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Investigation of the quantum well width on the size effect of PbSe/ZnSe multiple quantum well structures by non-epitaxial growth

V. Arivazhagan, M. Manonmani Parvathi, S. Rajesh *

Department of Physics, Karunya University, Coimbatore 641 114, India

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ABSTRACT

PbSe/ZnSe multiple quantum well (MQW) structures were prepared by non-epitaxial growth to investigate the impact of quantum well width (L_z) on the size effect. X-ray diffraction studies revealed the evaluation of PbSe nanocrystals phase about its critical layer thickness. Well-ordered and periodic structure of the MQW was confirmed through TEM and its interface morphology of L_z = 2.5 and 10 nm were studied. The discrete linear resonances in the absorption spectra and the corresponding blue shift reflect the quantum confinement effect. The effective QW band gap energies calculated from the infinite well approximation is compared to the experimentally observed values. Shift in longitudinal optical phonon from Raman scattering indicates stress induced size effect in PbSe/ZnSe MQW structures.

1. Introduction

Low dimensional semiconductors have great scientific and technological interest in the last few decades. Among these, Lead Selenide (PbSe) and its alloy has gained a great deal of attention due its remarkable structural, optical and electrical properties between bulk and nanostructures [1–4]. Third generation quantum dot (QD) solar cell expectations such as multiple exciton generation (MEG), fast hot electron transfer is possible in PbSe QDs [5,6]. The very large excitonic Bohr radius (46 nm) and low band gap (0.27 eV) of PbSe leads to strong quantum confinement. A wide knowledge of research works have been done on the formation of PbSe QDs or nanocrystals (NCs). Mostly PbSe QDs were formed through chemical route [2,6,7], meanwhile a few reports available on PbSe NCs by physical method [8,9]. Recently, Ten Cate et al. [10] studied the active carrier multiplication of PbSe QDs solids infilled with Al_2O_3 or Al_2O_3/ZnO compared with non-filled PbSe QDs. Size and composition dependent PbSe and PbS_xSe_{1-x} alloyed quantum dots show enhanced MEG due to quantum confinement [4]. PbSe was extensively studied as core shell QDs, ternary alloys with different stoichiometric for optoelectronic applications [2,11,12]. Synthesis of PbSe with different surface morphology such as nanorods and nanoparticle thin films are also the interest of current research. Alvi and Khan [9] synthesized a-$PbSe_{100-x}Cd_x$ nanoparticle and suggested the possible application in solar cells. Ram et al. [2] reported dielectric relaxation in $Se_{80}In_{20}$ alloys with an addition of Pb, which showed anomalous dielectric response for the composition of $Se_{80}In_5Pb_{15}$ due to Pb–Se polaron formation. It has been reported that multiple quantum well (MQW), superlattices or multilayer of semiconductor materials by physical methods leads to the quantum confinement effect [13–15]. However, for preparing those structure with good stability and periodicity, molecular beam epitaxy or metal–organic chemical vapour deposition (MOCVD) are most frequently applied [10,15]. These techniques are quite expensive and, in MOCVD normally use dangerous gases. Beside this, high quality crystalline ZnSe, GaAs or sapphire substrates are necessary for the epitaxial growth. Therefore a considerable research activity has been addressed for the preparation of low-dimensional structures by non-epitaxial film growth and application of less expensive vapour deposition [14,16]. With this consideration we report PbSe/ZnSe MQW structures prepared by non-epitaxial growth of simple thermal evaporation technique. The role of quantum well thickness on the size effect of PbSe/ZnSe MQW structure with good periodicity has been reported. The study show MQWs with good interface periodicity can be prepared by non-epitaxial growth. The enhanced optical absorption of UV–NIR region was reported along with its microstructural behaviour. The findings in the study came from the characterizations using HRXRD, TEM, optical absorption spectra and Raman scattering. Using these techniques, it was possible to study the quantum size effect with varying well thickness in PbSe/ZnSe MQW structure by non-epitaxial growth, in order to confirm the quantum size effect of PbSe with spacer ZnSe barrier layers.

