Ion-Molecule Reactions in Mixtures of Trimethylaluminum and Methylamines

Stephan B. H. Bach* and Denise C. Parent

Chemistry Division/Code 6110, Naval Research Laboratory, Washington, D.C., USA

The ion-molecule reactions of mixtures of trimethylaluminum and methylamines, to serve as a model system for group 13-15 semiconductor fabrication, were examined by using Fourier transform ion cyclotron resonance mass spectrometry. Sequential ion-molecule reactions leading to formation of multiple adducts were observed for each of the reactant mixtures investigated. Collision-induced dissociation was used to probe the adduct structures. There is evidence for hydrogen bonding between the amines and aluminum in most of the adducts studied. Rearrangement of the aluminum/nitrogen skeletons was not observed, although the aluminum/nitrogen bonds appear to be relatively strong, so that stable adducts can be formed. The monomethylamine and dimethylamine readily produce gas-phase neutral adducts with trimethylaluminum, which can be related to the basicities of the methylamines. (*J Am Soc Mass Spectrom* 1993, 4, 111-116)

Metalorganic chemical vapor deposition (MOCVD) is an outgrowth of metalorganic chemical vapor epitaxy (MOCVE) that finds its beginnings in the work of Manasevit [1]. This technology has shown rapid progress from the first demonstration of device-quality material to an emphasis on the devices themselves [2]. Little is understood, though, of the reactions that take the precursors from the gas phase to the formation of semiconductor devices on a surface.

This work is directed toward developing an understanding of the gas-phase interactions of the precursors utilized in the growth of group 13-15 semiconductor materials. These investigations also have the aim of suggesting possible new compounds that will reduce the impurities resulting from the incomplete decomposition of the precursors. This will involve identifying stable adduct species that could produce the desired semiconductor material with the degradation of a single precursor rather than using two or more precursors. A further goal is to investigate the role that ion-molecule reactions may play in determining the final composition of the materials that are incorporated into semiconductor devices. Ion-molecule reactions are most likely to be important in new MOCVD technolo-

gies, such as plasma-assisted MOCVD [3] and electron cyclotron resonance plasma-excited MOCVD [4], and in the laser-induced photochemistry [5] of MOCVD precursors used to initiate the reaction sequence that ultimately leads to the formation of the desired semiconductor material.

Interrante et al. [6] have shown that good quality aluminum nitride films can be produced in a chemical vapor deposition (CVD) reactor by using $((\text{CH}_3)_2\text{AlNH}_2)_3$, which is obtained by reacting trimethylaluminum (TMAI) and ammonia, and have identified the gas-phase products that occur during deposition. This group is also synthesizing other cyclic dialkylaluminum amides $(\text{R}_2\text{AlNH}_2)_n$ as precursors for high-purity AlN powder and thin films, as well as investigating the solution kinetics [7].

In our laboratory we have recently investigated [8] the fragmentation of TMAI and the ion chemistry in mixtures of TMAI and ammonia. The aluminum/ammonia adduct $(\text{CH}_3)_2\text{AlNH}_3^+$ and the diammonia adduct $(\text{CH}_3)_2\text{Al}(\text{NH}_3)_2^+$ were both observed. In extending this work, we hoped that the study of the gas-phase mixtures of methylamines and TMAI would provide insights into the gas-phase chemistry occurring among the group 13-15 precursors. Thus, TMAI serves as a model for other group 13 precursors (i.e., trimethylindium and trimethylgallium), whereas the methylamines can be considered as analogs to other group 15 precursors, such as those containing phosphorus and arsenic.

*Present address: Division of Earth and Physical Sciences, University of Texas at San Antonio, San Antonio, TX 78249-0063.

Address reprint requests to Denise C. Parent, Chemistry Division/Code 6110, Naval Research Laboratory, Washington, D.C. 20375-5000.

Experimental

The experiments were performed with a Fourier transform ion cyclotron resonance mass spectrometer, which has been described in detail elsewhere [9]. The experimental apparatus consists of a Nicolet FTMS-1000 data system (EXTREL-FTMS, Madison, WI), a 3-T superconducting magnet, and a custom vacuum system with a $1 \times 1 \times 2$ (z axis)-in. cell made of stainless steel, except for the trapping plates, which are composed of 90% transparent nickel mesh.

