CHAPTER VI

6. OPTICAL CHARACTERIZATIONS OF PbSe/ZnSe MULTIPLE QUANTUM WELL STRUCTURES

6.1. Absorption studies

6.1.1. Introduction

Optical absorption is a useful probe for determining the presence quantum confinement effects on the electronic structure as well as the overall absorption potential of the nanostructural materials if used in the context of solar cells. Also, a large blue shift and appearance of a discrete linear region in the optical absorption spectra are the easily measurable consequences of quantum size confinement (Choi et al. 2009, O.S.Heavens 1991). In a QW, the electrons and holes are still free to move in the direction parallel to the layers: hence, there are no discrete energy states for electrons and holes in the QWs, instead ‘sub-bands’ that starts at the energies calculated for the confined states (Takagahara and Takeda 1992b). Optical absorption measurements were performed on all the PbSe/ZnSe MQW structures as a function of photon energy including annealed samples (resulting modification in 2D nanostructure) to study the optical properties of the MQW structures. Optical measurements of reference PbSe and ZnSe was used to compare the absorption onset values. Infinite potential well approximation has been used to calculate the effective QW band gap for 2D PbSe/ZnSe MQW structures together with effective masses of electrons and holes.

6.1.2. Results and discussion

A schematic energy band diagram of PbSe/ZnSe MQW structure is shown in Fig. 6.1. Energy diagram clearly shows energy states of the lower band gap PbSe QW layers are confined within spacer ZnSe barrier with type I QW transition. Optical absorption spectra of 5 periods PbSe/ZnSe MQW structures as a function of photon energy along with reference ZnSe and PbSe thin films are shown in Fig. 6.2. The absorption onset of reference PbSe and ZnSe was found to be 2.6 and 0.8 eV
Fig. 6.1: *Energy band diagram of PbSe/ZnSe MQW structures.*

Fig. 6.2: *Optical absorption spectra of the 5 periods PbSe/ZnSe MQW structures with different $L_z$ along with reference PbSe and ZnSe thin films.*
which is in consistent with earlier works (Abe 2011). It can be noted that upon stacking of PbSe QW layers into ZnSe barrier, the absorption onset significantly red shifted in response with reference ZnSe film. It is noteworthy to state that the absorption edges of all the samples start with nearly same energy region which infers that ZnSe play a major role to absorb the energy. However, increasing $L_z$ leads to broadening of the absorption spectra towards reference PbSe thin film. No clear absorption or sub-band transition corresponds to PbSe phase was identified in 5 periods MQW structures.

Fig. 6.3 shows the optical absorption spectra of 10 periods PbSe/ZnSe MQWs as a function of incident photon energy. For comparison, absorption spectra of reference ZnSe (300 nm) and PbSe (200 nm) films are also provided. The inset in Fig. 6.3 is an enlarged view of the lower energy region of the graph which commonly used to show the clear shift in the absorption spectra of PbSe QDs (Wise 2000, Luther et al. 2007). All QW structures show two linear regions in the continuum of the absorption edge which is indicated by I and II in the inset of the Fig. 6.3. It can be seen that the absorption onset exhibits a progressive blue shift when $L_z$ decreases from 10 nm to 2.5 nm. The absorption edge lies in between the value of bulk PbSe and ZnSe band gaps and is shifted towards blue (higher energy) with smaller $L_z$. The lower energy features (I & II) in the inset correspond to the quantized sub band energy level transition within the QW which is clearly shown in the micro PL spectra (Fig. 6.7) discussed in next section. Feature II disappears when $L_z$ increases from 2.5 nm to 10 nm and attains the absorption of reference PbSe. This behaviour may be attributed to the lateral extension of the ground state exciton wave function in the QW plane resulting in a decrease of the quantum confinement (Yun et al. 2009). All absorption features along with the sharp absorption edge are shifted towards higher energy with decreasing $L_z$. This reflects a quantum confinement effect which results from the increase of the exciton binding energy.
**Fig. 6.3:** Optical absorption spectra of the 10 periods PbSe/ZnSe MQW structure with different $L_z$. The inset shows the enlarged view of the lower energy region of the spectra for clarity.

