# Synthesis, Characterization, and Chemical Vapor Deposition Properties of Primary and Secondary Neopentylstibine. New Antimony Precursors for MOCVD

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The primary and secondary neopentylstibines (neopentyl = $Me_3CCH_2$–) have been synthesized by the reduction of the corresponding dihalo- and monohaloantimony compounds, respectively. Neopentylstibine was prepared by the reduction of $(Me_3CCH_2)SbBr_2$ with lithium aluminum hydride (LAH). The primary stibine is highly air-sensitive and exhibits a vapor pressure of 5.5 Torr at 0 °C. Dineopentylstibine was synthesized by LAH reduction of $(Me_3CCH_2)_2SbI$. The secondary stibine is less sensitive to air than its primary congener but nonetheless decomposes when exposed to air. Dineopentylstibine is substantially less volatile than $(Me_3CCH_2)SbH_2$, exhibiting a vapor pressure of 0.5 Torr at 24 C. The detailed synthesis, spectroscopic characterizations, physical properties, and preliminary chemical vapor deposition experiments of these hydridic antimony compounds is described.

## Introduction

The production of semiconductor films by chemical vapor deposition techniques is an extremely active research area.[2] An ever-increasing demand for semiconductor materials specifically tailored to meet desired requirements fuels the efforts to understand materials production and fabrication. One of the most intriguing areas in semiconductors today is the antimonides, which find a wide variety of applications in infrared detectors, high-speed digital circuits, and quantum well structures.[3]

Although there is an increasing amount of ongoing work in antimonide-based semiconductors, these materials are less studied than other III–V systems such as InP and GaAs. This stems mostly from the difficulty associated with growing reproducible, high-quality antimonide films by metal organic chemical vapor deposition (MOCVD). There are at least two factors that affect the growth of antimonide-based thin films. First is the limited number of antimony sources currently available for use in CVD experiments. At this time, trimethylstibine ($Me_3Sb$) is the precursor of choice since it is the only volatile antimony source that is commercially available. Examination of the literature reveals that stibine ($SbH_3$),[4] triethylstibine ($Et_3Sb$),[5] and recently triisopropylstibine ($i$-$Pr_3Sb$)[6] have been explored as alternative antimony sources. Although these four sources have been used for the growth of acceptable films, each suffers from a drawback such as instability, low volatility, or high decomposition temperature. A second factor associated with antimonide film growth involves the relationship between the V/III ratio and the deposition temperature. Unlike the liberal growth conditions employed for GaAs that utilize a broad range of values for V/III ratios (always with excess $AsH_3$) over a wide temperature range, growth of antimonide films is more sensitive to the V/III ratio employed at a specific deposition temperature.[7] A slight variation of either parameter from its optimum value often results in either low growth rates or poor morphology and composition.

In view of the success of $t$-$BuAsH_2$[8] and $t$-$BuPH_2$[9] in the growth of GaAs and InP, it is surprising that primary ($RSbH_2$) and/or secondary stibines ($R_2SbH$) have not been examined as alternative precursors to $Me_3Sb$. Mechanistic studies have shown that hydrogen atoms bound to the group V atom often reduce carbon contamination in film growth.[8b] We believe the reasons organoantimony hydrides have not been considered as MOCVD precursors are related to the few known compounds of this type and to their lack of stability or volatility. To our knowledge, only two primary stibines and five secondary stibines have been reported in the literature to date. The methylstibines $Me_2SbH$ and $MeSbH_2$ are volatile liquids but reportedly decompose at room temperature and above −78 °C, respectively.[10] Of the two remaining alkylstibines, $(t$-$Bu)_2SbH$ has marginal volatility for MOCVD purposes (1 Torr a 24–25 °C) and has been isolated in low yields (17%),[11] whereas $(cyclohexyl)_2SbH$ could not be vacuum distilled at 1 Torr since it decomposed above 75 °C.[12] The arylstibines $(Ph)_2SbH$,[13] $(Ph)SbH_2$,[14] and $(mesityl)_2SbH$[15] have been synthesized in yields of 47, 95, and 68%, re-

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spectively. However, $(Ph)_2SbH$ has a low volatility (1 Torr at 118–120 °C), $PhSbH_2$ decomposes slowly at −70 °C under Ar with no boiling point data given, and $(mesityl)_2SbH$ is a solid that melts at 112–115 °C.

