Chalcogenide Letters Vol. 5, No. 11, November 2008, p. 273 – 276

PROPERTIES OF CdSe FILMS PULSE ELECTRODEPOSITED FROM NON- AQUEOUS BATH

K. R. MURALI*, K. CHITRA[a], P. ELANGO[a]
Electrochemical Materials Science Division, Central Electrochemical Research Institute, Karaikudi – 630 006, India
[a]*Dept of Physics, Government Arts College, Coimbatore, India*

CdSe thin films were pulse electrodeposited at room temperature and at different duty cycles in the range of 10 – 50 % from diethylene glycol bath. The precursors were 0.1 M $CdCl_2$, 0.1M SeO_2 and the deposition potential was – 0.85V(SCE). The films exhibited hexagonal structure. Optical absorption measurements indicated a direct band gap of 1.67 eV. The grain size increased from 10 – 30 nm and the surface roughness increased from 0.5 nm – 2.0 nm as the duty cycle increased from 10 – 50 %. The as deposited films exhibited photoactivity when used as photoelectrodes in Photoelectrochemical cells.

(Received

Keywords: Cadmium selenide, thin films, II-VI, pulse electrodeposition

1. Introduction

Cadmium selenide (CdSe) is well known as a II–VI compound semiconductor suitable for solar energy conversion with a photovoltaic cell because the band gap, i.e. 1.75 eV, is fit to the spectrum of sunlight [1]. Methods of the film processing can be classified into two major groups, viz., dry process and in wet process. The dry process includes techniques such as vacuum evaporation[2] chemical vapor deposition (CVD) [3]. These techniques, without exceptional, require high vacuumand/or temperature because it is necessary to produce gaseous precursor molecules or atoms. Besides the high energy needed for the film processing, emission of gaseous waste materials is another serious problem with these techniques. Because one can simply exclude the unwanted chemical species from the system, the gas-phase techniques have the advantages of the high controllability of the film growth and the feasibility to obtain a pure material. The gas-phase techniques benefit also from many variables tunable to achieve an intended film growth. The wet processes mainly have liquid-phase synthesis[3,4] chemical bath deposition and electrodeposition [5–8]. In wet method,electrochemical techniques provide numerous advantages,including: (a) it involves relatively simple and inexpensive equipment; (b) films can be fabricated on large and irregular surfaces; (c) the deposition occurs closer to equilibrium than in many high-temperature methods and inter-element diffusion is not a problem; (d) the process can be rather precisely controlled because of its electrical nature; (e) the toxic gaseous precursors do not have to be used unlike in chemical gas phase methods. In the present work, CdSe thin films were deposited by pulse electrodeposition using non aqueous electrolyte for the first time.

2. Experimental method

Thin CdSe films were deposited at different duty cycles in the range 10 – 50 % at room temperature. The precursors were AR grade 0.1 M $CdCl_2$, 0.1M SeO_2 in 20 ml of diethylene glycol. The details of pulse plating technique are given in an earlier paper[9].Titanium and

---

*Corresponding author: murailiramkrish@gmail.com

conducting glass substrates were used. The deposition potential was fixed at -0.85V(SCE). The thickness of the films estimated by Mitutoyo surface profilometer was in the range oh 0.9 – 1.2 μm as the duty cycle increased. The films were characterized by x-ray diffraction technique using Pro Xpert Panalytical x-ray diffractometer with Cu Kα radiation. Optical absorption measurements were made at room temperature using U3400 Hitachi UV-Vis-NIR spectrophotometer. Surface morphology of the films were studied by Molecular imaging systems Atomic Force microscope. Photoelectrochemical(PEC) measurements were made in 1M polysulphide (1M Na_2S, 1M NaOH, 1M S) electrolyte. Capacitance voltage measurements were made with PAR impedance analyser, the AC frequency was maintained at 10 kHz and the DC bias was varied in the range of 0.2 to -0.8V(SCE).

