Journal of Alloys and Compounds 505 (2010) 140–143

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Characterization of cadmium selenide films for photovoltaic applications

P.A. Chate [a,*], P.P. Hankare [b], D.J. Sathe [c]

[a] Department of Chemistry, J.S.M. College, Alibag, (M.S.) India
[b] Department of Chemistry, Shivaji University, Kolhapur, (M.S.), India
[c] Department of Chemistry, KIT's college of Engineering, Kolhapur, (M.S.) India

ARTICLE INFO

Article history:
Received 8 May 2010
Received in revised form 23 May 2010
Accepted 1 June 2010
Available online 11 June 2010

Keywords:
Chalcogenides
Nanostructure
Thin films
Chemical synthesis
Electrical properties
Photoelectrochemical cell

ABSTRACT

Crystalline cadmium selenide thin films have been deposited using dip technique. The precursor solution contains cadmium sulphate, sodium selenosulphate with maleic acid as a complexing agent. The deposited films undergo various characterization techniques. The crystalline phase of the deposited sample was hexagonal wurtzite-type. Compositional study indicates ratio of Cd:Se was close to 1:1. The direct optical band gap energy was found to be 1.90 eV. The construction of fabricated cell is CdSe|NaOH (1 M) + S (1 M) + Na_2S (1 M)|$C_{(graphite)}$. The photoelectrochemical characterization of the films is carried out by studying current–voltage characterization, capacitance–voltage and power output characteristics. The fill factor and efficiency of the cell were found to be 33.44% and 1.01%, respectively.

1. Introduction

II–VI semiconducting chalcogenides nanoparticles, especially sulphides and selenides have been investigated extensively owing to their interesting opto-electronic properties [1,2].

Cadmium selenide is a compound semiconductor material become important because of its major contribution in solar cells, photodetectors, light amplifiers, electro-photography, light emitting diodes, lasers, photoelectrochemical cells, electronic material based on the metal insulator semiconducting structure, gas sensors and biomedical imaging devices [3–9].

Electrical and optical properties of semiconducting films are very important from application point of view in various opto-electronic devices and these properties are extremely sensitive to ambient conditions and deposition technique used. Therefore, study of such properties of the films with respect to their different growing as well as ambient conditions is a matter of profound importance. Similarly, these properties depend on their crystallite size and/or the thickness of the film [10,11]. The nanocrystalline nature of the films leads to several interesting phenomena originating from the quantum confinement effect, along which and increasing in the optical band gap with a decrease in closely spaced semiconductor nanocrystals size is the most apparent [12–14].

Photoelectrochemical cells are simple in construction and have the advantage that they can be used for both solar to electrical and chemical energy conversions. Presently, one of the best materials for tailoring of band gaps is from the group of Cd-chalcogenide [15,16].

Pramanik and colleagues show variation of thickness with different bath parameters has been studied to obtain thickest deposition possible [17]. Murali et al. deposited CdSe thin films in the temperature range 5–30 °C from the precursors. The films exhibited hexagonal structure. Optical band gap was found to vary in the range of 1.65–2.1 eV as the substrate temperature is decreased from 30 °C to 5 °C [18]. Cerderia et al. deposited cadmium selenide thin film on Ti substrate using CBD. The photoluminescence and Raman spectra were studied [19].

With this view, we synthesize the nanocrystalline cadmium selenide thin film using a dip method. The film was studied for structural, compositional, optical, electrical and photoelectrochemical performance.

2. Experimental details

All the chemicals used for the deposition were analytical grade. It contains cadmium sulphate octahydrate, maleic acid, hydrazine hydrate, sodium sulphite, and selenium powder. All the solutions were prepared in double distilled water.

Sodium selenosulphate was prepared by following the method reported earlier [20].

In the experiments, 10 mL (0.2 M) cadmium sulphate octahydrate solution was taken in a 100 mL beaker; 2.5 mL (1 M) maleic acid, 5 mL (2%) hydrazine hydrate and 10 mL (0.2 M) sodium selenosulphate were added to the same reaction bath. The pH of the reactive mixture was 12.05. The total volume was made up to 50 mL with

* Corresponding author. Tel.: +91 0231 2693501.
E-mail addresses: pachate09@rediffmail.com, pachate04@rediffmail.com (P.A. Chate).