The objectives of this work have been to synthesize new primary and secondary stibines and to conduct a preliminary evaluation of their potential as MOCVD precursors. The neopentyl group ($Me_3CCH_2$–) was selected as the organic substituent in these compounds for three reasons: first, it contains no $\beta$-hydrogen atoms, thus eliminating a potentially low-energy decomposition pathway; second, the steric requirements of the substituent should hinder access to vacant coordination sites on the antimony that might be used in a migration, bimolecular, or surface-catalyzed decomposition process; third, it was anticipated that a five-carbon group should be small enough to allow a practical degree of volatility. In addition to the synthesis of these compounds, we have initiated studies to evaluate their ability to deposit InSb with $Me_3In$, to determine deposition parameters for a simple atmospheric reactor, and to measure gross impurities in the films.

## Experimental Section:

**General Techniques.** The compounds described in this paper were synthesized using a combination of Schlenk and vacuum-line techniques. Although no information is available on the toxicity of these compounds, the parent compound, $SbH_3$, is intensely toxic, and its derivatives should be regarded likewise until data are available to indicate otherwise. All glassware used in the synthetic work was washed in 6 M HCl, rinsed with distilled water, and oven-dried. It was observed that not employing the acid wash resulted in the partial decomposition of the stibines as evidenced by a darkening on the surface of the glass. Other manipulations were performed in a helium-filled Vacuum Atmospheres glovebox. Diethyl ether and tetraglyme were dried over sodium/benzophenone and distilled prior to use. Deuterated benzene (Aldrich) was dried over Na/K alloy and vacuum distilled. Lithium aluminum hydride (Aldrich) was used as received. Antimony tribromide was prepared by the careful addition of a stoichiometric amount of bromine to antimony powder suspended in a hexane solution. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker MSL-300 at 300.13 and 75.468 MHz, respectively. $^1H$ spectra were referenced to the residual protic peak of benzene at 7.15 ppm, while proton-decoupled $^{13}C$ spectra were referenced to the center of the benzene triplet at 128.000 ppm. Vapor pressure measurements were made using a capacitance manometer. Infrared spectra were recorded as either gases or neat liquids between potassium bromide plates on a Perkin-Elmer 1430 spectrophotometer. Absorption intensities were determined by the method of Durkin et al.[16] and are reported with the following abbreviations: w (weak), m (medium), sh (shoulder), s (strong), v (very). Elemental analyses were performed by E&R Microanalytical Laboratories, Corona, NY.

**Synthesis of $(Me_3CCH_2)SbBr_2$ (1).** The synthesis of 1 followed a procedure published by Sowerby and Breunig for the preparation of $PhSbBr_2$.[17] In a typical reaction, 1.00 g (2.98 mmol) of $(Me_3CCH_2)_3Sb$ was mixed in a flask with 2.16 g (5.96 mmol) of $SbBr_3$ and suspended in an oil bath at 140 °C. Upon melting of the two solids (approximately 80–90 °C), the melt turned black and solidified. Continued warming to 140 °C and heating for 24 h converted the black solid to a yellowish-brown oil. Vacuum distillation of the crude product through a short-path still afforded 2.56 g (81.0% yield) of slightly greenish-yellow oil: bp 53–57 °C ($4.0 \times 10^{-5}$ Torr); $^1H$ NMR $\delta$ 0.70 (s, 9 H, $SbCH_2C(C\mathit{H}_3)_3$), 2.59 (s, 2 H, $SbC\mathit{H}_2C(CH_3)_3$); $^{13}C\{^1H\}$ $\delta$ 32.60 ($SbCH_2C(\mathit{C}H_3)_3$), 32.83 ($SbCH_2\mathit{C}(CH_3)_3$), 58.24 ($Sb\mathit{C}H_2(CH_3)_3$); IR (neat) 2955 (s), 2930 (sh), 2875 (m), 2860 (m), 1465 (s), 1435 (w), 1400 (vw), 1380 (m), 1365 (s), 1265 (w), 1235 (s), 1130 (w), 1095 (vw), 1020 (vw), 1000 (vw), 740 (w), 605 (w) cm$^{-1}$. Elemental Anal. Calcd for $C_5H_{11}SbBr_2$: C, 17.03; H, 3.14; Br, 45.31. Found: C, 17.19; H, 3.07; Br, 45.66.

