

Composition and Band Gap Controlled AACVD of ZnSe and ZnS_xSe_{1-x} Thin Films Using Novel Single Source Precursors

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Abstract

Polycrystalline thin films of ZnSe and ZnS_xSe_{1-x} have been deposited on glass substrates by Aerosol Assisted Chemical Vapour Deposition (AACVD) from *bis*(diethyldiselenocarbamato)zinc(II) and a 1:1 and 1:0.75 mixtures of *bis*(diethyldiselenocarbamato)zinc(II) and *bis*(diethyldithiocarbamato)zinc(II) as precursors. All films were characterized by p-XRD, SEM, EDX, Raman spectroscopy, photoluminescence (PL and UV/Vis spectroscopy. The band gap of pure ZnSe thin films was found to be 2.25 whereas the band gap of ZnS_xSe_{1-x} films varied from 2.55 to 2.66 eV depending on the sulfur content in the films. PL emission spectra showed a clear blue shift for ZnS_xSe_{1-x} films compared to ZnSe due to the sulphur content in the films which increase the band gap. The band gap of ZnS_xSe_{1-x} can be controlled by sulfur to selenium ratio in the alloy. The morphology of the ZnSe thin films changed from small randomly shaped crystallites to triangles whereas the morphology of ZnS_xSe_{1-x} was mainly based on cuboids.

Keywords

Bis(diethyldiselenocarbamato)zinc(II), ZnSe, ZnS_xSe_{1-x}, AACVD, SEM

1. Introduction

Metal selenides are wide band gap materials and have applications in light-emitting devices, solar cells, sensors, and optical recording materials [1] [2] [3] [4]. ZnSe is ideal material for blue-green laser diodes [1] [2], mid-IR laser sources for remote sensing applications [5], and in optically controlled switching devices due to its large photo resistivity [6]. Zinc selenide thin films had been fabricated by photochemical deposition (PCD) [7], chemical bath deposition (CBD) [8] [9] and electrochemical deposition (ECD) [10], but all these methods have

their own drawbacks including higher annealing temperatures for PCD, controlling rate of reaction for CBD and the use of only conductive substrates for ECD [7].

Several reports have been published for the use of single-source precursors for the deposition of metal chalcogenide [11]-[22]. A range of chalcogenides have been deposited from $M[ESi(SiMe)_3]_2$ ($M = Zn, Cd, Hg$; $E = S, Se$ or Te) complexes as single source precursors [23] [24]. Metal complexes with the general formula $[M(R_2PSe_2)_n]$ ($M = Zn, Cd, Pb, In, Ga, Cu, Bi, Ni$; $R = ^iPr, Ph$) have been synthesised and used for the deposition of metal selenide thin films by CVD [25]. Other metal complexes used as single source precursors include: $[(M(E_2CNR_2)_2)]$ (symmetrical) or $[M(E_2CNRR')_2]$ (unsymmetrical) ($R, R' = alkyl, E = S, Se$; $M = Zn, Cd$) [22], mixed alkyl/dithio- or diseleno-carbamato complexes $[M(E_2CNRR')_2]$, where $R = Me, Et, Bu^t$ or Me_3CCH_2 , $M = Zn$ or Cd ; $E = S$ or Se ; $R' = Me$ or Et [26] [27] [28] [29], imino-*bis*(dialkylphosphineselenide) complexes $[M[(EP^iPr)_2N]_2]$ ($M = Cd, Zn$; $E = S, Se$) and $[M[(SePPh_2)_2N]_2]$ ($M = Cd, Zn$) [30] [31] [32] [33] [34].

