Compatibility and optoelectronic of ZnSe nano crystalline thin film

Taj Muhammad Khan[a)†] and Tayyaba BiBi[b)]

[a)] *National Institute of Laser and Optronics (NILOP), P.O. Nilore* 45650, *Islamabad, Pakistan*

[b)] *Department of Chemistry, Peshawar University, P.O. Peshawar* 45000, *Pakistan*

(Received 26 August 2011; revised manuscript received 12 June 2012)

We report the room temperature synthesis of zinc selenide (ZnSe) nano crystalline thin film on quartz by using a relatively simple and low cost closed space sublimation process (CSSP). The compatibility of the prepared thin films for optoelectronic applications was assessed by X-ray diffraction (XRD), atomic force microscope (AFM), scanning electron microscope (SEM), Raman spectroscopy, photoluminescence, and Fourier transform infrared spectroscopy (FT-IR). The XRD confirmed that the films were polycrystalline with the preferential orientation along the (111) plane corresponding to the cubic phase ($2\theta = 27.28^\circ$). The AFM indicated that the ZnSe film presented a smooth and compact morphology with RMS roughness 19.86 nm. The longitudinal optical phonon modes were observed at 247 cm^{-1} and 490 cm^{-1} attributed to the cubic structured ZnSe. The Zn–Se stretching band was confirmed by the FT-IR. The microstructure and compositional analysis was made with the SEM. The grain size, dislocation density, and strain calculated were co-related. All these properties manifested a good quality, high stability, finely adhesive, and closely packed structured ZnSe thin film for optoelectronic applications.

Keywords: thin film, Raman spectroscopy

PACS: 73.61.Ga, 74.25.nd, 78.30.Fs **DOI:** 10.1088/1674-1056/21/9/097303

1. Introduction

1.1. Research background

Thin films of group II–VI semiconductor compounds have attracted considerable attention due to their novel physical properties.[1,2] As a wide band-gap material, ZnSe is a talented candidate showing compatibility for optoelectronic devices based on the thin-film technology.[2,3] The substantial interest over the years owing to their wide range of applications in various optoelectronic applications and current developments go hand-in-hand with the explosion of scientific and technological breakthroughs in microelectronics, optics, and nanotechnology.[4−6] ZnSe is the most popular material for infrared applications because of its high refractive index (2.417–2.385 at 8–13 μm), low dispersion rate at infrared (IR) wavelengths, and towering transmission band from 0.60 μm to 20 μm. ZnSe is a competitive material compared to the other thin film materials owing its compatibility.[7]

Thin films of this material can be deposited by using a variety of methods, including pulsed laser ablation, electron beam deposition, magnetron sputtering, and atomic layer deposition.[8−10] While the closed space sublimation process (CSSP), which offers many advantages compared to the other sophisticated techniques, like reproducibility, simple mechanism, high deposition rate, and economically viability, is one of the fast synthesis methods to produce high quality thin films of large scale. Moreover, the co-evaporation of materials, easy substrate loading, and high deposition rate are its additional advantages. Nevertheless, thin films synthesized at higher temperature have been studied and investigated over the years including ZnSe; however, achieving high quality thin films at room temperature is rather challenging.

1.2. Research purposes

The basic aim of this research work is to present the room temperature (RT) synthesis of ZnSe thin film using a relatively simple and low cost traditional CSSP technique. The physical properties obtained are similar to that reported for higher temperatures. The compatibility of the room temperature ZnSe thin films for optoelectronic applications is investigated by using the diagnostic techniques, X-ray diffraction (XRD),

†Corresponding author. E-mail: tajakashne@gmail.com

© 2012 Chinese Physical Society and IOP Publishing Ltd

atomic force microscopy (AFM), Raman spectroscopy, Fourier transform infrared spectroscopy (FT-IR), photoluminescence (PL), and scanning electron microscope (SEM). The research findings for the room temperature thin film are reasonably good to contribute to the room temperature thin film technology.

