Low-Temperature Thermolysis Behavior of Tetramethyl- and Tetraethyldistibines

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The thermolysis behavior of tetramethyl- and tetraethyldistibine (Sb_2Me_4 and Sb_2Et_4) was investigated using a mass spectrometer coupled to a tubular flow reactor under near-chemical vapor deposition (CVD) conditions. Sb_2Me_4 undergoes a gas-phase disproportionation with an estimated activation energy of 163 kJ/mol. This reaction leads to the formation of methylstibinidine, SbMe , that reacts on the surface to produce antimony film and SbMe_3 . Unfortunately, this clean decomposition pathway is limited to a narrow temperature range of 300–350 °C. At temperatures exceeding 400 °C, SbMe_3 decomposes following a radical route with a consequent risk of carbon contamination. In contrast, Sb_2Et_4 disproportionates at the hot wall of the reactor. According to mass-spectrometric data, this reaction is significant starting at a temperature of 100 °C, with an apparent activation energy of 104 kJ/mol. Within the temperature range of 100–250 °C, the precursor decomposition leads to the formation of antimony films and SbEt_3 , whereas different molecular reaction pathways are significantly activated above 250 °C. The use of Sb_2Et_4 lowers the risk of carbon contamination compared to Sb_2Me_4 at high temperature. Therefore, Sb_2Et_4 is a promising CVD precursor for the growth of antimony films in the absence of hydrogen atmosphere in a wide temperature range. (J Am Soc Mass Spectrom 2008, 19, 1336–1342) © 2008 American Society for Mass Spectrometry

Antimony-containing compounds are extensively investigated as thermoelectric [1, 2], lasing [3], photo-detecting [4], magnetic [5, 6], and transparent electrode [7] materials for a wide range of applications. Most of the antimony-containing materials possess metastable compositions that impose low processing temperatures. Chemical vapor deposition (CVD) is considered as a nearly ideal, low-cost, and high throughput approach for device manufacturing; however, its application here is hindered by the lack of suitable, low-temperature antimony precursors [8]. Standard antimony precursors including SbMe_3 and SbEt_3 exhibit high thermal stability, which complicates the growth of materials such as InSb [9, 10]. These precursors were therefore judged not suitable as controllable antimony sources because of their strong Sb—C bond [11, 12]. The strength of the Sb—C bond was found to decrease with increasing ligand size [13], although the extremely low volatility of the resulting molecules represents a significant drawback [14]. Deuterated stibine (SbD_3) was proposed by Todd et al. [8] as a suitable carbon-free antimony source that allows deposition of antimony films at temperatures as low as 200 °C. SbD_3 shows an enhanced stability compared to that of SbH_3 at 23 °C, which allows its implementation as a CVD

precursor [8]. Tetramethyl- and tetraethyldistibine (Sb_2Me_4 and Sb_2Et_4) were also investigated as alternative precursors [11, 12, 15]. These showed low decomposition temperatures without carbon retention and enabled an accurate control of doping concentration as a result of the conveniently controllable vapor pressures. Dickson et al. [11] reported on the decomposition of Sb_2Me_4 at 300 °C in the presence of molecular hydrogen to yield pure antimony films, but no information was given on the kinetics or on the nature of the obtained decomposition products. A successful growth of InSb was demonstrated at 330 °C using Sb_2Et_4 in combination with InMe_3 [11]. In this case the deposition kinetics was limited by the cracking efficiency of InMe_3 . The low deposition temperature (330 °C) suppresses reaction at the hetero-interface for the growth of heterojunctions and superlattices.

In this study, the decomposition mechanism of two selected distibine compounds will be investigated with the objective to clarify the mechanism that is responsible for the low resulting deposition temperature and to evaluate the contamination risk as a function of the deposition temperature.

Experimental

Sb_2Me_4 [16] and Sb_2Et_4 [17] were prepared according to literature methods. Thermolysis reactions were investigated in a stainless steel tubular hot-wall reactor at

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$1\text{--}1.6 \times 10^{-5}$ mbar, whereas the precursor was delivered from an evaporator maintained at 0 and 25 °C for Sb_2Me_4 and Sb_2Et_4 , respectively, using 2 sccm of argon as carrier gas. The operating pressure range corresponds to conditions where GaSb was grown by CVD in earlier work [18, 19]. The residence time of gaseous molecules was estimated to be $<70 \mu\text{s}$. The tubular reactor has a high surface-to-volume ratio ($S/V = 0.5 \text{ mm}^{-1}$), which favors surface–gas interactions. A copper skimmer was used to extract a gas sample from the pyrolysis reactor to the ionization chamber, which is pumped down to $<5 \times 10^{-6}$ mbar. The sampled gas is then subjected to electron-impact ionization before analysis with a time-of-flight mass spectrometer (Kaesdorf, Munich, Germany), equipped with a reflectron. The mass resolution of this instrument is $m/\Delta m = 4000$ and the sensitivity is better than 10 ppm for most considered hydrocarbons in this study. The energy of the electron beam is tunable between 5 and 40 eV, and analysis with 10 and 20 eV was routinely used to minimize electronic fragmentation and to allow its discrimination from the thermally induced reactions. Setting the electron beam energy at nominally 10 eV allows minimizing the electron-induced fragmentation, although without completely succeeding to suppress it because of the energy spread of about 0.5 eV (full width at half-maximum).

