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ผลงานทางวิชาการ

นำเสนอผลงานแบบโปสเตอร์ในการประชุมวิชาการ "The 1^{st} ASEAN Plus Three Graduate Research Congress (AGRC 2012)" จัดโดย บัณฑิตวิทยาลัย มหาวิทยาลัยเชียงใหม่ ระหว่างวันที่ 1 – 2 มีนาคม 2555 ที่ The Empress Convention Center, The Empress Hotel, Chiang Mai, Thailand โดยมีรายละเอียด Proceeding ดังนี้

Effect of ZnO Anti-reflection Layer on Efficiency of ZnO Dye-sensitized Solar Cells

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Abstract

In this research, we investigated the effects of ZnO thin films as an anti-reflection layer for ZnO dye-sensitized solar cells (DSSCs). ZnO thin films were prepared by thermal evaporation and sparking technique with 0.5, 1.5 and 2.5 5 sparking cycles (1 cycles = 261.24 s) onto glass substrates. Surface morphology were investigated by field emission scanning electron microscopy (FE-SEM) and showed that sparking ZnO thin films have roughness surface with nanoparticles compared with thermal evaporation. The optical properties were measured via transmittance and reflectance using UV-vis spectroscopy. The optical reflective index and thickness of the films were obtained via ellipsometry. It was found that the films prepared by sparking technique can reduce reflection and also increase transmission of light more than that of the reference film and the film prepared by thermal evaporation. Also, the optical reflective index of the sparking films has value between that of the substrate and air. The thicknesses of sparking films are in the range of 20-100 nm. For the ZnO DSSCs assembly, the photoelectrochemical parameters of DSSCs were monitored under stimulated sunlight AM 1.5 with the radiant power of 100 mW/cm^2. The results showed that the solar cell with sparking film 1.5 cycles has a short circuit current density (J_{sc}) of 4.34 mA/cm^2 and the maximum efficiency (E_{ff}) of 0.8%, compared with the reference cell of 3.00 mA/cm^2, 0.43%, respectively. Moreover, the DSSCs with sparking films exhibited higher efficiency, suggesting an efficiency improvement due to anti-reflection layer**.**

Keywords

Anti-reflection coating, Dye-sensitized Solar Cells, Sparking technique, Thermal evaporation, ZnO thin films

Introduction

Recently, there is a promising type of solar cells called Dye-Sensitized Solar Cells (DSSCs) with less complicated production process and low production costs [1]. However, the conversion efficiency of DSSCs is still low because of some problems, such as the reflection of light on the skin, the recombination and trap carriers in the material and surface, power dispersion due to the resistance of cell (material, metal, electrode, etc) [2].

To improve the efficiency of solar cells, the loss mechanisms mentioned above have to be overcome. In this research, we focused on anti-reflection surface factor. The anti-reflection coating layer (ARCs) is transparent optical film applied to the surface of the lens and the equipment in order to reduce the reflection of light [3]. In solar cell technology, many methods were applied in coating process of ARCs on to the surface of silicon, $CuInGaSe_2$ (CIGS) and organic solar cell to improve the efficiency, such as dimond-like carbon film by the RF-PECVD (plasma enhanced chemical vapor deposition) [4], moth eye nano-scale coatings on the glass surface [5], PVC film moth eye pattern of nano-scale by hot embossing method [6], SiO_2 by thermal oxidation, ZnO/TiO_2 by sputtering deposition method and porous silicon (PS) by the electro-chemical etching method [7], ZnO nanorod by hydrothermal process [8], and bottom-up technique using an aqueous solution method [9].

Also, we can reduce the reflection and increase the transmission of light at the glass surface. When light penetrates to the dye molecules, it will increase the efficiency of DSSCs because the total flux of photons to photocurrent through the electrode were increased. This will result in increasing of short circuit current density (J_{sc}) as shown in the following equations (1)-(3) [2], [10], [11]:

$$J_{sc} = \int_0^{\infty} Q(E)N(E)dE \qquad (1)$$

$$J_{sc} = \int_{\lambda_1}^{\lambda_2} qF(\lambda)IPCE(\lambda)d\lambda \qquad (2)$$

$$J_{sc} = \int_{\lambda_1}^{\lambda_2} qF(\lambda)\left[1-R(\lambda)\right]Q_i(\lambda)d\lambda \qquad (3)$$

