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Structural and Optical Properties of Chemically Synthesised PbSe Nanorods

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Abstract

PbSe nanorods were synthesised through chemical bath deposition at room temperature (303K) and at elevated temperature 365K. XRD shows the synthesised PbSe were polycrystalline having cubic rock salt type structure. The most preferential growth direction was along (200) direction. SEM exhibits the shape and size oriented growth morphology. The optical measurements show excitonic absorption at 740nm and blue emission in the range 363nm- 397nm which are attributed to the strong quantum confinement of PbSe nanostructures.

Keywords: PbSe nanorods, chemical bath deposition, structure, quantum confinement and blue emission.

Introduction

Lead selenide is a promising IV-VI semiconductor because of its nice quantum modulated optical behaviour in the infrared range. Quantum confinement effects begin to appear at relatively large particle dimension owing to its large Bohr exciton radius (46nm). This results a strong confinement of electron-hole pair and larger optical nonlinearity[1,2]. Lead salts also exhibit multiple exciton generation and superlattice[2]. Exploiting the novel properties PbSe nanostructures are potentially employed in various opto-electronic devices such as IR detectors and sensors, near IR luminescence thermoluminescence, solar cells and chemical sensors[1-9]. Bulk PbSe has a rock salt crystal structure and is a direct band gap semiconductor with a band gap of 0.28eV. The small electron and hole masses of lead salts implies large confinement of energies that split equally between carriers. Hence the energy spacing become larger than the bulk which leads to suitable bandgap engineering in near IR and visible region.

Monodisperse PbSe nanocrystals are first reported by Murry *et al*[10] in 2001. In the following year other workers[11-13] also reported synthesis of colloidal PbSe NC. William *et al*[12] reported larger spherical PbSe NC (3-13nm) using a cheap and environmental friendly non coordiniting solvent 1-octadecene. Matt *et al*[13] described the structural, optical and electrical properties of spin casted, oleate-capped PbSe nanosrtuctures films that are treated thermally or chemically in solution of hydrazine, methaylamine, or pyridine to produce electronically coupled nanocrystals to be used for development of novel solar cells. PbSe nanostructures with a variety of shape such as starlike, nanorods, nanotubes, nanowires, nanorings, nanocubes and others are reported[1-9,14]. Recently octopod-like structures are also reported through solution route[1]. A number of studies have focussed on the chemical bath deposited films using sodium selenosulphate as Se source. Variation of deposition temperature can allow control of deposition reaction rates, solubility and convection and thus affect structural and optical properties[15-21]. Several workers Shandalov *et al*[17], Grozdanov *et al*[20], Pramanik *et al*[21] and other studied the effect of rise of growth temperature upto 80^0C where they expressed the improvement of crystallinity with increase of crystallite size and reduction of amorphous phases. However the work on growth temperature dependence of optical properties in co relation with the structural morphology is limited in PbSe nanostructures. The most important parameters in determining the shape, size and structure of PbSe nanocrystals are the concentration of the metal nanoparticles followed by the Pb:Se precursor ratio, pH, growth temperature as well as capping agents. Hence for better understanding the physical properties of PbSe nanocrystals in co relation with the growth characteristics, further more work are desirable. In this paper the effect of growth temperature on the structure as well as optical properties has been highlighted.

Material and Methods

Although there are various techniques to prepare PbSe nanostructures, chemical bath deposition offers a simple and cost-effective route for fabrication of high quality chalcogenide films. Most of the workers had done a variety of fundamental research work and thereby promoting the chemical route into an excellent synthesis technique in recent times[14-25]. In the present work PbSe nanocrystals were grown chemically as thin films on glass substrates. Initially a 0.1M sodium sulphite (Na_2SO_3) solution was mixed with a 0.1M freshly prepared Se solution under constant stirring for 6 hours to form the sodium selenosulphate (Na_2SeSO_3) solution. A clear 3% PVA (Poly Vinyl Alcohol) solution was prepared with constant stirring prior to deposition as a capping agent. Lead acetate solution (0.1M) was mixed with PVA solution where the ammonia was added to form clear dispersed metallic complex. The Na_2SeSO_3 solution was then mixed with the lead ion complex to form the final matrix solution. The reaction was carried out in an alkaline medium keeping pH at 9. Commercial glass slides were first

