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# Characteristics of nanocrystalline CdSe films

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## Abstract

CdSe films have been pulse electrodeposited on evaporated gold substrates with different duty cycles. The deposition of nanocrystalline films was carried out at 100°C for 10 min with precursors of CdSO<sub>4</sub>, SeO<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub>. TEM studies indicated a crystal size in the range 10–50 nm depending upon the duty cycle. The size of the nanoparticle could be controlled by the pulse parameters. Variation of grain size and band gap with duty cycle are in close agreement with the results reported earlier for the films prepared by electrodeposition and chemical bath deposition. Luminescence studies indicated room temperature emission in the wavelength range 520–410 nm depending on the duty cycle, the excitation wavelength was 570 nm.

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**Keywords:** CdSe; Thin films; Nanocrystals; Pulse plating

## 1. Introduction

The II–VI group compounds (CdSe, ZnSe, CdS, CdTe, etc.) are important because of their photovoltaic, photoelectrochemical and electroluminescent applications and have received much attention [1–3]. Recently, there have been many efforts to produce nanosized materials, because the electrical and optical properties can be varied via chemical control over size, stoichiometry and interparticle separation [4–7]. These materials have been synthesized by various techniques including pyrolysis of organometallic compounds, Sol–gel synthesis, chemical bath deposition, electrodeposition, etc. [8,9]. CdSe films have earlier been electrodeposited on gold-

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coated glass substrates at 120°C by dissolving the precursors in DMSO [9]. In the present work, CdSe films were deposited by pulse electrodeposition.

## 2. Experimental

The deposition bath consisted of 0.5 M CdSO<sub>4</sub> and 0.1 M SeO<sub>2</sub> (concentrations of the constituents selected on the basis of our earlier work [4]). Glass substrates were first boiled in chromic acid for 5 h, they were then washed thoroughly in triple distilled water and finally cleaned with acetone. These substrates were mounted in a vacuum evaporation unit. Gold was evaporated under a vacuum of 10<sup>-5</sup> Torr. After evaporating gold for 2 min, the substrates were taken out and used as cathode in the electrodeposition bath (the thickness of the evaporated gold film was 0.5 μm). Gold-coated glass substrates were kept in the electrolyte maintained at 100°C. A constant current density of 275 mA cm<sup>-2</sup> was used. The deposition was made for 10 min with a constant ON time of 1 s and the OFF time was varied from 1 to 15 s. The thicknesses of the films were estimated by gravimetric method. The films were characterized by X-ray diffraction studies using JEOL JDX-8030 X-ray diffraction unit and CuKα radiation. Optical absorption studies were carried out for the films with Hitachi UV–VIS–NIR spectrophotometer. Photoluminescence emission spectra was recorded at an excitation wavelength of 570 nm at room temperature.

## 3. Results and discussion

X-ray diffraction studies indicated hexagonal structure with peaks corresponding to (1 0 0), (0 0 2), (1 0 1), (1 1 0), (1 0 3) and (1 1 2) along with one Au line (Fig. 1). The crystallite size was estimated from the X-ray diffraction pattern by using Scherrer's formula, it was found to be in the range 10–30 nm. All the films irrespective of the duty cycle, have preferential orientation in (0 0 2) direction and the peaks corresponding to this orientation are found to increase in intensity as the duty cycle decreases (i.e. for longer OFF times). This is due to the fact that longer OFF times result in improved nucleation and crystallization as enough time is available for the species to settle down in the nucleation sites before the next set of species reach the cathode during the next ON pulse. In pulse plating, the pulsed current density remains considerably higher than the corresponding direct current plating, which leads to the higher population of adatoms on the surface during deposition than during continuous plating resulting in an increased nucleation rate and therefore a fine grained structure. High population of adatoms and high overpotentials on the surface enhance the creation of new nucleation centers. As the duty cycle increases, the conditions approach continuous plating [10,11] (Table 1).

