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Effect of Post-Heating Temperature on Efficiency of Dye Sensitized Solar Cell with ZnO:Al Thin Films Prepared by Sol-Gel Spin Coating

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ABSTRACT: *The prototype of Dye Sensitized Solar Cell had been successfully fabricated using ZnO:Al thin film and dye from red dragon fruit as a working electrode. ZnO:Al thin films were prepared using the method sol-gel spin coating with post-heating temperature variations. The XRD result confirms that all ZnO: Al have hexagonal structure with crystal sizes of 16 - 41 nm. SEM analysis showed the nanoparticle with particle size of 50-100 nm. The bandgap ranges from 3.16 to 3.40 eV. The efficiency of DSCC gradually improved with increasing the post-heating temperature. ZnO: Al with post-heating temperature of 600 ºC had the highest efficiency of 0.398%.*

Keywords: Dye Sensitized Solar Cell, ZnO:Al thin films, Sol-gel Spin coating

1. INTRODUCTION

Dye sensitized solar cell (DSSC) is a form of solar cell layer, originally invented by Gratzel in 1991.[1] The fabrication of DSSC is low cost and environmentally friendly which consists of several components, namely semiconductor oxide, dye, counter electrode and electrolyte.[2] The engineering of ZnO semiconductor for the DSSC working electrode is promising because it has an energy band gap of 3.37 eV and a binding energy of 60 meV which allows direct absorption of UV radiation.[3] The shortcomings of ZnO thin film has poor electrical characteristic like having a low conductivity value of 6.24×10^{-7} $(\Omega cm)s^{-1}$.[4] In order to enhance the physical, optical and electrical properties of ZnO, it is often doped with extrinsic dopant, using various types of group IIIA-doped metal materials such as B, Al, and Ga as foreign element doped into the ZnO structure.[5] Aluminum (Al) is chosen as a doping agent because it can increase the electrical conductivity of ZnO thin films to an order of 10^5 Ω.cm.[6] There are several techniques to fabricate thin film such as molecular beam epitaxy,[7] RF magnetron sputtering,[8] pulsed laser deposition,[9] spray pyrolysis,[10] physical vapor deposition,[11] and sol-gel spin coating.[12] A sol-gel spin coating method has several advantages, including not using a high vacuum space, low cost, homogeneous composition, controllable layer thickness and great microstructure.[13]

Research on aluminum doping ZnO thin films has been carried out by Jannane (2017)[14] with variations of aluminum doping concentration, the energy band gap value was affected by the doping concentrations. The crystal size, transmittance and energy band gap increase with the increasing of heating temperature.[15] The efficiency of DSSC not only influenced by aluminum doping concentration[16] but also annealing temperature.[17] Based on this, it is interested to conduct research on DSSC using Al doped ZnO thin film prepared by a sol-gel spin coating method with variation of post-heating temperatures and extract red dragon fruit as the natural dye sensitized.

2. EXPERIMENTAL

2.1. Synthesis of ZnO:Al thin films

ZnO:Al thin films was synthesized using a sol-gel spin coating method. Typically, 4 grams of zinc acetate dihydrate (ZnAc) and Al 1.0 % was dissolved into 20 mL isopropanol then stirred with a magnetic stirrer. After 10 minutes, diethanolamine (DEA) was added slowly. The molar ratio between DEA and ZnAc is 1:1. The gel solution was then dropped onto ITO glass substrate and then rotated by a spin coating with a speed of 1800 rpm. Finally, the sample was heated with temperature pre-heating of 250°C for 5 hours then post-heating with temperature variations of 400, 450, 500, 550 and 600°C for 5 hours.

2.2. Characterization of ZnO:Al thin films

The crystal properties of ZnO:Al thin films were evaluated using X-ray diffractometer (LabX XRD-6100, Shimadzu) with Cu K_α radiation (40kV, 30mA) of wavelength. 1.54 Å. A field emission scanning electron microscopy (FE-SEM, JEOL 6500) with accelerating voltage of 15 kV and working distance of 10 mm was used to observed the surface morphology of thin films. The optical properties of thin films were further investigated using UV-Vis spectrometer with both transmission and absorbance modes from wavelength of 300 to 700 nm.

2.3. Synthesis of Dye Sensitizer

Synthetic dye sensitizer was done by cutting red dragon fruit into small pieces and then put it into a beaker glass. After that, the red dragon fruit is crushed by mortar until smooth. Extraction was done by adding ethanol and then soaked for 24 hours in a dark place. Finally, the extract was filtered using filter paper and stored it in a under dark place

2.4. Fabrication of DSSC

The DSSC was fabricated by attaching a platinum counter electrode to a ZnO: Al thin film coated with dye from red dragon fruit which acted as a working electrode with a layer of separating surlyn. Sticking of surlyn was conducted by pressing the working electrode and the counter electrode under heating with at temperature of 70-80 °C in order to stick them perfectly. The working electrode that had been attached to the platinum counter electrode was injected with a liquid electrolyte solution through a small hole found in the platinum opposite electrode.

2.5. Efficiency measurement

Electrical testing was carried out by making an electrical circuit between the DSSC and the measurement, that is, a digital multimeter as shown in Figure 1**.** This test is based on the beam lighting method to determine the performance and the efficiency of the cells obtained when the solar cell object is exposed to light with a certain intensity at the top of the electrode (anode). DSSC outputs are Open-Circuit Voltage (Voc) and Short Circuit Current (Isc) DSSC. Then the fill factor (FF) and the DSSC efficiency are calculated (η).

3. RESULT AND DISCUSSION

3.1. Crystal Structure of ZnO: Al Thin Film

The diffraction pattern of ZnO: Al thin films with variation of post-heating temperatures is shown in Figure 2. The result confirm that all samples have the same crystal structure of hexagonal wurtzite.[18] All XRD pattern shows three peaks with the (100), (002) and (101) planes where a (101) plane has the highest intensity indicating the prefer the crystal growth.

Crystallite size of the samples with variation post-heating temperatures are calculated using the Scherrer's equation[19]:

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \qquad (1)$$

Where, D= crystallite size, λ= wavelength, β= FWHM (full width half maximum), θ= diffraction angle.

Table 1 shows the crystal size increases from 16 - 41 nm along with an increase in post-heating temperature from 400 - 550^{o} C. This was because increasing heating temperature will make compaction increase and grow large granule due to the incorporation of small grains.[20] When the post-heating temperature was increased continuously to 600 ^{o}C, the crystallite size decreased to 34 nm, this is due to aluminum doping blocking the density of the grain boundaries formed and the small granules coalition to form larger grain.[21]

3.2. Morphology of ZnO:Al Thin Film

Figure 3 shows representative scanning electron microscope images of ZnO:Al with variation of post-heating temperatures. The surface morphology of thin film contains a lot of tiny nanoparticle with homogenous distribution. It can be seen clearly that there is no obvious different of SEM images for different post-heating temperatures. The SEM images also exhibits that the grains totally covers the substrate without cracking and has a good interconnection each particle to the others. The grain size of nanoparticle is about 50-100 nm. Energy disperse spectroscopy (EDS) analysis was further conducted to confirm the success of Al doped into ZnO. As shown in the Figure 3d, a representative EDS result exhibits the peak of Al at energy 1.5 KeV with atomic concentration of 0.99%. This data confirm that Al has been successfully doped into ZnO lattice. The atomic concentrations of zinc (Zn) and oxygen (O) were 77.13% and 51.88 %, respectively.

3.3. Optical Properties of ZnO:Al Thin Films

Figure 4 and Figure 5 exhibits the transmittance and absorbance spectra, respectively. The transmittance spectrum of the ZnO:Al thin films in Figure 4 shows a sharp increase in the transmittance value for all samples that occurs in the wavelength range of approximately 350 to 400 nm which is the ultraviolet wavelength region. For ZnO:Al thin film samples heated at post-heating temperatures, the transmittance value is about 75 - 80% at a wavelength of about 600 to 700 nm and the reduction in heating of 500^{o}C. The high transmittance value of thin films is good and suitable for solar cell applications.[22] Figure 5 shows the absorbance edges of the samples heated at temperatures of 450 and 550^{o}C shift to a shorter wavelength region, while those of samples heated at post-heating temperatures of 500 and 600 ^{o}C shift to a longer wavelength region.

The energy band gap of the ZnO:Al thin film is furher calculated using the equation (2)[23]

$$(\alpha hv)^2 = C_D(hv - E_{opt}) \qquad (2)$$

Based on the Tauc Plot method in Figure 6, the energy band gap of the ZnO:Al thin films with variation post-heating temperatures could be obtained. Table 2 shows the energy band gap value increases from 3.16 - 3.40 eV with increasing the post-heating temperature from 400 -500 ^{o}C.[20] When the post-heating temperature is increased to 550 and 600 ^{o}C, the energy band gap value slightly decreases about 0.2 eV to be 3.20 eV. This phenomenon may be related to a thin film defects due to increase in heating temperature.[24]

3.4. Dye Spectrum of Red Dragon Fruit Extract

The absorbance spectrum of red dragon fruit solution tested with UV-Vis spectrophotometer is shown in Figure 8. It is clearly seen that the red dragon fruit dye has the absorbance at UV and visible light range with peak absorbance of 254 and 570 nm, respectively. The result indicates that the extract of red dragon fruit has a great potential to be used as the dye sensitizer for DSSC device.

3.5. DSSC Efficiency

The efficiency can be obtained by comparing the power produced by the prototype DSSC (P_{max}) with the power provided by the light source (P_{in}), as shown in equation (3) and (4).

$$\eta = \frac{P_{max}}{P_{in}} x\ 100\% = FF \frac{J_{sc}\ x\ V_{oc}}{P_{in}} x\ 100\% \qquad (3)$$

$$FF = \frac{J_{max}\ x\ V_{max}}{J_{sc}\ x\ V_{oc}} \qquad (4)$$

Where, η = DSSC efficiency (%), J_{sc} = current density (mA), V_{oc} = Voltage (mV), P_{in} = Input power (mW), FF = Fill Factor.

Table 3 lists the efficiency of ZnO:Al with temperature variations. The efficiency of DSSC shows the increasing trend with the increasing post-heating temperature. The maximum efficiency is 0.398% with temperature post heating of 600^{o}C. This is because of the increasing in post-heating temperature along with the energy supplied in the form of an increasing temperature which is used to form a better crystalline hexagonal wurtzite. To further investigate a higher efficiency with a higher temperature, the electrochemical impedance spectra analysis (EIS) was conducted in electrolyte solution of potassium chloride (KCl, 1M). The EIS data can be used to evaluate the charge transfer property by comparing the diameter of that semicircle in Figure 8. As can clearly observed, by increasing the temperature the diameter of semicircle becomes smaller indicating a better electron transfer. Further, the charge transfer resistance (R_{ct}) could be determined after fitting technique. The value of R_{ct} for heating at 600 ^{o}C is 6.5 kΩ which is lower than at 500 ^{o}C (7.6 kΩ) or 400 ^{o}C (9.5 kΩ). Therefore, the other reason for maximum efficiency at 600 ^{o}C post-heating temperature due to its lowest resistance that leading to most efficient charge transfer. We realize that presence efficiency is still relatively low but there is always room for improvement. Therefore, further research and development is needed in the future.

4. CONCLUSION

The DSSC prototype has been successfully fabricated using ZnO:Al thin film and dye from red dragon fruit extract as working electrodes. The XRD analysis confirmed that all sample had the hexagonal wurtzite structure. The band gap values of thin films were about of 3.16-3.40 eV. The surface morphology of as-fabricated thin films was nanoparticle with particle size less than 100 nm. We found that the efficiency of DSCC gradually improved with increasing the post-heating temperature. ZnO: Al with post-heating temperature of 600^{o}C had the highest efficiency of 0.398%. The main reasons for optimum efficiency at 600 ^{o}C were contributed by the better crystallinity and more efficient charge transfer properties. Further investigation is highly needed to improve the efficiency in the future.

5. Acknowledgments

Researcher would like to thank the Physics Laboratory and Chemistry Laboratory in Universitas Negeri Medan and supported by Indonesia Directorate of Research and Community Service.

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Figure

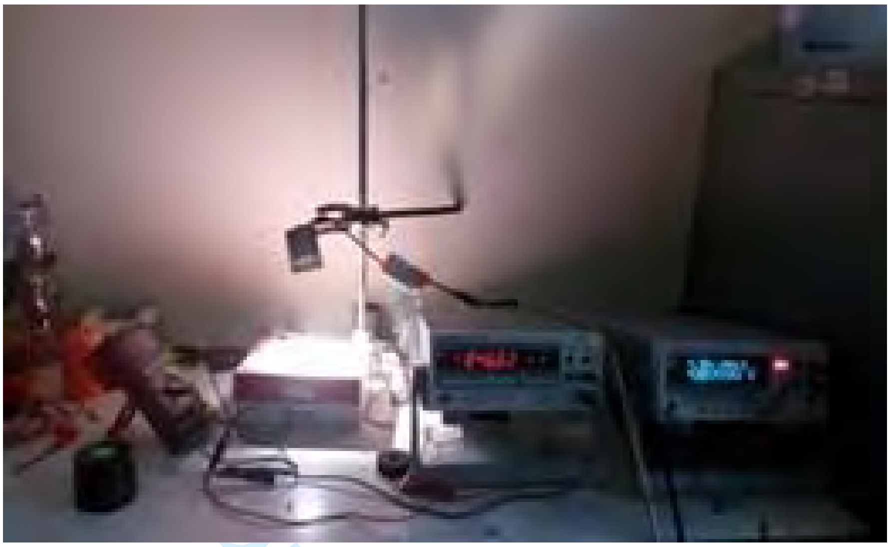

Figure 1: Measurement of DSSC efficiency

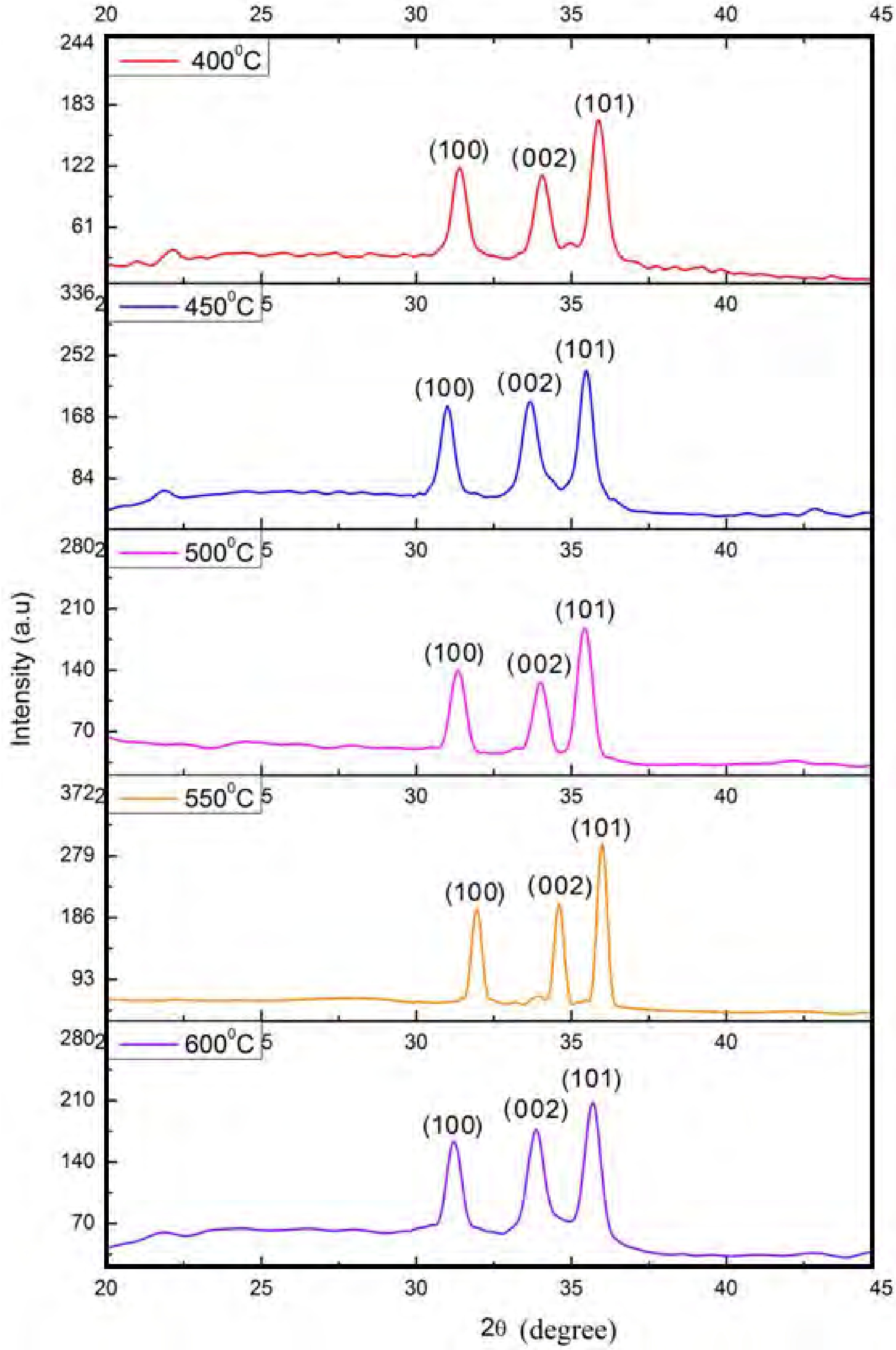

Figure 2. X-ray diffraction spectra of ZnO:Al thin films

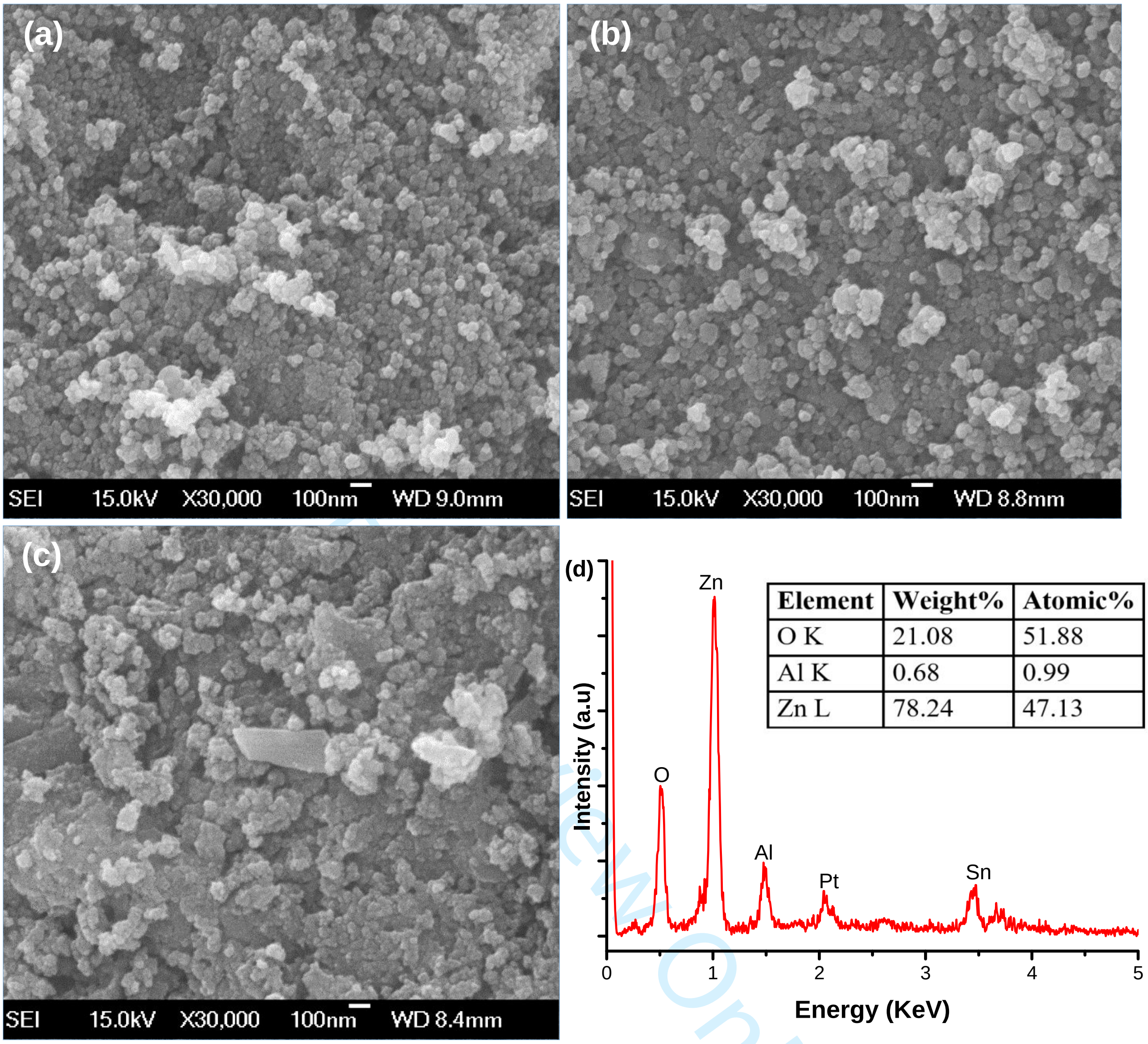

Figure 3. Representative SEM images of ZnO:Al thin films with different post-heating temperatures (a) 400 °C, (b) 500 ºC , (c) 600 ºC and (d) Energy disperse spectra (EDS) to show the presence of Al

