

# Molecular Design of Single-Source Precursors for 3-6 Semiconductor Films: Control of Phase and Stoichiometry in $\text{In}_x\text{Se}_y$ Films Deposited by a Spray MOCVD Process Using Single-Source Reagents

Henry J. Gysling\* and Alex A. Wernberg

Corporate Research Laboratories, Eastman Kodak Company, Rochester, New York 14650-2111

Thomas N. Blanton

Analytical Technology Division, Eastman Kodak Company, Rochester, New York 14652-3712

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Thin films of the 3-6 semiconductors  $\text{InSe}$  and  $\text{In}_2\text{Se}_3$  have been prepared by a spray MOCVD process using  $\text{Me}_2\text{InSePh}$  and  $\text{In}(\text{SePh})_3$ , respectively, as single-source precursors. The new compound,  $\text{Me}_2\text{InSePh}$ , was prepared by a redistribution reaction between  $\text{InMe}_3$  and  $\text{In}(\text{SePh})_3$  (2:1 molar ratio in toluene) and  $\text{In}(\text{SePh})_3$  was prepared by an oxidative addition reaction of diphenyl diselenide ( $\text{Ph}_2\text{Se}_2$ ) and indium powder in refluxing toluene. The fabrication of the films was carried out by ultrasonically nebulizing a toluene solution of the precursor and transporting the mist, in an argon carrier gas, into a heated reactor zone containing the substrate. With a  $\text{GaAs}(100)$  substrate at 408-477 °C the  $\text{InSe}$  films were primarily the known hexagonal phase with a low level of a new zinc blende-like cubic phase. When the substrate temperature was lowered to 309-365 °C, films of the new cubic phase ( $a = 5.72 \text{ \AA}$ ) were obtained. Solid-state pyrolysis of the  $\text{In}(\text{SePh})_3$  precursor, under an argon atmosphere, gives  $\text{In}_2\text{Se}_3$ ,  $\text{SePh}_2$ , and  $\text{Se}_2\text{Ph}_2$ . Highly (001) oriented thin films of hexagonal  $\text{In}_2\text{Se}_3$  have been prepared on a  $\text{GaAs}(100)$  substrate at temperatures between 470 and 530 °C. The films were characterized by X-ray diffraction and scanning electron microscopy.

## Introduction

The fabrication of films of refractory ceramics (e.g.,  $\text{TiC}$ ,<sup>1</sup>  $\text{AlN}$ ,<sup>2</sup>  $\text{TiB}_2$ ,<sup>3</sup>  $\text{BN}$ ,<sup>4</sup>  $\text{Zr}_3\text{N}_4$ ,<sup>5</sup>  $\text{Nb}_3\text{N}_4$ ,<sup>5</sup>  $\text{V}_4\text{C}_3$ ,<sup>6</sup>) and semiconductors (e.g., III-V,<sup>7</sup> II-VI,<sup>8</sup> and III-VI<sup>9</sup> materials) by use of single-source reagents has recently become an area of considerable research interest. The use of such molecular

precursor reagents that incorporate atomic bonds corresponding to those of the solid-state species may provide significantly improved processes for the fabrication of films due to the inherent control of stoichiometry and the resulting simplified fabrication equipment compared to multiple-source processes. In addition, such reagents generally allow deposition of the desired phase at temperatures lower than those of the conventional multiple source processes (e.g., the deposition of  $\text{TiC}$  at 200 °C using  $\text{Ti}(\text{neopentyl})_4$  versus conventional CVD processes using  $\text{TiCl}_4$ ,  $\text{H}_2$ , and a hydrocarbon, which operate at 1100-1350 °C, is an extreme example of the potential of single-source chemistry for low-temperature film fabrication<sup>1</sup>). The low substrate temperatures often used in CVD processes with such single-source precursor reagents may also result in the deposition of new phases (e.g.,  $\text{Nb}_3\text{N}_4$  deposited using  $\text{Nb}(\text{NEt}_2)_4$  at 300 °C,<sup>5</sup> cubic  $\text{GaN}$  deposited at 150 °C using  $\{\text{H}_2\text{GaNH}_2\}_{13}$ <sup>10</sup>).

Although chemical vapor deposition (CVD) and its various modifications have been the most widely used techniques for the deposition of thin films using molecular reagents, spray pyrolysis<sup>11</sup> is a somewhat more experimentally convenient process for precursors that have low volatility. Spray pyrolysis processes for the deposition of simple oxides using aqueous salt solution of the appropriate metals have been extensively reported in the literature (e.g.,  $\text{ZnO}$ <sup>11,12</sup> and  $\text{CuO}$ <sup>11,13</sup>). Aqueous solutions of multiple precursor reagents have also been used to deposit complex oxides (e.g., high- $T_c$  superconductors<sup>14</sup>) and

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chalcogenides (e.g., CdS,<sup>11,15</sup> CuInS<sub>2</sub>,<sup>11,16</sup> CuInSe<sub>2</sub><sup>11,17</sup>). For deposition of the chalcogenide films an appropriate sulfur or selenium ligand (i.e., thiourea, selenourea, sodium selenosulfate) was added to the solution of the metal salt. High-quality oriented films suitable for electronic device applications generally cannot be prepared by this type of process due to the poor growth characteristics associated with the use of these nonvolatile precursors.

