CdS sensitized ZnO electrodes in photoelectrochemical cells*

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Abstract
In this work, ZnO nanocrystalline thin films were obtained by evaporating Zn films using a thermal evaporation technique and then thermal treatment. The results show that after annealing at 300, 350, 400 and 450 °C for 6 h, the obtained ZnO thin films have macro-structures. The results show that at an annealing temperature of 450 °C, the ZnO thin film has the best optical properties for photo-electrodes. The incorporation of cadmium sulfide (CdS) into ZnO macro-structure thin films was investigated. A CdS thin film was vacuum-deposited onto the pre-deposited ZnO film by the thermal evaporation technique. The obtained ZnO and ZnO/CdS bilayer films were characterized by x-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM). The ZnO/CdS bilayer film was used in a photoelectrochemical (PEC) cell as a working electrode and a platinum electrode as a counter electrode. The electrolyte solution contained 1 M KCl and 0.1 M Na₂S. The results show that the cell with the ZnO/CdS bilayer electrode had significantly improved photoelectric properties in comparison with that of the pure ZnO thin films. The best thickness of the CdS thin film deposited on ITO/ZnO substrates was around 70 nm.

Keywords: Cadmium sulfide, Zinc oxide, photoelectrochemical cell

Classification numbers: 4.10, 4.11

1. Introduction
Zinc oxide has been widely investigated due to its properties of piezoelectricity, conductivity, optical absorption and emission, and catalytic activity. ZnO thin films have many applications in gas sensors, photocatalysis, dye-sensitized solar cells and piezoelectric devices [1]. Compared with TiO₂, ZnO is cheaper, more abundant in nature and easier to prepare due to its ease of crystallization and anisotropic growth. Moreover, ZnO has higher electronic mobility that would be favorable for electron transport, with reduced recombination loss when used in PEC [2]. However, the band gap of ZnO is so large (around 3.37 eV) [3] that it can only absorb a small part of visible light. To enhance the absorption of visible light, it is necessary to sensitize the nanoelectrodes. As a result, many sensitizers have been explored and dye sensitizers have been studied. In addition to dye sensitizers, semiconductors with a narrow band gap have recently attracted much attention due to their excellent properties, such as higher absorption, greater stability and adjustable band gap [4]. Combining two semiconductor particles offers an opportunity to sensitize a semiconductor material having a large band gap and energetically low-lying conduction band by another one having a small band gap and energetically high-lying conduction band [5]. Charge injection from one semiconductor into another can lead to efficient and longer charge separation, which is anticipated to have potential applications in photocatalysis and solar energy

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conversion [6]. Among the various semiconductors, CdSe, CdTe, CuInS₂, InP, etc are used as sensitizers [7], and CdS has shown much promise as an effective sensitizer [8]. CdS belongs to the II–VI group and is typically sulfur deficient [9]. 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 [10]. However, it has not been much studied in comparison with the sensitizers of dye-sensitized solar cells (DSSCs) [11]. In this study, CdS was used to sensitize ZnO nanostructures. In a ZnO/CdS nanocomposite, CdS acts as a visible sensitizer and ZnO, being a wide band semiconductor, is responsible for charge separation, which suppresses the recombination process. Hence, the prepared ZnO/CdS nanocomposite thin films can effectively capture the visible light and quickly transfer the photogenerated electrons into the ZnO conduction band. Finally, the sensitization of CdS on ZnO strongly ameliorates the photoelectric performance of the ZnO/CdS nanocomposite electrodes.

Various methods have been used for the production of ZnO nanostructures, such as chemical vapor deposition [12], thermal evaporation [13], pulse-laser deposition [14], dc and/or radio frequency (RF) sputtering [15], sol–gel and wet chemical methods. In this work we used a vacuum evaporation technique combined with a thermal process for the fabrication of ZnO films. In comparison with other techniques, thermal evaporation is a relatively simple one for large-scale uniform coating to produce clean, dense and strong adhesion to substrate thin films.

2. Experimental setup

A variety of substrates were used for different purposes. For photoelectrochemical (PEC) cell testing, patterned ITO on glass was used. For XRD and FE-SEM samples, silicon substrates were employed. 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. All of the substrates were subsequently treated with a glow discharge technique. A 500 nm thick layer of Zn was vacuum-deposited by thermal evaporation at a pressure of 10⁻² torr. The deposition rate was controlled at 1.5 nm s⁻¹. The thin film thickness in the range of 15–180 nm was measured during deposition using a conventional quartz crystal monitor. To obtain good crystallinity, the thin CdS films were annealed at 450 °C in air for 6 h.

The thin films of CdS were fabricated, by the same method as that for Zn film, onto the ZnO/ITO substrate, which was annealed at 450 °C. The deposition rate was 0.2 nm s⁻¹. The thin film thickness in the range of 15–180 nm was measured during deposition using a conventional quartz crystal monitor. To obtain good crystallinity, the thin CdS films were annealed at 450 °C in air for 2 h.

