Dialkyldiselenophosphinato-metal complexes – a new class of single source precursors for deposition of metal selenide thin films and nanoparticles

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Abstract. We report here a new synthetic approach for convenient and high yield synthesis of dialkyldiselenophosphinato-metal complexes. A number of diphenyldiselenophosphinato-metal as well as diisopropyldiselenophosphinato-metal complexes have been synthesized and used as precursors for deposition of semiconductor thin films and nanoparticles. Cubic Cu_{2-x}Se and tetragonal CuInSe₂ thin films have been deposited by AACVD at 400, 450 and 500 °C whereas cubic PbSe and tetragonal CZTSe thin films have been deposited through doctor blade method followed by annealing. SEM investigations revealed significant differences in morphology of the films deposited at different temperatures. Preparation of Cu_{2-x}Se and In₂Se₃ nanoparticles using diisopropyldiselenophosphinato-metal precursors has been carried out by colloidal method in HDA/TOP system. Cu_{2-x}Se nanoparticles (grown at 250 °C) and In₂Se₃ nanoparticles (grown at 270 °C) have a mean diameter of 5.0 ± 1.2 nm and 13 ± 2.5 nm, respectively.

1. Introduction
Semi-conducting materials like Cu₂Se, PbSe, CdSe, CuInSe₂ (CIS), CuGaSe₂ (CGS), CuIn_(1-x)GaxSe₂ (CIGS), Cu₂ZnSnS₄ (CZTS), Cu₂ZnSnSe₄ (CZTSe) and Cu₂ZnSn(S/Se)₄ (CZTSSe) are the leading absorber materials for solar photovoltaic applications. Solar cells based on potassium doped CIGS thin films have already demonstrated 20.8 % power conversion efficiency (PCE) [1]. Similarly, CZTS/Se materials are being explored as earth abundant solar absorber materials. Several approaches have been employed for the deposition of photo-absorbing semiconductor materials. CIGS based thin films showing maximum efficiency have been deposited via co-evaporation process, whereas hydrazine based solution processing technique has given best results for CZTSSe materials [2]. However, these processes either require high vacuum resulting in higher processing cost and significant loss of materials or involve use of toxic chemicals like hydrazine. Large scale applicability of these techniques is also limited by the difficulty in achieving precise control over the structure, morphology...
and stoichiometric composition of the deposited material over larger substrate area. Consequently, up-scaling of these technologies is presently a significant research challenge.

Chemical vapour deposition (CVD) is a process which employs thermal degradation of vaporized chemical reagents (i.e., precursors) to form thin solid films of target materials onto suitable substrates. Presently, it is regarded as the vital technology for commercial production of solar cells, light-emitting diodes (LEDs), photodetectors, injection lasers, quantum-well lasers, hetero-junction bipolar transistors and various other electronic and optoelectronic devices [3]. The major hindrances to the application of CVD include the unfavourable volatility of the precursors and difficulty in precisely controlling stoichiometry of the deposits. These limitations can be circumvented by aerosol assisted chemical vapour deposition (AACVD) method as aerosols in a stream of inert carrier gases, are used for delivery of the precursors onto substrate. There is no stringent requirement of volatility for AACVD precursors. They should however, be soluble in some solvent in order to generate their aerosols by employing any suitable technique like ultrasonic modulation.

Our previous research efforts involve the synthesis of metal-organic complexes belonging to xanthates, dithiocarbamates, diselenocarbamates, thiourea, selenourea, thiobiurets etc as single source precursors for deposition of high quality semiconductor thin films and nanoparticles. Use of single source precursors in AACVD process further simplifies these issues as it ensures the availability of all requisite elements of semiconductor material in judiciously designed precursor molecule. We have previously synthesized a number of selenophosphinate ligands and reported their use for deposition of semiconductor thin films and nanoparticles [4]. This report deals with an efficient and reproducible synthesis of diphenyldiselenophosphinato-metal precursors and their use for deposition of semiconductor photo-absorbing thin films and nanoparticles for solar photovoltaics applications.

