Synthesis and Characterization of (hfac)In(CH_3)$_2$: A Volatile Compound Useful for CVD of Indium and Indium-Containing Materials

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Introduction

Indium-containing materials are receiving increased attention for a variety of microelectronic applications. For example, they are playing an important role in the development of III−V semiconductor thin films for electronic and optoelectronic devices.[1] Indium is also being considered as a shallow-well dopant for integrated circuit junctions, since shallow device junctions enable high performance at lower switching voltages than are required for junctions of greater depth.[2] Copper−indium (Cu−In) alloys have also been examined for improved electromigration resistance, including the long-term performance and reliability of copper-based interconnects in ultralarge scale integrated (ULSI) devices.[3] For each of these applications, volatile indium precursors are highly desirable.

Historically, the most common indium source materials are trialkylindium(III), e.g. trimethylindium and triethylindium. These volatile precursors are extremely sensitive to oxygen and moisture, producing vigorous exothermic reactions, fire, and explosions when exposed to air.[4] Furthermore, for chemical vapor deposition (CVD) of In-containing alloys, trialkylindium precursors are not compatible with most commonly used coreactants. For example, copper CVD precursors that might be used in the formation of Cu−In alloys, such as (hfac)Cu^IL, where hfac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate and L = neutral Lewis base ligands, such as alkenes and alkynes, would not be compatible when mixing these two precursors. Detrimental redox reactions may occur when the alkylindium precursor and the copper precursor are co-injected or their vapors are mixed in the gas phase. The resulting formation of a less volatile species or formation of particles may adversely affect the CVD process. To alleviate these concerns, we have sought alternative indium-source materials with decreased oxygen and moisture sensitivity and greatly improved chemical compatibility with commonly used Cu CVD precursors.

Many metal β-diketonate compounds exhibit useful volatility and suitable thermal stability for uses as CVD precursors in deposition of metal and metal oxide thin films.[5−9] Once one alkyl group in trialkylindium is replaced with a β-diketonate ligand, the new complex stability to oxygen and moisture is expected to be significantly increased. Therefore, we believed that complexes of (β-diketonate)InR_2 are environmentally insensitive and simultaneously volatile enough to serve as safer indium sources when compared to trialkylindium compounds. To explore this concept, we synthesized and characterized (hfac)In(CH_3)$_2$ in this work. Herein, we report our preliminary findings on the synthesis and characterization of (hfac)In(CH_3)$_2$ and a preliminary examination of its utility as a CVD precursor.

Experimental Section

Trimethylindium was purchased from Strem Chemicals, Inc., and used directly without further purification. H(hfac) was purchased from Aldrich Chemical Co. and used as received. Two copper precursors, e.g. (hfac)CuL, where L = DMCOD or 1,5-dimethyl-1,5-cyclooctanediene and MHY or 2-methyl-1-hexen-3-yne, were made at ATMI, Inc., according to the literature procedure.[10,11] All hydrocarbons and ethereal solvents were dried and distilled over sodium and benzophenone. Infrared (IR) spectra were acquired on a Perkin-Elmer 1600 FT-IR spectrometer using KBr pellets. Thermal analyses were performed on a Rheometric Scientific STA-625, using Ar as carrier gas. Solution nuclear magnetic resonance (^{1}H and ^{13}C NMR) spectra were recorded on a Varian Gemini 200 NMR spectrometer by using the protic impurities of the deuterated solvents as reference for chemical shifts. Scanning electron micrographs (SEM) and spectra from energy dispersive spectroscopy (EDS) were recorded on a JEOL JSM-5800 scanning microscope.

Synthesis of (hfac)In(CH_3)$_2$. The general reaction was carried out under a steady flow of dinitrogen using standard Schlenk techniques. A Schlenk flask was charged with 4.8 g (30 mmol) of trimethylindium and 20 mL of diethyl ether. 1,1,1,5,5,5-Hexafluoro-2,4-pentanedione (6.20 g, 30 mmol) was added dropwise to the magnetically stirred solution at about −10 °C. Gas evolution was observed immediately. After completion of the addition, the solution was stirred for an additional 1 h at room temperature. Removal of volatiles gave 9.9 g (yield 94%) of white needle-shaped crystals. Colorless single crystals can be grown by sublimation of the compound at room temperature and atmospheric pressure. Mp: 63 °C. NMR (C_6D_6; δ, ppm): ^{1}H, −0.29 (s, 6H, In−C*H*$_3$) and 5.97 (s, 1H, −C*H*− of hfac); ^{13}C, −2.9 (s, −*C*H$_3$ of In−CH_3), 89.9 (s, −*C*H− of hfac), 117.7 (q, *C*F$_3$ of hfac), and 179.4 (q, −*C*(O)−CF_3 of hfac). FT-IR (KBr) (cm^{-1}): 2996 (w), 2921 (w), 1646 (s), 1610 (m), 1560 (m), 1534 (m), 1466 (s), 1261 (s), 1205 (s), 1148 (s), 1085 (m). Anal. Calcd for $C_7H_7F_6InO_2$: C, 23.89; H, 2.00. Found: C, 23.87; H, 1.81.