The surface morphology of the samples was investigated using a Hitachi field emission scanning electron microscope (FE-SEM). The ultraviolet-visible (UV-VIS) absorption spectra were measured using a Jasco UV-VIS-NIR V570 spectrometer, and x-ray diffractograms were recorded on a Siemens D-5000 diffractometer using CuKα radiation with a wavelength of 1.5406 Å. In photoelectric studies, a two-electrode PEC cell was used. This comprises ITO/ZnO or ITO/ZnO/CdS used as the working electrode (the working area is 1 cm²) and a platinum electrode separated by an electrolyte containing 1 M KCl and 0.1 M Na₂S. The photocurrent was measured on an Auto-Lab Potentiostat PGS-30. A halogen lamp was used as a light source.

3. Results and discussion

3.1. Morphology and structural characterization of the ZnO thin films and the ZnO/CdS bilayer films

Figure 1 shows the FE-SEM images of annealed ZnO thin film surfaces on silicon substrates at different temperatures.
From the figure, it is apparent that at an annealing temperature of 300 °C, the ZnO thin film consisting of sheet-like grains covers the substrate surface continuously and homogeneously. The average spaces between the sheet-like grains are 50–100 nm. The film has a coral-like structure with a very rough surface, which becomes visible after annealing at 350 °C. At an annealing temperature of 400 °C, the film has a particle-like structure with a grain size in the range of 50–100 nm. The smoother and approximately uniform surface can be observed at an annealing temperature of 450 °C with the grain size in the range of 100–200 nm. The increase in smoothness of the ZnO thin film with increased annealing temperature might originate from the increase in the grain size in the film due to thermal treatment [16]. Therefore, the surface roughness becomes smoother when the annealing temperature increases.

Figure 2 shows the XRD patterns of annealed ZnO thin films at different temperatures. It can be seen from figure 2(a) that the high intensity of diffraction peaks at the 2θ position of about 36.3°, 39.0° and 43.2° from zinc are found in the sample annealed at 300 °C, whereas for the ZnO thin film annealed at 350 °C, diffraction peaks at the 2θ position of 39.0° and 43.2° are shown with very low intensity. In particular, the peaks at the 2θ position of 36.3° and 54.3° disappeared (figure 2(b)).

As can be seen from figures 2(c) and (d), no diffraction peaks from zinc or other impurities are detected except for Si coming from the substrates at annealing temperatures of 400 and 450 °C. The diffraction peaks at the 2θ values of approximately 31.7°, 34.3°, 36.3°, 47.6°, 56.6° and 62.8° correspond to the (100), (002), (101), (102), (110) and (103) planes, respectively. They are indexed as a wurtzite structure of ZnO with cell constants of a = 0.324982 nm and c = 0.520661 nm (JCPDS card No. 36-1451). This is in good agreement with [17, 18]. These results indicate that the conversion to ZnO increases with the increase in annealing temperature. This means that the zinc films were completely transformed to ZnO. Furthermore, increasing the annealing temperature leads to enhancement of the intensity of the XRD peaks and the peaks become sharper (figure 2(d)). Hence, the morphology and crystallinity are improved. This is an indication of the enhancement of the crystalline nature of the films.
UV-VIS absorption spectra of a series of ZnO thin films with the annealing temperature at 300, 350, 400 and 450 °C. As can be seen from the figure, the ZnO thin films annealed at 300, 350 and 400 °C absorb light mainly within the wavelength range from 365 to 390 nm, whereas for the sample annealed at 450 °C, the absorption is obviously enhanced. The main absorption edge is estimated to be about 420 nm. In order to calculate the band gap of the ZnO films, the equation

\[ \alpha(h\nu) = C(h\nu - E_g)^m \]  

is applied [19], where \( C \) is a constant related to the refractive index and the electron/hole masses, \( \alpha \) is the absorption coefficient, \( h\nu \) is the energy of the incident photon, \( E_g \) is the band gap of the semiconductor, and \( m \) is 0.5 and 2.0 for a direct transition semiconductor and an indirect transition semiconductor, respectively. ZnO is a direct semiconductor and the \( m \) value is 0.5. The values of the optical band gap of the films are obtained by plotting \( (\alpha(h\nu))^2 \) versus \( h\nu \) (photon energy). The band gaps of the ZnO films are 3.23, 3.23, 3.20 and 3.19 eV, corresponding to the annealing temperatures at 300, 350, 400 and 450 °C, respectively (figure 5(b)). It is clearly seen that at an annealing temperature of 450 °C, the ZnO thin film has the best optical properties for photo-electrodes. This can be explained by the Lambert–Beer law [17],

\[ I = I_0 \exp(-\alpha d), \]  

where \( I, I_0, d \) and \( \alpha \) represent the transmission light intensity, incident light intensity, film thickness and absorption coefficient, respectively. According to equation (2), it can be easily determined that the increase in film thickness \( d \) causes the decrease in transmission light intensity \( I \) and results in high absorption of visible light (figures 6(d)–(f)).
Therefore, the modification of CdS thin films for ITO/ZnO would effectively capture the visible light.