immersed into dilute HCl (hydrochloric acid) overnight which were washed throughly with constant rubbing by soft tissue papers. Those glass substrates were then put into freshly prepared chromic acid for a few minutes for further fine cleaning. After that the substrates were washed under running water and put into dilute NaOH (sodium hydroxide) solution to neutralize any acid tracing on the glasses. Finally the substrates were rinsed with distilled water several times and dried. The The cleaned glass substrates were dipped into the final matrix solution to cast thin film of PbSe. The deposition time at room temperature was around 24 hours. It was observed that the reaction rate was very slow at room temperature. Rising the temperature upto 365K the reaction rate become fast and hence the substrates was dipped only for 10 minutes to cast thin films. The thin films were used for the X-ray diffraction (XRD) while the filtrated brownish colour solution for Scanning Electron Microscopy (SEM) as well as UV-VIS and Photoluminescence (PL) spectroscopy.

Results and Discussion

Structural characterization: The X-ray diffractograms were taken using a Philip's X-Ray diffractometer (XPERT PRO) using *Cu Kα (l= 1.5406Å)* radiation. The (*2q*) scanning was done in the range 10^0-80^0. The XRD pattern of a typical lead selenide nanostructure film grown at room temperature (303K) is shown in figure-1. The peak position shows that it possesses polycrystalline having cubic rock salt structure. The peaks are shown at (111), (200), (220), (311), (222) and (400) of cubic structure with lattice parameter *a*= 6.131Å which is consistent with the standard value *a*= 6.105Å (JCPDS card No. 78-1902). Other sharp reflections at 19.85^0 are corresponding to that of PVA which exhibits its higher order of abundance in the sample. Polymar having higher monomer may show its direct existence in the prepared materials[1,7].

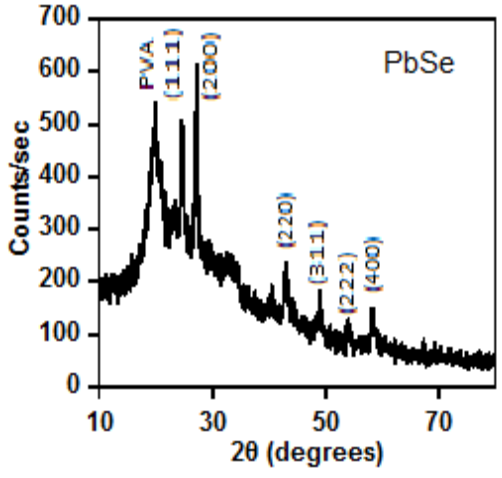

Figure-1
XRD trac of a typical PbSe thin film deposited at 303K

The structural morphology was also studied by SEM images. The low magnification SEM pictures exhibit randomly oriented small pieces of nanorods for PbSe deposited at room temperature as depicted in figure-2a and 2b. A close look however shows that those small nanorods were distributed inside some pockets of PVA ligands. A single rod measured a diameter of about 0.1 µm having average length of 0.5 µm for room temperature grown films. But the nanorods were found to change their shape oriented structural morphology on increase of deposition temperature. The aspect ratio of nanorods were changed significantly as the diameter of most of the rods become smaller and the length become longer with the rise of deposition temperature upto 365K (figure-2c and 2d) in the work. The rods were found to transform into pin like structures. It is also seen that those randomly oriented pins or rods have a tendency to form a star like microstructures following anisotropic growth mechanism. Some of nanorods which already formed bigger structure on agglomeration, changes into glazed nanosheets like structure on rise of temperature. A quite bigger microsheet is seen for PbSe deposited at 365K. Similar nanorods, nanosheets and star like particle structures of PbSe are also reported by other workers where they show the change of shape morphology on variation of growth temperature[1-8, 12-14].