Results and Discussion

Mass spectrometry was repeatedly used to support and to improve the understanding of the CVD process. Our previous work demonstrated its usefulness for the systematic evaluation of new families of CVD precursors [20], for the identification of the occurring reaction pathways under near-CVD conditions and for the determination of their activation energies [21]. Both precursors investigated in this study are highly volatile at 18 °C with partial pressures of 0.32 mbar for Sb_2Me_4 and 0.8×10^{-3} mbar for Sb_2Et_4 [11]. These compounds are also air-sensitive [22], which imposes careful handling under controlled atmosphere. Furthermore, Sb_2Et_4 is light-sensitive, indicating its higher reactivity [11].

Tetramethyldistibine

Figure 1 shows the recorded mass spectra at different temperatures. At 20 °C, the molecular ion peak presents the highest intensity. The degree of electron-induced fragmentation is very low, either leading to the loss of methyl groups with subsequent formation of Sb_2Me_3 and Sb_2Me_2 fragment ions, or to the scission of the Sb–Sb bond to form SbMe_2 fragment ion. The spectrum at 400 °C shows that the signals representing the precursor are substantially decreased, except for that corresponding to the SbMe_2 fragment ion, and that peaks attributed to SbMe_3 and SbMe have emerged. The reference spectrum of SbMe_3 below the temperature decomposition threshold exhibits the molecular peak signals

Figure 1. Mass spectra of Sb_2Me_4 collected after ionization with a 10 eV electron beam, CVD reactor at 20, 400, and 750 °C.

(highest intensity) in addition to signals arising from the electronic fragmentation with the loss of one methyl group. In this reference spectrum (available as supplementary materials, which can be found in the electronic version of this article), no signal could be attributed to SbMe fragment ion. Therefore, the increase of the SbMe_2 signal at 400 °C can be attributed to the formation of SbMe_3 whereas methylstibinidine (SbMe) is considered as a second product of the thermolysis reaction.

At the reactor temperature of 750 °C, C_4^- , C_3^- , C_2^- , and C_1^- species are detected, indicating the complete precursor thermolysis. Butene (C_4H_8) was identified as the major product of thermolysis at 750 °C, as clearly shown in the supplementary materials. The trend of individual peaks was presented as a function of the thermolysis temperature in Figure 2 for the most relevant species. The precursor molecule, represented by the peaks attributed to Sb_2Me_4 and its fragment ions Sb_2Me_3 and Sb_2Me_2 in Figure 2a, shows good stability up to a reactor temperature of 300 °C. Above this temperature, an abrupt decay was observed with a complete depletion starting at 450 °C. The thermolysis of Sb_2Me_4 was associated with the detection of SbMe_3 as dominant product, in terms of signal intensity, and SbMe as shown in Figure 2b. Figure 2c shows that SbMe_2 signal can be fitted with a sum of a decay component at 300 °C, corresponding to the precursor molecule, and to a peak with a maximum above 400 °C, which corresponds to the formation of SbMe_3 . Therefore, the detection of SbMe_2 ion is reasonably attributed to the fragmentation of SbMe_3 and Sb_2Me_4 .

The detection of SbMe_3 and SbMe molecules in the gas phase suggests the occurrence of an intramolecular disproportionation reaction as presented in Scheme 1. The activation energy of this reaction was estimated at $(163 \pm 4) \text{ kJ/mol}$ from the decay of the molecular peak when assuming a first-order kinetics with $A = 10^{13} \text{ s}^{-1}$ as the preexponential factor.

The low intensity of the peaks attributed to SbMe (Figure 1) and its early depletion (Figure 2b) hint at its

Figure 2. Temperature-dependent intensity of relevant species in the thermolysis of Sb_2Me_4 .

further reaction, probably on the wall of the reactor. This reaction is expected to result in the formation of an antimony deposit in addition to a methyl radical, which the profile is depicted as a function of the temperature in Figure 2d. The significant formation of methane (Figure 2e), starting at a temperature of 400 °C indicates

hydrogen abstraction from adjacent methyl ligands, probably on the surface where coating occurs. Several higher hydrocarbons have been detected above 500 °C, including butane, butene, propane, ethane, and ethene, from which ethane and ethene are shown in Figure 2f. At temperatures exceeding 600 °C, hydrogen and several unsaturated hydrocarbons were detected. These observations indicate the presence of several pathways with a high risk of carbon contamination in the case of the growth of antimony films from the thermolysis of Sb_2Me_4 at temperatures exceeding 400 °C.