**Table 6.1:** Optical band gap and confined energies of the PbSe/ZnSe MQW structure for 10 periods.

<table>
<thead>
<tr>
<th>Quantum well thickness (nm)</th>
<th>$E_g$ (eV)</th>
<th>$E_{0,e}$ (meV)</th>
<th>$E_{0,h}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
<td>Observed</td>
<td></td>
</tr>
<tr>
<td>2.5</td>
<td>2.35</td>
<td>2.35</td>
<td>621</td>
</tr>
<tr>
<td>5</td>
<td>1.55</td>
<td>2.1</td>
<td>155</td>
</tr>
<tr>
<td>7.5</td>
<td>1.37</td>
<td>1.75</td>
<td>69</td>
</tr>
<tr>
<td>10</td>
<td>1.32</td>
<td>1.65</td>
<td>39</td>
</tr>
</tbody>
</table>
To support this argument, we calculated the effective QW band gap for a 2D structure using the following infinite well approximation (Martelli et al. 1993),

$$E_{g\text{ QW}} = E_{g\text{ bulk}} + E_{0,e} + E_{0,h} \quad \text{(13)}$$

$$E_{0,e} = \frac{\hbar^2}{8m^*_e L_z^2}$$

$$E_{0,h} = \frac{\hbar^2}{8m^*_h L_z^2}$$

Where \((m^*_e)\) and \((m^*_h)\) are the effective masses of the electron and hole, respectively, with values equal to 0.097\(m_0\) and 0.120\(m_0\). \(L_z\) is the quantum well layer thickness. \(E_{0,e}\) and \(E_{0,h}\) are the quantized electron and hole energy, respectively. Here the bulk value of PbSe \((E_{g\text{ PbSe}})\) is taken as 1.2 eV from the reference PbSe absorption spectrum. The calculated QW band gap energies are compared with experimentally observed values in the absorption spectra and listed in Table 6.1. The calculated \(E_{g\text{ QW}}\) values approximately match with the observed values which confirm the fact that the observed band gap energy in the absorption is due to the quantum confinement effect. The discrete linear region in the absorption spectra (inset of Fig. 6.3) with the wide range (UV-NIR) favourably covers the desirable energy regions for conversion efficient solar cells. It is believed that this types of discrete energy levels will lead to multiple exciton generation when the confined regions of the PbSe band gap \((E_g)\) obey \(E_g \geq 2E_{g\text{ (bulk)}}\) (Luther et al. 2007). It is noteworthy to state that the observed value of \(E_{g\text{ QW}}\) is approximately two times larger than the reference band gap of 1.2 eV.

Fig. 6.4 shows optical absorption spectra of 20 periods PbSe/ZnSe MQW structure with various \(L_z\) as a function of incident photon energy. For comparison, the absorption spectra of reference ZnSe (300 nm) and PbSe (200 nm) films are also provided. It is noted that the absorption onset of the MQW structure lies in between reference ZnSe and PbSe thin films indicating the formation of type I QW structure in which carriers are confined in QW layers.
Fig. 6.4: Optical absorption spectra of the 20 periods PbSe/ZnSe MQW structure with different $L_z$. The inset shows an enlarged view of the lower energy region of the spectra for clarity.

Table 6.2: Optical band gap and confined energies of the PbSe/ZnSe MQW structure for 20 periods.

