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# Effect of ZnO Passivating Layer Using RF-Sputtered for Dye-Sensitized Solar Cells

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*Dye-sensitized solar cells(DSSCs) have a FTO/TiO<sub>2</sub>/Dye/Electrolyte/Pt-counter electrode structure, but a more than 10% electron loss occurs at each interface. A passivating layer between the Electrolyte/FTO glass interface can prevent the recombination of electrons. FTO glass was coated with ZnO thin films by RF-magnetron sputtering. Each film was deposited under different O<sub>2</sub>(Oxide) pressures. Under each pressure, the passivating layer showed a difference in thickness. The optical transmittance of the ZnO thin film depends on the thickness and grain size of ZnO thin film. A TiO<sub>2</sub>-nanoparticle upper layer was coated on the ZnO passivating layer by screen-printing. FTO showed relatively high intensity but the X-ray diffraction pattern revealed the presence of ZnO thin films. The conversion efficiency of the DSSCs were strongly affected by the passivating layer. The conversion efficiency measured the maximum conversion efficiency of 4.29% at O<sub>2</sub> 5 mTorr, which is due to the effective prevention of electron recombination with the electrolyte.*

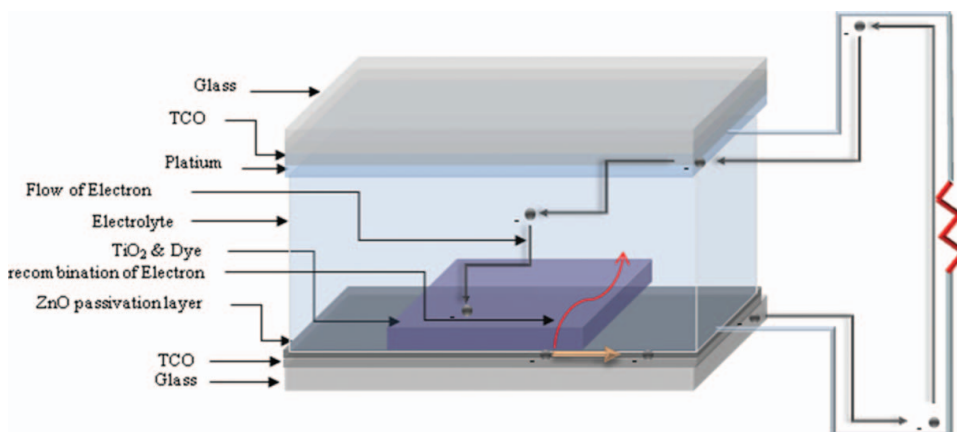
**Keywords** ZnO passivating layer; RF-magnetron sputter; DSSC; thin film

## 1. Introduction

Dye-sensitized solar cells have been studied intensively since the discovery of Dye-sensitized solar cells(DSSCs) in 1991 [1]. DSSCs have attracted considerable attention owing to their high efficiency, simple fabrication process, low production cost, and applicability to flexible substrates [2,3]. The cost effectiveness is an important parameter for producing DSSCs compared to the widely used conventional silicon solar cells. DSSCs consist of a wide bandgap nanoporous metal oxide film, such as TiO<sub>2</sub> deposited on a conducting oxide layer as an electron transport layer. Nanoparticle TiO<sub>2</sub> is commonly used in DSSCs to embed a high density of dye molecules onto the TiO<sub>2</sub> surface to enhance the photo-absorption process. Whereas, the highly porous structure of the TiO<sub>2</sub> layer might cause electrical recombination between the electrolyte and transparent conducting oxide (TCO) [4]. To avoid this problem, ZnO thin films are used as a compact layer in DSSCs [5]. In theory, ZnO has excellent electron collecting capability because the bandgap of ZnO is 3.4 eV, which suppresses electron mobility. In addition, ZnO also has good compatibility and can be prepared at room temperature. ZnO nanoparticles have a hexagonal structure,

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**Figure 1.** Structure of the ZnO passivating layer to prevent the recombination of electrons.

which promotes optical refraction [6]. Many studies have reported the electrode modification of DSSCs. Electrode modification is performed to decrease the number of electron losses at the interface between the TCO and electrolyte [7]. Electron transport was slower in more porous films. Therefore, the dense film between the  $\text{TiO}_2$  electrode and TCO can be a useful method. A dense film was found to lead to faster electron transport and slower recombination [8]. In this study, a ZnO passivating layer was prepared on FTO glass by RF(Radio Frequency)-magnetron sputtering. The RF-sputtered ZnO film structure acted as an effective short-circuit preventive layer (blocking layer) between the FTO( $\text{SnO}_2:\text{F}$ ) and electrolyte. The efficiency of the DSSC can be improved by the introduction of ZnO thin films as the electron-recombination blocking layer.