ZnS_xSe_{1-x} is found to be one of the best substituent for CdS as a buffer layer. When the sulphur composition is larger than 0.2, then it becomes another good candidate for cladding layers for blue laser diodes [35]. Polycrystalline ZnS_xSe_{1-x} thin films were deposited by co-evaporation of ZnS and ZnSe [36], by low-pressure metal-organic chemical vapour deposition (LP-MOCVD) process from the zinc alkyls dimethylzinc (DMZ) or diethylzinc (DEZ) and H_2Se and H_2S [37], and by molecular beam epitaxy (MBE) using radio-frequency (RF) plasma [38]. We have recently reported the deposition of CdSe and CdSSe thin films from molecular precursors by AACVD [39]. Herein we report the deposition of highly crystalline hexagonal ZnSe thin films from *bis*(diethyldiselenocarbamato)zinc(II) complex and ZnSSe composite from a mixture of *bis*(diethyldiselenocarbamato)zinc(II) and *bis*(diethyldithiocarbamato)zinc(II) complexes and their detailed optical and structural characterisation. To the best of our knowledge ZnSe or ZnSSe thin films have never been deposited by AACVD method from diselenocarbamato complexes of zinc.

2. Experimental

2.1. Synthesis of Precursors

Bis(diethyldiselenocarbamato)zinc(II) $[Zn(Se_2CNEt_2)_2]$ and *bis*(diethyldithiocarbamato)-zinc(II) $[Zn(S_2CNEt_2)_2]$ precursors were synthesised using method described in literature [27] [28] [29] [30]. In a typical synthesis sodium salt of diethyl dithiocarbamate ($[Na(S_2CNEt_2)]_2$) was reacted with zinc nitrate ($Zn(NO_3)_2$) in a water solution. The white precipitate of $[Zn(S_2CNEt_2)_2]$ was separated by filtration, washed with water and dried under vacuum.

2.2. Thermogravimetric Analysis

Thermogravimetric analysis measurements were carried out by a Seiko SSC/S200 model under a heating rate of $10^\circ C \cdot min^{-1}$ under nitrogen. Indium metal is used

as a reference to calibrate the instrument. TGA was performed by School of Chemistry, University of Manchester, micro-analysis team

2.3. Deposition of Thin Films

The depositions of thin films were carried out at 300°C and 350°C using 14 mmol of the $[\text{Zn}(\text{Se}_2\text{CNEt}_2)_2]$ precursor in 15 mL THF and for the deposition of ZnSSe; 1:1 ratio of $[\text{Zn}(\text{Se}_2\text{CNEt}_2)_2]$ (7 mmol) and $[\text{Zn}(\text{S}_2\text{CNEt}_2)_2]$ (7 mmol) in 15 mL THF and $[\text{Zn}(\text{Se}_2\text{CNEt}_2)_2]$ (5 mmol) and $[\text{Zn}(\text{S}_2\text{CNEt}_2)_2]$ (7 mmol) in 15 mL THF to reduce the amount of Se on the thin films at 350°C.

The depositions were carried out onto glass slides with the dimensions of 1 × 3 cm by AACVD. In a typical experiment, the precursor was dissolved in 15 mL THF in a two-necked 100 mL round-bottom flask. The flask was connected with an argon gas inlet carried the aerosols generated by a PIFCO ultrasonic humidifier to the reactor tube connected to other neck of the flask and placed in a Carbolite furnace. The gas flow rate was controlled at 160 Sccm through a Platon flow gauge. The precursor mist was thermolysed in the hot zone at the surface of glass substrate and resulted in the deposition of thin film as reported previously [39].

2.4. Characterisation of Thin Films

XRD patterns were recorded on a Bruker D8 AXE diffractometer (Cu-K α) from 20 to 80 degrees with a step size of 0.05. SEM studies were carried out by using a Philips XL 30 FEGSEM and EDAX analysis for the composition of films were carried out by using a DX4 instrument. TEM i were recorded on a Tecnai F30 microscope and Raman spectra were measured by Renishaw 1000 Micro Raman system. UV/Vis spectra were carried out by Perkin Elmer Lambda 1050 spectrophotometer. And PL spectra were taken by using HOIBO Fluorolog FL3 iHR at excitation wavelength of 400 nm.

3. Results and Discussion

Bis(diethyldithio/diselenocarbamate)zinc(II) complexes can easily be synthesised by a single step reaction and are stable at room temperature for periods of years as the complexes used in these experiments were synthesised 5 years ago. The analysis of the complexes after 5 years proved that no decomposition occurred. These complexes are soluble in common organic solvents such as toluene, THF, chloroform. Both decompose in the same the same manner and in the same temperature range (*vide infra*) making them suitable to be used as a mixture in different ratios to control the sulfur or selenium concentration in the alloy. The effect of precursor concentration and deposition temperature on the stoichiometric composition and morphology of the ZnSe and ZnSSe thin films were investigated.

