

Structural properties of CdSe nanocrystals in CdSe/Se multilayer

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CdSe/Se multilayer thin films were prepared using sequential thermal evaporation technique by varying the thickness of selenium sublayers. Identifying the prominent peaks observed in the XRD spectra of the top layer CdSe which corresponds to the (100) plane with wurtzite structure, the average size of the crystallites was calculated for the CdSe nanocrystals. Experimentally measured band gaps are larger than bulk band gap of CdSe. This confirms the presence of spin-orbit splitting of energy levels. Size of the crystallites was then calculated with the theoretical prediction of the effective mass approximation model (i.e., Brus model). It resulted in that the diameters of crystallites were much smaller than the Bohr exciton diameter (11.2 nm) of CdSe. Thus, the structural and optical properties of CdSe/Se multilayer thin films reveal the effect of quantum confinement of CdSe crystallites in Se matrix for various sublayer thicknesses. Confinement effect is more pronounced while sublayer thickness of selenium increases.

Keywords: CdSe; Structural; Multilayer.

1. INTRODUCTION

For more than past two decades there has been rapidly growing interest in the preparation of semiconductor nanometer- sized particles due to great variety of their potential applications in optoelectronic devices, solar cells, etc. The nano- structures of II–VI materials such as CdS [1], CdSe [2], CdTe [3] have attracted more attention for their great fundamental, experimental and applied properties. These composites are a good subject for studying quantum size effects in semiconductor quantum dots [4, 5]. Preparation of multi- layer (ML) thin films showed that the layers deposited in a step-by-step manner were smoother than those made in one step [6]. Hence, we chose thermal evaporation technique for fabrication of CdSe/Se ML thin films. CdSe has a large exciton Bohr diameter (11.2 nm), and therefore this semiconductor offers the possibility of studying quantum confinement effects in higher cluster size regimes [7]. Selenium is constructed of random chains, in such a way that all its atoms are twofold coordinated in chains with a constant dihedral angle, but this angle is changing its sign randomly [8]. This makes selenium a mixture of chain and ring fragments that allows both electrons and holes to attain measurable drift mobilities. This property of selenium will increase the strain and constraints to the adjacent layers in the multilayer systems. Moreover, the flexibility of selenium strongly reduces the requirements for matching the lattice constants of the

constituent materials in the fabrication of CdSe/Se multi- layers. In this paper, we report on changes in optical and structural properties of CdSe/Se ML thin films with respect to sublayer thickness of selenium. Moreover, quantum confinement effect due to spin-orbit coupling in CdSe/Se ML systems is also explained in view of layer thickness.

2. EXPERIMENTAL DETAILS

Chalcogenide MLs of CdSe/Se were deposited by means of physical vapor deposition technique. The CdSe/Se MLs were produced in a vacuum chamber at residual pressure of about 5×10^{-5} mbar. A consecutive evaporation was carried out from two independent molybdenum crucibles mounted in as far as possible distance from each other. CdSe and Se powders (99.99 % Aldrich Chem. Co.) were used as source materials.

Table 1 Preparation details of CdSe/Se multilayer thin film samples

S. No	Name of the sample	Total number of layers in the sample	Order of sublayers		Thickness of sublayers (Å)		Thickness ratio	Total thickness of the film (Å)
			Bottom layer	Top layer	Se	CdSe		
1	S 1	10	Se	CdSe	100	100	1:1	1000
2	S 2	10	Se	CdSe	200	100	2:1	1500
3	S 3	10	Se	CdSe	500	100	5:1	3000

