Chem. Mater. 1993, 5, 979–982

Low-Temperature Chemical Vapor Deposition of Sb Films Using $(i\text{-Pr})_2SbH$

Robert W. Gedridge, Jr.,* Kenneth E. Lee, and Charlotte Lowe-Ma

Chemistry Division, Research Department, Naval Air Warfare Center Weapons Division,
China Lake, California 93555

Received February 8, 1993. Revised Manuscript Received April 16, 1993

The new precursor diisopropylantimony hydride, $(i\text{-Pr})_2SbH$, was prepared by reaction of $(i\text{-Pr})_2SbBr$ with $LiAlH_4$ in diethyl ether and subsequently evaluated for use as a volatile Sb-source compound in the low-temperature organometallic vapor-phase epitaxial film growth of Sb-containing semiconductor materials. $(i\text{-Pr})_2SbH$, an extremely photosensitive volatile liquid, was used in an atmospheric pressure chemical vapor deposition reactor to grow polycrystalline Sb films on Si(100) and Si(111) substrates at temperatures as low as 200 °C. X-ray diffraction data indicated that the resulting Sb films were oriented in the [000*L*] direction. H_2 and Ar were used as carrier gases and the pyrolysis products were monitored by a residual gas analyzer. The Sb films were characterized by Auger electron spectroscopy and X-ray diffraction.

Introduction

Antimony-containing semiconductor materials are of interest for lasers, high-speed electronic devices, and infrared detectors operating in the 3–5 and 8–12-μm spectral ranges. InSb focal plane arrays are currently being used at observatories all over the world for infrared astronomical imaging.[1] A variety of binary, ternary and quaternary III/V semiconductor materials containing antimony have been grown by organometallic vapor phase epitaxy (OMVPE) using Me_3Sb as the antimony precursor.[2]

Alternative tertiary stibines such as $(CH_2{=}CH)_3Sb$,[3] $(i\text{-Pr})_3Sb$,[4] $(CH_2{=}CHCH_2)_3Sb$,[5] and $(t\text{-Bu})Me_2Sb$[6] have been previously evaluated for low temperature OMVPE film growth since Me_3Sb[7] is inefficiently pyrolyzed at temperatures lower than 400 °C. $(i\text{-Pr})_3Sb$ has been successfully used to grow InSb by OMVPE as low as 300 °C, the lowest reported InSb film growth temperature using a stable organoantimony precursor. However, the low vapor pressure (0.4 Torr at 25 °C) of $(i\text{-Pr})_3Sb$ and its inefficient pyrolysis at 300 °C result in low film growth rates (0.077 μm/h).[8]

Although SbH_3 has been used in the OMVPE growth of InSb at temperatures as low as 300 °C, it is unstable at room temperature and was generated at the point of use.[9] Higher homologues such as $MeSbH_2$,[10] Me_2SbH,[10] and $(t\text{-Bu})_2SbH$[11] are also unstable at room temperature. Recently, primary and secondary neopentyl stibines have been synthesized and used to deposit InSb.[12] However, these neopentyl stibines were believed to decompose in the stainless steel bubblers and this discouraged further investigation for OMVPE.[13] Therefore, a need for a volatile Sb-source compound that pyrolyzes at low temperatures still exists. We now report the pyrolysis and use of the new Sb-source compound $(i\text{-Pr})_2SbH$ in the chemical vapor deposition of Sb films as low as 200 °C.

Experimental Section

Organoantimony compounds should be handled with extreme caution since they are toxic.[14] Organic solvents were distilled under Ar from sodium/benzophenone. $SbCl_3$ (99.99% metal basis) was purchased from Alfa. Isopropyl Grignard, Br_2, and $LiAlH_4$ reagents were purchased from Aldrich and used as received. $(i\text{-Pr})_2SbBr$ was prepared according to the literature.[15] Elemental analyses were performed by E + R Microanalytical Laboratory, Inc. NMR spectra were recorded on C_6D_6 solutions with an Bruker AMX-400 spectrometer. ^{13}C spectra were obtained at 100.6 MHz with ^1H-coupled ^{13}C spectra obtained under gated decoupling conditions.

