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The aerosol assisted chemical vapour deposition of SnSe and Cu₂SnSe₃ thin films from molecular precursors†

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Tin selenide (SnSe) and copper tin selenide (Cu₂SnSe₃) thin films have been deposited onto glass substrates by AACVD using [Sn(Ph₂PSe₂)₂] or a mixture of [Sn(Ph₂PSe₂)₂] and [Cu(acac)₂] respectively.

Tin selenide (SnSe) is a p-type semiconductor with a direct band gap of 0.9 eV and an indirect band gap of 1.3 eV. The material finds application in optoelectronic devices,¹ as a thermoelectric material and in lithium ion batteries.² Various methods have been used for the deposition of SnSe thin films which include atmospheric pressure chemical vapour deposition (APCVD),³ pyrolysis,⁴ thermal evaporation⁵ and chemical bath deposition (CBD).⁶ Cu₂SnSe₃ is also a p-type semiconductor. In both cubic and wurtzitic forms, Cu₂SnSe₃ has a band gap close to 1.5 eV whereas the rhombohedral form has a direct band gap of 0.84 eV.⁷ Cu₂SnSe₃ has a high optical absorption co-efficient > 10⁴.⁸ Its Hole transport is chiefly controlled by the Cu–Se electro-conductive frame work.⁹ Cu₂SnSe₃ is based on earth abundant elements, has a simple crystal structure and phase diagram as compared to other quaternary chalcogenides. These features make Cu₂SnSe₃ an attractive candidate for variety of optoelectronic and solar energy applications.¹⁰ The uses of Cu₂SnSe₃ are being explored in: acousto-optic applications,¹¹ thermo-electronics,¹² and biomedical applications.

Cu₂SnSe₃ nanocrystals have been synthesized by employing a variety of techniques including: a microwave assisted polyol method,¹³ colloidal synthesis¹⁴ and flash evaporation methods.¹⁵ However, there are very few reports on the deposition of thin films. Kim *et al.* have recently reported the growth of Cu₂SnSe₃ crystals on soda lime glass substrate by the co-evaporation method.¹⁶ They studied the effect of substrate temperature on phase transformations between cubic and monoclinic phases

and determined optical properties. The precise control of both the morphology and stoichiometry of Cu₂SnSe₃ films remains a challenge. Chemical Vapour Deposition (CVD) is a promising technique for deposition of such films and can provide control over phase, morphology and microstructure. The utility of conventional CVD is limited by its dependence on volatile precursors. AACVD is a variant of CVD in which less or non-volatile precursors are flash evaporated. Sharma *et al.* have deposited SnSe thin films by AACVD at 490 °C and 530 °C using a diorganotin(IV)-2-pyridyl selenoate complex as single source precursor.¹⁷

Previously, we have reported the synthesis and use of selenophosphinate complexes for deposition of binary, ternary and quaternary metal chalcogenide thin films by AACVD.^{18,19} Krauss *et al.* reported the structure and the use of bis(diphenyldiselenophosphinato)lead(II) complex as a precursor for PbSe nanoparticles.²⁰ The deposition of CZTS thin films from diethyldithiocarbamate-complexes of Cu, Zn and Sn by AA-CVD has also been reported.²¹ Suitable mixtures of precursor materials with comparable thermal decomposition rate facilitate deposition and provide effective stoichiometric control especially in the deposition of more complex semiconductor materials.²¹ We have now synthesized a new complex bis(diphenylphosphine-diselenoato)tin(II) [Sn(Ph₂PSe₂)₂] and used it as a single source precursor for the deposition of tin selenide (SnSe) thin films by AACVD. We have also used it in combination with bis(2,4-pentanedionato)copper(II) [Cu(acac)₂] for the deposition of Cu₂SnSe₃ thin films.‡

The preparation of [Sn(Ph₂PSe₂)₂] complex was carried out in two steps. Potassium diphenylphosphinodiselenoate was prepared by the reaction of diphenylphosphine, elemental selenium and potassium hydroxide as reported by Gusarova *et al.*²² The ligand was then reacted with SnCl₂ to give corresponding [Sn(Ph₂PSe₂)₂] complex. The product was characterized by FTIR, NMR, mass spectrometry and elemental analysis. Thermogravimetric analysis of the complex showed decomposition between 350 °C and 400 °C to give a ~21% residue corresponding to SnSe (Fig. S1, ESI†).

The deposition of SnSe by AACVD was carried out by using a 0.19 mmol solution of [Sn(Ph₂PSe₂)₂] in THF (15 mL).