3.1. Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) of $[\text{Zn}(\text{Se}_2\text{CNEt}_2)_2]$ and $[\text{Zn}(\text{S}_2\text{CNEt}_2)_2]$ films

were studied from 10°C - 600°C under nitrogen. $[\text{Zn}(\text{S}_2\text{CNET}_2)_2]$ and $[\text{Zn}(\text{Se}_2\text{CNET}_2)_2]$ decomposed in one relatively sharp step with almost similar rate and resulted with ~8% and ~10% residual mass, which found to be half or less than half of the mass of the expected metal chalcogenides; ZnS (27%) or ZnSe (20%). The sharp transition shows a one-step decomposition for both complexes to give the metal chalcogenides and all the rest of impurities volatilised. The less quantity of the residue appears to be due to the volatility of sulphur and selenium at high temperatures. Decomposition of both precursors at similar temperature makes them highly suitable for depositing ZnSe, ZnS, and ZnSSe thin films by AACVD within a temperature range of 250°C to 350°C (**Figure 1**).

3.2. AACVD of ZnSe Thin Films

3.2.1. Powder X-Ray Diffraction for ZnSe Thin Films

Depositions were carried out at 300°C and 350°C using 14 mmol of the $[\text{Zn}(\text{Se}_2\text{CNET}_2)_2]$ precursor in 15 mL THF.

Films deposited at 300°C were slightly yellow and thick, p-XRD did not give any diffraction peaks indicating the amorphous nature of the deposited material whereas, films deposited at 350°C were thick adherent, specular golden in appearance. **Figure 2(a)** shows the p-XRD pattern of ZnSe thin films deposited at 350°C. The main peaks at about 27.3°, 45.2° and 53.6° correspond to cubic ZnSe (ICDD: 01-088-2345).

3.2.2. Scanning Electron Microscopy of ZnSe Films

Morphology of the films was studied using by SEM. **Figure 2(b)** shows the SEM images of the films with an inset at higher magnification. The films are based on

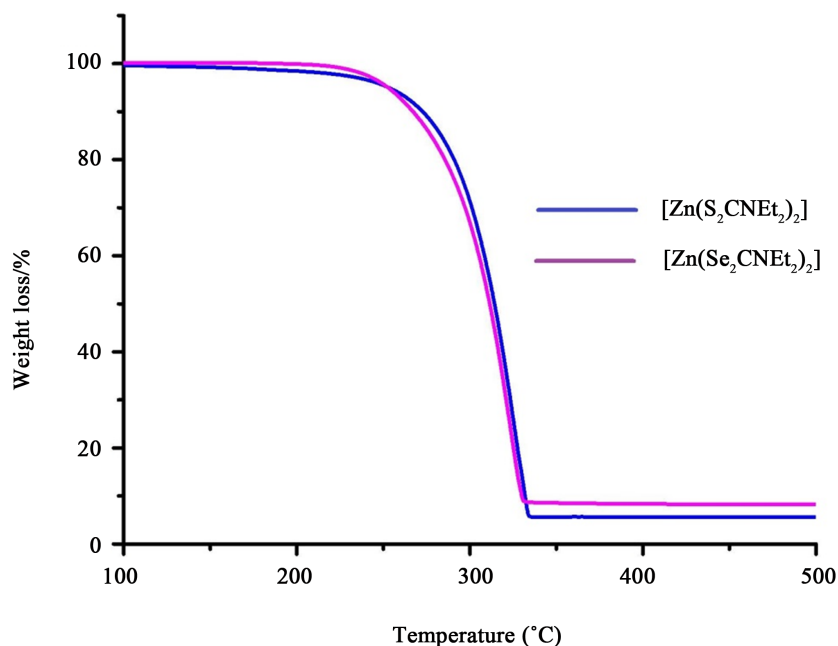


Figure 1. Thermogravimetric analysis of complexes $[\text{Zn}(\text{Se}_2\text{CNET}_2)_2]$ and $[\text{Zn}(\text{S}_2\text{CNET}_2)_2]$ under N_2 .