2. Experimental details

2.1. Material and methods

Zinc selenide thin films were prepared on quartz substrates by using the CSSP technique at room temperature. The step-by-step CSSP method was adopted, in which the substrates were rotated at a rate of 8 turn/min spending only 1/12 part time of each turn over the ZnSe source to produce thin films with smooth interfaces and good periodicities. The growth was carried out in a high vacuum system (Fig. 1) at the National Institute of Laser and Optronics (NILOP). Prior to deposition, the substrates were properly cleaned by high voltage glow discharge. For final cleaning, they were heated to 150 °C and rinsed with distilled water. The shutter was kept in front of the source till the evaporation rate and the pressure attained their constant values. It is utmost important for producing high quality thin films with the best mechanical and optical properties.



Fig. 1. (colour online) CSSP system for ZnSe thin film growth.

The chemicals used for the deposition of ZnSe thin films were of analytical reagent grade (99.999% purity, E-Merck). The experimental details are summarized in Table 1.

Table 1. Growth parameters for ZnSe thin films using CSSP.

Target (material)	ZnSe (99.999%)
Substrate	Quartz
Substrate temperature	300 ± 2 K (RT)
Substrate to target distance	25 cm
Current	150–200 A
Deposition time	15 min
Deposition rate	0.1–1.2 nm $\cdot$ s^{-1}
Vacuum	6.0×10^{-6} torr

2.2. Diagnostic techniques

The X-ray diffraction (XRD) was carried out with a Bruker D8 discover diffractometer equipped with the Cu $K\alpha$ radiation ($\lambda = 1.54186$ Å) as the X-ray source. The incident X-ray beam was collimated by a 1° divergence slit. The diffracted beam was collimated by a 0.2-mm receiving slit and a curved graphite monochromator, which diffracted the beam in a proportional counter. The measurements consisted of $\theta/2\theta$ scans performed in the 2θ angular range from 20° to 90° with an angular scan step of 0.02° and 4 s counting time. For all the diffractograms, the X-ray source was operated at 40 kV and 40 mA.

The surface morphology of the film was investigated by atomic force microscope (Quesant Universal SPM, Ambios Technology, USA) in contact. An AFM tip of silicon nitride with an approximate curvature radius of 10 nm was used.

A Fourier transform infrared interferometer (PMQ II, Carl Zeiss) was used to measure the transmittance (T) in the wavelength region of interest for optical applications (400–2500 cm^{-1}).

The Raman scattering measurements were performed with an He–Cd laser as the excitation source emitting at the wavelength of 442 nm and a triple grating spectrograph Raman system (μ-Ramboss MST-4000A, Dongwoo Optron Co. Ltd.) equipped with an air cooled charge coupled device (CCD). The scan acquisition mode was used to take the spectra by using the INDOR software. The PL spectrum was taken in the same way using 325 nm as the excitation wavelength and a 325 cut off filter.

The microstructures and the atomic composition were investigated by using the scanning electron microscopy (LEO 440i) attached with the energy dispersive X-ray spectroscopy (EDS).

3. Results and discussion

3.1. XRD analysis

XRD was performed at the grazing angle to obtain the information about the crystallographic structure, crystallinity, orientation, and crystallite grain size. The XRD pattern of ZnSe thin film deposited on quartz at room temperature is shown in Fig. 2. In the XRD pattern, the peak positions indicate that the deposited ZnSe film has a cubic (zinc blend) crystal structure, which is mono crystalline (single phase) with the preferred orientation along the (111) plane. Moreover, the presence of single sharp peak in the figure confirms the polycrystalline nature of the ZnSe thin film with high periodicity and crystanallity. The preferential orientation of the crystal plane (111) corresponds to the Bragg's reflection at $2\theta = 27.28°$.

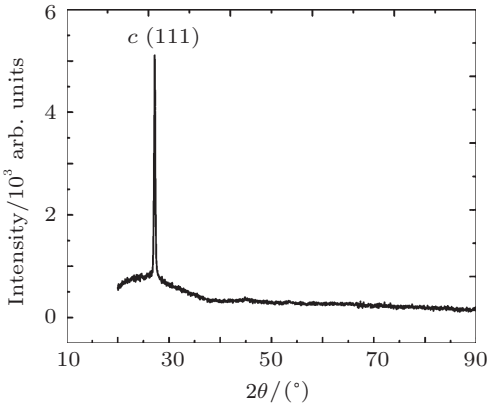


Fig. 2. XRD pattern of ZnSe thin film deposited on quartz substrate at room temperature.

