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Structural and optical properties of sonoelectrochemically deposited CdSe films

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The II-VI group compounds (CdSe, ZnSe, CdS, CdTe etc.) are important because of their photovoltaic, photoelectrochemical (PEC) and electroluminescent applications and have received much attention [1–3]. Recently there have been many efforts to produce nano-sized 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 coated glass substrates at 120 °C by dissolving the precursors in DMSO [9]. In the present work, CdSe films were deposited by pulse electrodeposition with and without sonication. Earlier there was a report [10] on the synthesis of CdSe powder by a combination of pulse plating and pulsed sonication, where the titanium substrate itself was pulse sonicated which prevented the growth of films; the films formed during a pulse were removed from the titanium substrate and the powder collected at the bottom. In this work, CdSe films were pulse plated at different duty cycles in the presence and absence of ultrasonic field.

The deposition bath consisted of 0.5 M $CdSO_4$ and 0.1 M of SeO_2 (concentrations of the constituents selected on the basis of our earlier work).

The duty cycle was varied in the range 9–50%. Time of deposition was maintained as 30 min. Titanium and conducting glass substrates were used for the deposition of the films. The deposition potential was −0.8 V(SCE). The films were deposited with and without ultrasonic field. The bath containing the precursors was placed in an ultrasonic trough and after setting the potential and fixing the duty cycle with the help of a microprocessor, the ultrasonic field was applied and deposition was carried out for a period of 30 min. For the films without sonication the ultrasonic field was not applied during deposition. Thickness of the films measured by gravimetry was around 2.5 μm. The films were characterized by X-ray diffraction technique with Cu K_α radiation. Optical absorption measurements were carried out using the films deposited on conducting glass substrates. XPS measurements were carried out using ESCALAB.

X-ray diffraction studies (Fig. 1) indicated hexagonai structures with peaks corresponding to (100), (002), (101), (110), (103) and (112). The peaks were found to become broader in the presence of sonication. 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 to 30 nm. The results are indicated in Table I. In general, pulse plating produces fine grained structure, but in the presence of both ultrasonic field and pulse potential, acceleration of mass transport, cleaning and degreasing of the electrode surface and increased reaction rates take place [11–13]. The combined effect is the reason for the reduction in the grain size.

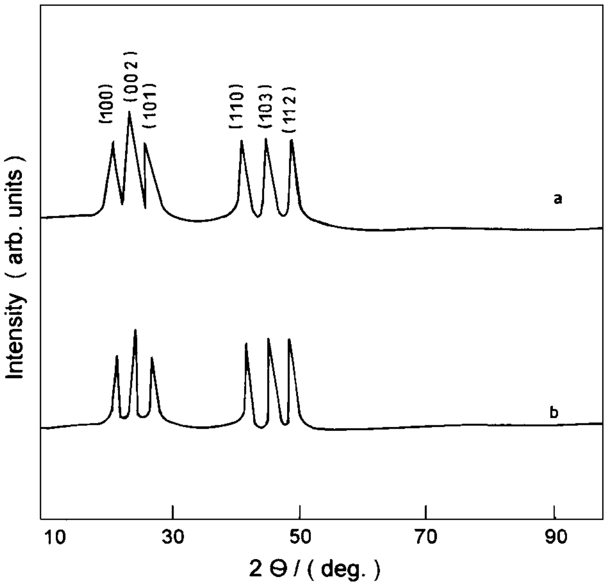

Figure 1 X-ray diffraction pattern of CdSe films pulse plated at a duty cycle of 6%: (a)without sonication and (b) with sonication.

