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ZnO/CdS BILAYER USED FOR ELECTRODE IN PHOTOVOLTAIC DEVICES

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Abstract. *In this article we present the fabrication and characterization of the nanoporous ZnO and/or ZnO/CdS thin films onto indium doped-tin oxide (ITO) substrates, based on the thermal evaporation technique followed by thermal treatment. The preparation method was relatively simple and low-cost for large scale uniform coating to produce clean, dense and strong adhesion to substrate thin films. The nanostructured ZnO and ZnO/CdS thin films were characterized by X-ray diffraction (XRD) and field emission scanning electron microscope (FE-SEM). The nanostructured ZnO/CdS bilayer film was used in a photo-electrochemical (PEC) cell as a working electrode and a Pt net as a counter electrode. The results show that the photovoltaic cell with nanostructured ZnO/CdS bilayer film electrode has significantly improved photoelectric capability in comparison with that of ZnO electrode.*

I. INTRODUCTION

Zinc oxide (ZnO) is an n-type semiconductor of wurtzite structure. ZnO thin films have many applications in gas sensors, photocatalysis, dye-sensitized solar cells and piezoelectric devices [1]. Unfortunately, the band gap of ZnO is so large (around 3.37eV) [2] that it can only absorb a small part of visible light. Therefore, it is necessary to sensitize the ZnO nanoelectrodes. Semiconductors with narrow band gap have recently attracted much attention due to their excellent properties, such as higher absorption, greater stability and adjustable band gap [3]. Among the various semiconductors, CdSe, CdTe, $CuInS_2$, InP, etc, are used as sensitizers .[4], CdS has shown much promise as an effective sensitizer [5]. It is the most widely studied nanocrystalline semiconductor as a photoanode in photoelectrochemical cells because of its suitable band gap, long lifetime, important optical properties, excellent stability and ease of fabrication [6]. In the semiconductor-sensitized solar cell (SSSC), a light-absorbing semiconductor deposited on the porous transparent oxide takes the place of the dye [3]. In this work, CdS was used to sensitize ZnO nanostructures.

Various methods have been used for the production of ZnO nanostructures such as chemical vapor deposition [7], thermal evaporation [8], pulse-laser deposition [9], DC and/or radio frequency (RF) sputtering [10], sol-gel and wet chemical method [11], hydrothermal method [12], etc. In this work we used vacuum evaporation technique combined with thermal process for fabrication of nanostructured ZnO films. In comparison

with various techniques, thermal evaporation is a relatively simple one for large scale uniform coating to produce clean, dense and strong adhesion to substrate thin films.

II. EXPERIMENTS

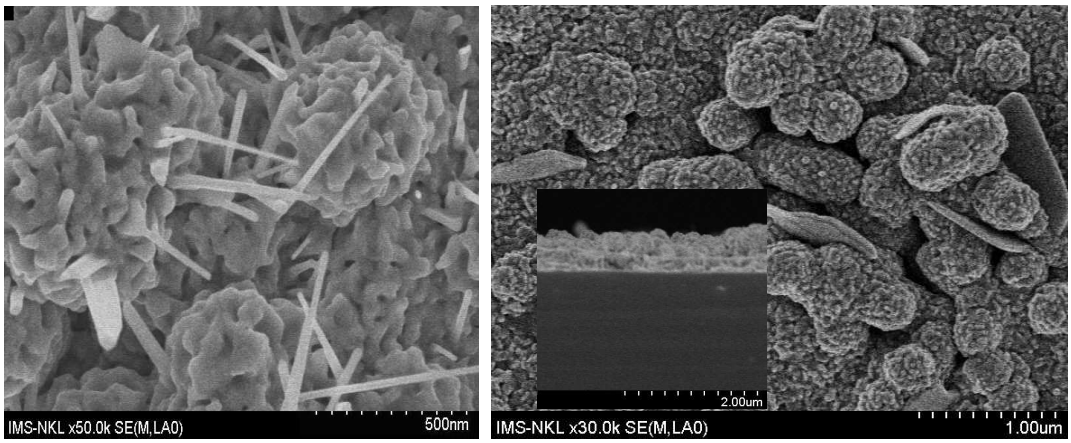
The optically transparent and electrically conductive indium tin oxide (ITO) coated glass substrate with a sheet resistance of 30 Ω per square was rinsed ultrasonically successively in acetone, ethanol, and distilled water. A 100 nm thick layer of Zn was deposited on ITO substrates by thermal evaporation at a pressure of 10^{-2} torr. Then the thin film Zn was annealed at 450°C in air for 7 h. Thin film of CdS with thickness of about 200 nm was fabricated, by the same method as that for Zn film, onto the pre-fabricated ZnO films. The deposition rate was 0.2 nm/s and the thin film thickness was measured during deposition using a conventional quartz crystal monitor. To obtain good crystallinity, the thin CdS films were annealed at 400°C in air for 1 h. The surface morphology of the samples was investigated by using a Field Emission Scanning Electron Microscope (FE-SEM) Hitachi S-4800. The Ultraviolet-visible (UV-VIS) absorption spectra was performed by using a Jasco UV-VIS-NIR V570 spectrometer, X-ray diffractograms were recorded on a Siemens D-5000 diffractometer using CuKα radiation with the wavelength of 1.5406 Å. In photoelectronic studies, a two-electrode PEC cell was used. This comprises ITO/ZnO or ITO/ZnO/CdS used as working electrode (working area is 1 cm^2) and a Pt net electrode separated by an electrolyte containing 1 M KCl and 0.1 M Na_2S. The photocurrent was measured on an Auto-Lab Potentiostat PGS-30. A halogen lamp of 300 W with visible filter in the wavelength range of 380-800 nm was used as an irradiation source. The illumination power density on the electrodes was of 20 $mW.cm^{-2}$ was used as an irradiation source in the Lab. The photoelectrochemical cells were irradiated by sunlight of power density of 100 $mW.cm^{-2}$ in open air.

