electrical resistance of 9.186 \(\Omega/\text{sq}\) and the highest transmittance of 90.047% at a wavelength of 800 nm.

Keywords: electrical resistance, fluorine-doped tin oxide (FTO), optical transmittance, sintering temperature, spray pyrolysis deposition method

1. Introduction

One of technology that can be used to convert solar energy into electricity is solar cells. However, solar cells are generally still based on silicon which is expensive, complicated manufacturing process, high technology, and low environment-friendliness. Therefore, researchers are looking for other alternatives to replace silicon-based solar cells, one of which is third-generation solar cells, namely dye sensitized solar cell (DSSC). DSSC requires cheaper production costs, because it does not require high and complicated technology. Furthermore, the DSSC’s materials can be easily obtained and can be reconfigured if its efficiency has decreased [1–4].

The main DSSC components are working electrodes, semiconductors, dyes, electrolytes and counter electrodes [5,6]. Until now the material that can be used as electrodes in DSSC is transparent conductive oxide (TCO) glass. Transparent conductive glass serves as a substrate, where the other DSSC components are attached, in charged to pass light directly from sunlight, and transmit electrons through the conductive layer on the glass [7,8]. Indium-doped tin oxide (ITO) is indeed the most TCO
type widely used in the DSSC solar cells application. However, indium is a material which the availability is limited in nature so the price is very expensive and unstable at high temperatures [9]. Fluorine-doped tin oxide (FTO) has been studied and became a promising candidate to replace indium because of its potential efficiency and higher electronic mobility in the DSSC solar cells application. In addition, the abundance of fluorine in nature and non-toxic characteristic makes fluorine more attractive than indium.

There are various techniques to deposit or overly conductive material on glass in the FTO manufacture. In this study spray pyrolysis method was used to make FTO by using OMRON NE-C28 nebulizer. The process that occurs in spray pyrolysis is an atomized solution into a droplet with an ultrasonic nebulizer, and then the droplet is flowed with a carrier gas. This method was chosen because it has several advantages, which were low cost with simple equipment, doping control easiness, high growth rate, uniformly distributed results, and can produce for large quantities [10]. In this study, the composition materials of FTO glass were varied by tuning the mass ratio (wt%) of NH₄F:SnCl₂·2H₂O and the sintering temperature. With this research, it is expected to produce FTO substrate which has a high optical transmittance and low electrical resistance value, thus it can be applied as electrodes in DSSC.

2. Research Method

The method that was used in this study was an experimental research method. Figure 1 shows the scheme of spray pyrolysis deposition method for this study. In this work, the deposition of precursor solutions was conducted by using the OMRON NE-C28 Nebulizer.

![Figure 1. Scheme of spray pyrolysis deposition method](image)

The precursor solution was made by tin (II) chloride (SnCl₂·2H₂O) and ammonium fluoride (NH₄F) which was dissolved in 100 ml of 96% ethanol. The 12 gram of SnCl₂·2H₂O was dissolved in ethanol and then stirred with a magnetic stirrer until homogeneous. NH₄F was varied according to the mass ratio variation of 2, 4, 6, 8, and 10 wt% which had the weight of 0.24, 0.48, 0.72, 0.96, and 1.2 gram, respectively. Each NH₄F samples were dissolved in ethanol and stirred with a magnetic stirrer until homogeneous. SnCl₂·2H₂O and NH₄F which had been dissolved was mixed into a tightly closed container and stirred with a magnetic stirrer for 5 hours.

Glass that had been cut into pieces of 20 x 20 x 3 mm, was inserted into a container that has been filled with ethanol, then put into a digital ultrasonic cleaner for 8 minutes. The aim was to remove impurities and increase the glass adhesion strength. After that, the glass was removed from container with tweezers.

The cleaned glass was placed on the hotplate, and chimney was placed above it. So, the atomized precursor solution did not spread to the environment. The chimney was connected to the nebulizer through a hose. The precursor solution was put into a 7 ml nebulizer. The temperature was set to still use the temperature controller at 400 °C for variations in the mass ratio of 2, 4, 6, 8, and 10 wt%. For
the next variation, the sintering temperatures were varied at 300, 350, 400, 450, and 500 °C for the regulated mass ratio at 4 wt%.