The TMAI and methylamines were introduced into the vacuum chamber via leak valves and maintained at static pressures between 1.0 and 2.0×10^{-8} torr for TMAI and between 2.0×10^{-8} and 1.0×10^{-7} torr for the methylamines. (All pressures reported are uncorrected for instrumental factors and ionization gauge response.) The TMAI samples were prepared by transferring small quantities from the shipping container into a sample container and performing several freeze/pump/thaw cycles to remove noncondensable gases. The methylamine samples were used without further purification. The purities of all samples were verified by their electron ionization (EI) mass spectra.

All of the ion-molecule reactions to be discussed were studied by isolating the reactant ion, using MS^n (tandem mass spectrometry) techniques, and varying the reaction time. Absolute or even relative rate constants were not determined, however, because the pressures of the various gases could not be calibrated. Two factors precluded accurate pressure calibrations: first, limited literature data on ion-molecule reactions with TMAI; second, difficulty in maintaining stable pressures of most of these compounds owing to their "stickiness."

The collision-induced dissociation (CID) experiments were carried out by applying a single frequency pulse (0.06–3.0-ms duration) to translationally excite the ion of interest, which undergoes subsequent collisions with either the reactant gases already present or with added argon. The pressure of argon was varied between 2.0×10^{-8} and 1.0×10^{-7} torr.

Results and Discussion

Evidence for Neutral-Neutral Reactions

The base peak in the EI mass spectrum of a mixture of TMAI and monomethylamine (MMAm) or dimethylamine (DMAm) is the adduct $(CH_3)_2AlNH_2CH_3^+$ or $(CH_3)_2AlNH(CH_3)_2^+$, respectively. These products appear immediately after ionization, with no subsequent reaction time, and are apparently due to neutral-neutral reactions of TMAI with the methylamines. The methyl group can be lost during the reaction or on ionization. The parent adduct was carefully searched for but not observed, suggesting either that the methyl is lost during adduct formation or that the parent ion is unstable. The results of the ion-

molecule reactions suggest the latter explanation is correct. In a previous study of the ion chemistry of $(CH_3)_3Al^+$, Kappes et al. [10] mentioned that neutral complexes were formed between TMAI and various neutrals including trimethylamine (TMAm); however, they did not indicate whether the parent ion of the neutral complex was actually detected. The strength of the neutral interaction appears to be correlated to the pK_b 's of the amines, which are 4.74 (NH_3), 3.36 (NH_2CH_3), 3.29 ($NH(CH_3)_2$), and 4.28 ($N(CH_3)_3$) [11]. In this work, the two methylamines that were observed to form neutral adducts are also the strongest bases. Because the Al center in TMAI has no electrons available for bonding, the methylamine must supply the electrons. The ability to donate electrons is one measure of basicity, thus the correlation with pK_b is to be expected.

These adduct ions are ejected when the reactant ion [i.e., $(CH_3)_2Al^+$ or the amine parent ion] is mass selected. Any neutral-neutral reaction products are not detected, because there is no other ionization event. The observation of the adduct ions arising from neutral-neutral reactions, although interesting, is independent of the ion-molecule chemistry to be discussed in the rest of this report.

Ion-Molecule Reactions

The generalized ion-molecule reaction scheme for mixtures of TMAI with MMAm, DMAm, or TMAm is depicted in Figure 1. (The numbers above the arrows refer to the reaction numbers in the following discussion.) For each amine, the primary ionic product is the aluminum/amine adduct $(CH_3)_2AlNH_x^+$ ($CH_3)_3Al^{3-x}^+$ (where $x = 2, 1$, and 0 for MMAm, DMAm, and TMAm, respectively), $\equiv [DMAI \cdot A]^+$ (DMAI is dimethylaluminum, and A is the amine). One observed pathway for the formation of this product is the reac-

Figure 1. A generalized schematic of the ion-molecule reactions observed in mixtures of TMAI with different amines (A), as well as the results of the CID experiments. Numbers above the arrows refer to the reactions in the text. Reaction 4 was not observed with TMAm, nor was reaction 4b with MMAm.

