interesting to investigate the effect of MZO sputtering time on performance of ZnO DSSCs.

Objective of the study

The aim of this study was to investigate the effect of $Mg_{0.2}Zn_{0.8}O$ sputtering time on efficiency of DSSCs which has ZnO/$Mg_xZn_{1-x}O$ as photoelectrode.

Research Methodology

The DSSC structures used in this experiment were shown as schematic diagram in Figure 1. In preparation of photoelectrodes, the ZnO paste was obtained by mixing of ZnO powder and polyethylene glycol solution with ZnO content of 50% by weight. The paste was screened on conductive glass (fluorine doped SnO_2 glass, FTO glass) which controlled the thickness of the films by adhesive tapes and heated at 400°C for 1 hour. The ZnO films on FTO were then coated with thin layer of MZO by radiofrequency magnetron sputtering technique from $Mg_{0.2}Zn_{0.8}O$ target. This particular composition was selected because the lattice structure of the films remains hexagonal similar to ZnO. The same lattice structure is important in order to avoid lattice mismatch and obtain smooth interface. Moreover, the conduction band minimum of MZO is higher than that of ZnO and increases with higher Mg composition (x). Therefore, the higher Mg composition gives the higher different value of conduction band minimum and should better prevent recombination process than that of lower Mg composition.

The target was prepared by mixing MgO (99.9%) and ZnO (99.9%) powders with Mg composition to 20 mole% and sintering at 1,200°C for 24 hours. The target was placed at a distance of 6 cm from the substrates. The deposition conditions were RF power of 150 W, base pressure less than 5.0×10^{-5} Torr, Ar pressure of 2.5×10^{-2} Torr and sputtering time varied from 0.5 to 30 minutes. After sputtering, the films were soaked in Eosin-Y dye ($C_{20}H_6Br_4Na_2O_5$) solution for 1 hour. The counterelectrodes were prepared by spreading H_2PtC_{16} in acetone solution on FTO and heating at 550°C for 1 hour. Finally, the photoelectrode and counterelectrode were assembled into DSSC using parafilm sheet as a spacer and some electrolyte, 0.03 M I_2 + 0.3 M LiI in propylene carbonate, was added between both electrodes. In optical characterization of MZO, the MZO films were deposited on quartz substrate with the same conditions as on FTO glass in order to obtain the energy band gap.

The transmittance spectra were investigated by UV-Visible spectroscopy (Varian model Carry 50). The film morphology was carried out by scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS) (JEOL model JSM-6335). Cell performance was measured under illumination of 100 mW/cm^2 solar simulator from xenon lamp with AM 1.5 filter (Solar Light CO. model XPS 400) and sourcemeter potentiostat (Keithley model 2611) in the frequency range of 0.4-105 Hz with the magnitude of the alternative signal of 10 mV.

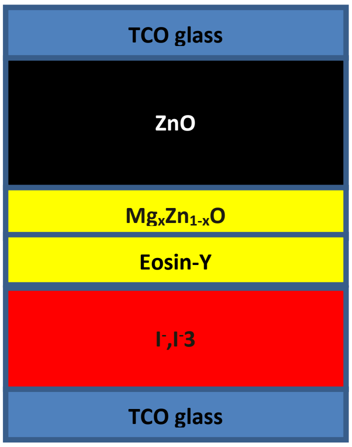
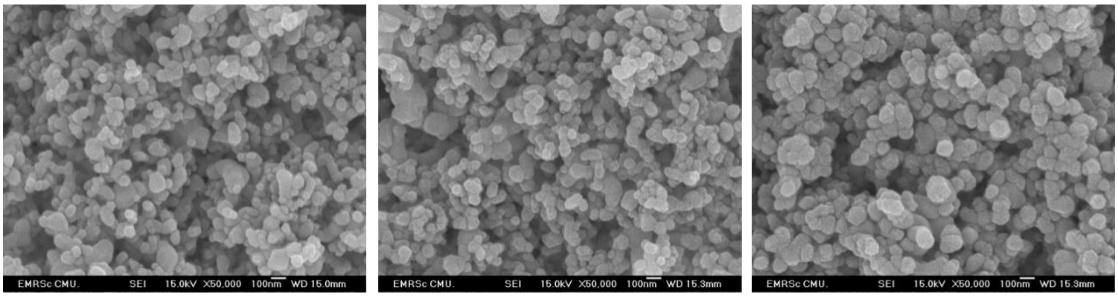


Figure 1 Schematic diagram of DSSC structures used in this experiment.

