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Quantum size effect on the layer by layer assembly of PbTe–InSe multilayer nanocomposite structures

M. Manonmani Parvathi [a], V. Arivazhagan [a, 1], S. Rajesh [b, *]

[a] Department of Physics, Karunya University, Coimbatore 641 114, India
[b] Department of Nanoscience and Technology, Karunya University, Coimbatore 641 114, India

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ABSTRACT

PbTe–InSe multilayer nanocomposite structures were prepared by thermal evaporation method using layer by layer assembly with different PbTe nanocrystal (NCs) layer thicknesses ranges from 5 to 20 nm. Cross sectional transmission electron microscopy images divulge the formation of PbTe NCs embedded within InSe matrix as an ordered PbTe–InSe multilayer structure. X-ray and electron beam diffractions from the multilayer structure exhibit eminent peak at (2 0 0) plane analogous to face-centred cubic PbTe. The absorption onset significantly blue shifted as long as 3 nm PbTe NCs were embedded in InSe matrix. The observed band gap is correlated with theoretically predicted effective band gap of three dimensionally confined PbTe NCs which confirm size dependent quantum confinement effect. PL spectra show dominant single emission at 1.6 eV corresponding to the band edge emission of PbTe NCs. The prospects to use this structure in p-i-n junction quantum dot solar cells are discussed.

1. Introduction

Semiconductor nanocrystals (NCs) have paid enormous deal of attention by many researchers due to their potential application in thin film optoelectronics such as solar cells [1], photodetecters [2] and light emitting devices [3] and thermoelectric applications [4]. The metal chalcogenide NCs have attracted significant attention due to their potential application in solar energy conversion and storage which are the most essential challenges to be addressed to meet the world rising demand for energy in future [5]. Amid many other metal chalcogenide NCs system, PbTe possesses unique features of size tuneable absorption and photoluminescence over a wide range covering the near infrared region to visible region. One of the next generation solar cell intentions for high conversion efficiency is based on multiple exciton generation and fast hot electron transfer. PbTe has been identified as a promising material for this aforementioned effect [6,7]. Consequential progress has been made by tuning the optical properties of NCs due to quantum size effect as well as in preparation of NCs to use in photovoltaics [8,9]. PbTe quantum wells (QWs) and NCs or quantum dots (QDs) prepared by solution methods (such as colloidal and self-assembled method) and their optical properties and device applications have been extensively explored [10–13]. In most of the studies, PbTe NCs are obtained by solution methods [13,14]. however, chemically synthesized NCs typically capped with long tail organic ligands cannot be directly implemented in electronic circuits due to weak inter-particle coupling which are momentous limits for device applications [15]. To conquer these problems, physical way of multilayer approach using layer by layer deposition process is preferred. Meantime, PbTe NCs prepared by multilayer approach using physical method such as molecular beam epitaxy [16] and thermal evaporation [17] are less studied compared to other Lead chalcogenides. Thermal evaporation is a simple, cost effective and versatile method to form complex nanocomposite structures with fine control over thickness through alternate layer by layer deposition.

In this work, we report the investigation of the PbTe NCs layer thickness on the size effect in multilayer assembly of PbTe–InSe nanocomposite structures for solar cell applications. There is a distinguished interest in PbTe due to large exciton Bohr radius ($a_B = 46$ nm) and tunable band gap from infra-red to visible region which are all together make this as robust aspirant material for use in solar cells [18]. Besides, there is an evolving interest in using two dimensional (2D) InSe thin film because of its optical band gap energy (1.3 eV at room temperature) in visible region [19]. So it is

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[*] Corresponding author.
E-mail address: drsrajesh@karunya.edu (S. Rajesh).
[1] Present address: Department of Physics and Technology, University of Bergen, Allégaten 55, 5007 Bergen, Norway.