0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2010.06.015

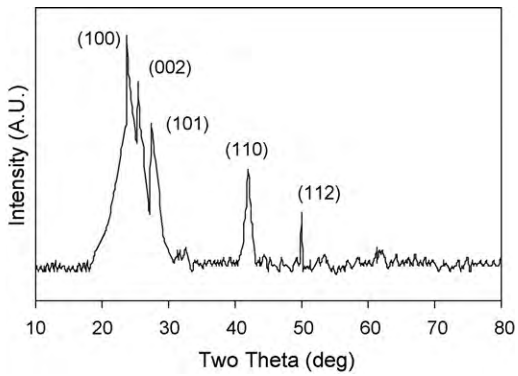

Fig. 1. XRD pattern of hexagonal cadmium selenide thin film.

double distilled water. The temperature of the bath was maintained at 278 K using ice bath. Individual solutions were cooled at 278 K and mixed to avoid precipitation. The solution was stirred vigorously before dipping stainless steel substrates, which were kept vertically slightly tilted in a reactive bath. The temperature of the bath was then allowed to increase up to 298 K very slowly. After 3 h, the slides were removed and washed several times with double distilled water. The deposited substrate were dried naturally, preserved in dark desiccators over anhydrous $CaCl_2$ and subjected to various characterizations. The thickness of cadmium selenide thin film was measured by weight difference method and found to be 0.4 μm.

3. Result and discussions

3.1. Structural characterization

Crystallographic studies of cadmium selenide thin film were characterized using a Phillips PW-1710 X-ray diffractometer with Cu $K\alpha_1$ line (λ = 1.54056 Å) in 2θ range from 10° to 80°. In general, cadmium selenide exist in two crystal structures namely, wurtzite and zinc blende. It has been reported that chemically deposited cadmium selenide films depending upon preparative parameters, show cubic hexagonal or mixed crystal structure [21–24]. Cadmium selenide prepared by present method are nanocrystalline in nature and have hexagonal crystal structure. Fig. 1 shows X-ray diffraction plot of film deposited at room temperature. The presence of a large number of peaks indicates that the films are crystalline in nature. The XRD pattern shows the highest intensity reflection peak at d = 3.735 Å (1 0 0). The diffraction angles were (25.38)° (0 0 2), (27.34)° (1 0 1), (41.94)° (1 1 0) and (50.04)° (1 1 2). The diffused background is due to some amorphous phase present in the cadmium selenide thin films. The lattice parameter of hexagonal phase was calculated using standard equation. The lattice parameter 'a and c' of film is found to be 4.304 and 7.044 Å, respectively [25]. The-crystallite size of cadmium selenide thin films was calculated using Scherrer's formula. The average crystallite size was calculated by resolving the highest intensity peak of (1 0 0) plane. The average crystallite size of cadmium selenide thin film was found to be 21.2 nm. The microstrain developed in the film was calculated and found to be 1.70×10^{-3}. The various structural parameters are cited in Table 1.

Table 1
Structural parameters of cadmium selenide thin films.

Name	Angle (2θ)	d (Å)	Assignments	Cell parameters (Å)	Crystallite size (nm)
	23.80	3.735	(1 0 0)		
	25.38	3.506	(0 0 2)		
CdSe	27.34	3.259	(1 0 1)	a = 4.304	
	41.94	2.152	(1 1 0)	c = 7.044	21.2
	50.04	1.821	(1 1 2)		

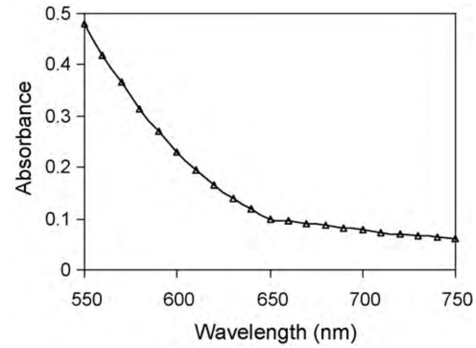

Fig. 2. Absorption spectrum of cadmium selenide thin film.

3.2. Compositional studies

Atomic absorption spectroscopy was used to determine the amount of cadmium in the film using calibration curve method. Previously weighed minute sample was dissolved in the minimum quantity of conc. HNO_3. Below pH 7, the selenium was precipitated as free element [26,27]. While nitrates of cadmium remain in the solution state. The precipitate was filtered through a Gooch crucible and subjected to selenium estimation using a standard gravimetric method. The filtrate containing cadmium nitrate was diluted to suitable dilution and estimated by atomic absorption spectroscopy. The elemental analysis shows percentage of Cd:Se was 49.46:50.54. It is close to 1:1.