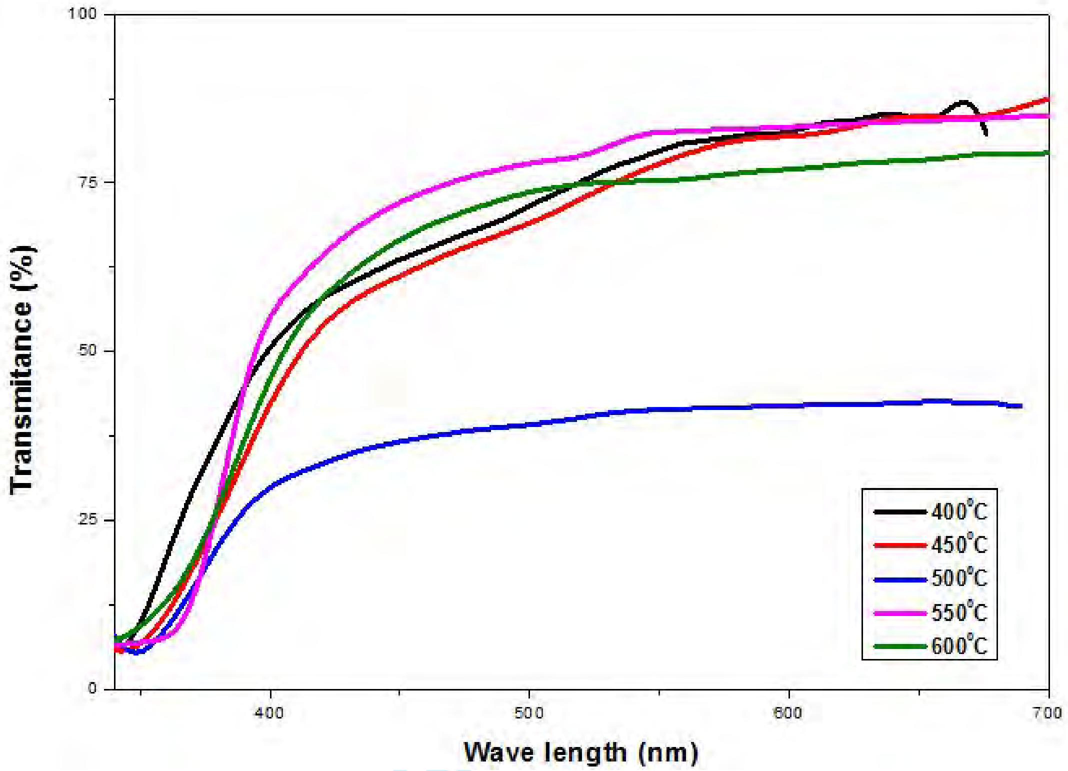

Figure 4. Transmittance spectrum of ZnO:Al thin films

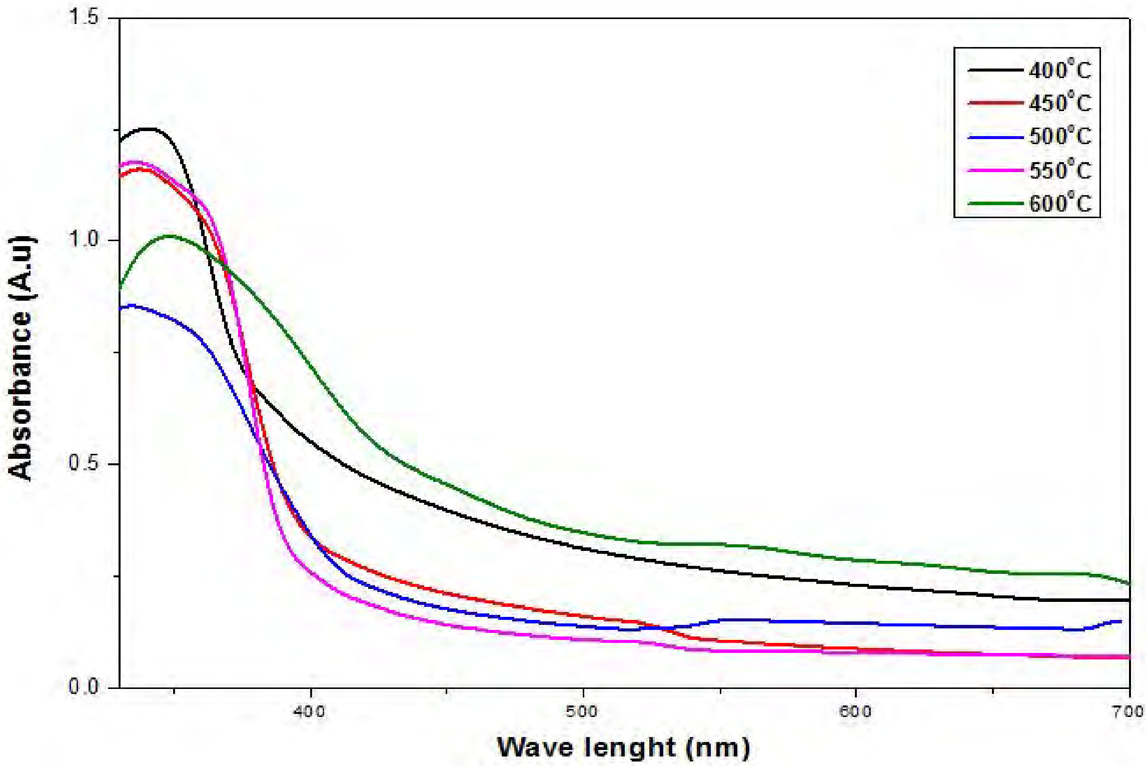

Figure 5. Absorbance Spectrum of ZnO:Al thin films

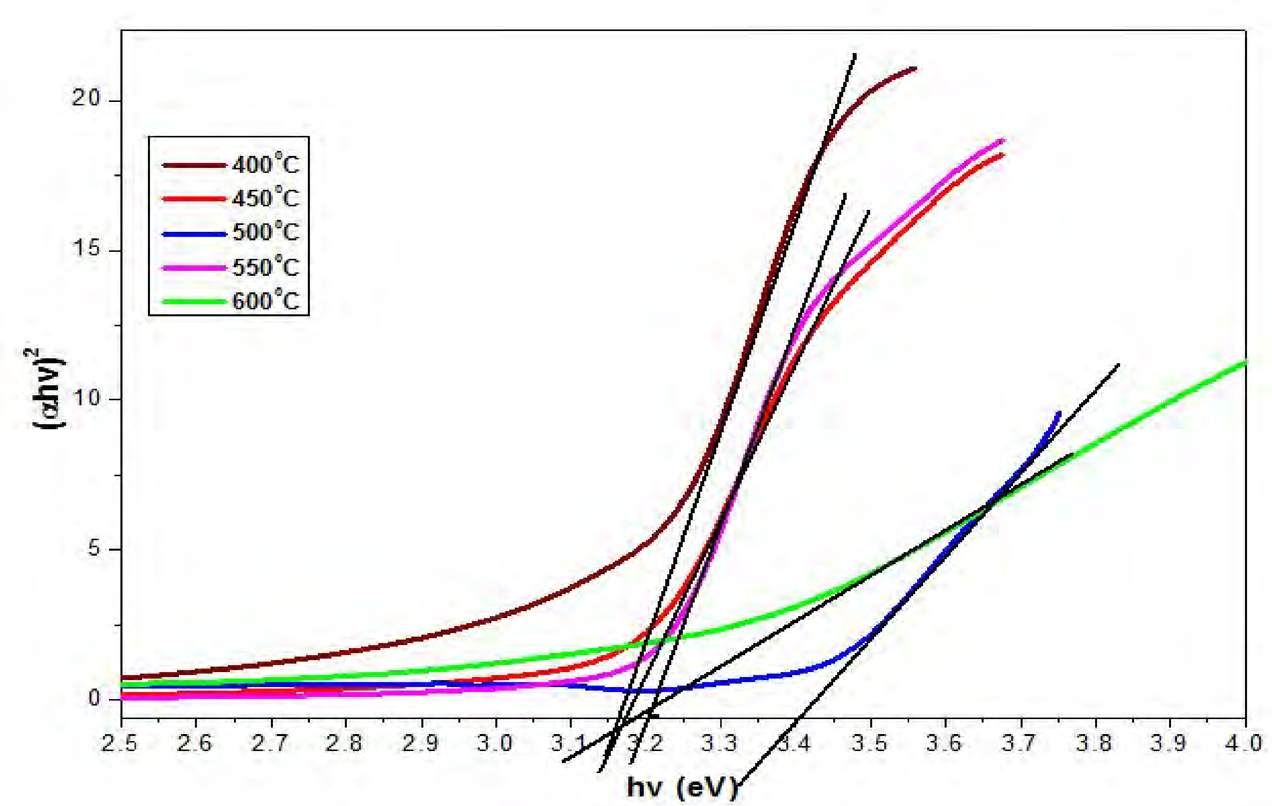

Figure 6. Energy band gap of ZnO:Al thin films using *Tauc Plot* method

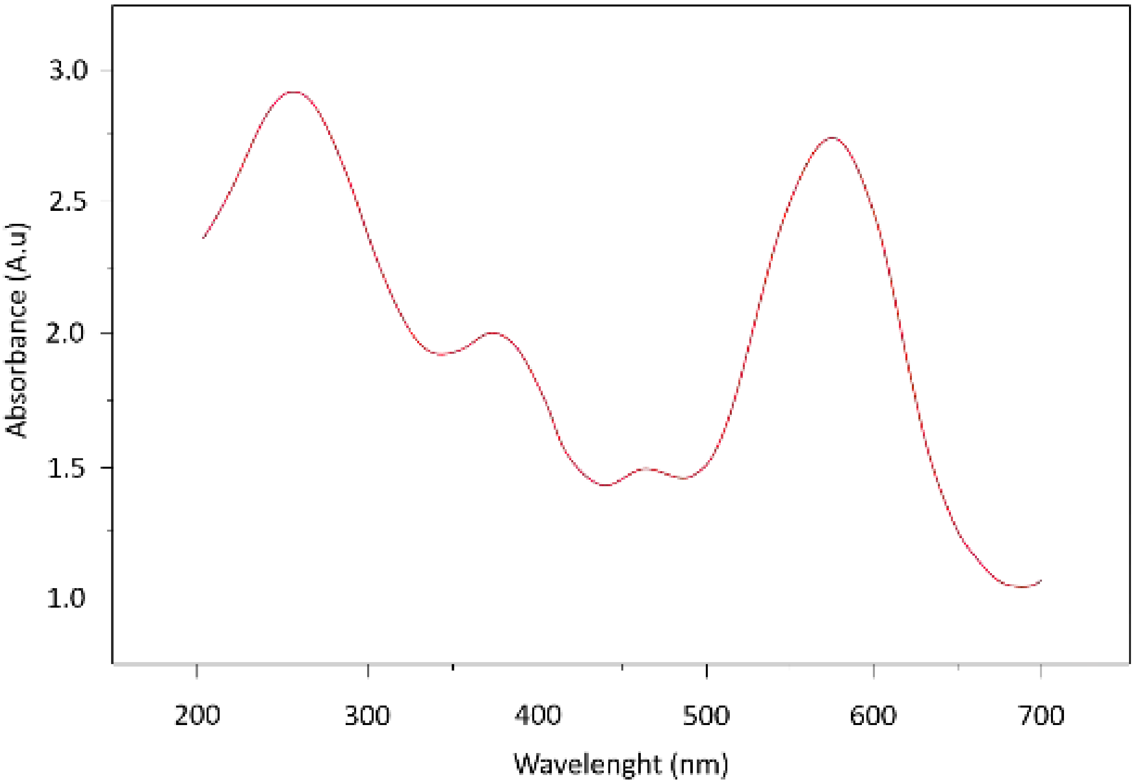

Figure 7. Absorbance of red dragon fruit dye

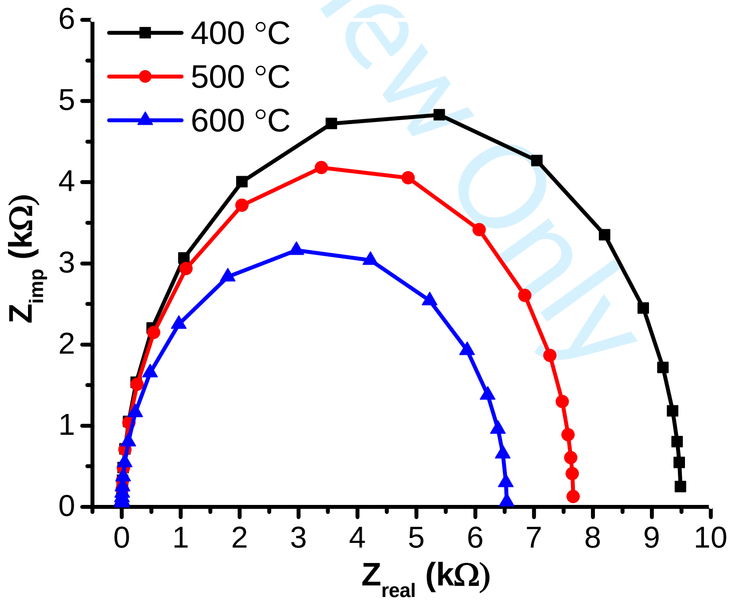

Figure 8. Electrochemical impedance spectra (EIS) of ZnO: Al thin films

Table

Table 1. Crystal size ZnO:Al thin film with variations post-heating temperature

Post-Heating temperature (°C)	Phase	Peak		Crystal size (nm)
		2θ (degree)	FWHM(degree)	
400	ZnO:Al	36.98	0.52	16
450	ZnO:Al	36.79	0.40	21
500	ZnO:Al	34.99	0.21	39
550	ZnO:Al	34.96	0.20	41
600	ZnO:Al	36.79	0.24	34

Table 2. Energy band gap of ZnO:Al thin films with variations of post-heating temperature.

Post-HeatingTemperature (°C)	Band Gap (eV)
400	3.16
450	3.17
500	3.40
550	3.20
600	3.20

Table 3. Values of voltage, current density, power, fill factor and efficiency of DSSC with variations of post-heating temperature

Post-Heating temperature (°C)	V_{oc} (V)	J_{sc} (mA/cm^2)	P_{max} (W/cm^2)	P_{in} (W/cm^2)	FF (%)	η (%)
400	0.45	0.350	0.031	36.5	19.644	0.084
450	0.45	0.450	0.052	36.5	25.925	0.143
500	0.45	0.487	0.068	36.5	31.339	0.188
550	0.50	0.650	0.094	36.5	28.941	0.257
600	0.55	1.168	0.250	36.5	22.605	0.398

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Keywords: Dye Sensitized Solar Cell, ZnO:Al thin films, Sol-gel Spin coating

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ZnO:Al thin films was synthesized using a sol-gel spin coating method. Typically, 4 grams of zinc acetate dihydrate (ZnAc) and Al 1.0 % was dissolved into 20 mL isopropanol then stirred with a magnetic stirrer. After 10 minutes, diethanolamine (DEA) was added slowly. The molar ratio between DEA and ZnAc is 1:1. The gel solution was then dropped onto ITO glass substrate and then rotated by a spin coating with a speed of 1800 rpm. Finally, the sample was heated with temperature pre-heating of 250°C for 5 hours then post-heating with temperature variations of 400, 450, 500, 550 and 600°C for 5 hours.

2.2. Characterization of ZnO:Al thin films

The crystal properties of ZnO:Al thin films were evaluated using X-ray diffractometer (LabX XRD-6100, Shimadzu) with Cu K_α radiation (40kV, 30mA) of wavelength. 1.54 Å. A field emission scanning electron microscopy (FE-SEM, JEOL 6500) with accelerating voltage of 15 kV and working distance of 10 mm was used to observed the surface morphology of thin films. The optical properties of thin films were further investigated using UV-Vis spectrometer with both transmission and absorbance modes from wavelength of 300 to 700 nm.

2.3. Synthesis of Dye Sensitizer

Synthetic dye sensitizer was done by cutting red dragon fruit into small pieces and then put it into a beaker glass. After that, the red dragon fruit is crushed by mortar until smooth. Extraction was done by adding ethanol and then soaked for 24 hours in a dark place. Finally, the extract was filtered using filter paper and stored it in a under dark place

2.4. Fabrication of DSSC

The DSSC was fabricated by attaching a platinum counter electrode to a ZnO: Al thin film coated with dye from red dragon fruit which acted as a working electrode with a layer of separating surlyn. Sticking of surlyn was conducted by pressing the working electrode and the counter electrode under heating with at temperature of 70-80 °C in order to stick them perfectly. The working electrode that had been attached to the platinum counter electrode was injected with a liquid electrolyte solution through a small hole found in the platinum opposite electrode.

2.5. Efficiency measurement

Electrical testing was carried out by making an electrical circuit between the DSSC and the measurement, that is, a digital multimeter as shown in Figure 1**.** This test is based on the beam lighting method to determine the performance and the efficiency of the cells obtained when the solar cell object is exposed to light with a certain intensity at the top of the electrode (anode). DSSC outputs are Open-Circuit Voltage (Voc) and Short Circuit Current (Isc) DSSC. Then the fill factor (FF) and the DSSC efficiency are calculated (η).