Optical absorption studies were made on the films. A plot of  $(\alpha h\nu)^2$  vs.  $h\nu$  exhibited a linear behavior indicating the direct band nature of the films (Fig. 2). The band gap value varies in the range 1.70–1.99 eV as the duty cycle is varied from 50% to 6%. As

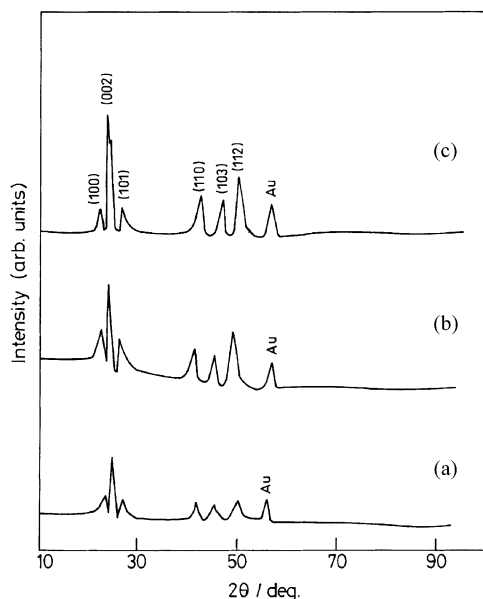


Fig. 1. XRD pattern of CdSe films deposited at different duty cycles: (a) 50%, (b) 15%, and (c) 6%.

Table 1

Effect of duty cycle for CdSe nanocrystals obtained by pulse plating

Duty cycle (%)	Diffacted angle ( $2\theta$ )	Full-width at half-maximum	Crystallite size (nm)
50	24.604	0.162	50.3
33	24.998	0.164	49.5
15	24.908	0.336	24.2
9	25.397	0.418	19.2
6	23.217	0.649	12.8

the duty cycle is decreased, a reduction in size of the particle is observed which results in a change in the band gap value. Assuming a spherical shape of a nanocrystal with radius  $R$ , the confinement energy  $\Delta E$  corresponding to the lowest transition is [12]

$$\Delta E = \hbar^2 \pi^2 / 2\mu R^2 - 1.8e^2 / \epsilon R,$$

where  $\mu$  is the reduced mass,  $\epsilon$  is the dielectric constant, and  $e$  is the electronic charge.

The band gap of bulk CdSe is 1.74 eV [12], the absorption maxima occurs at an energy  $E_1$  for the nanocrystalline films depending upon the radius  $R$ . The energy of quantum confinement  $\Delta E = E_1 - E_g$ . As the nanocrystal radius decreases the  $\Delta E$  increases, indicating an increase in band gap with decrease of particle size. Our experimental data on optical absorption have been used to calculate the crystallite

