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Quantum Confinement in Cadmium Selenide Multilayer Thin Films Using Physical Vapour Deposition Method

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Nanocrystals of CdSe have been produced in SiO_x matrix layer and in ZnSe heterostructure layer by thermal evaporation method. Structural studies were done by X-ray diffractometer. Quantum confinement effect of CdSe nanocrystals was analyzed from optical studies. Bulk CdSe has band-gap energy of 1.756 eV that can be shifted to larger values by reducing the crystal size to dimensions smaller than the Bohr radius of the exciton. Experimentally measured band-gap shifts with respect to the bulk value for quantum dot thin films are compared with the predictions of the effective mass approximation model (i.e., Brus model) and Quantum mechanical model. Sizes of the crystallites calculated from both models were coincident with each other.

Keywords: Multilayer thin films, Quantum Confinement, CdSe, ZnSe, SiO_x.

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1. INTRODUCTION

II-VI semiconductor particles with sizes of a few nanometers in matrix layer and in heterointerfaces show very attractive properties completely different from those of bulk materials [1]. They have potentials both for basic study of the three-dimensional quantum confinement effect in semiconductors and for applications in the field of optoelectronic devices. Number of devices make use of size controlled spectral tunability confinement induced concentration of the oscillator strength and ultra fast relaxation dynamics (optical data processing) [2-4] offered by nanocrystals. Since the first observations of quantum confinement in the optical absorption of semiconductor doped glasses [5], the nanocrystalline research has expanded immensely. The theory of quantization of hole states in a semiconductor nanocrystals has been developed taking into account band mixing effects [6, 7]. If the exciton Bohr radius is comparable to the dimensions of nanocrystallites, the confinement effects strongly modify hole energies and relax the selection rules for optical transitions which makes observation of a great number of electron-hole pair transitions possible. The presence of trap levels within the gap or on the surface of confined structures, together with the quantum confinement effect itself, strongly affect many properties of nanocrystalline materials and in particular, II – VI nanocrystals [8].

In the present work, CdSe/SiO_x and CdSe/ZnSe nanocrystalline multilayer structures are studied. We report a successful production of CdSe quantum confinement effect in thin film matrices from SiO_x and ZnSe by means of multilayer approach. The structural properties of the CdSe/SiO_x and CdSe/ZnSe were studied by X-ray diffraction method. The Optical properties of the same layers were studied by UV-VIS NIR spectrophotometer.

2. EXPERIMENTAL DETAILS

CdSe/SiO_x and CdSe/ZnSe nanocrystalline multilayer structures were prepared by consecutive thermal evaporation of CdSe(99.99 % Aldrich Chem. Co.,) and SiO_x (or) ZnSe from two independent molybdenum crucibles at a vacuum of 5×10^{-5} Pa. Corning 7059 glass substrates were used and sere not intentionally heated. The nominal film thickness and deposition rate were controlled by two calibrated quartz monitor detectors. The substrates were fixed at the greatest possible distance which was used to calculate the tooling factor of the instrument. A step-by-step procedure was applied in the deposition of a given layer in the multilayer stutures. In CdSe/SiOx sample, five layers of CdSe and four layers of SiOx were coated with the layer thickness of 50 Å and 1000 Å, respectively. In CdSe/ZnSe sample, five layers of CdSe and Si_x layers of ZnSe were coated with layer thickness of 80 Å and 500 Å, respectively. Structural studies of these samples (CdSe/SiO_x, CdSe/ZnSe) were recorded with X-ray (Shimadzu XRD-6000) diffractometer and transmission spectra were obtained using UV-VIS NIR spectrophotometer. The well coincidence between experimental data and calculated data has been proved.

3. RESULTS AND DISCUSSION

3.1 Structural Properties

Structural properties of CdSe/SiO_x and CdSe/ZnSe multilayer thin films coated under specific conditions were analyzed from X-ray diffraction spectra. The XRD profiles for the samples are shown in figure (i). A peak approximately at 23.4° and 22.7° in spectra referring to (100) plane (JCPDS-8-459) of CdSe material. This shows that CdSe/SiO_x and CdSe/ZnSe films are polycrystalline in nature with wurtzite structure. The broadness of the (100) diffraction line in the spectra indicated that the size of the CdSe crystallites in the films is small [9]. We obtained the value for size of crystallites in the range of 1-2 nm as in Table 1.