3. RESULT AND DISCUSSION

3.1. Crystal Structure of ZnO: Al Thin Film

The diffraction pattern of ZnO: Al thin films with variation of post-heating temperatures is shown in Figure 2. The result confirm that all samples have the same crystal structure of hexagonal wurtzite.[18] All XRD pattern shows three peaks with the (100), (002) and (101) planes where a (101) plane has the highest intensity indicating the prefer the crystal growth.

Crystallite size of the samples with variation post-heating temperatures are calculated using the Scherrer's equation[19]:

$$D = \frac{0.9\,\lambda}{\beta \cos \theta} \quad (1)$$

Where, D= crystallite size, λ= wavelength, β= FWHM (full width half maximum), θ= diffraction angle.

Table 1 shows the crystal size increases from 16 - 41 nm along with an increase in post-heating temperature from 400 - 550^{o} C. This was because increasing heating temperature will make compaction increase and grow large granule due to the incorporation of small grains.[20] When the post-heating temperature was increased continuously to 600 ^{o}C, the crystallite size decreased to 34 nm, this is due to aluminum doping blocking the density of the grain boundaries formed and the small granules coalition to form larger grain.[21]

3.2. Morphology of ZnO:Al Thin Film

Figure 3 shows representative scanning electron microscope images of ZnO:Al with variation of post-heating temperatures. The surface morphology of thin film contains a lot of tiny nanoparticle with homogenous distribution. It can be seen clearly that there is no obvious different of SEM images for different post-heating temperatures. The SEM images also exhibits that the grains totally covers the substrate without cracking and has a good interconnection each particle to the others. The grain size of nanoparticle is about 50-100 nm. Energy disperse spectroscopy (EDS) analysis was further conducted to confirm the success of Al doped into ZnO. As shown in the Figure 3d, a representative EDS result exhibits the peak of Al at energy 1.5 KeV with atomic concentration of 0.99%. This data confirm that Al has been successfully doped into ZnO lattice. The atomic concentrations of zinc (Zn) and oxygen (O) were 77.13% and 51.88 %, respectively.

3.3. Optical Properties of ZnO:Al Thin Films

Figure 4 and Figure 5 exhibits the transmittance and absorbance spectra, respectively. The transmittance spectrum of the ZnO:Al thin films in Figure 4 shows a sharp increase in the transmittance value for all samples that occurs in the wavelength range of approximately 350 to 400 nm which is the ultraviolet wavelength region. For ZnO:Al thin film samples heated at post-heating temperatures, the transmittance value is about 75 - 80% at a wavelength of about 600 to 700 nm and the reduction in heating of 500°C. The high transmittance value of thin films is good and suitable for solar cell applications.[22] Figure 5 shows the absorbance edges of the samples heated at temperatures of 450 and 550°C shift to a shorter wavelength region, while those of samples heated at post-heating temperatures of 500 and 600 °C shift to a longer wavelength region.

The energy band gap of the ZnO:Al thin film is furher calculated using the equation (2)[23]

$$(\alpha h v)^2 = C_D(hv - E_{opt}) \quad (2)$$

Based on the Tauc Plot method in Figure 6, the energy band gap of the ZnO:Al thin films with variation post-heating temperatures could be obtained. Table 2 shows the energy band gap value increases from 3.16 - 3.40 eV with increasing the post-heating temperature from 400 -500 °C.[20] When the post-heating temperature is increased to 550 and 600 °C, the energy band gap value slightly decreases about 0.2 eV to be 3.20 eV. This phenomenon may be related to a thin film defects due to increase in heating temperature.[24]

3.4. Dye Spectrum of Red Dragon Fruit Extract

The absorbance spectrum of red dragon fruit solution tested with UV-Vis spectrophotometer is shown in Figure 8. It is clearly seen that the red dragon fruit dye has the absorbance at UV and visible light range with peak absorbance of 254 and 570 nm, respectively. The result indicates that the extract of red dragon fruit has a great potential to be used as the dye sensitizer for DSSC device.

3.5. DSSC Efficiency

The efficiency can be obtained by comparing the power produced by the prototype DSSC (P_{max}) with the power provided by the light source (P_{in}), as shown in equation (3) and (4).

$$\eta = \frac{P_{max}}{P_{in}} x\ 100\% = FF \frac{J_{sc}\ x\ V_{oc}}{P_{in}} x\ 100\% \quad (3)$$

$$FF = \frac{J_{max}\ x\ V_{max}}{J_{sc}\ x\ V_{oc}} \quad (4)$$

Where, η = DSSC efficiency (%), J_{sc} = current density (mA), V_{oc} = Voltage (mV), P_{in} = Input power (mW), FF = Fill Factor.

Table 3 lists the efficiency of ZnO:Al with temperature variations. The efficiency of DSSC shows the increasing trend with the increasing post-heating temperature. The maximum efficiency is 0.398% with temperature post heating of 600°C. This is because of the increasing in post-heating temperature along with the energy supplied in the form of an increasing temperature which is used to form a better crystalline hexagonal wurtzite. To further investigate a higher efficiency with a higher temperature, the electrochemical impedance spectra analysis (EIS) was conducted in electrolyte solution of potassium chloride (KCl, 1M). The EIS data can be used to evaluate the charge transfer property by comparing the diameter of that semicircle in Figure 8. As can clearly observed, by increasing the temperature the diameter of semicircle becomes smaller indicating a better electron transfer. Further, the charge transfer resistance (R_{ct}) could be determined after fitting technique. The value of R_{ct} for heating at 600 °C is 6.5 kΩ which is lower than at 500 °C (7.6 kΩ) or 400 °C (9.5 kΩ). Therefore, the other reason for maximum efficiency at 600 °C post-heating temperature due to its lowest resistance that leading to most efficient charge transfer. We realize that presence efficiency is still relatively low but there is always room for improvement. Therefore, further research and development is needed in the future.

4. CONCLUSION

The DSSC prototype has been successfully fabricated using ZnO:Al thin film and dye from red dragon fruit extract as working electrodes. The XRD analysis confirmed that all sample had the hexagonal wurtzite structure. The band gap values of thin films were about of 3.16-3.40 eV. The surface morphology of as-fabricated thin films was nanoparticle with particle size less than 100 nm. We found that the efficiency of DSCC gradually improved with increasing the post-heating temperature. ZnO: Al with post-heating temperature of 600°C had the highest efficiency of 0.398%. The main reasons for optimum efficiency at 600 °C were contributed by the better crystallinity and more efficient charge transfer properties. Further investigation is highly needed to improve the efficiency in the future.

5. Acknowledgments

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Comments to authors

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Keywords:	Dye Sensitized Solar Cell, ZnO:Al thin films, Sol-gel Spin coating, Red dragon fruit extract

Effect of Post-Heating Temperature on Efficiency of Dye Sensitized Solar Cell with ZnO:Al Thin Films Prepared by Sol-Gel Spin Coating

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ABSTRACT:

Dye Sensitized Solar Cell (DSSC) has a great potential to harvest the solar light into electricity. In this report, a prototype of DSSC had been successfully fabricated using ZnO:Al thin film and dye from red dragon fruit as a working electrode. ZnO:Al thin films were prepared using the method sol-gel spin coating with post-heating temperature variations. The XRD result confirms that all ZnO: Al have hexagonal structure with crystal sizes of 16 - 41 nm. SEM analysis showed the nanoparticle with particle size of 30-80 nm. The bandgap ranges from 3.16 to 3.40 eV. The EIS analysis reveals that charge transfer resistance greatly decreases with the rise of temperature. The efficiency of DSCC gradually improved with increasing the post-heating temperature. ZnO: Al with post-heating temperature of 600 ºC had the highest efficiency of 0.398%.

Keywords: Dye Sensitized Solar Cell, ZnO:Al thin films, Sol-gel Spin coating, red dragon fruit extract

1. INTRODUCTION

Dye sensitized solar cell (DSSC) is one of the solar cell types that originally invented by Gratzel in 1991.[1] The fabrication of DSSC is low cost and environmentally friendly. It consists of several components, namely semiconductor oxide, dye, counter electrode and electrolyte.[2] The engineering of ZnO semiconductor for the DSSC working electrode is promising because it has an energy band gap of 3.37 eV and a binding energy of 60 meV which allows direct absorption of UV radiation.[3] The shortcomings of ZnO thin film has poor electrical characteristic like having a low conductivity value of 6.24 x 10^{-7} (Ωcm)s^{-1}.[4] In order to enhance its physical, optical and electrical properties, it is often doped with extrinsic dopant from group IIIA such as B, Al, and Ga as foreign element doped into the ZnO structure.[5] Aluminum (Al) is chosen as a doping agent because it can increase the electrical conductivity of ZnO thin films to an order of 10^5 Ω.cm.[6] There are several techniques to fabricate thin film such as molecular beam epitaxy,[7] radio frequency (RF) magnetron sputtering,[8] pulsed laser deposition,[9] spray pyrolysis,[10] physical vapor deposition,[11] and sol-gel spin coating.[12] A sol-gel spin coating method has several advantages, including not using a high vacuum space, low cost, homogeneous composition, controllable layer thickness and great microstructure.[13]

Research on aluminum doping ZnO thin films has been carried out by Islam and co-workers [14] with variations of aluminum doping concentration, the energy band gap value was affected by the doping concentrations. The crystal size, transmittance and energy band gap increase with the increasing of heating temperature.[15] The efficiency of DSSC not only influenced by aluminum doping concentration[16] but also annealing temperature.[17] Recently, Bekele et al. had successfully utilized root extract of *Kniphofia schemperi* as natural dye for DSSC.[18] Based on these considerations, it is interested to conduct research on DSSC using Al doped ZnO thin film prepared by a sol-gel spin coating method with variation of post-heating temperatures and extract red dragon fruit as the natural dye sensitized.

2. EXPERIMENTAL

2.1. Synthesis of ZnO:Al thin films

ZnO:Al thin films was synthesized using a sol-gel spin coating method.[19] Typically, 4 grams of zinc acetate dihydrate (ZnAc) and Al 1.0 % was dissolved into 20 mL isopropanol then stirred with a magnetic stirrer. After 10 minutes, 1.72 mL diethanolamine (DEA) was added slowly as a stabilizer agent. The gel solution was then dropped onto ITO glass substrate and then rotated by a spin coating with a speed of 5000 rpm. And then, the sample was heated on the top of a hotplate with temperature pre-heating of 250 °C for 5 minutes to remove the excess liquid. Finally, the sample was annealed in an electric furnace with temperature variations of 400, 450, 500, 550 and 600 ^{o}C for 5 hours.

2.2. Characterization of ZnO:Al thin films

The crystal properties of ZnO:Al thin films were evaluated using X-ray diffractometer (LabX XRD-6100, Shimadzu) with Cu K_{α} radiation (40kV, 30mA) of wavelength. 1.54 Å. A field emission scanning electron microscopy (FE-SEM, JEOL 6500) with accelerating voltage of 15 kV and working distance of 10 mm was used to observed the surface morphology of thin films. The optical properties of thin films were further investigated using UV-Vis spectrometer with both transmission and absorbance modes from wavelength of 300 to 700 nm. Electrochemical impedance spectroscopy was performed using Biologic SP-300 Potentiostat.

2.3. Preparation of Dye Sensitizer

The extract of dye sensitizer was done by cutting red dragon fruit into small pieces and then put it into a beaker glass. After that, the red dragon fruit is crushed by mortar until smooth. Extraction was done by adding ethanol and then soaked for 24 hours in a dark place.[18] Finally, the extract was filtered using filter paper and stored it in a under dark place.

2.4. Fabrication of DSSC

The DSSC was fabricated by attaching a platinum counter electrode to a ZnO: Al thin film coated with dye from red dragon fruit which acted as a working electrode with a layer of separating surlyn. Sticking of surlyn was conducted by pressing the working electrode and the counter electrode under heating with at temperature of 70-80 ^{o}C in order to stick them perfectly.[20] The working electrode that had been attached to the platinum counter electrode was injected with a liquid electrolyte solution through a small hole found in the platinum opposite electrode.

2.5. Efficiency measurement

Electrical testing was carried out by making an electrical circuit between the DSSC and digital multimeter as shown in Figure 1. This test is based on the beam lighting method to determine the performance and the efficiency of the cells obtained when the solar cell is exposed to light with a certain intensity at the top of the electrode (anode).[21] DSSC outputs are Open-Circuit Voltage (Voc) and Short Circuit Current (Isc) DSSC. Then the fill factor (FF) and the DSSC efficiency were calculated (η).

3. RESULT AND DISCUSSION

3.1. Crystal Structure of ZnO: Al Thin Film

The diffraction pattern of ZnO: Al thin films with variation of post-heating temperatures is shown in Figure 2. The result confirm that all samples have the same crystal structure of hexagonal wurtzite according to database with JCPDF No. #36-1451.[22] All XRD pattern shows three peaks with the (100), (002) and (101) planes where a (101) plane has the highest intensity indicating the prefer the crystal growth.

Crystallite size of the samples with variation post-heating temperatures are calculated using the Scherrer's equation.[23]

$$D = \frac{0.9\,\lambda}{\beta\cos\theta} \qquad (1)$$

Where, D= crystallite size, λ= wavelength, β= FWHM (full width half maximum), θ= diffraction angle.

Table 1 shows the crystal size increases from 16 - 41 nm along with an increase in post-heating temperature from 400 - 550^{o} C. This was because increasing heating temperature will make compaction increase and grow large granule due to the incorporation of small grains.[24] When the post-heating temperature was increased continuously to 600 ^{o}C, the crystallite size decreased to 34 nm, this is due to aluminum doping blocking the density of the grain boundaries formed and the small granules coalition to form larger grain.[25]

3.2. SEM and EDS analyses of ZnO:Al Thin Film

Figure 3 shows representative scanning electron microscope images of ZnO:Al with variation of post-heating temperatures. The surface morphology of thin film contains a lot of tiny nanoparticle with homogenous distribution. It can be seen clearly that there is no obvious different of SEM images for different post-heating temperatures. The SEM images also exhibits that the grains totally cover the substrate without cracking and has a good interconnection each particle to the others. The average particle size of nanoparticles annealed at 400, 500 and 600 ^{o}C are 38±7, 50±10, and 66±12 nm, respectively. Energy disperse spectroscopy (EDS) analysis was further conducted to confirm the success of Al doped into ZnO. As shown in the Figure 3d, a representative EDS result exhibits the peak of Al at energy 1.5 KeV with atomic concentration of 0.99%. This analysis confirms that Al as an extrinsic dopant has been successfully doped into ZnO structure. The atomic concentrations of zinc (Zn) and oxygen (O) were 47.13% and 51.88 %, respectively.

3.3. Optical Properties of ZnO:Al Thin Films

Figure 4 and Figure 5 exhibits the transmittance and absorbance spectra, respectively. The transmittance spectrum of the ZnO:Al thin films in Figure 4 shows a sharp increase in the transmittance value for all samples that occurs in the wavelength range of approximately 350 to 400 nm which is the ultraviolet wavelength region. For ZnO:Al thin film samples heated at post-heating temperatures, the transmittance value is about 75 - 80% at a wavelength of about 600 to 700 nm and the reduction in heating of 500 °C. The high transmittance value of thin films is good and suitable for solar cell applications. Figure 5 shows the absorbance edges of the samples heated at temperatures of 450 and 550 °C shift to a shorter wavelength region, while those of samples heated at post-heating temperatures of 500 and 600 °C shift to a longer wavelength region.

The energy bandgap of the ZnO:Al thin film is further calculated using the equation (2) [26]

$$(\alpha h v)^2 = C_D(hv - E_{opt}) \quad (2)$$

Where α= absorption coefficient, ν= frequency, C_D = proportionality constant, h = Planck's constant, and E_{opt} = optical bandgap.

Based on the Tauc Plot method in Figure 6, the energy band gap of the ZnO:Al thin films with variation post-heating temperatures could be obtained. Table 2 shows the energy band gap value increases from 3.16 - 3.40 eV with increasing the post-heating temperature from 400 -500 °C. When the post-heating temperature is increased to 550 and 600 °C, the energy band gap value slightly decreases about 0.2 eV to be 3.20 eV. This phenomenon may be related to a thin film defects due to increase in heating temperature.[27]

3.4. Dye Spectrum of Red Dragon Fruit Extract

The absorbance spectrum of red dragon fruit solution tested with UV-Vis spectrophotometer is shown in Figure 7. It is clearly seen that the red dragon fruit dye has the absorbance at UV and visible light range with peak absorbance of 254 and 570 nm, respectively. The result indicates that the extract of red dragon fruit has a great potential to be used as the dye sensitizer for DSSC device.

3.5. DSSC Efficiency

The efficiency can be obtained by comparing the power produced by the prototype DSSC (P_{max}) with the power provided by the light source (P_{in}), as shown in equation (3) and (4).

$$\eta = \frac{P_{max}}{P_{in}} x\ 100\% = FF\frac{J_{sc}\ x\ V_{oc}}{P_{in}} x\ 100\% \quad (3)$$

$$FF = \frac{J_{max}\, x\, V_{max}}{J_{sc}\, x\, V_{oc}} \quad (4)$$

Where, η = DSSC efficiency (%), J_{sc} = current density (mA), V_{oc} = Voltage (mV), P_{in} = Input power (mW), FF = Fill Factor.

Table 3 lists the efficiency of ZnO:Al with temperature variations. The efficiency of DSSC shows the increasing trend with the increasing post-heating temperature. The maximum efficiency is 0.398% with temperature post heating of 600 ^{o}C. This is because of the increasing in post-heating temperature along with the energy supplied in the form of an increasing temperature which is used to form a better crystalline hexagonal wurtzite. The absorption spectra in Figure 5 exhibits that ZnO: Al with annealing temperature of 600 ^{o}C had the highest absorption in the visible light region among other temperatures which might be the other reason to show the highest efficiency. To further investigate a higher efficiency with a higher temperature, the electrochemical impedance spectra analysis (EIS) was conducted in electrolyte solution of potassium chloride (KCl, 1M). The EIS data can be used to evaluate the charge transfer property by comparing the diameter of that semicircle in Figure 8. As can clearly observed, by increasing the temperature the diameter of semicircle becomes smaller indicating a better electron transfer. Further, the charge transfer resistance (R_{ct}) could be determined after fitting technique. The value of R_{ct} for heating at 600 ^{o}C is 6.5 kΩ which is lower than at 500 ^{o}C (7.6 kΩ) or 400 ^{o}C (9.5 kΩ). Therefore, the other reason for maximum efficiency at 600 ^{o}C post-heating temperature due to its lowest resistance that leading to most efficient charge transfer. We realize that presence efficiency is still relatively low but there is always room for improvement. Therefore, further research and development is needed to conduct in the future.

4. CONCLUSION

The DSSC prototype has been successfully fabricated using ZnO:Al thin film and dye from red dragon fruit extract as working electrodes. The XRD analysis confirmed that all sample had the hexagonal wurtzite structure. The band gap values of thin films were about of 3.16-3.40 eV. The surface morphology of as-fabricated thin films was nanoparticle with particle size less than 100 nm. We found that the efficiency of DSCC gradually improved with increasing the post-heating temperature. ZnO: Al with post-heating temperature of 600^{o}C had the highest efficiency of 0.398%. The main reasons for optimum efficiency at 600 ^{o}C were contributed by the better crystallinity and more efficient charge transfer properties.