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. 3 shows the above plot for films deposited at a duty cycle of 6% with and without sonication. A band gap value

TABLE I Effect of sonication on the crystallite size for CdSe nanocrystals obtained by pulse plating

	Crystallite size (nm)	
Duty cycle (%)	Without sonics	With sonics
50	50.3	45.2
33	49.5	43.3
15	24.2	19.4
9	19.2	14.1
6	12.8	10.0

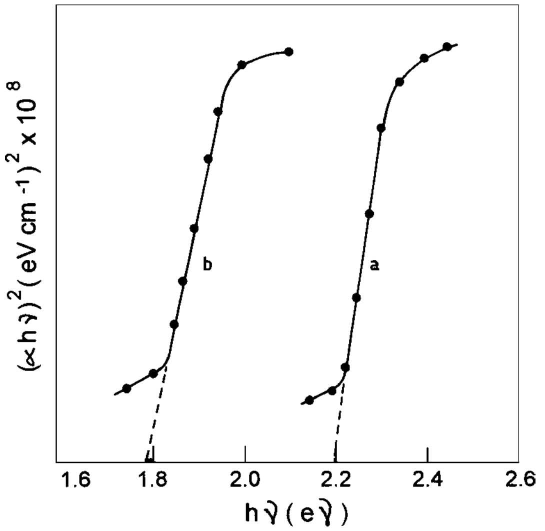

Figure 2 $(\alpha h\nu)^2$ vs. $h\nu$ plots of CdSe films deposited at a duty cycle of 6%: (a) with sonication and (b) without sonication.

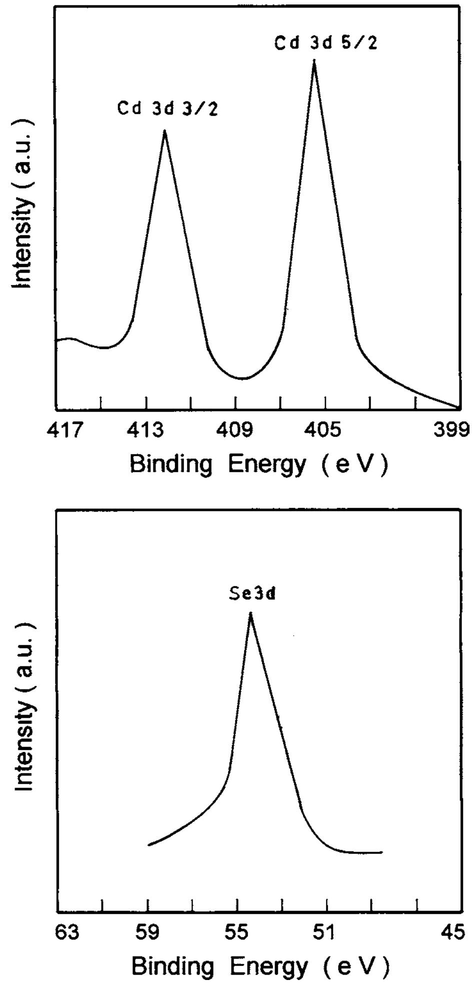

Figure 3 XPS data on CdSe films deposited at 6% duty cycle and with sonication.

of 2.2 eV was obtained for the films deposited with ultrasonics at a duty cycle of 6%. The band gap value for bulk CdSe is 1.65 eV. This increase in band gap is due to size quantization effects. The band gap values obtained for the films deposited at different duty cycles with and without sonication is shown in Table II.

TABLE II Effect of sonication on the band gap of CdSe films

	Band gap (eV)	
Duty cycle (%)	Without sonics	With sonics
50	1.72	1.85
33	1.75	1.94
15	1.78	1.99
9	1.78	2.08
6	1.79	2.20

To examine the chemical composition of the films, the XPS spectra of the CdSe films grown at different bath temperatures were measured and are indicated in Fig. 3. Fig. 3a exhibits the detailed spectra of Cd3d and Se3d regions respectively. The two strong peaks at 411.8 and 405.1 eV correspond to $Cd3d_{3/2}$ and $Cd3d_{5/2}$ binding energies. The peak at 54.3 eV (Fig. 3b), measured in the Se energy region is attributed to the Se3d transition. The energies for Cd and Se are in good agreement with the literature [14].

A novel, simple and efficient method for obtaining nanocrystalline CdSe films has been demonstrated. The crystal size is found to decrease with sonication. 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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