**Synthesis of $(Me_3CCH_2)SbH_2$ (2).** Although several different reaction schemes were attempted in order to prepare 2, only one will be described in depth based on its superiority to the others. These deficient schemes will be discussed later in the paper. To 0.112 g (2.95 mmol) of lithium aluminum hydride suspended in 8 mL of tetraglyme stirred at −25 °C, 1.07 g (3.03 mmol) of $(Me_3CCH_2)SbBr_2$ in 8 mL of tetraglyme at 0 °C was added dropwise via cannula with stirring. Immediately upon introduction of the dibromide to the lithium aluminum hydride solution, a darkening was observed with a small evolution of gas. Addition of the dibromide solution was made over a period of 5–10 min. Following addition, the reaction flask was suspended in an ice bath and evacuated on a high-vacuum line. Volatile materials from the reaction were trapped and fractionated by passing through a −78 °C trap and a −196 °C trap. The contents of the −78 °C trap were examined and found to be a white solid that melted with slight warming (approximately −50 °C). Transfer of the volatile liquid to a tared container afforded 340 mg (57.6% yield) of liquid identified as 2. $^1H$ NMR $\delta$ 0.86 (s, 9 H, $SbCH_2C(C\mathit{H}_3)_3$), 1.62 (t, $^3J = 4.8$ Hz, 2 H, $SbC\mathit{H}_2C(CH_3)_3$), 1.70 (t, $^3J = 4.8$ Hz, 2 H, $Sb\mathit{H}_2$); $^{13}C\{^1H\}$ $\delta$ 21.04 ($Sb\mathit{C}H_2C(CH_3)_3$), 31.34 ($SbCH_2C(\mathit{C}H_3)_3$), 31.70 ($SbCH_2\mathit{C}(CH_3)_3$); IR (gas) 2965 (vs), 2915 (sh), 2875 (w), 1870 (vs), 1470 (m), 1365 (m), 1240 (m), 1140 (m), 810 (m), 790 (w), 645 (w), 575 (w). Elemental Anal. Calcd for $C_5H_{13}Sb$: C, 30.81; H, 6.72; Sb, 62.47. Found: C, 31.08; H, 6.49; Sb, 62.52.

**Synthesis of $(Me_3CCH_2)_2SbH$ (3).** The preparation of the secondary stibine 3 was accomplished by the reduction of the previously reported $(Me_3CCH_2)_2SbI$.[18] To 0.065 g (1.6 mmol) of LAH suspended in 5 mL of diethyl ether at −50 °C, 1.75 g (4.48 mmol) of $(Me_3CCH_2)_2SbI$ in 10 mL of diethyl ether was added slowly with stirring. The mixture was then held at −50 °C for 2 h, followed by gradual warming to ambient temperature. Following stirring overnight, the diethyl ether was removed in vacuo at −20 °C (0.01 Torr) to leave an oily residue. This residue was transferred to a short-path still by cannula and vacuum distilled to afford 0.673 g (56.8% yield) of a colorless liquid: bp 11–12 °C (0.01 Torr); $^1H$ NMR $\delta$ 0.98 (s, 18 H, $SbCH_2C(C\mathit{H}_3)_3$), 1.28 (m, 2 H, $^2J = 12.0$, $^3J = 5.5$ Hz, $SbC\mathit{H}_2C(CH_3)_3$), 2.03 (m, 2 H, $^2J = 12.0$, $^3J = 5.5$ Hz, $SbC\mathit{H}_2C(CH_3)_3$), 2.13 (quintet, 1 H, $^3J = 5.5$ Hz, $Sb\mathit{H}$); $^{13}C\{^1H\}$ $\delta$ 28.72 ($Sb\mathit{C}H_2C(CH_3)_3$), 32.09 ($SbCH_2C(\mathit{C}H_3)_3$), 32.90 ($SbCH_2\mathit{C}(CH_3)_3$); IR (neat) 2955 (vs), 2940 (sh), 2900 (m), 2870 (m), 1840 (s), 1470 (s), 1385 (m), 1365 (m), 1240 (s), 1140 (sh), 1130 (m), 1100 (w), 1020 (w), 1005 (w), 790 (m), 755 (w), 740 (w), 650 (w), 555 (w). Elemental Anal. Calcd for $C_{10}H_{23}Sb$: C, 45.32; H, 8.75; Sb, 45.94. Found: C, 45.14; H, 8.87; Sb, 46.08.