2. Experimental
Diphenylphosphine, Se powder ~ 100 mesh, indium (III) chloride, gallium (III) chloride, copper (II) chloride, copper (I) chloride, tin (II) chloride, zinc (II) chloride, toluene and dichloromethane were purchased from Sigma-Aldrich and used as received. Ethanol and methanol used as solvents in these reactions were also used without carrying out further drying steps. All synthetic manipulations were carried out under an inert atmosphere of nitrogen using standard Schlenk line techniques. $^1$H NMR spectra were recorded on Bruker AC400 FT-NMR spectrometer and a Kratos Concept 1S instrument was used to record mass spectra. Elemental analyses were performed by University of Manchester microanalysis facility. Melting points were recorded using a Stuart melting point apparatus and are uncorrected.

2.1. Deposition of thin films
Glass slides (1 x 3 cm) were used as substrates for the deposition of thin films. Any possible contamination on the substrates was removed by thoroughly cleaning the substrates and sonicating them in acetone for half an hour. An improvised AACVD kit was used for the deposition of thin films. Typical deposition experiment involved dissolving 150 mg of the precursor (or a suitable combination of precursors while depositing the ternary and the quaternary thin films) in 15 mL toluene taken in a two-necked 100 mL round-bottom flask. The flask was connected with a gas inlet which allowed the argon carrier gas to flow through the solution and carry the aerosols generated by a PIFCO ultrasonic humidifier. A piece of reinforced tubing connected the flask to the reactor tube and argon flow rate was controlled at 150 mL/min through a Platon flow gauge. The reactor tube containing 6-8 glass substrates was positioned in a Carbolite furnace. Carrier gas transferred aerosols generated in the flask to the hot zone of the reactor. Thermolysis of both the solvent and the precursor at the hot substrate surface due to thermally induced reactions lead to deposition onto substrates. Deposition experiments were performed at different temperatures i.e., 400, 450 and 500 °C at a constant argon flow rate on substrates for 1.5 h. Some of the thin films were deposited through doctor blade method followed by annealing at different temperature under argon gas flow. p-XRD patterns were recorded on a Bruker D8 AXE diffractometer (Cu-Kα) from 20 to 80 degrees with a step size of 0.05. Morphology and
microstructure of thin films were investigated by using a Philips XL 30 FEGSEM and film composition was studied by EDX analysis using a DX4 instrument.

2.2 Growth of nanoparticles
Nanoparticles were grown by thermolysis of molecular precursors, respectively in HDA/ODE and TOP. Colloidal method, previously reported for growth of CuIn\textsubscript{n-1}\textsubscript{x},Ga\textsubscript{x},Se\textsubscript{2} nanoparticles, was employed with slight modification [5]. UV-Vis-NIR absorption spectra of as grown nanoparticles were recorded in dry toluene using HELIOS \(\lambda\) spectrophotometer. Bruker D8 AXE diffractometer (Cu-K\(\alpha\)) was used to obtain p-XRD patterns of the films of nanoparticles obtained through drop cast method. Phase identification was performed by comparing the p-XRD patterns with the standard ICDD patterns using DIFFRACplus EVA software package. Size and morphology of as synthesized nanoparticles was determined by high resolution transmission electron microscopy (HRTEM). TEM samples were prepared by evaporating a dilute toluene solution of the nanoparticles on carbon coated copper grids (S166-3, Agar Scientific) and TEM images of the nanoparticles were recorded on Philips CM 200 and Tecnai F30 TEM, operated under accelerating voltage of 200 kV and 300 kV, respectively. Stoichiometric composition of the materials was determined by EDX analysis.

