CHAPTER IV

4. EXPERIMENTAL DETAILS

This chapter describes experimental procedures on the growth of PbSe/ZnSe MQW structures and preparation of reference single layer PbSe and ZnSe thin films. Sample preparation for cross sectional TEM analysis also described. The chapter clearly describes the variables of the structures and post deposition thermal annealing. The details of various characterization tools used to study the PbSe/ZnSe MQW structures are clearly described.

4.1. Source materials and substrates

Source materials with good trace metal basis are important one to prepare good quality of thin films by thermal evaporation technique. A high purity PbSe in the form as an ingot and ZnSe powder were purchased from Sigma Aldrich with 99.99% trace metal basis. This compound semiconductor of PbSe and ZnSe were used as active QW layer and barrier layer, respectively. Two individual molybdenum boats (200 Å) were used to place the source materials as an evaporator to prepare the structures.

As discussed in section 3.1, thermal evaporation has been chosen with one of the reasons of less expensive and hence it is not required any particular kind of substrates like what epitaxial growth requires. In this thesis work, glass substrates were used to grow both reference and MQW structures. However, to prepare cross sectional TEM specimen, Si (1 1 1) wafer were used since cross sectional view on conducting substrates like Si is preferred.

4.2. Preparation of PbSe and ZnSe single layer thin films

Reference PbSe and ZnSe single layer thin films with different thicknesses were prepared by thermal evaporation technique to make characterization of PbSe/ZnSe MQW structures in an ordered manner. The source material of PbSe was placed in a Molybdenum boat (200 Å) with the distance of separation of the boat and substrates was 30 cm and heated with applying current at vacuum pressure
Fig. 4.1: Schematic of the dual source vacuum chamber used to Prepare PbSe/ZnSe MQW structures.

of $10^6$ torr and deposited on unheated glass substrates with different thickness. The thicknesses of the films say 50 nm to 200 nm was prepared while the thicknesses of the films were monitored using *in-situ* quartz crystal thickness monitor. A constant rate of evaporation ranging 1x3 Å/sec was maintained throughout the experiment. The procedure was repeated to prepare reference ZnSe thin films with the thickness of 100, 200 and 300 nm which is the barrier material of this research work. However, the characterization of these thin films are not categorized separately in this thesis but provided with the result of MQW structures for clear comparison. Schematic view of the vacuum chamber used to prepare reference PbSe, ZnSe and PbSe/ZnSe MQW structures are shown in Fig. 4.1.

4.3. **Growth of PbSe/ZnSe multiple quantum well structures**

A simple thermal evaporation technique was used to prepare the MQW structures on ultrasonically cleaned glass substrates and Si wafers (for TEM analysis) kept at room temperature. The source materials of PbSe and ZnSe were placed in two individual molybdenum boats and the distance between the boats and
Fig. 4.2: Schematic views of the PbSe/ZnSe MQW structures with different QW periods, a) 5, b) 10 and c) 20. The structure were grown with different QW thickness ranges from 2.5 to 10 nm.

Table 4.1: Thickness and periods variation of PbSe/ZnSe MQW structures growth.

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<thead>
<tr>
<th>Periods</th>
<th>Thickness</th>
<th>Total thickness</th>
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<tbody>
<tr>
<td></td>
<td>PbSe (QW)</td>
<td>ZnSe (Barrier)</td>
</tr>
<tr>
<td>5</td>
<td>2.5 nm</td>
<td>25 nm</td>
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<tr>
<td></td>
<td>5 nm</td>
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<td></td>
<td>7.5 nm</td>
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substrates was kept at 30 cm. Initially ZnSe was deposited on the substrate with a thickness of 100 nm to act as a buffer layer. Then a PbSe quantum well layer was deposited with a thickness of 2.5 nm followed by a 25 nm ZnSe barrier layer at a vacuum of $10^{-6}$ torr. The cycle was repeated to 5, 10 and 20 double layers of PbSe/ZnSe MQW without breaking the vacuum. The MQW structure was prepared with various PbSe quantum well layer thicknesses $L_z$ ranging from 2.5 nm to 10 nm with the increment of 2.5 nm, while the optimized barrier layer thickness was maintained as 25 nm in all the structures. The layer thicknesses were monitored and controlled using an *in-situ* quartz crystal thickness monitor. A constant rate of evaporation ranging between 1-3 Å/sec was maintained throughout the experiment. It is one of the aims of this thesis work to prepare MQW structure with good periodic structure and thickness reproducibility. Hence care was taken on quartz crystal monitor like cleaning and tooling factor with almost same level of vacuum. Source shutter was used during each and every layer deposition to prevent excess deposition of the materials that already vaporized to control the uniformity and thickness. It is noteworthy to state that path way of the vapour is important to obtain the uniform 2D layers which were controlled by evaporation rate in order to avoid isolated heap or cluster formation. The QW thickness and periods for various PbSe/ZnSe MQW structures grown are tabulated in Table 4.1