tion of DMAI^+ with the neutral amine as follows:

A second pathway that was also observed is

Because this adduct product is also observed with ammonia, the methyl is presumably lost from the TMAI moiety. This does not preclude the loss of methyl from the amine in these reactions, however. One would expect reaction 1 to be more rapid than reaction 2, owing to steric hinderance in the interaction between neutral TMAI and the methylamine cation, which must pass through an intermediate with a fourfold coordinate Al center. The reaction of DMAI^+ and the neutral methylamine can simply form the adduct without any rearrangement necessary. The relative rates could not be experimentally verified, however, because we could not calibrate the pressures of all of the compounds used, as noted previously.

The $[\text{DMAI} \cdot \text{A}]^+$ adducts undergo a second addition reaction with the neutral amine to yield the diamine adduct $(\text{CH}_3)_2\text{Al}(\text{NH}_x(\text{CH}_3)_{3-x})_2^+ \equiv [\text{DMAI} \cdot \text{A}_2]^+$, as shown in reaction 3;

Reactions 1 and 3 were also observed in an older study [10] of DMAI^+ reacting with TMAM.

With the exception of TMAM, the aluminum/amine adduct $[\text{DMAI} \cdot \text{A}]^+$ also reacts with TMAI to form a dialuminum adduct, $(\text{CH}_3)_2\text{AlNH}_x(\text{CH}_3)_{3-x}\text{Al}(\text{CH}_3)_3^+ \equiv [\text{DMAI} \cdot \text{A} \cdot \text{TMAI}]^+$, as follows:

The nonreactivity of TMAM in this reaction could be due to experimental factors (i.e., the relative pressures of TMAI and TMAM were such that reaction 4a was not competitive with reaction 3). With DMAM, an additional product $(\text{CH}_3)_2\text{AlNH}_x(\text{CH}_3)_{3-x}\text{Al}(\text{CH}_3)_2^+ \equiv [\text{DMAI} \cdot \text{A} \cdot \text{DMAI}]^+$ was also observed:

corresponding to methyl loss from the dialuminum adduct formed in reaction 4a. This methyl loss product

was more intense than the adduct formed in reaction 4a. It is also the only reaction, in addition to reaction 2, where neutral loss was observed.

The diamine adducts $[\text{DMAI} \cdot \text{A}_2]^+$ formed in reaction 3 reacted further with TMAI via reaction 5,

to produce a diamine/dialuminum adduct $(\text{CH}_3)_2\text{Al}(\text{NH}_x(\text{CH}_3)_{3-x})_2\text{Al}(\text{CH}_3)_3^+ \equiv [\text{DMAI} \cdot \text{A}_2 \cdot \text{TMAI}]^+$.

The ion adducts, because they undergo no fragmentation, contain excess energy equal to the bond strength of the new bond(s) [12].¹ The disposal of this energy can take several forms: It can be emitted in the form of infrared photons; it can be accommodated by the product in its internal modes; or it can be removed by thermalizing collisions. These adducts have a large number of internal degrees of freedom ($3n - 3 = 45$ for the smallest adduct), many of which will be low-frequency bending modes. This will lead to long lifetimes for the adduct ions. The observation of adduct ions between DMAI^+ and the methylamines is not surprising when compared with previous work in Fourier transform mass spectrometry (FTMS). We have observed adduct formation to occur relatively efficiently when the neutral reagent has a permanent dipole moment [9], as is the case for the methylamines.

Methyl loss on adduct formation is only observed when TMAI is one of the reactants. Reactions 2 and 4b are examples of ion-molecule reactions where methyl loss is observed. The major exception is reaction 5, where TMAI is seen to complex without methyl loss. This suggests that geometric factors are important in determining the stability of these adducts, at least for the smaller adducts.