**Chemical Vapor Deposition Experiments.** Silicon or gallium arsenide (100) wafers with a thickness of 0.4 mm were cut into pieces ranging from 10 to 20 mm/side. The pieces were then degreased with detergent, washed with distilled water, isopropyl alcohol, boiling trichloroethylene, and isopropyl alcohol, and finally blown dry with a stream of nitrogen. The piece of cleaned wafer (polished side up) was then placed on a static, graphite susceptor within an atmospheric pressure, vertical growth, Pyrex reactor. A smaller piece of substrate (polished side down) was placed on top of the clean wafer to serve as a mask. The vertical reactor contained three separate inlets arranged in a triangular fashion with spacing between the inlets of approximately one inch. For all CVD growth runs, the graphite susceptor was positioned about 2.5 in. below the inlets and inductively heated with an rf source operating between 250 and 800 kHz to calibrated temperatures of 350–450 °C depending on conditions of the growth run. Using Cajon Ultra-Torr fittings and stainless steel flexible tubing, two glass bubblers (one containing trimethylindium, Alfa, electronic grade, and the other containing a neopentylantimony source) were connected to two of the reactor inlets. The third inlet was connected to a hydrogen flow source (push gas). Flows through both bubblers and the push gas were controlled with calibrated flowmeters. The hydrogen carrier and push gas were reagent grade

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and passed through a molecular sieve cartridge. Gas flows for the two antimony sources, trimethylindium, and the push gas were in the ranges 50–150 standard cm$^3$/min (sccm), 25–50 sccm, and 0.5–2.0 L/min, respectively, depending on conditions of the specific growth run. During growth runs both trimethylindium and $(Me_3CCH_2)_2SbH$ were maintained at ambient temperature (ca. 23 °C), while $(Me_3CCH_2)SbH_2$ was held at 0 °C. Following the termination of a growth run, the susceptor was heated for an additional 3–5 min with purging after stopping the source flows; purging was then continued as the system was allowed to cool to ambient temperature. The substrate was subsequently removed from the reactor and characterized. A total of eight individual growth runs were made for each antimony source ($(Me_3CCH_2)_2SbH$ and $(Me_3CCH_2)SbH_2$).

**Characterization of Thin Films.** The thin films grown by the chemical vapor deposition experiments were characterized by Auger electron spectroscopy (AES) and X-ray diffraction (XRD). The Auger spectra were obtained on a Physical Electronics Industries Model 10-155 equipped with a cylindrical mirror analyzer. Spectra of as-mounted films were recorded, followed by sputtering with Ar$^+$ ions for 2 min at a pressure of $5 \times 10^{-5}$ Torr with a beam energy of 700 eV and a beam current of 16 $\mu$A to remove carbon and oxygen contaminants from the surface of the film. Data from the sputtered samples are reported here. A reference spectrum for InSb was obtained on a piece of molecular beam epitaxy (MBE) grown InSb (bulk mobility $2 \times 10^5$ cm$^2$/V s) and gave an In/Sb ratio of 1.13. X-ray diffraction patterns were obtained on Philips 12045 $\theta$–$2\theta$ diffractometer equipped with Cu K$\alpha$ radiation. Thickness measurements were obtained with a Sloan Dektak 900051 profilometer.

## Results and Discussion:

Both $(Me_3CCH_2)SbH_2$ and $(Me_3CCH_2)_2SbH$ were synthesized by reduction of the corresponding organoantimony halide species with lithium aluminum hydride. The two stibines have been prepared and isolated in 57–58% yield (reaction scales involving up to 3 g of product or approximately 10–15 mmol). A scheme showing the reaction is depicted in eq 1. Although eq 1 describes the

$$(Me_3CCH_2)_ySbX_{3-y} + LiAlH_4 \xrightarrow[\text{low temperature}]{Et_2O \text{ or tetraglyme}} (Me_3CCH_2)_ySbH_{3-y} \quad (1)$$

$$\text{for } y = 2, X = I$$

$$\text{for } y = 1, X = Br$$

reduction of only the bromide and iodide species, it is worth noting that we attempted the reduction of both dineopentylchlorostibine and neopentyldichlorostibine. However, in our hands these compounds produced little or no isolable Sb–H containing products. Thus, it would appear that the nature of the halide is crucial for optimizing the yield of the antimony hydride complex. Also, we have found no dependence on the stoichiometry of $LiAlH_4$ used (0.25–1.0 equiv of $LiAlH_4$/equiv of haloantimony compound) with respect to the yield of Sb–H compound obtained.