4.4. Post deposition thermal annealing

Post thermal annealing was performed in order to produce PbSe nanocrystals (NCs) within ZnSe barrier (PbSe NCs embedded in ZnSe) or PbSe nanoclusters at the interfaces of PbSe/ZnSe MQW structure. After preparation of PbSe/ZnSe MQW structures, the samples were undergone thermal annealing with different temperature and time duration. Initially the samples were annealed at 100, 250 and 300°C for about 20 minutes and 40 minutes. It is noteworthy to state that thin films from thermal evaporation technique will easily re-evaporated upon annealing. The samples annealed at 40 minutes lost the thickness by means of re-evaporation of the layers. The samples annealed at 250°C for about 20 minutes showed interesting
quantum size effect behaviour from the optical absorption spectra and hence 250°C for about 20 minutes were taken for all the quantum well structure. The formation of NCs or clusters in QW structure may arise from the following mechanism. Thermal annealing facilitates movement of constituent atom and interface reconstruction on the QW layer which leads to the formation of sphere like quantum structures.

4.5. Cross sectional TEM sample preparation

All samples investigated by cross-sectional TEM were prepared in the following way using particular care to minimize mechanical and thermal exposure of the sensitive layers. It totally involves seven steps which are summarized as follows with photographs as given in Fig. 4.3 and 4.4:

1. A first steps is cutting the sample into two equal slices with 2mm width and 4-6mm length which is shown in Fig. 4.3. Since the slices will be finally embedded in Cu tube with an inner diameter of 2.12mm. So that the cleaved sample slices must be smaller than the tube diameter. Cleaving the sample prevents damaging of the original sample surface which may occur by sawing the sample.

2. Second step is forming a sandwich stack which is shown in Fig. 4.4. The two slices of the samples are glued together. So that the film layers face each other. For gluing GATAN two component epoxy glue is used. Then annealed a sample stack in an oven at a temperature of 120°C for few minutes. A final sandwich stack consists of Si/(PbSe/ZnSe)$_{\text{MQW}}$/glue/(PbSe/ZnSe)$_{\text{MQW}}$/Si.

3. The next step is embedding the stack in a Cu tube which is shown in Fig. 4.3. Before inserting the stack in a tube, fill a droplet of epoxy glue into the tube. Then the stack has to be loaded into the tube and centre it. Then place the tube standing on the heating plate at a temperature of 120°C for few minutes.

4. Then cutting the tube into disk using diamond wire saw with the thickness of 300-400μm.
Fig. 4.3: Photographs of different steps involved to prepare the TEM samples (steps 1-3).

Fig. 4.4: a) Photograph of sliced specimen disk mounting on a support (step 4&5) and b) dimpling.
**Fig. 4.5:** a) PIPS Ion mill and b) Optical microscope images of ion-milled TEM specimen.
5. The disk are ground and polished on one side, subsequently flip over other side using rotor with running water and abrasive paper. For that the disk is to be mounted on the support using wax is shown in fig 4.4a. The disk is to be grounded down to a thickness of 80-100μm.

6. This process involves grinding and polishing the specimen disk with diamond particles using dimple grinder and is shown in fig 4.4b. In this step, the thickness of the specimen to be reduced to 80μm.

7. The final step is the ion milling process. For this process, a GATAN precision ion polishing system (PIPS) is used and is shown in fig 4.5a. In this process two Ar ion beams mill the dimple ground sample in such a way that a hole results at the desired position. The specimen is thinned in an ion-mill under persistent liquid nitrogen (LN₂) cooling until a hole has formed in the centre. At this point the edges of the hole are transparent for electrons (thickness: 10-100 nm). The ion-mill is operated at 4 kV; 1mA; and at an incident angle of the argon-ions of 13° in the double sector thinning mode.

