Chem. Mater. **1998,** *10,* 3467−3470

Bis(bis(trimethylsilyl)methyl)tin(IV) Chalcogenides as Possible Precursors for the Metal Organic Chemical Vapor Deposition of Tin(II) Selenide and Tin(II) Telluride Films

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Received April 3, 1998. Revised Manuscript Received August 18, 1998

Two air- and light-stable compounds, bis(bis(trimethylsilyl)methyl)tin(IV) selenide and telluride, $[Sn\{(SiMe_3)_2CH\}_2(\mu\text{-}E)]_2$ (E = Se (**1**) and Te (**2**)), were investigated as possible precursors for metal organic chemical vapor deposition (MOCVD). Their sublimation rate was measured by thermal gravimetric analysis in the 190−260 °C range and was found to be as high as 2 mg/min at 260 °C at 14 mbar. MOCVD experiments were conducted using both compounds as precursors at 300−600 °C and 1 Torr under a flow of a 1:1 He/H_2 mixture. Strong selectivity of the decomposition reaction was found toward the metallic surfaces (copper, silver, gold) with respect to nonmetallic surfaces (quartz, silicon with natural oxide layer). A thin layer (≈10 nm) of conducting seeding layer was used for the deposition of carbon-free film of SnTe, using **2** as a precursor. The films were examined by scanning electron microscopy, X-ray diffraction, and X-ray photoelectron spectroscopy analyses.

Introduction

Tin and lead chalcogenides and their ternary alloys, such as $Pb_{1-x}Sn_xTe$, have semiconducting properties with a naturally narrow band gap. Thin films of these compounds are promising materials for the fabrication of mid-IR (3−14 μm) photodetectors, light-emitting diodes and diode lasers, and memory in switching devices.[1]

Different techniques, including thermal evaporation, molecular beam epitaxy (MBE), and laser ablation,[1,2] were applied for the deposition of thin films of tin(II) selenide and tin(II) telluride. To our knowledge, only one paper has been devoted to the metal organic chemical vapor deposition (MOCVD) of these compounds.[3] Tetramethyltin, dimethyltellurium, and hydrogen selenide were used as precursors for this process. On the other hand, CVD has a number of advantages, including high deposition rates, good step coverage, and uniform deposition over large surfaces.

The investigated complexes, bis(bis(trimethylsilyl)methyl)tin(IV) chalcogenides, $[Sn\{(SiMe_3)_2CH\}_2(\mu\text{-}E)]_2$ (E = Se (**1**) and Te (**2**)) (Figure 1), are volatile in a vacuum and stable to air and light. This allowed us to consider them as potential precursors for the MOCVD process of Sn and Se (or Te) containing films. These complexes can also belong to the class of single-source precursors because they have both elements (Sn and either Se or Te) in one molecule.

The concept of the single-source precursor has drawn the attention of many research groups in recent years.[4] A single-source precursor, which after decomposition gives a film of the desired element ratio, can significantly reduce the number of deposition parameters and simplify the whole deposition process. Such precursors were found for the deposition of many different materials, including metals (e.g. CoGa), semiconductors (e.g. InN), and insulators (e.g. $(Al_2O_3)_x(SiO_2)_y$).[5]

Organometallic compounds containing the element combination Sn/E (E = S, Se, Te) are known.[6] The four-membered motif of the type $[Sn(\mu\text{-}E)]_2$ encountered in **1** and **2** is frequently observed in the chemistry of solid-

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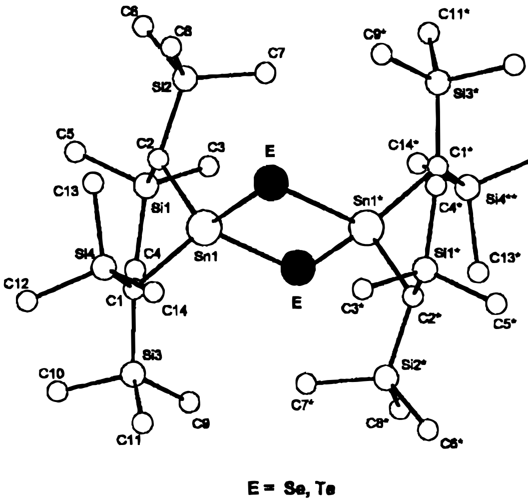

