Vacuum 99 (2014) 95–98

Contents lists available at SciVerse ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Rapid communication

Complementary NIR absorption of ZnSe induced by multiple PbSe submonolayers by vacuum deposition technique

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

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

ARTICLE INFO

Article history:
Received 6 April 2013
Received in revised form
24 April 2013
Accepted 3 May 2013

Keywords:
ZnSe–PbSe
UV–NIR absorption
NIR emission
TEM
Raman scattering

ABSTRACT

The paper reports the possibilities to utilize the full solar spectrum (UV–NIR) by combining two different materials which have wide transparency over visible and NIR region. Simple vacuum deposition was preferred to produce ZnSe thin films with multiple 2D PbSe submonolayers (ML). Cross sectional TEM image proves the PbSe ML are well in order and has good periodicity at the interfaces of ZnSe layers which exactly matches with SAXS profile. Optical absorption of ZnSe shows the absorption in visible region while insertion of PbSe ML lead to enhancement of absorption in NIR region. A Photoluminescence spectrum of ZnSe–PbSe reveals the emission at NIR region which supports the absorption studies. In addition, Raman scattering was performed to study the presence of strain in the ZnSe layers.

Continuous tuning of the structural and optical behaviour of a compound semiconductor system is facilitated by the development of nanostructured materials. Zinc Selenide (ZnSe) is a promising II–VI semiconductor material for wide range of application in optoelectronic devices such as blue-green light emitting diodes, lasers, non-linear optical crystals and thin film solar cells [1–3]. It has a large band gap of 2.7 eV, exciton binding energy of 21 meV, small Bohr radius of 4.5 nm and is transparent to visible spectrum. Several research works have been reported on the preparation of ZnSe thin films using various techniques [1,2,4–7]. Similarly several materials have been doped with ZnSe to improve its electrical, optical, structural and recently magnetic properties. A few heterostructure and superlattice based ZnSe reports available with GaAs, SnO_2, CdSe, Si, ZnS materials to enhance its optical behaviour [8,9]. However, in all these work ZnSe used to behave more active only in the visible region. Recently, ZnSe based ternary alloys and compounds are of great interest as a solar cell absorbing layer which efficiently covers visible region to enhance the conversion efficiency. It is well known for last few decades that the research on PbSe quantum dots are paid great deal of attention because of its possibility to create as much as seven excitons from single photon of absorbed sun light [10,11]. However, optical absorption of PbSe quantum dots can be tuned in NIR region and absorption coefficient in visible region is very less. Recent solar cells research focuses on utilizing the full solar spectrum (visible-near infrared (NIR)), carrier multiplication and fast hot electron transport [3,10,12]. Yun D.Q et al. [3] reported polymer ZnSe and PbSe nanocrystal hybrid photovoltaic solar cells to tune the absorption of ZnSe in NIR region. Abe [13] has reported that PbSe–ZnSe composite enhance the optical absorption in desirable range for solar cell application. This paper reports the enhanced absorption of ZnSe at NIR region by introducing PbSe submonolayers (ML) at the interfaces. The nature of ZnSe will absorb the energy in visible region and quantum confined PbSe ML will give complementary NIR absorption to ZnSe towards full solar spectrum utilization. In addition to this, size dependent properties of ZnSe–PbSe stacks are also discussed to substantiate the complementary absorption.

A vacuum deposition technique was used to prepare ZnSe–PbSe compound thin films on ultrasonically cleaned glass substrates and on Si wafer (for TEM analysis) kept at room temperature. A high purity PbSe ingot and ZnSe powder (both from Sigma Aldrich, 99.99%) were placed in two individual molybdenum boats. Initially ZnSe was deposited on the substrate with a thickness of 100 nm. Then a PbSe ML was deposited with a thickness of 5 nm (8 times less than its Bohr radius) followed by a 25 nm ZnSe layer at a vacuum of 10^{-6} torr. The cycle was repeated for 10 such pairs of PbSe–ZnSe layers without breaking the vacuum. The layer thicknesses were monitored and controlled using an *in-situ* quartz crystal thickness monitor. The structural analysis was carried out using PANalytical (PW3040/60) high resolution X-ray diffractometer (HRXRD) using Cu-$K\alpha$ radiation with the range of 2θ between 20 and 60° and Small angle X-ray scattering (SAXS) was done using

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* Corresponding author. Tel.: +91 (0)4222614300; fax: +91 (0)422261430.
E-mail address: drsrajesh@karunya.edu (S. Rajesh).

