

## Effect of $Mg_xZn_{1-x}O$ Sputtering Time on Efficiency of ZnO Dye-Sensitized Solar Cells

### ผลของเวลาในการสเปตเตอร์ริง $Mg_xZn_{1-x}O$ ต่อประสิทธิภาพของเซลล์แสงอาทิตย์ชนิดสีย้อมไวแสง ที่มี ZnO เป็นฐาน

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#### Abstract

In this work  $Mg_xZn_{1-x}O$  (MZO) thin layer films prepared by using 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 ZnO dye-sensitized solar cell (DSSCs). The effect of barrier layer was investigated in term of MZO layer films thickness by varying sputtering time. The MZO films were characterized by scanning electron microscope, energy dispersive spectroscopy and UV-visible spectroscopy. The DSSCs were investigated by using J-V characteristic measurement. It was found that DSSCs with 1 minute MZO sputtering time exhibited the highest power conversion efficiency of 0.73% which was higher than that without MZO film. It was concluded from the experiment that the MZO films layer could reduce the electron recombination but the increasing of MZO resistance with the longer sputtering time resulting in low current density and low efficiency of DSSCs.

#### บทคัดย่อ

ในงานนี้ฟิล์มบางของ  $Mg_xZn_{1-x}O$  (MZO) ซึ่งเตรียมโดยใช้ RF-magnetron sputtering จากเป้าสาร  $Mg_{0.2}Zn_{0.8}O$  ถูกใช้เป็นชั้นของกั้นแสงกั้นระหว่างสารกึ่งตัวนำและสีย้อมเพื่อช่วยในการปรับปรุงประสิทธิภาพของเซลล์แสงอาทิตย์ชนิดสีย้อมไวแสงชนิดซิงค์ออกไซด์(DSSCs) ผลของกั้นแสงกั้นถูกศึกษาในเทอมของความหนาของชั้น MZO โดยการเปลี่ยนเวลาในการสเปตเตอร์ ทำการวิเคราะห์ ฟิล์ม MZO ด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด สเปกโทรสโกปีพลังงานกระจาย และยูวีวิสิเบิลสเปกโทรสโกปี ทำการวิเคราะห์ DSSCs โดยใช้การวัดลักษณะเฉพาะของ J-V พบว่าที่เวลาในการสเปตเตอร์ 1 นาทีจะได้ค่าประสิทธิภาพสูงสุด 0.73% ซึ่งมากกว่าเซลล์ที่ไม่มีชั้นของฟิล์ม MZO จากการทดลองสรุปได้ว่าผลของชั้นฟิล์ม MZO สามารถช่วยลดการไหลย้อนกลับของอิเล็กตรอนได้ แต่ความต้านทานของฟิล์ม MZO ที่มีค่ามากขึ้นตามระยะเวลาในการสเปตเตอร์ที่นานขึ้นมีผลทำให้ความหนาแน่นกระแสและประสิทธิภาพของเซลล์แสงอาทิตย์ชนิดสีย้อมไวแสงลดลง

**Keywords:** dye-sensitized solar cell, ZnO,  $Mg_xZn_{1-x}O$

**คำสำคัญ:** เซลล์แสงอาทิตย์ชนิดสีย้อมไวแสง, ซิงค์ออกไซด์, แมกนีเซียมซิงค์ออกไซด์

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## Introduction

Dye-sensitized solar cells (DSSCs) are metal-oxide wide-band-gap solar cells which have some interesting advantages such as low production cost, ease of fabrication and environmental friendly. The major progress of DSSCs was done by the work of Grätzel. (Grätzel, 2003; O'Regan, Grätzel, 1991). The typical structure of DSSCs composes of photoelectrode, electrolyte and counterelectrode. The photoelectrode contains semiconductor with adsorbed dye on transparent conducting glass. The electrolyte is a solution of redox reaction. The counterelectrode contains catalyst film on transparent conducting glass. The mechanism of electron transport in this solar cell starts with electrons in the highest occupied molecular orbital level (HOMO) which are excited by photon to lowest unoccupied molecular orbital level(LUMO) in dye layer. Then, the excited electrons are injected to conduction band of semiconductor and pass through the transparent conducting glass to external circuit. After that, the electrons come back to cell at counterelectrode and are recaptured by electron acceptors in electrolyte solution. By recapturing electrons, electron acceptors are reduced into electron donors which, finally, regenerated the dye molecule (Grätzel, 2003).