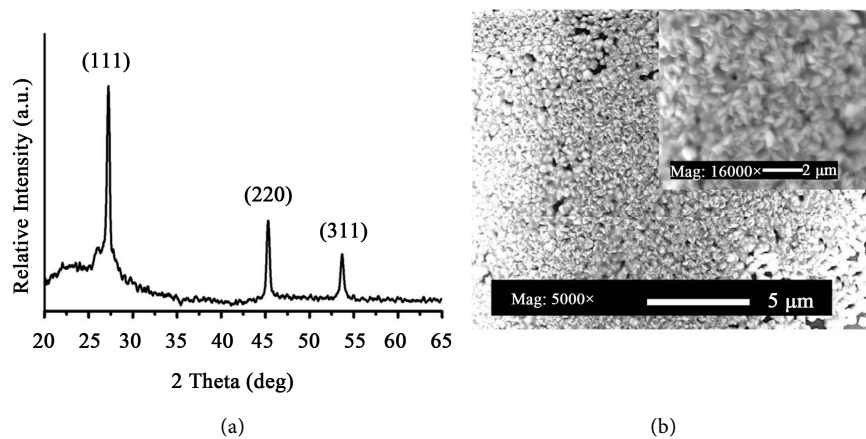


Figure 2. (a) p-XRD pattern of ZnSe thin films deposited at 350°C by AACVD. Peaks are labelled with cubic ZnSe (ICDD: 01-088-2345); (b) SEM images of ZnSe films with an inset at higher magnification.

small (100 - 300 nm) random crystallites thickly packed together. EDX analysis showed Zn:Se ratio as 49.44:50.55, which is very close to the 1:1 ratio expected for ZnSe.

3.2.3. Raman and PL Spectra of ZnSe Films

Raman spectra showed peaks at 205, 253, 412 and 498 cm^{-1} which are close to the Raman peaks for the TO, LO and 2LO phonon modes of ZnSe (~ 206 , 252 and 493 cm^{-1}) [40]-[45] (**Figure 3(a)**).

PL spectra showed a very strong emission between 530 to 580 nm (**Figure 3(b)**). The emission maximum shift towards the higher energy, as compared to the bulk values, is due to the smaller size of crystallites and large surface defects and Zn vacancies at the interstitial sites [46].

3.3. AACVD of Zinc Sulfoselenide ($\text{ZnS}_x\text{Se}_{1-x}$) Thin Films

3.3.1. p-XRD of ZnSSe Thin Films

The deposition was carried out at 300°C and 350°C but no deposition occurred at 300°C. Thick specular yellow films were obtained at 350°C using 1:1 and 1:0.75 ratios of $[\text{Zn}(\text{Se}_2\text{CNET}_2)_2]$ and $[\text{Zn}(\text{S}_2\text{CNET}_2)_2]$ precursors. The p-XRD patterns of $\text{ZnS}_x\text{Se}_{1-x}$ thin films deposited using 1:1 ratio of mixture are shown in **Figure 4**. The p-XRD patterns were indexed using the standard patterns for cubic $\text{ZnSe}_{0.5}\text{S}_{0.5}$ (ICDD: 04-001-6856) space group F-43m, lattice parameters, $a = b = c = 5.500 \text{ \AA}$. The main peaks at 2θ : 28.07 (111), 32.53 (200), 46.67 (220), 55.35 (311) and 58.04 (222) are slightly shifted from the standard pattern. Minor peaks are due to the contamination of binary phases as ZnS and ZnSe (**Figure 4**).