$(i\text{-Pr})_2SbH$. To a stirring slurry of 0.330 g (8.69 mmol) of $LiAlH_4$ in 15 mL of Et_2O at −78 °C was added dropwise (drop time = 30 min) in the dark a solution of 2.502 g (8.693 mmol) of $(i\text{-Pr})_2SbBr$[15] in 15 mL of Et_2O. After the addition was complete, the slurry was warmed to room temperature slowly and stirred at room temperature overnight. All the volatiles from the off-white slurry were collected in a liquid nitrogen trap under vacuum. The solvent from the condensed colorless fraction was fractionally distilled off using a 35–40 °C water bath. $(i\text{-Pr})_2SbH$, an extremely

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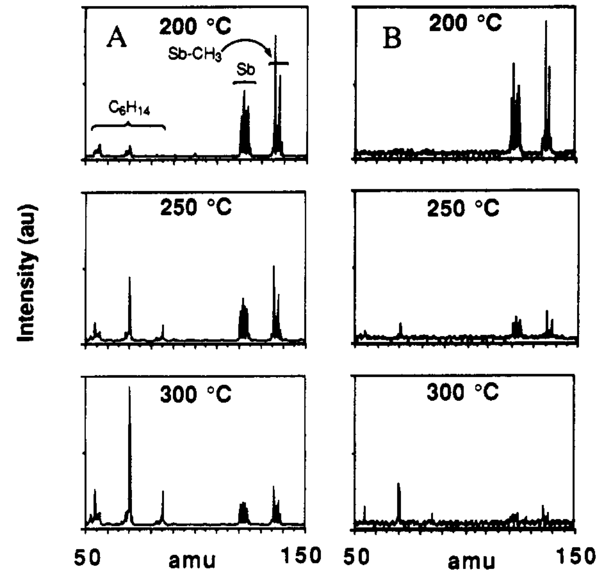

Figure 1. Mass spectra between 50 and 150 *m/e* for (i-Pr)$_2$SbH pyrolysis at various temperatures in (A) H_2 and (B) Ar.

air- and light-sensitive colorless liquid, was fractionally distilled at 32–33 °C at 6 Torr (1.010 g, 56% yield based on (i-Pr)$_2$SbBr). (i-Pr)$_2$SbH can also be fractionally distilled at 43 °C at 16 Torr. (i-Pr)$_2$SbH showed no evidence of decomposition after storage for 4 days in the dark at 0 °C. (i-Pr)$_2$SbH starts to decomposes within minutes after exposure to sunlight. While (i-Pr)$_2$SbH can be stored in a stainless steel bubbler in the dark for several weeks without significant decomposition, long-term stability is unknown. ^{1}H NMR (C_6D_6) 3.53 ppm (t of m, 1H, Sb–H, $^3J_{HH}$ = 3.6, $^4J_{HH}$ = 0.5 Hz), 2.05 ppm (septet of d, 3H, CH–Sb, $^3J_{HH}$ = 3.6, $^3J_{HH}$ = 7.3 Hz), 1.41 ppm (d, 6H, CH_3, $^3J_{HH}$ = 7.3 Hz), 1.27 ppm (d, 6H, CH_3, $^3J_{HH}$ = 7.3 Hz). ^{13}C NMR (C_6D_6) 25.5 ppm (q of m, CH_3, $^1J_{CH}$ = 126 Hz), 24.2 ppm (q of m, CH_3, ^1JCH = 126 Hz), 15.2 ppm (d of m, CH, $^1J_{CH}$ = 134 Hz). Anal. Calcd for $C_6H_{15}Sb$: C, 34.49; H, 7.24; Sb, 58.27. Found: C, 34.45; H, 7.10; Sb, 58.05.