The efficiency of DSSCs is quite low compared with silicon solar cells. The highest efficiency of DSSCs with titanium dioxide ( $\text{Ti}_2\text{O}$ ) as photoelectrode has been recorded to be 15% (Diamant Y et al., 2003). However, the investigation on zinc oxide (ZnO) as an alternative photoelectrode has been intensively carried out due to its band gap, electron affinity, and electron injection efficiency which are nearly the same as  $\text{TiO}_2$ . In addition, in ZnO electron

lifetime is significantly higher and the recombination rate is lower than that of  $\text{TiO}_2$ .(Choopun et al., 2002; Diamant et al., 2003; Raksa et al., 2009) However, the power conversion efficiencies of DSSCs based on ZnO are lower than that of  $\text{TiO}_2$ . Since the recombination of electron in conduction band of semiconductor to electron acceptor in electrolyte is one problem that decreased the power conversion efficiency of DSSCs then in order to suppress this process, thin potential barrier layer was introduced to the interface between semiconductor layer and dye to act as a blocking layer for preventing charge recombination in DSSCs.

Phathaitep Raksa has reported an improvement of efficiency by coating thin layer of CuO on ZnO photoelectrode. The higher efficiency of DSSCs based on ZnO with CuO layer than that of without CuO layer has explained in terms of CuO barrier layer as a potential step in energy band diagram because CuO has higher conduction band level than ZnO but lower than LUMO level of Eosin-Y dye(Raksa et al., 2009). Also, it has been reported the efficiency improvement by coating ZnO or  $\text{Al}_2\text{O}_3$  on  $\text{TiO}_2$  photoelectrode (Kim et al., 2003; Wu et al., 2008).

$\text{Mg}_x\text{Zn}_{1-x}\text{O}$  (MZO) is one of an interesting material for potential barrier due to a small lattice mismatch with ZnO and controllable energy band gap by controlling Mg composition. The energy band gap of MZO is in the range of 3.3 to 4.0 eV for hexagonal phase. In addition, the conduction and valence band offset between ZnO and MZO ( $\Delta E_c/\Delta E_v$ ) has been reported to be approximately 70/30 (Choopun S et al., 2002). Beside that Pengpad. A et al. have reported the efficiency improvement of ZnO DSSCs by using MZO thin films as a barrier layer between semiconductor layer and electrolyte (Pengpad et al., 2011) Thus, it is

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  $400^\circ C$  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  $1,200^\circ C$  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  $5.0 \times 10^{-5}$  Torr, Ar pressure of  $2.5 \times 10^{-2}$  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  $H_2PtCl_6$  in acetone solution on FTO and heating at  $550^\circ C$  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  $100 \text{ mW/cm}^2$  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.



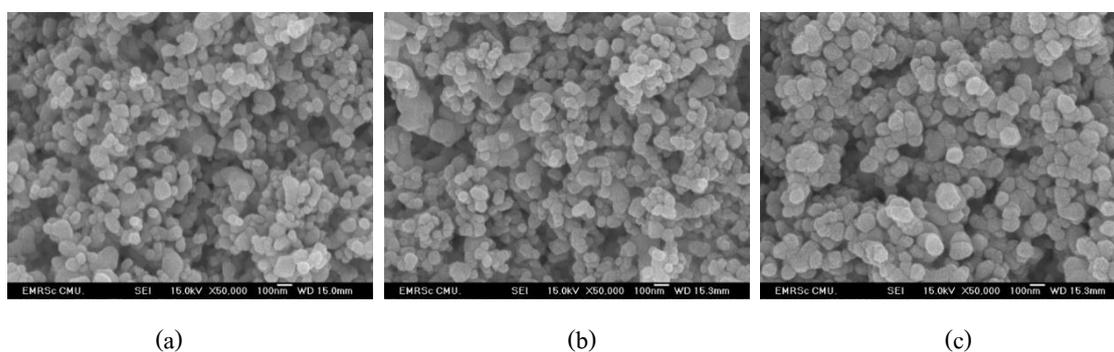
**Figure 1** Schematic diagram of DSSC structures used in this experiment.