Recently, Wold et al.<sup>18</sup> reported that films of improved quality could be obtained by using precursors that can be vaporized during the spray pyrolysis process. In this modification by Wold et al.,<sup>18</sup> the solution droplets vaporize prior to reaching the heated substrate surface to allow vapor-phase transport of the molecular precursor reagent to the substrate surface. This process is, therefore, essentially a CVD process in which transport of the precursor into the reactor is effected by a solvent mist with the final transport to the substrate surface being in the vapor phase. We shall refer to this fabrication process as spray MOCVD to reflect the above considerations. Wold et al. have reported the deposition of various oxide films by this spray MOCVD process using ethanol solutions of volatile acetylacetonates (e.g., ZrO<sub>2</sub>,<sup>18a</sup> Cr<sub>2</sub>O<sub>3</sub>,<sup>18b</sup> TiO<sub>2</sub>,<sup>18c</sup> Y<sub>2</sub>O<sub>3</sub>,<sup>18d</sup> La<sub>2</sub>O<sub>3</sub>,<sup>18d</sup> La<sub>2</sub>CuO<sub>4</sub>,<sup>18d</sup> and Fe<sub>2</sub>O<sub>3</sub><sup>18e</sup>).

The fabrication of thin films of III-VI semiconductors<sup>19</sup> has been the subject of relatively few reports in the literature. Amorphous films of InSe, a layer-type semiconductor, have been prepared by thermal evaporation<sup>20</sup> and radio frequency (rf) sputtering.<sup>21</sup> The electrical, optical, photoelectric and photovoltaic characteristics of these films have been evaluated, and their possible applications include switching devices, photovoltaics, and nonlinear optics.<sup>19a,20</sup>

Films of In<sub>2</sub>Se<sub>3</sub>, which exists as four crystalline modifications,<sup>22</sup> have been prepared by thermal evaporation<sup>23</sup> and an electrochemical method in which alternate layers

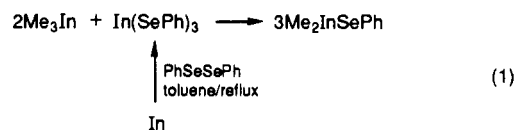
of Se and In were electrodeposited onto a titanium substrate with subsequent thermal annealing.<sup>24</sup> Relatively limited data are available for this material (i.e., bandgap of the  $\beta$  phase, 1.39 eV,<sup>23a</sup> resistivity,<sup>22a,23a</sup> and photoluminescence<sup>25</sup> properties, and structural and phase transformation studies.<sup>22b,c23a,26</sup>

Thin films of In<sub>2-x</sub>Ga<sub>x</sub>S<sub>3</sub> ( $x = 0-2$ ), prepared by spray pyrolysis from aqueous solutions of reagents (e.g., InCl<sub>3</sub>, GaCl<sub>3</sub>, and thiourea in 1:1 methanol-water), are of poor crystalline quality due to the low volatility of the precursors.<sup>27</sup> Nomura et al. have recently reported single-source precursors for the preparation of films of InS<sup>9c</sup> and  $\beta$ -In<sub>2</sub>S<sub>3</sub>.<sup>9a-c</sup> Using *n*-BuIn(S-*i*-Pr)<sub>2</sub>,<sup>9a-c</sup> these workers were able to prepare oriented films of In<sub>2</sub>S<sub>3</sub> by a chemical vapor deposition process. Kanatzidis et al.<sup>28</sup> have reported the synthesis of anionic In/Se cluster species (i.e., {In<sub>2</sub>Se<sub>21</sub>}<sup>4-</sup> and {In<sub>3</sub>Se<sub>15</sub>}<sup>3-</sup> and suggested their use as precursors for InSe and In<sub>2</sub>Se<sub>3</sub> films. Solid-state pyrolysis of [PPh<sub>4</sub>]<sub>4</sub>{In<sub>2</sub>Se<sub>21</sub>} has been shown to give  $\beta$ -In<sub>2</sub>Se<sub>3</sub> in the temperature range 350-536 °C.<sup>28b</sup>

In earlier work we reported the fabrication of thin films of III-V (i.e., GaP, GaAs<sup>7d,29</sup>) semiconductor films by various solution- and vapor-phase processes using single-source precursor reagents. We report here the fabrication of oriented films of the III-VI semiconductors InSe and In<sub>2</sub>Se<sub>3</sub> by a spray MOCVD process using Me<sub>2</sub>InSePh and In(SePh)<sub>3</sub>, respectively, as single-source precursors and the characterization of the films by X-ray diffraction and scanning electron microscopy. We demonstrate the ability to control the film phase and stoichiometry in such III-VI materials by molecular design of the single-source precursor reagents.

## Results and Discussion

**Fabrication of InSe Films Using the Single-Source Precursor Me<sub>2</sub>InSePh.** A single-source precursor for film fabrication by the spray MOCVD process ideally incorporates the bonds found in the desired solid-state phase, contains the appropriate atomic stoichiometry of the elements in the target phase and has solubility in a suitable transport solvent and sufficient volatility to allow the vapor transport required for the deposition of high-quality films using this process. Such a molecular precursor reagent for InSe films, Me<sub>2</sub>InSePh, was prepared using a redistribution reaction between InMe<sub>3</sub> and In(SePh)<sub>3</sub> in toluene (eq 1).