where Q(E) is a quantum efficiency for photons with energy E, N(E) is the flux of photons with energies in the range of E and E + dE, q is the charge of electrons, F(λ) is spectral solar flux (flux of the solar spectrum), IPCE(λ) is the external quantum efficiency, R(λ) is reflection of light, $Q_i(\lambda)$ is internal quantum efficiency. The Efficiency (E_{ff}) of the variation of solar energy can be calculated from the following equation (4), (5):

$$E_{ff} = \frac{I_{max}V_{max}}{P_{in}} = \frac{I_{sc}V_{oc}FF}{P_{in}} \qquad (4)$$

$$FF = \frac{I_{max}V_{max}}{I_{sc}V_{oc}} \qquad (5)$$

where the fill factor (FF) is a measure of the quality of the equipment used, P_{in} is the sum of the radiation incident on the solar cell, I_{sc} is the short circuit current, V_{oc} is the open circuit voltage, I_{max} is the current at maximum power, V_{max} is the voltage at maximum power.

In this work, the effects of ZnO thin film anti-reflection layer of light for DSSCs were investigated. ZnO thin films were prepared by thermal evaporation and the sparking process on the glass substrate.

Methodology/Experimental design

ZnO thin films sample were prepared by thermal evaporation [12] and sparking technique [13] onto glass substrates. The glass substrates were sonically cleaned in acetone, distilled water and ethanol, and then dried at room temperature. In thermal evaporation, high purity ZnO powder was used as source and the distance between source and substrate was 10 cm. The heating filament was a convention tungsten boat. The pressure was evacuated until a vacuum of about $1x10^{-5}$ torr was achieved. Sparking technique was prepared from the two sharp tips zinc wire (ϕ 0.38 mm, purity 99.97 %.) with nine couples of tips in the sparking plate. The tips were horizontally at 3 mm spacing and 2 mm above the center of the substrate. The sparking process occurred with

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apply high voltage when the 25 nF capacitor was changed to 10 kV for two sharp tips and connected it by rotating control switch. The experiment was done repeatedly 0.5 cycles, 1.5 cycles, 2.5 cycles in ambient air (1 cycles = 261.24 s). Then the samples from two techniques were annealed at 450°C for 1 hr in air.

The surface morphology was characterized by field emission scanning electron microscopy (FE-SEM). The optical properties were studied by measurement of transmittance and reflectance via UV-vis spectroscopy. In addition, the refractive index and films thickness were obtained via ellipsometry. For ZnO DSSC preparation, the DSSC structures are composed of ZnO thin films/glass/ fluorine-doped tin oxide (FTO)/ZnO as a photoelectrode, Eosin Y as a dye sensitizer, iodine/iodide solution as an electrolyte and Pt / fluorine-doped tin oxide (FTO)/glass as a counterelectrode as shown in Fig 1. Then, the photoelectrochemical characteristics of the DSSCs were tested under stimulated sunlight AM 1.5 with the radiant power of 100 mW/cm^2.

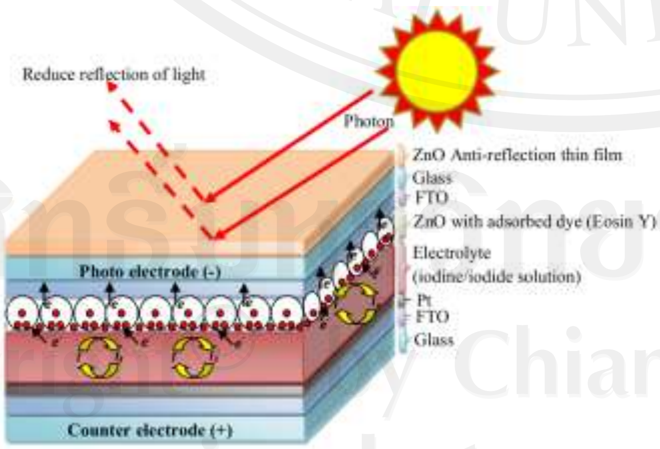

Fig.1 Structure of DSSCs with anti-reflection layer

Results and Discussion

Fig.2(a) showed FE-SEM image of ZnO thin film which prepared by thermal evaporation. The topography surface roughness and grain size of the evaporation films are bigger than those of the sparking films (Fig.2(b)-(d)). Fig.2(b)-(d) showed porosity with nanoparticle structure of ZnO film of different sparking cycles. The average of nanoparticle size is about 20-30 nm, which depends on annealing temperature [13]. Also, density of nanoparticle increases with number of sparking cycles as shown in Fig.2.