The average grain size D of ZnSe crystallites is estimated by using the Debye–Scherrer formula[11]

$$D = \frac{0.9\lambda}{\mathrm{FWHM}\cos\theta}, \tag{1}$$

where λ is the X-ray wavelength of the Cu $K\alpha$ radiation, and θ is the Bragg angle. The grain size of the crystallites for the c (111) plane is about 16.34 nm.

By utilizing the average grain size D, the dislocation density δ is calculated using the following relation:[12]

$$\delta = \frac{1}{D^2}, \tag{2}$$

where D is in units of nm. The δ value calculated is 3.89×10^{15} m^{-2}. This is in agreement with the other experimental results and research reports.

The interplanar distance d of the (111) plane is identified by using the Brag's diffraction condition[13]

$$2d\sin\theta = n\lambda, \tag{3}$$

where θ is the angle between the normal of the diffracting plane and the incident X-ray, and n is the order of the diffracted beam, which is taken to be one for the first order diffraction. The lattice parameter c of the as-deposited room temperature ZnSe thin film is calculated using the formula for the cubic crystal structure. For the cubic crystal system, the lattice parameter c is related to d with the following equation:[14]

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{c^2}, \tag{4}$$

where h, k, and l are the Miller indices, and c is the lattice parameter along the z direction. The lattice parameter c and the interplanar distance d calculated from the XRD patterns are $c = 5.65$ Å and $d_{111} = 3.23$ Å, respectively.

The train value for the film is calculated using the following relation:[15]

$$\varepsilon = \left(\frac{\lambda}{D\cos\theta} - \mathrm{FWHM}\right)\frac{1}{\tan\theta}. \tag{5}$$

The value of strain so-calculated for the room temperature ZnSe thin film is about 1.23×10^{-3}.

Our XRD results and calculations confirm the better crystalline structure of our room temperature ZnSe thin film grown on the quartz substrate by CSSP compared with those grown at higher temperatures. In addition, crystalline structure, film composition, and luminescence properties of the CSSP deposited film are better for optoelectronics applications than that deposited by using the successive ionic layer adsorption and reaction (SILAR) method, where the film has poor crystallinity and Se deficient as reported by Kale *et al.*[16]

3.2. AFM analysis

For the analysis of the surface morphology of ZnSe thin films, AFM was employed. AFM images of the ZnSe thin film are shown in Fig. 3. The best ordering and the surface uniformity are observed for the films deposited at room temperature. The 2D and the 3D AFM images presented in Fig. 3 reveal that the films deposited on quartz at room temperature have the uniform and smooth morphology. The surface presents a compact surface and a low roughness with the root mean square (RMS) value of 19.86 nm.

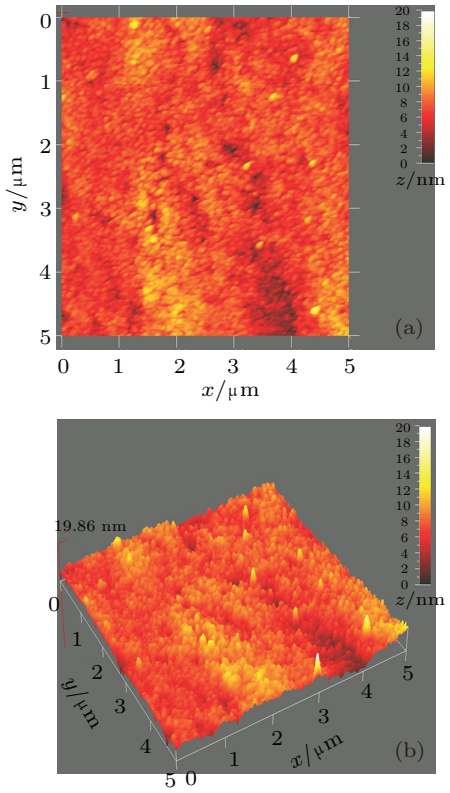


Fig. 3. (colour online) The (a) 2D and (b) 3D AFM images of ZnSe thin film deposited on quartz at room temperature.

3.3. FT-IR analysis

The FT-IR is a very important technique to probe functional groups and chemical bondings in bulk semiconductors and thin films. The defects and the impurity contents can also be characterized by using this diagnostic technique. FT-IR measurements have been carried-out to understand the molecular structure of the ZnSe thin film deposited at room temperature.