Figure 1. Molecular structure of $[Sn\{(SiMe_3)_2CH\}_2(\mu\text{-}E)]_2$ (E = Se, Te).[9]

state chalcogenates as well as in molecular compounds.[7] However, most of these complexes are air- and light-sensitive or have low volatility. For example, complexes $[\{(tert\text{-butyl})_2SnE\}_2]$ (E = S, Se, and Te) are reported to be especially air- (Se, Te) and light-sensitive (S, Se, Te).[7a] Linear and cyclic perphenylated and benzylated derivatives of tin chalcogenides, $(R_3Sn)_2E$ (E = S, Se, and Te) and $(R_2SnE)_3$ (E = S and Se) and pyridineselenolate complexes such as $[Sn(\mu\text{-}SeNC_5H_4)_2]_2$, can be used as single-source precursors for the preparation of powders of SnS, SnSe, and SnTe by pyrolysis in an inert atmosphere.[8]

Except for the pyridineselenolate complexes, their vapor pressure is too low for any possible application in the MOCVD process. To our knowledge none of the volatile compounds have been successfully employed in MOCVD experiments for the deposition of SnE films.

Recently we reported on the synthesis of **1** and **2** from the stannylene $[\{(SiMe_3)_2CH\}_2Sn]$ and elemental chalcogene.[9] The most important features of these compounds are their straightforward synthesis with good yields, *high volatility* at reduced pressure, and *air*- and *light-stability*. The compounds may therefore hold some promise as single-source precursors for the deposition of Sn/chalcogene films in the MOCVD experiments. The main goal of this research was to estimate the applicability of these new compounds to the MOCVD process.

Experimental Section

Synthesis and characterization of **1** and **2** was done as reported earlier.[9]

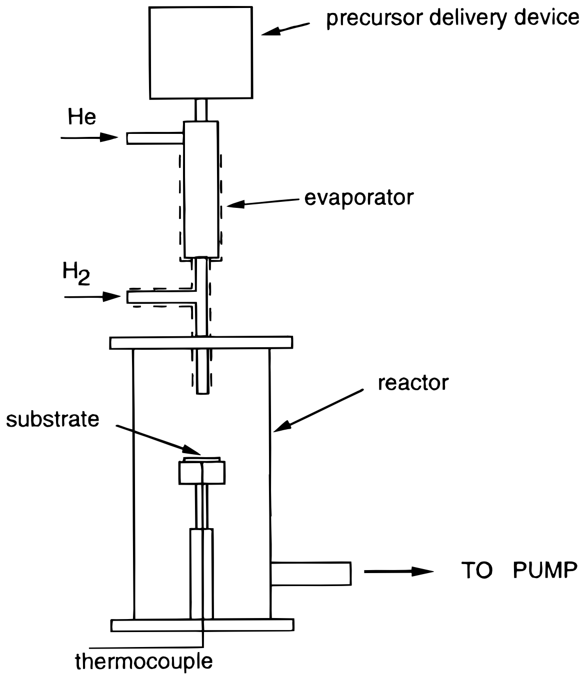

Figure 2. General scheme of the CVD setup used for the film deposition experiments.

Table 1. Parameters of the MOCVD Process Which Were Kept Constant during All Deposition Experiments

evaporation temp	210 °C	He flow	50 cm^3(STP) min^{-1}
time of deposn	45 min	H_2 flow	50 cm^3(STP) min^{-1}
amt of the precursor for one deposn	50 mg	total pressure in the reactor	0.5 mbar

Thermogravimetric analysis (TGA). A 951 Thermogravimetric Analyzer by DuPont Instruments, Inc., was used for the thermogravimetric analysis (TGA) of the complexes at reduced pressure (14 mbar) in the temperature range of 20–300 °C with a temperature ramp of 10 deg/min. The evaporation rate was calculated as the first derivative of weight with respect to time.

MOCVD Experiments. The deposition process was investigated in a vertical cold wall CVD reactor. The general scheme of the CVD setup is shown in Figure 2. The complexes were loaded under ambient atmosphere. The powder of the precursor was delivered at a constant rate of approximately 1.1 mg/min to the preheated stainless steel evaporator, where it evaporated completely. The vapor of the precursor was carried to the reactor through the heated stainless steel tubes by the flow of helium. Two stainless steel screens located in the evaporator were used to prevent influx of stray particles from the evaporator to the reactor. The deposition parameters, which were kept constant during all deposition processes, are summarized in Table 1. The substrates were rinsed in deionized water and washed with acetone (99.6%) and mounted with silver paint on a stainless steel susceptor, which was heated resistively. Hydrogen and helium of UHP/ZERO grade were used without further purification. A mass-flow controller controlled their flow with an accuracy of ±1 cm^3(STP) min^{-1}. The temperature of substrates was controlled by a thermocontroller with an accuracy of ±2 °C.