## 2. Experimental Procedures

ZnO passivating layer were prepared by RF-magnetron sputtering using a ZnO target (99.99% purity, LTS Research Lab., Inc), 2" in diameter and 1/4" thickness. FTO ( $20 \times 20 \text{ mm}^2$   $9 \Omega/\text{sq}$   $\text{SnO}_2:\text{F}$ ) glass was used as the substrates. The substrate surface was cleaned with ethanol and sonification in isopropyl alcohol. The FTO glass substrates were inserted in an RF-magnetron sputter chamber. The distance from the target to the substrate was 10 cm. The base pressure in the chamber was  $5 \times 10^{-6}$  torr. The RF power was 80 W. The ZnO passivating layer was deposited with different working  $\text{O}_2$  pressures.

The  $\text{TiO}_2$  powders were manufactured by a sol gel method, and  $\text{TiO}_2$  pastes were prepared for screen-printing [9]. An  $\sim 8\text{--}10 \mu\text{m}$ -thick  $\text{TiO}_2$ -nanoparticle upper layer was coated on the ZnO passivating layer using a screen-printing method. A  $\text{TiO}_2$  film was sintered at  $480^\circ\text{C}$  for 15 min in air. And the  $\text{TiO}_2$  working electrodes were immersed into the 0.5 mM dye complex of N-719 ruthenium(II) (Cis-di (thiocyanato) - N,N' - bis (2,2'-bipyridyl-4-carboxylic acid-4'-tetrabutylammonium carboxy late) in an ethanol solution for 24 hours. The counter electrodes were prepared by dropping a 5 mM  $\text{H}_2\text{PtCl}_6$  ethanol solution onto FTO glass and heating at  $500^\circ\text{C}$  for 30 minutes. The dye-adsorbed  $\text{TiO}_2$  electrodes and Pt-counter electrodes were assembled for the cell using hot-melt sealant and were laminated for 10 minutes at  $120^\circ\text{C}$ . The electrolyte was inserted through a hole in the

counter electrode and the hole was sealed with hot-melt sealant and slide deck glass. The active area of the solar cells was  $0.25 \text{ cm}^2$ .

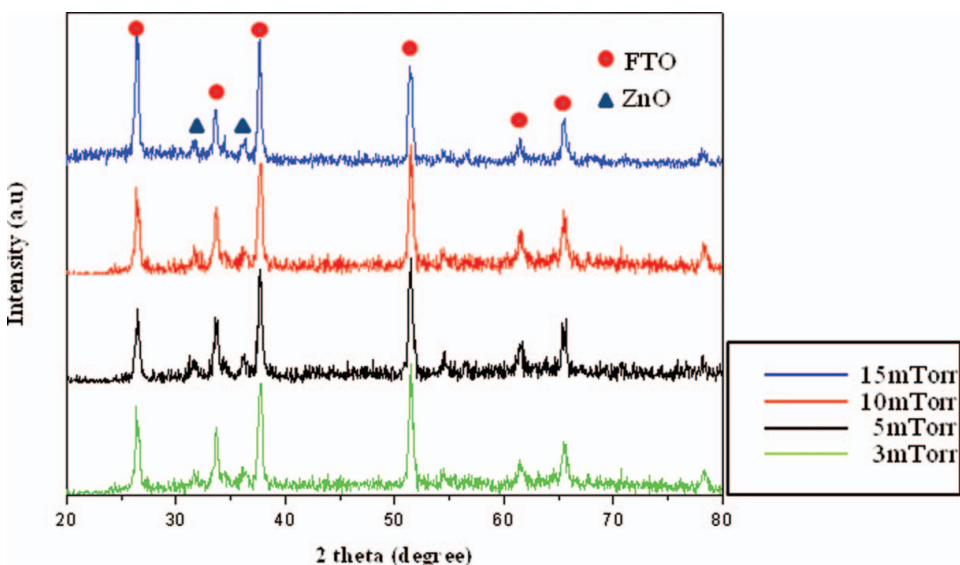
X-ray diffraction (XRD, Rigaku D/MAX-2200) patterns of mesoporous materials were collected on a Rigaku diffractometer using Cu K $\alpha$  radiation. The morphology and particle size of the TiO $_2$  thin film were examined by field-emission scanning electron microscopy (FE-SEM, HITACHI S-4700). The transmittance of the passivating layer and absorbance of the DSSC cell was measured using a UV spectrometer (Agilent, UV-vis 8453). The photocurrent-voltage measurements were taken using an I-V solar simulator (McScience, Solar simulator).