0042-207X/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.vacuum.2013.05.001

(PW3050/60) with the angles of 0.5–5°. The cross sectional TEM image was taken by JEOL 2010F Transmission electron microscopy operating at 200 kV in bright field mode. Cross sectional TEM sample was prepared using a Gatan PIPS ion mill using focussed Ar^+ ion beam milling [14]. The optical absorption spectra were recorded using a UV–VIS–NIR spectrophotometer (Jasco-570) in the wavelength range of 200–2500 nm. Room temperature Photoluminescence analysis was carried out with a photoluminescence (PL) setup using 325 nm and 532 nm continuous laser with the beam spot of 1 μm. Raman scattering was done using LabRAM HR 800 micro Raman spectrometer with 514.12 nm laser source.

Fig. 1 shows the bright field cross sectional TEM image of ZnSe thin films with 5 nm thick multiple 2D PbSe ML. As observed in Fig. 1, the sample composes of a 25 nm thick layer of ZnSe and 5 nm thin PbSe ML. A good periodicity and ordering of the layered ZnSe–PbSe structure can be seen in the TEM image. In the structure, a 2D PbSe sub mono layer formation is evident through the characteristic dark contrast of the PbSe and lighter contrast of the ZnSe layers. The thickness of the PbSe and ZnSe is consistent throughout as predicted based upon the rate of evaporation during deposition.

Fig. 2 shows HRXRD pattern of ZnSe–PbSe thin films and inset in the figure shows the SAXS profile of the structure. The typical polycrystalline nature of the material was observed from the pattern. 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° corresponds to (2 2 0) and (3 1 1) crystallographic planes. The week intense peak at $2\theta = 29.2°$ and 41.1° is assigned to be the crystallographic phases of cubic PbSe [15] corresponds to (2 0 0) and (2 2 0) reflections respectively. The average crystalline size of ZnSe was calculated using Debye Scherer's formula, $D = 0.9\lambda/\beta\cos\theta$, which estimated as 15 nm. The lattice constant 'a' for cubic ZnSe is calculated using the relation, $1/d^2 = h^2 + k^2 + l^2/a^2$, is 5.53 A°. The periodic arrangement of PbSe ML at ZnSe interfaces were studied by SAXS shown in the inset of Fig. 2. The strong and sharp 1st and 2nd order diffraction maxima with satellites suggest that the ZnSe–PbSe has well-defined periodicity with smooth and abrupt interfaces as revealed in TEM. The Bragg's reflection at lower angle ($2\theta = 0.5–2°$) indicates the formation of the superlattice (SL) structure [16] of the system. The existence of the second order satellite peaks at higher angles is due to crystalline nature of the layers along with abrupt interface.

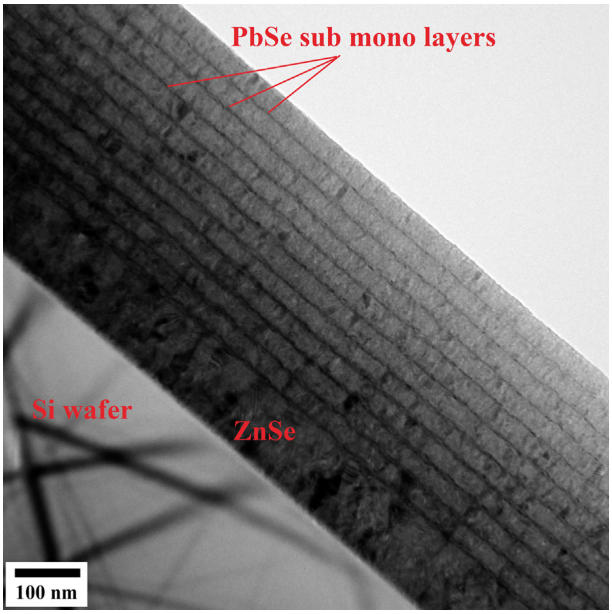

Fig. 1. Bright field cross sectional TEM image of ZnSe with 2D multiple PbSe ML.

