

CdS FILMS PULSE PLATED FROM NON-AQUEOUS BATH

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Cadmium sulphide(CdS) films were deposited from ethylene glycol bath by the pulse plating technique using CdCl₂ and S at 90°C on conducting glass substrates. The films exhibited cubic structure. The peaks increased in height and became sharper as the duty cycle increased. Optical absorption measurements indicated direct band gap values in the range 2.39 – 2.80 eV were obtained as the duty cycle is decreased. Raman spectra exhibited LO phonons. The films exhibited higher photo outputs compared to earlier reports.

(Received November 4, 2008; accepted November 12, 2008)

Keywords: CdS, II-VI, thin films, pulse electrodeposition

1. Introduction

CdS is a II–VI compound semiconductor and has an energy band gap of 2.42 eV at room temperature. CdS is one of the important materials for application in electro-optic devices such as photoconducting cells, photosensors, transducers, laser materials, optical wave-guides and non-linear integrated optical devices [1]. CdS thin films used as window material for CdS/CdTe solar cells continues as a subject of intense research in order to obtain cells with higher efficiencies [2]. In this type of solar cells, fabrication of CdS films with low resistivity is very important because it helps to decrease the device sheet resistance and to obtain the space charge region in the active zone, i.e., into the CdTe film. CdS films can be deposited by techniques such as vacuum evaporation, sputtering, spray pyrolysis, electrodeposition and chemical bath deposition (CBD) techniques[3-7]. In this work, CdS films were pulse electrodeposited for the first time from ethylene glycol bath and their properties are presented and discussed.

2. Experimental Methods

CdS films were pulse plated on conducting glass substrates at different duty cycles in the range of 10 – 50 % using AR grade CdCl₂ and S in ethylene glycol solution maintained at 90°C. Thickness of the films measured by Mitutoyo surface profilometer varied in the range of 0.9 – 1.2 micrometres. The films were characterized by x-ray diffraction technique using CuK α radiation and Xpert PANalytical x-ray diffraction unit.

Optical absorption measurements were made using Hitachi U3400 UV-Vis-NIR spectrophotometer. Laser Raman studies were made using 633nm He-Ne laser with 15% laser power and Renishaw Invia laser Raman Microscope.

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3. Results and discussion

X-ray diffraction(XRD) pattern of the CdS films deposited at different duty cycles is shown in Fig.1. The XRD pattern indicates the formation of polycrystalline films with the cubic structure. Peaks corresponding to the (100), (002), (100) and (200) reflections were observed in all the cases. It is observed from the figure that the height of the peaks increase with duty cycle and the width of the peak decreases with increase of duty cycle. For a duty cycle of 6%, the peaks are not well defined and peaks begin to appear only for duty cycles in the range of 6 – 50 %. This is understandable since, at a duty cycle of 6% , the flux of ions are available for a very short time for deposition and the thickness of the film is very small around 0.1 μ m. At higher duty cycles, the flux of ions are available for a longer period and hence the thickness increases.

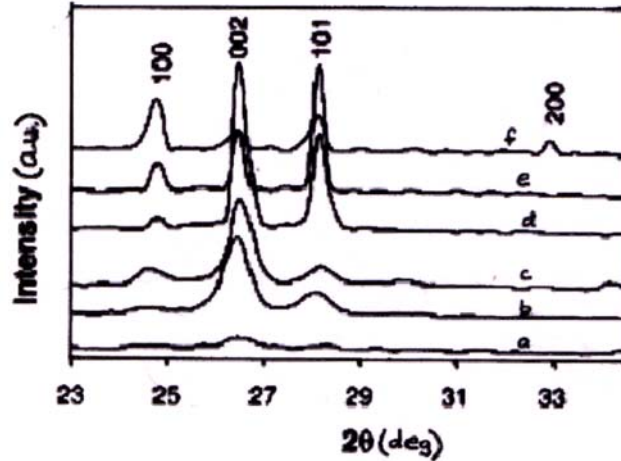


Fig.1. XRD patterns of CdS films deposited at different duty cycles(a) 6 % (b) 9 % (c) 15% (d) 25 % (e) 33 % (f) 50 %

The grain size was calculated using Scherrer's equation:

$$D = 0.9 \lambda / \beta \cos \theta \quad (1)$$

where D is the grain size, λ is the wavelength of CuK α radiation, θ is the diffraction angle and β is the full width at half maximum. It is observed that the grain size increases with increase of substrate temperature.