### 3. Results and Discussion

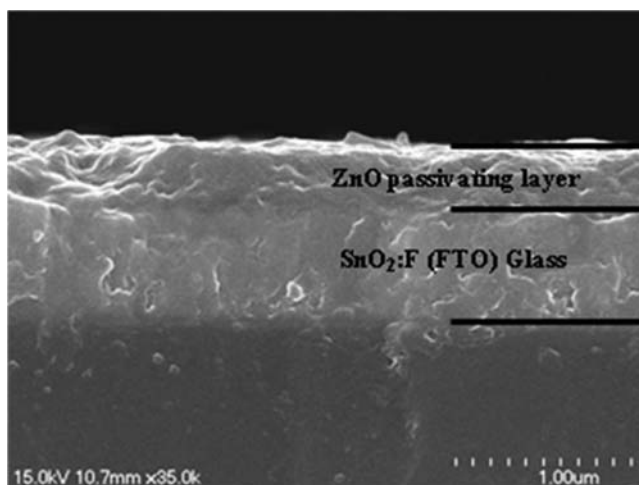
XRD of the deposited ZnO passivating layer revealed a crystalline structure in Fig. 2. The films were crystalline, and they showed mixed characteristics of FTO and ZnO. It is found that all the films have a polycrystalline hexagonal wurtzite structure with (100) and (101) orientation [10]. The XRD patterns of the samples prepared at 3 mTorr, 5 mTorr, 10 mTorr, and 15 mTorr showed similar crystalline properties.

There are slight differences in the deposition rate with the working pressure (3 mTorr, 5 mTorr, 10 mTorr, and 15 mTorr), there was no significant difference in thickness between each pressure. In Fig. 3, cross-section FE-SEM images show clearly that the film consists of three parts. The top part is the ZnO passivating layer 240 nm-thick, compared with bare FTO glass. The middle one is the FTO layer, and lowest one is the glass substrate.

Figure 4 shows FE-SEM images of the ZnO passivating layers. From the surface FE-SEM images, the average grain size was decreased as the working pressure increasing. The SEM results show that a high working pressure produces a small grain size. It might be expected that higher working pressure have a lower nucleation rate. ZnO particles were