Anisotropic growth of semiconductors has been achieved using multiple surfactants exploiting inherent differences of different growth rates between different crystal directions. Usually the shape of fcc nanocrystal is determined by the ratio of growth rate along <100> direction to that of <111> direction[1,4,7]. Several workers explained on the basis of XRD and HRTEM results that the (200) lattice plane is always oriented perpendicular to the growth direction along <100> in both simple rods and branched structures[4,14,24]. In the present work the XRD shows the most preferred orientation along (200) of the cubic rock salt structure of PbSe. Therefore it is expected that the nanorods grows along <100> direction during synthesis. The dimension and structure of PbSe nanocrystals changes signnificantly corresponding to bath temperature, growth time and precursor concentration. Increasing bath temperature, reaction time and molar concentration of precursor solution the growth of nanorods along axial and radial direction can be increased. The overall rod morphology however also dependent on the acetate and the polymar capping agent. PVA is expected to play a key role not only in bringing the quantum confinement but also the stabilization of PbSe nanorods.

Optical characterization: The UV-VIS spectroscopy was used to study the absorption spectra in the range from 350nm-900nm. The spectra exhibit a prime absorption at 740nm both irrespective of growth temperature at 303K and 365K as shown in figure- 3. It can be attributed to the excitonic absorption which shows a considerable blue shift because of strong confinement of PbSe nanocrystal.

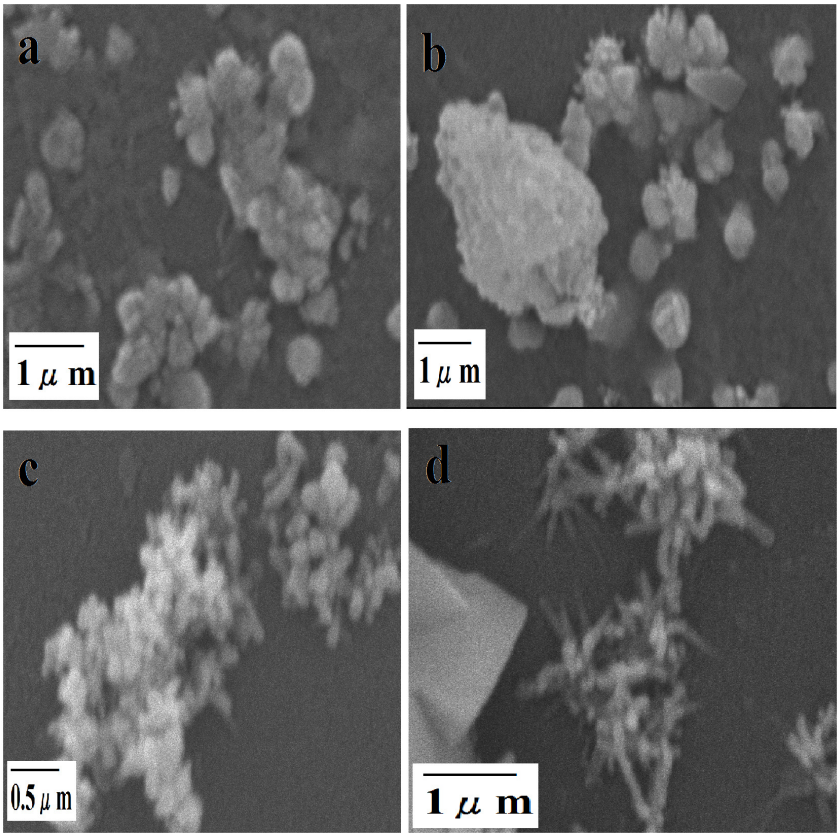

Figure-2
SEM images of PbSe nanorods synthesised at 303K (a,b) and 365K (c,d)