Scheme 1

Scheme 2

Comparing the mass-spectroscopic results obtained for Sb_2Me_4 and SbMe_3 shows an advantageous low temperature ($\sim 300^\circ\text{C}$) and slightly lower activation energy (163 kJ/mol) of the decomposition process for Sb_2Me_4 . In fact, SbMe_3 was reported to significantly decompose at a temperature of 400°C [23, 24], with an activation energy of 171 kJ/mol [25]. The decomposition products of Sb_2Me_4 — SbMe and SbMe_3 —are already observed at 300°C , which is in agreement with the early investigation by Dickson et al. [11], who reported on the growth of Sb films at 300°C from this precursor in the presence of hydrogen.

Within the narrow temperature range of 300 – 350°C , no hydrocarbon products were detected as depicted in the temperature-dependent profiles in Figure 2, whereas a significant fraction of the precursor has already decomposed, which might be attributed to the deposition of antimony forming exclusively SbMe_3 as product. The ligand exchange between adsorbed SbMe is assumed to form SbMe_3 that can desorb from the surface in addition to the formation of an antimony deposit. The increase of the rate of this reaction with increasing temperature leads to the depletion of SbMe from the gas phase. It is anticipated that the growth of carbon-free antimony films can be expected in this temperature range (300 – 350°C) also in the absence of molecular hydrogen. To

date, this was demonstrated only in the presence of molecular hydrogen by Dickson et al. [11].

The produced SbMe_3 from the thermolysis of Sb_2Me_4 undergoes further decomposition above 400°C to form a series of hydrocarbons including methyl radical, methane, and ethane. These species were reported during the thermolysis study of SbMe_3 [24–26]. The formation of these species was attributed to the homolytic scission of the Sb—C bond to release CH_3 radical that further reacts following hydrogen abstraction or recombination to form a variety of hydrocarbons. The growth of carbon-free antimony films above 400°C is expected to require the use of additional molecular hydrogen flow to facilitate the formation of methane as the major product of the thermolysis. This agrees with the investigation of Larson et al. [23, 24], who reported the decomposition threshold of SbMe_3 at 400°C in inert atmosphere with significant recombination to form C_2 - and C_3 -species. The occurrence of radical recombination constitutes a high risk of carbon contamination, in that unsaturated hydrocarbons might form. The presence of D_2 or H_2 decreases the decomposition threshold to approximately 350°C and suppresses the formation of C_2 - and C_3 -species. CH_3D was observed as the predominant decomposition product of SbMe_3 in D_2 atmosphere [23, 24].

Tetraethyldistibine

The mass spectrum obtained with Sb_2Et_4 at 30°C shows the presence of the expected precursor molecule and the corresponding electron-induced fragments: Sb_2Et_3 , Sb_2Et_2 , and Sb_2Et , in addition to fragments with one Sb atom. $\text{Et}_2\text{Sb—O—SbEt}_2$, the oxidation

Figure 3. Mass spectra of Sb_2Et_4 collected after ionization with a 10 eV electron beam, CVD reactor at 30, 300, and 650°C .

product of Sb_2Et_4 , was also detected with a relatively low intensity. The formation of this molecule as reported by Breunig [22] and Dickson et al. [11], despite the taken precautions, shows the extremely high affinity of Sb_2Et_4 toward oxygen. The decomposition path of Sb_2Et_4 will be discussed while ignoring the presence of the small fraction of $\text{Et}_2\text{Sb}-\text{O}-\text{SbEt}_2$, with the assumption that no significant interaction takes place.

At the reactor temperature of 300 °C, Sb_2Et_4 was almost completely thermally decomposed and molecules with a single antimony atom were formed. The relative intensities of the peaks attributed to SbEt_3 , SbEt_2 , and SbEt correspond to the reference spectrum of SbEt_3 , which is given as supplementary materials. Therefore, it is assumed that the decomposition of Sb_2Et_4 occurs with surface trapping of the reactive antimony-containing intermediates, as illustrated in Scheme 2. Above 650 °C, no antimony-containing species were detected as depicted in Figure 3.

The temperature scan in Figure 4a shows that reaction (2) is significantly observed starting at a temperature of 100 °C and is terminated at 300 °C. The activation energy of this reaction was calculated to be (104 ± 7) kJ/mol from the decay of the molecular peak with

Scheme 3

increasing temperature. For this calculation, a first-order kinetics and a preexponential factor of $A = 1 \times 10^{13} \text{ s}^{-1}$ were assumed. A significant production of SbEt_3 starts above 100 °C, as shown in Figure 4b, and attains its maximum at 250–300 °C, which is the temperature of the complete depletion of Sb_2Et_4 .

