

Effect of etching and annealing on performance of CdS nanostructures photoelectrochemical solar cells

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Nanostructures of CdS in thin films form have been achieved via chemical bath deposition followed by wet chemical etching process. Studies have been made by using scanning electron microscopy (SEM), atomic force microscopy (AFM) and UV-vis spectroscopy techniques. SEM study reveals that the length of nanowires increases upon increment of etching time. AFM image shows that annealing of the photoelectrode leads to the fusion of small crystallites, resulting in agglomeration. Optical absorption study shows the presence of direct transition and band gap energies are found to be 2.58, 2.43, 2.40 and 2.38 eV, respectively, for the as-deposited and annealed films. Photoelectrochemical (PEC) investigations are carried out using cell configuration as n-CdS/(1M NaOH + 1M Na₂S + 1M S)/C. Performance of the PEC cell is found to be improved on annealing and wet chemical etching.

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1. Introduction

As an alternative and clean energy source, photoelectrochemical (PEC) solar cells have attracted great scientific and technological interest and have been extensively investigated in the past decades. It has been found by several researchers that growth and treatment parameters, such as the film thickness, microstructure, annealing, aging, etching and photo-electrochemical etching, influence the performance of the PEC solar cells fabricated, including their efficiency of performance. Hence, research is being carried out in different laboratories to investigate the influence of these parameters in an attempt to increase the efficiency of the PEC solar cells. One-dimensional (1D) semiconductor nanostructures (such as nanotubes, nanorods, nanowires and nanobelts) have recently received considerable attention because of their unique electronic, optical, mechanical properties and their potential applications in nanodevices [1–3]. Among group II–VI semiconductors, CdS with a direct bandgap of 2.42 eV is considered to be an excellent material for various optoelectronic applications in the visible range of the electromagnetic spectrum. Some of these applications include nonlinear optical devices, LEDs, and solar cells [4–6]. It has also been used as an alternative to dye-sensitization of TiO₂ electrode [7]. CdS in a nanocrystalline thin films form can be prepared by a variety of methods (both physical and chemical) like sol–gel [8], electrostatic deposition [9], gas evaporation [10], micelles [11], chemical bath deposition (CBD) [12] and etc. The CBD process is a simple and inexpensive technique to obtain homogeneous, hard, adherent, transparent and stoichiometric CdS nanocrystals thin films. Earlier, we have reported about the thin film of CdS nanowires formation at room temperature (300 K). In present paper, effect of etching time and annealing

temperatures on PEC and optical properties of CdS nanostructured thin films is reported.

2. Experimental detail

In the present study analytical grade reagents were used without any further purification. Preparation method of CdS nanostructures consisted of two steps. In the first step films of CdS nanoparticle were prepared by CBD. The nanoparticle films were converted into fibril-like nanowire using chemical etching in second step.

The nanostructures of CdS in thin film form was synthesized by the reaction of CdSO₄ with thiourea in presence of complexing agent NH₄OH in the method reported previously [13]. The freshly prepared as-grown samples were etched in hydrochloric acid (HCl) for 5, 15 and 30 second by the procedure described earlier [13]. Besides, the as-grown samples were also annealed at different temperatures (100, 150 and 200 °C) for an hour under air. After annealing the heater of furnace was switched off and left to cool until room temperature was reached.

The thickness of CdS film was measured with the help of weight difference method employing sensitive electronic microbalance (Citizen: CX-265). Thickness of film was 435 nm. The surface morphology of the films was characterized by scanning electron microscopy (SEM; JEOL-JSM 5600) and atomic force microscopy (AFM; DIAFM-4). The transmission data in the range 400–700 nm were obtained with Perkin Elmer, Lambda-35 spectrometer. The PEC cell was constructed using as-grown, etched and annealed films of CdS onto Ti as photoelectrode, and polysulfide as an electrolyte with graphite as the counter electrode. The photocurrent and photovoltages were measured under different load

conditions with constant intensity of illumination (100 mW/cm^2) from a 50 W tungsten-halogen lamp.