5. Acknowledgments

Researcher would like to thank the Physics Laboratory and Chemistry Laboratory in Universitas Negeri Medan and supported by Indonesia Directorate of Research and Community Service.

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Figure

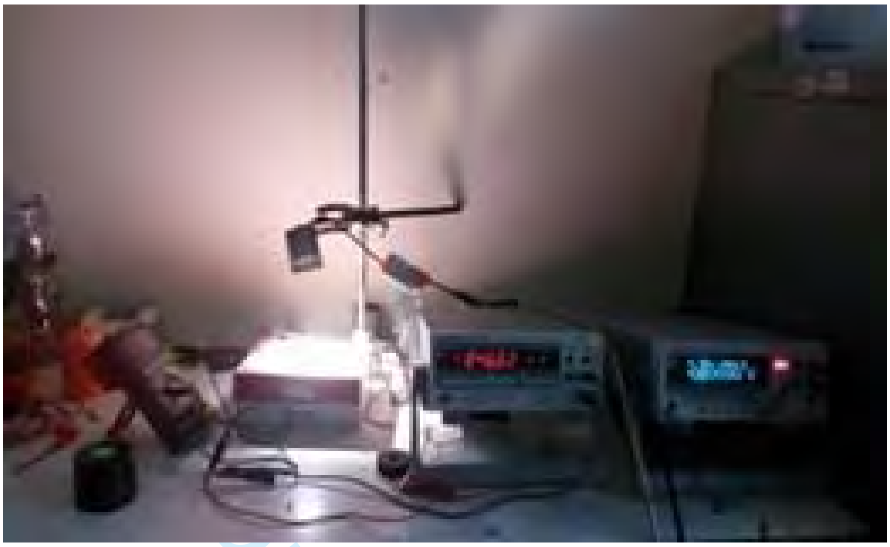


Figure 1: Measurement of DSSC efficiency

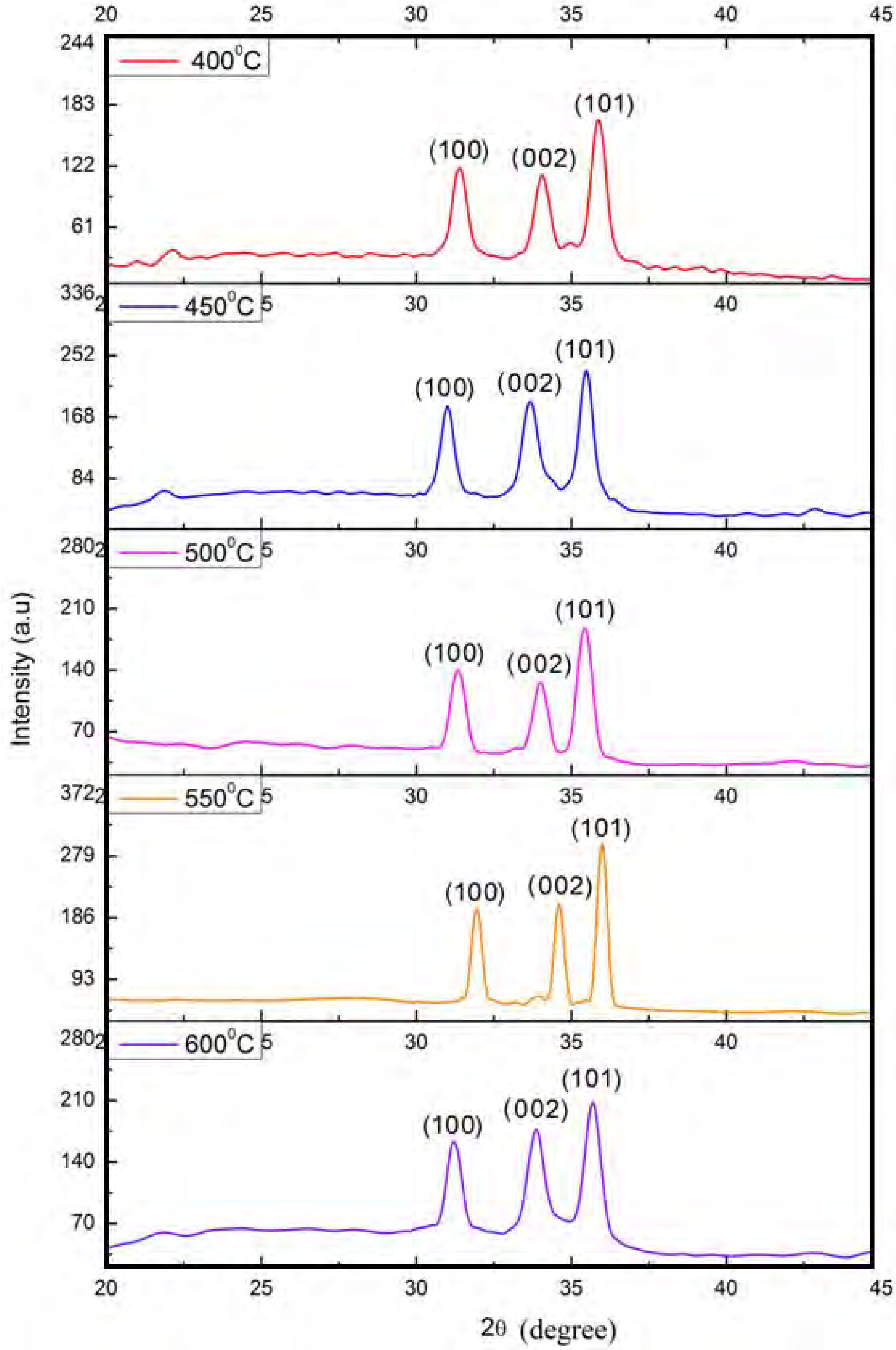
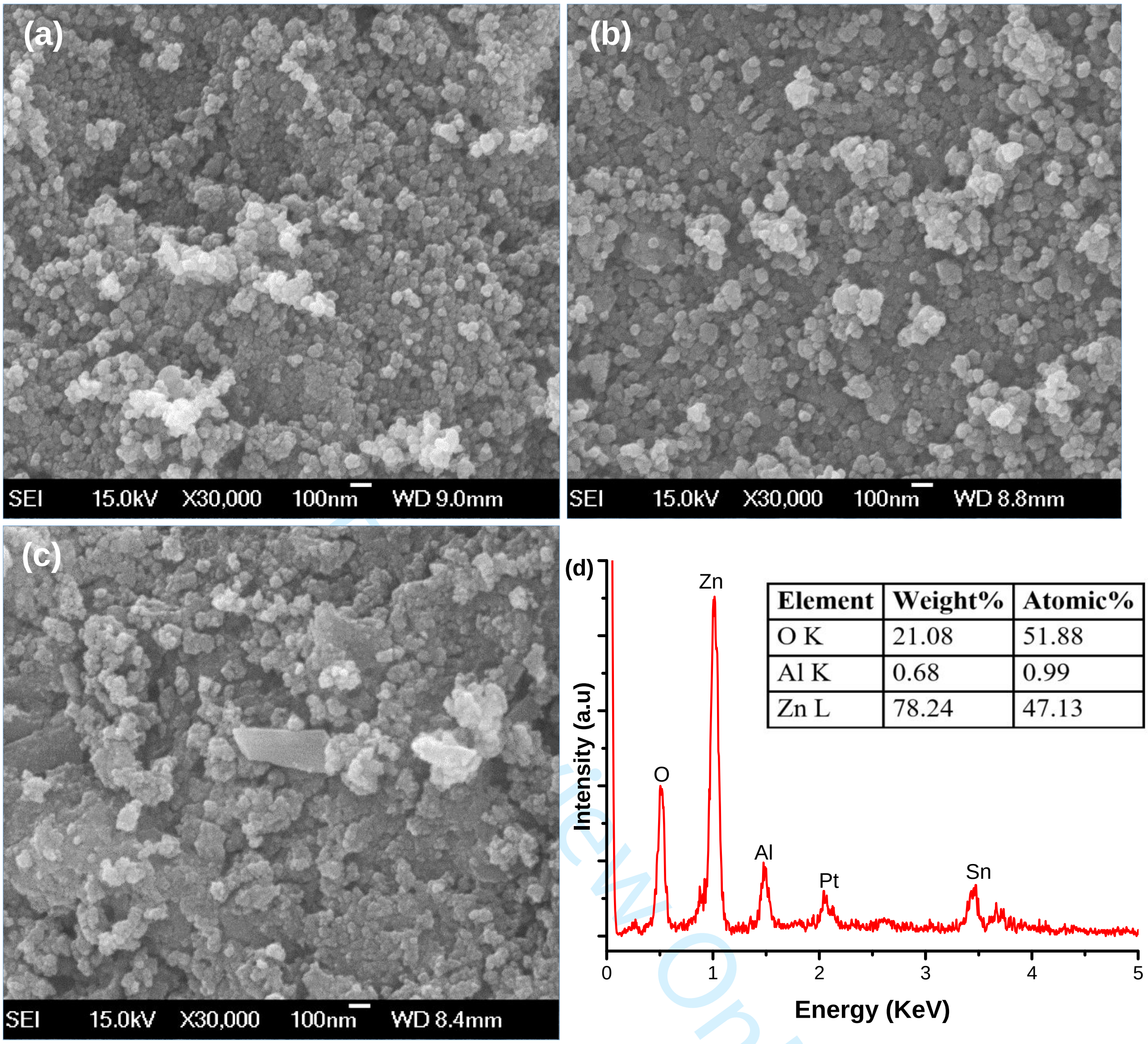


Figure 2. X-ray diffraction spectra of ZnO:Al thin films



Element	Weight%	Atomic%
O K	21.08	51.88
Al K	0.68	0.99
Zn L	78.24	47.13

Figure 3. Representative SEM images of ZnO:Al thin films with different post-heating temperatures (a) 400 °C, (b) 500 ºC , (c) 600 ºC and (d) Energy disperse spectra (EDS) to show the presence of Al