III. RESULTS AND DISCUSSION

III.1. Morphology and structural characterizations of nanostructure ZnO/CdS bilayer films

The FE-SEM images of the surface of nanostructured ZnO film is presented in Fig. 1(a). The surface of nano-particle CdS film on the ITO/ZnO substrate is shown in Fig. 1(b). From Fig. 1(a) it is seen that the film consists of flower-like grains continuously and homogeneously deposited on the substrate surface. As shown in Fig. 1(b) a homogeneous CdS film with good quality deposited onto ITO/ZnO substrate and a very rough surface was observed. The film has a nanoporous structure which is supposedly beneficial to diffusion of electrolytes and effective scattering of incident sunlight when it is applied to photoanodes of SSSC. Therefore, the thermal evaporation technique can effectively improve the distribution of CdS nanoparticles on the ITO/ZnO surface and into the porosity of the thin film. This may favor the absorption of irradiation light by semiconductor .

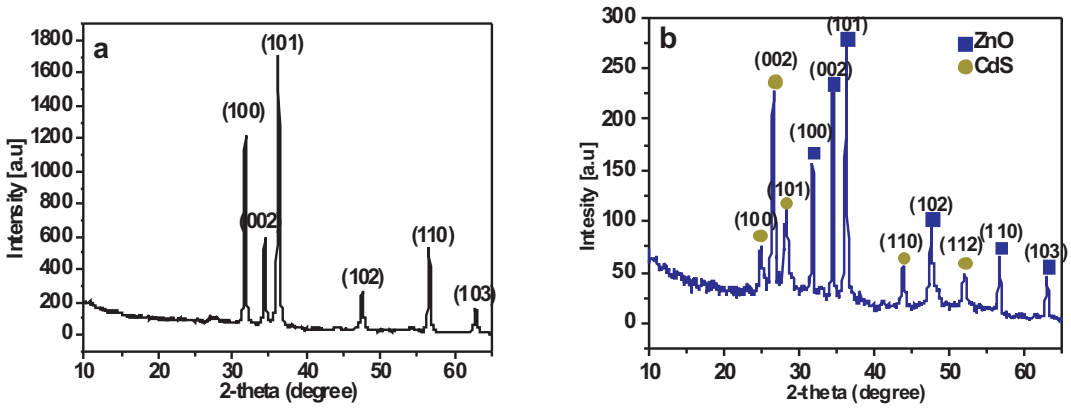
The XRD patterns of ZnO film and ZnO/CdS bilayer film on glass substrates are shown in Fig. 2(a) and Fig. 2(b), respectively. Peaks in Fig. 2(a) with 2θ values of 31.62°, 34.28°, 36.42° and 47.40° exactly identified for the hexagonal wurtzite structure of ZnO. This is in good agreement with references [1]. Fig. 2(b) shows peaks at 2θ of about 24.83°,



(a) (b)

Fig. 1. FE-SEM images of the nanostructured ZnO (a), ZnO/CdS films (b). The inset shows the cross-sectional of the ZnO/CdS bilayer

26.52°, 28.21°, 36.65°, 43.73° and 51.87° corresponding to the (100), (002), (101), (102), (110) and (112) planes, respectively and identified to a hexagonal phase for CdS. This result agrees well with Ref. [13]. There are no peaks for other zinc compounds detected in the spectra. This result clearly shows that ZnO/CdS bilayer film had been successfully prepared.