3. Results and discussion

3.1. Synthesis of precursor complexes
Synthesis of dialkyldiselenophosphinates has been carried out by many research groups involving diverse synthetic strategies. Lindner et al synthesized \([\text{Ph}_3\text{PSi(Me)}_2]\) through lithiation of diphenylphosphine chloride and this intermediate was subsequently reacted with trimethylsilylchloride at -78°C [6]. Insertion of metallic Se into this species yielded \([\text{Ph}_3\text{PSe}]_2\text{Se}\). As similar intermediates \((\text{R}_3\text{PSeCl})\) can also be synthesized via Benkeser reaction [7], we had previously synthesized a number of diisopropylselenophosphinates and used these compounds as ligands for synthesis metal-organic complexes. However, low reaction yields and lower solubility of these ligands in MeOH, the reaction medium for complexation reaction, remained as issues. In order to overcome these problems, our research efforts were diverted towards synthesis of \([\text{R}_3\text{PSe}]^2\)- anion which was in-situ stabilized by using excess triethylamine (NEt\(_3\)) to yield \([\text{R}_3\text{PSe}]_2(\text{HNEt}_3)^+\) (where \(\text{R} = \text{Ph}, \text{Pr}, \text{Bu}\)). These ligand salts were isolated in good yield and undergo metathesis reaction with metal halides to give corresponding dialkyldiselenophosphinatometal complexes. We have used this approach for synthesis dialkyldiselenophosphinato-metal complexes of a number of metals including Cu, Zn, Pb, In, Ga, Cd and Ni and these complexes have been used as single source precursors for deposition of binary metal selenide thin films and nanoparticles [8]. This method still required longer reaction periods (~ 30 h) under drastic reflux and sometimes suffered with low-yield.

Our quest to develop even simpler and reproducible synthetic strategy for preparation of dialkyldiselenophosphinato-metal complexes led us to a newer method based on the synthesis of potassium diselenophosphinophosphate by reaction of diphenylphosphine, elemental selenium and potassium hydroxide as reported by Gusarova et al [9]. This diselenophosphinic ester salt was then reacted with metal halides to give corresponding dialkyldiselenophosphinatometal complexes. Diphenyldiselenophosphinato- metal complexes with general formula \(\text{M}_x[\text{Ph}_3\text{PSe}]_y\) (where \(\text{M} = \text{Cu}, \text{In}, \text{Ga}, \text{Pb}, \text{Zn}, \text{and Sn}\)) were thus synthesized and characterized accordingly.

3.2. Deposition of thin films
In a recent report, we have described the deposition of Cu\(_2\)Se and In\(_2\)Se\(_3\) thin films onto glass substrates by AACVD using the diisopropylselenophosphinato-metal complex \(\text{Cu}_4[\text{Pr}_3\text{PSe}]_4\) and \(\text{In}[\text{Pr}_3\text{PSe}]_3\) as single source precursors [10]. Ternary \(\text{CuInSe}_2\) and \(\text{CuGaSe}_2\) thin films were also deposited by using 1:4 molar ratios of \(\text{Cu}_4[\text{Pr}_3\text{PSe}]_4\) and \(\text{In}[\text{Pr}_3\text{PSe}]_3\), \(\text{Cu}_4[\text{Pr}_3\text{PSe}]_4\) and \(\text{Ga}[\text{Pr}_3\text{PSe}]_3\) complexes, respectively. Furthermore, the same complexes were also used for deposition of CIGSe (CuIn\(_{0.7}\)Ga\(_{0.3}\)Se\(_2\)) thin films by using 1:2:2 ratio of the copper, indium and gallium.
complexes, respectively. Present work deals with the deposition of Cu$_{2-x}$Se and CuInSe$_2$ thin films by AACVD process. Furthermore, PbSe and CZTSe thin films have been deposited by doctor blading the precursor complexes onto glass substrates and subsequent annealing of the as deposited thin films in an argon atmosphere at various temperatures.

