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STRUCTURAL AND OPTICAL PROPERTIES OF PULSE PLATED CADMIUM SELENIDE FILMS

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ABSTRACT

Cadmium Selenide (CdSe) thin fil ms were pulse electrodeposited at room temperature and at different duty cycles in the range of 6 – 50 % at a current density of 100 mA cm^{-2}. XRD patterns of films deposited at different duty cycles exhibit the cubic structure. The peak widths decreased with increase of duty cycle. The crystallite size increased from 8 to 20 nm. Microstructural parameters like dislocation dneisty and strain were calculated.The transmission spectra exhibit interference fringes. Refractive index calculated by the envelope method varied in the range of 2.5 to 3.3.The optical band gap increased from 1.75 eV to 2.12 eV with increase of duty cycle. Nyquist plots were used to calculate the charge transfer reistance and double layer capacitance. Preliminary studies on the Photoelectrochemical cells using the films deposited at different duty cycles have yielded photo output without post annealing.

INTRODUCTION

Semiconductor nanocrystalline materials have been extensively investigated in the last decade because of their potential applications in many areas. Semiconductor Nanocrystallites belong to the state of matter in the transition region between molecules and solids. Their properties depend upon the size of the nanocrystallites (Hodes, et al., 2003). Nanocrystalline semiconductor materials have been used in photovoltaic, photoconductive and sensor applications. Amongst the II-VI compounds, CdSe is a direct band gap semiconductor with a band gap of 1.70 eV. The Nanocrystalline form of CdSe is being actively investigated owing to the quantum size effect and luminescent properties (Coe, et al., 2002). CdSe thin films have been deposited earlier by several techniques like thermal evaporation (Pathinettam Padiyan, et al., 2002), pulse laser deposition (Hernandez-Perez, et al., 2008), electrodepsoition (Murali, et al., 1991), spray pyrolysis (Yu. et al., 2007), successive ionic layer adsorption (SILAR) (Tigau, et al., 2005) and chemical bath deposition (Gopakumar, et al., 2010). In an earlier report on pulse deposited CdSe films, the films were deposited by constant potential method. In this work CdSe films were deposited by the pulse electrodeposition technique at a constant current density and at different duty cycles.

EXPERIMENTAL METHODS

CdSe films were pulse electrodepsited at room temperature using a current density of 100 mA cm^{-2} and at different duty cycles in the range 6 – 50 %. The films were deposited on tin doped Indium oxide (ITO) glass substrates at room temperature from Analar grade precursors (0.2 M $CdSO_4$ and 5 mM SeO_2). The thickness of the films estimated by Mitutoyo Surface profilometer varied from 300 nm – 900 nm with increase of duty cycle. The films were characterized by x-ray diffraction to study the structural properties using X'pert Pro PANanalytical x-ray diffraction unit with Cu Kα radiation. Optical absorption studies were made with Hitachi U3400 UV-VIS-NIR spectrophotometer. Surface morphology was studied with Molecular imaging system Atomic force microscope. Resistivity of the films was measured at room temperature by two probe method. For this purpose, Indium ohmic contact was provided at the centre of the top surface. Laser Raman studies was made with Renishaw Invia Laser Raman Microscope. Photoluminscence studies were made at room temperature by using an excitation wavelength of 350 nm.

RESULTS AND DISCUSSION

X-ray diffraction pattern of the films deposited at different duty cycles indicated the peaks corresponding to the cubic phase (Fig.1). Peaks were observed for the (111), (220) and (311) reflections. The microstructural parameters were estimated from the above data. The crystallite size was calculated using Scherrer's equation

$$\text{Crystallite size } D = 0.9\,\lambda / \beta \cos\theta$$

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where, λ is the wavelength of x-ray radiation, β is the full width at half maximum and θ is the diffraction angle.

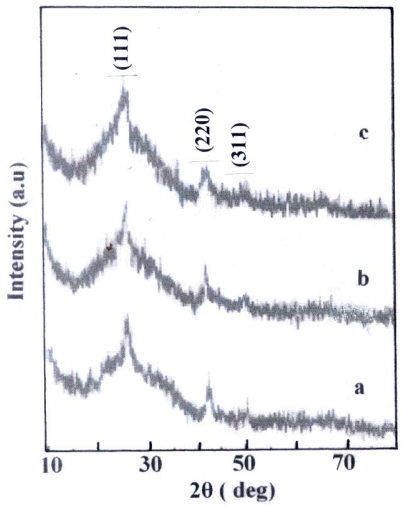

Fig.1 X-ray diffraction pattern of CdSe films deposited at different duty cycles (a) 50 % (b) 33 % (c) 15 %

The lattice parameter was calculated using,

$$1/d^2 = 1/a^2 (h^2 + k^2 + l^2)$$

where, h,k,l are the miller indices, d is the lattice spacing and 'a' is the lattice parameter.

The strain and dislocation density were calculated using the following relations,

$$\text{Strain } (\varepsilon) = \beta \cos\theta/4$$
$$\text{Dislocation density } (\delta) = 15\varepsilon/aD$$

All the above microstructural parameters are given in Table-1. It is generally known that the strain and dislocation density decrease as the particle size increases. Strains are inherent and natural components of nano grained materials. Due to the large number of grain boundaries and the concomitant short distance between them, the intrinsic strains associated with such interfaces are always present in nanophase films. Moreover, the increasing surface energy contributes to the varying magnitude of strain.