The final hole should be as small as possible. The optical image of the sample after ion milling process is shown in fig 4.5b. Fig. 4.3-4.5 shows different steps involved to prepare cross sectional TEM specimen. Finally, the specimen was cooled for about 20 minutes. The choice of the substrate has to be selected carefully. Extremely hard substrates (e.g., sapphire) require a long grinding-process until their thickness is reduced sufficiently. Since the duration of the mechanical treatment also should be kept to a minimum, less hard substrates such as silicon are used to prepare PbSe/ZnSe MQW structures. With the above described procedures, cross-sectional TEM specimens of different QW thickness and period were prepared and used for TEM imaging.
4.6. **Structural studies**

4.6.1. **Transmission Electron Microscopy**

High-resolution transmission electron microscopy (TEM) was used extensively in the following work to study the structure of the PbSe/ZnSe MQW structures and formation of PbSe NCs or clusters upon annealing. This method characterizes the interface periodicity like uniform height, continuity of layers, crystalline structure as well as the size and distribution of the PbSe nanophase within the ZnSe barrier upon annealing. Appropriate sample preparation is key to obtaining high-resolution images (section 4.5). The specimen prepared (as described in section 4.5) was then inserted into a JEOL 2010 TEM for nanostructural imaging with an accelerating voltage of 200 kV. Selected area electron diffraction patterns are obtained in addition to real-space imaging of the specimens to enable confirmation of crystalline phases present in the nanocomposites, as well as their spatial distribution and grain structure.

4.6.2. **High resolution X-ray diffractometer**

One of the most widely used techniques for evaluating the crystallinity and structure of films and powders is X-ray diffraction. This method of analysis serves to corroborate the phase information gained from SAED. The technique in the present work allowed the evolution of film crystallinity and phase development to be monitored as a function of QW thickness, period and thermal processing. The HRXRD used in the following studies is a PANalytical X’Pert PRO ((PW 3040/60) containing a Cu Kα source with an X-ray wavelength of 1.54 Å. The run conditions consisting of a 2θ step size of 0.05° and a scanning range of 20 to 60°. A goniometer of X’celerator was used here for high resolution.

4.7. **Optical studies**

4.7.1. **UV-Vis-NIR spectrophotometer**

Optical absorbance measurements were obtained using a UV-VIS-NIR spectrophotometer (Jasco-570) in the wavelength range of 200-2500 nm. The range
of wavelengths that can be studied with this instrument ranges from 250 to 2500 nm in steps of 1 nm increments. The band gap behaviour of PbSe/ZnSe MQW structures with changes in QW thickness, QW period and thermal annealing was also examined. The fundamental absorption edge in most chalcogenide follows an exponential law. Above the exponential tail, the absorption coefficient has been reported to obey the following relation,

$$\alpha(h\gamma) = d^{-1} \ln \left( \frac{h\gamma}{A} \right)^{-1}$$

(10)

where ‘d’ is the thickness of the samples and A is the absorption of the sample.

4.7.2. Micro-Photoluminescence spectrometer

Micro-Photoluminescence of the PbSe/ZnSe MQW structures were analysed using a LabRAM HR micro PL. The sample was placed on a substrate holder and the excitation beam was focussed with the spot diameter of 1μm. The PL was performed using 325 or 532 nm continuous laser at room temperature. The power density at the sample was 200 W/cm² and PL signal is collected using CCD camera. The PL signal was processed digitally and plotted as PL intensity versus wavelength.

4.7. Raman scattering

Further structural insight was obtained by means of vibrational spectroscopy using a Jobin Yvon Horiba Lab-Ram HR800 micro-Raman spectrometer under laboratory ambient conditions. Excitation of the specimens was produced using a water-cooled argon ion laser with a wavelength of 514.12 nm laser nm as the excitation sources in order to observe specific resonances in the films. Spectra were collected at room temperature in a backscattering geometry through a 10x microscope objective producing a 100 μm diameter spot with a 30 mW intensity at the sample. An air-cooled Si-CCD array was used for detection with the overall spectrometer systems providing a wavenumber resolution of 2 cm⁻¹.