Examination of the evolution of low-mass peaks with increasing temperature does not show any significant production of hydrocarbons below 250 °C, which clearly indicates that the only product of reaction (2) is elemental antimony and SbEt_3 . This suggests the exchange of ethyl groups on the surface as illustrated in Scheme 3 as the dominant deposition mechanism at temperatures in the range of 100–250 °C. Interestingly, Dickson et al. [11] noticed the degradation of Sb_2Et_4 in the liquid phase when exposed to daylight at temperatures as low as 50 °C to produce SbEt_3 and metallic antimony deposit.

Our recent investigation shows that SbEt_3 is remarkably stable up to a reactor temperature of 400 °C in similar conditions [21]. Therefore, the observed decay of the intensity of SbEt_3 above 250 °C in Figure 4 cannot be attributed to its thermal decomposition. This result rather indicates that the path leading to the formation of SbEt_3 became unfavorable at higher temperatures. It is concluded that a competing decomposition mechanism, with the reaction represented in Scheme 2, builds up at temperatures exceeding 250 °C.

At temperatures above 250 °C, where the formation of SbEt_3 is not favored, several hydrocarbons were detected with different trends as a function of the temperature. The presence of *n*-butane, ethene, ethane, and ethyl radical, shown in Figure 5, indicates the competing radical and molecular route for the release of the ligand from the surface. The radical route involves the scission of the $\text{Sb}-\text{C}$ bond and the formation of gas-phase ethyl radicals, whereas the molecular route involves the β -hydride elimination by releasing ethene and forming surface hydrogen. The surface hydrogen might react with an adjacent ethyl group to form ethane. Since no hydrogen was detected it is assumed that all hydrogen produced during the β -hydride elimination is used to form ethane. A recombinative desorption of adjacent ethyl groups leads to the formation of *n*-butane, which is detected in its molecular form, but

Figure 4. Temperature-dependent intensity of relevant antimony-containing species in the thermolysis of Sb_2Et_4 . The curve fitting the depletion of Sb_2Et_4 (upper diagram) is included with the profiles of the species containing one antimony atom (lower diagram). (a) Sb_2Et_4 and associated fragment ions; (b) SbEt_3 intermediate and associated fragment ions.

Figure 5. Temperature-dependent intensity of relevant produced hydrocarbon species. Ethene, ethyl radicals, and C_3H_7 (most intense fragment ion of *n*-butane) were measured using the ionization energy of 10 eV; whereas ethane, which was not detected at 10 eV because of the low intensity (see supplementary materials), was measured with 20 eV.

also by its most intense fragment C_3H_7 during ionization at 10 eV attributed to the energy spread [21]. From the relative intensities of ethene and ethyl radical, it can be concluded that the radical route is less favorable than the molecular route and it is observed in a limited temperature range.

A comparative study of the thermolysis of Sb_2Et_4 and $SbEt_3$ shows a clear advantage of Sb_2Et_4 in terms of decomposition temperature and activation energy. Based on the mass spectrometric data, the possibility to grow antimony films using Sb_2Et_4 can be expected at a

temperature of 100 °C with an activation barrier of 104 kJ/mol, which contrasts with $SbEt_3$ that requires a temperature of 400 °C and presents a barrier of 183 kJ/mol [21]. Regarding the decomposition mechanism, Sb_2Et_4 offers a wide temperature range of 100–250 °C, where a clean reaction path is dominant that produces exclusively elemental Sb and $SbEt_3$. The decomposition path above 250 °C is mainly dominated by a molecular route with formation of ethane, ethene, and *n*-butane. It is worth noting that these species were also observed during the thermolysis of $SbEt_3$, but at temperatures exceeding 400 °C [21, 26]. Therefore, a carbon-free antimony film is expected when using Sb_2Et_4 as precursor.

Conclusion

The thermal behavior of two distibine compounds (Sb_2R_4 ; R = Me, Et) was investigated under near-CVD conditions. Both precursors exhibit low decomposition temperature and activation energies when compared to traditional antimony sources, which was attributed to the occurrence of an intramolecular disproportionation reaction. The Sb_2Me_4 precursor exhibits a homogeneous intramolecular disproportionation to form gas-phase $SbMe$ and $SbEt_3$, whereas Sb_2Et_4 seems to undergo this reaction with a surface trapping of the reactive $SbEt$. These precursors offer a particularly convenient temperature range where the formed alkylstibinidine molecules that undergo ligand exchange on the hot surface to release SbR_3 and form Sb deposit. This clean decomposition path is expected to enable the growth of pure films at low temperature and might be considered as a strategy for other elements. Further investigations on the surface reactions and on CVD deposition of Sb films are suggested.

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