3. Results and Discussions

3.1. Analysis of optical transmittance at various sintering temperatures

Transmittance is the ability of a material to transmit light at a certain wavelength. The purpose of FTO glass fabrication is to be applied as a substrate on DSSC type solar cells that work in the visible light region, so that a UV-Vis spectrophotometer is used to determine the FTO glass transmittance value of 4% fixed mass ratio with temperature variations of 300, 350, 400, 450 and 500 °C at the visible wavelength of 400-800 nm.

![Figure 2. The optical transmittance of 4 wt% FTO as functions of wavelength at various sintering temperatures](image)

Figure 2 shows that the best transmittance value is 82.971% obtained at sintering temperature of 500 °C at the wavelength of 800 nm. At sintering temperature of 300, 350, and 400 °C, the transmittance range ranges from the lowest to the highest, as 60.345-82.349%, 65.964-81.635%, and 61.259-78.284%, respectively. At sintering temperatures of 300, 350, and 400 °C the highest transmittance values obtained at each temperature tended to decrease from 82.349, 81.635, and 78.284%, because the higher the temperature, the more thermal energy received by droplets (atomized precursor solution) so that the granules expand and the size becomes larger. The larger the size of the grain causes the conductor layer formed on the surface of the substrate to be thicker so that it can cause light to be transmitted by the FTO glass to be less and the transmittance value decreases.

At sintering temperatures of 450 and 500 °C, the transmittance range ranges from the lowest to the highest, that are 51.474-80.047%, and 57.53-82.971%. At sintering temperature of 450 and 500 °C the highest transmittance value obtained at each temperature tends to rise again, from 80.047 to 82.971%. This phenomenon because the sintering temperature is too high and make the energy absorbed by the droplet exceed so that many droplets that evaporate before reaching the substrate surface. Because the number of droplets attached to the surface of the substrate is less, the conductor layer formed becomes thinner so that the glass transmittance value of the FTO rises again. This is also in line with the research that has been done previously that the higher the temperature of the substrate causes a little precursor attached to the glass because a lot of it evaporates [11].
3.2. Analysis of electrical resistance at various sintering temperatures

Electrical resistance is the inhibition amount of a material in flowing electrons. In this study the FTO glass is expected to have the lowest possible electrical resistance in order to increase the DSSC efficiency [8,12,13]. Resistance test was carried out using 4-point probe method with PROHEX digital multi tester. Figure 3 showed that the lowest resistance value was obtained at 400 °C sintering temperature which is 11.131 Ω/sq. At sintering temperatures of 300, 350 and 400 °C the electrical resistance tended to decrease from 12,391, 12,080, and 11,131 Ω/sq, respectively. According to this result, the decreasing of electrical resistance was followed by decreasing of transmittance (FTO glass more opaque). The tendency of the resistance values at temperatures 300, 350, and 400 °C decreases because the increasing of sintering temperature forms a tetragonal crystal structure according to the rutile pattern SnO₂ [14]. Increasing the sintering temperature also makes the bigger crystal diameter so that the grain boundaries get smaller and cause electrons to flow easily and the resistance value decreases.

![Figure 3. Correlation of sintering temperature to FTO electrical resistance value at mass ratio of 4 wt%](image)

At substrate temperatures of 450 and 500 °C the resistance values rose again that was 13.298 to 17.389 Ω/sq. This is because of at the temperature that has passed the optimum precursor solutions many evaporate occurred. The vapor then agglomerated to form a powder that had very low adhesion, so it was not deposited on the glass surface. Because of this, the conductor layer formed on the surface of the glass was thinner and contained fewer precursor solutions so that its electrical resistance properties increase.