Film Growth and Pyrolysis. Sb films were grown in a cylindrical horizontal quartz CVD reactor (4.5 cm by 40 cm). The graphite susceptor was inductively heated by a 2.5-kW Lepel Corp. RF generator. The temperature was measured using a calibrated thermocouple embedded in the susceptor and controlled by a Research Inc. Micristar digital controller-programmer. A Dycor MA200 residual gas analyzer (RGA) was used to monitor the depositions and the gaseous byproducts. All the mass spectral data were collected at a 50-eV electron impact energy. In calculating the relative percent decomposition, mass spectral peak intensities were corrected based on the intensity of the unvarying background water peak in the RGA. Si(100) and 4°-off-axis Si(111) substrates were first degreased then etched with a 10% HF solution. The substrates were blown dry with N_2 then heated for 1 hr at 350 °C with a 200–500 sccm flow of carrier gas prior to the deposition. Ar and H_2 were passed through a glass bubbler, wrapped in Al foil to keep out light, containing the (i-Pr)$_2$SbH precursor held between 18 and 23 °C. Flow rates of 40 and 13 sccm, measured by a calibrated Matheson flow meter, were used for the depositions. X-ray diffraction data were obtained using a Scintag PAD V (2θ:θ) diffractometer (220-mm radius) equipped with a N_2(l) cooled solid-state Ge detector and Cu-target X-ray tube. A Perkin-Elmer PHI 600 scanning Auger microprobe was used to determine the elemental composition of the as-deposited films.

Results and Discussion

Pyrolysis Studies. (i-Pr)$_2$SbH was pyrolyzed under H_2 (Figure 1A) and Ar (Figure 1B) onto cleaned Si substrates mounted on the susceptor. Background mass spectra were recorded by the RGA with (i-Pr)$_2$SbH flowing through the reactor at room temperature. Although the parent peak for (i-Pr)$_2$SbH was not observed in any of the mass spectra, peaks at *m/e* of 121 and 123 were clearly observed for the two major isotopes of Sb (Figure 1). In addition, peaks at 122 and 124 were also observed for the Sb–H fragments. The highest *m/e* peaks were observed in the 136–138 region, and these are believed to be Sb-CH_3 recombination fragments. Many peaks due to the isopropyl fragments were also observed and this severely hindered our ability to distinguish between propane (C_3H_8) and propene (C_3H_6) in the mass spectra. Therefore, peaks from the *m/e* = 121–124 region were used to monitor pyrolysis since no other peaks from the organic byproducts overlapped this region. The pyrolysis was monitored by the RGA from low temperature to higher temperatures (complete pyrolysis) and back down to low temperatures.

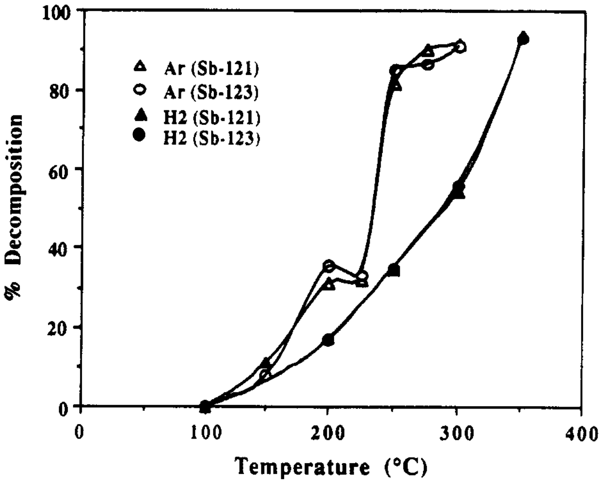

Figure 2. Plot of percent decomposition of (i-Pr)$_2$SbH versus susceptor temperature, based on relative intensities of the two major isotopes of Sb.

The onset pyrolysis of (i-Pr)$_2$SbH in H_2 occurs above 100 °C (Figure 2). Complete pyrolysis was observed just above 350 °C with a monotonically increasing pyrolysis curve between 100 and 350 °C. An increase in the intensity and number of peaks around *m/e* of 29 and 40, corresponding to various hydrocarbon fragments, occurs during pyrolysis. We were unable to make definitive assignments to these organic fragment peaks. However, the parent peak of 2,3-dimethylbutane (C_6H_{14}) and the peak for the parent minus a CH_3 were clearly observed at *m/e* of 86 and 71, respectively (Figure 1A). Formation of C_6H_{14} may occur by recombination of two isopropyl radicals (eq 1) or by a reductive elimination of two isopropyl groups from (i-Pr)$_2$SbH (eq 2).

$$2C_3H_7 \rightarrow C_6H_{14} \quad (1)$$

$$(C_3H_7)_2SbH \rightarrow C_6H_{14} + SbH \quad (2)$$

The onset pyrolysis of (i-Pr)$_2$SbH in Ar also occurs above 100 °C (Figure 2). However, complete pyrolysis in Ar was observed around 300 °C, about 50 °C lower than in H_2. This suggests that there may be a carrier gas dependence in the pyrolysis of (i-Pr)$_2$SbH. Furthermore, the pyrolysis curve exhibits a shoulder in the region between 200 and 225 °C. This behavior has been observed before when there are competing homogeneous gas-phase and heterogeneous reactions.[3] The homogeneous gas-phase process appears to take over above 225 °C. Again, an increase in the intensity and number of peaks around *m/e* of 29 and 40 occurs during pyrolysis. H_2 and 2,3-dimethylbutane were clearly observed during pyrolysis in Ar (Figure 1B).