3. Results and discussion

In our previous communication, we have reported the conversion of CdS nanoparticles into nanorod/nanowire via this simple aqueous chemical growth route. The average diameter of the CdS nanoparticle is estimated to be 6.6 nm whereas it is 5.8 nm for CdS nanowire sample. A detailed description about size of CdS nanoparticle and nanowire measurement is given elsewhere [13].

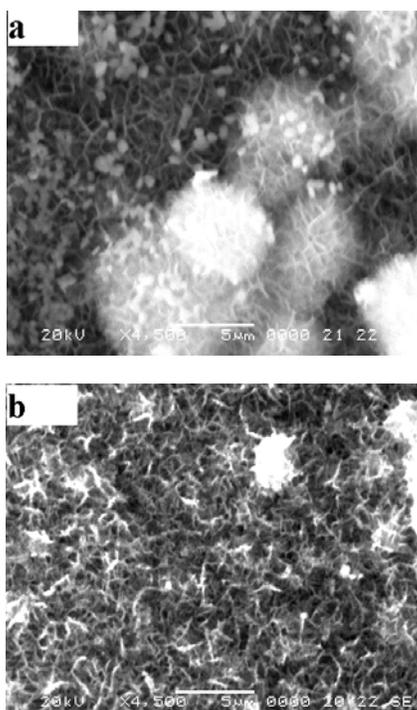


Fig. 1. SEM micrograph of CdS nanorod/nanowire after chemical etching (a) for 5 second (b) for 15 second.

3.1 Morphology of nanofilms and formation mechanism of nanostructures

It has been reported that the morphology of etched semiconductor materials depends on the etching condition [14]. The morphology of as-grown sample (clusters of nanoparticles) changed drastically when the samples were etched in hydrochloric acid (commercially available 36%) using optimized etchant parameters such as concentration (0.1 M) of etchant, temperature (283K) and time of etching process. Fig. 1 (a) shows the SEM micrograph of the CdS nanowires, fabricated by CBD for deposition time of 5 hrs followed by chemical etching for 5 second. The micrograph shows interconnect fibril-like wires with incorporated clusters of CdS nanoparticle. The nanowires have widths in the range of 50-150 nm and have lengths of the order of a few micrometers. Interestingly, the length of nanorods/nanowires increases upon increasing the time (15 second) of etching process, however other etchant

parameters were kept same as for above sample (Fig. 1b). We believe that the formation of nanorods/nanowires from the CdS clusters is either by dissolution-condensation (recrystallization) process [15] or by due to Ostwald ripening. We think that in our experiment, the CdS molecules first dissolved into the solvent (HCl acid) and then diffuse through the solvent and deposited onto the preferential surface (002) resulting in the growth of nanorods/nanowires. A detail of the formation mechanism of nanowire is reported earlier [13]. Morphological study is also done for annealed samples. Fig. 2 (a) shows the AFM picture of as-grown sample which also confirms the spherical shaped morphology of clusters of CdS nanoparticles. As the annealing temperature increased, larger particles were formed, probably due to melting of boundaries between particles. Fig. 2 (b) shows AFM image of CdS sample annealed at 473K.

3.2 Optical studies

UV-visible transmission spectra of as-grown and annealed samples at different temperatures (373, 423 and 473 K) recorded in the wavelength range of 400-700 nm is shown in Fig. 3. For annealed film electrodes, transmittance was decreased slightly which is common in semiconducting thin films, as reported by other [16]. It is also noted from the spectra that the absorption edge shifts to longer wavelength slightly as annealed temperature increases.