1:0.75 molar ratio of $[\text{Zn}(\text{Se}_2\text{CNET}_2)_2]$ and $[\text{Zn}(\text{S}_2\text{CNET}_2)_2]$ precursor mixture at 350°C produced thin orange adherent films. The p-XRD patterns showed good matching with cubic $\text{ZnSe}_{0.5}\text{S}_{0.5}$ (ICDD: 04-001-6856). The main peaks were observed at 2θ : 28.07 (111), 32.53 (200), 46.67 (220), 55.35 (311) and 58.04 (222) similar to those observed for films deposited from 1:1 mixture. Again the films

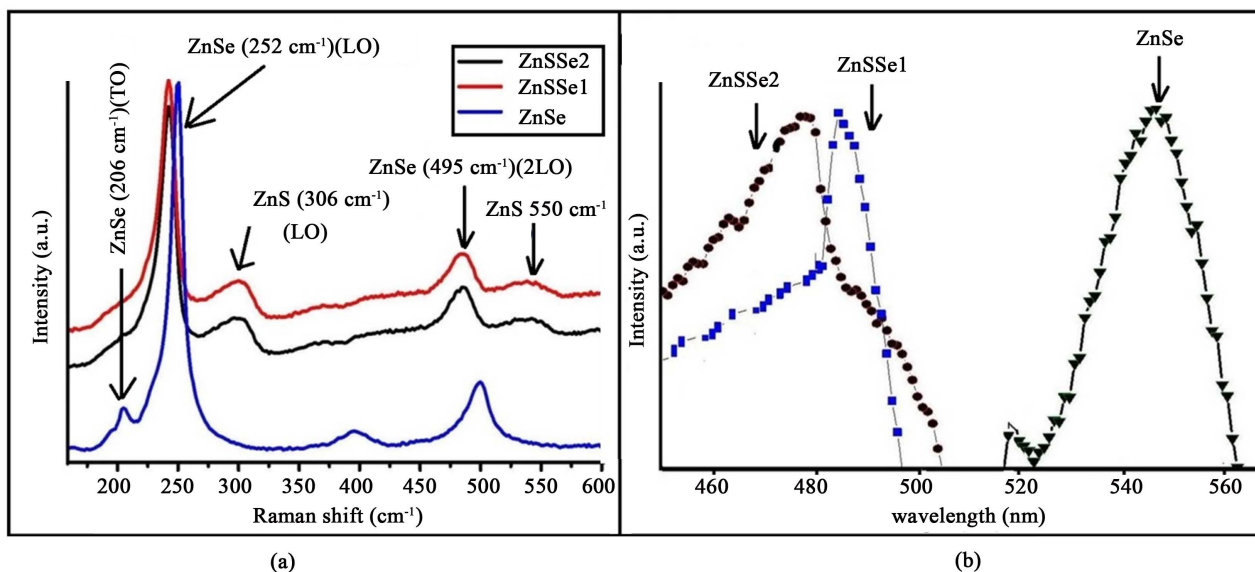


Figure 3. (a) Raman spectra of ZnSe, ZnSSe1, and ZnSSe2 thin films deposited at 350°C by AACVD, ZnSSe1, ZnSSe2 are films deposited using 1:1 and 1:0.75 mmol of $[\text{Zn}(\text{S}_2\text{CNET}_2)_2]$ and $[\text{Zn}(\text{Se}_2\text{CNET}_2)_2]$ precursors at 350°C; (b) Photoluminescence spectra of ZnSe, ZnSSe1, and ZnSSe2.

