CHAPTER 5

STRUCTURAL AND OPTICAL PROPERTIES OF
CdSe/ZnSe MULTILAYER THIN FILMS
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5.1 INTRODUCTION

Confined electron and hole motions in three dimensional spaces lead to quantum size effects. This effect is observable if the size of the particle is smaller than Bohr excitonic radius which acts as a natural length scale of the electron-hole pair. Quantum confinement effect is described from the discrete energy level structures and electron transitions that can be shifted to higher energies upon particle size decrease. Noteworthy efforts have been dedicated in the literature to understand thoroughly the influence of quantum confinement effects. (Memming.R. 2001; Brus.L. 1986; Efros.A.L. 1982; Melvin et al. 2013; Bawendi et al. 1990; Wang.Y. 1991). As compared to III-V materials, II-VI wide band gap materials such as CdSe, ZnSe, ZnS have much larger excitonic binding energies. Much attention has been paid to the properties of the CdSe/ZnSe systems, which have been considered as an attractive system for green-blue opto-electronic applications (Pejova 2008; Maehashi et al. 2001; Shubina et al. 1998; Kurtz et al. 2002; Kapitonov et al. 2005; Pejova et al. 2005; Ohishi et al. 2000). Mostly molecular beam epitaxy (MBE) (Cardona 1963; Baldereschi et al. 1971) and chemical route (Kurtz et al. 2002; Yu.P.Y. 1999) have been used to prepare CdSe/ZnSe systems by various research groups. Series of profound works by other researchers (Chinyama et al. 1999; Reiss et al. 2003; Kim.S. et al. 2003) have been devoted to correct assignments of higher-energy transitions detected in the photoluminescence and optical spectra of CdSe quantum dots (QDs) in various size regimes. Remarkably
Pejova (2008) has analyzed all the possible transitions between valance bands and conduction band quantitatively in CdSe and ZnSe quantum dot layers. In the present work, alternative CdSe and ZnSe thin film layers are stacked over glass substrates using physical vapor deposition method. Moreover the changes that take place in structural and optical properties of CdSe/ZnSe multilayer (ML) thin films have been thoroughly studied by varying the sublayer thicknesses as well as the number of sublayers. As the layers deposited in a step-by-step manner were smoother than those made in one step (Norris et al. 1996), thermal evaporation technique was adopted for fabrication of CdSe/ZnSe ML thin films. The main advantage of this approach is the possibility for a precise control of the sublayer thickness during the deposition process. 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 (Ekimov et al. 1993). ZnSe was chosen mainly because of its smaller lattice mismatch corresponding to CdSe and common-anion heterostructures to give a better compromise between the confinements of electrons and holes (P.Y. Yu 1999). In the present work, quantum confinement effects in CdSe/ZnSe ML thin films based on spin-orbit splitting of valance band, higher excited electronic states and shift in band gap energies are explained. Structural and optical properties of the prepared samples have been investigated in connection with quantum size effects.

5.2 EXPERIMENTAL DETAILS

CdSe/ZnSe nanocrystalline ML thin films were prepared by consecutive thermal evaporation of CdSe and ZnSe (99.99% Aldrich Chem. Co.,) materials from two independent molybdenum crucibles in vacuum condition at a pressure of $5 \times 10^{-5}$ mbar. Glass substrates were used for coating thin film samples and were not intentionally heated. The sublayer thickness and deposition rate of both materials were measured during deposition by calibrated DTM (Digital Thickness Monitor) whose quartz crystal head was fixed close to the substrates. The substrates were fixed at the greatest possible distance (for which the tooling factor was calculated)
from the source materials. A step-by-step procedure was applied in the deposition of each sublayer in the multilayer structures. CdSe and ZnSe single layer thin films with 50 nm thickness and CdSe/ZnSe multilayer samples (further referred to as Z1, Z2 and Z3) with different sublayer thicknesses were prepared. Four layers of ZnSe and three layers of CdSe materials were coated alternatively with thicknesses 50 and 10 nm respectively in the first sample Z1. The same thickness ratios of CdSe and ZnSe layers were maintained but additionally three more layers (2 layers of CdSe and 1 layer of ZnSe) were coated in sample Z2. In sample Z3, the sublayer thickness of CdSe is reduced to 1 nm. Details about the sample preparation are given in Table 5.1 with sublayer thicknesses and number of layers in CdSe/ZnSe ML samples.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Name of the Sample</th>
<th>Total Number of Layers in the sample</th>
<th>Order of sublayers</th>
<th>Thickness of Sublayers (Å)</th>
<th>Total Thickness of the film (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CdSe</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>500</td>
</tr>
<tr>
<td>2</td>
<td>ZnSe</td>
<td>1</td>
<td>-</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>3</td>
<td>Z1</td>
<td>7</td>
<td>ZnSe</td>
<td>ZnSe</td>
<td>2300</td>
</tr>
<tr>
<td>4</td>
<td>Z2</td>
<td>10</td>
<td>ZnSe</td>
<td>CdSe</td>
<td>3000</td>
</tr>
<tr>
<td>5</td>
<td>Z3</td>
<td>10</td>
<td>ZnSe</td>
<td>CdSe</td>
<td>2550</td>
</tr>
</tbody>
</table>