3.3. Optical characterization

The optical properties were studied by taking absorption spectra of films using a Hitachi-330 (Japan) double beam spectrophotometer. The optical absorption spectrum of cadmium selenide film was studied in the wavelength of 450–750 nm. Fig. 2 shows the variation of optical absorption with wavelength. The absorptivity was found in the range of 10^4 cm^{-1}. Based on obtained optical absorbance, the square of absorption co-efficient (α^2) is plotted as a function of photon energy (hν) in Fig. 3. It can be seen that the films have a steep optical absorption feature, indicating good homogeneity in the shape and size of the grains and lower defects density near the band edge. As can be seen, α^2 vary almost linearly with hν above band gap energy. According to following equation for direct inter-band transition can be applied [28];

$$\alpha^2 = A(h\nu - E_g) \quad (1.1)$$

where A is a constant. The band gap energy is obtained by extrapolating the straight-line portion of the curve to zero absorption co-efficient. The band gap value of the cadmium selenide was found to be 1.90 eV, which exceeds the reported value for bulk cadmium

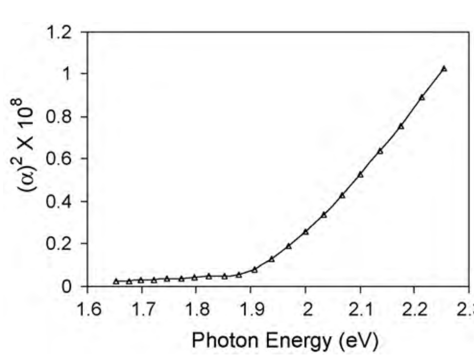

Fig. 3. Plot of (α^2) with respect to photon energy.

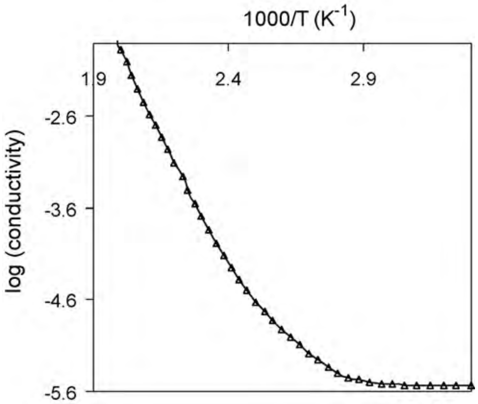

Fig. 4. The variations of log (conductivity) with inverse temperature.

selenide (1.75–1.8 eV [29,30]). The small increase of the band gap in comparison with bulk material could be related with small grain size and/or to stress due to deformation of the film [31].

3.4. Electrical properties

The electrical resistance measurements were carried out in the temperature range 300–525 K on a Zintek 502 BC milliohmmeter using two-probe method. At room temperature the specific conductance was found to be in the order of 10^{-6} ($\Omega\,cm^{-1}$), which agrees well with the earlier reported value [24]. The low value of conductivity may be attributed to the nanocrystalline nature of thin film, crystallite boundary discontinuities, presence of surface states and small thickness of the film. It is observed that the conductivity on the film increases with increasing in temperature. This indicates the semiconducting behavior of the thin film. The electrical conductivity variation with temperature during heating and cooling cycles were found to be different and this shows that the 'as deposited' films undergo an irreversible change due to annealing out of non-equilibrium defects during first heating. A plot of log (conductivity) versus inverse absolute temperature for the cooling and heating curve is shown in Fig. 4. A plot shows that electrical conductivity has two linear regions, an intrinsic region setting at low temperature, characterized by small slope (300–350 K). High temperature region is associated with extrinsic conduction due to the presence donor states. The activation energy is calculated using exponential form of Arrhenius equation. The activation energies are 0.234 and 0.640 eV for low and high temperature region, respectively [32].

3.5. Photoelectrochemical performance

A PEC cell with configuration n-CdSe|NaOH (1 M) + S (1 M) + Na_2S (1 M)|C $_{(graphite)}$ was formed. Even in the dark, photoelectrochemical cell shows dark voltage and dark current. The polarity of this dark voltage was negative towards semiconductor electrode. The sign of the photovoltage gives the conductivity type of cadmium selenide. This suggests that cadmium selenide is a n-type conductor.