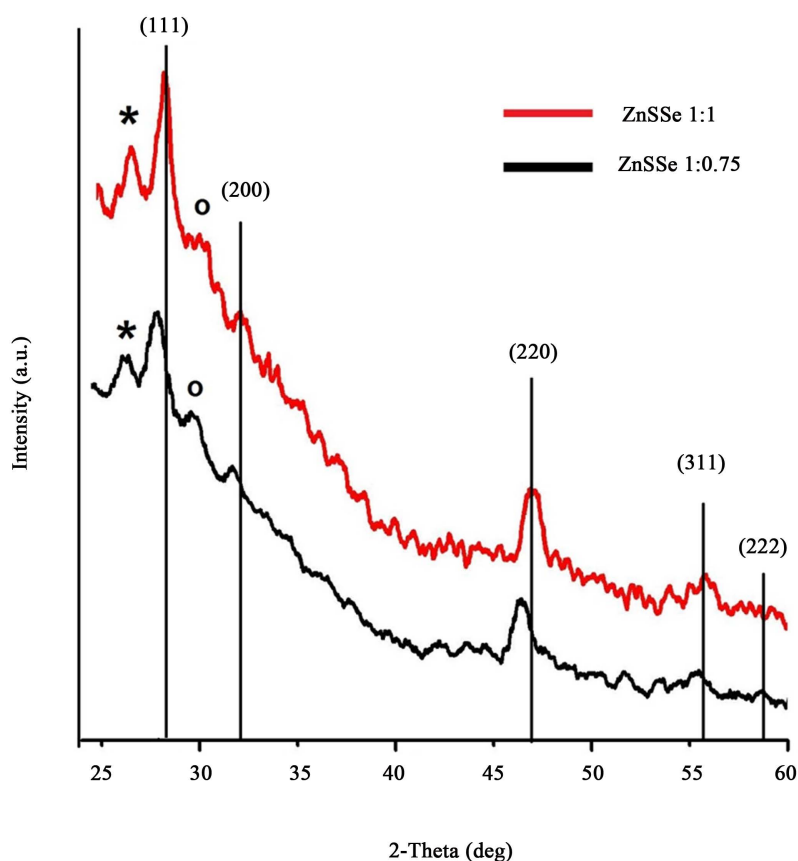


Figure 4. p-XRD patterns of ZnSSe thin films deposited at 350°C using 1:1 and 1:0.75 mmol of $[\text{Zn}(\text{S}_2\text{CNET}_2)_2]$ and $[\text{Zn}(\text{Se}_2\text{CNET}_2)_2]$ precursors. Sticks pattern is the reference patterns for cubic $\text{ZnSe}_{0.5}\text{S}_{0.5}$ (ICDD: 04-001-6856). (*) shows ZnSe peaks and (°) shows the ZnS peaks.

had minor contamination of ZnS and ZnSe phases. The p-XRD patterns showed good agreement with the reported X-ray diffraction data related to the ZnS_xSe_{1-x} thin films for different x-values (x= 0, 0.2, 0.4, 0.6). It can be noted that the higher the x-value the more the (1 1 1) peak shifts from the ZnSe (1 1 1) peak to ZnS(1 1 1) peak as reported [35].

3.3.2. Morphology of ZnS_xSe_{1-x} Thin Films

The SEM images of ZnS_xSe_{1-x} thin films deposited using 1:1 ratio of [Zn(Se₂CNET₂)₂] and [Zn(S₂CNET₂)₂] precursor mixture showed irregular shaped crystallites which showed some kind of tetragonal morphologies (Figure 5). EDX result showed the ratio of Zn: S: Se: 47.34:36.68:13.98 giving a stoichiometric formula of Zn_{1.0}Se_{0.77}S_{0.30}. The EDX results gave good explanation for the larger deviation of the p-XRD patterns peaks from the ZnS patterns than the ZnSe pattern. Morphology of the ZnS_xSe_{1-x} films deposited using 1:0.75 molar ratio of [Zn(Se₂CNET₂)₂] and [Zn(S₂CNET₂)₂] is based on a mixture of irregular and cubic crystallites.

EDX results showed the ratio of Zn: S: Se: 49.25:23.84:26.91 giving a stoichiometric formula of Zn_{1.0}Se_{0.48}S_{0.54}. The elemental map of the films showed uniform distribution of elements on the entire area of the substrate (Figure 6).

3.3.3. Raman Spectroscopic Studies of ZnS_xSe_{1-x} Thin Films

Raman spectra of ZnS_xSe_{1-x} thin films deposited using 1:1 ratio of [Zn(Se₂CNET₂)₂] and [Zn(S₂CNET₂)₂] precursor mixture showed strong peaks at 240 cm⁻¹ which shifted from the ZnSe peaks at (253 cm⁻¹) and the peak at 300 cm⁻¹ corresponds to ZnS phases (306 cm⁻¹). Similarly the peak at 490 cm⁻¹ corresponds to the Raman mode of ZnSe (498 cm⁻¹). Other peak observed at 550 cm⁻¹ was closer to the peak for ZnS (546 cm⁻¹) (Figure 3(a)) [31] [32] [33] [34] [35] [37]. The Raman spectra of the ZnS_xSe_{1-x} films deposited using 1:0.75 molar ratio of [Zn(Se₂CNET₂)₂] and [Zn(S₂CNET₂)₂] showed strong peaks at 240 cm⁻¹ which is shifted from the ZnSe peak at 252 cm⁻¹ along with peaks at 300 cm⁻¹ which correspond