Structures of Neutral Complexes of Aluminum Compounds

Before beginning a discussion of the CID results and what they imply about the adduct ion structure, it is useful to review what is known about neutral adducts of aluminum compounds, such as TMAI and AlX_3 (where X is a halogen), with various other molecules. Most of the structural information comes from gas-phase electron diffraction studies [13]. Generally, the aluminum compound/neutral adduct can be described as an electron pair donor/acceptor complex, with the neutral containing an electron-rich atom, such as N, P, O, or S, which then forms a dative bond to the Al atom by donating electrons into an empty orbital on the

¹For the reaction of TMAI with TMAM the $\Delta H_f^\circ(g)$ of the adduct $(\text{CH}_3)_3\text{Al}(\text{CH}_3)_3$ was determined to be -30.69 kcal/mol, which gives an indication of the magnitude of this excess energy.

aluminum. This bond is weaker than a normal covalent bond. In these complexes the aluminum is fourfold coordinate, giving it a formal negative charge, whereas the donor atom has lost electron density, giving it a formal positive charge. The donor atom also has a coordinate number that is one greater than it has in the isolated neutral (i.e., four for nitrogen).

There are several adducts that do not fit this picture, however. The dimers of TMAI and DMAIH have bridging methyl or hydrogen groups, respectively, and some degree of Al-Al bonding [13]. Thus, the aluminum atoms in these complexes are fivefold coordinate. Hydrogen bonding is also observed in the complex of TMAI with BH_3 [13]. AlH_3 is found to complex twice with TMAM, forming a trigonal bipyramid in which the aluminum is also fivefold coordinate [14].

Another class of aluminum compounds are those having the composition R_2AlY , where Y is a halogen atom or radical such as OR, SR, or NR_2 . (These compounds differ from those preceding in that the two constituents are no longer stable, free molecules.) The aluminum is bonded to two carbon (or hydrogen) atoms and the electron donor atom and hence is threefold coordinated. In the gas phase these compounds form cyclic oligomers, with a ring consisting of alternating donor atoms and fourfold coordinated aluminum atoms. The ring bonds are all equivalent, suggesting a resonance between covalent and donor-acceptor bonds [13].

Collision-Induced Dissociation of Adduct Ions

Most of the adduct product ions were produced in sufficient quantities for CID studies to glean information about their structures. The aluminum/amine adducts $[\text{DMAI} \cdot \text{A}]^+$ formed by all three methylamines yield the fragment ions DMAI^+ , MMAI^+ , and Al^+ on CID. The amine cation A^+ was never observed, which imposes an upper limit of 7.82 eV [the ionization potential (IP) of TMAM] on the IP of DMAI. In addition, the aluminum/amine adducts also undergo the following fragmentation process:

or

With MMAM, the ionic product is $(\text{CH}_3)_2\text{AlH}^+ \equiv \text{DMAIH}^+$, whereas with DMAM and TMAM, the ionic product is $(\text{A-H})^+$, $\text{N}(\text{CH}_3)_2^+$, or $(\text{CH}_3)_2\text{NCH}_2^+$, respectively. [For TMAM, the two DMAIH^+ and $(\text{A-H})^+$ products have the same nominal mass. The resolution of the FTMS is sufficient to allow the two products to be differentiated.] Note that this result allows us to bracket the unknown IP of $(\text{CH}_3)_2\text{AlH}$ between 6.7 eV (the IP of HNCH_3) and 5.7 eV [the IP of $(\text{CH}_3)_2\text{NCH}_2$].

The products of reaction 6 suggest that the aluminum/amine adduct has a bridging hydrogen atom structure, that is, a $\text{C}_2\text{-Al-H-N}$ skeleton and not the $\text{C}_2\text{-Al-N}$ skeleton that might be expected from the preceding discussion of neutral adduct structure. (Note that this structure is not likely for TMAM, as discussed in more detail later.)

Collision-induced dissociation of the diamine adducts regenerates the $[\text{DMAI} \cdot \text{A}]^+$ adduct for all three methylamines.

in addition to producing the other fragment ions observed in CID of $[\text{DMAI} \cdot \text{A}]^+$. The diamine adduct is most likely formed by the methylamine "attacking" the positive aluminum center, forcing the three groups attached to the aluminum out of the $\text{C}_2\text{-Al-X}$ plane to form a tetrahedral complex analogous to that reported by Anderson et al. [12] for the neutral complex of TMAI with TMAM (to cite one example). Similar geometric changes have been observed in matrix isolation studies by Picoos and Ault [15] of the neutral complex of trimethylgallium and arsine.