CAUTION! *Inhalation of volatile In-containing materials may be hazardous to humans, and handling in well-ventilated areas is strongly recommended.*

X-ray Crystallographic Studies. Single crystals were grown by sublimation of (hfac)In(CH_3)$_2$ at room temperature and atmospheric pressure. Colorless crystals were selected and cleaved to nearly cubic shape and mounted in a thin-walled capillary tube. Crystallographic data are summarized in Table 1. About 75% of a full sphere of data, which provided a high degree of redundancy, was collected using a

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(1) Zanella, P.; Rossetto, G.; Brianese, N.; Ossola, F.; Porchia, M. *Chem. Mater.* **1991**, *3*, 225−242.
(2) Baum, T. H.; Xu, C. Y. U.S. Patent (pending), 1998.
(3) Harper, J. A.; Hu, C. K. *Mater. Res. Soc. Bull.* **1994**, *8*, 41 (Special Issue on Copper Metallization, XIX).
(4) Leman, J. T.; Barron, A. R. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; John Wiley & Sons: New York, 1995; pp 1531−1542.
(5) Sievers, R. E.; Sadlowski, J. E. *Science* **1978**, *201*, 217−223.
(6) Brooks, K. C.; Turnipseed, S. B.; Barkley, R. M.; Sievers, R. E.; Tulchinsky, V.; Kaloyeros, A. E. *Chem. Mater.* **1992**, *4*, 912−16.
(7) Kodas, T. T.; Hampden-Smith, M. J. In *The Chemistry of Metal CVD*; VCH: New York, 1994; and the references wherein.
(8) Xu, C. Y.; Baum, T. H.; Rheingold, A. L. *Chem. Mater.* **1998**, *10* (9), 2329−31.
(9) Chi, K. M.; Shin, H. K.; Hampden-Smith, M. J.; Kodas, T. T.; Duesler, E. N. *Inorg. Chem.* **1992**, *31*, 424.
(10) Doyle, G.; Eriksen, K. A.; Van Engen, D. *Organometallics* **1985**, *4*, 830.
(11) Doppelt, P. French Patent, FR 9,703,029, 1997.

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Table 1. Crystallographic Data and Structure Refinement for $(hfac)In(CH_3)_2$

empirical formula	$C_7H_7F_6InO_2$
fw	351.95
T	−50 °C
λ	0.710 73 Å
cryst syst	tetragonal
space group	$I4_1/a$
a	20.2201(2) Å
b	20.2201(2) Å
c	11.72720(10) Å
β	90
V	4794.69(8) Å^3
z	16
ρ(caldd)	1.950 g cm^{-3}
μ	2.032 mm^{-1}
final R indices $[I > 2\sigma(I)]^{a,b}$	R1 = 0.0301 wR2 = 0.0762
R indices (for all data)	R1 = 0.0386, wR2 = 0.0914

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2}$.

Siemens Smart CCD detector. The data were averaged, and corrections for Lorenzian, polarization, and absorption effects were applied. The tetragonal space group was uniquely determined by systematic absences in the diffraction data.

The structure was solved by heavy-atom methods and refined by full-matrix, least-squares methods. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized conditions. Both trifluoromethyl groups were rotationally distorted over two positions; the unprimed atoms were refined at 70% occupancy. All software is contained in the SHELXTL program library (version 5.01).

Studies on CVD of Cu−In Alloys. Chemical vapor deposition (CVD) of Cu−In films was studied using (hfac)Cu(MHY) and (hfac)-$In(CH_3)_2$ as precursors with dual bubblers in a quartz bell-jar CVD reactor. No carrier gas or reactive gas was used. Platinum-coated silicon wafers were used as the substrates. The reactor pressure was maintained between 0.9 and 2.0 Torr during the deposition process. The bubbler temperature was held at 60 °C for both the In and Cu precursors. The copper film was deposited at a substrate temperature of 200 °C; after 5 min, a metallic and reflective copper film was physically observed on the surface. The copper precursor bubbler was manually closed and the substrate temperature was increased to 300 °C before further film growth. The In precursor bubbler was manually opened for 10 min to form a Cu−In film on the heated substrate. The process was stopped and the film was cooled to room temperature before removal from the CVD reactor. Subsequently, the deposited film was analyzed by energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM).