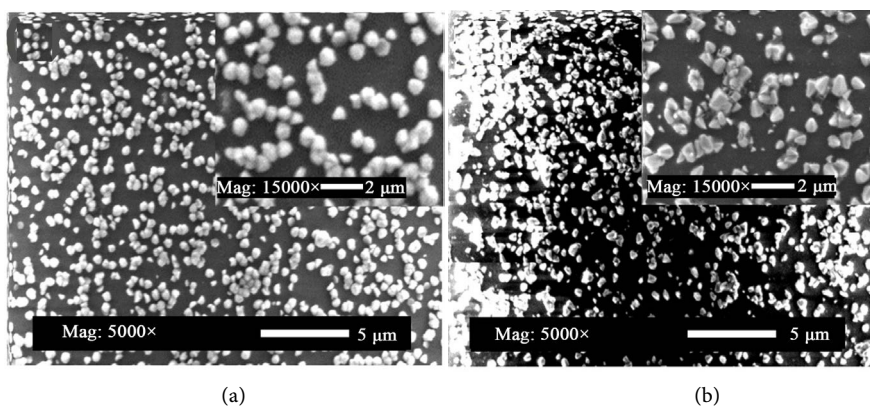


Figure 5. (a) and (b) are the SEM images (5000× magnification) of ZnS_xSe_{1-x} films obtained at 350 °C using 1:1 and 1:0.75 molar ratio [Zn(Se₂CNET₂)₂] and [Zn(S₂CNET₂)₂] precursor mixtures. Inset shows images at 15000x magnification.