Lattice parameters 'a' and 'c' were calculated using the relation,

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

The lattice strain(ϵ) is calculated using the relation,

$$\epsilon = (\beta \cos \theta) / 4 \quad (3)$$

It is observed that the strain values decrease as the duty cycle increases, indicating better crystallinity for the films deposited at higher duty cycles

The dislocation density was calculated from the relation,

$$\delta = 15\epsilon/aD \quad (3)$$

The dislocation density varies in the range of 4.5×10^{-14} to 1.5×10^{-14} lines/m as the duty cycle increases.

Optical absorption measurements indicated an absorption spectra as shown in Fig.2. The relationship of the absorption coefficient and the incident photon energy of semiconductor are given by the following equation [8]

$$\alpha h\nu = A(h\nu - E_g)^n \quad (4)$$

where α is absorption coefficient, $h\nu$ is the energy of the incident photon, n is 0.5 and 2.0 for a direct transition semiconductor and indirect transition semiconductor, respectively. The CdS is the direct semiconductor, which has a very small absorption coefficient. By plotting the graph of $(\alpha h\nu)^2$ versus $h\nu$, it is possible to determine the nature of transition involved. The extrapolation of straight line portions of the plot ($\alpha h\nu$ greater than E_g) to the zero absorption coefficients gives measurement of energy gap [10]. This plot is given in Fig. 3. Direct band gap values in the range 2.39 – 2.80 eV were obtained as the duty cycle is decreased.

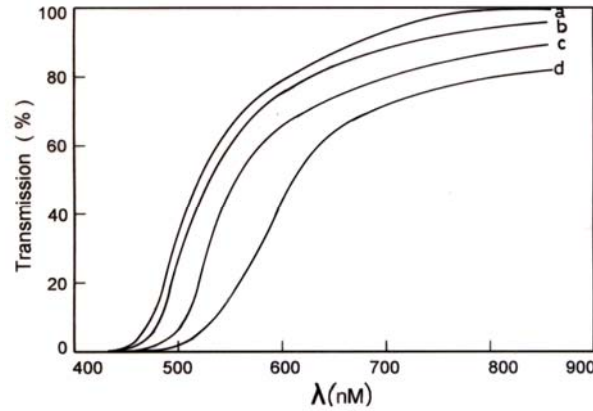


Fig.2. Absorption spectra of CdS films deposited at different duty cycles
(a) 9 % (b) 15 % (c) 33 % (d) 50 %

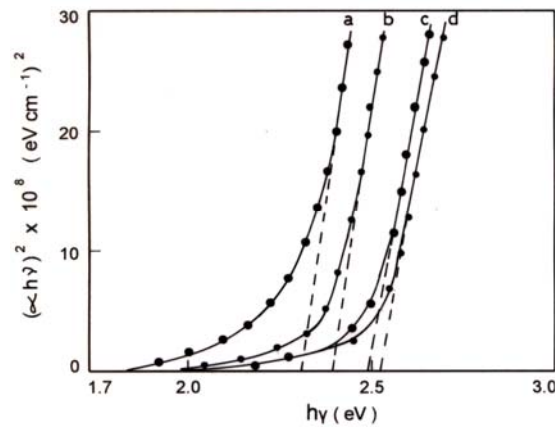


Fig.3. $(\alpha h\nu)^2$ versus $h\nu$ plot of CdS films deposited at different duty cycles
(a) 9 % (b) 15 % (c) 33 % (d) 50 %

different duty cycles is due to the variation of This is due to the decrease in particle size with decrease of duty cycle. The variation of band gap at crystallite size with duty cycle. Strong and weak confinements were noticed for the films. For strong confinement, the exciton energy is given by,

$$E_s = E_g + \frac{h^2 \pi^2}{2\mu^2} - \frac{1.786.e^2}{4\pi.R\epsilon_0\epsilon} - 0.248E_{Ry}^*$$

where E_g is the band gap of bulk CdS, the second term is related to the quantum localization energy, the third term represents the Coloumb energy and the fourth term represents the correlation energy in which ERy^* is the effective Rydberg energy and can be written as

$$\left\{ \frac{\mu \cdot e^4}{2(4\pi\epsilon_0\epsilon)^2 \hbar^2} \right\}$$

where, μ is the reduced effective mass, ϵ is the dielectric constant for CdS and ϵ_0 is the permittivity of free space. The estimated band gap of 2.80 eV due to strong confinement matches with the band gap value obtained from absorption measurements for the films deposited with 9 % duty cycle.