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Table 1 – Size of the Crystallites from XRD data

№	**Sample**	**2θ(deg)**	***d*(Å)**	**FWHM(deg)**	**Strain(e)**	**Stress(*S*) (dyn/cm²)**	***D* (nm)**
1	CdSe/SiO_x	23.40	3.79856	6.680	0.0212	21.2	1.19
2	CdSe/ZnSe	22.70	3.91409	6.0666	0.0522	52.2	1.31

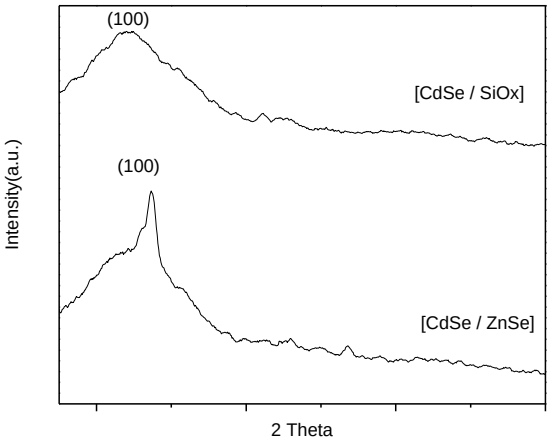

Fig. 1 – XRD profile for the samples CdSe/SiO_x and CdSe/ZnSe

The X-ray diffraction data were also used to calculate the average size of the CdSe crystallites. It was done by using Debye-Scherer broadening formula.

$$D = \frac{\lambda\beta}{\Delta(2\theta)\cos\theta}\ \text{Å} \qquad (1)$$

where D is the crystallite size, λ is the wavelength of X-ray, β is the full width at half maximum (FWHM) after correcting the instrument peak broadening (β expressed in radians), and θ is the Bragg's angle. This method provides an estimation of the CdSe crystallite size with a maximum error of about 20 % [9].

3.2 Optical Properties

CdSe/SiO_x and CdSe/ZnSe films coated on glass substrates were subjected to optical absorption using Hitachi 3010 UV-VIS-NIR spectrophotometer in the range of 190 nm - 2500 nm. In bulk CdSe material, the conduction band is non degenerate and almost isotropic whereas the valance band (mostly constituted of the selenide anion P orbital) [10] is threefold orbitally degenerate.

An important question at this point is what would be the effects of quantum confinement on the degenerate valance band of CdSe material. Based on the works done by Baldereschi & Lipari [11], the transitions close to the band gap value confirm the quantum confinement. In Fig. 2(a) &2(b), it is observed that the two transitions close to the band gap value. Two direct band to band transitions are indeed observed in CdSe/SiO_x UV spectra at 2.05 eV and 2.4 eV whereas in CdSe/ZnSe UV spectra, they were observed at 2.125 eV and 2.5 eV. This splitting of band gap confirms the quantum confinement of CdSe nano crystallites.

In Fig. 3, transmission spectra of CdSe-SiO_x and CdSe-ZnSe films were shown. A shift, which is marked

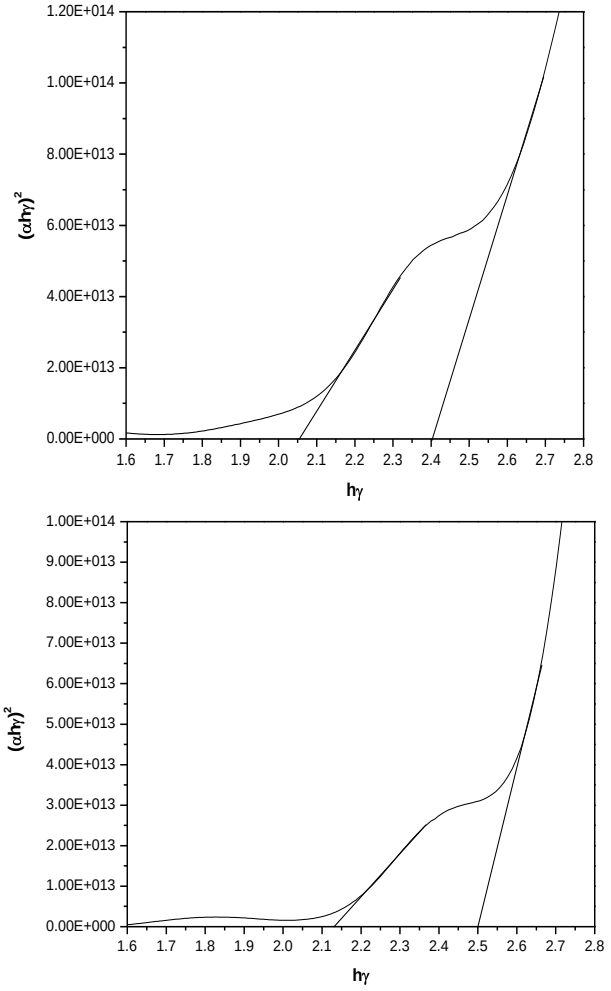

Fig. 2 – Band gap graph for CdSe/SiO_x (a) and CdSe/ZnSe (b)