(a) (b)

Fig. 2. The XRD patterns of ZnO film (a) and ZnO/CdS bilayer (b)

III.2. Absorption spectra of the ZnO and ZnO/CdS bilayer thin films

Light absorption property is one of the most important properties for photo-electrodes which may determine the overall conversion efficiency of solar cell. Fig. 3 shows the UV-VIS absorption spectra of ZnO thin film and CdS thin film on the ZnO substrate. As it can be seen from the figure, the ZnO thin film absorbs light mainly in the wavelength range from 365 nm to 380 nm. The absorption edge of ZnO/CdS bilayer film falls into the visible region at the wavelength of about 540 nm. The absorption edge for the CdS film on ZnO substrate was shifted to longer wavelength region, known as red-shift.

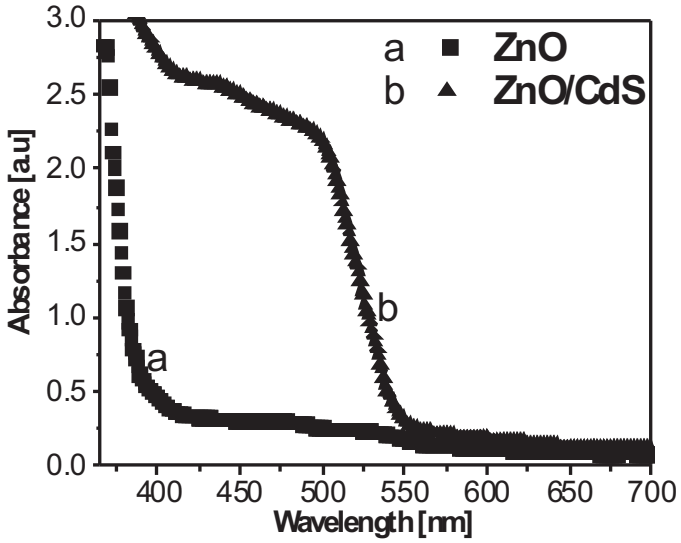


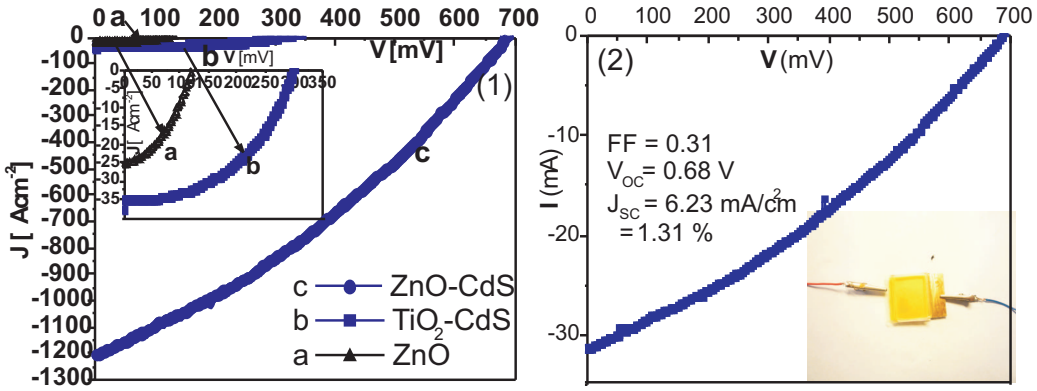
Fig. 3. UV-VIS absorption spectra of nanostructured ZnO and ZnO/CdS bilayer films.

III.3. Photoelectronic performance of nanostructured ZnO/CdS bilayer films

Figure 4 shows the photocurrent-potential behaviors of the photoelectrochemical cell with each of the prepared samples used as working electrodes in turn under illumination. The photocurrent-potential behavior of ITO/TiO_2/CdS was our previously result in Ref. [14]. From figure 4, it is can be seen that the open-circuit photovoltage (V_{oc}) and the short-circuit photocurrent density (J_{sc}) of ITO/ZnO, ITO/TiO_2/CdS and ITO/ZnO/CdS are (117 mV, 27 μA.cm^{-2}), (300 mV, 35 μA.cm^{-2}) and (680 mV, 1200 μA.cm^{-2}), respectively. This is clearly seen that the photo-electrochemical cell made from films consisting only of ZnO has very low values for V_{oc} and J_{sc} whereas on coating a thin film of CdS, both V_{oc} and J_{sc}' increase dramatically. The resulting nanoporous ZnO/CdS film produced a photocurrent of 1200 μA.cm^{-2}, which was three time more than that of macroporous ZnO/CdS [15]. Figure 4b presents the photocurrent-potential behavior of ITO/ZnO/CdS with working area of 5 cm^2 under irradiation of sunlight with energy

density of 100 mW.cm^{-2} in open air. The open-circuit photovoltage and the short-circuit photocurrent density were of 680 mV and 6.23 mA.cm^{-2}, respectively. The fill-factor of our PEC was of 0.31-0.33 then the energy conversion efficiency was of 1.3-1.4%.