Figure 1A shows the p-XRD patterns of the Cu$_{2-x}$Se thin films deposited at 400 °C, 450 °C and 500 °C by AACVD process. XRD analyses revealed that the berzelianite phase of cubic Cu$_{2-x}$Se (standard ICDD pattern 06-0680) has been deposited at all the temperatures. All the films showed a preferred orientation along (111) plane while other major peaks were observed at (220), (311) planes at 44.6 and 52.9 on 2-theta axis. Sharp and narrow peaks demonstrated good crystallinity of the deposited material. Microstructural studies through SEM images showed growth of randomly shaped grains having distinct grain boundaries for films deposited at 400 °C (Fig. 1B) and 450 °C (Fig. 1C). Larger grains having triangular faceting were observed in the thin film deposited at 500 °C (Fig. 1D). EDX analyses showed that the films had a Cu deficient morphology and this deficiency was even more pronounced for thin film deposited at 500 °C.

Deposition of CuInSe$_2$ has been carried out by AACVD using 1:4 molar ratio of Cu$_4$[Ph$_2$PSe$_2$]$_4$ and In[Ph$_2$PSe$_2$]$_3$, respectively at 450 °C and 500 °C. p-XRD patterns of as deposited thin films are shown in Figure 2A which revealed deposition of tetragonal phase of CuInSe$_2$ (standard ICDD pattern 040-1487). Preferred orientation of deposited material along (112) plane was observed which is typical for copper chalcogenide materials deposited through CVD. SEM imaging used to study microstructure of thin films revealed deposition of rice like grains deposited at 450 °C (Fig. 2B) whereas films deposited at 500 °C exhibited somewhat spherical grains with distinct grain boundaries. 1:1:2 atomic ratio for Cu, In and Se was demonstrated by EDX analyses in both the films.

Lead selenide (PbSe) thin films have been deposited by doctor blading the complex Pb[Ph$_2$PSe$_2$]$_2$ onto glass substrate and then annealing the films in argon atmosphere at different
temperatures. Weakly adhered dark brown films were obtained at all deposition temperatures. Figure 3A shows the p-XRD patterns for as deposited thin films at 400 °C, 450 °C and 500 °C. Phase analyses demonstrates that these p-XRD patterns can be indexed to clausthalite phase of cubic PbSe (standard ICDD pattern 06-0356). Thin films deposited at all temperatures had preferred orientation along (200) plane. SEM image of the thin film deposited at 400 °C (Fig. 3B) showed deposition of small sized cubic PbSe crystallites with poor coverage of the film. However, densely populated films were obtained at 450 °C (Fig. 3C) and the film deposited at 500 °C (Fig. 3D) showed linearly arranged streaks of PbSe cubes fully covering the glass substrate. EDX analyses demonstrated 1:1 ratio of the lead and selenium atoms within the error limits of EDX technique. No individual differences were observed in the stoichiometric composition of individual grains.

Figure 2. (A) p-XRD patterns of CuInSe$_2$ thin films deposited by AACVD using 1:4 molar ratio Cu$_4$[Ph$_2$PSe$_2$)$_4$ and In[Ph$_2$PSe$_2$]$_3$ complexes at (a) 450 °C and (b) 500 °C indexed with standard ICDD pattern 040-1487 for tetragonal CuInSe$_2$ (B) SEM image of as deposited PbSe thin film at 450 °C and (C) at 500 °C.