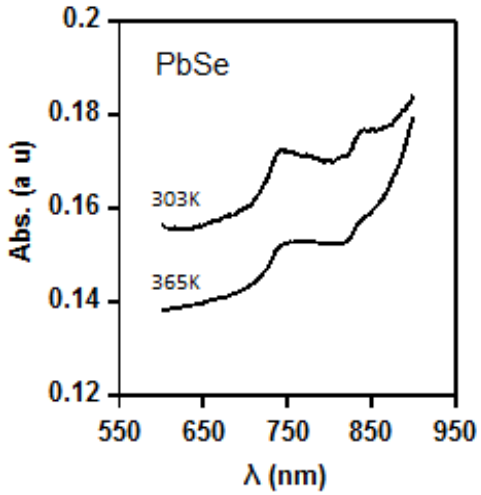

Figure-3
UV-VIS absorption spectra of PbSe nanorods

The quantum confined -states in conduction and valence band can be conceptualized in an envelope function defined by a particle in a box of size and shape of the nanocrystals. The size dependent that quantum-confined state becomes descrete and equally spaced in the respective bands. The electronic interband transitions are possible between the electrons and holes for the perfectly symmetric bands in bulk as well as for the quantum confined states for the same quantum numbers[3,6]. The broad absorption peak reveals the transition in quantum regime is much broader than bulk. This broader transtion may be due to mainly inhomogeneous boardening effect. The inhomogeneous boardening effects arise owing to the distribution of different size and aspect ratios of nanorods which can translate into a small distribution of wavelengths rather than perfoming as a single discrete transition[24]. As self assembled PbSe nanocrystals are generally small relative to that of bulk exciton radius, the quantization energies of electrons and holes are large compare to columb binding energy. The band gap estimated as 1.7eV which is enhanced significantly over that of bulk. Several other workers reported the large blue shift of excitonic absorption of chemically bath deposited PbSe nanostructures[3,4,6,8,24]. The absorption spectra also shows a broad hump around at 840 nm which is attributed to defect states[8]. On increasing the bath temperature upto 365K the defects are found to be considerably reduced.

The PL spectroscopy of synthesised PbSe nanorods shows non symmetrical blue emisssions which is depicted in figure-4. It shows two distinct peaks at 368 nm and 397 nm superimposed to give average larger full with at half maximum (FWHM) for the nanorods synthesised at room temperature (303K). This type

of non symmetrical blue emission at 359nm was reported by Cheng *et al* for PbSe nanowires[8] . The photoluminescence also supports the strong quantum-confined effect of the synthesised nanorods. Both the PL peaks are found to further blue shifted to 363 nm and 394 nm along with the enhancement of their intensities on increasing the bath temperature (365K). The improvement in PL characteristics is attributed to the small diameter and larger length of the nanorods at high growth temperature[24]. Straight nanorods have potential in fabrication of field effect transistor (FET) for possible use in complementary logic circuits.

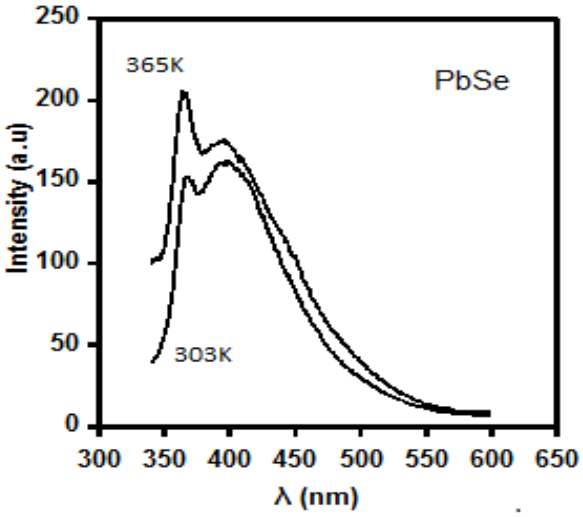

Figure-4
PL spectra of PbSe nanorods

Conclusion

Chemically synthesised PbSe nanorods show a strong quantum confinement in PVA matrix. XRD shows the polycrystalline nature of PbSe having cubic rock salt type structure. It shows the most preferred orientation for growth mechanism is along (200) direction. The SEM images show the short rod type structural morphology at room temperature (303K). The diameter of most of the rods become smaller and the length become longer with the rise of deposition temperature upto 365K. It is also seen that randomly oriented rods have a tendency to form a star like as well as glazed sheet type bigger microstructures following anisotropic growth mechanism. The absorption spectra exhibit a prime absorption at 740nm irrespective of growth temperature which can be attributed to the excitonic transition. The PL spectroscopy shows a non symmetrical blue emisssion at 368 nm and 397 nm for room temperature grown PbSe which are further shifted to 363 nm and 394 nm along with the enhancement of their intensities on increasing the bath temperature. The optical observations clearly exhibit the considerable blue shifts and threby confirm the strong confinement of PbSe nanocrystal. PVA is expected to play a key role for bringing the quantum confinement amongs PbSe nanorods with the necessery stabilization. Hence this approach can be employed for the thermodynamically and kinetically controlled synthesis of shape and size oriented PbSe nanostructures.

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