Both stibines are colorless, volatile liquids at room temperature and are soluble in hydrocarbons and ethers. The vapor pressure of $(Me_3CCH_2)_2SbH$ is 0.5 Torr at 24 °C, whereas that of the substantially more volatile $(Me_3CCH_2)SbH_2$ is 5.5 Torr at 0 °C. In addition to these physical properties, the two liquids turn to white solids when exposed to air but are nonpyrophoric in small quantities. Both compounds exhibit surprising stability at ambient temperatures in the absence of light as evidenced by the primary stibine showing no darkening or formation of noncondensable gas when stored under vacuum for 2 months and the secondary stibine remaining unchanged over a period of 3 months when stored under an argon atmosphere. However, we have observed a blackening of the walls of a tube containing either of the hydrides when exposed to fluorescent light for a period of at least 2 weeks. In the case of $(Me_3CCH_2)_2SbH$, we have determined a photodecomposition product to be the distibine, $(Me_3CCH_2)_4Sb_2$ (confirmed by NMR and X-ray crystallography).[19] We believe this product to arise from the evolution of $H_2$ along with the coupling of two $(Me_3CCH_2)_2Sb-$ fragments.

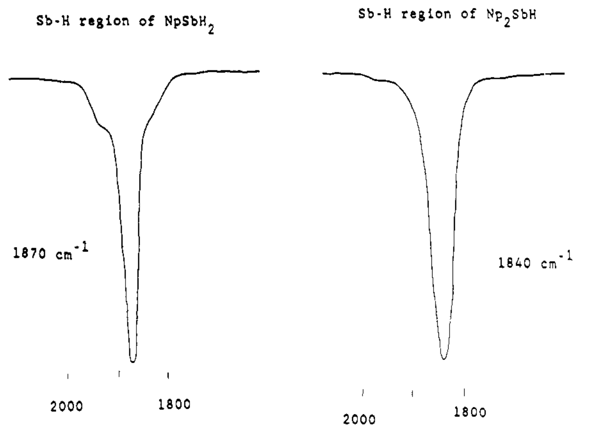

**Figure 1.** Infrared spectra of $(Me_3CCH_2)SbH_2$ and $(Me_3CCH_2)_2SbH$ showing the Sb–H region.

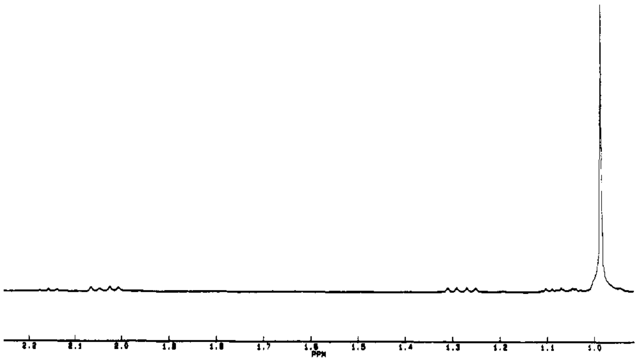

**Figure 2.** $^1H$ NMR spectrum of $(Me_3CCH_2)_2SbH$.

In addition to their physical properties, the two stibines have been characterized by infrared and NMR spectroscopy. The infrared spectra of the two hydrides are dominated by a very intense absorption associated with the Sb–H stretch. For the neat liquid $(Me_3CCH_2)_2SbH$, the Sb–H stretch is observed at 1840 cm$^{-1}$. In the case of $(Me_3CCH_2)SbH_2$ in the gas phase, the band is centered at 1870 cm$^{-1}$. The two Sb–H regions are shown in Figure 1. These values compare favorably with $SbH_3$, which exhibits a central Sb–H stretch at 1890 cm$^{-1}$ [20] and is some 230 cm$^{-1}$ lower in energy than the corresponding neopentylarsines.