Fig.3 showed the optical transmittance spectra of the films as a function of wavelength. The optical transmittance in the visible region decreased for thermal evaporation coating film and increased for sparking films. Especially, the sparking films of 0.5 cycles and 1.5 cycles showed an increase of light transmission compared with reference and evaporation film. An inset in Fig.3 showed the plot of $(\alpha h\nu)^2$ versus energy $h\nu$ in order to obtain energy gap (E_g), where α is the absorbance coefficient and $h\nu$ is the photon energy [14]. The E_g of 3.25, 3.25, 3.24, and 3.20 eV were estimated for the evaporation, sparking 2.5 cycles, sparking 1.5 cycles and sparking 0.5 cycles, respectively. The E_g of the samples slightly increased with higher film thickness.

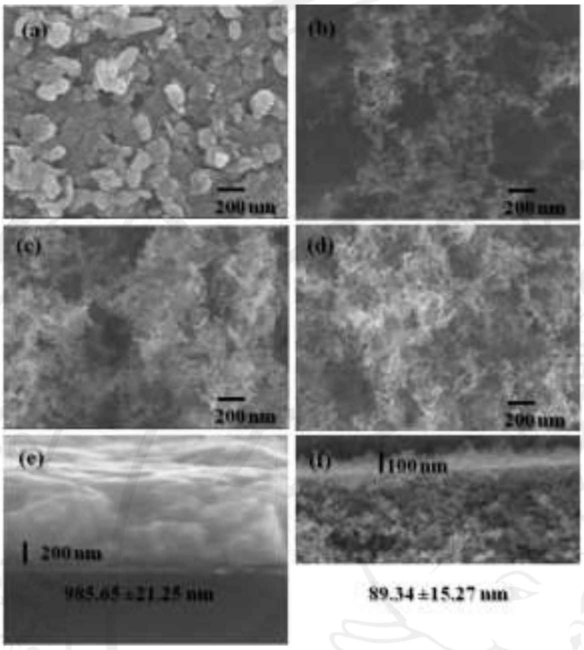

Fig.2 FE-SEM image of ZnO thin films prepared (a) by thermal evaporation and by sparking process at (b) 0.5cycles, (c) 1.5 cycles, and (d) 2.5 cycles. And the cross section image of ZnO thin films prepared (e) by thermal evaporation, (f) sparking process 1.5 cycles.

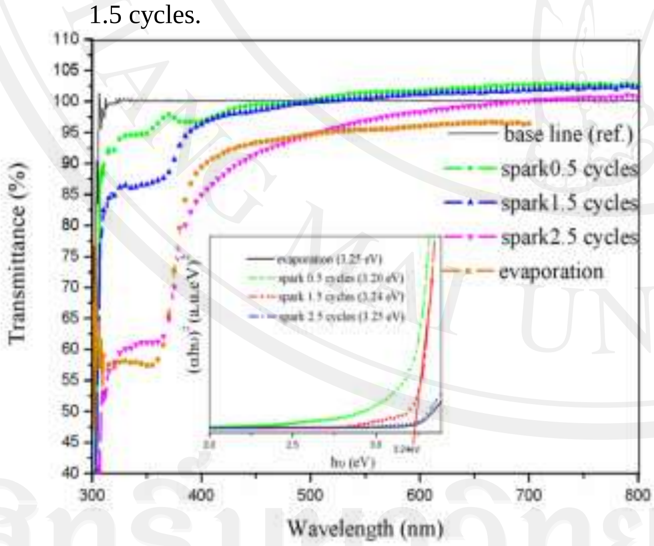

Fig.3. Optical transmittance spectra of ZnO thin films prepared by thermal evaporation and sparking technique at 0.5, 1.5, and 2.5 sparking cycles. Inset is the plot for estimation of the energy gaps of the films.