X-ray Diffraction (XRD) measurements were performed on a X-ray diffractometer D-5000 by Siemens, Inc., in Θ - 2Θ mode. Cu $K\alpha$ radiation was used. The instrumental resolution is 0.02°.

Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Analysis (EDX). The samples were examined using a JEOL Electron Probe Microanalyzer JXA-840A equipped with a Kevex Microanalytical System.

X-ray Photoelectron Spectroscopy (XPS). Carbon concentration in the films was determined using a Perkin-Elmer

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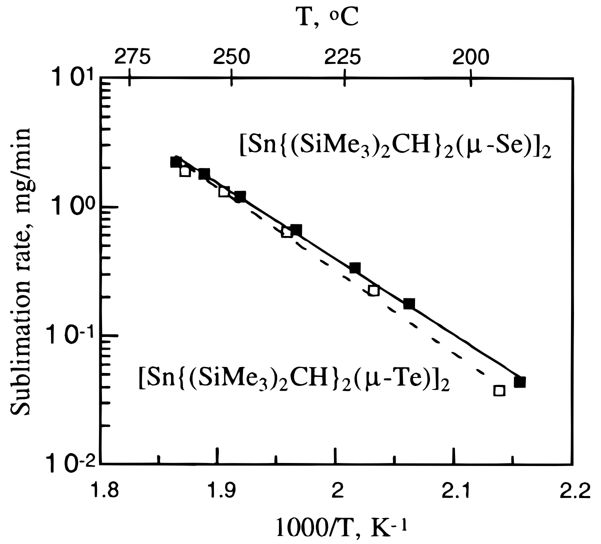

Figure 3. Arrhenius plots of the sublimation rate of $[Sn\{(SiMe_3)_2CH\}_2(\mu\text{-}Se)]_2$ and $[Sn\{(SiMe_3)_2CH\}_2(\mu\text{-}Te)]_2$ complexes.

ESCA system 5100 series with an Al anode. The instrument detection limit for this element is about 1 at. %. Surface contamination was removed by Ar^+ beam sputtering with accelerating voltage of 3 keV.

Results and Discussion

Investigation of the Precursor Volatility. The volatility at reduced pressure of complexes **1** and **2** was confirmed by TGA experiments at 14 mbar. The residue found at 275 °C was only about 3 mass %. The sublimation rates for both complexes were calculated from the TGA data in the temperature range of 190–260 °C, and the Arrhenius plots are shown in Figure 3. The observed value of the sublimation rate as high as about 2 mg/min at 260 °C can be considered high enough for application of the complexes in the MOCVD process. The enthalpies of evaporation of $\{\{(SiMe_3)CH\}_2SnSe\}_2$ and $\{\{(SiMe_3)CH\}_2SnTe\}_2$ complexes were found to be 112.24 and 122.43 J/mol, respectively. The sublimation process of **1** and **2** from a boat was also investigated at a constant temperature of 210 °C in dynamic vacuum (≈1 mbar) under a 10 cm^3(STP) min^{-1} flow of He. The sublimation was almost complete with a residue of less than 1 mass %.

Deposition Experiments. To evaluate **1** and **2** as MOCVD precursors, we carried out a series of deposition experiments using different substrates. No deposition was found on quartz and silicon with a natural oxide layer in the temperature range of 300–600 °C, neither using He as a carrier gas nor using H_2. Increasing the total pressure in the reactor from 0.5 to 40 mbar did not induce precursor decomposition either.

On the other hand, thick gray films could be obtained using both precursors on (100) oriented copper substrates as low as 400 °C for **1** and 300 °C for **2**.

The XRD performed on the film obtained from **2** revealed the presence of some amount of the tin telluride phase SnTe, along with Cu_3Sn and $Cu_{2-x}Te$ phases, as shown in Figure 4. For the film obtained from **1**, Cu–Sn alloy, Cu_2Se, and $Cu_{41}Sn_{11}$ phase are all present. This result clearly shows the selectivity of the decomposition reaction of **1** and **2** toward the metallic surfaces.