* Corresponding author. Tel.: +91 4222614300; fax: +91 4222614301.
E-mail address: drsrajesh@karunya.edu (S. Rajesh).

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2. Experimental details

Thermal evaporation technique was used to prepare PbSe/ZnSe MQW structure on ultrasonically cleaned glass substrates and Si wafers at room temperature. A high purity PbSe ingot and ZnSe powder (both from SigmaAldrich, 99.99%) were used as source materials. At first ZnSe was deposited on the substrates with a thickness of 100 nm to act as a buffer layer. Then a thin PbSe quantum well (QW) 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 for 20 pairs of PbSe/ZnSe MQW structure without breaking the vacuum. The MQW structure was prepared with various PbSe quantum well layer thickness (L_z) ranging from 2.5 nm to 10 nm (less than its exciton Bohr radius of 46 nm) with the increment of 2.5 nm. 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. The structural analysis of the MQW was carried out with a PANalytical X'pert PRO (PW 3040/60) high resolution X-ray diffractometer (HRXRD) using Cu Kα radiation. Transmission electron microscopy (TEM) studies were done using a Philips CM 30 TEM operating at 200 kV. Cross sectional TEM samples were prepared using a Gatan PIPS ion mill using focussed Ar^+ ion beam milling. The optical absorption spectra were recorded using a UV–VIS–NIR spectrophotometer (Jasco-570) in the wavelength range of 200–2500 nm. A Raman scattering was done using LabRAM HR 800 micro Raman spectrometer with 514.12 nm laser source.

3. Results and discussion

3.1. Structural studies

The HRXRD patterns of MQW with different L_z are shown in Fig. 1. The typical polycrystalline nature of the material was observed from the patterns. High intense and well pronounced peak observed at $2\theta = 27.35°$ is associated with (1 1 1) plane of cubic zinc blende structure of ZnSe (JCPDS: 70-0777). The secondary phases of ZnSe also observed at 45° and 54° corresponding to (2 2 0) and (3 1 1) crystallographic planes. No significant changes in angular positions and full width half maximum (FWHM) of ZnSe peaks were observed in all the samples and no diffraction corresponds to PbSe phase identified in lower L_z of 2.5 and 5 nm. Further increasing L_z virtually starts to exhibit PbSe peak at 29.20° corresponding to (2 0 0) plane and it becomes well resolved at L_z = 10 - nm. The weak intense peaks with increasing L_z at 25.6 and 41° is associated with (1 1 1) and (2 2 0) plane of cubic PbSe phase (JCPDS: 78-1903). The angular positions of these peaks are well in agreement with previous work on PbSe thin films [17]. The appearance of well resolved PbSe peaks above the critical layer thickness (~8 nm) calculated using empirical formula [18], $h_c = a_{QW}/2\varepsilon$, ($a_{QW}$ – lattice constant of the quantum well, ε – lattice mismatch) alludes the improved crystallinity of PbSe. The average crystalline size of (2 0 0) oriented PbSe and (1 1 1) oriented ZnSe was calculated using Debye Scherer's formula,

$$D = k\lambda/\beta\cos\theta \quad (1)$$

where k is the shape factor that was taken equal to 0.9, λ is the wavelength of X-ray used (1.54 Å), β is the full width half maximum (FWHM) of the peak and θ is the Bragg diffraction angle. The calculated crystalline size of PbSe and ZnSe are 6 nm and 15 nm respectively for L_z = 10 nm. The lattice constant 'a' is calculated using the relation, $1/d^2 = h^2 + k^2 + l^2/a^2$, are 5.53 Å and 6.07 Å for cubic ZnSe and PbSe respectively. The decrease in lattice constant of PbSe and increase in ZnSe from its bulk value (5.44 Å (ZnSe) and 6.12 Å (PbSe)) indicates the presence of compressive and tensile strain respectively in the layers.