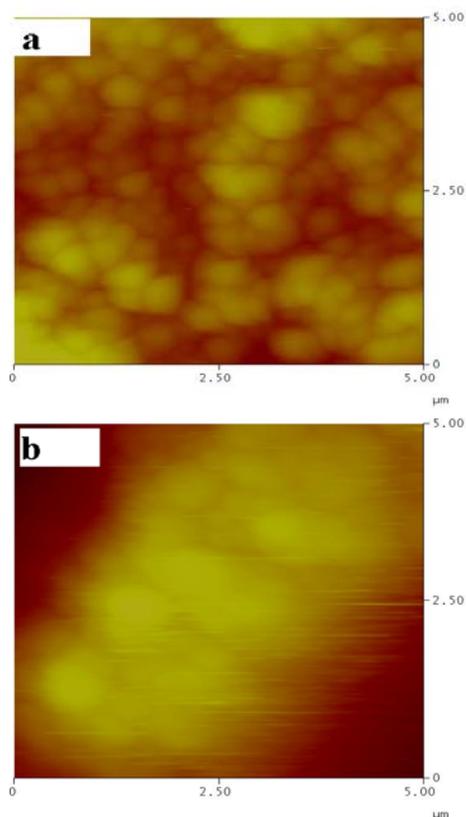


Fig. 2. AFM image of CdS nanoparticles (a) as-grown and (b) annealed at 473K.

It is also noted from the spectra that the absorption edge shifts to longer wavelength slightly as annealed temperature increases. This shift corresponds to decrease in the optical band gap i.e. increase in size. The fundamental absorption, which corresponds to electron excitation from the valance to conduction bands, can be used to determine the value of the optical band gap. The band gap has been calculated by extrapolating the linear region of the plots $(ahv)^2$ vs hv on the energy axis, as shown in Fig. 4. The band gap values are estimated to be 2.58, 2.43, 2.40 and 2.38 eV for as-grown and annealed (at 373, 423 and 473 K for 1 hrs) CdS samples respectively.

3.3 Photoelectrochemical performance

Fig. 5 and Fig. 6 show photovoltaic output characteristics of the PEC solar cells under illumination with 100 mW/cm^2 white light from a tungsten-halogen lamp, for photoelectrodes with a thickness of 435 nm, before and after heat and etching treatments. Table 1 gives details of the PEC solar cell efficiency (η) obtained when films both as-grown and heat- and surface-treated, are used as the photoelectrode in the solar cell. The efficiency η (in %) and fill factor (FF) of PEC cell were calculated from the relation

$$\eta = \frac{V_{oc} I_{sc} FF}{P_{input}} \times 100$$

$$FF = \frac{I_m V_m}{I_{sc} V_{oc}} \quad (1)$$

where P_{input} is the input light energy and V_{oc} and I_{sc} are open circuit voltage and short circuit current respectively. I_m and V_m are values of maximum current and voltage at the maximum power point, respectively. Series resistance R_s and shunt resistance R_{sh} were estimated from slope of power output characteristics using the relation [17]

$$\left(\frac{dI}{dV}\right)_{I=0} = \left(\frac{1}{R_s}\right) \quad \text{and}$$

$$\left(\frac{dI}{dV}\right)_{V=0} = \left(\frac{1}{R_{sh}}\right) \quad (2)$$

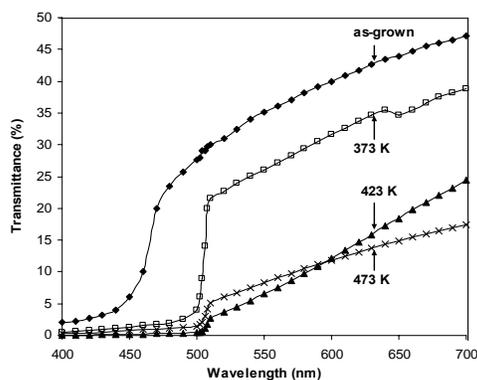


Fig. 3. Optical transmission spectra of as-grown and annealed (at 373, 423 and 473 K for 1 hrs) CdS thin films.