In contrast to pyrolysis in H_2, 2,3-dimethylbutane was only a minor organic byproduct formed during pyrolysis in Ar. The formation of H_2 may result from a variety of reductive elimination or free-radical processes.

From the available pyrolysis data, we were unable to unequivocally determine if propane or propene were formed during pyrolysis. As a result, it is unclear whether free-radical, β-hydrogen elimination, reductive elimination, or some combination of these processes dominate the pyrolysis of this novel compound. More detailed pyrolysis experiments are in progress using $(i\text{-Pr})_2SbH$ and $(i\text{-Pr})_2SbD$ with He, H_2, and D_2 carrier gases in a flow tube pyrolysis reactor with a time-of-flight mass spectrometer to monitor the gaseous byproducts.[16] These studies have indicated that propene and propane are the major byproducts formed during pyrolysis of $(i\text{-Pr})_2SbH$ in H_2 and He.

Chemical Vapor Deposition of Sb Films. Sb films were grown for preliminary evaluation of $(i\text{-Pr})_2SbH$ as a precursor for low-temperature OMVPE growth of Sb-containing semiconductor materials. Polycrystalline Sb films were grown on Si(100) at 350 °C using H_2 as the carrier gas. These films were highly reflective and the SEM photographs revealed faceted Sb crystallites in the shape of flattened rhombohedral basal pinacoids on the Si substrates (Figure 3A). Polycrystalline Sb films were also grown under similar conditions but at 200 °C. These films were dull gray and the SEM photographs showed that the substrates were covered with submicron-sized Sb crystallites (Figure 3B). The Auger spectra of both films showed the composition of the films to be only Sb with no detectable carbon within the limits of Auger (~1%). By comparison, we were unable to deposit Sb at 200 °C under similar conditions using $(i\text{-Pr})_3Sb$.

X-ray diffraction from the Sb films grown on Si(100) at 350 °C under a H_2 ambient revealed that the films were highly oriented in the [0001] direction in comparison to the standard powder diffraction pattern[17] and peaks other than (000*L*) were extremely weak (Figure 4). The observed diffraction data are consistent with the SEM photographs which show the {0001} faces of the crystallites parallel to the Si substrate. Rocking about ω at the position for maximum diffraction by the Sb (0006) reflection yielded only one relatively sharp peak, indicating little angular distribution of the [0001] directions of the crystallites. From omega rocking curves, the {0001} faces of the Sb crystallites were observed to be parallel to the Si (100) surface. X-ray diffraction of the Sb films grown on Si(100) at 200 °C under a H_2 ambient revealed that the crystallites on the film were again oriented in the {000*L*} direction but to a lesser degree than the films grown at 350 °C (Figure 4A). Growth on 4°-off-axis Si(111) and/or under Ar gave polycrystalline films with similar orientations as observed with Si(100) substrates.

Conclusions

$(i\text{-Pr})_2SbH$ is a promising new Sb-source compound for low-temperature OMVPE of Sb-containing semiconductor materials. Although $(i\text{-Pr})_2SbH$ is extremely photosensitive, it has a greater vapor pressure than $(i\text{-Pr})_3Sb$ and can be readily synthesized. Our pyrolysis studies were inconclusive in determining the gas-phase pyrolysis mechanism for $(i\text{-Pr})_2SbH$. $(i\text{-Pr})_2SbH$ was used in our CVD reactor to grow polycrystalline Sb films oriented in the [0001] direction on Si substrates as low as 200 °C. Auger analysis on these Sb films showed no detectable carbon impurities within the limits of AES. By comparison, we were unable to grow Sb films at 200 °C under similar conditions using $(i\text{-Pr})_3Sb$. Recently, epitaxial layers of