The tris(phenylselenolato)indium(III) was prepared by the oxidative addition of diphenyl diselenide with indium

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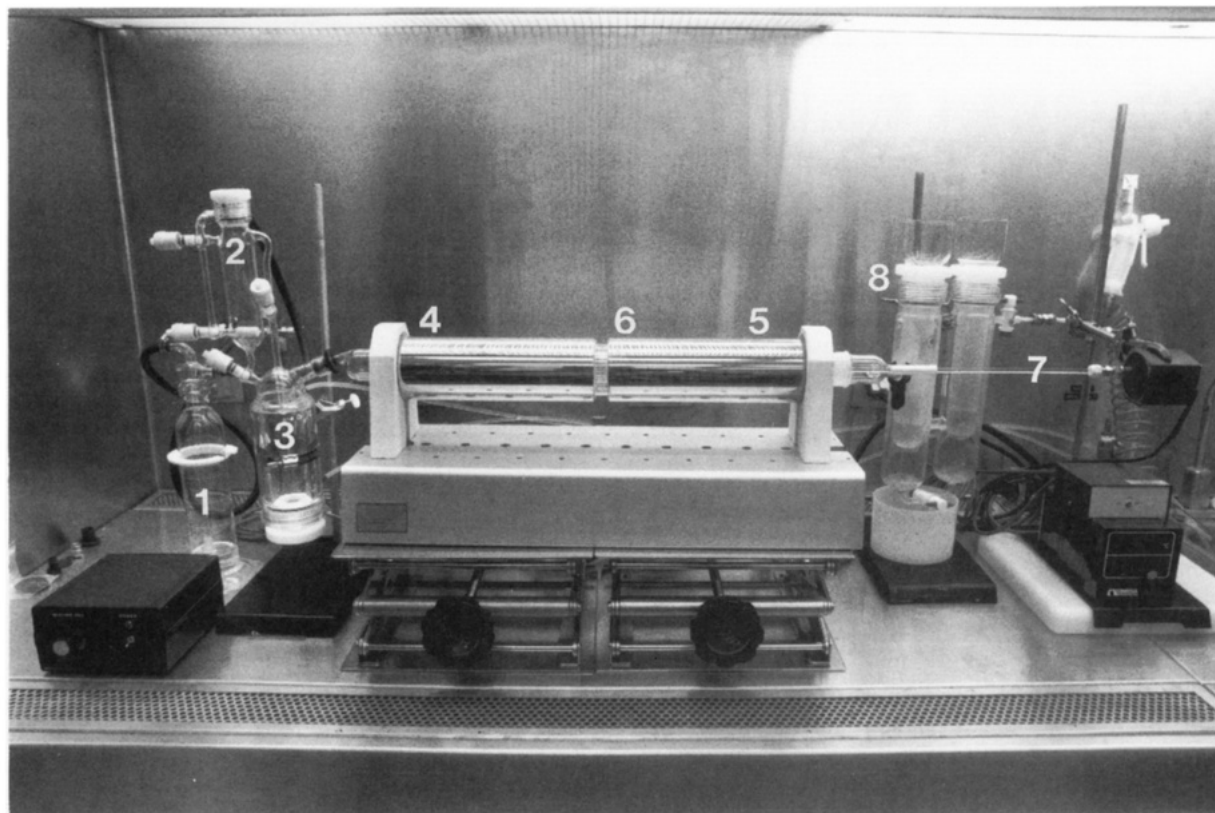
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**Figure 1.** Spray MOCVD reactor: (1) bubbler for solvent saturation; (2) reservoir containing precursor solution; (3) nebulization chamber; (4) lower-temperature zone of the reactor; (5) high-temperature zone of the reactor; (6) substrate position; (7) rotating glass rod attached to the quartz sample holder; (8) dry ice/acetone trap for exit mist.

powder in refluxing toluene as previously described by Tuck et al.<sup>30</sup> Such redistribution reactions have been routinely used to prepare organometallic halides of gallium and indium<sup>31</sup> and, recently, have been used to prepare single-source 3–5 precursors (e.g.,  $\{\text{Bu}_2\text{InP}(t\text{-Bu})_2\}_2$ ,  $\{\text{Bu}_2\text{GaAs}(t\text{-Bu})_2\}_2$ <sup>32</sup>). The product of the above reaction, obtained as a white solid after recrystallization from hexane, is probably dimeric or trimeric (e.g.,  $\{\text{Me}_2\text{InSb}(t\text{-Bu})_2\}_3$ ,<sup>7c</sup>  $\{\text{Me}_2\text{InP}(i\text{-Pr})_2\}_2$ ,<sup>7f</sup>  $\{\text{Me}_2\text{InP}(i\text{-Pr})_2\}_3$ ,<sup>7f</sup>  $\{\text{Me}_2\text{InAsMe}_2\}_3$ ,<sup>33a</sup>  $[\text{Me}_2\text{In}(\text{PPh}_2)]_2$ <sup>33b</sup>) although suitable crystals could not be obtained for an unequivocal X-ray diffraction study.

Thin films of InSe were obtained from this precursor using the spray MOCVD apparatus shown in Figure 1; 200 mL of a 0.0086 M solution of the precursor was transferred, in a glovebox, into the nebulization chamber (Figure 1–2). After attachment of this chamber to the reactor assembly illustrated in Figure 1, a mist of the solution was passed into the heated zone of the reactor using ultrasonic nebulization and an argon flow rate of 4.5 SLM. With a GaAs(100) substrate heated to 365 °C, a film of a cubic  $\text{In}_x\text{Se}_y$  phase (lattice constant  $a = 5.72 \text{ \AA}$ ) was obtained. The X-ray diffraction pattern of this film is shown in Figure 2A. The composition of this new cubic phase cannot be unambiguously assigned since the elemental analyses (Se:In = 1.2) and the diffraction patterns obtained

for the films do not correspond to any of the reported  $\text{In}_x\text{Se}_y$  phases. This suggests that the film formed at low temperature (Figure 2A) contains not only the cubic phase but also an amorphous phase rich in selenium. The experimental evidence and the known reactivity of these precursors are consistent with the new cubic phase being either InSe or  $\text{In}_2\text{Se}_3$  and having a zinc blende-type structure. Using a substrate temperature of 309 °C, a film with an essentially identical X-ray diffraction pattern was obtained. Scanning electron micrographs of a film prepared at 365 °C (Figure 3A, surface; Figure 3B, cross section) show that film growth occurs preferentially in the direction perpendicular to the substrate surface.