The FT-IR transmission spectrum of ZnSe thin film in the range of our interest (400–2500 cm^{-1}) is displayed in Fig. 4. The FT-IR analysis reveals that the characteristic ζ stretching bonding vibration mode occurs at wave number 660 cm^{-1}.[17] The other peaks are observed at 786 cm^{-1}, 880 cm^{-1}, 992 cm^{-1}, 1378 cm^{-1}, and 1580 cm^{-1}. The observed peaks at 786 cm^{-1}, 880 cm^{-1}, and 992 cm^{-1} correspond to the C–H bending modes. While the peak observed at 1378 cm^{-1} corresponds to the NO_2 stretching mode. The C≡C stretching vibration mode occurs at 2317 cm^{-1}. The weak peak at 1580 cm^{-1} is assigned to the O–H characteristic vibration resulting from a small quantity of H_2O expected to be present on the sample.[17]

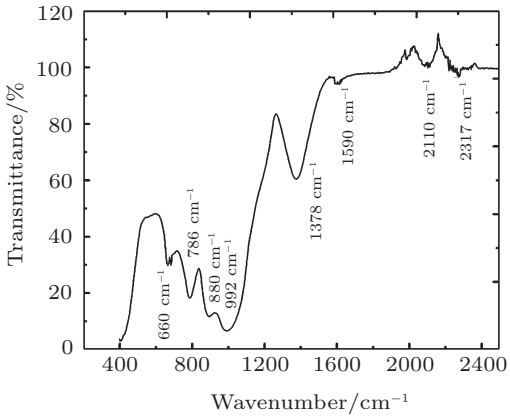


Fig. 4. FT-IR spectrum of ZnSe thin film deposited on quartz at room temperature.

3.4. Raman spectroscopy analysis

We measured the room temperature Raman spectrum in the desired range from 100 cm^{-1} to 700 cm^{-1}. The spectrum for the room temperature ZnSe film is shown in Fig. 5. From this figure, it is well evident that the ZnSe optical absorption peaks (Raman shifts) are at 247 cm^{-1} and 490 cm^{-1}. These are the longitudinal optical phonon modes 1LO and 2LO of the ZnSe cubic structure.[18,19] As the 1LO band is the most intensive in the Raman spectrum excited by the 442 nm line, the energy of this line should be close to the optical band gap. The observed modes are well consisted with the other experimental results.[20,21] It confirms the formation of single phase cubic (zinc blend) polycrystalline structure in the ZnSe thin film deposited on the quartz substrate at room temperature and supports our XRD results.

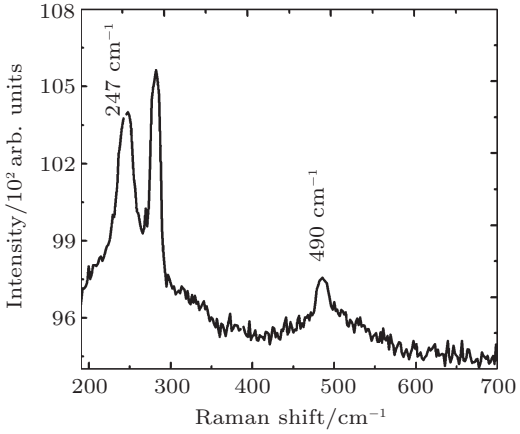


Fig. 5. Raman spectrum of ZnSe thin film deposited on quartz at room temperature.

Moreover, for polar semiconductors, the 490 cm^{-1} phonon mode is well known and is the so-called LO

phonon replica in ZnSe.[22] For amorphous Se, it has been reported that it exhibits an optical absorption at 256 cm^{-1}, while the crystalline Se obtained after annealing exhibits the absorption at 240 cm^{-1}. So the observed phonon peaks at 247 cm^{-1} and 490 cm^{-1} are the phonon bands of the ZnSe thin film.

By comparing with the XRD data, it can be well established that the two results are well consisted to each other. Moreover, the observed longitudinal vibrational phonon modes for the room temperature ZnSe thin film manifest the improved crystallinity as shown in the XRD results.