Current–voltage (*I*–*V*) characteristics of photoelectrochemical cell in dark have been studied at 303 K and shown in Fig. 5. The characteristics are non-symmetrical indicating the formation of rectifying type junction. The Butler–Volmer relation can be applied to the cadmium selenide electrolyte interface and observed magnitude of symmetry factor shows rectifying Schottky type of junction.

The measurements of capacitance as a function of applied voltage provided useful information such as type of conductivity, depletion layer width and flat band potential. Flat band potential can be obtained using Mott–Schottky relation by standardizing

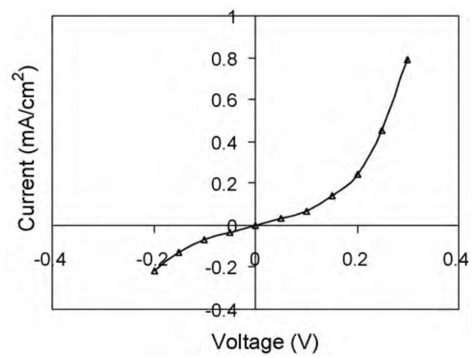

Fig. 5. *I*–*V* characteristics of cadmium selenide photoelectrode.

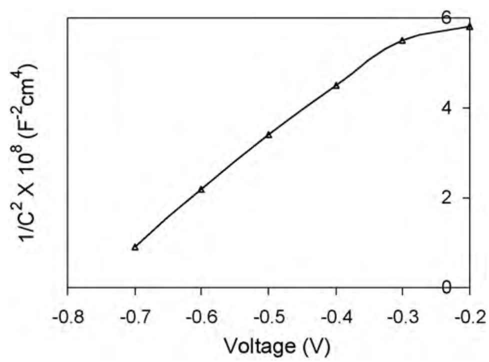

Fig. 6. *C*–V characteristics of cadmium selenide photoelectrode.

with saturated calomel electrode (SCE);

$$C^{-2} = [2/q\varepsilon\varepsilon_0 N_d]\ (V - V_{fb} - kT/q) \quad (1.2)$$

where symbols have their usual meaning. The variation of C^{-2} with voltage for representative samples is shown in Fig. 6. Intercepts of plots on voltage axis determine the flat band potential value of the junction. The flat band potential value is found to be −0.765 V (SCE) for CdSe–polysulphide redox electrolyte, which is a measure of electrode potential at which band bending is zero. The non-linear nature of the graph is an indication of graded junction formation between CdSe and polysulphide electrolyte. Non-planar interface, surface roughness, ionic adsorption on the photoelectrode surface may be possible reasons for deviation from linearity in *C*–*V* plot.

Fig. 7 shows the photovoltaic power putout characteristics for a cell under illumination of 30 mW/cm^2. The maximum power output of the cell is given by the largest rectangle that can be drawn inside the curve. The open circuit voltage and short circuit current are found to be 220 mV and 282 μA, respectively. The calculation shows the fill factor is 33.44%. The power conversion efficiency is

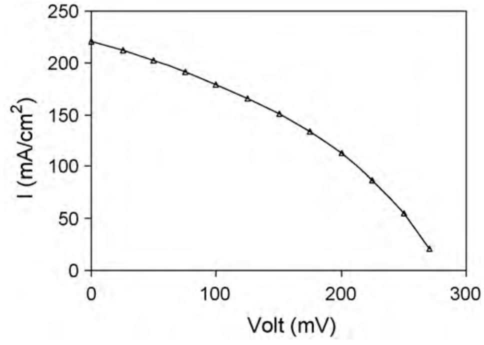

Fig. 7. Power output curves for cadmium selenide photoelectrode.

found to be 1.01%. The value of series resistance and shunt resistance was found to be 503 Ω and 603 Ω, respectively.

4. Conclusions

The deposition of cadmium selenide thin films from maleic acid bath at room temperature is possible. The films deposited on stainless steel substrates. The deposited cadmium selenide thin films are nearly stoichiometric, crystalline with hexagonal crystal structure having a band gap with 1.9 eV. An electrical property shows two types of conduction mechanism with semiconducting nature. The material shows promising photo-response when tested in polysulphide electrolyte. Current–voltage plot suggests formation of rectifying type junction. Capacitance–voltage plot indicate graded junction formation between CdSe and electrolyte.