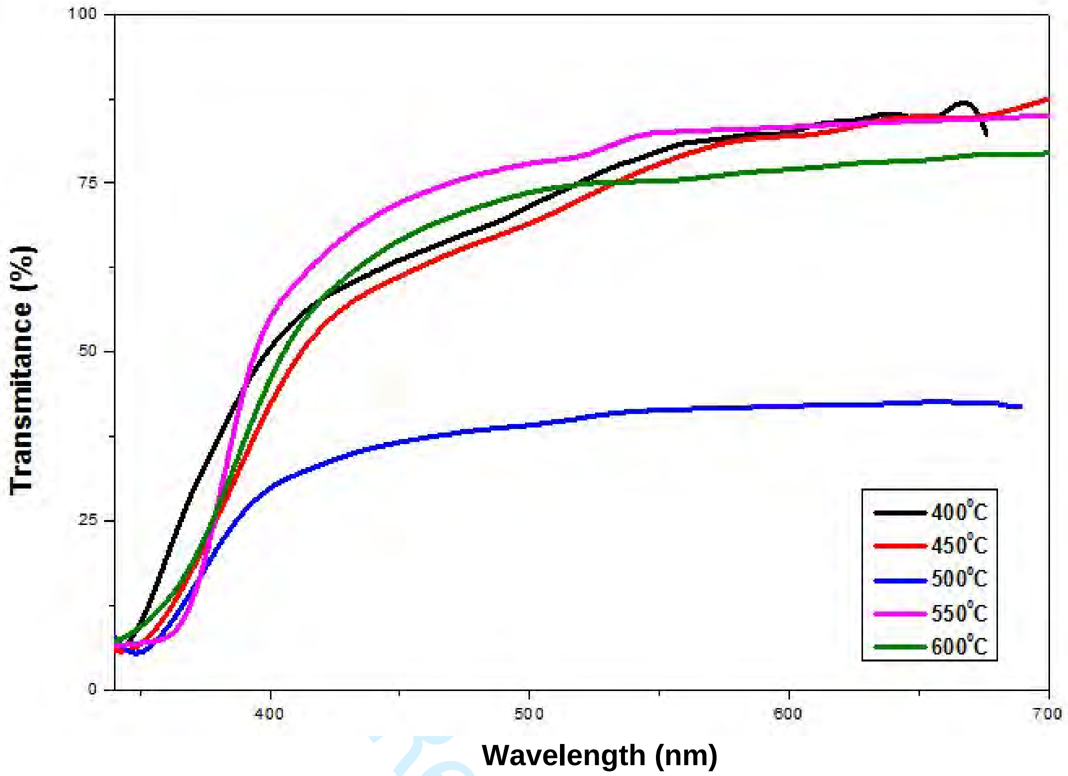


Figure 4. Transmittance spectrum of ZnO:Al thin films

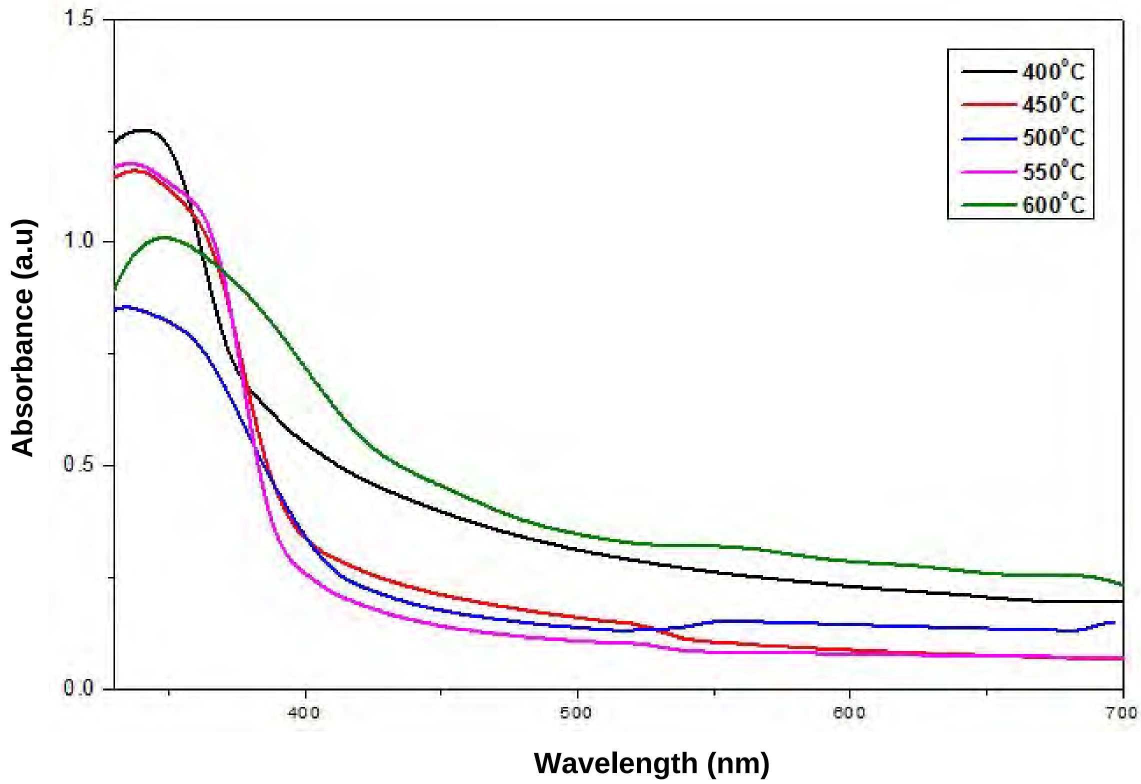


Figure 5. Absorbance Spectrum of ZnO:Al thin films

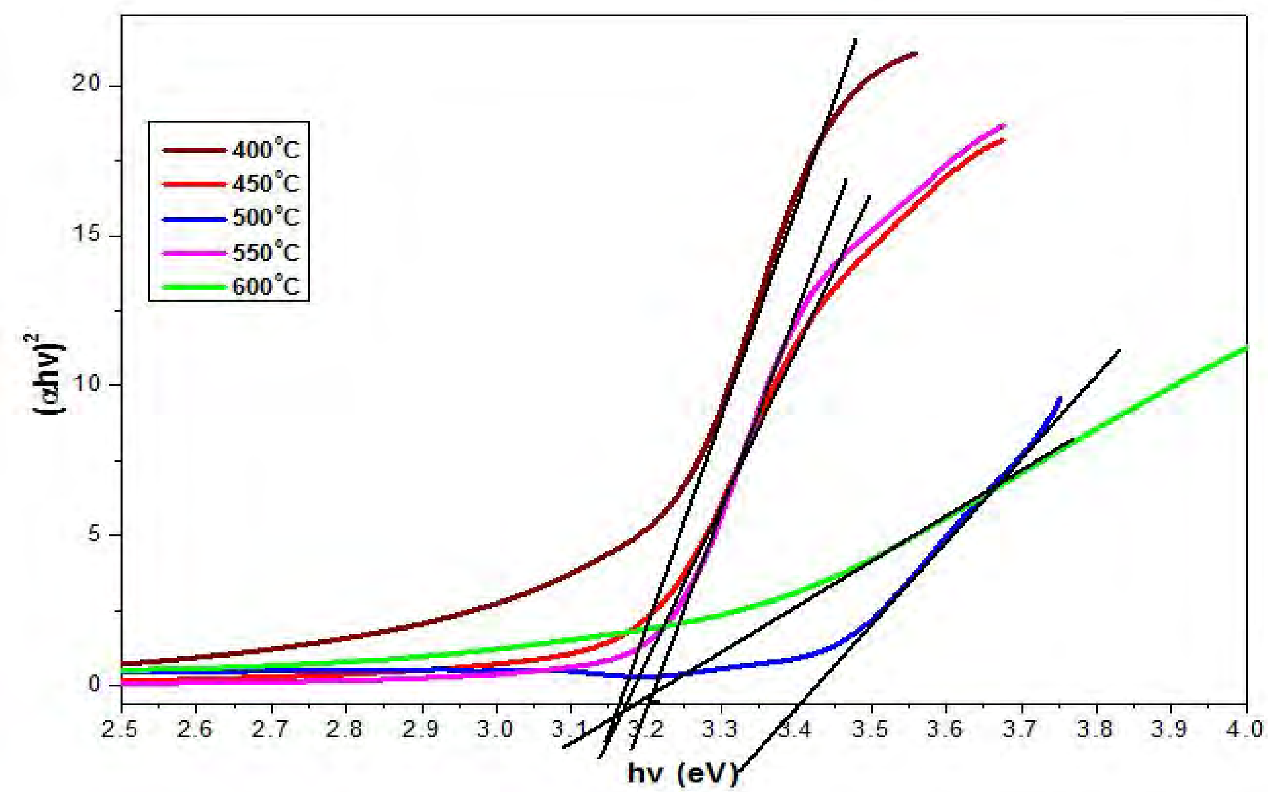


Figure 6. Energy band gap of ZnO:Al thin films using *Tauc Plot* method

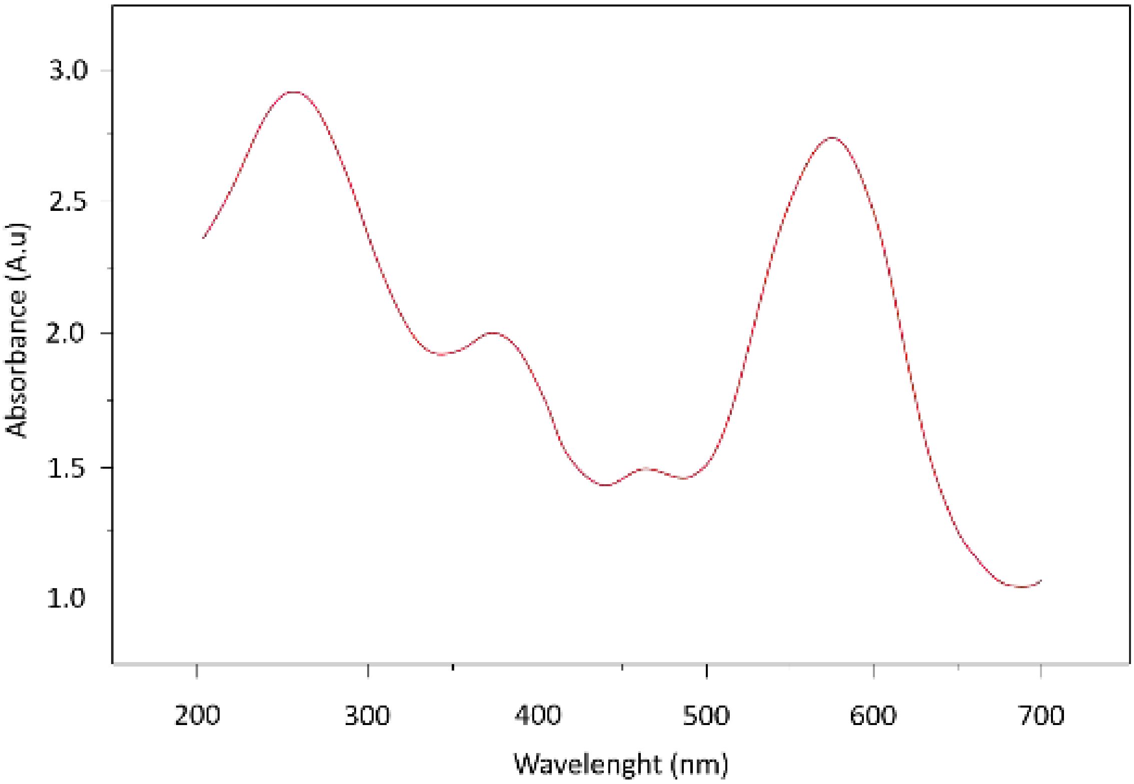


Figure 7. Absorbance of red dragon fruit dye

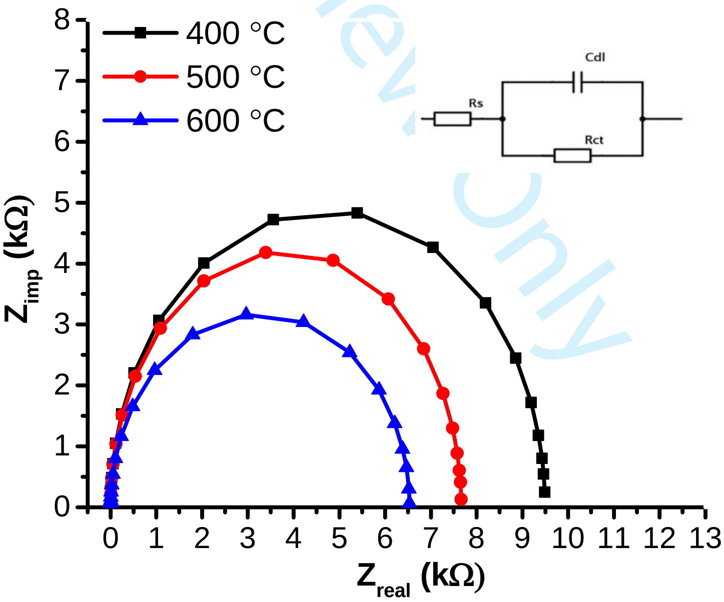


Figure 8. Electrochemical impedance spectra (EIS) of ZnO: Al thin films

Table

Table 1. Crystal size ZnO:Al thin film with variations post-heating temperature

Post-Heating temperature (°C)	Phase	Peak		Crystal size (nm)
		2θ (degree)	FWHM(degree)	
400	ZnO:Al	36.98	0.52	16
450	ZnO:Al	36.79	0.40	21
500	ZnO:Al	34.99	0.21	39
550	ZnO:Al	34.96	0.20	41
600	ZnO:Al	36.79	0.24	34

Table 2. Energy band gap of ZnO:Al thin films with variations of post-heating temperature.

Post-HeatingTemperature (°C)	Band Gap (eV)
400	3.16
450	3.17
500	3.40
550	3.20
600	3.20

Table 3. Values of voltage, current density, power, fill factor and efficiency of DSSC with variations of post-heating temperature

Post-Heating temperature (°C)	V_{oc} (V)	J_{sc} (mA/cm^2)	P_{max} (W/cm^2)	P_{in} (W/cm^2)	FF (%)	η (%)
400	0.45	0.350	0.031	36.5	19.644	0.084
450	0.45	0.450	0.052	36.5	25.925	0.143
500	0.45	0.487	0.068	36.5	31.339	0.188
550	0.50	0.650	0.094	36.5	28.941	0.257
600	0.55	1.168	0.250	36.5	22.605	0.398

Reviewer: 1

Recommendation: Minor revision

Siregar et al. investigate the effect of different annealing temperatures on efficiency of dye sensitized solar cell with ZnO:Al thin films prepared by sol-gel spin coating. They found that temperature was significantly affect the efficiency of DSSC. I would like to recommend this manuscript to be published in journal of physical science. However, there are several issues need to be addressed by authors before publication, as follows.

1. The introduction part should be revised by adding some recently reports. Moreover, some of the references are out of date. The authors should update their references like within last 5 years.

Authors response:

Thanks for your suggestion. The authors have updated the reference of manuscript with the latest ones.

2. Please change Wave length in Figure 4 and 5.

Authors response:

Thanks for your suggestion. The authors have modified it.

3. Equation 2 should be explained in more detail manner.

Authors response:

Thanks for your suggestion. The authors have done so.

4. The authors should provide an equivalent/Randle circuit to EIS data in Figure 8.

Authors response:

Thanks for your suggestion. The authors have done so, as inserted in Figure 8.

5. Overall, there are a lot of grammatical error in this manuscript. Please carefully check throughout the manuscript.

Authors response:

Thanks for your comment. The authors have improved the English of this manuscript.

Reviewer: 2

In this article, Effect of Post-Heating Temperature on Efficiency of Dye Sensitized Solar Cell with ZnO:Al Thin Films Prepared by Sol-Gel Spin Coating is reported. The manuscript is clear and well-written. However, there are some points that need to be either clarified before re-consideration of the manuscript.

1. Please indicate the jcpdf number from the XRD results

Authors response:

Thanks for your suggestion. The authors have added the JCPDF Number in the manuscript.

The result confirm that all samples have the same crystal structure of hexagonal wurtzite according to database with JCPDF No. #36-1451.22

2. Did the authors calculate the particle size distribution from the SEM images? is there any significant difference?

Authors response:

Thanks for your suggestion. The authors have calculated the particle size distribution. We found that the average particle size of nanoparticles annealed at 400, 500 and 600 ^{o}C are 38±7, 50±10, and 66±12 nm, respectively. By considering the standard deviation value, there is no a significant different on particle size between 400 ^{o}C and 500 ^{o}C or 500 ^{o}C and 600 ^{o}C. But there is an obvious different for 400 ^{o}C and 600 ^{o}C.

Reviewer: 3

After exhaustive review of your manuscript (with Manuscript ID:JPS-OA-21-0034) entitled ’’ Effect of Post-Heating Temperature on Efficiency of Dye Sensitized Solar Cell with ZnO:Al Thin Films Prepared by Sol-Gel Spin Coating’ and submitted to the Journal of Physical Science, I have suggested the following detail comments.

Detailed comments:

1. Let the abstract include introductory sentence. The abstract is the concise summary of the manuscript comprises of introductory sentence, objectives, brief description of methodology, major findings and conclusions in short. In this regard, the abstract lacks introductory sentence.

Authors response:

Thanks for your suggestion. The authors have modified abstract part.

2. Let the abstract include some of your findings concerning charge transfer analysed using EIS analysis. I recommend you include one more keyword, that is , 'Red dragon fruit extract'

Authors response:

Thank you for your great suggestion. The authors have done so.

3. For your narrations under introduction part, I suggest you to include the currently published papers in Dye sensitized solar cells such as https://doi.org/10.1155/2021/6648325

Authors response:

Thanks for your suggestion. The authors have added in ref. 18

4. Define the abbreviations such as RF in page 1 line 24.

Authors response:

Thanks for your suggestion. The authors have done so.

5. Under methodology section (section 2.1), purpose of adding DEA to the blend of zinc acetate and Al need to be mentioned

Authors response:

Thanks for your suggestion. The authors have added the purpose of adding DEA in the section 2.1.

6. Actually it is expected to optimize the proportions of DAE and ZnAc for its best performance. The rationale behind mixing 1:1 ratios of DAE and ZnAc in the method section need to clearly indicate.

Authors response:

Thanks for your suggestion. The authors have optimized the ratio of DAE and ZnAc in our previous study (un-published yet).

7. Please provide related references to ascertain the credibility of the method you have used for section 2.1. 2.3,2.4 and 2.5

Authors response:

Thanks for your suggestion. The authors have done so.

8. If your solution was gel, how could you manage to get uniform film using spin coater with spinning speed of 1800 rpm? Usually high spinning speed is required for gel or thick solutions. Please check the spinning speed you have used. 9. You have mentioned two types of heating treatments for sample in the methodology part: pre-heating and post-heating. Please state the purpose of pre-heating and post-heatings

Authors response to point No 8 and 9:

Thanks for your suggestion. The authors have modified the section 2.1 as follows:

ZnO:Al thin films was synthesized using a sol-gel spin coating method.19 Typically, 4 grams of zinc acetate dihydrate (ZnAc) and Al 1.0 % was dissolved into 20 mL isopropanol then stirred with a magnetic stirrer. After 10 minutes, 1.72 mL diethanolamine (DEA) was added slowly as a stabilizer agent. The gel solution was then dropped onto ITO glass substrate and then rotated by a spin coating with a speed of 5000 rpm. Finally, the sample was heated on the top of a hotplate with temperature pre-heating of 250 oC for 5 minutes *to remove the excess liquid. Finally, the sample was annealed in an electric furnace with temperature variations of 400, 450, 500, 550 and 600 oC for 5 hours.*

10. Subtopic 2.3 (page 3): Use the term 'preparation' or 'extraction' instead of the term ‘synthesis’ in subtopic 2.3. You cite references for this sub section too. Include currently published work here: https://doi.org/10.1155/2021/6648325,

Authors response:

Thanks for your suggestion. The authors have done so.

11. In section 2.5, let all the details of phovoltaic parameter measurements be mentioned. Also mention the model of the sun simulator and its power intensity (Pin). You have also used electrochemical impedance spectroscopy (EIS) to analyse the performance your DSSCs, but you did not mention about this technique in the methodology part. You should include procedures of EIS analysis in the methodology section.

Authors response:

Thanks for your suggestion. The authors have added EIS analysis in the section 2.5

12. In section 2.5, at the fourth line delete unrelated word ‘object’.

Authors response:

Thanks for your suggestion. The authors have deleted it.

13. You have analysed the performance of your DSSCs devices and their components using XRD, SEM-EDS, UV-Vis, J-V characteristics and EIS. That is good, but in the result and discussion part your document is expected show how each analysis support each other towards your findings. Let the ‘Result and discussion’ part be revised again to show some sorts of relationship among each and every analysis results to towards the performance of fabricated DSSCs.

Authors response:

Thanks for your suggestion. The authors have modified the results and discussion with some related characterizations with the efficiency. As follows:

Table 3 lists the efficiency of ZnO:Al with temperature variations. The efficiency of DSSC shows the increasing trend with the increasing post-heating temperature. The maximum *efficiency is 0.398% with temperature post heating of 600 oC. This is because of the increasing in post-heating temperature along with the energy supplied in the form of an increasing temperature which is used to form a better crystalline hexagonal wurtzite. The absorption spectra in Figure 5 exhibits that ZnO: Al with annealing temperature of 600 oC had the highest absorption in the visible light region among other temperatures which might be the other reason to show the highest efficiency. To further investigate a higher efficiency with a higher temperature, the electrochemical impedance spectra analysis (EIS) was conducted in electrolyte solution of potassium chloride (KCl, 1M). The EIS data can be used to evaluate the charge transfer property by comparing the diameter of that semicircle in Figure 8. As can clearly observed, by increasing the temperature the diameter of semicircle becomes smaller indicating a better electron transfer. Further, the charge transfer resistance (Rct) could be determined after fitting technique. The value of Rct for heating at 600 oC is 6.5 kΩ which is lower than at 500 oC (7.6 kΩ) or 400 oC (9.5 kΩ). Therefore, the other reason for maximum efficiency at 600 oC post-heating temperature due to its lowest resistance that leading to most efficient charge transfer. We realize that presence efficiency is still relatively low but there is always room for improvement. Therefore, further research and development is needed to conduct in the future.*

14. Section 3.2: your subtopic is ‘Morphology of ZnO Al thin films’, but the content under the subtopic is not only about the SEM Images and Morphology, but also elemental composition analysis using EDS. Please use the subtopic. "SEM and EDS analysis of ZnO:Al Thin film"

Authors response:

Thanks for your suggestion. The authors have modified so.

15. Please look at the data in Figure 3d. The sum of atomic percentages of all elements found in ZnO:Al thin film should not exceed 100%. Your discussion at the bottom of section3.2 has no a harmony the data in Figure3d. Please revise this part very well.

Authors response:

Thanks for your correction. The authors have revised it.

"As shown in the Figure 3d, a representative EDS result exhibits the peak of Al at energy 1.5 KeV with atomic concentration of 0.99%. This analysis confirms that Al as an extrinsic dopant has been successfully doped into ZnO structure. The atomic concentrations of zinc (Zn) and oxygen (O) were 47.13% and 51.88 %, respectively."

16. You have calculated the average crystallite size of your material using XRD data in section 3.1. Please make sure that the size you have described in section 3.2 is in agreement with the one you explained in section 3.1.

Authors response:

Thanks for your suggestion. The authors have calculated the particle size from the SEM images using J software. It is important to note that crystallite size is different with the particle size.

17. In the body of the manuscript you have not cited Figure 7. You have to cite and discuss this missed figure. And also you have miss-referred Figure 8. It must be Figure 7.

Authors response:

Thanks for your correction. The authors have revised it.

18. At the bottom of section3.3: With increasing the post-heating temperatures from 550 to 600, the bandgap values of the ZnO:Al thin films were slightly decreased by about 0.2 eV. You should relate changes in band gap with findings (with performance of your DSSCs).

Authors response:

Thanks for your suggestion. The authors found that there is no a relationship between the bandgap energy with the efficiency.

19. Section 3.4: In the body of the manuscript you have not cited figure 7. You have to cite and discuss this missed figure. And also you have miss-referred Figure 8. It must be Figure 7.

Authors response:

Thanks for your correction. The authors have revised it.

20. The alignment of Equation numbers from 1 up to 4 must be uniform throughout from right side of margin.

Authors response:

Thanks for your suggestion. The authors have modified it.

21. Remove the last sentence in Conclusion section. Recommendation statement must not be included in the conclusion. Always conclusion is to be drawn based your findings only.

Authors response:

Thanks for your suggestion. The authors have removed it.

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Effect of Post-Heating Temperature on Efficiency of Dye Sensitized Solar Cell with ZnO:Al Thin Films Prepared by Sol-Gel Spin Coating

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Keywords:	Dye Sensitized Solar Cell, ZnO:Al thin films, Sol-gel Spin coating, Red dragon fruit extract

Effect of Post-Heating Temperature on Efficiency of Dye Sensitized Solar Cell with ZnO:Al Thin Films Prepared by Sol-Gel Spin Coating

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ABSTRACT:

Dye Sensitized Solar Cell (DSSC) has a great potential to convert solar light into electricity. In this report, a prototype of DSSC had been successfully fabricated using ZnO:Al thin film and dye from red dragon fruit as a working electrode. ZnO:Al thin films were prepared by a sol-gel spin coating method with variation of post-heating temperatures. The XRD result confirms that all ZnO: Al thin films have a hexagonal structure with crystal sizes of 16 - 41 nm. SEM analysis showed the nanoparticles with particle size of 30-80 nm. The bandgap ranges from 3.16 to 3.40 eV. The EIS analysis reveals that charge transfer resistance greatly decreases with the rise of temperature. The efficiency of DSCC gradually improved with increasing the post-heating temperature. ZnO: Al with a post-heating temperature of 600 ºC had the highest efficiency of 0.398%.

Keywords: Dye Sensitized Solar Cell, ZnO:Al thin films, Sol-gel spin coating, red dragon fruit extract

1. INTRODUCTION

Dye sensitized solar cell (DSSC) is one of the solar cell types that originally invented by Gratzel in 1991.[1] The fabrication of DSSC is low cost and environmentally friendly. It consists of several components, namely, semiconductor oxide, dye, counter electrode and electrolyte.[2] The engineering of ZnO semiconductor for the DSSC working electrode is promising because it has an energy bandgap of 3.37 eV and a binding energy of 60 meV which allows direct absorption of UV radiation.[3] ZnO thin film has poor electrical characteristic like having a low conductivity value of 6.24 x 10^{-7} $(\Omega cm)s^{-1}$.[4] To enhance its physical, optical and electrical properties, it is often doped with extrinsic dopant from group IIIA such as B, Al, and Ga as foreign element doped into the ZnO structure.[5] Aluminium (Al) is chosen as a doping agent because it can increase the electrical conductivity of ZnO thin films to an order of 10^5 Ω.cm.[6] There are several techniques to fabricate thin film such as molecular beam epitaxy, radio frequency (RF) magnetron sputtering, pulsed laser deposition, spray pyrolysis, physical vapor deposition, and sol-gel spin coating. [7-12] A sol-gel spin coating method has several advantages, including not using a high vacuum space, low cost, homogeneous composition, controllable layer thickness, and great microstructure.[13]

Islam et. al studied Al-doped ZnO and they found that the energy bandgap value was affected by the doping concentrations. [14] The crystal size, transmittance and energy bandgap increase with the increasing of heating temperature.[15] The efficiency of DSSC is not only influenced by Al concentration but also annealing temperature.[16, 17] Recently, Bekele et al. had successfully utilized the root extract of *Kniphofia schemperi* as the natural dye for DSSC.[18] Based on these considerations, it is interested to conduct research on DSSC using Al doped ZnO thin film prepared by a sol-gel spin coating method with variation of post-heating temperatures and extract red dragon fruit as the natural dye sensitized.

2. EXPERIMENTAL

2.1. Synthesis of ZnO:Al Thin Films

ZnO:Al thin film was synthesized using a sol-gel spin coating method.[19] Typically, 4 grams of zinc acetate dihydrate and Al 1.0 % was dissolved into 20 mL isopropanol and then stirred with a magnetic stirrer. After 10 minutes, 1.72 mL diethanolamine (DEA) was added slowly as a stabilizer agent. The gel solution was then dropped onto ITO glass substrate and then rotated by a spin coating with a speed of 5000 rpm. Finally, the sample was heated with temperature of 250 °C for 5 minutes to remove the excess liquid. Finally, the sample was annealed in an electric furnace with temperatures of 400, 450, 500, 550, and 600 °C for 5 hours.