The structural properties of the samples were analyzed by X-Ray diffractometer (Shimadzu 6000) and Scanning Electron Microscopes (FEI Quanta FEG 200 & JEOL – JSM 6390). The absorption and emission properties of the samples were studied by using UV-VIS spectrophotometer (JASCO V-550) and Photo Luminescence spectrometer (Fluorolog – 3 HJY) respectively.
5.3. RESULTS AND DISCUSSION

5.3.1 Structural Properties

Identification of the nanocrystalline phases and the determination of the average crystallite sizes of CdSe/ZnSe ML thin film samples coated under specific conditions were carried out from X-ray diffraction spectra (Figure 5.1). It has been shown that the X-ray diffraction spectra of the samples Z1, Z2 and Z3 are having the prominent peaks approximately at $27^\circ$ [JCPDS-80-0021] referring to (111) plane of the ZnSe with zinc-blende structure.

Figure 5.1 X-Ray Diffraction Spectra of CdSe/ZnSe multilayer thin film samples Z1, Z2 and Z3 with (111) plane of ZnSe
The peak in the XRD spectra of sample Z1 and Z2 are sharp whereas in sample Z3, the peak appears broad due to decrease in thicknesses of CdSe sublayers. Broadness of the peaks in the XRD profile indicates that the size of the particles is very small (Lifshitz et al. 1998). In order to calculate the average nanocrystallite diameter, the Debye – Scherrer’s equation as given in equation (4.1) is employed. In this calculation, θ and β are the position and FWHM of the prominent peak after correcting the instrument peak broadening using Origin software. Size of the particles is calculated as 20, 8 and 2 nm for the samples Z1, Z2 and Z3 respectively as given in Table 5.2.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Sample</th>
<th>2θ(deg)</th>
<th>d(Å)</th>
<th>FWHM (deg)</th>
<th>Strain (ε)</th>
<th>D (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Z 1</td>
<td>27.35</td>
<td>3.25</td>
<td>0.40</td>
<td>0.0024</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>Z 2</td>
<td>27.43</td>
<td>3.26</td>
<td>1.01</td>
<td>0.0055</td>
<td>8</td>
</tr>
<tr>
<td>3</td>
<td>Z 3</td>
<td>27.10</td>
<td>3.28</td>
<td>4.80</td>
<td>0.0116</td>
<td>2</td>
</tr>
</tbody>
</table>