[21] The $^1H$ NMR spectrum for $(Me_3CCH_2)_2SbH$ in Figure 2 shows a singlet for the methyl groups while the methylene protons and antimony hydrogen form an AA′BB′X system. The two nonequivalent methylene hydrogens occur at 1.28 and 2.03 ppm (showing $^2J_{AB} = 12.0$ Hz and $^3J_{AX} = {}^3J_{BX} = 5.5$ Hz) and are due to the different magnetic environments imposed by the pyramidal structure and the reduction in symmetry resulting from having only two neopentyl groups bound to the antimony center. The antimony hydrogen resonance is identified by the quintet pattern at 2.13 ppm with a coupling of 5.5 Hz. A $^{13}C\{^1H\}$ spectrum from $(Me_3CCH_2)_2SbH$ shows the expected three

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**Table I. XRD Data for InSb Film Grown Using $(Me_3CCH_2)_2SbH$**

| $2\theta_{obsd}$ | $d_{obsd}$, Å | $d_{lit}$, Å | identity | orientation ($I/I_0$, %) |
|---|---|---|---|---|
| 23.70 | 3.751 | 3.74 | InSb[a] | 111 (98) |
| 28.70 | 3.108 | 3.109 | Sb[b] | 101 (100) |
| 39.30 | 2.291 | 2.290 | InSb | 220 (44) |
| 46.50 | 1.951 | 1.953 | InSb | 311 (26) |
| 48.40 | 1.879 | 1.878 | Sb | 006 (13) |
| 51.70 | 1.767 | 1.770 | Sb | 022 (10) |

[a] See ref 22. [b] See ref 23.

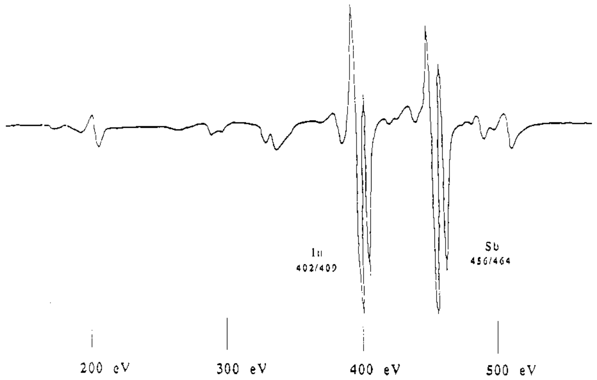

**Figure 3.** Auger spectrum of InSb film employing trimethylindium and $(Me_3CCH_2)_2SbH$ as precursors.

resonances with the methylene ($-CH_2$) carbon appearing at 28.72 ppm. This chemical shift for the methylene carbon is some 9.10 ppm upfield from $(Me_3CCH_2)_3Sb$[18] and can be attributed to the shielding nature of the hydrogen atom. The $^1H$ spectrum for $(Me_3CCH_2)SbH_2$ is much simpler than that observed for $(Me_3CCH_2)_2SbH$ in that both the methylene hydrogens and the antimony hydrogens appear as triplets at 1.62 and 1.70 ppm respectively. The $^{13}C\{^1H\}$ spectrum for $(Me_3CCH_2)SbH_2$ also shows three resonances. However, the methylene carbon exhibits a further upfield shift of 7 ppm from that of the methylene carbon in $(Me_3CCH_2)_2SbH$ with a chemical shift of 21.04 ppm.

Our ultimate interest in these compounds has been to explore their potential utility as precursors for use in MOCVD. Specifically, we have carried out preliminary investigations of both stibines in conjunction with trimethylindium in attempts to grow indium antimonide films in a very simple reactor. Our goal has been to demonstrate growth of indium antimonide films and to identify whether these compounds had potential as an alternative antimony source compound.