When the substrate temperature was held between 408 and 476 °C, the resulting films contained both a low level of the above cubic phase and a major level of the known hexagonal InSe phase<sup>34</sup> (JCPDS No. 34-1431: 3.41, 2.94, 2.40, and 1.97 Å; these peaks are reported to be broad as observed in the X-ray diffraction pattern of the high-temperature film prepared in this work (Figure 2B)). Elemental analyses of this film indicate the stoichiometry is much closer to that expected for a monophasic InSe film (Se:In = 1.05). Scanning electron micrographs of a film prepared at 476 °C (Figure 4A, surface; Figure 4B, cross section) shown an oriented growth with thin needles interspersed between larger platelets. The thin needles could possibly be the minor cubic phase with the larger platelets being the major InSe hexagonal phase.

**Fabrication of  $\text{In}_2\text{Se}_3$  Films Using the Single-Source Precursor  $\text{In}(\text{SePh})_3$ .** Tris(benzene-selenolato)indium(III), which can be readily prepared by an oxidative addition type reaction between indium powder and diphenyl diselenide in refluxing toluene,<sup>30</sup> was

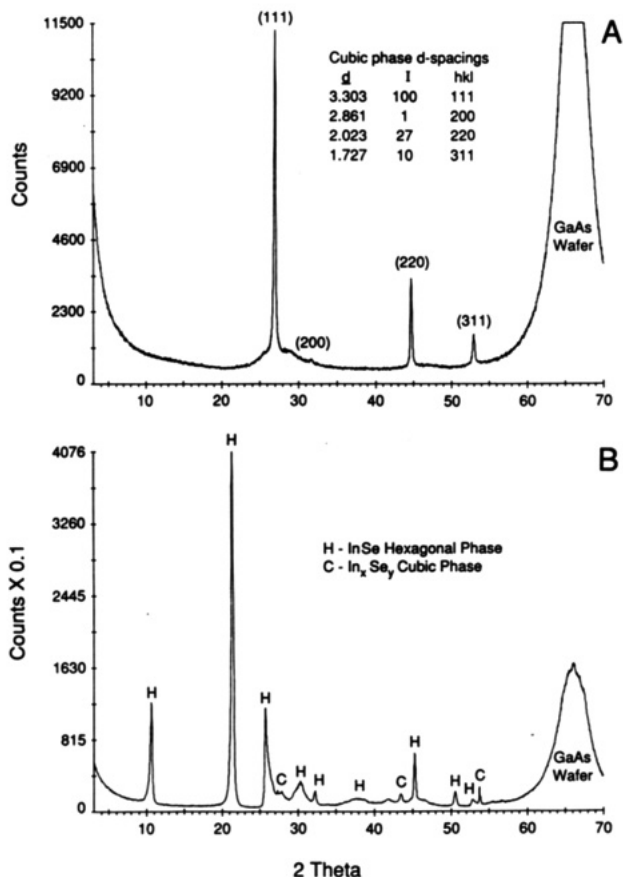
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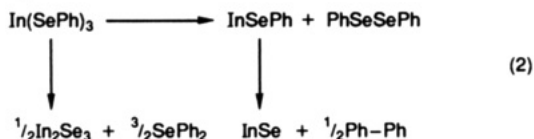
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**Figure 2.** X-ray diffraction patterns of  $\text{In}_2\text{Se}_3$  films deposited on GaAs(100) substrates using the  $\text{Me}_2\text{InSePh}$  precursor: (A) 365 °C; (B) 476 °C.

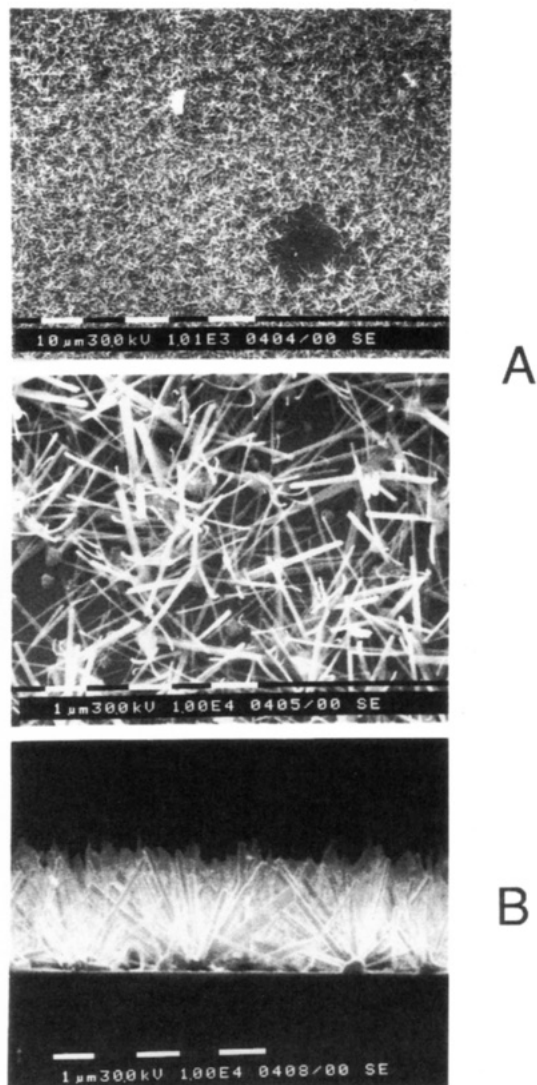
selected for initial evaluation as a single-source reagent for  $\text{In}_2\text{Se}_3$  films. The 3:1 Se:In ratio in this compound suggested that it could either decompose to the desired  $\text{In}_2\text{Se}_3$  phase or, via an initial reductive elimination reaction to the In(I) derivative  $\text{InSePh}$ , decompose to  $\text{InSe}$  (eq 2). A number of stable In(I) compounds have been isolated and structurally characterized.<sup>35</sup>