3.3. Analysis of optical transmittance at various mass ratios

Figure 4 showed that the highest transmittance obtained was 90.216% which was obtained at the 650 nm wavelength for 10 wt% sample. At the mass ratio of 2, 4, and 6 wt%, the transmittance ranged from the lowest to the highest, as 55.965-77.426%, 61.259-76.284%, and 43.098-70.128%, respectively. At the mass ratio of 2, 4, and 6 wt%, the highest transmittance values tend to decrease with increasing mass ratios because the increasing amount of fluorine doping which was administered, then the precursor concentration is increasing. In the higher number of mass ratios causes many F atoms to enter the SnO₂ crystal structure either by filling in the O atomic vacancy or by occupying the position of the Sn (substitution) atom. With increasing F atoms entering the SnO₂ crystals, the number of free electrons increased so that it increased the concentration of the charge carrier and reduced the amount of light passed on by the glass FTO. This was also in accordance with previous studies that increasing the free charge carrier can be a reason to reduce transmittance when doping levels increase [15].
Figure 4. The optical transmittance of FTO at 400 °C sintering temperature as functions of wavelength with various mass ratios

At the mass ratio of 8 and 10 wt%, the transmittance ranged from 63,031-90,047%, and 75,001-90,216%. At higher mass ratios (8 and 10 wt%) the highest transmittance values obtained tend to increase with increasing mass ratios. This phenomenon was caused by the increasing NH₄F crossed the certain limits, the amount of doping fluorine became excessive and there was no longer a charge carrier so that the value of light passed in the FTO glass rose and increased the transmittance value again.

3.4. Analysis of electrical resistance at various mass ratios

Figure 5 showed that the lowest electrical resistance was obtained at the 6 wt% sample that was 8.794 Ω/sq. But according to the inverse nature, the mass ratio of 6 wt% had the lowest transmittance among variations in the other mass ratios, only 43-70%. While the highest electrical resistance value was obtained at a mass ratio of 10 wt%, but had the highest transmittance value of 75-90%. It can be seen at a mass ratio of 2, 4, to 6 wt% which tends to decrease the resistance because the higher mass ratio, the more fluorine doping in the conductor layer. At high amount of fluorine, more F⁻ anions substituted with O²⁻ anions so it created more free electrons and decreased the resistance value.

After decreasing to a certain extent, at the mass ratio of 8 and 10 wt%, the resistance value had a tendency to rise again i.e. from 9,186 to 15,273 Ω/sq, because the excess F atom did not occupy the right position of the SnO₂ crystal lattice so it could not contribute to increase the cargo carrier concentration. This excessive doping was not able to produce more free electrons because the atoms in
the lattice were full and nothing can be inserted or substituted again, but with more F atoms causing more boundaries scattering so that the resistance value decreases. This was also in accordance with the results that have been done previously that the increasing in the return resistance after a certain level of fluorine content was the limit of fluorine doping in the tin oxide lattice SnO$_2$ [16].

3.5. Analysis of Scanning Electron Microscopy (SEM)

Figure 6 depicted the scanning electron microscopy (SEM) image for any variation. At sintering temperature of 300 °C, the conductive layer formed was not uniform and there were many glass surfaces that were not covered by a conductive layer and created black holes. The holes could act as sinks that absorbed and blocked the moving electrons so that the electrical resistance increased. But with the formation of a non-dense conductive layer, it allowed light through the glass so that at the variation of 300 °C sintering temperature the transmittance is high.

At the sintering temperature of 400 °C, the conductive layer was flat and covered the entire glass surface. The layers were very tightly formed so the light was difficult to penetrate the glass and cause the transmittance value decreased. However, the dense and big granules allowed the electrons easily to flow so that the resistance was low. At the sintering temperature of 500 °C, the conductive layer was uniform and very tight, but the size of the granule was small and caused a high optical transmittance. The smaller granule size produced more granule boundaries. The granule boundary was a barrier for electrons to flow so that with a small granule size for sintering temperature of 500 °C, the electrical resistance increased.
4. Conclusions
The FTO glass was successfully fabricated by spray pyrolysis deposition method. The best results were obtained at the sintering temperature of 400 °C with the mass ratio of 8 wt%, which the electrical resistance value was 9.186 Ω/sq and the highest optical transmittance was 90.047% at a wavelength of 800 nm. By increasing sintering temperature, the transmittance and electrical resistance decreased to a certain value and rose again after beyond the boundary. By increasing NH₄F mass ratio, the transmittance value and resistance value decreased to a certain value and rose again after beyond the boundary.