There is more possibility for stress to be one of the causes for quantum size effects in multilayer system due to heap arrangement. Therefore, approximate level of microstrains for CdSe/ZnSe ML thin films were calculated using the relation (Suchitra Sen et al. 1974) as given in equation (4.6).
Values of microstrains for the samples Z1, Z2 and Z3 were obtained as $2.4 \times 10^{-3}$, $5.5 \times 10^{-3}$ and $11.6 \times 10^{-3}$ respectively as tabulated in Table 5.2 which shows that increasing microstrain in CdSe layers decreases crystallite sizes. Microstrain in sample Z1 is comparatively small so that size of the particle in sample Z1 exceeds the Bohr exciton diameter (11.2 nm) of CdSe. Surface images of CdSe/ZnSe ML thin films as Z1, Z2 and Z3 were recorded using scanning electron microscope (SEM) as shown in Figure 5.2 (a), (b) and (c) respectively. Usually when CdSe material is coated over ZnSe matrix as a thin layer under some conditions, quantum islands will appear on the surface (Yu.P.Y. 1999; Zhou-yao et al. 1987; Arizpe-Chávez et al. 2000). To examine this, top layers in samples Z2 and Z3 were coated with CdSe material while it was ZnSe in sample Z1. The particles were distributed like islands in the SEM images of samples Z2 and Z3 (Figure 5.2 (b) and (c)) whereas the surface of the sample Z1 is observed like domains as expected.
Figure 5.2 Scanning Electron Microscope images of CdSe/ZnSe ML samples showing domains (a) and distribution of the particles on the surface with clear surroundings (b & c).
Images of HRSEM and composition ratios of CdSe and ZnSe recorded using Energy Dispersive Analysis of X-rays (EDX) of sample Z2 are shown in Figures 5.3 and 5.4. The layer formation in CdSe/ZnSe ML thin films is confirmed from HRSEM - FEI Quanta FEG 200. The edges of the ML samples are scratched using micro blades to view the arrangements of CdSe and ZnSe sublayers. From the scale given at the bottom of Figure 5.3, the sublayer thickness of CdSe and ZnSe materials could be inferred to be less than 100 nm. These values coincide well with the values of sublayer thicknesses in sample Z2 which is calculated by DTM.

Figure 5.3 HRSEM image of sample Z2 showing layer formation

The existence of Cd, Zn and Se was proved by EDX spectrum. The peaks located at 1.3 keV and between 11 and 12 keV confirm the presence of selenium characteristic lines K and L. The detected elements of Cd, Se and Zn in the spectra are related to CdSe and ZnSe composed materials. The elemental composition of CdSe/ZnSe ML sample Z2 was analysed by XPS survey spectrum which is given in Figure 5.5.
Figure 5.4 EDX spectra of sample Z2 showing composition ratios of CdSe and ZnSe

Figure 5.5 X-ray Photoelectron spectrum of CdSe/ZnSe ML thin film sample Z2
All the peaks were calibrated using C (1s) signal at 284.5 eV as the reference. The peaks at 10, 59.7 and 408.7 eV in the XPS survey are the characteristic peaks of Zn, Se and Zn respectively. Furthermore, Se (LMM1 & LMM2) augur lines were also observed in the survey. The XPS results confirmed the elemental composition of CdSe/ZnSe ML thinfilms and are consistent with the already reported model for CdSe/ZnSe sample. Though the XRD and SEM methods revealed the morphological properties of the multilayer systems with some approximations, the phenomena like spin-orbit coupling, splitting of valance bands, energy level shifting etc., could not be characterized by these techniques. Therefore, confinement effects of CdSe/ZnSe systems were mostly discussed with optical absorption and emission spectra (Pejova 2008; Chinyama et al. 1999; Reiss et al. 2003; Kim.S. et al. 2003).

5.3.2 Optical Properties

Absorption spectra of CdSe, ZnSe single layer thin films and CdSe/ZnSe ML samples Z1, Z2 and Z3 are shown in Figures 5.6 and 5.7 respectively. There is a blue shift observed in the absorption edges of ML samples from 690 to 550 nm as the size of the particle reduces. Substructures are seen in the absorption spectra of CdSe/ZnSe ML samples Z1,Z2 and Z3 (Figure 5.7) but not in the spectra of CdSe and ZnSe single layer thin films (Figure 5.6), which may be related to electronic transitions between discrete hole and electron energy levels in the valance and conduction bands of CdSe nanocrystals due to spin-orbit coupling (Arizpe-Chávez et al. 2000). Valence bands of CdSe often show remarkable complexities. These complexities in hole dispersion relations are mainly due to the fact that the valence band originates from anionic p-orbitals.
Figure 5.6 Absorption spectra of CdSe and ZnSe single layer thin films with layer thickness 50 nm each.

Figure 5.7 Absorption Spectra of CdSe/ZnSe ML thin films indicating the blue shifts in the absorption edges.
This band is three-fold degenerate and therefore effects of spin and orbital angular momentum coupling are very significant (Maehashi et al., 2000; Nesheva et al., 2002; Ohishi et al., 2000). Moreover the spin-orbit interaction splits the valance band of CdSe into an upper and lower component. The quantitative analysis to characterize the band-to-band electronic transitions and the transitions between the discrete hole and electron states has been carried out with the optical absorption and transmission spectra (shown in Figure 8.2) of the prepared CdSe/ZnSe ML films. Absorption co-efficients of the prepared ML samples can be calculated with experimentally measured optical transmission data as given in equation 4.2.