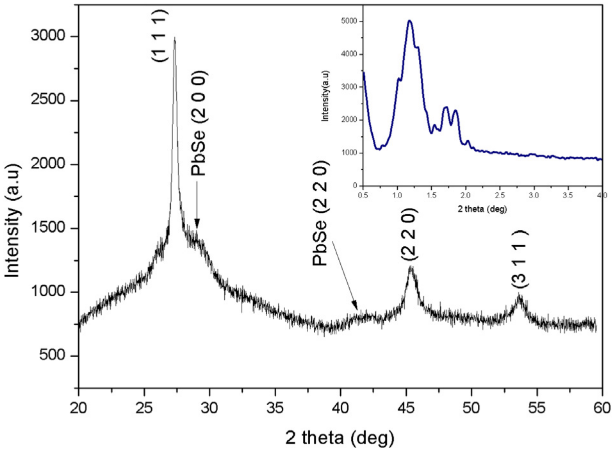

Fig. 2. HRXRD pattern of ZnSe with PbSe ML. Inset shows SAXS profile of the structure.

Fig. 3 shows the optical absorption spectra of ZnSe–PbSe film along with reference ZnSe (300 nm thick) film as a function of wavelength. The inset of Fig. 3 is an enlarged view of the lower energy region of the spectrum. The absorption onset of ZnSe is 500 nm (2.5 eV) which is widely reported band gap value of the material [1,2,4]. It is noted that the PbSe ML were stacked in the ZnSe film is significantly red shifted in response with reference ZnSe. It also exhibits two absorption feature in NIR region at 1.5 and 1 eV. It is noteworthy to state that the ZnSe film shows only the absorption tail within the UV region and no absorption takes places in NIR region (interference only). So that the absorption feature at NIR region is speculated from PbSe ML. Obviously further broadening of the spectral range from UV to NIR is obtained by inserting PbSe ML. It is one of the challenges that solar cell researchers are focussing to enhance the absorption region towards utilizing full solar spectrum (UV–NIR). Hence it is expected that stacking of PbSe ML at the interfaces of ZnSe may full fill the requirements. The lower energy features correspond to the quantized sub band energy level transition in the PbSe ML. The effective PbSe ML band gap (E_g

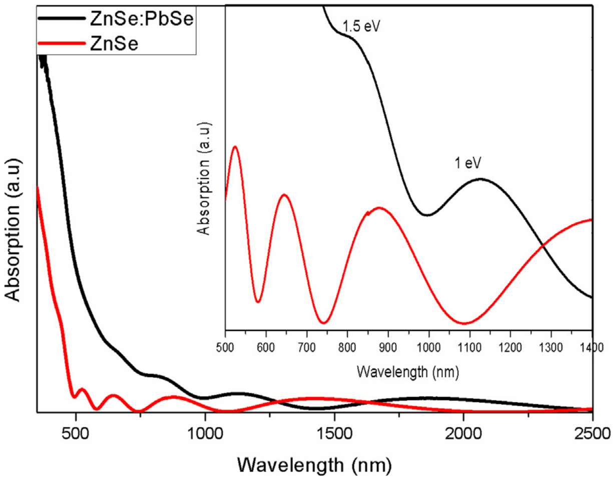

Fig. 3. Optical absorption spectra of ZnSe and ZnSe–PbSe ML. Inset shows an enlarged view of the NIR region absorption.