The transmission spectra (Fig.2) of the films deposited at different duty cycles was studied in the wavelength range of 450 – 2500 nm at room temperature. The spectra exhibit interference fringes. The refractive index was calculated using the envelope method (Ilican, et al., 2007). The refractive index values in the range of 2.5 – 3.3 at 700nm are in close agreement with the bulk values. The absorption co-efficient (α) was estimated from the transmission spectra. In order to find out the nature of the band gap of the CdSe films, α and hν values were used to fit in with the following equation.

$$\alpha h\nu = A (h\nu - E_g)^{1/2}$$

where E_g is the band gap of CdSe films, α is the absorption co-efficient, A is a constant and hν is the photon energy. The $(\alpha h\nu)^2$ vs hν plots (Fig.3) for all the films exhibit linear regions, extrapolation of the linear regions yields direct band gap in the range of 1.75 to 2.12 eV.

Table 1 Microstructural parameters of CdSe films deposited at different duty cycles

Duty cycle (%)	Lattice Spacing d ( )	Crystallite size D(nm)	δ (x 10^{15}) lines/ m^2	Strain ε x 10^{-3}	Lattice parameter 'a' (nm)
6	3.491	8	1.34	4.34	6.05
15	3.493	12	0.59	2.88	6.06
33	3.497	17	0.30	2.04	6.05
50	3.499	20	0.21	1.73	6.06

Composition of the films studied by EDAX indicated that the Cd concentration was slightly in excess for all the duty cycles. The composition of the films varied from Cd (51.1%), Se (48.9%) at 50 % duty cycle to Cd (50.5 %), Se (49.5 %) at 6 % duty cycle.

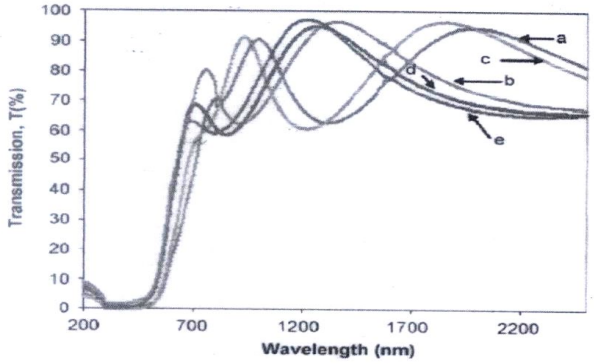

Fig.2 Transmission spectrum of CdSe films deposited at different duty cycles(a) 50 % (b) 33 % (c) 15 % (d) 10 % (e) 6 %

To investigate the properties of the interface between CdSe and the polysulphide electrolyte Impedance studies were made in dark. Fig.4 shows the Nyquist plot for the CdSe films deposited at different duty cycles. This semicircle behaviour can be attributed to the porous structure formed by randomly oriented flakes of the photoelectrode (Lavos-Valerto, et al., 2004). The equivalent circuit includes a solution resistance (R_s), a charge transfer resistance (R_{ct}) and the double layer capacitance (C_{ct}). Thin films with low R_{ct} and high C_{ct} are suitable for photoelectrodes in a Photoelectrochemical cell. It is observed that the values of R_{ct} decreases from 850 ohms to 430 ohms but the value of C_{ct} increases from 0.37 μF to 1.67 μF with increase of duty cycle. This is due to the better crystallinity of the films deposited at higher duty cycles.

Preliminary studies on the photoelectrodes deposited at different duty cycles have resulted in photo output without post annealing treatment. For the films deposited at 50 % duty cycle a V_{oc} of 0.55 V and J_{sc} of 6.0 mA cm^{-2} was obtained.

CONCLUSIONS

Nanocrystalline CdSe films with grain size in the range of

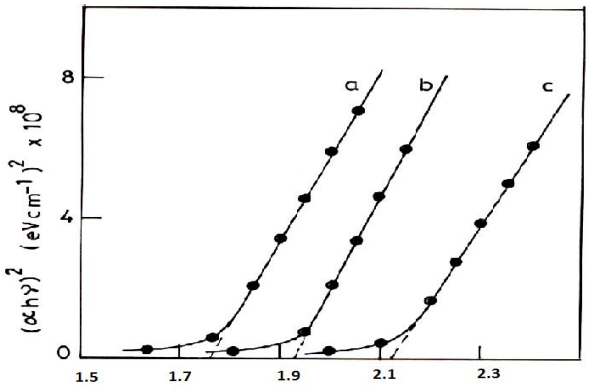

Fig.3 Variation of band gap with wavelength for CdSe films deposited at different duty cycles (a) 50 % (b) 15 % (c) 6 %

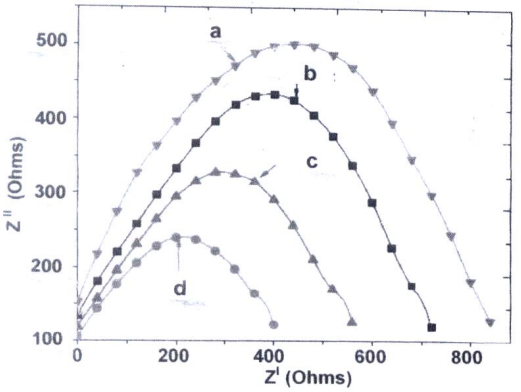

Fig.4 Nyquist plot of CdSe films deposited at different duty cycles (a) 6 % (b) 15 % (c) 33 % (d) 50 %

8 to 20 nm can be easily obtained by the contstant current pulse electrodeposition. Films with band gap in the range of 1.75 to 2.12 eV. Films with refractive index in the range of 2.5 to 3.3 can be obtained.

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