Result

1. Photoelectrode Characteristics

Figure 2 showed FE-SEM images of (a) ZnO films, (b) ZnO/MZO films at sputtering time of 10 min and (c) ZnO/MZO films at sputtering time of 30 min. The clusters of nanoparticles structure was observed and ZnO/MZO films exhibited similar morphology as ZnO film. This indicated that the MZO film did not change the morphology of ZnO film. The average nanoparticle size of the films was about 130 nm. Figure 3. showed EDS spectrum of ZnO/MZO films at the sputtering time of 10 min. Mg signal along with Zn, and O signal was clearly observed indicating an existence of Mg in the film. It should be noted that the EDS spectrum was obtained from the sample that composed of two layers; thin MZO films and ZnO film.



(a) (b) (c)

Figure 2 SEM images of (a) ZnO film, ZnO/MZO film at sputtering time of (b) 10 and (c) 30 min.

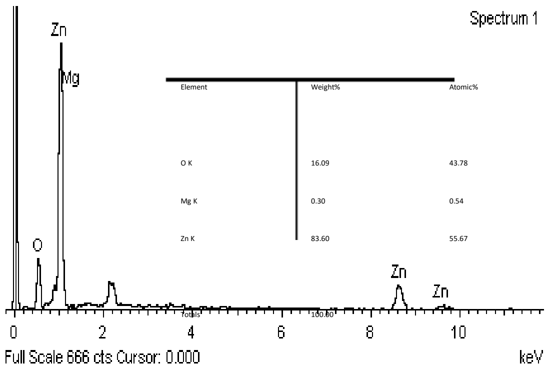


Figure 3 EDS spectrum of ZnO/MZO film at the sputtering time of 10 min

2. Optical properties of MZO thin films

The transmittance spectra of MZO films on quartz substrate with different sputtering time was shown in Figure 4. The absorption edges were clearly observed at around 250-350 nm which was corresponded to the energy band gap of the MZO films. The value of energy band gap was extracted from transmittance spectra by plotting $(\alpha h\nu)^2$ vs photon energy and extrapolating the linear portion of the curve to zero. The energy band gap of the MZO films was estimated to be 3.64 eV compared to 3.3 eV of ZnO (Fujita et al., 2005; Choopun et al., 2002; Caglar et al., 2009). Therefore, the energy band diagram can be drawn as Figure 5. by using the reported ratio of conduction and valance band offset (ΔEC/ΔEV) of 70/30.

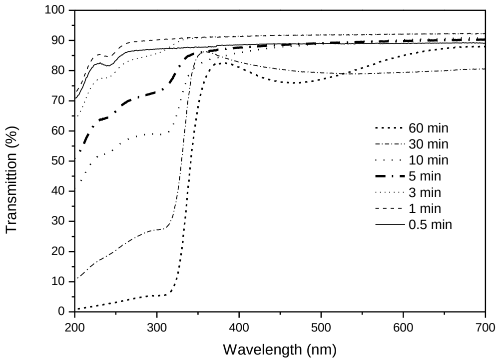


Figure 4 Transmittance spectra of $Mg_{0.2}Zn_{0.8}O$ films with different sputtering time.

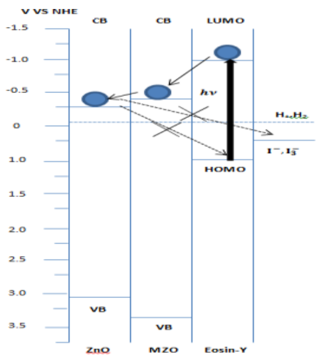


Figure 5 The energy level diagram of MZO photoelectrode.