<table>
<thead>
<tr>
<th>QW thickness ($L_z$) nm</th>
<th>QW band gap energy $E_{g\text{, QW}}$ (eV)</th>
<th>Calculated</th>
<th>Observed</th>
<th>$E_{0,e}$ (meV)</th>
<th>$E_{0,h}$ (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>1.92</td>
<td>1.83</td>
<td>601</td>
<td>502</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>1.20</td>
<td>1.57</td>
<td>155</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>7.5</td>
<td>0.98</td>
<td>1.23</td>
<td>69</td>
<td>55</td>
<td></td>
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<tr>
<td>10</td>
<td>0.87</td>
<td>0.96</td>
<td>39</td>
<td>31</td>
<td></td>
</tr>
</tbody>
</table>
Reference ZnSe film shows interference fringes beyond its fundamental absorption edge whereas MQW structures show exciton resonances. The inset of the Fig. 6.4 is an enlarged view of the lower energy region of the graph (without spectra of reference films) to show the QW resonances clearly. The effect of QW thickness and result analysis of 10 periods MQW structures are same for 20 periods MQW structures. To calculate the effective QW band of PbSe/ZnSe MQW structures, the equation given in eqn.13 was used.

The calculated QW band gap energies are compared with experimentally observed values in the absorption spectra and are listed in Table 6.2. The calculated $E_{g,QW}$ values approximately matches with the observed values confirm the fact that the observed band gap energy in the absorption is due to the quantum confinement effect. In comparison with 10 periods PbSe/ZnSe MQW structure, the observed and calculated values of $E_{g,QW}$ is less which is associated with increasing total thickness of the QW layers.

6.1.3. Conclusion

Quantum confinement effect from the optical absorption characterization of PbSe/ZnSe MQW structures with different QW periods range from 5 to 20 as a function of $L_z$ was studied. The absorption onset of the MQW structure lies in between reference ZnSe and PbSe thin films indicating the formation of type I QW structure in which carrier are confined in QW layers. The absorption onset exhibits a progressive blue shift when $L_z$ decreases from 10 nm to 2.5 nm. The lower energy features correspond to the quantized sub band energy level transition within the PbSe QW was observed. When $L_z$ increases from 2.5 nm to 10 nm, some of the lower energy features disappear and attains the absorption of reference PbSe which is due to lateral extension of the ground state exciton wave function in the QW plane. All absorption features along with the sharp absorption edge are shifted towards higher energy with decreasing $L_z$ reflects a quantum confinement effect. In addition, the quantum confinement effect is confirmed from the infinite potential
well approximation. The well resolved resonance in the absorption spectra favourably covers the full solar spectrum (0.6-2.5eV), which will be useful for potential applications in high conversion efficiency solar cells.
6.2. Photoluminescence studies

6.2.1. Introduction

QW structures are show increasing importance in the development of smaller, faster, and efficient optoelectronic devices. The primary motivation for using QW structures is to change the potential energy of electrons and holes at the material interfaces. Because phenomena at surfaces and interfaces in QW structures tend to dominate the behaviour of excitations in the heterostructures, many microelectronic devices is limited by the nature of heterojunctions. Smooth and atomically abrupt interfaces are necessary for good optical and electrical reflection, uniform quantum confinement and high carrier mobility. Even more importantly, defects and impurities at the interfaces provide new states for electrons and holes, altering their motion, life time and transition energies. PL is the spontaneous emission of light from a material under optical excitation which is a useful analysis to study the surface and interface properties of the QW system (Romcevic et al. 2009, Wang, Zhang and Zhang 2012). When light of sufficient energy is incident on a material, photons are absorbed and electronic excitations takes place. Eventually, these excitations relax and the electrons return to the ground state. Features of the emission spectrum can be used to identify surface, interface properties and interface roughness. The intensity of the signal provides information on the quality of surface and interface. The energy distribution and density of interface states can be ascertained by studying the excitation intensity dependence of the PL spectrum. PL measurements of PbSe/ZnSe MQW structures were done using micro-photoluminescence setup with the excitation sources of 325 and 532 nm laser source and results are discussed below.