3.5. Photoluminescence analysis

The PL spectrum provides information related to transition energies, which can be used to determine electronic energy levels. Moreover, the PL intensity gives information of relative rates of radiative and non-radiative recombinations.

Figure 6 shows the room temperature PL emission spectrum of ZnSe thin film. This spectrum shows a strong ultraviolent (UV) emission peak at 382 nm and a visible-blue emission peak at 764 nm. The strong emission at 382 nm is attributed to the recombination of excitons.[23] The visible emission at 764 nm is assigned to the recombination of photon-generated holes with charge of specific defects. Furthermore, it may be due to the presence of native defects like zinc and selenium vacancies or interstitials, which are likely to be introduced during the growth process. Self activated centers arising from complexes of zinc vacancies and shallow donors (selenium interstitials) may occur around 2.2 eV.[24] The emission band observed in the present case at 764 nm may also be attributed to the above complexes.

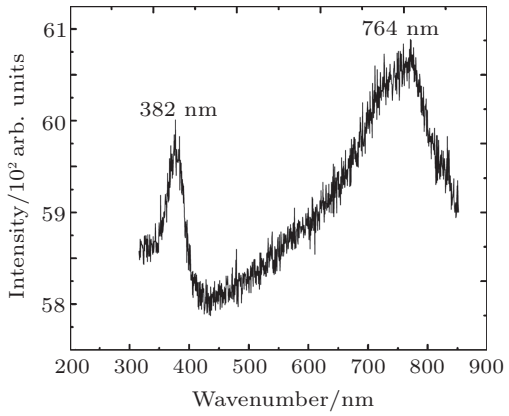


Fig. 6. PL spectrum of ZnSe thin film deposited on quartz at room temperature.

3.6. SEM analysis

For morphological and elemental analyses of the CSSP deposited ZnSe thin film, we employed the scanning electron microscopy attached with the energy dispersive X-ray spectroscopy (EDS).

A high-resolution SEM micrograph of the room temperature ZnSe film is displayed in Fig. 7. The SEM micrograph reveals the smooth surface morphology. Small spots are also observed in the micrograph; however, they are actually aggregation of smaller islands.

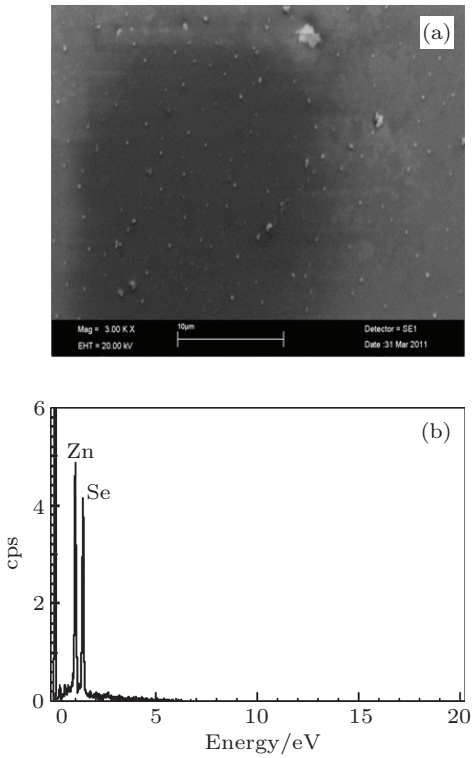


Fig. 7. (a) SEM micrograph and (b) EDS spectrum of ZnSe deposited on quartz at room temperature.

The composition of Zn and Se in the ZnSe thin film was estimated by EDS. Figure 7 shows the EDS spectrum of the ZnSe nano crystalline thin film deposited on quartz by CSSP at room temperature. The spectrum shows only peaks for Zn and Se, which clearly shows that the film is of high purity containing only Zn and Se elements with no impurity. The elements in the sample are found to be Zn (65.65%) and Se (354.35%).

4. Conclusion and outlook

In summary, the room temperature synthesis of ZnSe thin film on quartz by using the closed surface sublimation process was successfully demonstrated.

The films were highly crystalline with the preferential orientation along (111) corresponding to the cubic phase ($2\theta = 27.28°$). The film presented a smooth and compact surface morphology with roughness of RMS value 19.86 nm. The optical phonon modes 247 cm^{-1} and 490 cm^{-1} confirmed the formation of the cubic structured ZnSe. The photoluminescence emissions were observed at 382 (excitonic emission) nm and 764 nm. The SEM data confirmed the formation of the high purity ZnSe thin film. The FT-IR study established the strong Zn–Se stretching bond at 660 cm^{-1}.