## Result

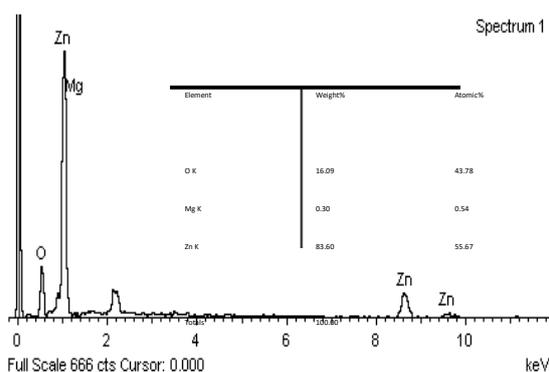
### 1. Photoelectrode Characteristics

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.



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

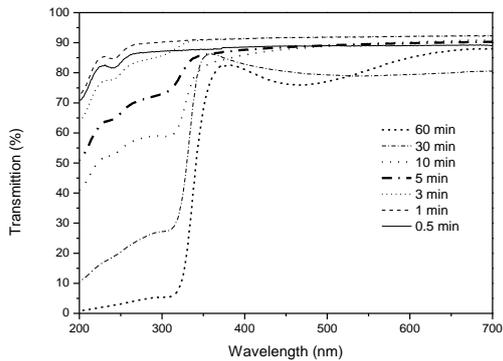


**Figure 3** EDS spectrum of ZnO/MZO film at the sputtering time of 10 min

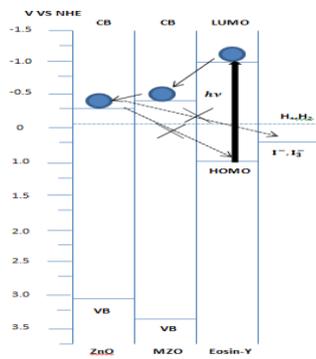
### 2. Optical properties of MZO thin films

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 ( $\Delta E_C/\Delta E_V$ ) of 70/30.



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

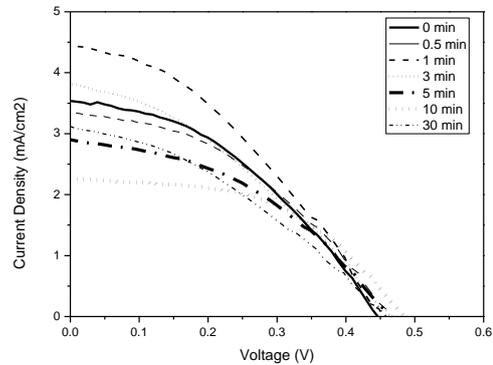


**Figure 5** The energy level diagram of MZO photoelectrode.

### 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 ( $J_{sc}$ ), open circuit voltage ( $V_{oc}$ ), fill factor (FF), thickness and power conversion efficiency ( $\eta$ ) 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 ( $\eta$ ) which determined from the measured J–V curves.

Sputtering Time (min)	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF	Thickness ( $\mu$ m)	$\eta$ (%)
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 <sub>0.2</sub> Zn <sub>0.8</sub> O (This work)		ZnO/Mg <sub>0.3</sub> Zn <sub>0.7</sub> O (Pengpad et al., 2011)		TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (Wu et al., 2008 )	
Sputtering time (min)	$\eta$ (%)	Sputtering time (min)	$\eta$ (%)	Sputtering time (min)	$\eta$ (%)
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<sub>x</sub>Zn<sub>1-x</sub>O (MZO) thin layer films prepared by RF-magnetron sputtering from Mg<sub>0.2</sub>Zn<sub>0.8</sub>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 varying 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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