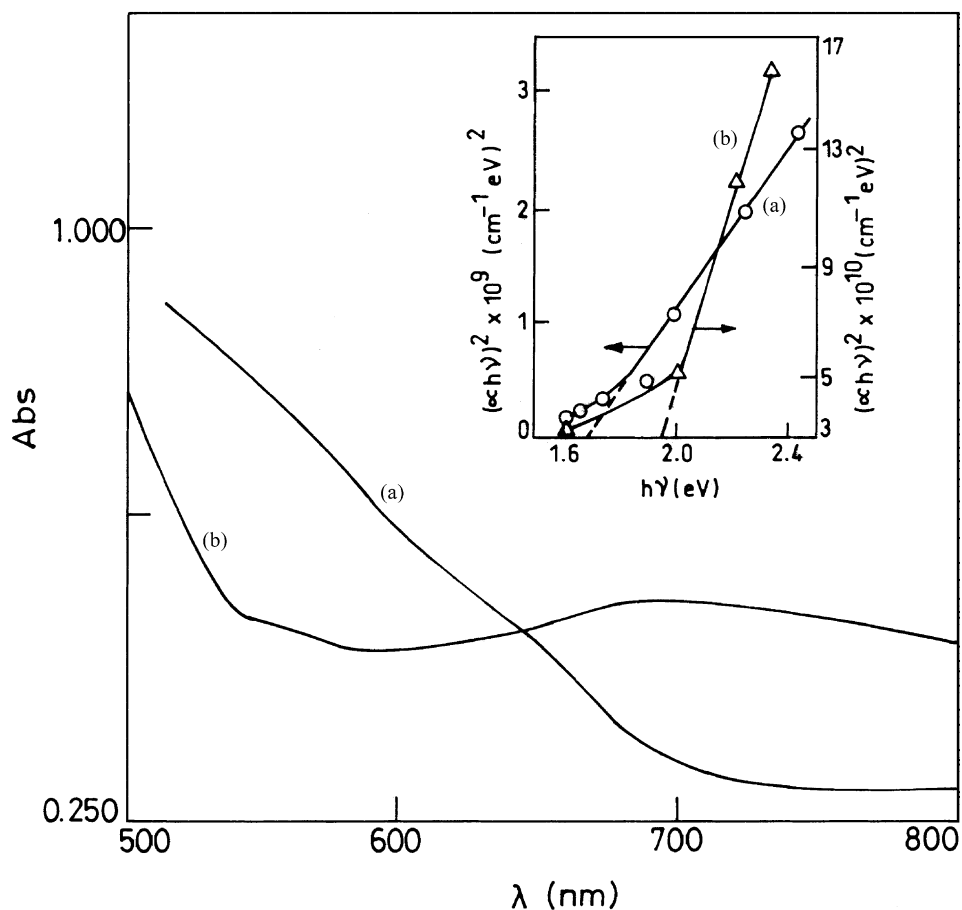


Fig. 2. Optical absorption spectra of CdSe: (a) polycrystalline thin film, and (b) nanocrystalline thin film deposited at 6% duty cycle.

size by employing the above equation. The values are nearly equal to the value of the crystallite size obtained from XRD data.

The luminescence spectra of the films deposited at different duty cycles was recorded. The emission spectra peaks at 520 nm for the films deposited at 50% duty cycle. This peak is observed to shift towards blue region (410 nm) as the duty cycle decreases to 6% (Fig. 3). This may be due to the increase in band gap due to decrease in particle size. The lowest energy transition for a nanocrystal is still an excitonic transition; however, it has a much more complex electronic structure due mainly to the finite size of the crystallite. In this size regime surface states can influence the optical properties due to  $e-h$  defects, which act as localized trap centers. The large surface-to-volume ratio in strongly confined nanocrystals results in a significant contribution of surface trap states to the optical and electronic properties [13,14]. As

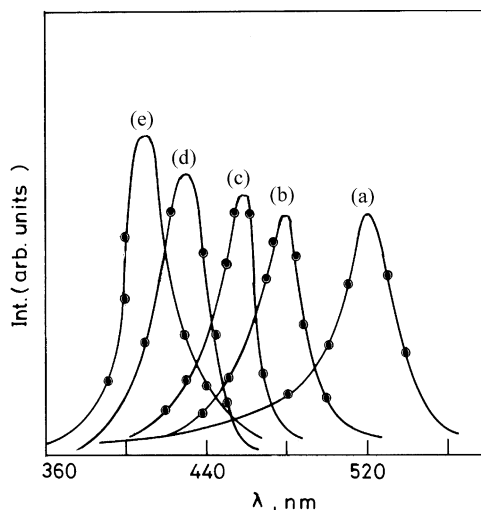


Fig. 3. Luminescence emission spectra of CdSe films deposited at different duty cycles: (a) 50%, (b) 33%, (c) 15%, (d) 9%, and (e) 6%.

the crystallite size increases, the distribution of these surface state density also decreases resulting in the change in the luminescence spectrum.

#### 4. Conclusion

A novel, simple and efficient method for obtaining nanocrystalline CdSe films has been demonstrated. The crystal size is found to vary with duty cycle. Further, small size crystallites can be obtained by increasing the deposition current density. Better crystallinity can be achieved by pulse reversal during the OFF time. Further work is in progress towards achieving this goal.

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