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foreseen that combining both InSe and PbTe will lead to absorb the energy from both visible (InSe) and NIR (PbTe) region with carrier multiplication. The PbTe–InSe multilayer structure have been studied along with buffer and capping layer of the same matrix material which can be recouped with p-n type semiconductor when it is fabricated as p-i-n junction solar cells (i-QDs region). The primary contributions of quantum confined PbTe NCs phase within amorphous InSe matrix have been proclaimed in this paper.

2. Experimental details

Simple thermal evaporation technique was used to prepare layered and uniformly distributed PbTe NCs within the amorphous InSe thin film matrix using layer by layer deposition approach. The samples were grown on both ultrasonically cleaned glass substrates and on Si wafer (for TEM analysis) kept at ambient temperature. A high purity PbTe (Alfa Aesar 99.99%) in the form of an ingot and InSe metal powder (Sigma Aldrich, 99.99%) were placed in two individual molybdenum boats. The distance between the boats and substrates was kept at 30 cm. The chamber was evacuated with a vacuum of 10^{-6} torr. The structures were prepared by alternate deposition of PbTe and InSe layers. Initially InSe was deposited on the substrate with a thickness of 100 nm to act as a buffer layer. The NCs layer of 3 nm thick PbTe were deposited followed by 10 nm thick InSe matrix layer to form PbTe–InSe nanocomposite structures. The cycle was repeated to 5 double layers of PbTe–InSe multilayer without breaking the vacuum. The structure was prepared with various PbTe NCs layer thicknesses (L_w) ranging from 3 nm to 20 nm, whereas the optimized InSe matrix layer thickness (L_b) was fixed as 10 nm in all the structures. In all the PbTe–InSe structures, 50 nm thick InSe capping layer were deposited to avoid the damage of the NCs arrays. The layer thicknesses were monitored and controlled using an *in-situ* quartz crystal thickness monitor. A constant rate of evaporation ranging between 1 and 3 Å/s was maintained throughout the experiment.

Structural analysis of the PbTe–InSe multilayer structures was carried out with a PANalyticalX'pert PRO (PW 3040/60) high resolution X-ray diffractometer (HRXRD) using Cu Kα radiation ($\lambda = 1.54$ Å) with 2θ ranging between 20 and 60°. To confirm the PbTe NCs layers formation with uniform distribution and thicknesses, cross sectional TEM studies were done using a JEOL 2010F TEM operating at 200 kV. Cross sectional TEM samples were prepared using a Gatan PIPS ion mill with a focussed Ar^+ ion beam [20]. Atomic force microscopic (AFM) analysis on the formation of PbTe NCs at the interfaces was analysed using A100-AFM (A.P.E. Research). Optical absorption spectra were recorded using a UV-VIS-NIR spectrophotometer (Jasco-570UV/VIS/NIR) in the wavelength range of 200–2500 nm. Room temperature photoluminescence (PL) analysis was carried out using a Photoluminescence spectroscopy with the excitation wavelengths of 500 nm at room temperature.

3. Results and discussion

Fig. 1 shows cross-sectional TEM images of the PbTe–InSe multilayers with 3 nm (Fig. 1a) and 10 nm (Fig. 1b) thick PbTe NCs layers. It apparently shows that PbTe NCs are isolated (black spots) and the layers are sandwiched by the InSe matrix layer. The differences in contrasts are due to density of the individual material (dark-PbTe and light-InSe). It is obvious from TEM that 3 nm thin PbTe NCs layer consists of sparse density of PbTe NCs with the diameter of >5 nm and height of ~3 nm (growth direction) embedded in amorphous InSe matrix layer. The 10 nm thick PbTe–InSe structure consists of defined PbTe NCs with the size of 5 nm which consistent with crystalline size obtained from XRD pattern. The thin layers of PbTe are deposited on the rough surface of the matrix layer underneath. Hence, one can expect that PbTe layer in the multilayer PbTe–InSe nanocomposite structure described will be disrupted and nanosized region will be formed. Such a uniformly distributed PbTe NCs embedded in amorphous InSe matrix by thermal evaporation techniques are quite alluring for the next generation optoelectronics such as p-i-n junction quantum dot/quantum well solar cells. Inset of Fig. 1b shows the selected area electron diffraction (SAED) pattern of PbTe–InSe composite structure for $L_w = 5$ nm and $L_b = 10$ nm. SAED consists of arc diffraction rings corresponding to PbTe and exhibit multi-crystalline nature of the sample. Also weaker reflections from the PbTe crystallites can be seen in higher order ring. However, no diffraction corresponds to InSe observed indicates the amorphous nature of InSe. The SAED pattern matches with the standard XRD pattern confirm the formation of PbTe NCs with preferred orientation and denoted with (h k l) accordingly.