3. Results and discussion

XRD patterns of the films deposited at different duty cycle is shown in Fig.1. The peaks corresponding to hexagonal CdSe were observed. Crystallite size calculated using the Debye Scherrer equation is found to increase with increase of substrate temperature. The crystallite size increased from 15 – 30 nm as the duty cycle increased from 10 – 50 %. The prominent peaks corresponding to (002), (100), (101), (102),(110), (103), (200), (112), (201) and (202) are observed in all cases. It is observed that as the annealing temperature increases the intensity of the peaks also increase due to improved crystallinity. The lattice constants 'a' and 'c' calculated using the XRD data are 4.304°A and 7.044 °A, which are in close agreement with the ASTM data.

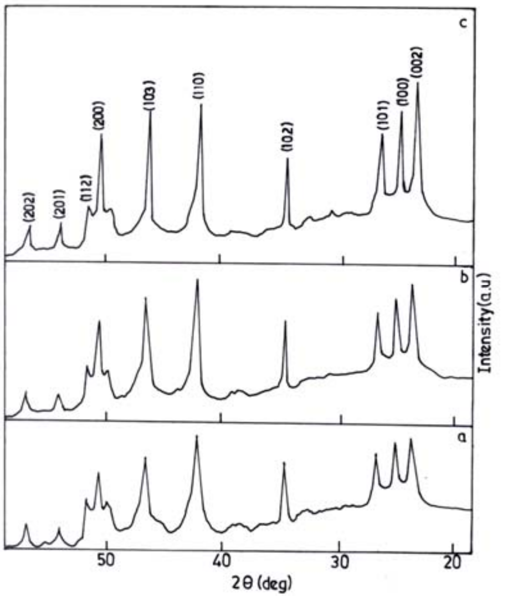

Fig.1. X-ray diffraction pattern of CdSe films deposited at different duty cycles
(a) 10% (b) 33 % (c) 50 %

To determine the band gap of the CdSe films deposited at different duty cycles, transmission spectra of the CdSe films deposited on conducting glass substrates were recorded. The energy gap obtained by extrapolating the linear portion of the $(\alpha h\nu)^2$ vs hν plot to the energy axis yielded a direct band gap value of 1.67 eV(Fig.2). This value is similar to the value obtained on thin film CdSe [10].

Surface morphology of the films indicated an increase of grain size with duty cycle. The grain size increased from 10 – 30 nm as the duty cycle increased from 10 – 50 %. The surface roughness increased from 0.5 nm – 2.0 nm as the duty cycle increased. Fig.3 shows the Atomic force micrograph of CdSe films deposited at different duty cycle.

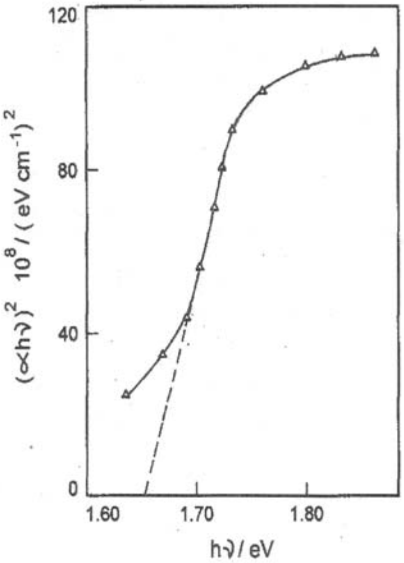

Fig.2. $(\alpha h\nu)^2$ vs $h\nu$ plot of CdSe films deposited at a duty cycle of 50 %

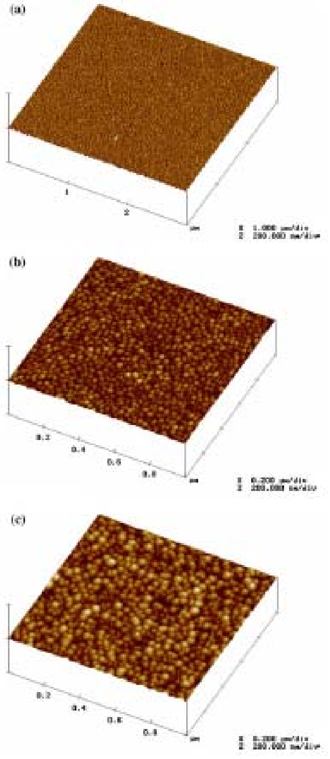

Fig.3. Atomic force micrographs of CdSe films deposited at different duty cycles (a)10 % (b) 33% (c) 50 % X-axis – 0.2μm/div, z-axis – 200 nm /div.