2.2. Characterizations of ZnO:Al Thin Films

The crystal properties of ZnO:Al thin films were evaluated using X-ray diffractometer (LabX XRD-6100, Shimadzu) with Cu K_α radiation (40kV, 30mA) of wavelength. 1.54 Å. A field emission scanning electron microscopy (FE-SEM, JEOL 6500) with accelerating voltage of 15 kV and working distance of 10 mm was used to observe the surface morphology of the thin films. The optical properties of thin films were further investigated using UV-Vis spectrometer with both transmission and absorbance modes from the wavelength of 300 to 700 nm. Electrochemical impedance spectroscopy was performed using Biologic SP-300 Potentiostat. The characterizations were conducted in Indonesia and Taiwan.

2.3. Preparation of Dye Sensitizer

The extract of dye sensitizer was done by cutting red dragon fruit into small pieces and then put it into a beaker glass. After that, the red dragon fruit is crushed by mortar until smooth. Extraction was done by adding ethanol and then soaked for 24 hours in a dark place.[18] Finally, the extract was filtered using filter paper and stored it in a under dark place.

2.4. Fabrication of DSSC

The DSSC was fabricated by attaching a platinum counter electrode to a ZnO: Al thin film coated with dye from red dragon fruit which acted as a working electrode with a layer of separating surlyn. Sticking of surlyn was conducted by pressing the working electrode and the counter electrode under heating with at temperature of 70-80 ^{o}C to stick them perfectly.[20] The electrolyte was injected through a small hole found in the counter electrode.

2.5. Efficiency Measurement

Electrical testing was carried out by assembling an electrical circuit between the DSSC and digital multimeters as shown in Figure 1. [21] This test is based on the beam lighting method to determine the performance and efficiency of the cells obtained when the solar cell is exposed to light with a certain intensity at the top anode. DSSC outputs are open-circuit voltage (V_{oc}) and short circuit current (I_{sc}) DSSC. Then, the fill factor (FF) and the DSSC efficiency (η) were calculated.

Figure 1: Measurement efficiency of DSSC

3. RESULTS AND DISCUSSION

3.1. Crystal Structure of ZnO: Al Thin Film

The diffraction pattern of ZnO: Al thin film with variation of post-heating temperatures is shown in Figure 2. The result confirm that all samples have the same crystal structure of hexagonal wurtzite according to the database with JCPDF No. #36-1451.[22] All XRD pattern shows three peaks with (100), (002), and (101) planes where a (101) plane has the highest intensity indicating the prefer the crystal growth.

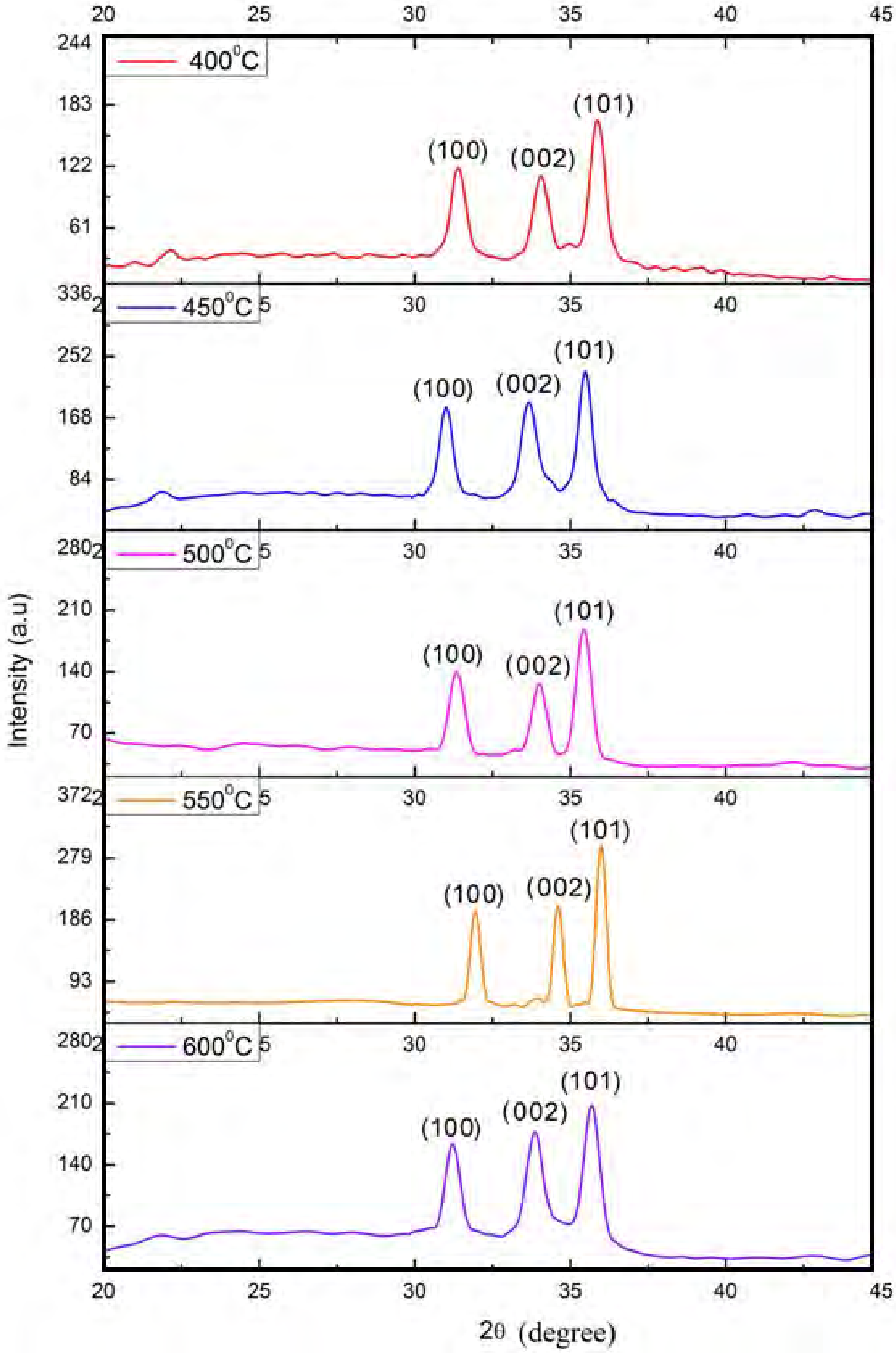

Figure 2: X-ray diffraction spectra of ZnO:Al thin films

Crystallite size of the samples with variation post-heating temperatures are calculated using the Scherrer's equation.[23]

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \quad (1)$$

Where, D= crystallite size, λ= wavelength, β= FWHM (full width half maximum), θ= diffraction angle.

Table 1 shows the crystal size increases from 16 - 41 nm along with an increase in post-heating temperature from 400 - 550^o C. This was because increasing heating temperature will make compaction increase and grow large granule due to the incorporation of small grains.[24] When the post-heating temperature was increased to 600 ^{o}C, the crystallite size decreased to 34 nm due to aluminium as dopant block the grain boundaries .[25]

Table 1: Crystal size ZnO:Al thin film with variation post-heating temperatures

Temperature (^{o}C)	Crystal size (nm)
400	16
450	21
500	39
550	41
600	34

3.2. SEM and EDS analyses of ZnO:Al Thin Film

Figure 3 shows scanning electron microscope images of ZnO:Al. The surface morphology of thin film contains a lot of tiny nanoparticle with homogenous distribution. It can be seen clearly that there is no obvious different of SEM images for different post-heating temperatures. The SEM images also exhibit that the grains totally cover the substrate without cracking and have a good interconnection between each particle. The average particle size of nanoparticles annealed at 400, 500 and 600 ^{o}C are 38±7, 50±10, and 66±12 nm, respectively. Energy disperse spectroscopy (EDS) analysis was further conducted to confirm the success of Al doped into ZnO. As shown in the Figure 3d, a representative EDS result exhibits the peak of Al at energy 1.5 KeV with atomic concentration of 0.99%. This analysis confirms that Al as an extrinsic dopant has been successfully doped into ZnO structure. The atomic concentrations of zinc (Zn) and oxygen (O) were 47.13% and 51.88 %, respectively.

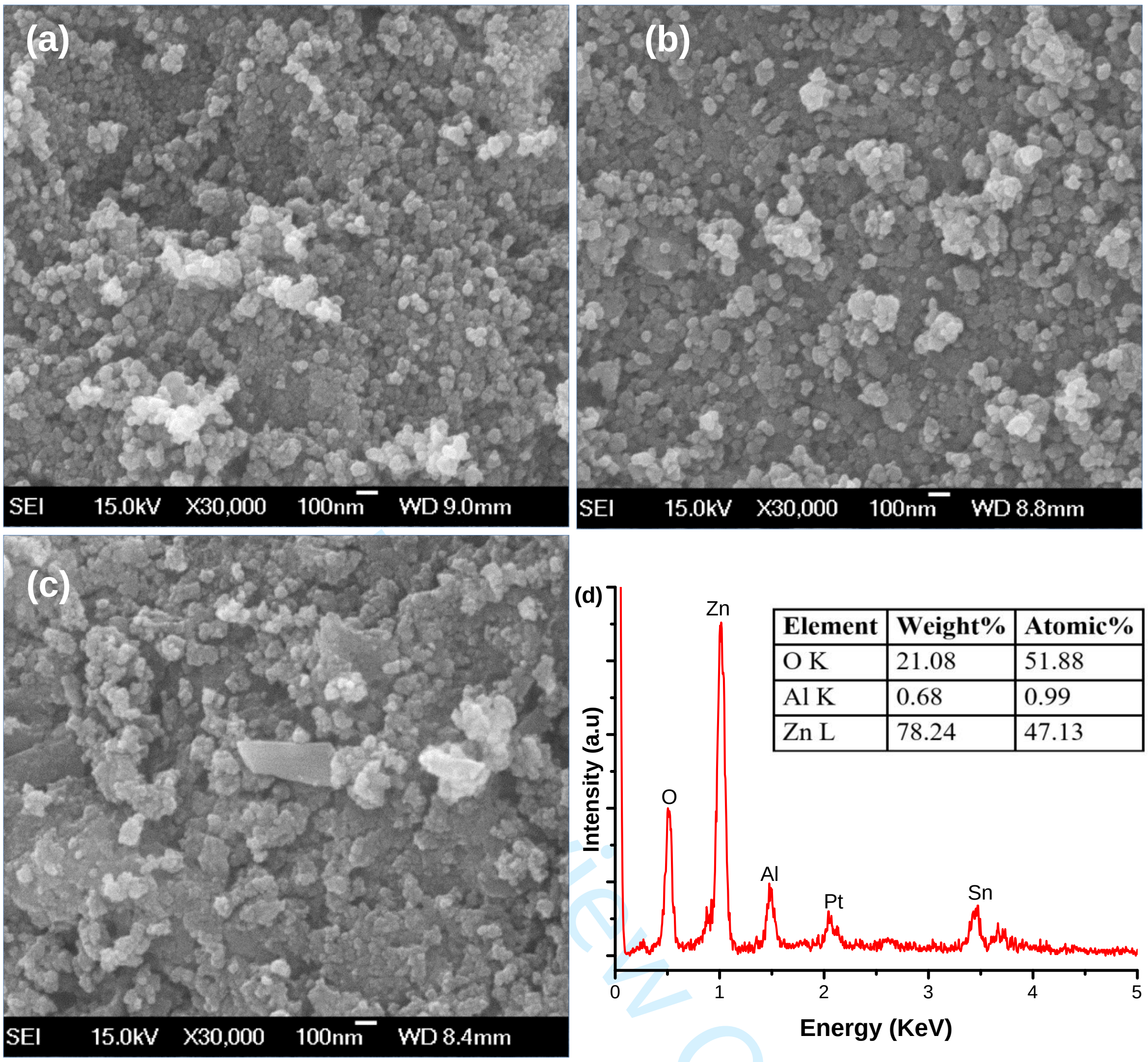

Figure 3: SEM images of ZnO:Al thin films (a) 400 °C, (b) 500 ºC , (c) 600 ºC and (d) Energy disperse spectra (EDS) to show the presence of Al

3.3. Optical Properties of ZnO:Al Thin Films

Figure 4 and Figure 5 exhibit the transmittance and absorbance spectra, respectively. The transmittance spectrum of the ZnO:Al thin films in Figure 4 shows a sharp increase in the transmittance value for all samples that occurs in the wavelength range of approximately 350 to 400 nm, which is the ultraviolet wavelength region. For ZnO:Al thin film samples heated at post-heating temperature, the transmittance value is about 75 - 80% at a wavelength of about 600 to 700 nm and the reduction in heating of 500 ºC. The high transmittance value of thin films is good and suitable for solar cell applications. Figure 5 shows the absorbance edges of the samples heated at temperatures of 450 and 550 ºC shift to a shorter wavelength region, while those of samples heated at post-heating temperatures of 500 and 600 °C shift to a longer wavelength region.

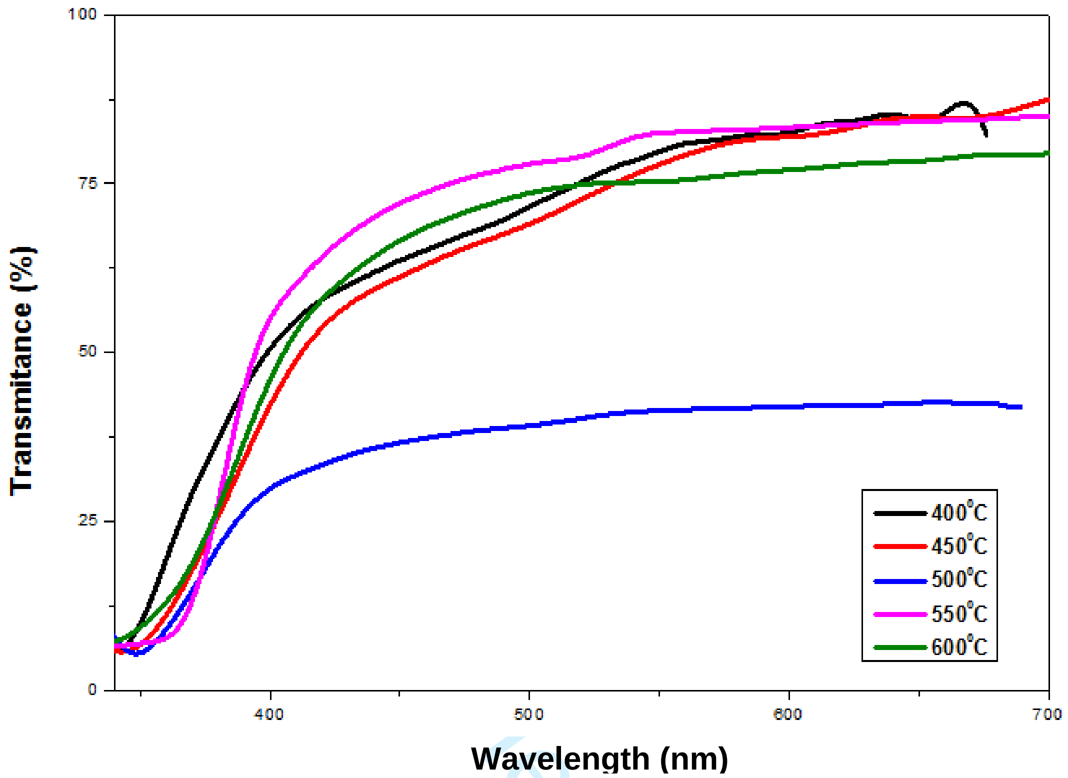

Figure 4: Transmittance spectrum of ZnO:Al thin films

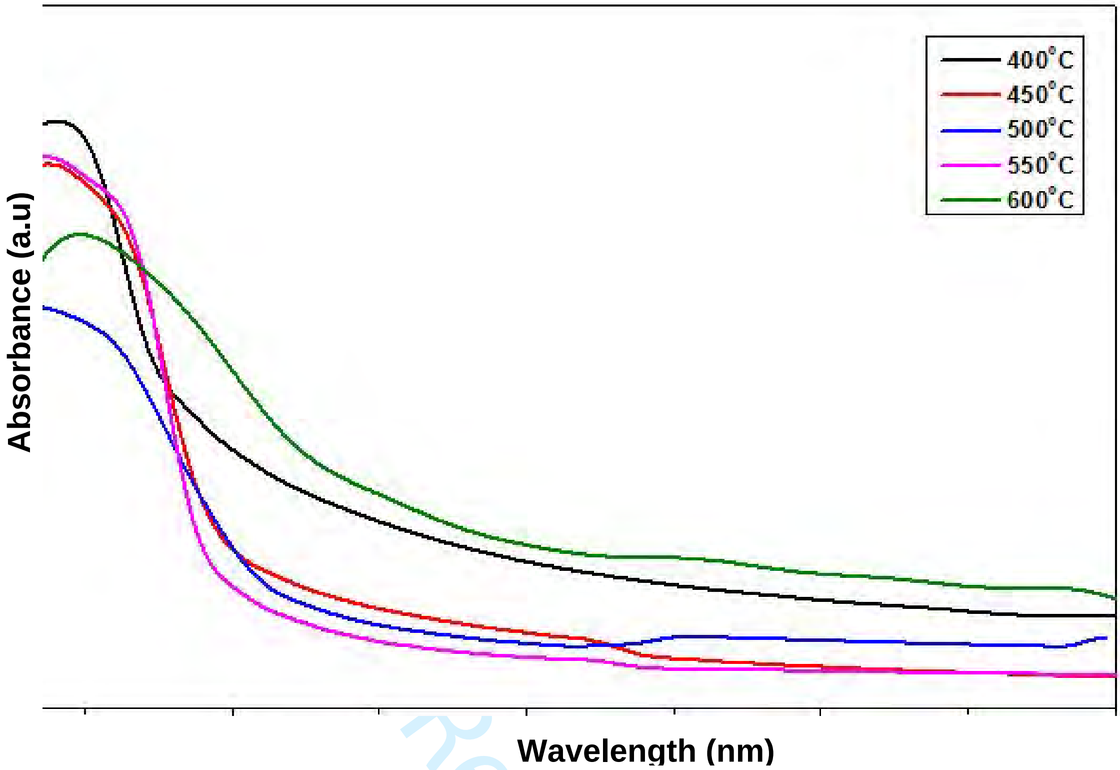

Figure 5: Absorbance Spectrum of ZnO:Al thin films

The energy bandgap of the ZnO:Al thin film is further calculated using equation (2).[26]

$$(\alpha h v)^2 = C_D(hv - E_{opt}) \quad (2)$$

Where, α= absorption coefficient, ν= frequency, C_D = proportionality constant, h = Planck's constant, and E_{opt} = optical bandgap.