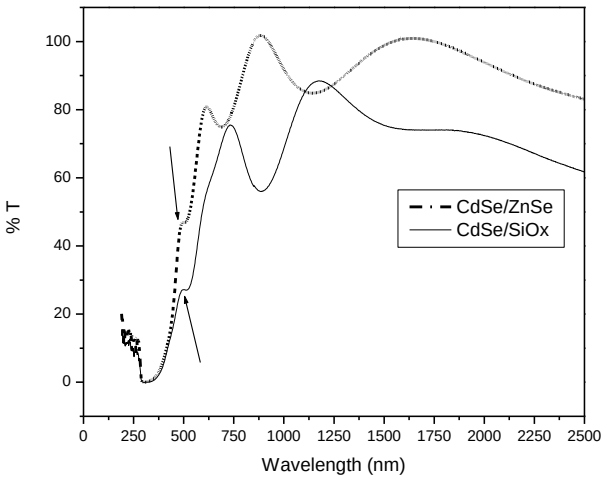

Fig. 3 – Transmission spectra of the samples CdSe/SiO_x and CdSe/ZnSe

by arrow mark, towards lower wavelength region is observed in both spectra. Shift in the transmission spectra indicates the degeneracy of valance band of CdSe material.

3.2.1 The effective mass approximation – Brus Model

If the size of a CdSe crystals becomes smaller than the exciton radius, i.e, 5.6 nm for CdSe bulk material, the band gap energy increases due to quantum confinement [12]. Hence it has been generally proven that the quantum confinement effect should be observable if the radius of nano crystallites becomes less than the Bohr excitonic radius for corresponding material. Using the relation,

$$E_{sh} = \frac{2\hbar^2\pi^2}{\mu d^2} \qquad (2)$$

where d is the average size of nanocrystals, $\mu = 0.38\ m_e$[13] is reduced electron – hole mass, the value of $d = 5.2$ nm and 4.6 nm have been obtained for the samples CdSe/SiOx and CdSe/ZnSe respectively and tabulated in Table 2.

Table 2 – Size of the crystallites from UV-Vis data by Brus model

S.No	Sample	Band gap(E_g)	Shift in Band gap (E_{shift})	D (nm)
1	CdSe/SiO_x	2.05	0.294	5.19
2	CdSe/ZnSe	2.125	0.369	4.64

3.2.2 Quantum Mechanical Model

Based on the work of Yu, W., Qu L., Guo W., [14], the condition for strong quantum confinement is $Q_{dot} << Q_b$ where Q_{dot} is radius of quantum dot and Q_b is exciton Bohr radius (CdSe = 5.6 nm).By using the given relation [14],

$$E_{ob} = E_g + \pi^2(Q_b/Q_{dot})^2\, R_y^* - 1.786\,(Q_b/Q_{dot})\, R_y^* - 0.248\, R_y \qquad (3)$$

where E_{ob} = Energy calculated from UV/VIS spectrum, E_g = bang gap (CdSe = 1.756 eV) for bulk material Q_b = exciton Bohr radius (CdSe = 5.6 nm), Q_{dot} = radius of crystallite, R_y^* = Rydberg constant (CdSe = 0.016 eV), the size of the crystallites were calculated and well coincidence between the crystallite size calculated from Brus model and Quantum mechanical model has been shown in Table 3.

Table 3 Size of the crystallites from UV-Vis data by Quantum mechanical model

S.No	Sample	Band gap(E_g)	Shift in Band gap(E_{shift})	R (nm)
1	CdSe/SiOx	2.05	0.294	3.25
2	CdSe/ZnSe	2.125	0.369	2.9

4. CONCLUSION

A new method of producing CdSe quantum dots in SiOx thinfilm matrix and in lattice matched heterostructure layer ZnSe has been proposed in this study. Well expressed quantum confined effects in the optical properties of CdSe have been observed. This method gives the possibility of preparing nanocrystals of various semiconductors with a relatively narrow size distribution in relatively short times than conventional method. It is very useful especially in case of semiconductors such as Se which form nanocrystals of very different sizes in a standard crystallization procedure. Further studies carried out in order to produce II-VI semiconductor nanocrystals with suitable sublayers.

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