Thin films of the quaternary material CZTSe were deposited by the doctor blade method using 0.5:1:1 molar ratio of Cu$_4$[Ph$_2$PSe$_2$]$_4$, Zn[Ph$_2$PSe$_2$]$_2$, and Sn[Ph$_2$PSe$_2$]$_2$ precursors, respectively. The films were later annealed at 500 °C under argon atmosphere for 2 hours. Figure 4A shows p-XRD pattern of CZTSe of the as deposited film which fairly matches with the standard ICDD pattern 052-0868 for tetragonal phase of Cu$_2$ZnSnSe$_4$. Relatively broader peaks suggest deposition of small sized crystallites and absence of any peaks from binary or ternary phases indicates deposition of monophasic CZTSe onto thin films. Morphological studies of the films by SEM imaging (Fig. 4B & 4C) revealed deposition of nano-sized globular clusters onto thin films. Stoichiometric ratio of Cu, Zn, Sn and Se was found to be Cu$_{1.91}$Zn$_{1.13}$Sn$_{1.00}$Se$_{4.28}$ as determined by EDX analyses. These values are fairly close to the expected Cu$_2$ZnSnSe$_4$ stoichiometry. Selected area EDX elemental mapping (Fig. 4D) confirmed uniform distribution of Cu, Zn, Sn and Se throughout the film.
Figure 3. (A) p-XRD patterns of PbSe thin films deposited by doctor blading the suspension of Pb[Ph$_2$PSe$_2$]$_2$ complex and annealing at (a) 400 °C (b) 450 °C and (c) 500 °C indexed with standard ICDD pattern 06-0356 for cubic phase of PbSe (B) SEM image of as deposited PbSe thin film at 400 °C (C) at 450 °C and (D) at 500 °C.

Figure 4. (A) p-XRD patterns of CZTSe thin film deposited by doctor blading the suspension of Cu$_4$[Ph$_2$PSe$_2$]$_4$, Zn[Ph$_2$PSe$_2$]$_2$ and Sn[Ph$_2$PSe$_2$]$_2$ complexes onto glass substrates and annealing at 500 °C. Vertical lines below show standard ICDD pattern 052-0868 for tetragonal CZTSe (B) & (C) SEM images of as deposited CZTSe thin film (D) EDX elemental mapping showing uniform distribution of Cu, Zn, Sn and Se in the film.
3.3. Growth of nanoparticles

Colloidal method was chosen for growth of semiconductor nanoparticles from dialkyldiselenophosphinato-metal precursors as this method provides better control over crystallite size and stoichiometric composition of the nanoparticles. In a previous report, we have described colloidal preparation of CuInSe$_2$, CuGaSe$_2$, and CuIn$_{1-x}$Ga$_x$Se$_2$ nanoparticles from diisopropyldiselenophosphinato-metal precursors [5]. In present work, we report the preparation of Cu$_{2-x}$Se and In$_2$Se$_3$ nanoparticles from diisopropyldiselenophosphinato-metal complexes as single source precursors.

![Figure 5](image.png)

Figure 5. (A) p-XRD patterns of cubic Cu$_{2-x}$Se nanoparticles synthesized from (a) 0.15 g (0.11 mmol) precursor at 250 °C (b) 0.3 g (0.22 mmol) precursor at 250 °C and (c) 0.15 g (0.11 mmol) precursor at 300 °C indexed with the standard ICDD pattern 006-680 for cubic Cu$_{2-x}$Se phase (ICDD 00-006-0680) are shown in Figure 5A. Mean diameter of the nanoparticles was calculated using Scherrer equation and it was found that the mean diameter of nanoparticles synthesized from 0.22 mmol precursor at 250 °C was 14.4 nm, which is in good agreement with the results obtained from TEM images. It was observed that higher precursor concentration and reaction temperature leads to increase in mean diameter of the nanoparticles, as evident from the stronger XRD peaks. Figure 5B (a) shows TEM images of the HDA capped Cu$_{2-x}$Se nanoparticles grown from 0.3 g (0.22 mmol) of [Cu$_4$(iPr$_2$PSe)$_2$$_4$] precursor at 250 °C. Well defined Cu$_{2-x}$Se nanocrystals were observed in TEM images while HR-TEM image (Figure 5B (b) clearly shows lattice fringes. Interplaner distances were found to be 0.33 nm which are consistent with the known value for d$_{111}$ interplaner distance of cubic Cu$_{2-x}$Se nanoparticles.