The results presented are promising, showing that the traditional CSSP technique can be employed at room temperature for the controlled synthesis of stichiometric ZnSe thin film of high quality and good periodicity. This technique can be extended to other II–VI semiconductors to prepare their thin films at room temperature, thus leading to more industrial optoelectronics applications.

Acknowledgements

The authors acknowledge their departments for helping and providing the required experimental facilities for this research work.

References

[1] Bhargava R 1997 *Properties of Wide Bandgap II-VI Semiconductors* (INSPEC: London)

[2] Yun D Q, Feng W, Wu H C, Liu X Z and Qiang J F 2010 *Chin. Phys.* B **19** 017304

[3] Itoh S, Nakano K and Ishibashi A 2000 *J. Cryst. Growth* **1029** 214

[4] Venkatachalam S, Jeyachandran Y L, Sureshkumar P, Dhayalraj A, Mangalaraj D, Narayandass S K and Velumani S 2007 *Materials Characterization* **58** 794

[5] Khawaja E E, Durrani S M A, Hallak A B, Salim M A and Sakhawah M H 1994 *J. Phys.* D: *Appl. Phys.* **27** 1008

[6] Toda A, Nakamura F, Yanashima K and Ishibashi A 1997 *J. Cryst. Growth* **170** 461

[7] Liang W Z, Ji Y D, Nan T X, Huang J, Zeng H Z, Du H, Chen C Land Lin Y 2012 *Chin. Phys.* B **21** 067701

[8] Subbaiah Y P V, Prathap P, Devika M and Ramakrishna K T R 2005 *Physica* B: *Physics of Condensed Matter* **365** 240

[9] Perna G, Capozzi V, Plantamura M C, Minafra A, Biagi P F, Orlando S, Marotta V and Giardini A 2002 *Applied Surface Science* **186** 521

[10] Riveros G, Gomez H, Henriquez R, Schrebler R, Marotti R E and Dalchide E A 2001 *Solar Energy Mater Sol. Cells* **70** 255

[11] Trindade T, Brien P O and Pickett N L 2001 *Synthes. Chem. Mater.* **13** 3843

[12] Bailey R E, Smith A M and Nie S 2004 *Physica* E **25** 1

[13] Jeong T S, Yu P Y, Hong K J, Kim T S, Youn C J, Choi Y D, Lee K S and Yoon M Y 2003 *J. Cryst. Growth* **249** 9

[14] Venkatachalam S, Jeyachandran Y L, Sureshkumar P, Dhayalraj A, Mangalaraj D, Narayandass S K and Velumani S 2007 *Materials Characterization* **58** 794

[15] Kale R B and Lokhande C D 2004 *Journal of Materials Research Bulletin* **39** 1829

[16] Kumara P and Singh K 2009 *Journal of Optoelectronic and Biomedical Materials* **1** 59

[17] Mahalingam T, Kathalingam A, Velumani S, Lee S, Sun M H and Deak K Y 2006 *J. Mater. Sci.* **41** 3353

[18] Jones R N 1986 *Chemical, Biological and Industrial Applications of Infrared Spectroscopy* (ed. Durig J R) (Chichester: John Wiley & Sons) pp. 1–50

[19] Takenaka T and Fukuzaki H 1979 *J. Raman Spectrosc.* **8** 151

[20] Guziewicz M, Godlewski E, Kopalko M, Eusakowska K and Dynowska E 2004 *Thin Solid Films* **446** 234

[21] Trindade T, Brien P O and Pickett N L 2001 *Prop. Chem. Mater.* **13** 3843

[22] Kumar P and Singh K 2009 *Journal of Optoelectronic and Biomedical Materials* **1** 59

[23] Shen J L, Chang I M, Shu Y M, Chen Y F, Chang S Z and Lee S C 1994 *Phys. Rev.* B **55** 1678

[24] Kanemitsu Y, Yamamoto A, Matsue H, Masumoto Y, Yamaga S and Yoshikawa A 1992 *Appl. Phys. Lett.* **60** 1330