6.2.2. Results and discussion

Micro PL spectrum of reference ZnSe thin film with the thickness of 200 nm is shown in Fig. 6.5. The sample was excited using 325 nm laser at room temperature. The strong peak at 2.23 eV of the reference ZnSe film was assigned to
be a band edge luminescence due to radiative recombination of electrons localized at ground state ($1E_s$). Several authors have reported PL emission of ZnSe with this region corresponding to the band gap value of 2.7 eV. The FWHM of the emission peak is 0.38 eV. The sharp and homogeneous broadening of the PL peak indicates the quality of the ZnSe film (Akimoto, Miyajima and Mori 1989). Fig. 6.6 shows room temperature micro PL spectrum of PbSe/ZnSe MQW structure of $L_z=2.5$ nm with 5 periods. Well resolved two emission peaks are observed at 1.86 and 2.35 eV. The emission at high energy region is attributed to be the ZnSe band edge luminescence of PbSe/ZnSe MQW structure. The low energy emission peak at 1.86 eV is associated with the emission from PbSe. One can see that the $1E_s$ peak was slightly blue shifted in response with reference ZnSe film. The FWHM of the $1E_s$ peak is 0.3 eV which is less than that of $1E_s$ emission of reference ZnSe thin film.

Fig. 6.5: Micro PL spectrum of reference ZnSe thin film excited at 325 nm laser.
Fig. 6.6: Micro PL spectrum of PbSe/ZnSe MQW structure of $L_z=2.5$ nm with 5 periods. The samples were excited at 325 nm laser.

The FWHM of the peak associated with PbSe is 0.15 eV and is interesting to observe the intensity of the peak corresponds to PbSe is almost same as ZnSe emission and this is associated with such an ultra-small QW layers with the total thickness of ~12.5 nm. However, total thickness of PbSe increases with QW periods leads to decrease in intensity of PbSe emission that will be discussed in 10 and 20 periods MQW structures (Fig. 6.7 -6.11).

Fig. 6.7 shows the normalized room temperature micro PL spectra of $L_z=2.5$ nm MQW structures of 10 periods along with the PL spectrum of a reference ZnSe thin film. It can be seen that, as long as the 2.5 nm PbSe QWs formed, the PL peak becomes significantly red shifted with response to the reference ZnSe band edge luminescence. The peaks centred at 2.12 eV assigned to be the radiative recombination of electrons localized at excited state ($1E_s$) of ZnSe. Formation of 2D PbSe/ZnSe MQWs results in the appearance of sub band transition within the QW at lower energy region of 1.73 eV.
Fig. 6.7: Normalized micro PL spectrum of the PbSe/ZnSe MQW structure along with the reference ZnSe thin film. The samples were excited at 325 nm laser.

The sub band transition peak at lower energy region in PL spectrum is consistent with the linear region at 2.0 eV in the absorption spectrum of \( L_z = 2.5 \) nm (see inset of Fig. 6.3). The emission peak position and intensity corresponds to 2D layers of PbSe is less than that of 5 periods QW structures attributed to the total thickness increment of PbSe QW layer. For \( L_z = 2.5 \) nm, a shoulder in the high energy region of 2.37 eV in the \( 1E_s \) emission peak causing inhomogeneous broadening associated with interface induced new transition energy level (Rajalakshmi et al. 2012). Fig. 6.8 shows micro PL spectrum of PbSe/ZnSe MQW structure of \( L_z = 10 \) nm with 10 periods. There is no significant peak shift with respect to the reference ZnSe film for \( L_z = 10 \) nm. The observed peak position of 2.23 eV remains same as reference ZnSe thin film. However, the FWHM of the peak is 0.85 eV which is 2 times greater than reference ZnSe.
Fig. 6.8: Micro PL spectrum of PbSe/ZnSe MQW structure of $L_z=10$ nm with 10 periods. The samples were excited at 325 nm laser.