Fig.4 showed the optical reflectance spectra of (a) ZnO thin film substrate prepared by evaporation and sparking at 0.5, 1.5, 2.5 cycles together with glass substrate. It was found that the sparking films clearly reduce light reflection and increased the light trapping upon wide wavelength compared with thermal evaporation film and reference. Moreover, the figure showed that sparking 1.5 cycles is the lowest reflectance of light. Fig.4 (b) showed the optical reflectance spectra of DSSCs coated with ZnO thin films which act as anti-reflection coating layer (ARCs). It was found that the reflectivity of films of the DSSCs was slightly increased than that of the film substrate. However, the sparking film clearly reduces light reflection compared with thermal evaporation film and reference film. Thus, ZnO ARCs prepared by sparking process can reduce reflection and increase transmission of light. In addition, fig.4 showed oscillation of reflectance because of the effect of interference of light at interface of ZnO thin film and substrate, due to the film roughness. Also, it makes constructive interference and destructive interference of light [3].

Fig.5. shows the plot of the refractive index of ZnO thin films on FTO glass substrate versus wavelength. The result showed the refractive index of sparking films lower than that of substrate and evaporation film. Especially, sparking 1.5 cycles and sparking 2.5 cycles have refractive index value between that of the substrate and air. Usually, anti-reflection coating must have a refractive index approximately midway between that of air ($n \approx 1$) and the solar selective absorber [15].

ZnO film thickness was shown in table 1. The evaporation ZnO thin film is thicker than sparking films and thickness of sparking film increase

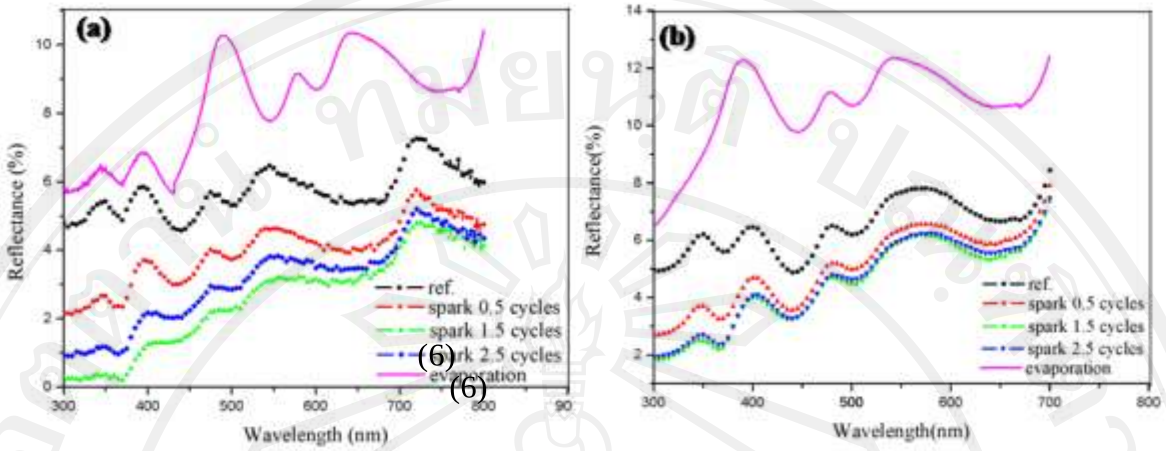

Fig.4 Reflection spectra of (a) ZnO thin films prepared by thermal evaporation and by sparking technique at 0.5, 1.5, 2.5 sparking cycles and (b) DSSCs composed of coated ZnO thin films as an anti-reflection layer.

with increasing amount of sparking cycle. The thickness of ARCs is chosen to produce destructive interference of light form interface to reduce the light reflection, so that the wavelength in the film is one quarter the wavelength of the incoming.

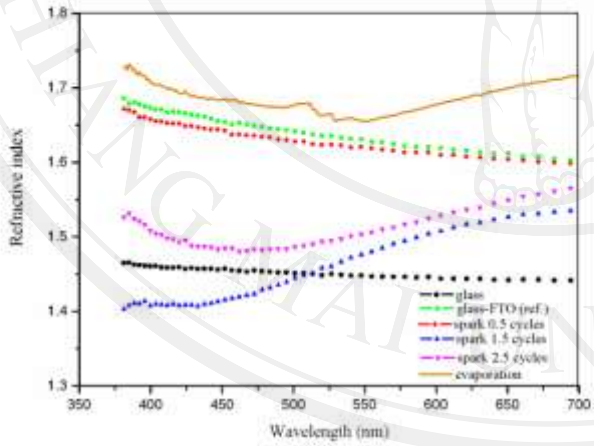

Fig.5 Refractive index of ZnO thin films on FTO glass substrate obtained via ellipsometry.