Glass substrates were kept at greatest possible distance from the source materials. The sublayer thickness and deposition rate of both materials were measured during de- position process using calibrated DTM (Digital Thickness Monitor) whose quartz crystal head was fixed close to the substrates. CdSe/Se ML samples were prepared with different sublayer thicknesses of Se. In samples S1, S2 and S3, sublayer thickness of CdSe was maintained at 10 nm whereas the thicknesses of Se sublayers were 10, 20 and 50 nm, respectively. The main objective in the present work is to analyze the changes that take place in structural and optical properties of CdSe/Se MLs by varying the thick- ness of Se sublayers. The complete detail about the sample preparation is given in Table 1. The substrates were not objectively heated during the deposition of each sublayer of the CdSe/Se multilayer structures. The structural properties of the samples were analyzed by X-ray diffractometer (Shimadzu 6000) and Scanning Electron Microscope (JEOL-JSM 6390). The absorption and emission properties of the samples were studied by using UV-Vis spectrophotometer (JASCO V-550) and Photoluminescence spectrometer (FLUOROLOG-3 HJY), respectively.

3. RESULTS AND DISCUSSION

3.1 Structural properties

Identification of the nanocrystalline phases and the determination of the average crystallite sizes of CdSe/Se multilayer thin film samples coated with different sublayer thicknesses were carried out from X-ray diffraction spectra (Fig. 1). Crystallization of one kind of sublayers in multilayer thin films may not destroy its artificial periodicity if the structure of second constituent material is rigid enough to restrict the crystal growth. Therefore, we chose selenium as the second constituent material due to its structure of constructed random chains and rings [9]. The top layer in all the CdSe/Se ML samples is coated with CdSe material to protect the selenium sublayers from slow evaporation. It has been shown that the X-ray diffraction of CdSe/Se ML films has the prominent peak approximately at 23.5° in all the spectra [JCPDS-02-0330] referring to (100) plane of the for samples S1, S2 and S3, respectively. Fiber-like structures are observed on the morphology of all the samples. These structures might be due to the selenium sublayer matrices.

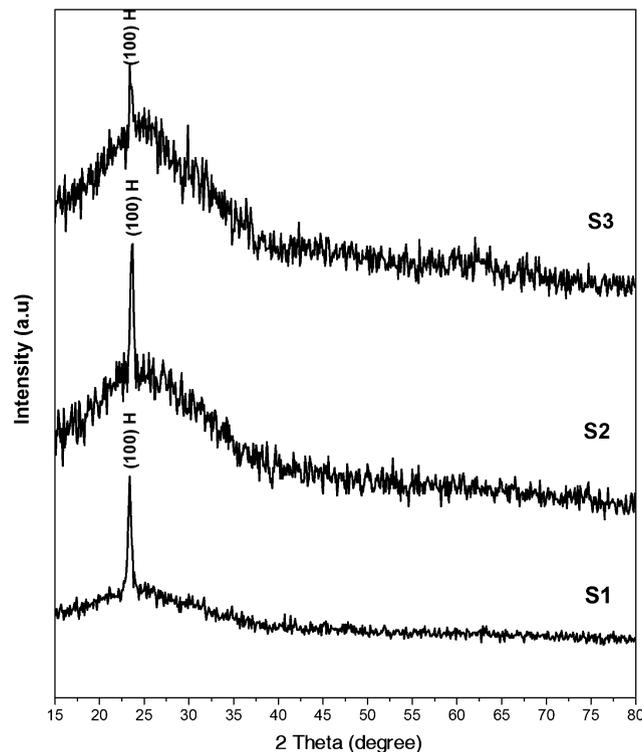


Fig. 1 X-ray diffraction spectra of CdSe/Se multilayer thin film samples with different sublayer thicknesses of selenium. Symbol 'H' represents CdSe with wurtzite structure.