The room temperature Raman spectra of the CdS films are shown in Fig.4. The Raman spectra of the CdS films exhibit a well-resolved line at approximately 300 cm^{-1} , corresponding to the first order scattering of the longitudinal optical (LO) phonon mode. CdS can take both hexagonal wurtzite and cubic zinc blende structures, and it was reported that for both the structures, the zone-center longitudinal-optical A1(LO) phonon frequency is about 305 cm^{-1} [9]. The FWHMs of the 1 LO peak are 27.8, 23.7, and 20.6 cm^{-1} , for 10%,25% and 50 % duty cycle, respectively. These values are much larger than that (6.5 cm^{-1}) for melt grown single-crystal CdS. Usually, very large width indicates poor crystallinity (lack of long-range order) in the films, but the well-defined peak indicates the crystalline nature of the films. Hence, the large FWHM in the present case can be attributed to a polycrystalline effect in the as-deposited film [10]. The broad second-order scattering of LO phonons is also visible at approximately 600 cm^{-1} , regardless of duty cycle. The main characteristic of the Raman spectra of our films is the broadening of the LO peak in the samples deposited at lower duty cycle. The peak position did not change much with change in duty cycle and remained almost constant.

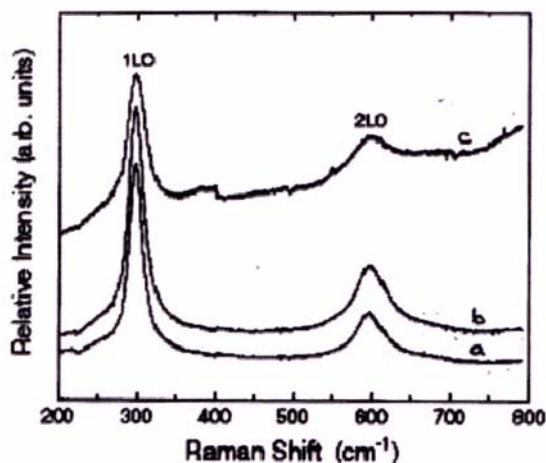


Fig. 4. Raman spectra of CdS films deposited at different duty cycles (a) 50% (b) 33% (c) 15%

Photoelectrochemical (PEC) cells were prepared using the films deposited at different duty cycles on titanium substrates heat treated at different temperatures. The films were lacquered with polystyrene in order to prevent the metal substrate portions from being exposed to the redox electrolyte. These films were used as the working electrode. The electrolyte was 1 M polysulphide. This electrolyte was chosen, as it is well known that CdS electrode has reasonable stability and yield respectable outputs in polysulphide. The light source used for illumination was an ORIEL 250 W tungsten halogen lamp. A water filter was introduced between the light source and the PEC cell to cut off the IR portion. The intensity of illumination was measured with a CEL suryamapi, whose readings are directly calibrated in mWcm^{-2} . The intensity of illumination was varied changing the distance between the source and the cell. The power output characteristics of the cells were measured by connecting the resistance box and an ammeter in series and the voltage output was measured across the load resistance. The photocurrent, dark current and output voltage were measured with a HIL digital multimeter.

The CdS photoelectrodes were dipped in the electrolyte and allowed to attain equilibrium under dark conditions for about 10 minutes. The dark current and voltage values were

noted. The cells were then illuminated by the light source and the current and voltage were measured for each setting of the resistance box. The photocurrent and photovoltage were calculated as the difference between the current under illumination and the dark current, and voltage under illumination and dark voltage respectively.

The as deposited films did not exhibit any photoactivity. They were post heat treated in argon atmosphere for 10 min in the temperature range of 450 - 525°C. The power output characteristics of the PEC cells made using the photoelectrodes deposited at different duty cycles after post heat treatment is shown in Fig.5. The films exhibited higher photo output compared to earlier report on electrodeposited CdS films[11].

4. Conclusions

The results of this investigation clearly shows that CdS films with band gap values in the range of 2.39 – 2.80 eV can be obtained. The photo output of photoelectrochemical cells obtained with these films are higher than the values obtained with electrodeposited CdS films.

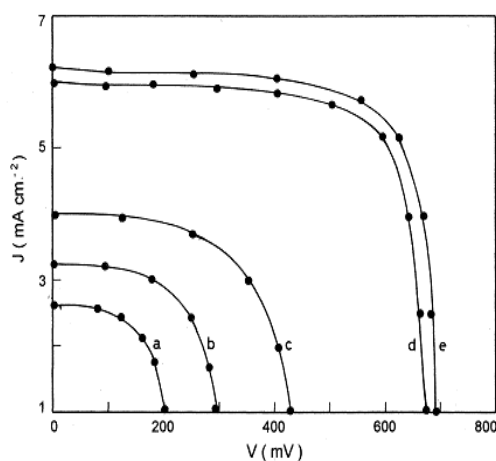


Fig.5 – Load characteristics of CdS electrodes deposited at different duty cycles and post heat treated at 525°C (a) 6 % (b) 9 % (c) 15 % (d) 33 % (e) 50 %

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