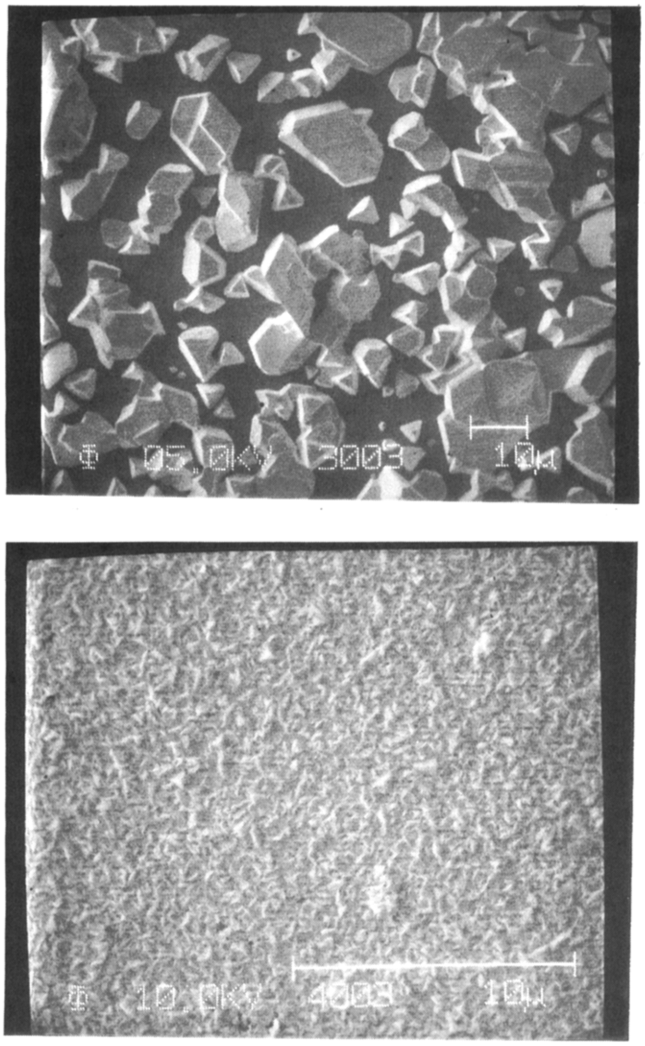

Figure 3. (A, top) Sb films grown on Si(100) at 350 °C under a H_2 ambient for 30 min. (B, bottom) Sb films grown on Si(100) at 200 °C under a H_2 ambient for 2 h.

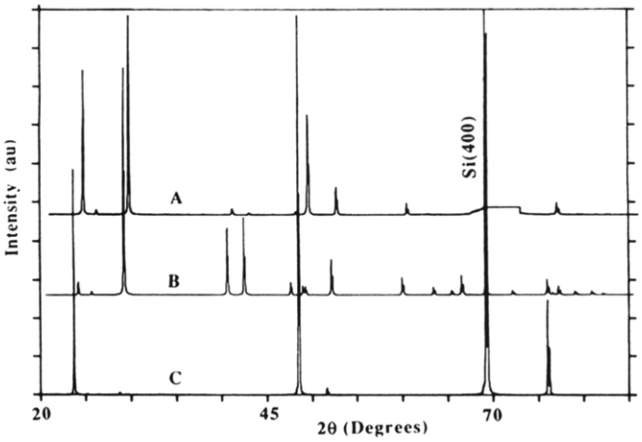

Figure 4. X-ray diffraction patterns are offset for clarity. (A) X-ray diffraction pattern of the Sb films grown on Si(100) at 200 °C under H_2. (B) Calculated X-ray diffraction powder pattern for randomly oriented Sb.[19] (C) X-ray diffraction pattern of the Sb films grown on Si(100) at 350 °C under H_2.

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InSb have been grown by OMVPE using $(i\text{-Pr})_2SbH$ with Me_3In as low as 300 °C and characterization of these films is in progress.[18]

Acknowledgment. This work was supported by the Office of Naval Research and the Office of Naval Technology. We thank R. Z. Dalbey for Auger data collection and manipulation. K.E.L. thanks the American Society for Engineering Education for support from a postdoctoral fellowship.

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