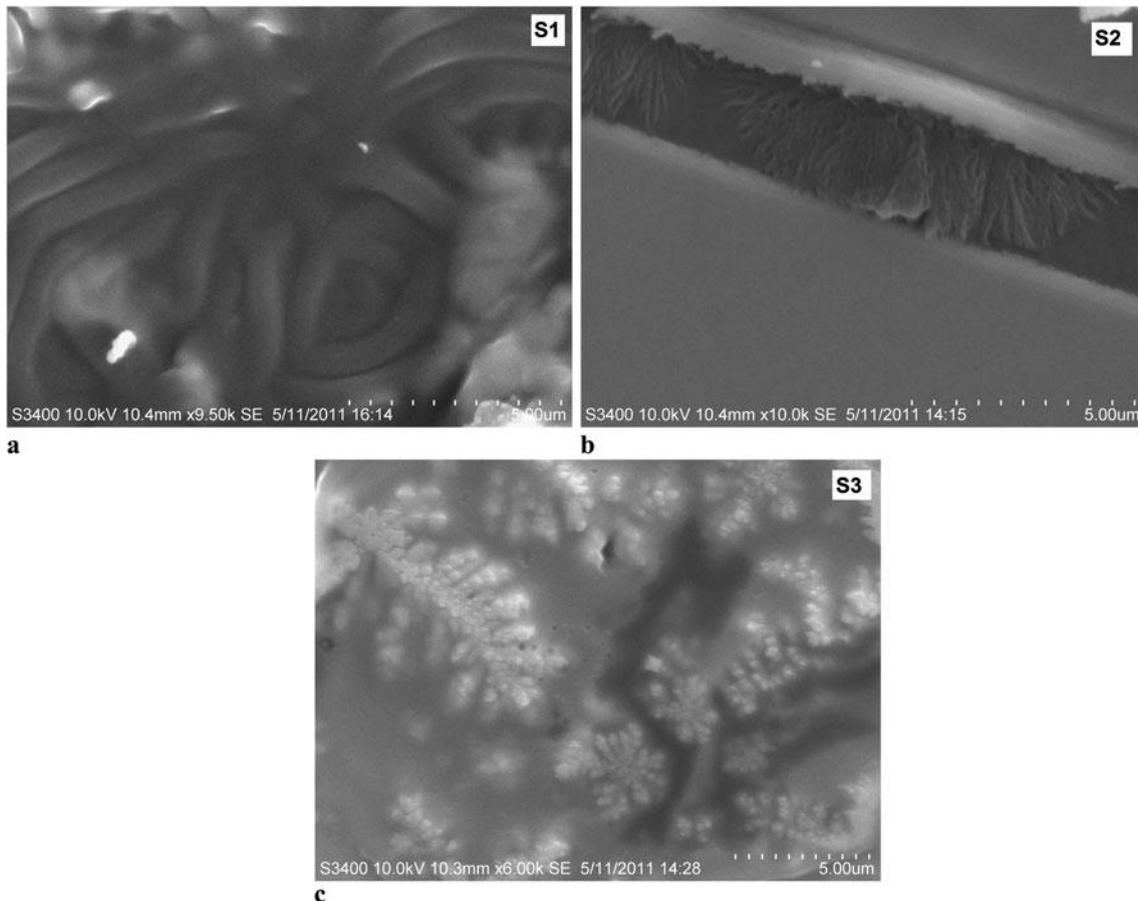


Fig. 2 Scanning electron microscope images of CdSe/Se ML samples S1, S2 and S3 showing nanostructures.

3.2 Optical properties

Absorption and transmission spectra of CdSe/Se ML samples are shown in Figs. 3 and 4. A gradual red shift is observed in the absorption edges (shown in Fig. 3) from 670 to shift (marked by arrow marks) is observed in the transmission onset of spectra (Fig. 4) of CdSe/Se samples which may be due to the splitting of energy bands due to spin-orbit coupling. However, the quantitative analysis to characterize the band-to-band electronic transitions is carried out with the optical absorption and transmission spectra of the prepared CdSe/Se ML films. Absorption coefficients of the prepared ML samples can be calculated with experimentally measured optical transmission values (T) as follows:

the absorption edge of the CdSe/Se ML samples. Moreover, it is inferred from absorption spectra of samples S1, S2 and S3 that when the thickness of Se sublayer increases, absorption edge of the CdSe/Se ML samples decreases. An abrupt In the equation, d is the thickness of the thin films noted from DTM. Transition energies between valance bands and conduction band of CdSe/Se ML samples S1, S2 and S3 were calculated by plotting a typical graph between energies

It has been generally proved that the quantum confinement effect should be observable if the radius of nanocrystallites becomes less than the Bohr excitonic radius of the corresponding material. The shift in band gaps due to quantum confinement effect in CdSe/Se ML samples is described theoretically by the effective mass approximation. Size of the crystallites was calculated from the shift in energy gap by using Brus equation.