The dialuminum adduct $[\text{DMAI} \cdot \text{A} \cdot \text{DMAI}]^+$, produced by reaction 4b in the DMAM system, yields predominantly DMAIH^+ on CID:

Observation of this product also suggests that the aluminum/amine adduct is hydrogen bonded, with the second DMAI bonded to the nitrogen. The CID process presumably involves loss of a neutral aluminum/amine adduct, which implies that the Al-N and Al-H bonds are stronger than the N-H bond. It is interesting to note that although a second TMAI adds to the nitrogen as in reaction 4, a second amine adds to the aluminum. Thus, Al-N bond formation is favored over Al-Al and N-N bond formation, which again indicates a strong Al-N bond.

Alternative structures for the adducts formed by reactions 1 or 2 and 4b can be considered. If the $[\text{DMAI} \cdot \text{A}]^+$ adduct is conventionally bonded, with a $\text{C}_2\text{-Al-N}$ skeleton, then reaction 6 involves transfer of a hydrogen from the amine to DMAI during the CID process. Addition of a second DMAI to the $[\text{DMAI} \cdot \text{A}]^+$ adduct (reaction 4b) would be at the aluminum and not at the nitrogen, which is already fourfold coordinate. Reaction 8 would also involve transfer of hydrogen from the amine to the aluminum. This scenario seems less likely than the hydrogen-bonded structure with direct bond cleavage.

The most interesting CID process is that of the dialuminum/diamine adducts $[\text{DMAI} \cdot \text{A}_2 \cdot \text{TMAI}]^+$, which in each case regenerate $[\text{DMAI} \cdot \text{A}]^+$,

by losing a stable aluminum/amine neutral adduct. Loss of a single amine or aluminum moiety was not observed, even at the lowest CID energies; however, these dialuminum/diamine adducts represent two very different cases. With MMAM or DMAm one can postulate the following reaction sequence: The aluminum/amine adduct is hydrogen bonded; the second amine coordinates to the aluminum center; and the second TMAI coordinates to the first amine at the nitrogen center, giving an ion with the structure shown in Structure 1. The CID process involves cleavage of the Al-H bond. The addition of the second amine probably does not involve hydrogen bonding, because one would then expect to also see fragmentation into dialuminum/amine adduct plus amine products.

The picture becomes less clear when considering the case of TMAM. This amine has no acidic hydrogens, in contrast to MMAM or DMAm. The aluminum/amine adduct presumably has a $\text{C}_2\text{-Al-N}$ skeleton, and the second amine can coordinate to the aluminum center. The difficulty arises when considering the point of attachment of the second TMAI. Both nitrogens and the aluminum are already fourfold coordinate. Attack of the TMAI at one of the nitrogen centers, to form a linear or cyclic N-Al-N-Al backbone, rather than at the aluminum center, which would produce a branched $(\text{N})_2\text{-Al-Al}$ structure, is consistent with the primary CID fragment being the aluminum/amine adduct. If

Structure 1

Structure 2

attachment occurred at the aluminum, one would expect to preferentially lose a single moiety (an amine or TMAI, requiring cleavage of one bond) instead of losing an adduct (requiring cleavage of two bonds). The postulated structure (Structure 2) has a fivefold coordinated nitrogen. This is rather surprising, because fivefold coordinated nitrogens are unknown, whereas several examples of fivefold coordinated aluminums have been found [13]; however, this is the only structure consistent with the CID results.

Summary

We have observed many reactions between the MOCVD precursors examined in this study. Adducts due to neutral reactions occurring on mixing of the precursors were observed by EI ionization. The neutral adducts $(\text{CH}_3)_3\text{AlNH}_2\text{CH}_3$ and $(\text{CH}_3)_3\text{AlNH}(\text{CH}_3)_2$ are possibly stable enough that they could be produced in macroscopic quantities. These products are similar to the adduct aluminum precursor $\text{H}_3\text{AlN}(\text{CH}_3)_3$, which is commercially available (American Cyanamid Co., Wayne, NJ).