Based on the Tauc Plot method in Figure 6, the energy bandgap of the ZnO:Al thin films with variation post-heating temperatures could be obtained. Table 2 lists that the energy bandgap value increases from 3.16 - 3.40 eV with increasing the post-heating temperature from 400 - 500 °C. When the post-heating temperature was increased to 550 and 600 °C, the energy bandgap value slightly decreased to3.20 eV. This phenomenon may be related to defects in thin film due to rise of heating temperature.[27]

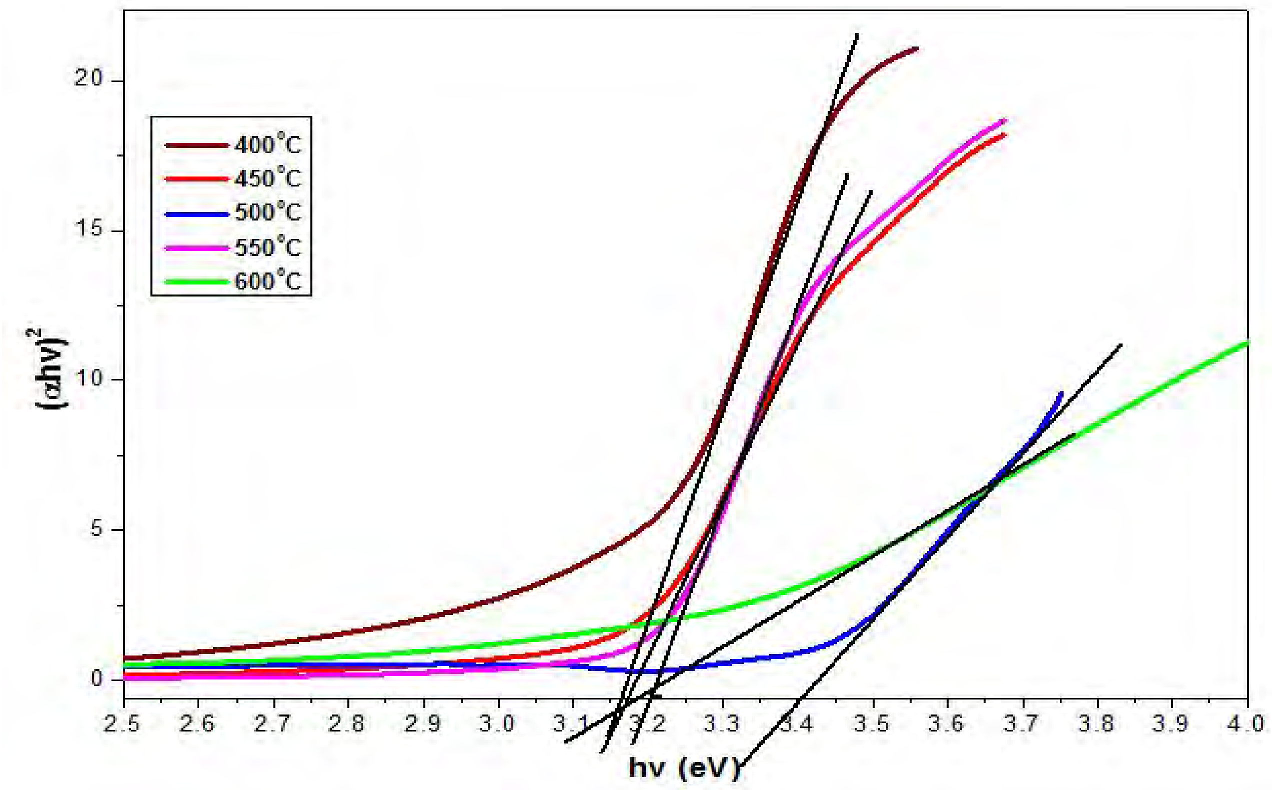

Figure 6: Energy bandgap of ZnO:Al thin films using Tauc Plot

Table 2: Energy bandgap of ZnO:Al thin films

Temperature (°C)	Bandgap (eV)
400	3.16
450	3.17
500	3.40
550	3.20
600	3.20

3.4. Dye Spectrum of Red Dragon Fruit Extract

The absorbance spectrum of red dragon fruit solution was tested with UV-Vis spectrophotometer. Figure 7 clearly shows that the red dragon fruit dye has the absorbance at UV and visible light range with peak absorbance of 254 and 570 nm, respectively. The result indicates that the extract of red dragon fruit has a great potential to be used as the dye sensitizer for DSSC device.

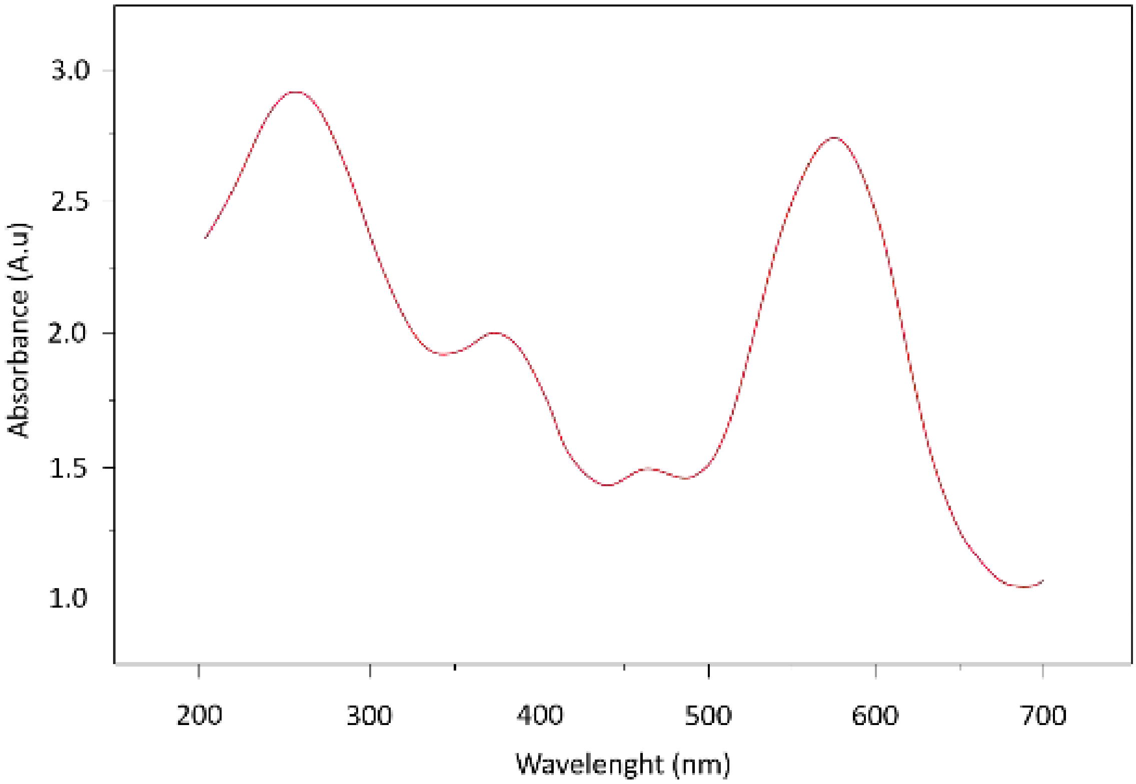

Figure 7: Absorbance of red dragon fruit dye

3.5. DSSC Efficiency

The efficiency can be obtained by comparing the power produced by the prototype DSSC with the power of light source (P_{in}), as shown in equation (3) and (4).

$$\eta = \frac{P_{max}}{P_{in}} x\ 100\% = FF \frac{J_{sc}\ x\ V_{oc}}{P_{in}} x\ 100\% \quad (3)$$

$$FF = \frac{J_{max}\ x\ V_{max}}{J_{sc}\ x\ V_{oc}} \quad (4)$$

Where, η = DSSC efficiency (%), J_{sc} = current density (mA), V_{oc} = Voltage (mV), P_{in} = Input power (mW), FF = Fill Factor.

As listed in Table 3, the efficiency of DSSC increases with the rise of post-heating temperature. The maximum efficiency is 0.398% at a temperature of 600 ^{o}C. The reasons for this could be explained. First, a better crystallinity as proved by XRD analysis. Second, the absorption spectra in Figure 5 exhibits that ZnO: Al with annealing temperature of 600 ^{o}C had the highest absorption in the visible light region among other temperatures. To further investigate a higher efficiency with a higher temperature, the electrochemical impedance spectra analysis (EIS) was conducted in electrolyte solution of potassium chloride (KCl, 1M). The EIS data can be used to evaluate the charge transfer property by comparing the diameter of that semicircle in Figure

8. The charge transfer resistance (R_{ct}) could be determined after fitting technique. The value of R_{ct} for heating at 600 °C is 6.5 kΩ, which is lower than at 500 °C (7.6 kΩ) or 400 °C (9.5 kΩ). Therefore, the other reason for maximum efficiency at 600 °C post-heating temperature is due to its lowest resistance that leading to most efficient charge transfer. We realize that presence efficiency is still relatively low but there is always room for improvement. Therefore, further research and development is needed to conduct in the future.

Table 3: Values of voltage, current density, power, fill factor and efficiency of DSSC

Temperature (°C)	V_{oc} (V)	J_{sc} (mA/cm^2)	P_{max} (W/cm^2)	FF (%)	η (%)
400	0.45	0.350	0.031	19.644	0.084
450	0.45	0.450	0.052	25.925	0.143
500	0.45	0.487	0.068	31.339	0.188
550	0.50	0.650	0.094	28.941	0.257
600	0.55	1.168	0.250	22.605	0.398

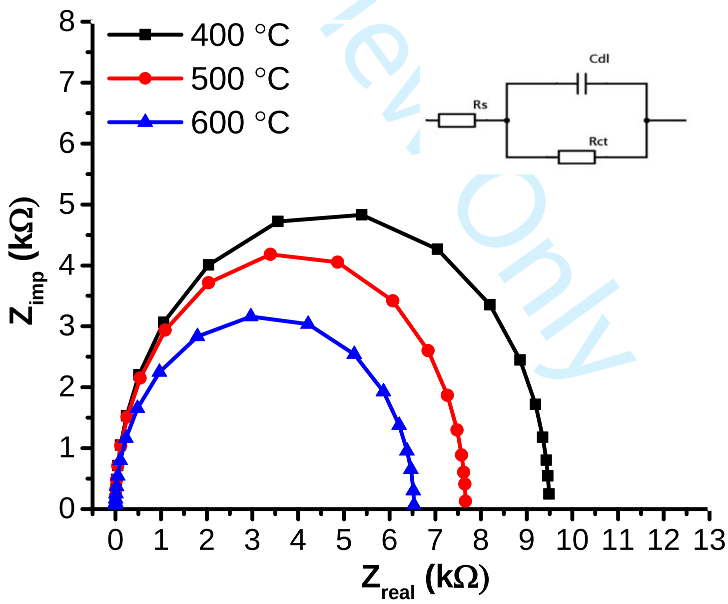

Figure 8: Electrochemical impedance spectra (EIS) of ZnO: Al thin films

4. CONCLUSION

The DSSC prototype has been successfully fabricated using ZnO:Al thin film and dye from red dragon fruit extract as working electrodes. The XRD analysis confirmed that all samples had the hexagonal wurtzite structure. The bandgap values of thin films were about of 3.16-3.40 eV. The surface morphology of ZnO:Al thin films was nanoparticle with particle size less than 100 nm. We found that the efficiency of DSCC gradually improved with increasing the post-heating temperature. ZnO: Al with post-heating temperature of 600 ^{o}C had the highest efficiency of 0.398%. The optimum efficiency was contributed by the better crystallinity, more efficient charge transfer, and higher absorption properties.

5. ACKNOWLEDGMENT

This work was supported by Indonesia Directorate of Research and Community Service (No. 027/UN33.8/LL/2018).

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Journal of Physical Science, Vol. 32(2), 57–70, 2021

Effect of Post-Heating Temperature on Efficiency of Dye-Sensitized Solar Cell with ZnO:Al Thin Films Prepared by Sol-Gel Spin Coating

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ABSTRACT: *Dye-sensitized solar cell (DSSC) has a great potential to convert solar light into electricity. In this article, a prototype of DSSC had been successfully fabricated using ZnO:Al thin film and dye from red dragon fruit as a working electrode. ZnO:Al thin films were prepared by a sol-gel spin coating method with variation of post-heating temperatures. The XRD result confirms that all ZnO:Al thin films have a hexagonal structure with crystal sizes of 16 nm to 41 nm. SEM analysis showed the nanoparticles with particle size of 30 nm to 80 nm. The bandgap ranges from 3.16 eV to 3.40 eV. The EIS analysis reveals that charge transfer resistance greatly decreases with the rise of temperature. The efficiency of DSSC gradually improved with increasing the post-heating temperature. ZnO:Al with a post-heating temperature of 600°C had the highest efficiency of 0.398%.*

Keywords: dye sensitised solar cell, ZnO:Al thin films, sol-gel spin coating, red dragon fruit extract

1. INTRODUCTION

Dye-sensitized solar cell (DSSC) is one of the solar cell types that originally invented by Gratzel in 1991.[1] The fabrication of DSSC is low cost and environmentally friendly. It consists of several components, namely, semiconductor oxide, dye, counter electrode and electrolyte.[2] The engineering of ZnO semiconductor for the DSSC working electrode is promising because it has an energy bandgap of 3.37 eV and a binding energy of 60 meV which allows direct absorption of UV radiation.[3] ZnO thin film has poor electrical characteristic like having a low conductivity value of 6.24×10^{-7} $(\Omega.cm)s^{-1}$.[4] To enhance its physical, optical and electrical properties, it is often doped with extrinsic dopant from group IIIA such as B, Al and Ga as foreign element doped into the ZnO structure.[5] Aluminium (Al) is chosen as a doping agent because it can increase the electrical conductivity of ZnO thin films to an order of 10^5 Ω.cm.[6] There are several techniques to fabricate thin film such as molecular beam epitaxy, radio frequency (RF) magnetron sputtering, pulsed laser deposition, spray pyrolysis, physical vapour deposition, and sol-gel spin coating.[7–12] A sol-gel spin coating method has several advantages, including not using a high vacuum space, low cost, homogeneous composition, controllable layer thickness and great microstructure.[13]

Islam et al. studied Al-doped ZnO and they found that the energy bandgap value was affected by the doping concentrations.[14] The crystal size, transmittance and energy bandgap increase with the increasing of heating temperature.[15] The efficiency of DSSC is not only influenced by Al concentration but also annealing temperature.[16,17] Recently, Bekele et al. had successfully utilised the root extract of *Kniphofia schemperi* as the natural dye for DSSC.[18] Based on these considerations, it is interested to conduct research on DSSC using Al-doped ZnO thin film prepared by a sol-gel spin coating method with variation of post-heating temperatures and extract red dragon fruit as the natural dye sensitized.

2. EXPERIMENTAL

2.1 Synthesis of ZnO:Al Thin Films

ZnO:Al thin film was synthesised using a sol-gel spin coating method.[19] Typically, 4 g of zinc acetate dihydrate and Al 1.0 % was dissolved into 20 ml isopropanol and then stirred with a magnetic stirrer. After 10 min, 1.72 ml diethanolamine (DEA) was added slowly as a stabiliser agent. The gel solution was then dropped onto indium tin oxide (ITO) glass substrate and then rotated by a spin coating with a speed of 5,000 rpm. Finally, the sample was heated with temperature of 250°C for 5 min to remove the excess liquid. Finally, the sample was annealed in an electric furnace with temperatures of 400°C, 450°C, 500°C, 550°C and 600°C for 5 h.

2.2 Characterisations of ZnO:Al Thin Films

The crystal properties of ZnO:Al thin films were evaluated using X-ray diffractometer (LabX XRD-6100, Shimadzu) with Cu K_α radiation (40 kV, 30 mA) of wavelength 1.54 Å. A field emission-scanning electron microscopy (FE-SEM, JEOL 6500) with accelerating voltage of 15 kV and working distance of 10 mm was used to observe the surface morphology of the thin films. The optical properties of thin films were further investigated using UV-visible (UV-vis) spectrometer with both transmission and absorbance modes from the wavelength of 300 nm to 700 nm. Electrochemical impedance spectroscopy was performed using Biologic SP-300 Potentiostat. The characterisations were conducted in Indonesia and Taiwan.

2.3 Preparation of Dye Sensitizer

The extract of dye sensitizer was done by cutting red dragon fruit into small pieces and then put it into a beaker glass. After that, the red dragon fruit is crushed by mortar until smooth. Extraction was done by adding ethanol and then soaked for 24 h in a dark place.[18] Finally, the extract was filtered using filter paper and stored in a under dark place.

2.4 Fabrication of DSSC

The DSSC was fabricated by attaching a platinum counter electrode to a ZnO:Al thin film coated with dye from red dragon fruit which acted as a working electrode with a layer of separating surlyn. Sticking of surlyn was conducted by pressing the working electrode and the counter electrode under heating with temperature of 70°C to 80°C to stick them perfectly.[20] The electrolyte was injected through a small hole found in the counter electrode.

2.5 Efficiency Measurement

Electrical testing was carried out by assembling an electrical circuit between the DSSC and digital multimeters as shown in Figure 1.[21] This test is based on the beam lighting method to determine the performance and efficiency of the cells obtained when the solar cell is exposed to light with a certain intensity at the top anode. DSSC outputs are open-circuit voltage (V_{oc}) and short-circuit current (I_{sc}) DSSC. Then, the fill factor (FF) and the DSSC efficiency (η) were calculated.

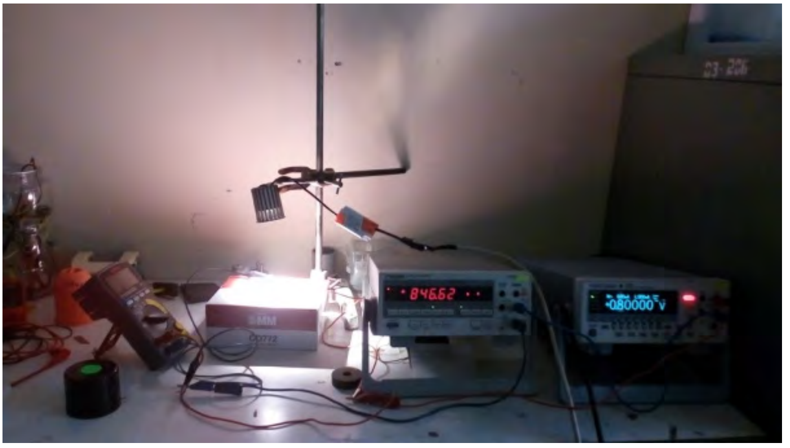


Figure 1: Measurement efficiency of DSSC.

3. RESULTS AND DISCUSSION

3.1 Crystal Structure of ZnO:Al Thin Film

The diffraction pattern of ZnO:Al thin film with variation of post-heating temperatures is shown in Figure 2. The result confirm that all samples have the same crystal structure of hexagonal wurtzite according to the database with JCPDF No. #36-1451.[22] The XRD pattern shows three peaks with (100), (002) and (101) planes where a (101) plane has the highest intensity indicating the preferred crystal growth.

Crystallite size of the samples with variation post-heating temperatures are calculated using the Scherrer's equation.[23]

$$D = \frac{0.9\,\lambda}{\beta \cos \theta} \tag{1}$$

Where, D = crystallite size, λ = wavelength, β = FWHM (full width half maximum), θ = diffraction angle.