Despite the low vapor pressure of $(Me_3CCH_2)_2SbH$ at ambient temperature (0.5 Torr), we were able to obtain films of polycrystalline indium antimonide on a silicon (100) substrate. Typical growth conditions employed a deposition temperature of 400 °C and an approximate V/III ratio of 3.5. The polycrystalline nature of the indium antimonide was confirmed by X-ray diffraction patterns and showed no preferred orientation.[22] A listing of observed $2\theta$ values, $d$ values, materials, and crystallographic orientation appears in Table I. In addition to the peaks associated with indium antimonide, we also observed peaks for antimony and/or indium. We attribute this to the simple design of our reactor, which does not allow for fine control of deposition parameters. Examination of the films by Auger electron spectroscopy showed various ratios of indium to antimony. Figure 3 shows an Auger spectrum for our best film obtained at the previously stated growth conditions. Central to the spectra are peaks at 402/409 eV for indium and 456/464 eV for antimony. In this spectrum, the In/Sb ratio of 1.08 compares favorably to 1.13 from a sample of MBE-grown indium antimonide analyzed in our spectrometer. A small peak at 277 eV indicates carbon contamination in this film to be a minimum of 1%, the approximate detection level of Auger spectroscopy. Nomarski photographs of these films exhibited a poor morphology with large grains (approximately 1-μm diameter) and numerous defects. This may be attributed to the nature of our reactor, incorrect growth conditions, or a 20% lattice mismatch between silicon and indium antimonide. Profilometry results indicated a low growth rate that varied from 0.1 to 0.3 μm/h.

**Table II. XRD Data for InSb Film Grown Using $(Me_3CCH_2)SbH_2$**

| $2\theta_{obsd}$ | $d_{obsd}$, Å | $d_{lit}$, Å | identity | orientation ($I/I_0$, %) |
|---|---|---|---|---|
| 23.70 | 3.751 | 3.74 | InSb | 111 (100) |
| 28.70 | 3.108 | 3.109 | Sb[b] | 102 (31) |
| 39.30 | 2.291 | 2.290 | InSb | 220 (34) |
| 39.95 | 2.255 | 2.248 | Sb | 014 (9) |
| 41.95 | 2.152 | 2.152 | Sb | 110 (6) |
| 46.40 | 1.955 | 1.953 | InSb | 311 (18) |
| 48.20 | 1.886 | 1.878 | Sb | 006 (14) |
| 51.60 | 1.770 | 1.770 | Sb | 022 (5) |
| 56.75 | 1.621 | 1.620 | InSb | 400 (2) |
| 59.40 | 1.555 | 1.555 | Sb | 204 (1) |
| 62.50 | 1.485 | 1.486 | InSb | 331 (3) |

[a] See ref 22. [b] See ref 23.

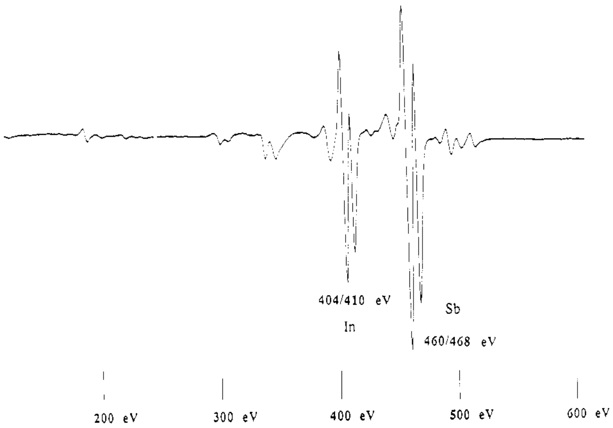

**Figure 4.** Auger spectrum of InSb film employing trimethylindium and $(Me_3CCH_2)SbH_2$ as precursors.

Similarly, we have employed $(Me_3CCH_2)SbH_2$ in attempts to grow films of indium antimonide. The primary stibine was of particular interest to us due to its enhanced volatility in comparison to $(Me_3CCH_2)_2SbH$. In our growth runs, we were able to obtain the deposition of polycrystalline indium antimonide on either a silicon or gallium arsenide (100) substrate at 350 °C. A typical run employed a V/III ratio of approximately 5.5–6. The polycrystalline nature of the film was established by XRD with no preferred orientation exhibited (data given in Table II). Profilometry results indicated an increase in growth rate, as compared to $(Me_3CCH_2)_2SbH$, with values ranging from 0.4–0.6 μm/h. Examination of the films by Auger spectroscopy showed an In/Sb ratio that varied from 0.64 to 1.40 depending on growth conditions. However, the Auger spectra contained no evidence of carbon in the 270-eV region indicating that the amount of carbon present was below the Auger detection limit of approximately 1% (see

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(22) Joint Committee on Powder Diffraction Standards (JCPDS), File Card No. 6-0208.