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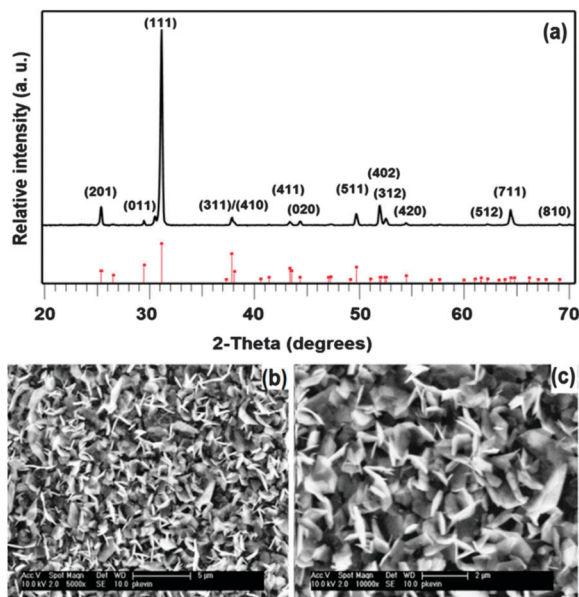


Fig. 1 (a) p-XRD pattern of SnSe thin film deposited from $[\text{Sn}(\text{Ph}_2\text{PSe}_2)_2]$ precursor at 400 °C. Vertical lines below show standard ICDD pattern 00-048-1224 for orthorhombic SnSe (b) and (c) SEM images of as deposited thin film at 400 °C.

Deposition was carried out at 350 and 400 °C with an Ar flow rate of 180 sccm for 45 min. No deposition occurred at 350 °C whereas dark brown, well adhered films were obtained on glass substrates at 400 °C. Fig. 1a shows p-XRD pattern of SnSe thin films deposited at 400 °C. The pattern is indexed to the standard ICDD pattern 00-048-1224 of orthorhombic SnSe with preferred orientation along (111) plane. SEM images (Fig. 1b and c) show the uniform morphology of microcrystalline SnSe thin films. The morphology of the films is based on irregular sheets with an average size of *ca.* 1.5 μm . Relative atomic percentage of Sn and Se atoms determined by EDX measurements was found to be 48:52 which is fairly close to the expected value of individual grains. The band gap of SnSe was found to be 1.1 eV (Fig. S2, ESI[†]) which is close to that reported previously for this material.¹

The deposition of Cu_2SnSe_3 was carried out by using a mixture of $[\text{Cu}(\text{acac})_2]$ (0.38 mmol) and $[\text{Sn}(\text{Ph}_2\text{PSe}_2)_2]$ (0.19 mmol) in 15 mL THF at three different temperatures (350, 400 and 450 °C) for 1 hour. Deposition at 350 °C produced no thin films whereas those at 400 and 450 °C produced uniform, shiny dark brown films. The p-XRD patterns (Fig. 2a) of the thin films deposited at 400 °C and 450 °C correspond to the standard ICDD pattern 03-065-4145 for cubic Cu_2SnSe_3 phase with space group $F\bar{4}3m$.

Films deposited at 400 °C had a uniform morphology (Fig. 3a) whereas two distinct types of crystallites were seen in those deposited at 450 °C. The films deposited at 400 °C consist of clusters of nanocrystalline flakes whilst the images of those deposited at 450 °C show larger semispherical crystallites thinly scattered in a background of irregularly shaped nanocrystallites. EDX analysis showed the chemical composition as Cu:Sn:Se 2.1:1.0:2.9 for thin films deposited at 400 °C and Cu:Sn:Se 1.9:1.0:2.6 for the films deposited at 450 °C. These results

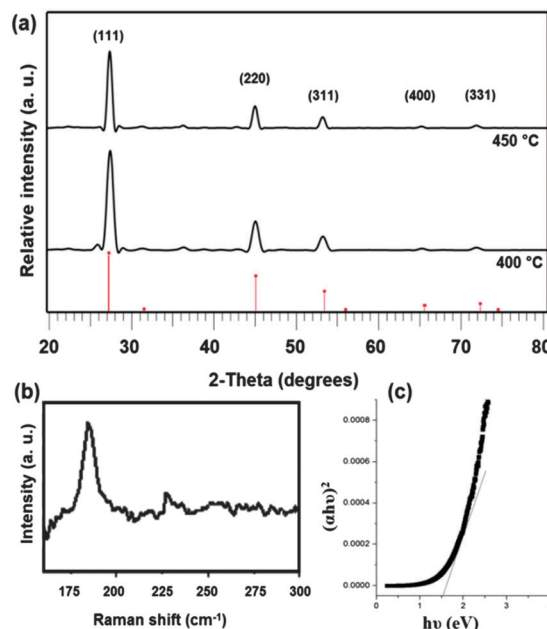


Fig. 2 (a) p-XRD pattern of Cu_2SnSe_3 thin film deposited from $[\text{Sn}(\text{Ph}_2\text{PSe}_2)_2]$ and $[\text{Cu}(\text{acac})_2]$ precursors at 400 and 450 °C indexed with standard ICDD pattern 03-065-4145 for cubic Cu_2SnSe_3 (b) Raman spectrum and (c) band gap plot for Cu_2SnSe_3 thin film deposited at 400 °C.