Fig. 2 shows the 2D and 3D AFM images of 20 nm thick PbTe NCs single layer on amorphous InSe matrix. It can be clearly seen from Fig. 2a that PbTe NCs are spread on the surface of the InSe matrix. The surface roughness from the 3D view indicates the PbTe NCs height (20 nm) on the InSe matrix is well in agreement with the experimental condition. These PbTe NCs can be confined three dimensionally when capping with InSe matrix and multilayer assembly. It is noteworthy to state that 10 nm InSe may not completely cover the 20 nm thick PbTe NCs layer in the multilayer structure. Nevertheless, the surface roughness of InSe will lead to PbTe NCs to be partially isolated and partially in contact with each other. Top and bottom layers are thick enough to completely cover the 20 nm thick PbTe NCs layer. The EDAX chemical characterization spectra of PbTe–InSe multilayer nanocomposites samples are shown in Fig. 3 with 5 nm thick PbTe (Fig. 3a) and 20 nm thick PbTe (3b) layers. Pb, In, Te and Se peaks are only present in the system. No other elemental composition are identified shows the purity of the structure. It can be clearly seen from the spectra that a significant rise of the peak intensity corresponding to 'Pb and Te' was observed with increasing PbTe NCs layers thickness.

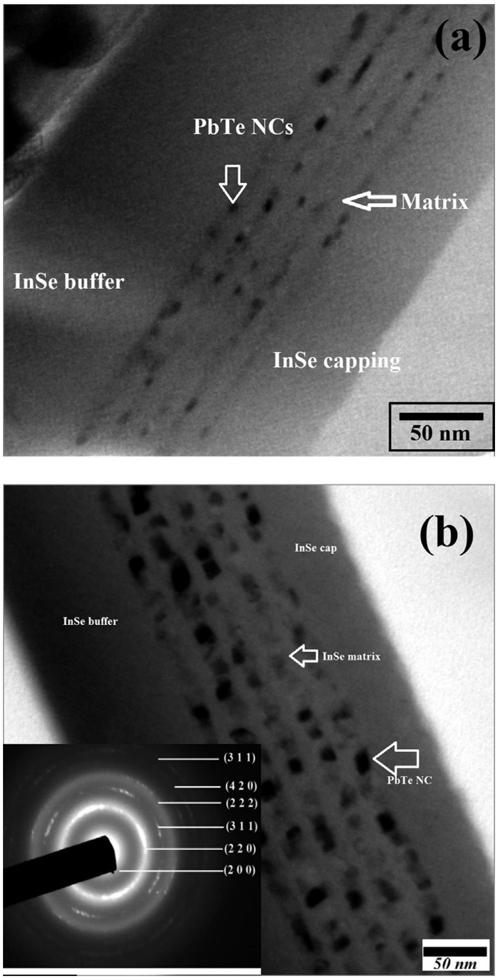

Fig. 1. Bright field cross-sectional TEM images of PbTe–InSe multilayer nanocomposites, a) 3 nm thick PbTe NCs layers and b) 10 nm thick PbTe NCs layers. Fig. 1b (inset), SAED of PbTe–InSe composite for $L_w = 5$ nm. The positions of the ring indexes to the rock salt cubic PbTe.