Thermolysis of 0.3 g (0.22 mmol) of Cu$_4$(iPr$_2$PSe)$_2$$_4$ in HDA/TOP system at 250 °C yielded brown Cu$_{2-x}$Se nanoparticles. UV-Vis absorption spectrum of as grown nanoparticles showed band edge at 860 nm. XRD patterns of the HDA capped nanoparticles prepared at different temperatures as compared to standard ICDD pattern for cubic Cu$_{2-x}$Se phase (ICDD 00-006-0680) are shown in Figure 5A. Mean diameter of the nanoparticles was calculated using Scherrer equation and it was found that the mean diameter of nanoparticles synthesized from 0.22 mmol precursor at 250 °C was 14.4 nm, which is in good agreement with the results obtained from TEM images. It was observed that higher precursor concentration and reaction temperature leads to increase in mean diameter of the nanoparticles, as evident from the stronger XRD peaks. Figure 5B (a) shows TEM images of the HDA capped Cu$_{2-x}$Se nanoparticles obtained from thermolysis of 0.22 mmol of [Cu$_4$(iPr$_2$PSe)$_2$$_4$] precursor at 250 °C. Well defined Cu$_{2-x}$Se nanocrystals were observed in TEM images while HR-TEM image (Figure 5B (b) clearly shows lattice fringes. Interplaner distances were found to be 0.33 nm which are consistent with the known value for d$_{111}$ interplaner distance of cubic Cu$_{2-x}$Se nanoparticles.
Indium selenide nanoparticles were grown by thermolysis of the $\text{[In}^{(\text{iPr}_2\text{PSe}_2)_3}\text{]}$ precursor at 270 °C in HDA/TOP system. The TEM image of nanoparticles grown at 270 °C for 2 hour showed well formed equi-axed crystallites with an average size of 5.0 ± 1.2 nm (Figure 6B a & b). Crystallographic phase of the nanoparticles was studied by powder X-ray diffraction. XRD pattern of the HDA capped nanoparticles (Figure 6A) corresponds to the hexagonal $\text{In}_2\text{Se}_3$ phase (ICDD pattern 00-012-0117). Preferred orientation along (102) lattice plane was observed in the material and broader diffraction peaks indicated formation of very small nanoparticles. This was also supported by TEM images of the nanoparticles. Previously we have synthesized InSe nanoparticles with an average size of 6.4 nm by thermolyzing single source precursor $\text{[In(Se}_2\text{CNEt}_2)_3\text{]}$ in TOPO at 250 °C [11]. However, in this study, phase present in the nanoparticles could not be defined due to poor crystallinity of the material. In a later report, hexagonal ‘wafer-like’ nanocrystals with average diameter of 141 nm (± 24 nm) were synthesized by reaction of $\text{In(OAc)}_3$ and Se in HDA at 300 °C [12]. In this report, longer reaction durations (18 h) were employed which might be the cause of the formation of larger nanocrystals.

Figure 6. (A) p-XRD pattern of HDA capped $\text{In}_2\text{Se}_3$ nanoparticles grown at 270 °C from $\text{[In}^{(\text{iPr}_2\text{PSe}_2)_3}\text{]}$ precursor. Vertical lines below show standard ICDD pattern 00-012-0117 for hexagonal $\text{In}_2\text{Se}_3$ (B) (a) TEM and (b) HR-TEM images of HDA capped $\text{In}_2\text{Se}_3$ nanoparticles grown at 270 °C.

4. Conclusions
We have devised a new strategy for facile and reproducible synthesis of dialkyldiselenophosphinato-metal complexes. These complexes have been successfully utilized as single source precursors for deposition of binary metal selenide thin films and nanoparticles. Deposition of ternary and quaternary monophasic thin films has also been carried out using these precursors. These dialkyldiselenophosphinometal complexes are a useful addition to the family of selenide molecular precursors as they exhibit fair air and moisture stability. Furthermore, they undergo clean decomposition in AACVD experiments as well as in HDA/TOP system yielding phase pure metal.
selenide thin films and nanoparticles. Future work will involve deposition of thin films and nanoparticles of multinary semiconductor materials like Cu$_2$ZnSn(S/Se)$_4$.

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