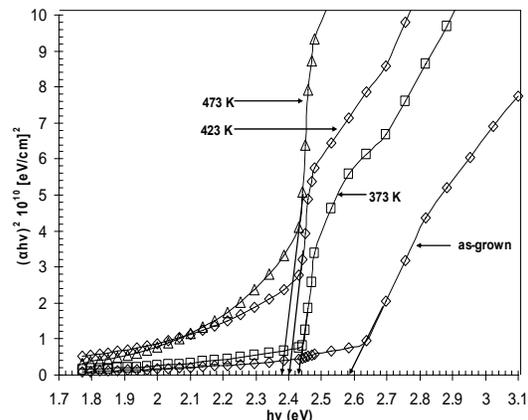


Fig. 4. Variation of $(ahv)^2$ with energy of as-grown and annealed (at 373, 423 and 473 K for 1 hrs) CdS thin films.

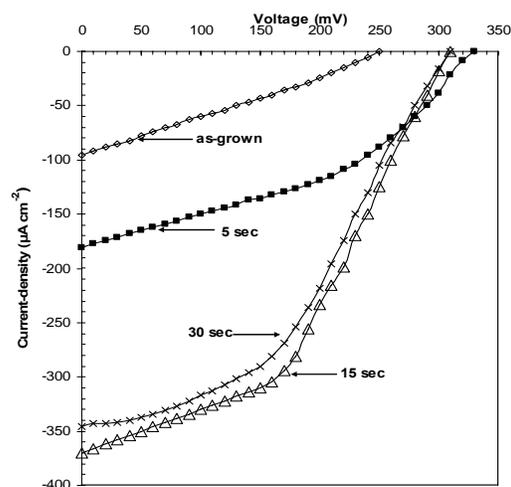


Fig. 5. Photovoltaic output characteristics for n-CdS/IM (NaOH-Na₂S-S)/C PEC cells of (a) as-grown (b) after 5 sec etching (c) after 15 sec etching (d) after 30 sec etching.

From the Table 1 it is observed that V_{oc} , I_{sc} , efficiency and fill factor continuously increased with increasing etching time duration. The best results were obtained for a 15 sec etch. The main effect of a short etch (5 sec) is to increase short-circuit current I_{sc} by 2 times. It is seen from the morphological study that after a short etching time period the nanoparticles become in well ordered and forming a fibril-like interconnected network of nanorod/nanowire due to Ostwald ripening [18]. Moreover, because of the occurrence of ostwald-ripening the length of nanowires possibly increases due to longer time periods (15 sec) of etching. The film consisting of one-dimensional nanostructures can easily transport the photoelectrons by providing the direct conduction paths for the electrons from the point of generation to the collection, also maintaining a high surface area for more light harvesting. The decreased path length of the electron travel will avoid the effect of recombination as compared

to that in the nanocrystalline film [19]. Further, etching process contributes to increase in the junction area and reduce the surface states, leading to the enhancement of the solar power-conversion efficiency [20]. Longer etching results in a decrease in all the solar cell parameters due to excessive etching which damage the film surface. The increase in conversion efficiency obtained due to annealing comes about because of the following reasons. Annealing of the photoelectrode leads to the fusion of small crystallites, resulting in agglomeration. This reduces the grain boundary area.

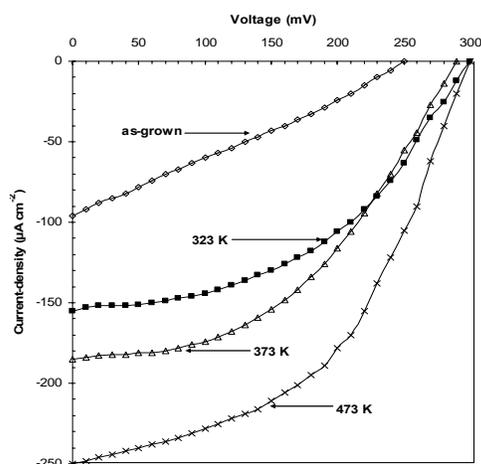


Fig. 6. Shows photovoltaic output characteristics of the as-grown and annealed (373, 423 and 473K for 1 hrs) CdS film photoelectrodes.

Table 1. Performance of CdS nanostructure photoelectrodes etched/annealed at different conditions.