Results and Discussion

The volatile, air- and moisture-stable $(hfac)In(CH_3)_2$ was synthesized by a reaction of trimethylindium with 1 equiv of (hfac)H in diethyl ether. This reaction resulted in the formation of $(hfac)In(CH_3)_2$ in high yield. After completion of the reaction, removal of the ethereal solvent under vacuum gave white needle-shaped crystals, exhibiting satisfactory elemental analysis without further purification. When an excess amount of (hfac)H was used in the reaction, the only product formed was (hfac)-$In(CH_3)_2$. This observation indicates that the displacement reaction provides only monodisplacement of a methyl group and is consistent with that reported for the reaction of trialkylindium with acetic acids or other Brønsted acids (HX where X is a nitrogen or oxygen donor base).[4] This monodisplacement can be attributed to coordinative saturation of the metal center. We examined the sensitivity of $(hfac)In(CH_3)_2$ to moisture and oxygen. The complex was exposed to air for 2 days. Unlike trialkylindium compounds, no reactions were observed either visually or by the ^{1}H NMR study. Therefore, $(hfac)In(CH_3)_2$ is insensitive to oxygen, moisture, and even to more acidic species, such as (hfac)H, because of the coordinative saturation of the metal center.

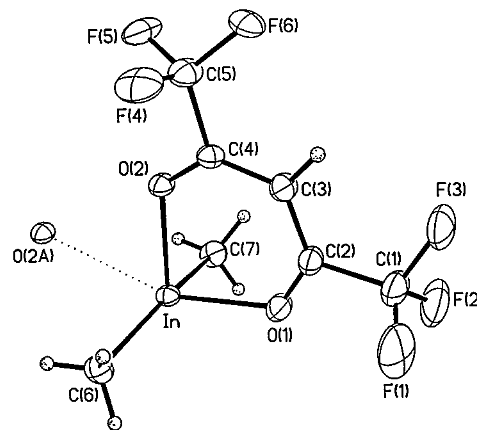

Figure 1. Molecular structure of $(hfac)In(CH_3)_2$ drawn with 30% thermal ellipsoids.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $(hfac)In(CH_3)_2$

In−C(7)	2.136(3)	In−C(6)	2.143(3)
In−O(2)	2.304(2)	In−O(1)	2.310(2)
O(1)−C(2)	1.246(4)	O(2)−C(4)	1.273(4)
C(1)−C(2)	1.574(5)	C(2)−C(3)	1.406(5)
C(3)−C(4)	1.401(4)	C(4)−C(5)	1.563(4)
C(7)−In−C(6)	159.6(2)	C(7)−In−O(2)	97.37(12)
C(6)−In−O(2)	99.85(11)	C(7)−In−O(1)	95.71(13)
C(6)−In−O(1)	97.64(12)	O(2)−In−O(1)	81.18(8)
C(2)−O(1)−In	128.0(2)	C(4)−O(2)−In	126.8(2)

The compatibility of $(hfac)In(CH_3)_2$ with (hfac)CuL was also examined, where L = DMCOD or MHY. When the indium complex and a copper species were mixed in C_6D_6 in a NMR tube, no color changes were observed visually. ^{1}H NMR study indicated that the spectrum of the mixture was a simple addition of the two individual NMR spectra of $(hfac)In(CH_3)_2$ and (hfac)-CuL. This observation indicated that no reactions occurred between $(hfac)In(CH_3)_2$ and (hfac)CuL compounds when they were mixed in solution. In a separate control experiment, trimethylindium was mixed with (hfac)CuL in C_6D_6. A light yellow precipitate was observed immediately, and the yellow precipitate slowly turned into black. Further studies revealed that redox reactions occurred, resulting in the formation of Cu metal (black particles) and $(hfac)In(CH_3)_2$. The air-stable (hfac)-$In(CH_3)_2$ appears to be readily compatible when mixed with (hfac)CuL solutions exhibiting no degradation and/or ligand exchange. Therefore, $(hfac)In(CH_3)_2$ may be employed as an In source for the CVD of Cu−In alloys.

The molecular structure of $(hfac)In(CH_3)_2$ in the solid state was determined by single-crystal X-ray diffraction (XRD). An ORTEP plot of the molecular structure is shown in Figure 1. Several selected bond lengths and angles are listed in Table 2. Two methyl groups and a chelating hfac ligand are coordinated to the indium central atom. Through long-range interactions within the crystal lattice, two indium molecules form weakly associated dimers (see Figure 2). The In−O(2a) distance 2.869(2) Å is significantly longer than the intramolecular distances of 2.304(2) and 2.310(2) Å. The two methyl groups and oxygen atoms O(1) and O(2a) form the base of a distorted square pyramid. Both of the trans basal plane angles are slightly less than 160°; the two methyl groups are positioned away from the apical group, while the basal oxygen atoms are positioned