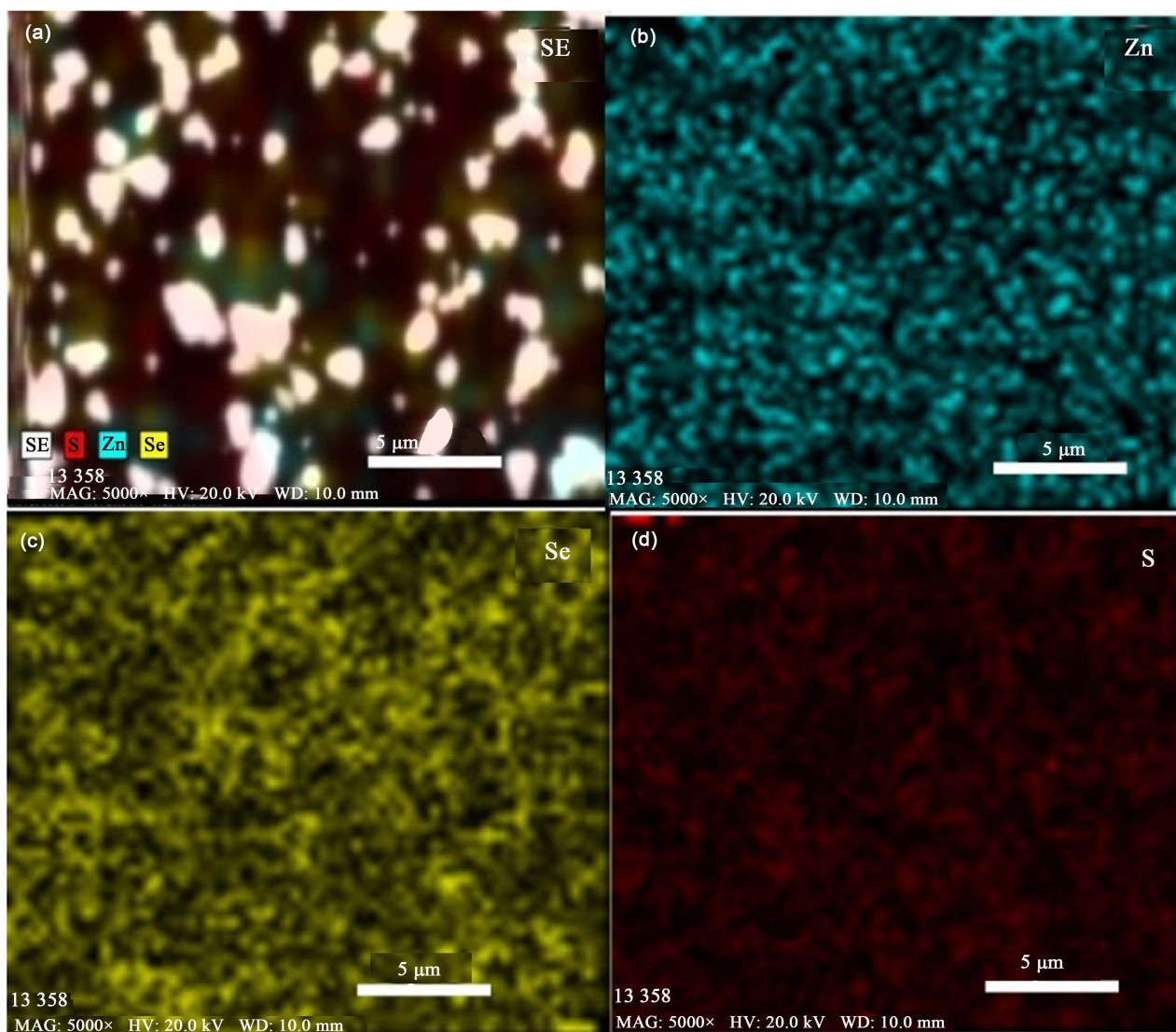


Figure 6. Elemental mapping of (a) ZnSSe films obtained at 350°C with stoichiometric formulae $Zn_{1.0}Se_{0.48}S_{0.54}$ deposited from 1:0.75 molar ratio of $[Zn(Se_2CNET_2)_2]$ and $[Zn(S_2CNET_2)_2]$ precursor mixtures; (b) Distribution of Zn; (c) Distribution of Se and; (d) Distribution of S.

to ZnS peak at 306 cm^{-1} [47]. Other peaks are similar to those observed for the films obtained from 1:1 mixture.

3.3.4. PL Spectra of ZnSSe Films

PL spectra of the ZnS_xSe_{1-x} films deposited using two different precursor mixture concentrations (1:1 and 1:0.75 molar ratio of $[Zn(Se_2CNET_2)_2]$ and $[Zn(S_2CNET_2)_2]$ mixture) showed less intense emission than the ZnSe films. The Se rich ZnSSe films showed PL at about 485 nm which gave a band gap of about 2.55 eV. Whereas the one with 1:1 ratio of S:Se showed PL absorption about 465 nm which gave an average band gap of 2.66 eV. Both values found to be higher than the band gap for ZnSe (2.25 eV) (Figure 3(b)). PL absorption showed that the absorption shifted towards blue region because of the presence of S and PL ab-

sorption decreases with increase in S content in the ZnSSe films. PL spectra measured for these films showed blue shift compared to ZnSe films and showed band gap around 2.4 eV (referred as ZnSSe1). The values showed good agreement with the reported values of $\text{ZnS}_x\text{Se}_{1-x}$ thin films with increase in value of S content [33].

4. Conclusion

The band gap of ZnSe had been tuned from 2.25 eV to 2.66 eV by increasing the sulfur content in the alloy ($\text{ZnS}_x\text{Se}_{1-x}$). XRD and Raman spectra showed the purity of ZnSe and confirmed the formation of ternary phase (ZnSSe). The morphology of the films was changed by addition of sulphur into the selenium precursor. The recent use of thin film absorber layers in solar energy conversion devices has led to the real possibility of sustainable and inexpensive replacements for silicon-based photovoltaics based on compound semiconductors. Our new manuscript shows how band gap tuning can be achieved from the doping of sulphur or selenium in metal chalcogenide thin films. Chemical vapour deposition (CVD) techniques to produce these films are currently highly sought-after as they have the potential for eventual scale up should these materials for solar cells be the solution to the renewable energy problem.

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