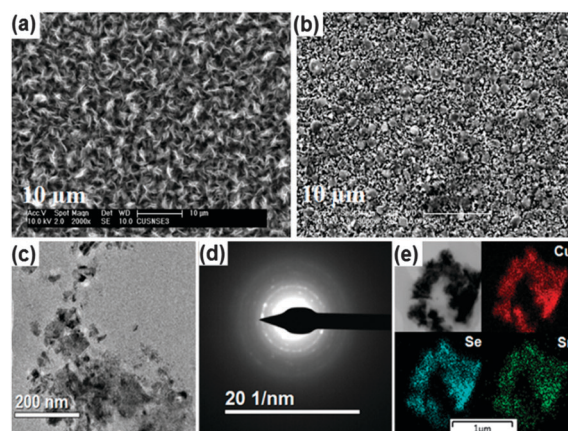


Fig. 3 SEM images of Cu_2SnSe_3 thin films deposited at (a) 400 °C and (b) 450 °C. (c) TEM image (d) SAED pattern and (e) EDX elemental of a single Cu_2SnSe_3 particle.

clearly show that the films deposited at 400 °C are of better quality being uniform in morphology and having better stoichiometry. The Raman spectrum of the thin films deposited at 400 °C is given in Fig. 2b which shows a strong peak at $\sim 180.6 \text{ cm}^{-1}$ with a minor peak at 232 cm^{-1} . These peaks correspond with the reported values (179.9 and 231.6 cm^{-1}) for A_1 and A_2 symmetry modes of Cu_2SnSe_3 .¹⁵ The absence of peaks at 150 and 260 cm^{-1} for CuSe and SnSe shows the deposition of pure Cu_2SnSe_3 . Fig. 2c shows the band gap of the films deposited at 400 °C as $\sim 1.5 \text{ eV}$. This value is in agreement with that reported previously for Cu_2SnSe_3 .^{23–25}

The deposited material was scratched from the films deposited at 400 °C and was further investigated by using transmission



electron microscopy (TEM). TEM image (Fig. 3c) show similar flake like crystals as observed in SEM. Selected area electron diffraction (SAED) pattern showed distinct rings suggesting the polycrystalline nature of the material (Fig. 3d). Elemental mapping of a single particle as shown in Fig. 3e exhibited even distribution of Cu, Sn and Se in the crystal.

A new complex, $[\text{Sn}(\text{Ph}_2\text{PSe}_2)_2]$ has been synthesised and used as single source precursor in combination with $[\text{Cu}(\text{acac})_2]$ for the deposition of monophasic tin selenide (SnSe) and copper tin selenide (Cu_2SnSe_3) thin films onto glass substrates by AACVD at 400 °C and 450 °C. This is the first deposition of thin films of this material by AACVD which has potential applications in photovoltaics and optoelectronics.

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Notes and references

‡ Synthesis of $[\text{Sn}(\text{Ph}_2\text{PSe}_2)_2]$: Ethanolic solution of KOH (1.5 mmol in 5 mL) and metallic Se powder ~100 mesh (0.158 g, 2.0 mmol) were added to ethanolic solution of diphenylphosphine (1.05 mmol in 6 mL EtOH) at room temperature under nitrogen. Vigorous stirring of the suspension was carried out at room temperature for ~5 minutes until all the Se dissolved. Colourless solution thus obtained was filtered and concentrated in rotary evaporator. The residue upon grinding in Et_2O (10 mL) gave potassium diphenylphosphinodiselenoate as white powder upon decanting the solvent and washing with Et_2O . Methanolic solution of SnCl_2 was added drop wise to a solution of 1.911 g (5 mmol) of potassium diphenylphosphinodiselenoate in 100 mL methanol. The precipitate formed was filtered, washed with hot methanol and dried. Yield (91%). Elemental analysis calc. (%) for $\text{C}_{24}\text{H}_{20}\text{P}_2\text{Se}_4$: C 35.81, H 2.50, P 7.70, Sn 14.75; found: C 34.94, H 2.65, P 7.30, Sn 15.01; FTIR 3049 cm^{-1} (Ar–C–H), 685 cm^{-1} (P–C) and 539 cm^{-1} (P=Se); ^1H NMR (400 MHz, CDCl_3 , Me_4Si) δ = 7.81 ppm (dd, 8H, J 3.9, 7.1, 8.9, 4 \times *o*-Ph), 7.44 ppm (m, 12H, 4 \times *p*-Ph and 4 \times *m*-Ph); ^{13}C NMR δ = 127 ppm & 132 ppm (–Ph); APCI-MS: $[\text{Ph}_2\text{PSe}_2]^+ = m/z$ 344.8.

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