(23) JCPDS No. 5-0562.

Figure 4). No attempts were made to quantify carbon contamination using more sensitive techniques since the presence of excess antimony in the film and the poor morphology (granular in nature), as seen from visual inspection and Nomarski micrographs, indicated we had not optimized the deposition conditions. Nevertheless, the absence of carbon at the percent level in these films, together with the stability and volatility of the primary stibine, suggests it is a suitable candidate for further growth studies under more controlled conditions.

## Conclusions:

From this study we have found that stable, volatile primary and secondary antimony hydrides can be synthesized in reasonably good yields. These compounds are significantly more stable and/or volatile than other organoantimony hydrides reported in the literature. This may be attributed to the presence of large organic substituents with no β-hydrogens. Our studies have also shown that these hydrides are transportable and can be used to deposit InSb. In particular, these compounds can be used with trimethylindium to deposit InSb at moderately low temperatures for organostibines (400 °C for $(Me_3CCH_2)_2SbH$ and 350 °C for $(Me_3CCH_2)SbH_2$). The primary stibine is extremely attractive because of its high volatility and low decomposition temperature, characteristics of interest in growing ternary antimonides or metastable antimonide-based materials.

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**Registry No.** 1, 129135-92-8; 2, 129135-94-0; 3, 129135-93-9; $(Me_3CCH_2)_3Sb$, 99715-60-3; $SbBr_3$, 7789-61-9; $(Me_3CCH_2)_2SbI$, 141612-23-9; $Me_3In$, 3385-78-2; InSb, 1312-41-0.

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# Synthesis and Evaluation of Copolymers of (*tert*-Butoxycarbonyloxy)styrene and (2-Nitrobenzyl)styrene Sulfonates: Single-Component Chemically Amplified Deep-UV Imaging Materials

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Copolymers of (*tert*-butoxycarbonyloxy)styrene (*t*-BOC-styrene) and (2-nitrobenzyl)styrene sulfonates were prepared to give hydrophobic, photosensitive materials. Exposure to ultraviolet light converted the pendant 2-nitrobenzyl sulfonate esters to sulfonic acid moieties, and this photogenerated acid catalyzed the removal of the *t*-BOC groups on subsequent heating. The resulting material was a copolymer of 4-hydroxystyrene and styrenesulfonic acid, which was hydrophilic and soluble in aqueous base. Copolymers with different compositions (monomer ratios) and molecular weights were synthesized, and the resulting materials were analyzed by thermal and spectroscopic methods and evaluated for lithographic performance as positive tone resists. As the percentage of the photosensitive 2-nitrobenzylstyrene sulfonate monomer was increased, the lithographic sensitivity improved but the thermal stability of the copolymers decreased. The photoresponse of some of the materials was inhomogeneous, apparently the result of inhomogeneous distribution of acid-generating monomers in the polymers.

## Introduction

The needs of the semiconductor industry continue to give impetus to the investigation of new chemistries for photoresists. These needs include the resolution of smaller features, improved sensitivity (or photospeed), and greater process latitude (the ability to tolerate more variation in processing conditions).[1] Chemically amplified deep UV photoresists are one promising class of materials for patterning in the submicron regime (0.25–1.0 μm).[2] Deep-UV is defined as light in the wavelength range 220–280 nm, though typically 248-nm KrF excimer laser radiation is employed. Chemical amplification refers to the increase in sensitivity achieved by harnessing the effect of each absorbed photon to catalytic resist chemistry.[3] A typical chemically amplified resist contains two components: a matrix polymer and a photoactive additive. Absorption of light by the photoactive compound generates the catalytic agent, usually a strong acid. Subsequent heating drives an acid-catalyzed chemical reaction of the matrix polymer, generally a deprotection or cross-linking reaction. The end result is different solubility properties for the exposed and unexposed areas of the resist film, allowing formation of the desired image.

A chemically amplified resist we have studied previously consists of poly[(*tert*-butoxycarbonyloxy)styrene-*co*-sulfur dioxide] (PTBSS) and a photoacid generator.[3d] We have

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