$\text{In}(\text{SePh})_3$  is a pale yellow, air-stable solid (mp = 148 °C (recrystallized from toluene)) that is soluble in polar solvents and sufficiently soluble in toluene (ca. 0.01 M) for its use in the spray MOCVD process. Tuck et al.<sup>36</sup> have also reported that the molecular structure of tris(benzeneselenolato)indium(III) is a homopolymer with linear chains formed by indium and selenium atoms running parallel to the  $a$  axis of the unit cell with each indium coordinated by six selenium atoms and each selenium bridging two indium atoms. This compound has been reported to vaporize as the monomer on the basis of its field desorption mass spectrum ( $m/e$ : molecular ion, 586;  $\text{InSe}(\text{SePh})_2^{2+}$  (506), and  $\text{Se}_2\text{Ph}_2^{2+}$  (314)).<sup>36</sup> We find,

(35) (a) Tuck, D. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 1, p 684. (b) Mabrouk, H. E.; Tuck, D. G. *Can. J. Chem.* 1989, 67, 746. (c) Annan, T. A.; McConville, D. H.; McGarvey, B. R.; Ozarowski, A.; Tuck, D. G. *Inorg. Chem.* 1989, 28, 1644. (d) Geloso, C.; Mabrouk, H. E.; Tuck, D. G. *J. Chem. Soc., Dalton Trans.* 1989, 1759.

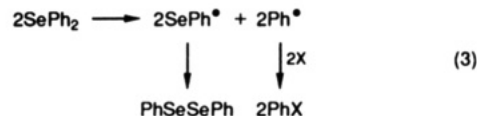
(36) Annan, T. A.; Kumar, R.; Mabrouk, H. E.; Tuck, D. G. *Polyhedron* 1989, 8, 865.



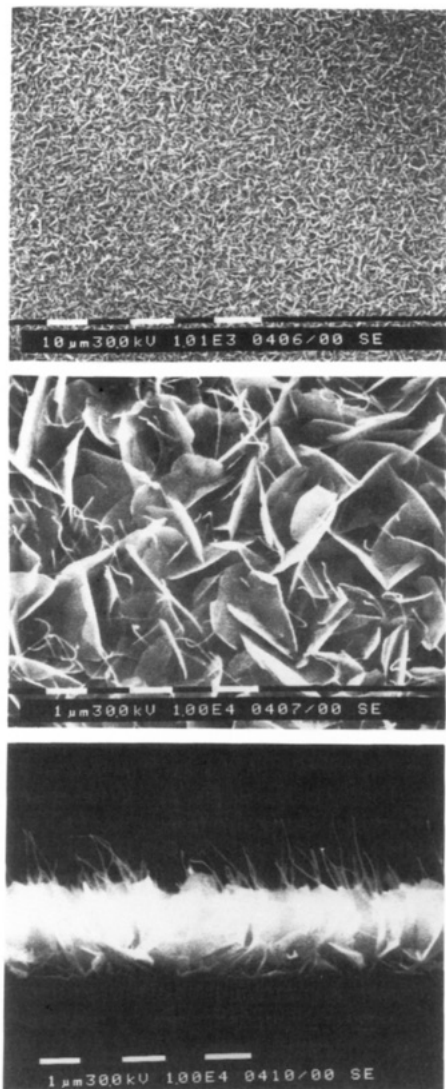
**Figure 3.** Scanning electron micrographs of  $\text{In}_2\text{Se}_3$  film prepared on 365 °C GaAs(100) substrate: (A) surface view; (B) cross section view.

however, under our measuring conditions, that its fdms has a weak molecular ion and an intense 1015 peak ( $\text{In}_2(\text{SePh})_5^{2+}$ ) as well the 506 peak, a 429 peak ( $\text{In}(\text{SePh})_2^{2+}$ ), and peaks due to  $\text{Ph}_2\text{Se}_2^{2+}$  (314, medium),  $\text{SePh}_2^{2+}$  (234, weak),  $\text{SePh}^+$  (157, medium),  $\text{In}_2\text{Ph}(\text{SePh})_4^{2+}$  (935, weak) and  $\text{In}(\text{SePh})_4^{2+}$  (743, weak), suggesting that it volatilizes as the dimer.