Table 1 shows the crystal size increases from 16 nm to 41 nm along with an increase in post-heating temperature from 400°C to 550°C. This was because increasing heating temperature will make compaction increase and grow large granule due to the incorporation of small grains.[24] When the post-heating temperature was increased to 600°C, the crystallite size decreased to 34 nm due to aluminium as dopant block the grain boundaries.[25]

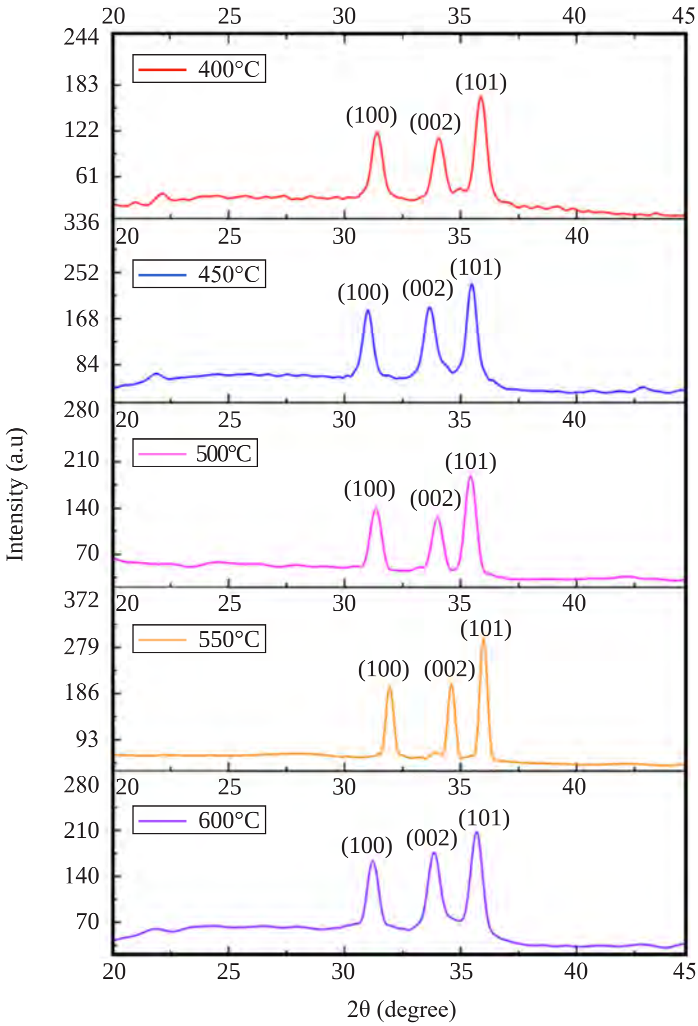


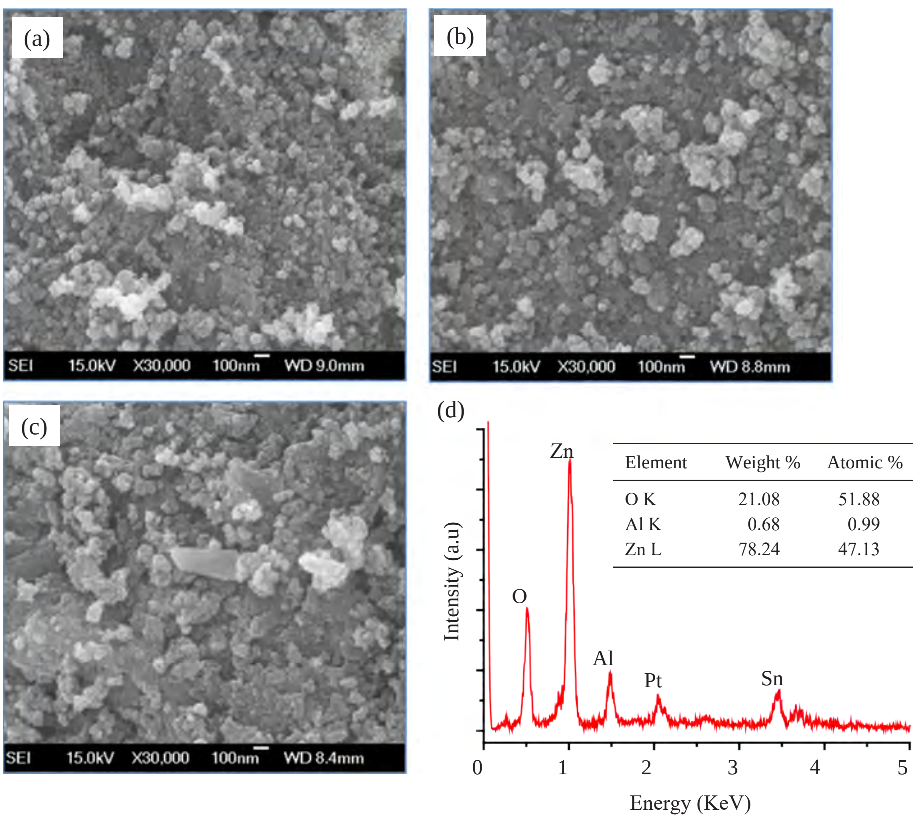
Figure 2: X-ray diffraction spectra of ZnO:Al thin films.

Table 1: Crystal size ZnO:Al thin film with variation post-heating temperatures

Temperature (°C)	Crystal size (nm)
400	16
450	21
500	39
550	41
600	34

3.2 SEM and EDS Analyses of ZnO:Al Thin Film

Figure 3 shows SEM images of ZnO:Al. The surface morphology of thin film contains a lot of tiny nanoparticles with homogenous distribution. It can be seen clearly that there is no obvious different of SEM images for different post-heating temperatures. The SEM images also exhibit that the grains totally cover the substrate without cracking and have a good interconnection between each particle. The average particle size of nanoparticles annealed at 400°C, 500°C and 600°C are 38±7 nm, 50±10 nm and 66±12 nm, respectively. Energy disperse spectroscopy (EDS) analysis was further conducted to confirm the success of Al-doped into ZnO. As shown in Figure 3(d), a representative EDS result exhibits the peak of Al at energy 1.5 KeV with atomic concentration of 0.99%. This analysis confirms that Al as an extrinsic dopant has been successfully doped into ZnO structure. The atomic concentrations of zinc (Zn) and oxygen (O) were 47.13% and 51.88%, respectively.



Element	Weight %	Atomic %
O K	21.08	51.88
Al K	0.68	0.99
Zn L	78.24	47.13

Figure 3: SEM images of ZnO:Al thin films at (a) 400°C, (b) 500°C, (c) 600°C and (d) EDS to show the presence of Al.

3.3 Optical Properties of ZnO:Al Thin Films

Figures 4 and 5 exhibit the transmittance and absorbance spectra, respectively. The transmittance spectrum of the ZnO:Al thin films in Figure 4 shows a sharp increase in the transmittance value for all samples that occurs in the wavelength range of approximately 350 nm to 400 nm, which is the ultraviolet wavelength region. For ZnO:Al thin film samples heated at post-heating temperature, the transmittance value is about 75% to 80% at a wavelength of about 600 nm to 700 nm and the reduction in heating of 500°C. The high transmittance value of thin films is good and suitable for solar cell applications. Figure 5 shows the absorbance edges of the samples heated at temperatures of 450°C and 550°C shift to a shorter wavelength region, while those of samples heated at post-heating temperatures of 500°C and 600°C shift to a longer wavelength region.

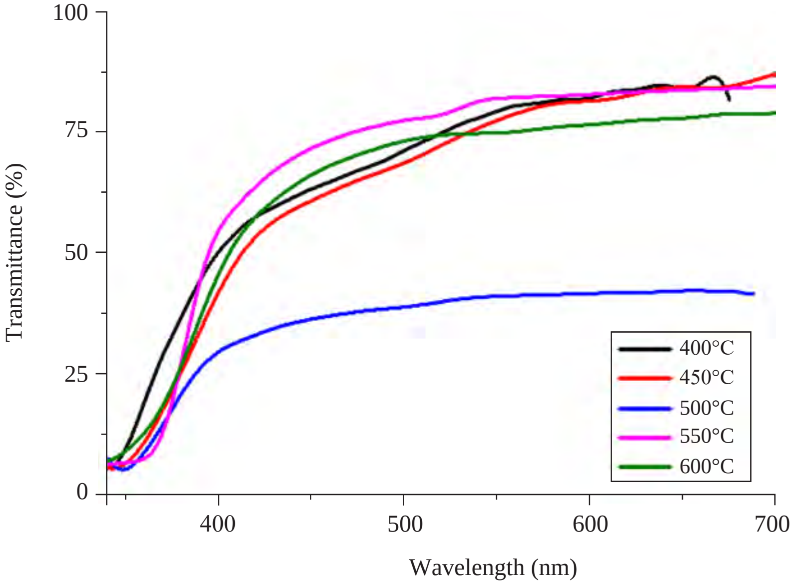


Figure 4: Transmittance spectrum of ZnO:Al thin films.

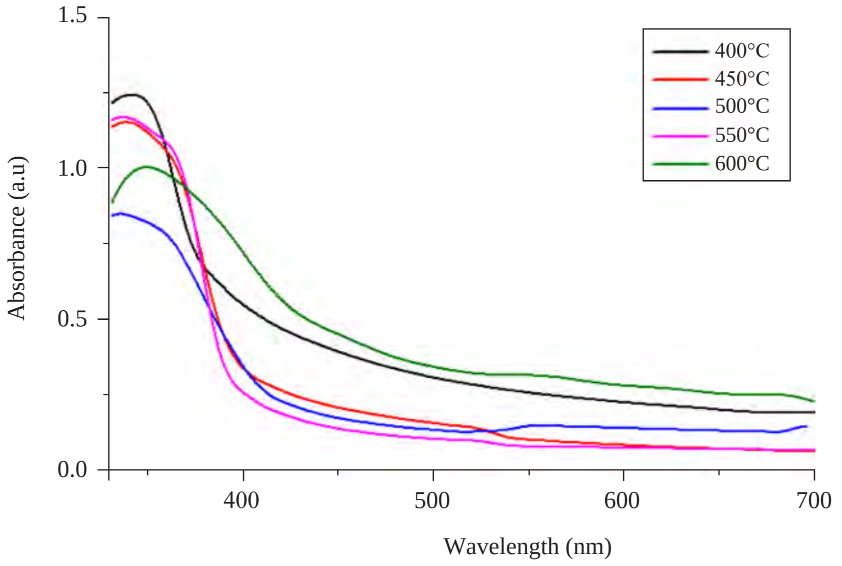


Figure 5: Absorbance spectrum of ZnO:Al thin films.

The energy bandgap of the ZnO:Al thin film is further calculated using Equation 2.[26]

$$(\alpha hv)^2 = C_D\,(hv - E_{opt}) \qquad (2)$$

Where, α = absorption coefficient, v = frequency, C_D = proportionality constant, h = Planck's constant and E_{opt} = optical bandgap.

Based on the Tauc Plot method in Figure 6, the energy bandgap of the ZnO:Al thin films with variation post-heating temperatures could be obtained. Table 2 lists that the energy bandgap value increases from 3.16 eV to 3.40 eV with increasing the post-heating temperature from 400°C to 500°C. When the post-heating temperature was increased to 550°C and 600°C, the energy bandgap value slightly decreased to 3.20 eV. This phenomenon may be related to defects in thin film due to rise of heating temperature.[27]

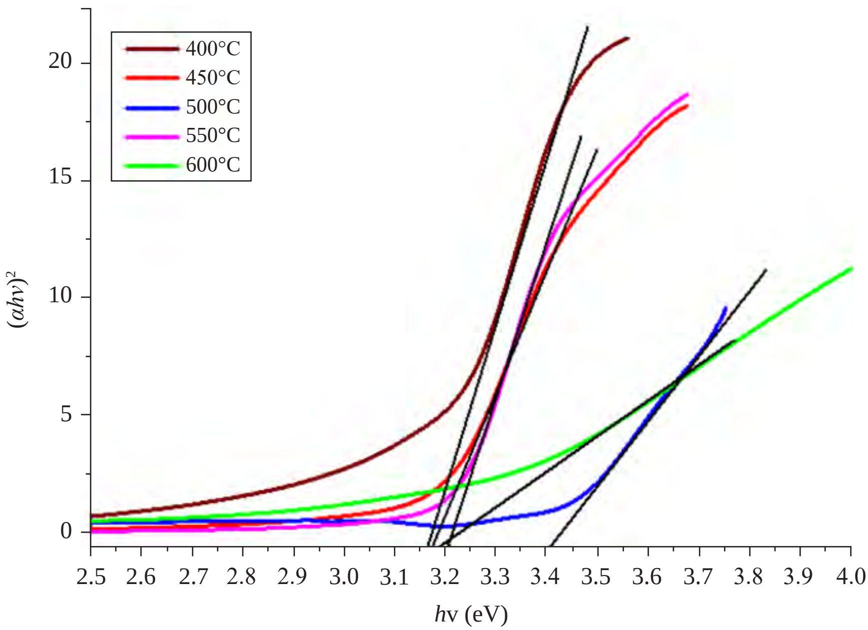


Figure 6: Energy bandgap of ZnO:Al thin films using Tauc Plot.

Table 2: Energy bandgap of ZnO:Al thin films.

Temperature (°C)	Bandgap (eV)
400	3.16
450	3.17
500	3.40
550	3.20
600	3.20

3.4 Dye Spectrum of Red Dragon Fruit Extract

The absorbance spectrum of red dragon fruit solution was tested with UV-vis spectrophotometer. Figure 7 shows that the red dragon fruit dye has the absorbance at UV and visible light range with peak absorbance of 254 nm and 570 nm, respectively. The result indicates that the extract of red dragon fruit has a great potential to be used as the dye sensitizer for DSSC device.

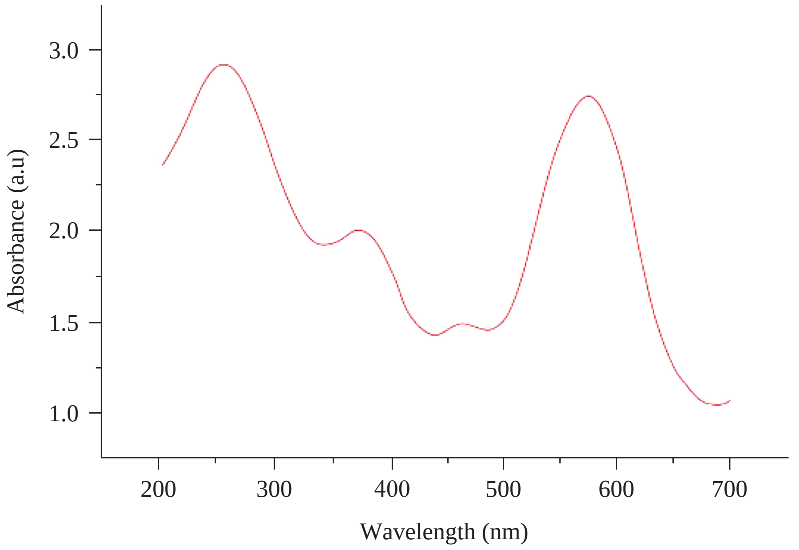


Figure 7: Absorbance of red dragon fruit dye.

3.5 DSSC Efficiency

The DSSC efficiency can be obtained by comparing the power produced by the prototype DSSC with the power of light source (P_{in}), as shown in Equations 3 and 4.

$$\eta = \frac{P_{max}}{P_{in}} \times 100\% = FF \frac{J_{SC} \times V_{OC}}{P_{in}} \times 100\% \quad (3)$$

$$FF = \frac{J_{max} \times V_{max}}{J_{SC} \times V_{OC}} \quad (4)$$

Where, η = DSSC efficiency (%), J_{sc} = current density (mA), V_{oc} = voltage (mV), P_{in} = input power (mW) and FF = fill factor.

As listed in Table 3, the efficiency of DSSC increases with the rise of post-heating temperature. The maximum efficiency is 0.398% at a temperature of 600°C. The reasons for this could be explained: first, a better crystallinity as proved by XRD analysis; and second, the absorption spectra in Figure 5 exhibits that ZnO:Al with annealing temperature of 600°C had the highest absorption in the visible light region among other temperatures. To further investigate the higher efficiency with a higher temperature, the electrochemical impedance spectra (EIS) analysis was conducted in electrolyte solution of potassium chloride (KCl, 1M). The EIS data can be used to evaluate the charge transfer property by comparing the diameter of that semicircle in Figure 8. The charge transfer resistance (R_{ct}) could be determined after fitting technique. The value of R_{ct} for heating at 600°C is 6.5 kΩ, which is lower than at 500°C (7.6 kΩ) or 400°C (9.5 kΩ). Therefore, the other reason for maximum efficiency at 600°C post-heating temperature is due to its lowest resistance that leading to most efficient charge transfer. We realised that presence efficiency is still relatively low but there is always room for improvement. Therefore, further research and development is needed to conduct in the future.

Table 3: Values of voltage, current density, power, fill factor and efficiency of DSSC.

Temperature (°C)	V_{oc} (V)	J_{sc} (mA/cm^2)	P_{max} (W/cm^2)	FF (%)	η (%)
400	0.45	0.350	0.031	19.644	0.084
450	0.45	0.450	0.052	25.925	0.143
500	0.45	0.487	0.068	31.339	0.188
550	0.50	0.650	0.094	28.941	0.257
600	0.55	1.168	0.250	22.605	0.398

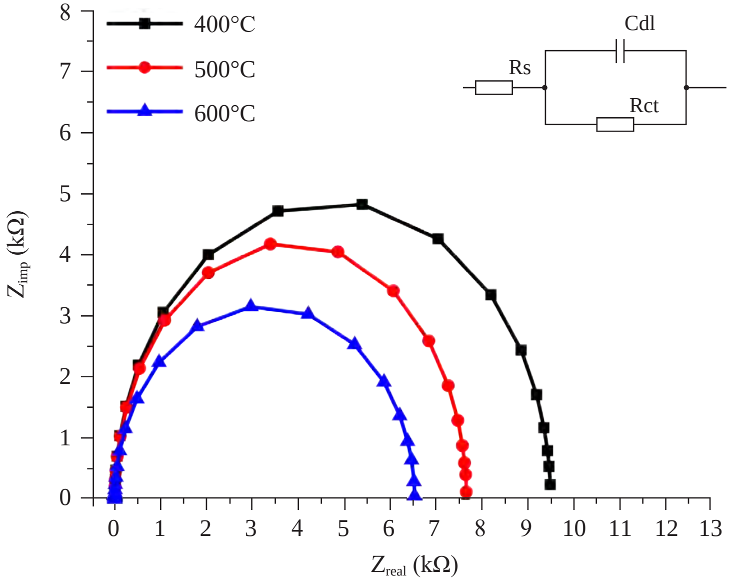


Figure 8: EIS of ZnO:Al thin films.

4. CONCLUSION

The DSSC prototype has been successfully fabricated using ZnO:Al thin film and dye from red dragon fruit extract as working electrodes. The XRD analysis confirmed that all samples had the hexagonal wurtzite structure. The bandgap values of thin films were about of 3.16 eV to 3.40 eV. The surface morphology of ZnO:Al thin films was nanoparticle with particle size less than 100 nm. We found that the efficiency of DSCC gradually improved with increasing the post-heating temperature. ZnO:Al with post-heating temperature of 600°C had the highest efficiency of 0.398%. The optimum efficiency was contributed by the better crystallinity, more efficient charge transfer and higher absorption properties.

5. ACKNOWLEDGEMENTS

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