References

[1] P. Mandal, R.S. Shrinivasa, S.S. Talwar, S.S. Major, Appl. Surf. Sci. 254 (2008) 5028.
[2] V.I. Klimov, J. Phys. Chem. B 110 (2006) 16827.
[3] A. Meskauskar, J. Viscakasi, Thin Solid Films 36 (1976) 113.
[4] A.A. Yadav, M.A. Barote, E.U. Masumdar, Chalcogenide Lett. 6 (2009) 149.
[5] K. Subba, Y.K. Su, S.J. Chang, F.S. Juang, K. Ohdaira, Y. Shiraki, H.P. Liu, I.J. Chen, A.K. Bhatnagar, Cryst. Growth 224 (2001) 74.
[6] R. Wang, H. Jakobson, R. Kou, J. Tang, R. Fineman, D. Yu, Y. Lu, Chem. Mater. 18 (2006) 4231.
[7] J.W. Edmund, E.M. Dale, R.N. Donalad, B.E. Arthur, F.G. John, T.F. Kucch, Cryst. Growth 148 (1995) 63.
[8] A.S. Khomane, P.P. Hankare, Alloys Compd. 489 (2010) 605.
[9] E. Hendry, M. Koeberg, F. Wang, H. Zhang, C. Donega, D. Vanmaekal-bergh, M. Bornn, Phys. Rev. Lett. 96 (2006) 7408.
[10] L.E. Brus, J. Chem. Phys. 80 (1984) 4403.
[11] G.A. Ozin, Adv. Mater. 68 (1992) 612.
[12] P. Nemec, M. Simurda, I. Nemec, P. Formanek, Y. Nemcova, D. Sprinzl, F. Trojanek, P. Maly, Phys. Status Solidi A 8 (2008) 1.
[13] G. Hodes, Phys. Chem. 9 (2007) 2181.
[14] G. Hodes, Chemical Deposition of Semiconductor Films, Marcel Dekker, Inc., Basel, New York, 2003.
[15] S.M. Pawar, A.V. Mohalkar, K.Y. Rajpure, C.H. Bhosale, Sol. Energy Mater. Sol. Energy 92 (2008) 45.
[16] V.D. Das, L. Damodare, J. Appl. Phys. 81 (1997) 1552.
[17] A. Mondal, T.K. Chaudhuri, P. Pramanik, Sol. Energy Mater. 7 (1983) 431.
[18] K.R. Murali, P. Elango, P. Gopalakrishnan, Mater. Chem. Phys. 96 (2006) 103.
[19] F. Cerderia, I. Torriani, P. Mostisuke, V. Lemos, F. Decker, Appl. Phys. 46 (1988) 107.
[20] P.P. Hankare, A.H. Manikshete, D.J. Sathe, P.A. Chate, K.C. Rathod, Mater. Chem. Phys. 113 (2009) 183.
[21] R.S. Mane, C.D. Lokhande, Thin Solid Films 304 (1997) 56.
[22] S. Erat, H. Metin, M. Ari, Mater. Chem. Phys. 111 (2008) 114.
[23] S.S. Kale, C.D. Lokhande, Mater. Chem. Phys. 103 (2000) 62.
[24] R.B. Kale, C.D. Lokhande, Appl. Surf. Sci. 223 (2004) 343.
[25] J.B. Chaudhari, N.G. Deshpande, Y.G. Gudage, A. Ghosh, V.B. Huse, R. Sharma, Appl. Surf. Sci. (2008) 6810.
[26] Zhu Junjie, Liao Xu Chang, Wang Jun, Chen Hong Yuan, Mater. Res. Bull. 36 (2001) 1169.
[27] P.P. Hankare, P.A. Chate, D.J. Sathe, P.A. Chavan, V.M. Bhuse, Mater. Sci.: Mater. Electron. 20 (2009) 374.
[28] H.T. Grahn, Introduction to Semiconductor Physics, World Scientific Publishing, Singapore, 1999.
[29] H.E. Esparza-Ponce, J. Hernández-Borja, A. Reyes-Rojas, M. Cervantes-Sánchez, Y.V. Vorobiev, R. Ramírez-Bon, J.F. Pérez-Robles, J. González-Hernández, Mater. Chem. Phys. 113 (2009) 824.
[30] C.D. Lokhande, E.H. Lee, K.D. Jung, Q.S. Joo, Mater. Chem. Phys. 91 (2005) 200.
[31] K.R. Murali, V. Swaminathan, D.C. Trivedi, Sol. Energy Mater. Sol. Cells 81 (2004) 113.
[32] E.U. Masumdar, V.B. Gaikwad, V.B. Pujari, P.D. More, L.P. Deshmukh, Mater. Chem. Phys. 77 (2002) 669.