Photoelectrochemical cells were made by dipping the CdSe films deposited at different duty cycle in 1M polysulphide electrolyte. The illumination intensity was varied in the range of 20 – 100 mW cm^{-2}. Fig.4 shows the load characteristics of the CdSe films deposited at a duty cycle of 50 % and illuminated with different intensities. It is observed that both V_{oc} and J_{sc} increase with intensity. A plot of $\ln J_{sc}$ vs V_{oc} yielded a straight line. Extrapolation of the line to the y-axis yields a J_0 value of 1.5 x 10^{-7}A cm^{-2}, the ideality factor (n) was calculated from the slope of the straight line and it was found to be 2.5. The special feature of this work is that, PEC output is obtained for the electrodes without any post heat treatment.

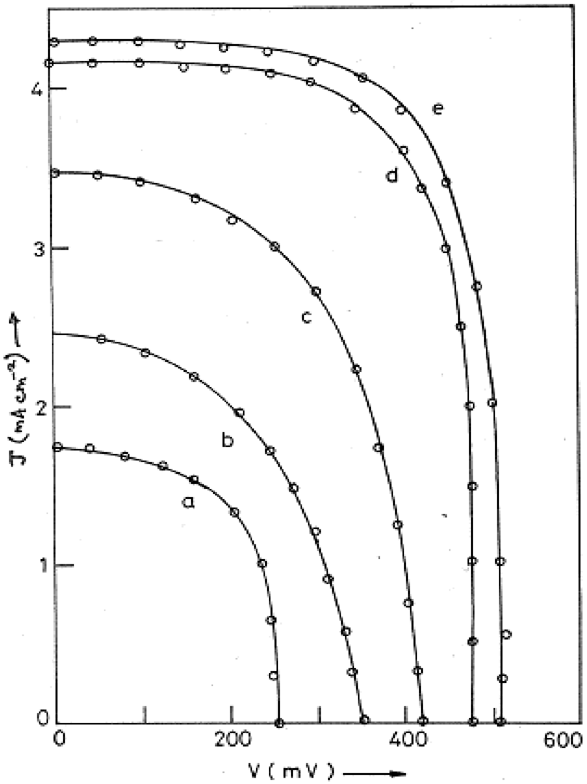

Fig.4 – Load characteristics of CdSe films deposited at 50 % duty cycle for different illumination intensities (a)20mW cm^{-2} (b) 40 mW cm^{-2} (c) 60 mW cm^{-2} (d) 80 mW cm^{-2} (e)100 mWcm^{-2}

4. Conclusions

The results of this investigation clearly indicate that CdSe films with grain size in the range of 10 – 30 nm can be deposited from non aqueous bath. The films are photoactive without any post heat treatment.

References

[1] K. Rajeshwar, Adv. Mater **4**, 23 (1992).
[2] M. Fujii, T. Kawai, S. Kawai, Solar Energy Mater **18**, 23(1988).
[3] A.C. Jones, Chem. Soc. Rev **26**, 101(1997).
[4] Chen Jin-jun, Ye Zhao-pei, Zhao Zhi-yao, Chemistry (TAIPEI) **56**, 223(1998).
[5] V. Swaminathan, V. Subramanian, K.K. Murali, Thin Soild Films **359**, 113(2000).
[6] A.V. Kokate, U.B. Suryavanshi, C.H. Bhosale, Solar Energy **80**, 156(2006).
[7] P. Nemec, M. Simurda, I.Nemec, D.Sprinzl, P.Formanek, P.Maly, J.Cryst.Growth, **292**, 78(2006).
[8] M. Dhanam, Rajeev R. Prabhu, P.K. Manoj, Mater.Chem.Phys. **107**, 289(2008).
[9] K. R. Murali, M. Balasubramanian, Materials Sci and Engg, **A 43**, 118 (2006).
[10] K.R. Murali, A. Austine, B. Jayasutha, D. C. Trivedi,Solar energy mater.solar cells, **90**,753(2006)