3.3. Photoelectronic performance of ZnO thin films and ZnO/CdS bilayer films

Figure 7 shows the photocurrent behaviors with time for the ZnO film and ZnO/CdS bilayer film electrodes performed under light on/off illumination at 0.2 V. It shows that initial photocurrent decay appeared with light-on illumination. The photocurrent decay is an indication of recombination of photogenerated charge carriers though the surface states [21]. As can be seen from the figure, the photocurrent generation was prompt and the current was stable in the time interval of the pulsed illumination in both ZnO/CdS and ZnO electrodes. The ZnO/CdS electrode shows significantly higher photocurrent than that of the pure ZnO electrode.

Figure 8 shows the photocurrent-potential behaviors of the photoelectrochemical cell with each of the prepared samples used as working electrodes in turn. It is clear that the coupling of CdS with ZnO ameliorates the photoelectric performance of the ZnO/CdS bilayer films. Figure 9 shows the short-circuit photocurrent ($J_{sc}$) and the open-circuit photovoltage ($V_{oc}$) of the ITO/ZnO and ITO/ZnO/CdS with different thicknesses of CdS film. The variation in $V_{oc}$ and $J_{sc}$ is likely due to the differences in the thickness of the CdS thin films. It is clear that in the thickness range of 15–70 nm, the $V_{oc}$ and $J_{sc}$ of the film electrodes under illumination increase with the increase in the thickness of the CdS thin films and approach maximum values of $V_{oc} = 465$ mV and $J_{sc} = 412 \mu$A (70 nm CdS film electrode), as shown in figure 9. Conversely, the $V_{oc}$ and $J_{sc}$ decrease as the thickness of the CdS thin films increases in the thickness range of 70–180 nm.

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 formed between the CdS and ZnO [20]. The light from the halogen lamp generates electron-hole pairs in the CdS. The electrons from the conduction band of the CdS are quickly transferred to the conduction band of the ZnO. Once the electrons diffuse into the conduction band of the ZnO, the probability of their decay is small because there is no free hole in the 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, charge separation is achieved.

In photoelectrochemical measurement, in order to avoid recombination, the photogenerated holes must reach the counter electrode along continuous paths without recombining with electrons. Simultaneously, the generated photoelectrons quickly transport to the counter electrode via the external circuit. Finally, the electron cycle is ended via the redox couple in the electrolyte [8].

It is clearly seen that the coupling of ZnO with CdS can significantly enhance the separation of electron and hole.

However, as discussed above, the amounts of $V_{oc}$ and $J_{sc}$ of the ZnO/CdS electrodes depend on the thickness of the CdS thin films deposited on the ITO/ZnO substrates. It is well known that light absorption with a suitable wavelength results in the creation of a bound electron–hole pair—the exciton. Mobile charge carriers are generated when the electron and hole of an exciton at the interface between the ZnO thin film and CdS thin film are separated. Only those excitons created...
within a diffusion length from the charge separation region can effectively generate charge carriers. This means that only a thin slab having a suitable thickness around the interface is contributing to the current. Increasing the thickness of the CdS thin films will increase the light absorption leading to greater exciton generation, as shown in figure 6, but not the charge separation and thus the efficiency of the photoelectrochemical cell [20]. Moreover, the increase in the thickness of the CdS thin films would require a longer time for the electrons to reach the interface. Furthermore, the excess CdS nanoparticles cannot effectively absorb light and inject electrons, but act as a potential barrier for charge transfer [22]. Therefore, the probability of recombination or trapping of the generated holes would be higher, causing the photocurrent to decrease. In contrast, for the CdS films of less than 70 nm, a decrease in the thickness will decrease the values of $V_{oc}$ and $J_{sc}$ due to lower absorption of the CdS films. Hence, the 70 nm CdS thin film seems to be a better candidate for a photovoltaic solar cell. This result agrees very well with our earlier results [20]. Qualitatively, the main reason is that the thickness might be suitable for light generated electrons and holes to travel over a shorter path and thus recombination losses are greatly reduced. Therefore, an enhanced charge transport route is desirable to achieve efficient electron conduction. In addition, the rough surface of the 70 nm CdS thin film, as shown in figure 3, can lead to an increased contact area to the electrolyte, which might give rise to an increase in the electrical conductivity.

4. Conclusion

ZnO thin films have been successfully prepared by the thermal evaporation technique combined with a thermal process. At an annealing temperature of 300 °C, the ZnO thin film consisted of sheet-like grains. The coral-like structure appeared after annealing at 350 °C. At an annealing temperature of 400 °C, the ZnO thin film is uniform with a grain size in the range of 50–100 nm. At an annealing temperature of 450 °C, the smoother and approximately uniform surface can be seen with the size of about 100–200 nm. Zinc films were completely transformed into ZnO. ZnO/CdS bilayer films have been successfully fabricated by a thermal evaporation technique. The prepared ZnO/CdS bilayer films have better photoelectrochemical performance than ITO/ZnO film. This would mean that ZnO macroporous structures sensitized by CdS thin films can be used to fabricate high efficiency photovoltaic devices. The best thickness of the CdS thin film deposited on ITO/ZnO substrates is around 70 nm.

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