3. J-V Characteristics of ZnO DSSCs

Figure 6 showed J-V characteristic of ZnO DSSCs with different sputtering time. The important photoelectrochemical parameters such as short circuit current density (Jsc), open circuit voltage (Voc), fill factor (FF), thickness and power conversion efficiency (η) which determined from the J-V curves were shown in Table 1. The highest power conversion efficiency is 0.73% was obtained from DSSCs with MZO film which coat by RF magnetron sputtering at 1 min which was higher than DSSCs without MZO film. And the decreasing of current density and power conversion efficiency with long sputtering time was observed.

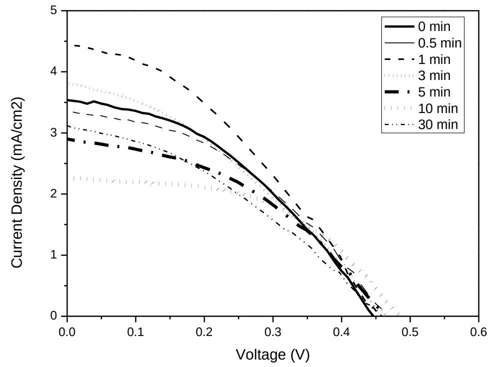


Figure 6 J-V characteristic of ZnO/$Mg_xZn_{1-x}O$ DSSCs with different sputtering time.

A comparison between the results obtained in this work and other similar work is shown in Table 2. It can be seen that introducing of Al_2O_3 barrier layer in TiO_2 DSSC and introducing of $Mg_{0.3}Zn_{0.7}O$ barrier layer in ZnO DSSCs give an improvement of power conversion efficiency at some optimum thickness. The results show that an introducing of $Mg_{0.2}Zn_{0.8}O$ and $Mg_{0.3}Zn_{0.7}O$ barrier layer in ZnO DSSCs exhibited the highest power conversion efficiency at the same 1 minute sputtering time.

Table 1 Summary of the photoelectrochemical parameters such as short current density (JSC), open circuit voltage (VOC), fill factor (FF), Thickness and the overall power conversion efficiency (η) which determined from the measured J–V curves.

Sputtering Time (min)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	Thickness (µm)	η (%)
0	3.54	0.44	0.41	13.95	0.62
0.5	3.36	0.46	0.41	14.01	0.63
1	4.47	0.45	0.37	14.25	0.73
3	3.82	0.46	0.35	14.53	0.61
5	2.90	0.46	0.42	14.78	0.56
10	2.26	0.48	0.51	15.28	0.54
30	1.83	0.48	0.48	17.69	0.43

Table 2 Comparison of the power conversion efficiency between this work and other similar work.

ZnO/ $Mg_{0.2}Zn_{0.8}O$ (This work)		$ZnO/Mg_{0.3}Zn_{0.7}O$ (Pengpad et al., 2011)		TiO_2/Al_2O_3 (Wu et al., 2008)	
Sputtering time (min)	η (%)	Sputtering time (min)	η (%)	Sputtering time (min)	η (%)
0	0.62	0	0.75	0	3.93
0.5	0.63	0.5	0.80	2	4.30
1	0.73	1	0.82	4	5.91
3	0.61	3	0.80	6	4.03
5	0.56	5	0.74	12	2.79
10	0.54	10	0.74	30	1.21
30	0.49				

Discussions and Conclusions

In this study, $Mg_xZn_{1-x}O$ (MZO) thin layer films prepared by RF-magnetron sputtering from $Mg_{0.2}Zn_{0.8}O$ target were used as a barrier layer between semiconductor layer and dye for efficiency improvement of DSSCs. The effect of barrier layer was investigated in term of MZO layer film thickness by verying sputtering time The results showed that the MZO film did not change the morphology of ZnO film. DSSCs with 1 minute MZO sputtering time exhibited the highest power conversion efficiency of 0.73% which was higher than DSSCs without MZO film. The DSSCs with longer sputtering time exhibited lower current density and efficiency. The efficiency improvement of DSSCs could be explained in term of the suppression of back electron transfer in recombination process. The lower current density was caused by the lower electron injection due to higher resistance of MZO film.

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