Transition energies between valance bands and conduction band of CdSe/ZnSe ML samples Z1, Z2 and Z3 were calculated by plotting a typical graph between energy($h\nu$) and $(\alpha h\nu)^2$ as shown in Figure 5.7 by using the following relation (Tauc.J, 1979) as given in equation 4.3. More than one band-to-band electronic transitions were observed in Fig. 5.8 (a), (b) and (c) which is due to the presence of spin-orbit split of valance band. This mixing of energy states arise upon particle size decrease. Now it is very important to assign the energies observed in Figure 5.8 to their respective electronic transitions. As mentioned earlier, valance band of CdSe semiconductor splits into energetically higher and lower components which are usually labeled as $\Gamma_7^v$ and $\Gamma_8^v$ as a result of spin-orbit interaction. These two low lying hole states are separated by a value $\Delta$ which is similar to $\Delta_0$ in the case of bulk material (Pejova et al. 2005).
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(a)

\[(a_hv)^2 \times 10^2 \text{eV}^2 \text{cm}^{-2}\]

Energy (eV)

(b)

\[(a_hv)^2 \times 10^2 \text{eV}^2 \text{cm}^{-2}\]

Energy (eV)
Based on the model proposed by Chestnoy et al. (1986), the valance band components $\Gamma_7^\nu$ and $\Gamma_8^\nu$ are expected to give rise to a set of discrete hole states separately as depicted in Figure 5.9 (Baldereschi et al. 1971). This proposed model has made the task of assigning the electronic transitions with the energy values quite straightforward. According to the energy order, the obtained energy values (referred as $E$ and $E_g$ in Table 5.3) in sample Z1 (2.23 and 1.84 eV), Z2 (2.34 and 1.96 eV) and in Z3 (2.62 and 2.25 eV) given in Figures 5.8 (a), (b) and (c) may be attributed to transitions taking place between $1S_{\nu}$-$1S_{\nu}$ and $1S_{\nu}$-$1S_{\nu}$ energy states respectively (Pejova et al. 2005; Woggon et al. 1996). The energy values corresponding to the $1S_{\nu}$-$1S_{\nu}$ and $1S_{\nu}$-$1S_{\nu}$ transitions in ML samples Z1, Z2 and Z3 are not equal since the shift of energy states mainly depends upon the size of the particles.
Figure 5.9 The discrete hole and electron states arising from valence and conduction bands in the case of CdSe semiconductor.
But the energy differences (E - E\textsubscript{g}) between these two transitions in the ML samples are more or less equal as given in Table 5.3. By analyzing (αh\nu)^2 versus h\nu dependence in the energy region of Figure 5.8 (b), the third electronic transition is observed just above 1S\textsubscript{A}-1S transition. According to Woggon et al. (1996), the third transition energy 2.55 eV in ML sample Z2 may be due to the result of transition which takes place between 1P-1P energy levels. The energy values along with their assigned electronic transitions reported in the present work are in good agreement with the reports given by other researchers (Pejova 2008; Cardona 1963; Baldereschi et al. 1971; Yu.P.Y. 1999; Ekimov et al. 1993; Norris et al. 1996; Lifshitz et al. 1998). For precise predictions, the size of the particles was calculated from the energy gap (E\textsubscript{g}) values using Brus effective mass approximation as given in equation 4.4.

The average size of the nanocrystallites calculated using equation (4.4) is 12, 7 and 4 nm for samples Z1, Z2 and Z3 respectively. As it can be inferred from Table 5.3, the confinement energies (E-E\textsubscript{g(bulk)}) for the samples Z1,Z2 and Z3 are large which states that the prepared ML samples are strongly quantized (Pejova et al. 2005). Moreover, it is evident that the nanocrystallite sizes (D) of the CdSe/ZnSe ML samples are much smaller than the Bohr exciton diameter (D\textsubscript{B}) of CdSe (11.2nm) (Sharma et al., 2005). If D / D\textsubscript{B} <<2, the film exhibits a single particle confinement behavior in which electrons and holes are independently confined. Hence, the prepared CdSe/ZnSe ML samples confirm the presence of strong quantum confinement effect.
Table 5.3: Size of the crystallites from UV – Vis data by Brus model