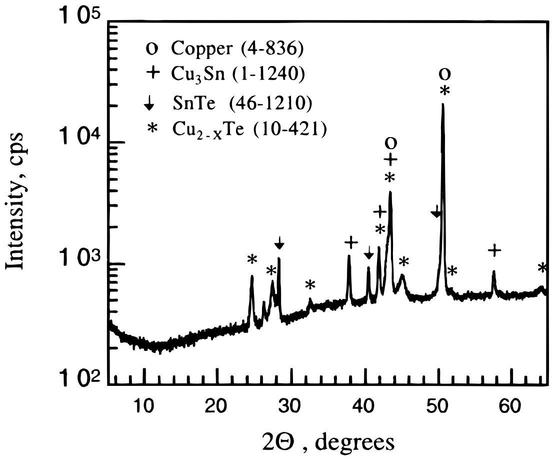

Figure 4. X-ray diffractogram of the film obtained from **2** at 300 °C on copper substrate (numbers in brackets are the numbers of JCPDS files for the observed phases).

Two other metallic surfaces, quartz substrates covered by sputtered gold, and silver metal films 85–90 nm thick were each used in order to investigate the selectivity of the deposition.

Only very thin films could be obtained using **1** on gold and silver layers up to 500 °C. However, even 300 °C was high enough for decomposition of **2** on silver, and 400 °C was enough on gold. XRD data for both films are shown in Figure 5 a and b, where mixed phases of Sn, Te, and either Ag or Au can be seen.

It can be seen from these results that **1** is more thermally stable than **2** and also that the decomposition reaction of **2** has different selectivity toward different metallic surfaces.

The amount of the SnTe phase in the films can be increased by decreasing the thickness of the initial metal layer. This can be demonstrated by deposition of a film on a thin (100 nm) Cu layer that was thermally evaporated on a silicon substrate. XRD analysis of this film (Figure 5c) revealed that the film consisted of SnTe with an admixture of Cu_2Te phase, while on the copper substrate a mixture of different phases was found.

Such an increase of the amount of SnTe phase in the films can take place only if the metal layer is necessary for the initial stage of SnTe film growth. It is known from the literature that metal surfaces can favor the nucleation of the metal film during MOCVD.[10] To clarify the role of the metal substrates in our case, we deposited films using **2** as a precursor at 400 °C on a very thin seeding layer (≈10 nm) of gold sputtered over quartz substrate. An XRD pattern of the resulting film is shown in Figure 6. Only the SnTe phase can be detected in the film. The calculated lattice parameter $a_o = 6.3369 \pm 0.0020$ Å agrees with the JCPDS data of $a_o = 6.3275$ Å (file 46-1210). The SEM image of the film is shown in Figure 7. The film consisted of 50.5 at. % Sn and 49.5 at. % Te according to the EDX data, with the amount of gold below the detection limit (≈0.4 at. %). The concentration of carbon determined by XPS was below the detection limit of the analysis (≈1 at. %).

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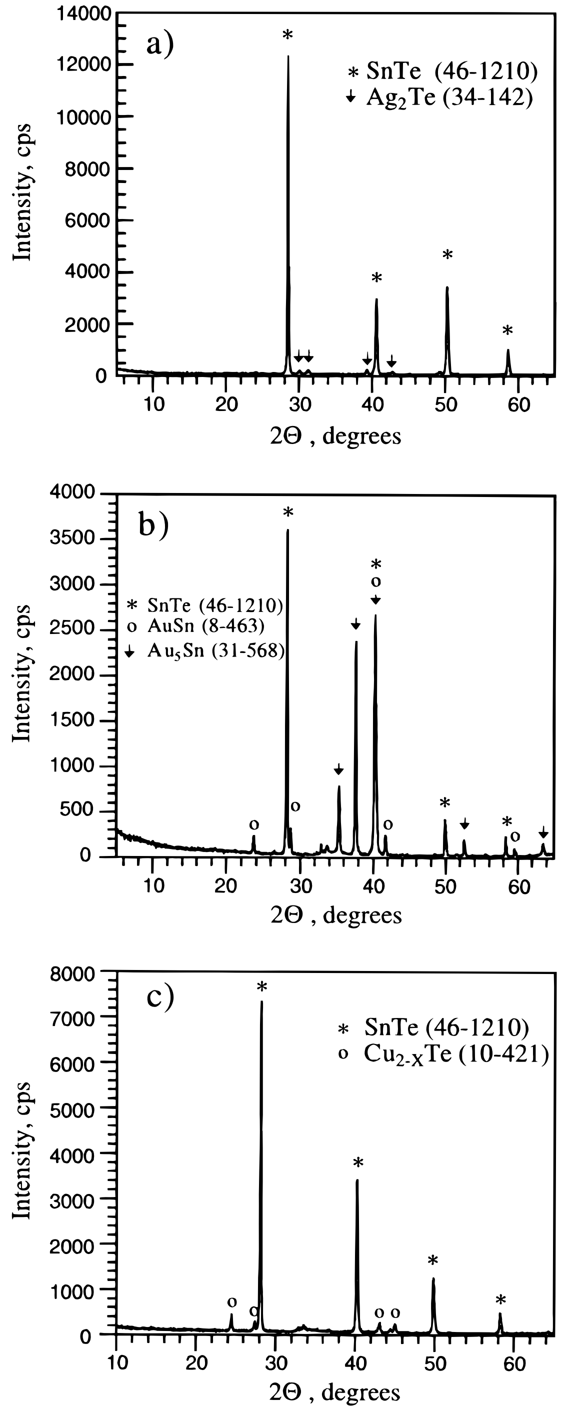