References
[1] Banyamin Y Z, Kelly J P, West G and Boardman J 2014 Electrical and Optical Properties of Fluorine Doped Tin Oxide Thin Films Prepared by Magnetron Sputtering Coatings 4
[2] Sutanto B, Arifin Z, Suyitno, Hadi S, Pranoto L M and Agustia Y V 2016 Enhancement ZnO nanofiber as semiconductor for dye-sensitized solar cells by using Al doped AIP Conference Proceedings vol 1717
[3] Arifin Z, Suyitno S, Hadi S and Sutanto B 2018 Improved Performance of Dye-Sensitized Solar Cells with TiO2 Nanoparticles/Zn-Doped TiO2 Hollow Fiber Photoanodes Energies 11
[4] Sutanto B and Indartono Y S 2018 Numerical approach of Al₂O₃-water nanofluid in photovoltaic cooling system using mixture multiphase model IOP Conference Series: Earth and Environmental Science vol 168 p 12003
[5] Agustia Y V, Suyitno, Arifin Z and Sutanto B 2016 Effect of acidity on the energy level of curcumin dye extracted from Curcuma longa L. AIP Conference Proceedings vol 1717
[6] Sutanto B, Arifin Z and Suyitno 2018 Structural characterisation and optical properties of aluminum-doped zinc oxide nanofibers synthesized by electrospinning J. Eng. Sci. Technol. 13 715–24
[7] Suyitno, Arifin Z, Ahmad A S, Argatya T S and Ubaidillah 2014 Optimization Parameters and Synthesis of Fluorine Doped Tin Oxide for Dye-Sensitized Solar Cells Appl. Mech. Mater. 575 689–95
[8] Widiyandari H, Purwanto A, Diharjo K, Suyitno and Hidayanto E 2013 Fluorine doped-tin oxide prepared using spray method for dye sensitized solar cell application AIP Conf. Proc. 1554 147–9
[9] Muruganathanth G, Ravichandran K, Saravanakumar K, Ravichandran A T and Sakthivel B 2011 Effect of solvent volume on the physical properties of undoped and fluorine doped tin oxide films deposited using a low-cost spray technique Superlattices Microstruct. 50 722–33
[10] Thangaraju B 2002 Structural and electrical studies on highly conducting spray deposited fluorine and antimony doped SnO₂ thin films from SnCl₂ precursor Thin Solid Films 402 71–8
[11] Yadav A, Masumdar E, Moholkar A, Neumann-Spallart M, Rajpure K and Bhosale C 2009 Electrical, structural and optical properties of SnO₂:F thin films: Effect of the substrate temperature vol 488
[12] Ooyama Y and Harima Y 2012 Photophysical and electrochemical properties, and molecular structures of organic dyes for dye-sensitized solar cells ChemPhysChem 13 4032–80
[13] Graetzel M 2006 Photovoltaic performance and long-term stability of dye-sensitized mesoscopic solar cells Comptes Rendus Chim. 9 578–83
[14] Arifin Z, Soeparman S, Widhiyanuriyawan D and Suyitno S 2017 Performance Enhancement of Dye-Sensitized Solar Cells Using a Natural Sensitizer Int. J. Photoenergy 2017 2704864
[15] Shanthi S, Anuratha H, Subramanian C and Ramasamy P 1998 Effect of fluorine doping on structural, electrical and optical properties of sprayed SnO₂ thin films J. Cryst. Growth 194 369–73
[16] Obaida M, Moussa I and Boshta M 2015 Low sheet resistance F-doped SnO₂ thin films deposited by novel spray pyrolysis technique Int. J. ChemTech Res. 8 239–47