<table>
<thead>
<tr>
<th>S.No</th>
<th>Sample</th>
<th>$E(\Gamma^\gamma\gamma^\gamma)/\Gamma^\gamma\gamma^\gamma$ eV</th>
<th>$E_g(\Gamma^\gamma\gamma^\gamma)/\Gamma^\gamma\gamma^\gamma$ eV</th>
<th>$(E-E_g)$ eV</th>
<th>$(E-E_{g(bulk)})$</th>
<th>Shift in Band Gap</th>
<th>D (nm)</th>
<th>D/D_B</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Z 1</td>
<td>2.23</td>
<td>1.84</td>
<td>0.39</td>
<td>0.47</td>
<td>0.10</td>
<td>12</td>
<td>1.07</td>
</tr>
<tr>
<td>2</td>
<td>Z 2</td>
<td>2.34</td>
<td>1.96</td>
<td>0.38</td>
<td>0.58</td>
<td>0.22</td>
<td>7</td>
<td>0.63</td>
</tr>
<tr>
<td>3</td>
<td>Z 3</td>
<td>2.62</td>
<td>2.25</td>
<td>0.37</td>
<td>0.86</td>
<td>0.51</td>
<td>4</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Size of the crystallites calculated from effective mass approximation is not precisely matched with the size of the crystallites calculated from X-ray diffraction spectra. In order to explain the observed discrepancy one should take into account that the full width at half maximum of X-ray diffraction peaks depends not only on the nanocrystal size but also on existing microstrains and deformations in the nanocrystal arrangement (Suchitra Sen et al. 1974).

Photoluminescence spectroscopy is one of the powerful techniques to characterize the optical properties of semiconductor quantum structures in ML systems (Kako et al., 2002; Kammerer et al., 2001). Figure 5.10 shows the photoluminescence spectra of CdSe and ZnSe single layers along with CdSe/ZnSe ML samples Z1, Z2 and Z3. The intense bands of CdSe and ZnSe single layer films are shifted from the bands of ML samples towards lower wavelength side due to the band structure alignment of CdSe/ZnSe systems. Position of PL peak in sample Z1 lies at 2.32 eV whereas in the samples Z2 and Z3 the peak positions are shifted to 2.92 eV due to decrease in particle size. This implies that the emission peaks can be tuned from green region to blue region by reducing the size of the particles. There is a splitting of the emission maximum observed with the bands centered on 2.85 and 2.98 eV in the samples Z2 and Z3.
Figure 5.10 Photoluminescence Spectra of CdSe/ZnSe ML samples along with CdSe and ZnSe single layers
This may be due to the emissions from the spin-orbit split up of neighboring energy states. The FWHM of the ML samples is another noteworthy entity. FWHM of the ML samples are larger than 200 meV, 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 (Mao et al., 2005). The FWHM of the CdSe/ZnSe ML sample Z2 and Z3 are the largest, because the size of the particle in these samples is smallest and the quantum confinement effect is most notable.

5.4 CONCLUSION

CdSe/ZnSe multilayer thin films using thermal evaporation technique under specific conditions promise the presence of quantum confinement phenomenon. Evidences for quantum confinement are observed in the structural and optical properties of the prepared samples. XRD studies are used to calculate the average size of the particles due to the observed (111) plane of ZnSe. Due to stacked arrangement of CdSe and ZnSe layers, stress developed in the samples results in the confinement of particles. Crystallite sizes (12 - 4 nm) were calculated with the predictions of the effective mass approximation model (i.e., Brus model). It shows that the diameter of crystallites are smaller than the Bohr exciton diameter (11.2nm) of CdSe. Spin-orbit split of valance band was identified from the absorption spectra of the samples and electronic transitions which were calculated from $(\alpha h\nu)^2$ versus $(h\nu)$ relation. Upon particle size decrease, the PL peak is shifted from green region to blue region. It is analyzed that the sublayer thickness of CdSe material changes the properties of CdSe/ZnSe multilayer systems. It is concluded that the size of the particle plays an important role in quantum confinement effect and energy gap increases with increasing the number of layers and decreasing the sub layer thicknesses.