Condition of films	Etching time (s)/Annealing temperature (K)	R_s (Ω)	R_{sh} (K Ω)	I_{sc} (μA)	V_{oc} (mV)	FF (%)	η (%)
As-grown	-	1666	2.5	96	250	28.0	0.006
Etched	5	909	2.86	181	330	40.0	0.024
Etched	15	454	3.3	370	310	44.0	0.05
Etched	30	500	3.0	346	310	43.0	0.046
Annealed	373	1111	3.3	155	300	45.76	0.021
Annealed	423	666	3.9	185	290	46.97	0.025
Annealed	473	605	5.0	250	310	48.77	0.038

This in turn leads to an increase in diffusion length of the charge carriers because of the decrease in scattering from the grain boundaries. Annealing also removes any excess Cd, so that excess Cd atoms which act as acceptors/recombination centers are reduced, thus improving the effective carrier concentration [21].

4. Conclusions

Nanostructures of CdS in the film form have been successfully synthesized by CBD method followed by electroless chemical etching technique. From the present study, we investigated the influence of different etching time periods and annealing temperatures on the cell performance. It is found that surface treatment techniques (etching and annealing) leads to enhancement of efficiency-1/ from 0.006 to .046% for the wet etching and 2/ from 0.006 to 0.038% for the annealing of photoelectrodes.

References

- [1] A. M. Morales, C. M. Liber, Science **279**, 208 (1998).
- [2] Z. W. Pan, Z. R. Dai, Z. L. Wang, Science **291**, 1947 (2001).
- [3] W. U. Huynh, J. J. Dittmer, A. P. Alivisatos, Science **295**, 2425 (2002).
- [4] X. Duan, C. Niu, V. Sahi, J. Chen, J. W. Parce, S. Empedocles, J. L. Goldman, Nature **425**, 274 (2003).
- [5] Y. K. Liu, J. A. Zapien, C. Y. Geng, Y. Y. Shan, C. S. Lee, S. T. Lee, App. Phys. Lett. **85**, 3241 (2004).
- [6] J. Zhang, F. Jiang, L. Zhang, J. Phys. Chem. B **108**, 7002 (2004).
- [7] Y. C. Shen, H. H. Deng, J. H. Fang, Z. H. Lu, Colloids Surf., A Physicochem. Eng. Asp. **175**, 135 (2000).
- [8] A. V. Rao, G. M. Pajonk, N. N. Parvathy, Mater. Chem. Phys. **48**, 234 (1997).
- [9] O. V. Salata, P. J. Dobson, P. J. Hull, J. L. Hutchinson, Thin Solid Films **251**, 1 (1994).
- [10] T. Arai, T. Yoshida, T. Ogawa, J. Appl. Phys. **26**, 396 (1987).
- [11] P. Lianos, J. K. Thomas, Chem. Phys. Lett. **125**, 299 (1986).
- [12] H. Moualkia, S. Hariech, M. S. Aida, Thin Solid Films, **518**, 1259 (2009).
- [13] J. K. Dongre, V. Nogriva, M. Ramrakhiani, App. Sur. Sci., **255**, 6115 (2009).
- [14] J. J. Kelly, D. Vanmaekelbergh, Electrochemistry of Nanomaterials ed G. Hodes, Wiley-VCH, Weinheim p. 114, 2001.
- [15] G. Cao, Nanostructure and Nanomaterials, first ed., Imperial College Press, London, 2004.
- [16] V. R. Shinde, C. D. Lokhande, R. S. Mane, S.-H. Han, Appl. Surf. Sci. **245**, 407 (2005).
- [17] T. J. Coutts, Thin Solid Films **50**, 99 (1978).
- [18] W. Z. Ostwald, J. Phys. Chem. **34**, 495 (1900).
- [19] A. R. Rao, V. Datta Nanotechnology **19**, 445712 (2008).
- [20] V. D. Das, L. Damodare Mater. Chem. and Phys. **56**, 48 (1998).
- [21] V. Damodara Das, D. Ravi Shankar, Sur. and Coat. Tech. **146-147**, 498 (2001).

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