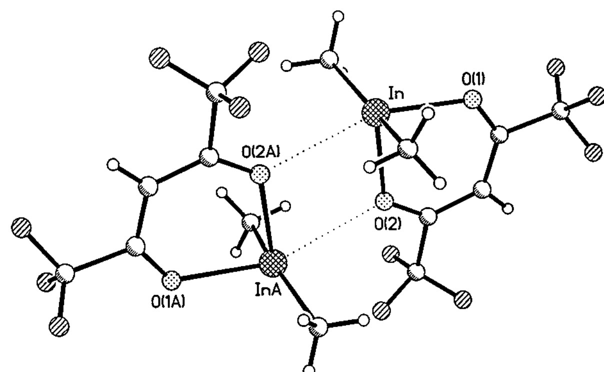

Figure 2. Ball-and-stick drawing of (hfac)In(CH_3)$_2$, emphasizing the formation of an intermolecular dimer.

toward the apical atom. For comparison, trimethylindium was found to exist as a loosely associated tetramer in the solid state,[12,13] and (CH_3COO)In(CH_3)$_2$ existed as an infinite polymeric species through the intermolecular In−O interactions of the molecules in the upper and lower layers.[4,14,15]

The volatility and thermal stability of the (hfac)In(CH_3)$_2$ was qualitatively examined by simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) with a heating rate of 10 °C/min using Ar as purge gas (25 mL/min). A melting endotherm was observed at 63 °C, and the material was transported intact below 118 °C under atmospheric pressure. Again the compound is readily sublimed at room temperature and atmospheric pressure. We therefore concluded that this molecular precursor exhibits good volatility and thermal stability, as required for its use as a CVD precursor.

The growth of Cu−In films was carried out through a multiple-precursor route using dual bubblers in a quartz bell-jar CVD reactor that was described previously elsewhere.[16,17] The experimental details were described in the Experimental Section. At first, copper films were grown on Pt-coated substrates at 200 °C for 5 min from (hfac)Cu(MHY). The film was visually reflective. Then, the substrate temperature was raised to 300 °C. Indium was deposited onto the copper film from (hfac)In(CH_3)$_2$ for 10 min. After being cooled to room temperature, the film was removed from the reactor and analyses were performed. The thin films were analyzed by energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM). EDS data (see Figure 3) revealed the presence of copper and indium within the films; a semiquantitative analysis indicated that indium content is roughly 10%. Scanning electron micrographs showed a smooth film texture with grain sizes ranging from 0.1 to 0.2 μm. Therefore we successfully deposited Cu−In alloy from (hfac)Cu(MHY) and (hfac)In(CH_3)$_2$ via a multiple-precursor route.

(12) Blake, A. J.; Cradock S. *J. Chem. Soc., Dalton Trans.* **1990**, 2393.
(13) Amma, E. L.; Rundle, R. E. *J. Am. Chem. Soc*. **1958**, *80*, 4141.
(14) Einstein, F. W. B.; Gilbert, M. M.; Tuch, D. G. *J. Chem. Soc., Dalton Trans.* **1973**, 248.
(15) Habeeb, J. J.; Tuck, D. G. *Can. J. Chem*. **1974**, *52*, 3950.
(16) Doppelt, P.; Baum, T. H. *Chem. Mater.* **1995**, *7* (12), 2217.
(17) Doppelt, P.; Baum, T. H. *Thin Solid Films*, **1995**, *270*, 480−482.

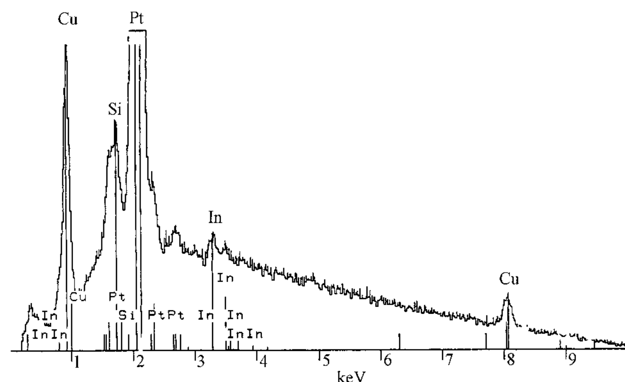

Figure 3. EDS data for a Cu−In film grown on Pt-coated silicon wafer from the precursors of (hfac)Cu(MHY) and (hfac)In(CH_3)$_2$ at 300 °C.

Conclusion

In summary, a new molecule of the (β-diketonate)InR_2 class of precursors was synthesized and characterized. This material is suitable for chemical vapor deposition of In-containing thin films and represents a promising alternative to the commonly used trialkylindium precursors. The new indium precursor is advantageous being air- and moisture-stable, highly volatile, thermally stable, and compatible with Cu CVD precursors. Preliminary CVD film growth using this newly developed precursor provides increased safety and handling while exhibiting effective reliability for the deposition of In-containing materials.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure of (hfac)In(CH_3)$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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