Thickness of the minimum reflection is calculated by equation (6) [3],

$$d_1 = \frac{\lambda_0}{4n_1} \qquad (6)$$

where d_1 is the thickness of film, λ_0 is wavelength, n_1 is refractive index of thin films. Sparking 1.5 cycles has minimum reflection when we calculated thickness by above equation and used refractive index 1.52 at wavelength of 632.8 nm from Fig.5. The thickness of sparking 1.5 cycles must have 104.08 nm but we also obtained via ellipsometry of 59.17 nm and approximately thickness by FE-SEM cross section from Fig.2(f) of 89.34 nm. Because the above equation used for thin film which has uniform and smooth surface, but we have roughness surface thin film as shown in Fig.2. However, sparking 1.5 cycles has minimum reflection for ARCs.

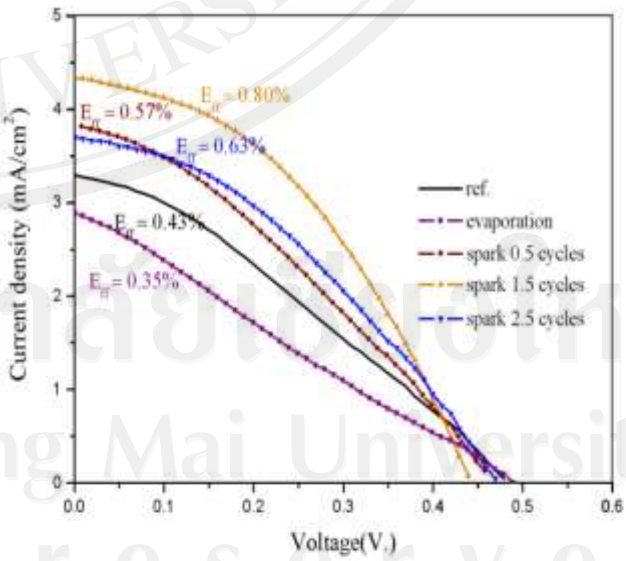

Fig.6 J-V characteristics of the DSSCs without ARC (Ref.) and ZnO thin film with ARC.

Table 1
Photovoltaic parameters of ZnO thin films ARCs coated on DSSCs compared with bare DSSCs. And thicknesses of ZnO thin films were obtained via ellipsometry at 632.8 nm wavelength.

Sample	J_{sc}(mA/cm^2)	V_{oc}(V)	FF(%)	E_{ff}(%)	Thickness (nm)
ref.	3.00	0.46	31.29	0.43	-
evaporation	2.89	0.49	24.58	0.35	1065.95±12.90
sparking 0.5	3.82	0.46	32.95	0.57	19.29±2.02
sparking 1.5	4.34	0.47	41.83	0.80	59.17±3.15
sparking 2.5	3.70	0.47	36.74	0.63	92.32±4.78

Fig.6 showed J-V characteristics of the bare DSSCs (Ref.) and ZnO thin film with ARCs. The result confirmed that sparking films coated on DSSCs have higher efficiency than evaporation film and reference cell. The figure also showed that sparking 1.5 cycles has the highest efficiency of 0.8% compared with reference cell of 0.43% which increase efficiency to 86.04% compared to reference cell. Thus, the efficiency can be improved due to ZnO sparking film. Also, we can reduce the reflection and increase the transmission of light to the dye molecules resulting in improvement of efficiency. Because of the total flux of photons increased, short circuit current (I_{sc}) was increased too. I_{sc} of sparking films are higher than evaporation film and reference cell, especially sample sparking 1.5 cycles has I_{sc} of 4.34 mA/cm^2 compare with reference cell that has I_{sc} of 3.00 mA/cm^2, which increase I_{sc} to 44.67% compared reference cell.

Conclusion

ZnO thin films as an anti-reflection layer were successfully prepared by sparking technique. It was found that DSSCs with sparking film of 1.5 cycles exhibited the highest efficiency and also higher than the reference cell without anti-reflection layer. The improvement of efficiency by ARCs can be explained by reduction of light reflection and having the optical reflective in between the value of the substrate (FTO-glass) and air. Thus, ZnO thin films ARCs prepared by sparking technique could be successfully used for efficiency improvement of DSSC.

Acknowledgement

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