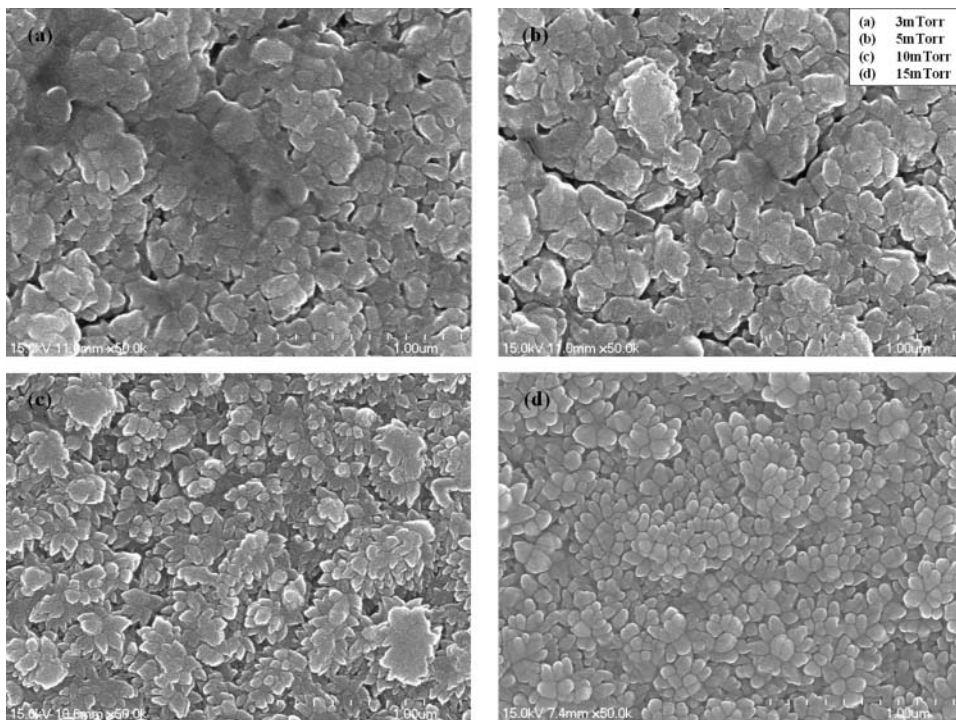
**Figure 2.** XRD patterns according to the oxide pressure used to prepare the ZnO passivating layer showed a hexagonal wurtzite structure (3 mtorr, 5 mtorr, 10 mtorr and 15 mtorr).



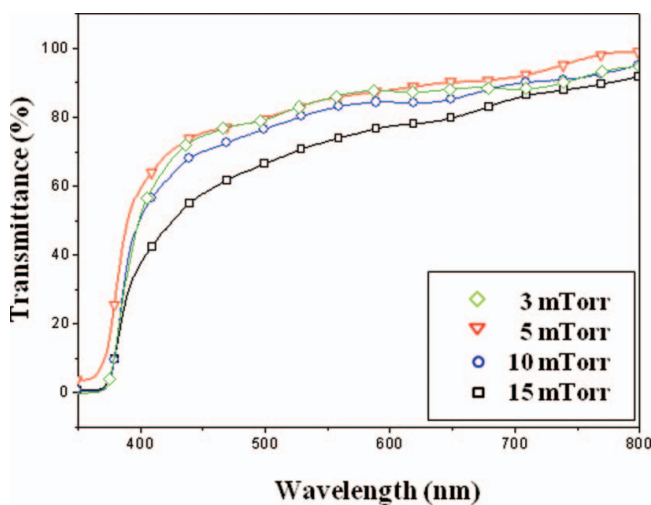
**Figure 3.** FE-SEM images showing cross-section view of the ZnO passivating layer.

observed when the ZnO passivating layer was deposited at higher working pressures, and a compact ZnO film was deposited at higher working pressures.

Figure 5 shows the transmission spectra of the FTO glass on the deposited ZnO passivating layers. The light transmitted through the ZnO thin film decreased with increasing

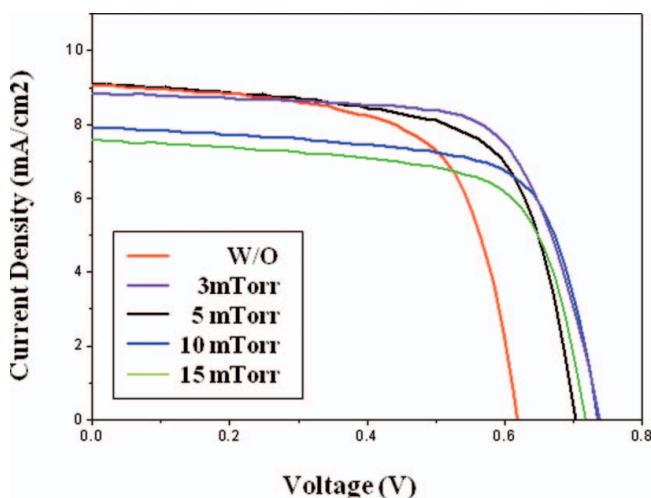


**Figure 4.** FE-SEM images of deposited ZnO passivating layer with various deposition pressure on 80 W RF power. (3 mTorr, 5 mTorr, 10 mTorr, 15 mTorr).