The strength of interaction of the neutral adducts is postulated to closely follow the basicity of the methylamines, $\text{MMAM} \approx \text{DMAm} > \text{TMAM} \approx \text{NH}_3$. The two methylamines that readily form the neutral adduct are also the two strongest bases. Ammonia and TMAM were not observed to form neutral adducts in our work.

The reactions between DMAI^+ and the methylamines, as well as ammonia [8], result in the formation of a variety of adducts that contain up to four compo-

nents. Under CID, most of the adducts simply regenerated the initial reactants. Evidence for hydrogen bonding in the initial DMAI/amine adduct was observed. This leads us to conclude that the adducts produced are simply acid/base pairs and that the strength of interaction depends mostly on the relative acidity and basicity of the reaction partners. In some cases, the Al-N bond that is formed can be relatively strong, although methyl loss is not usually observed. For example, the dialuminum/diamine adducts appear to lose a stable $[\text{TMAI} \cdot \text{A}]$ neutral on CID.

From this work and other similar studies it becomes apparent how little is known about the gas-phase chemistry of the MOCVD precursors and how great the impact of that chemistry can be. The observation of the neutral gas-phase adducts and the ready formation of ion-molecule adducts shows that these types of species are relevant when considering the likely pathways for the incorporation of unwanted impurities. The gas-phase stability of the adducts hints that these species may also be more stable on the deposition surface than previously thought and therefore would be a problem in the production of high-quality materials for solid-state devices.

Acknowledgments

We thank Herb Nelson for his interest and support during this project. This work was funded by the Office of Naval Research.

References

1. Manasevit, H. M. *Appl. Phys. Lett.* **1968**, *12*, 156-159.
2. DeBaars, S. P.; Maa, B. Y.; Dapkus, P. D.; Danner, A. D.; Lee, H. C. *J. Crystal Growth* **1986**, *77*, 188-193.
3. Heinecke, H.; Brauers, A.; Lüth, H.; Balk, P. *J. Crystal Growth* **1986**, *77*, 241-249.
4. Zembusto, S.; Sasaki, T. *J. Crystal Growth* **1986**, *77*, 250-256.
5. (a) Zhang, Y.; Stuke, M. *J. Crystal Growth* **1988**, *93*, 143-150; (b) Horwitz, J. S.; Villa, E.; Hsu, D. S. Y. *J. Phys. Chem.* **1990**, *94*, 7214-7219.
6. (a) Interrante, L. V.; Lee, W.; McConnell, M.; Lewis, N.; Hall, E. *J. Electrochem. Soc.* **1989**, *136*, 472; (b) Sauls, F. C.; Interrante, L. V.; Jiang, Z. *Inorg. Chem.* **1990**, *29*, 2989; (c) Amato, C. C.; Hudson, J. B.; Interrante, L. V. *Appl. Surf. Sci.* **1992**, *54*, 18.
7. Interrante, L. V.; Sigel, G. A.; Garbaskas, M.; Hejna, C.; Slack, G. A. *Inorg. Chem.* **1989**, *28*, 252.
8. Bach, S. B. H.; McElvany, S. W. *Organometallics*, to be submitted.
9. Parent, D. C.; McElvany, S. W. *J. Am. Chem. Soc.* **1989**, *111*, 2393-2401.
10. Kappes, M. M.; Uppal, J. S.; Staley, R. H. *Organometallics* **1982**, *1*, 1303.
11. Huheey, J. E. *Inorganic Chemistry: Principles of Structure and Reactivity*; Harper & Row: New York, 1978; Chapter 7.
12. Anderson, G. A.; Forgaard, F. R.; Haaland, A. *Acta Chem. Scand.* **1972**, *26*, 1947.
13. Haaland, A. In *Stereochemical Applications of Gas-Phase Electron Diffraction*, Part B; Hargittai, I.; Hargittai M., Eds., VCH Publishers, Inc.: New York, 1988; Chapter 8.
14. Mastryukov, V. S.; Golubinskii, A. V.; Vil'kov, L. V. *Zh. Strukt. Khim.* **1979**, *20*, 921. (English translation: *J. Struct. Chem. USSR*, **1979**, *20*, 788.)
15. Picos, E. A.; Ault, B. S. *J. Phys. Chem.* **1991**, *95*, 6827.