Fig. 6.9: Micro PL spectra of PbSe/ZnSe MQW structure of different $L_z$, a) 2.5, b) 5, c) 7.5 and d) 10 nm with 10 periods. The samples were excited at 532 nm laser.
Fig. 6.10: Micro PL spectrum of PbSe/ZnSe MQW structure of $L_z=2.5$ nm with 20 periods. The samples were excited at 325 nm laser.

It is expected that in the case of $L_z=10$ nm, the emission of PbSe/ZnSe MQW associated with top layer of ZnSe result broadened FWHM than $L_z=2.5$ nm. In comparison with absorption spectrum of $L_z=10$ nm, the absorption peak position of 0.9 eV (Fig. 6.3) is beyond the recorded region to observe the emission in the range less than 1 eV. Hence, PL with the excitation of 532 nm laser was performed to study the band edge luminescence of PbSe QW layer and discussed as follows. Fig. 6.9 depicts room temperature micro PL spectra of PbSe/ZnSe MQW structures of different $L_z$ with 10 periods excited at 532 nm laser. It is evident from Fig. 6.9 that all the samples clearly show two emissions at 1.16 eV (1060 nm) and 1.13 eV (1093 nm) which is assigned to be the the radiative recombination of electrons localized at excited ($1E_s$) and ground ($G_s$) states of PbSe respectively. There is no change in PL peak position in response with $L_z$, but intensity of the peak increase with decreasing $L_z$. There are two reasons for the luminescence yield arises, (i) may attributed to the peak like density of states of low dimensional system as well as the efficient carrier trapping at the interface due to large band gap and lattice mismatch and (ii) surface sates usually act as the non-radiative recombination centres. ZnSe
compensates most of the vacancies on the surface of the PbSe and non-radiative recombination sites are passivated with high QW thickness. Fig. 6.10 depicts micro PL spectrum of PbSe/ZnSe MQW structure of $L_z=2.5$ nm with 20 periods. The sample was excited using 325 nm laser at room temperature. As observed in 5 and 10 periods PbSe/ZnSe MQW structure, two PL features are observed. A well resolved PL peak at 2.2 eV was associated with band edge luminescence of ZnSe and a shoulder like emission at lower energy region of 1.9 eV was associated with the PbSe QW sub-band transition.

![Micro PL spectrum of PbSe/ZnSe MQW structure of $L_z=10$ nm with 20 periods. The samples were excited at 325 nm laser.](image)

**Fig. 6.11:** Micro PL spectrum of PbSe/ZnSe MQW structure of $L_z=10$ nm with 20 periods. The samples were excited at 325 nm laser.

PL spectrum of $L_z=10$ nm with 20 periods is shown in Fig. 6.11. The PL feature is as same as observed for $L_z=10$ nm with 10 periods while the FWHM is increased to 0.15 eV.
6.2.3. Conclusion

Micro PL studies of PbSe/ZnSe MQW structures with different $L_z$ and periods were presented. Impact of excitation source is also described on the emission from QW layer. PL spectrum of ZnSe showed a strong PL emission at 2.23 eV which was associated with radiative recombination of electrons localized at ground state. PL spectrum of $L_z=2.5$ nm with 5 periods MQW structure showed two PL resonances corresponding to $1E_s$ of ZnSe and strong emission from PbSe QW layers. As long as the 2.5 nm PbSe QWs formed in 10 periods MQW structures, the PL peak becomes significantly red shifted with response to the reference ZnSe band edge luminescence. Formation of 2D PbSe/ZnSe MQWs results sub-band transition within the QW lower energy region together with $1E_s$ emission of ZnSe. For $L_z=10$ nm, there is no emission corresponds to PbSe was observed with $1E_s$ of ZnSe. However, $L_z=10$ showed 2 times greater broad FWHM of $1E_s$ emission. Emission at MQWs with 20 periods showed the same PL features as 10 period structures. The PL features are consistent with the corresponding absorption spectrum for $L_z=2.5$ nm infer the quantum size effect of the PbSe/ZnSe MQW structures.