**Figure 5.** Optical transmittance of the ZnO passivating layers.

oxide pressure at over 5 mTorr. The optical transmittance of the ZnO passivating layer prepared at 5 mTorr was the highest. At 550 nm, the 5 mTorr oxide pressure showed an transmittance of 85.89% to that of the bare FTO glass sample. And, the 3 mTorr have almost the same transmittance at 550 nm. In contrast, an increase in the working pressure of the ZnO passivating layer above 10 mTorr leads to a decrease in the optical transmittance, at 82.55% at a 550 nm wavelength. The transmittance of the ZnO passivating layer decreased remarkably at a 15 mTorr working pressure. When the particle size increases, ZnO thin films have a higher transmittance. These results slightly increase in optical band-gap of ZnO film and it due to the small grain size of the polycrystalline ZnO film [11–13]. At



**Figure 6.** I-V characteristics of the DSSCs using the ZnO passivating layer and W/O passivating layer.

**Table 1.** Effect of the ZnO passivating layer on the performance of DSSCs.

Sample	Jsc (mA/cm <sup>2</sup> )	Voc (V)	FF (%)	Efficiency ( $\eta$ )
W/O passivation	9.08	0.62	65	3.66
3 mTorr	8.39	0.73	69	4.14
5 mTorr	9.09	0.70	67	4.29
10 mTorr	7.92	0.74	69	4.06
15 mTorr	7.58	0.72	68	3.72

wavelengths of 350 nm and 550 nm, the dye N-719 absorbs a considerable amount of Photovoltaic(PV). Therefore, a 550 nm wavelength is very important for DSSCs.

Figure 6 shows the photocurrent density—voltage (I-V) curves of the DSSCs with TiO<sub>2</sub> passivating layer fabricated with different deposition rates under 100 mW/cm<sup>2</sup> illumination in an AM 1.5G condition. One of the most important parameters for a solar cell is its photoelectric conversion efficiency. The fill factor (FF) is an important component of solar cells. When the I-V curves approach a square shape, the FF is higher. In addition, solar cells with a high FF have a stable output voltage and current compared to the cell with the same Voc and Jsc, and they produce more power. Table 1 lists the efficiency, FF, open circuit voltage, and integral photocurrent for the corresponding solar cells. From Fig. 6, the DSSC using the ZnO passivating layer showed higher conversion efficiency with a FF of 67%, photocurrent density (Jsc) of 9.09 mA/cm<sup>2</sup>, an open circuit potential (Voc) of 0.7 V, and a cell conversion efficiency of 4.29%. From Fig. 6, the DSSC using a ZnO passivating layer at 5 mTorr showed high photocurrent density and a FF of 9.09 mA/cm<sup>2</sup> and 67. The Jsc is related to the optical transmittance of the passivating layer. A high transmittance cell have high Jsc. [14] As a result, the highest conversion efficiency,  $\eta$ , was 17.2% higher than that of the DSSC fabricated without a passivating layer. This was attributed to the decreased conductivity for electron transfer from the nonporous TiO<sub>2</sub> layer to the FTO electrode, which suggests that a ZnO layer can act as a high-quality stable electron collector as a passivating layer.

#### 4. Conclusion

This study examined the properties of dye-sensitized solar cells based on dense ZnO films deposited by RF-magnetron sputtering. Compare to the DSSC prepared without a passivating layer, the DSSC with the ZnO passivating layers showed a high FF and high conversion efficiency. The DSSC with the passivating layer deposited under 5 mTorr oxide pressure showed a high photocurrent density and stable FF (9.09 mA/cm<sup>2</sup>, 67%). The DSSC fabricated on the FTO electrode with the ZnO passivating layer showed the highest conversion efficiency of 4.29%, due to the prevention of the electron transfer to the electrolyte. Additional oxide pressure (3 mTorr, 10 mTorr and 15 mTorr) resulted in a decrease in efficiency and photocurrent density. The improved conversion efficiency might be associated with the improved surface density and particle size of the passivating layer. The effect of the passivating layer on an ionic liquid electrolyte on a thin layer ZnO layer was investigated. A ZnO passivating layer coated on FTO is a promising electrode for high-efficiency DSSCs because it prevents the recombination of electrons from the FTO to the electrolyte.

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