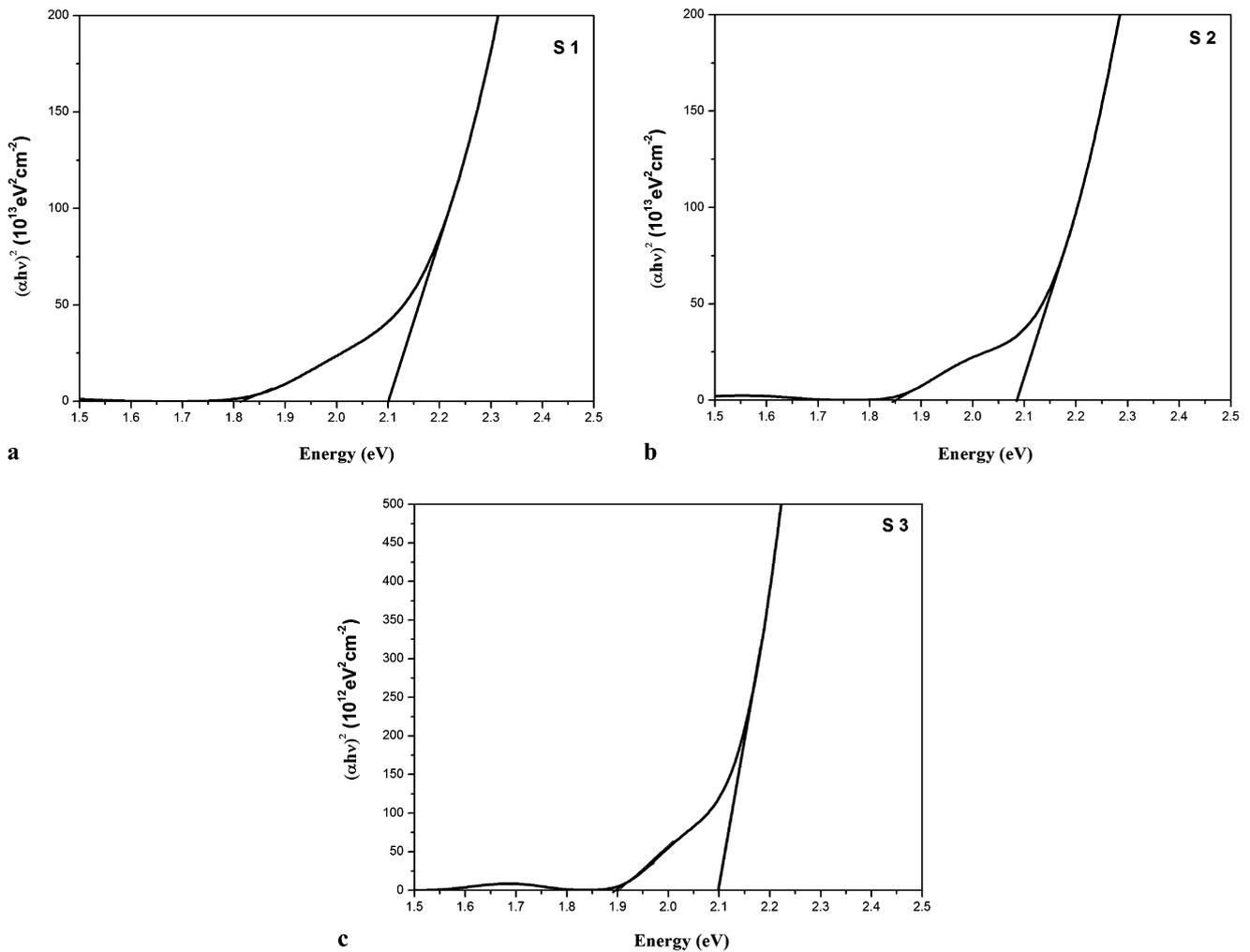


Fig. 5 The plots of (αhv) vs. $(\alpha hv)^2$ for the samples S1 (a), S2 (b) and S3 (c) with $\Gamma^V - \Gamma^V$ and $\Gamma^V - \Gamma^V$ transitions.

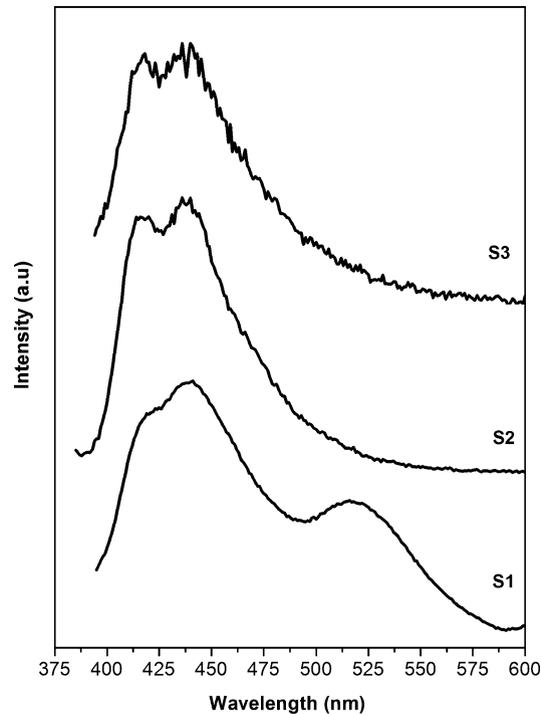


Fig. 6 Photoluminescence spectra of CdSe/Se ML samples.

transition [18]. The luminescence spectrum of sample S1 consists of an additional relatively weak band in the green region at 532 nm along with an intense band in the blue region. The FWHM of the ML samples is another note-worthy entity. FWHM of all the CdSe/Se ML samples are larger than 40 nm, which is far larger than that of ordinary bulk semiconductor sample. The main reason of this phenomenon is the size fluctuation of the quantum dots [19]. The FWHM of the weak band in sample S1 is large and can be due to potential effects, inhomogeneous broadening due to size distribution, a distribution in electron-hole distances and charge coupling with phonons. There is a splitting of the emission maximum observed with the bands centered on 420 and 440 nm in all spectra. This may be due to the emissions from the spin-orbit split of excited energy state. The large Stokes shift between the absorption maximum and the PL band may be due to the presence of at least one deep trap- ping site and electron-hole recombination via trap state [20].

4. CONCLUSION

It is observed that increasing the layer thickness of selenium increases the band gap in CdSe/Se ML samples. The main reason for this phenomenon is the structure of selenium. As mentioned earlier in this article, selenium is constructed with chains and rings structure on the surface. When thickness of the selenium sublayer increases, the depth of the surface wells (where CdSe is filled) on the surface of selenium also increases. So that alternating periodical stacking of Se and CdSe sublayers with few nanometers thickness in CdSe/Se ML samples promise the opportunity to analyze quantum confinement effect. We conclude that quantum confinement effect is more enunciated if the thickness of selenium sublayer is greater than the thickness of CdSe layers. This method gives the possibility of preparing nanocrystals of various

semiconductors with a relatively smaller size distribution in relatively shorter times than the conventional method. Further studies will be carried out in order to produce II–VI semiconductor nanocrystals with different materials.

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