Thermal gravimetric analysis of the precursor in flowing nitrogen gave a weight residue of ca. 35% at 450 °C (versus a theoretical weight residue of 40.01% for  $\text{In}_2\text{Se}_3$  and 33.24% for  $\text{InSe}$ ), a value consistent with the formation of  $\text{In}_2\text{Se}_3$  and partial volatilization of the precursor or, alternatively, formation of a mixture of the two phases. Preparative scale pyrolysis of solid  $\text{In}(\text{SePh})_3$  under an Ar atmosphere at 450 °C established that  $\text{In}_2\text{Se}_3$  was the sole solid-state product (X-ray diffraction phase identification), with  $\text{SePh}_2$  and  $\text{Se}_2\text{Ph}_2$  being the only two volatile products identified by gc/ms. We suggest that  $\text{SePh}_2$  is the initial pyrolysis product and the  $\text{Se}_2\text{Ph}_2$  is generated by the vapor phase decomposition of this selenide:



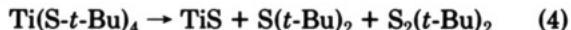
No products resulting from the phenyl radical, an expected



**Figure 4.** Scanning electron micrographs of  $\text{In}_x\text{Se}_3$  film prepared on 476 °C GaAs(100) substrate: (A) surface view; (B) cross section view.

product of the thermolysis of  $\text{SePh}_2$ , were observed by GC/MS. This is most probably due to the high reactivity of the phenyl radicals, resulting in their adsorption onto the reaction vessel walls [i.e., X (eq 3)].

A related homoleptic thiolate,  $\text{Ti}(\text{S}-t\text{-Bu})_4$ , has been shown to act as a single-source precursor for amorphous TiS films in a low-pressure CVD process at 130 °C.<sup>37</sup> Bulk pyrolysis of this precursor was shown to produce similar decomposition products:



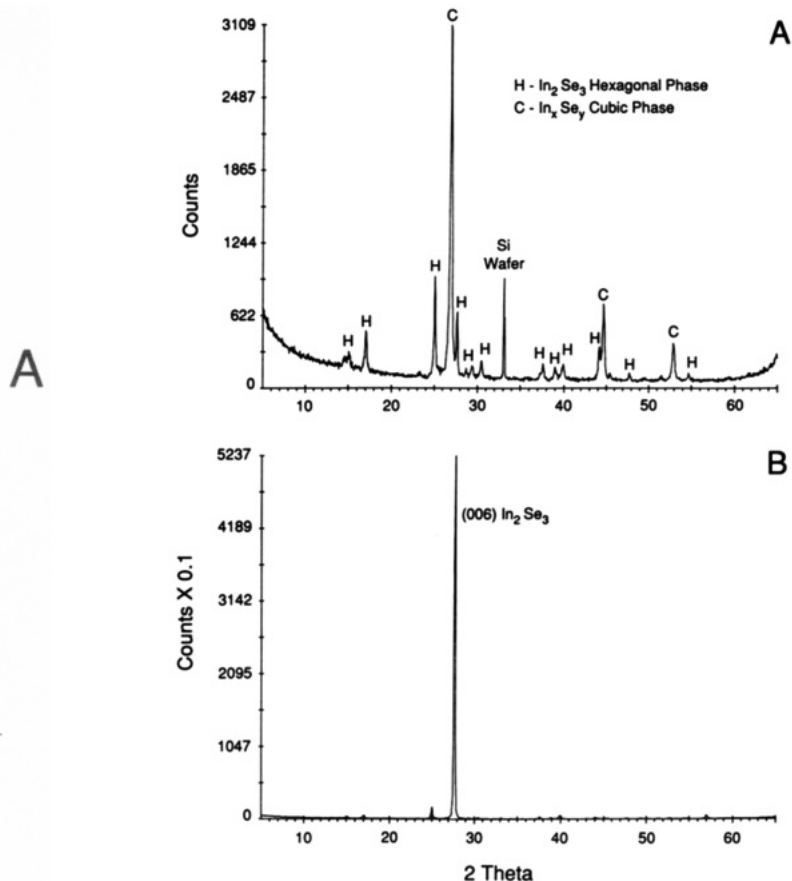
In contrast, the polymeric but nonvolatile methyl thiolates  $[\text{M}(\text{SMe})_2]_n$  ( $\text{M} = \text{Zn}, \text{Cd}$ )<sup>38</sup> and the dimeric, volatile complex  $[\text{Cd}(\text{S}-2,4,6-(t\text{-Bu})_3\text{C}_6\text{H}_2)_2]_2$ <sup>39</sup> gave only MS and the corresponding  $\text{SR}_2$  as pyrolysis products.

Thin films of  $\text{In}_2\text{Se}_3$  were obtained from  $\text{In}(\text{SePh})_3$  using the spray MOCVD apparatus shown in Figure 1; 200 mL of a 0.01 M solution of the precursor was loaded, in a glovebox, into the nebulization chamber (Figure 1–2). After attachment of this chamber to the reactor assembly

(37) Bochmann, M.; Hawkins, I.; Wilson, L. M. *Chem. Commun.* 1988, 344.

(38) (a) Osakada, K.; Yamamoto, T. *Chem. Commun.* 1987, 1117. (b) Osakada, K.; Yamamoto, T. *Inorg. Chem.* 1991, 30, 2328.

(39) Bochmann, M.; Webb, K.; Harman, M.; Hursthouse, M. B. *Angew. Chem., Int. Ed. Eng.* 1990, 29, 638.