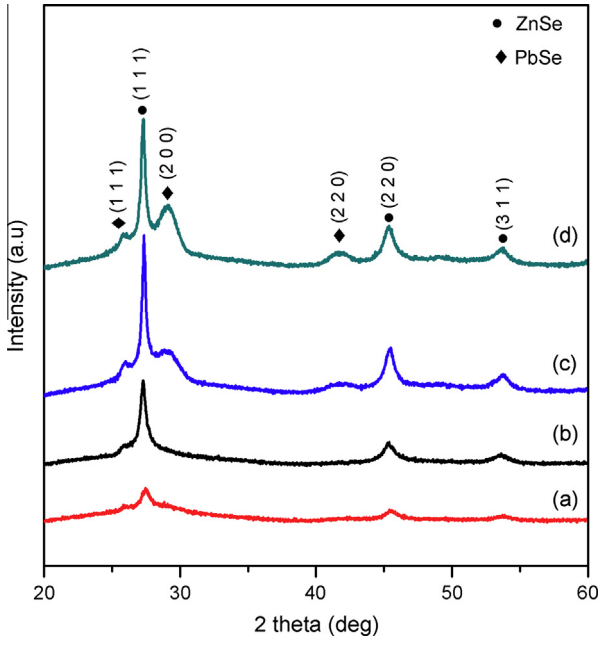

Fig. 1. HRXRD pattern of PbSe/ZnSe MQW structure with different L_z, (a) L_z = 2.5 - nm, (b) L_z = 5 nm, (c) L_z = 7.5 nm and (d) L_z = 10 nm. The symbols ● and ♦ represent orientation of the ZnSe and PbSe phases respectively.

Bright field cross sectional TEM micrographs of PbSe MQW with L_z = 2.5 and 10 nm is shown in Fig. 2. It is clearly seen that the good periodicity and well ordering of the PbSe/ZnSe MQW structure. The layers are continuous across the field of view. The spatial distribution of the nanocrystalline PbSe layers with L_z = 2.5 nm follows the pattern of the surface morphology of the barrier layer as shown in Fig. 2b. The curvature and stress at the rough surface will affect reaction rates at a solid interface because the existence of different environment at different reaction sites [19]. Hence, the structure described will be disturbed and two dimensional PbSe NCs layers were formed. Fig. 2c and d are the TEM images of PbSe/ZnSe MQW for L_z = 10 nm. It is evident that the interface of L_z = 10 nm are more smooth with uniform thickness throughout. No interface fluctuations are seen as in L_z = 2.5 nm since the QW thickness is high enough. The light and dark contrast in the images is due to density difference of both the materials. The periodicity of the PbSe and ZnSe layers in the MQW structures are retained based upon the rate of evaporation during deposition.

3.2. Absorption studies

Fig. 3 shows optical absorption spectra of 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 carrier are confined in QW layers. Reference ZnSe film shows interference fringes beyond its fundamental absorption edge whereas MQW structures show exciton resonances. The inset of Fig. 3 is an enlarged view of the lower energy region of the graph (without reference films spectra) to show the QW resonances clearly. Fig. 4 is the energy band diagram of PbSe/ZnSe MQW structure. It is obviously seen that the absorption onset exhibits progressive blue shift with decreasing L_z. The lower energy absorption features correspond to the quantized sub band energy level transition within the QW. All absorption features along with sharp absorption edge are shifted towards higher energy with decreasing L_z reflects quantum confinement effect [20,21]. An infinite well approximation method [22] was used to calculate the effective QW band gap ($E_{g\ QW}$) for 2D structure to substantiate the aforesaid statement,

$$E_{g\ QW} = E_{g\ bulk} + E_{0,e} + E_{0,h} \quad (2)$$

where $E_{0,e} = h^2/8m_e^*L_z^2$ and $E_{0,h} = h^2/8m_h^*L_z^2$. The effective masses of the electron (m_e^*) and hole (m_h^*) values are $0.097m_0$ and $0.120m_0$. L_z