The open-circuit photovoltage of 680 mV and the photocurrent of 1200 μA produced by nanoporous ZnO/CdS bilayer film of 1 cm^2-illuminated area show that the nanosize CdS effectively sensitized the nanoporous ZnO. This can be explained as follows, the electron affinity of the CdS is higher than that of the ZnO. Therefore, according to Anderson's model, a type-II heterojunction is well formed between CdS and ZnO [16]. The electrons from the conduction band of CdS are quickly transferred to the conduction band of ZnO. Once the electrons diffuse into the conduction band of ZnO, the probability of its decay is small because there can be no free hole in ZnO under visible excitation. As a result, the electrons accumulate in the conduction band of the ZnO and the holes accumulate in the valence band of the CdS. In this way, the charge separation is achieved [16]. The redox couple in the electrolyte, after reducing the oxidized dye, can be renewed in the counter-electrode, making the photoelectrochemical cell regenerative [5]. It is clearly seen that the coupling of ZnO with CdS can significantly enhance the separation of the electron and hole pairs, therefore, ameliorate the photoelectric performance of the ZnO/CdS bilayer films. These results are promising for improving the efficiency of photovoltaic devices.



(a) (b)

Fig. 4. Photocurrent-potential (J -V) behaviors of ZnO (a), TiO_2/CdS (b) and the ZnO /CdS (c) electrodes, respectively. The inset shows zoom in (J-V) of ZnO and TiO_2/CdS electrodes. (b)Photocurrent-potential (J -V) behaviors of Photovoltaic cells irradiated by sunlight in open air. The inset shows the image of device.

IV. CONCLUSIONS

Nanoporous ZnO/CdS thin films have been successfully prepared by a thermal evaporation technique combined with thermal process. This method is relatively simple and low-cost technique for large scale uniform coating nanoporous thin film on the substrate. The PEC using the nanoporous ZnO/CdS bilayer thin film as an electrode produced the

energy conversion efficiency of 1.3-1.4%. The nanoporous ZnO/CdS bilayer thin film produced photocurrent density of 6.23 $mA.cm^{-2}$ has possessed more excellent photoelectrochemical performance than that of ITO/ZnO, ITO/TiO_2/CdS films and macroporous ZnO/CdS. It is believed that nanostructured CdS films effectively sensitizing ZnO nanoporous structures can be used in fabricating high efficiency photovoltaic devices.

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REFERENCES

[1] Y. Jiang, M. Wu, X. Wu, Y. Sun, and H. Yin, *Materials Letters* **63** (2009) 275.
[2] N. Boukos, C. Chandrinou, K. Giannakopoulos, G. Pistolis, and A.Travlos, *Applied Physics A* **88** (2007) 35.
[3] G. Hodes, *The Journal of Physical Chemistry C* **112** (2008) 17778.
[4] D. Liu and P.V. Kamat, *The Journal of Physical Chemistry* **97** (1993) 10769.
[5] Y-J. Chi, H-G. Fu, L-H. Qi, K-Y. Shi, H-B. Zhang, and H-T.Yu, *Journal of Photochemistry and Photobiology A: Chemistry* **195** (2008) 357.
[6] J. Touscaronková, D. Kindl, and J. Touscaronek, *Physica Status Solidi (a)* **142** (1994) 539.
[7] H. Jianhua and R.G. Gordon, *J. Appl. Phys.* **71** (1992) 351309.
[8] M. Jin, J. Feng, Z. De-heng, M. Hong-lei, and L. Shu-ying, *Thin Solid Films* **357** (1999) 98.
[9] P.M. Verghese and D.R. Clarke, *J. Mater. Res.* **14** (1999) 1039.
[10] J-L. Chung, J-C. Chen, and C-J. Tseng, *Journal of Physics and Chemistry of Solids* **69** (2008) 535-539.
[11] J. Liu, X. Huang, J.Duan, H. Ai, and P.Tu, *Materials Letters* **59** (2005) 3710.
[12] C. Meijuan, T. Yiwen. L. Bihui, and L. Lijuan, *J. Nanosci. Nanotechnol.* **9** (2009) 1505.
[13] A. Aguilera, V. Jayaraman, S. Sanagapalli, S. Singh, V. Jayaraman, K. Sampson, and V. P. Singh, *Solar Energy Materials & Solar Cells* **90** (2006) 713.
[14] T.C. Dang, D.L. Pham, H.C. Le, and V. H. Pham, *Adv. Nat. Sci.: Nanosci. Nanotechnol.* **1** (2010) 0150021.
[15] T.C. Dang, D.L. Pham, H.L. Nguyen, and V. H. Pham, *Adv. Nat. Sci: Nanosci Nanotechnol.* **1** (2010) 0350101.
[16] J. Nayak, S. N. Sahu, J. Kasuya, and S. Nozaki, *Applied Surface Science* **254** (2008) 7215.

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