**Figure 5.** X-ray diffraction patterns of  $\text{In}_2\text{Se}_3$  films deposited on Si(100) substrate using the  $\text{In}(\text{SePh})_3$  precursor: (A) 400 °C; (B) 550 °C.

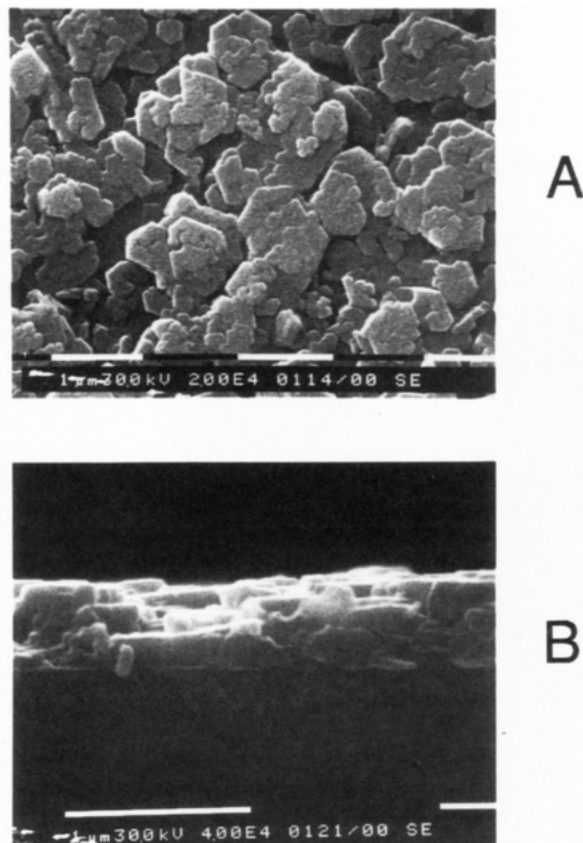
illustrated in Figure 1, a mist of the solution was passed into the heated zone of the reactor using ultrasonic nebulization and an argon flow rate of 4.5 SLM. With the inlet side of the reactor (Figure 1–4) at 320 °C and either a GaAs(100) or a Si(100) substrate at temperatures exceeding 460 °C, a highly (00 $l$ ) oriented hexagonal  $\text{In}_2\text{Se}_3$  was obtained (X-ray diffraction pattern fit with JCPDS 23–294; Figure 5B). X-ray diffraction of a film deposited at 400 °C on a Si(100) substrate (Figure 5A) shown the presence of both randomly oriented hexagonal phase of  $\text{In}_2\text{Se}_3$  as well as the new cubic  $\text{In}_x\text{Se}_y$  phase that was also obtained using the  $\text{Me}_2\text{InSePh}$  precursor as described above. Formation of the cubic  $\text{In}_x\text{Se}_y$  phase from this selenium-rich precursor does not exclude the InSe composition for this phase since In(III) compounds are known to undergo reductive elimination reactions to give In(I) derivatives (eq 2).

Scanning electron micrographs of the film deposited at 466 °C show highly oriented polycrystalline film growth (Figure 6A) with a rather rough surface morphology (Figure 6B). A deposition rate of ca. 1.5  $\mu\text{m}/\text{h}$  is estimated from the cross section micrograph (Figure 6B).

## Conclusions

Films of the III–VI semiconductors InSe and  $\text{In}_2\text{Se}_3$  have been fabricated by a spray MOCVD process using single-source precursors. Film stoichiometry and phase can be controlled by appropriate molecular design of the single source precursor reagent.

A new cubic phase of  $\text{In}_x\text{Se}_y$ , with a zinc blende-type structure, has been prepared by the spray MOCVD process using the single-source precursor  $\text{Me}_2\text{InSePh}$ . New phases of solid-state materials obtained with single-source pre-



**Figure 6.** Scanning electron micrographs of  $\text{In}_2\text{Se}_3$  film deposited at  $550^\circ\text{C}$  on a GaAs substrate: (A) surface view; (B) cross section view.

cursors, which contain the atomic bonding pattern of the target solid-state material, have also recently been observed by other workers (i.e., cubic GaN and  $\text{Nb}_3\text{N}_4$ —see Introduction). The ability to form such new phases using single-source precursors may be the result of the low-temperatures often used in film deposition with such molecular reagents.

The spray MOCVD process has been shown to produce highly oriented thin films of  $\text{In}_2\text{Se}_3$  using  $\text{In}(\text{SePh})_3$  as a single-source precursor. Further optimization of this film fabrication process could result in smoother films, suitable for detailed electrical and optical characterization.

### Experimental Section

**Materials.**  $\text{InMe}_3$  was obtained from Strem Chemicals and  $\text{In}(\text{SePh})_3$  was prepared by the reaction of indium powder (Alfa Products) with diphenyl diselenide (Aldrich Chemical Co.) in refluxing toluene as previously described.<sup>30</sup> Toluene and hexane used in the syntheses were distilled under argon from sodium/benzophenone directly into the Schlenk flasks containing the reactants.<sup>40</sup>

**Synthesis of  $\text{Me}_2\text{InSePh}$ .** Trimethylindium (1.59 g, 10 mmol) and  $\text{In}(\text{SePh})_3$  (2.91 g, 5 mmol) were loaded into a Schlenk flask in a glovebox. After removal from the glovebox, 150 mL of dry toluene was added to the flask under argon, and the resulting solution was refluxed for 30 min and then stirred at room temperature for 10 h to effect the redistribution reaction (eq 1).