Figure 5. XRD pattern of the film obtained from **2** at 400 °C on *(*a) Ag/SiO_2, (b) Au/SiO_2, and *(*c) Cu/Si substrates.

Conclusions

The volatility of the two air- and light-stable Sn/Se(Te) complexes, **1** and **2**, was investigated and proved to be high enough for MOCVD process.

A series of MOCVD experiments using **1** and **2** showed strong selectivity of the decomposition reaction toward the metallic substrates. It can be concluded that **1** is more thermally stable than **2**, and hardly can be used as a precursor for the thermal MOCVD process. The thin film growth is either promoted by the conductivity of the metallic surface helping in the redox process or by the reaction of the precursors with the metals forming chalcogenides or tin containing alloys. The composition of these various phases can be controlled by the nature of the metal layer and by their thickness. A very thin film of the metal can actually be used as a seeding layer initiating the growth of the tin chalcogenide; e.g., SnTe films free from carbon contamination can be grown on gold seeding layers at 400 °C using **2** as a precursor. Hence, the complex $[Sn\{CH(SiMe_3)_2\}_2(\mu\text{-}Te)]_2$ can be considered as the first single-source precursor for the deposition of SnTe thin films by MOCVD. However, we can expect interaction and diffusion of the seeding layer metal in the SnTe films based on the results of the depositions on thicker metal layers. Inert conducting seeding layer material should be found in order to apply the above-mentioned process for the manufacturing of the SnTe-based devices.

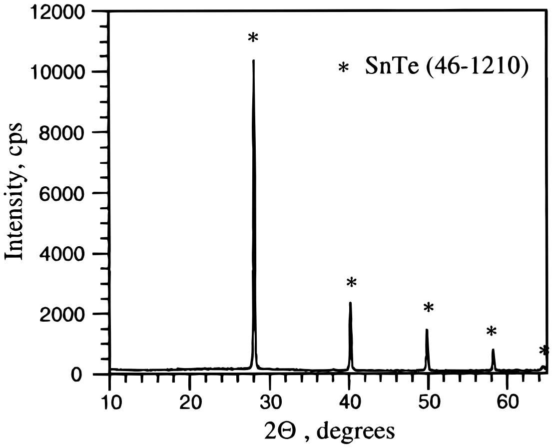

Figure 6. X-ray diffractogram of the film obtained at 400 °C from **2** on 10 nm gold seeding layer sputtered over quartz substrate.

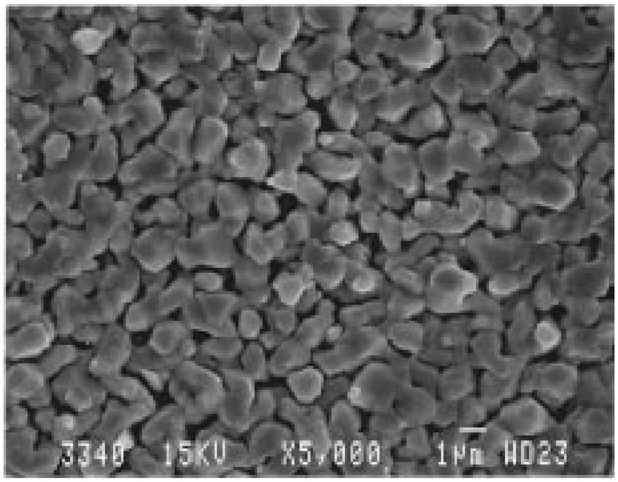

Figure 7. Electron scanning micrograph of the film obtained at 400 °C from **2** on 10 nm gold seeding layer sputtered over quartz substrate.

Acknowledgment. K.-H.D. and I.S.C. are grateful for the partial financial support by MARTECH/FSU. J.J.S. acknowledges the support through the DFG (Heisenberg fellowship), Fonds der Chemischen Industrie, and the Prof. Werdelmann Foundation administered by the Stifterverband für die Deutsche Wissenschaft.

CM980247J