Preparation of Phase-Pure InSe Thin Films by MOCVD Using a New Single-Source Precursor $[(Me)_2In(\mu\text{-}SeMe)]_2$

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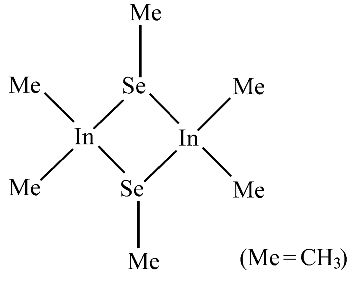
Recently, the preparation of indium selenide thin film has been an active research subject of considerable interest due mainly to its potential for optoelectronic or photovoltaic applications.[1,2] Researches on InSe thin films prepared by metal-organic chemical vapor deposition (MOCVD) method reveal that indium selenide has a hexagonal lamellar structure, and that their electrical, optical, and structural properties are known to strongly depend on their organometallic precursors, film preparation technique, deposition temperature, and post-deposition annealing process.[3]

The most difficult task in the preparation has been to obtain stoichiometric InSe; while In_2Se_3 was successfully grown by MOCVD using $In(SeR)_3[R=Ph, C(SiMe_3)_3]$, the growth of phase-pure InSe has not been observed despite the use of a single-source precursor, containing In and Se atoms in their ratio of 1 : 1, such as $[Me_2In(\mu\text{-}SePh)]_2$, $[(^tBu)_2In(\mu\text{-}Se\text{-}^tBu)]_2$. They typically lead to different stoichiometric or selenium deficient compounds in a single precursor MOCVD process.[4-7]

Present study deals with an experimental investigation to prepare a phase-pure InSe thin film using a new single-source precursor$[(Me)_2In(\mu\text{-}SeMe)]_2$ as shown below;



Synthesis of $[(Me)_2In(\mu\text{-}SeMe)]_2$: This relatively simple precursor was synthesized by reacting trimethyl indium (Morton Metalorganics: 0.995 g, 6.25 mmol) and dimethyl diselenide (Aldrich; 1.175 g, 6.25 mmol) in a 70 mL pentane solution at room temperature according to the similar reaction using trimethyl aluminum and dimethyldiselenide, reported by Oliver and coworkers.[8] All synthetic works were carried out in a double vacuum line and a glove box under argon. The product (yield: 90%) was rather easily characterized by ^1H, ^{13}C NMR (Varian Gemini 2000), mass (Micromass, Autospec EBE), and IR (Jasco, FT-IR 5300) spectroscopies: **$[(Me)_2In(\mu\text{-}SeMe)]_2$**: white powder, mp 154 °C, EI-MS m/z 463 ($M^+\text{-}CH_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 0.117 (s, 3H), 2.052 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ –1.700, 0.053; FT-IR 2950, 1428, 1280, 1158, 900, 680-720, 521, 481 cm^{-1}.

TG/DSC (Setaram, LABSYS) thermograms indicate that it melts at 154 °C and starts to decompose at about 200 °C. Assuming the loss of methyl groups, overall weight loss is expected to be 18.8%, but it was found to be 40%, indicative of decomposition accompanying sublimation of the precursor. Thin film deposition on GaAs substrates was performed using a horizontal flow CVD system under low pressure in a purified argon flow at a chamber pressure of 20 mTorr. In a typical deposition experiment, the precursor contained in a bubbler was heated to 80 °C and the substrate to 250-370 °C.

Surprisingly, the X-ray diffraction (XRD) (Scintag, XDS-2000) pattern of the resulting black colored thin film coincides quite well with that of the known hexagonal InSe (JCPDS No. 34-1431), in which the In : Se ratio is 1 : 1, and it is noteworthy that there are no other phases such as In_2Se_3, In_3Se_4, and In_2Se as shown in Figure 1.

In separate experiments, the In : Se ratio was reexamined by X-ray photoelectron spectroscopy (XPS) (VG Scientific Ltd., ESCALAB MK-11), but result was consistent with above one, and there were no appreciable amounts of carbon or oxygen impurities except them due to surface contamination during the experimental process. In order to get

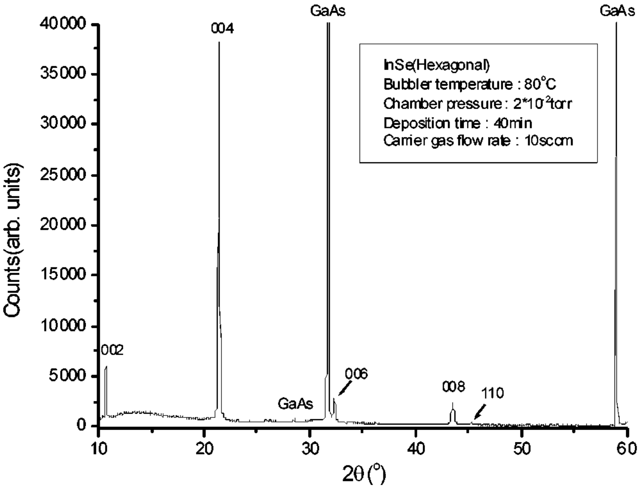


Figure 1. XRD of InSe film grown at 315 °C using $[(Me)_2In(\mu\text{-}SeMe)]_2$.

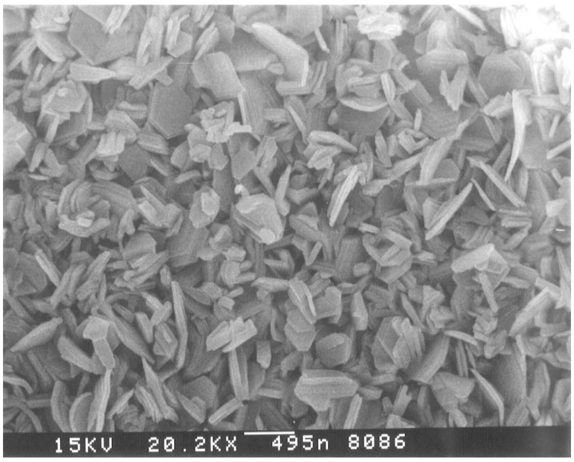


Figure 2. SEM image of InSe film grown at 315 °C using $[(Me)_2In(\mu\text{-}SeMe)]_2$.

information about the decomposition process, a gas mixture was collected during the solid state thermolysis of the precursor and analyzed by gas phase IR spectroscopy. Its major components were easily identified to be methane and ethane gases with a trace amount of dimethyl selenoketon compound, by comparing known gas phase IR spectra.[9] As predicted, there were no other infrared spectral evidences for methyl selenol, dimethyldiselenide, and trimethyl indium compounds, which might lead to different stoichiometric indium selenide compounds.

The band gap of the InSe thin films was found to be 1.187 eV on the basis of photoluminescence data, which is suitable for optoelectronic and photovoltaic applications.[3,10]

Scanning electron micrographs (I.S. I-DS 130 SEM) of the InSe films show that they have typical polycrystalline structure as shown in Figure 2 and that the InSe particles have a mean size of 445 nm with relatively narrow size distribution.

Thus, a new single-source precursor $[(Me)_2In(\mu\text{-}SeMe)]_2$ was synthesized and characterized. Using this precursor, phase-pure InSe thin films without any other indium selenide phase were successfully grown at 270-370 °C by lowpressure metal-organic vapor deposition method.

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