The solvent was then removed under vacuum and the residue was extracted with 200 mL of hot hexane. The hexane extract was filtered through a medium porosity glass frit under argon, concentrated to 35 mL under vacuum and cooled to  $-20^\circ\text{C}$  to

give a white precipitate. After the supernatant solution was removed by cannula, the white solid was vacuum dried to give 3.2 g (70.9%) of product. Anal. Calcd (found) for  $\text{C}_8\text{H}_{11}\text{InSe}$ : C, 31.93 (32.37); H, 3.68 (3.67); In, 38.15 (37.73).

**Physical Methods.** X-ray diffraction (XRD) phase identification and planar orientation measurements were made using a Rigaku RU-300 Bragg-Brentano diffractometer with a copper rotating anode, diffracted beam monochromator tuned for  $\text{Cu K}\alpha$  radiation, and a scintillation detector. Diffraction patterns were collected using step scans with the step size set to  $0.02^\circ 2\theta$  per step.

Samples for XRD analysis were  $1 \times 1 \text{ cm}^2$  and were mounted in a sample holder by placing clay on the backside of the substrate and leveling the sample with the sample holder reference plane by pressing the sample holder and sample flush on a piece of photographic plate glass. No measurable relaxation of the clay after compression was observed for this method of XRD sample preparation.

Peak position and intensity data were determined using a second-derivative peak search routine. The resultant  $d$ -spacing and intensity data were then compared to the JCPDS powder diffraction file<sup>41</sup> for phase identification and assessment of preferred orientation.

**Scanning Electron Micrographs.** The samples were prepared for SEM examination by coating the samples with 100 Å of a Au/Pd alloy using a Polaron E5100 sputter coater. The coating was applied at 2.5 kV and 20 mA for 60 s. The samples were then placed in a Philips 515 SEM and examined at an accelerating voltage of 30 kV and a spot size of 20 nm.

**Elemental Analyses.** The coated substrates were placed in 25-mL Erlenmeyer flasks, and 1.0 mL of aqua regia was added to each flask to dissolve the In/Se coatings. The sample solutions were quantitatively transferred to 10 mL volumetric flasks with distilled water. Calibration standards were prepared in 10% aqua regia. Samples and standards were analyzed on a Jarrell-Ash ICAP 9000, an inductively coupled argon plasma-atomic emission spectrographic instrument. The analytical wavelengths used for the In and Se analyses were 230.606 and 196.026 nm, respectively.

**Fabrication of the Films.** The solutions used for the film deposition were prepared in a Vacuum Atmospheres glovebox using toluene (Sure/Seal solvent, Aldrich Chemical Co.). After loading the solutions (200 mL) into the sample reservoir (Figure 1-2) in the glovebox, it was attached to the reactor and flushed for 5 min with argon. The reactor was vented into a  $-78^\circ\text{C}$  trap to condense the solvent, unreacted precursor, and organic reaction products.

**InSe Films.** A mist of a 0.0086 M toluene solution of  $\text{Me}_2\text{InSePh}$  was passed into the heated zone of the reactor using ultrasonic nebulization and an argon flow rate of 4.5 SLM. With the inlet side of the reactor (Figure 1-4) at  $280^\circ\text{C}$  and the GaAs(100) substrate at  $309\text{--}365^\circ\text{C}$ , a film of cubic  $\text{In}_2\text{Se}_3$  was obtained (X-ray diffraction, Figure 2A). With a substrate temperature of  $408\text{--}475^\circ\text{C}$ , the films were primarily the known hexagonal phase of InSe (JCPDS No. 34-1431) with the minor amount of the cubic  $\text{In}_2\text{Se}_3$  phase still present (Figure 2B).

**$\text{In}_2\text{Se}_3$  Films.** A mist of a 0.0086 M toluene solution of  $\text{In}(\text{SePh})_3$  was passed into the heated zone of the reactor using ultrasonic nebulization and an argon flow rate of 4.5 SLM. With the inlet side of the reactor (Figure 1-4) at  $320^\circ\text{C}$  and the Si(100) substrate at  $550^\circ\text{C}$ , a highly (001) oriented hexagonal  $\text{In}_2\text{Se}_3$  film was obtained (X-ray diffraction fit with JCPDS No. 23-294; Figure 5B). At lower temperatures ( $400^\circ\text{C}$ ) both a randomly oriented hexagonal phase of  $\text{In}_2\text{Se}_3$  as well as the cubic  $\text{In}_2\text{Se}_3$  phase were identified in the films by X-ray diffraction (Figure 5A).

**Acknowledgment.** We thank Gabriel Braunstein and Debasis Majumdar for recording RBS and Auger spectra, respectively, and for their helpful discussions.

**Registry No.** InSe, 1312-42-1;  $\text{In}_2\text{Se}_3$ , 12056-07-4;  $\text{In}(\text{SePh})_3$ , 115399-94-5;  $\text{Me}_3\text{In}$ , 3385-78-2;  $\text{Me}_2\text{InSePh}$ , 142188-45-2; GaAs, 1303-00-0;  $\text{SePh}_2$ , 1132-39-4;  $\text{Se}_2\text{Ph}_2$ , 1666-13-3.

(40) Gysling, H. J.; Thunberg, A. L. In *Physical Methods of Chemistry*, 2nd ed.; Rossiter, B. W., Hamilton, J. F., Eds.; Wiley: New York, 1986; Vol. I, pp 373-487.

(41) Joint Committee on Powder Diffraction Standards, Powder Diffraction File Sets 1-40, JCPDS-ICDD, Swarthmore, PA.