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Electron impact ionization and ion chemistry in trimethylaluminum and in trimethylgallium

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Abstract

Ionization of trimethylaluminum and trimethylgallium by electron impact from threshold to 70 eV and the gas-phase reactions of the resulting ions with their parent molecules are studied by using Fourier transform mass spectrometry. The total ionization cross sections rise from thresholds near 10 eV to $1.3 \pm 0.1 \times 10^{-15}$ and $1.2 \pm 0.1 \times 10^{-15}$ cm^2, respectively, at 70 eV. The most abundant product ions of dissociative ionization are $M(CH_3)_2^+$ ($M =$ Al or Ga). Most of the ions generated by the electron impact ionization except $M(CH_3)_2^+$ and M^+ react readily with the parent molecules yielding $M(CH_3)_2^+$ and M^+ as the principal product ions, with rate coefficients of $(2–6) \times 10^{-10}$ cm^3 s^{-1}. Clusters with two metal atoms were observed with relatively small branching ratios or reaction rates. (Int J Mass Spectrom 202 (2000) 345–349) © 2000 Elsevier Science B.V.

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1. Introduction

Aluminum (Al) and gallium (Ga) play important roles in the semiconductor industry. III–V semiconductors with Al or Ga as the III element have quite different properties compared to Si in terms of higher electron mobility, direct band gap and possible hetero junctions [1]. Aluminum oxide is an excellent dielectric material against the diffusion of alkaline ions and radiation damage as well as chemical attack [2,3]. These semiconductors have been manufactured mainly using techniques of chemical vapor deposition (CVD), reactive sputtering, molecular beam epitaxy, etc. The technique of plasma enhanced chemical vapor deposition (PECVD) using trimethylaluminum (TMA) [1,4–6] or trimethylgallium (TMG) [7,8] has also been used as it permits lower temperature deposition. In contrast to the aforementioned techniques such as CVD, which primarily involves neutral reactive species, PECVD generates significant charged species as well as neutral radicals that can drastically alter the reaction chemistry. In this article, we examine the electron impact ionization and the subsequent ion-molecule reactions of TMA and TMG, respectively, which are closely related to the properties of the plasma gas-phase processes using these two compounds.

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2. Experiment

All experiments are performed on a modified Extrel Fourier-transform mass spectrometer (FTMS) equipped with a cubic ion cyclotron resonance trapping cell (5 cm on a side) and a 2 T superconducting magnet [9]. TMA (98%, Strem Chemicals, Inc.) or TMG (99+%, Strem Chemicals, Inc.) is mixed with argon (99.999%, Matheson Research Grade) with a ratio about 1:2 to a total pressure of 10 or 200 Torr, respectively, as determined by capacitance manometry. The mixture is admitted through a precision leak valve into the FTMS system. Ions are formed by electron impact in the trapping cell at pressures in the 10^{-7} Torr range. An electron gun (Kimball Physics ELG2, Wilton, NH) irradiates the cell with a few hundred picocoulombs of low-energy electrons. The motion of the ions is constrained radially by the superconducting magnetic field and axially by an electrostatic potential (1 V) applied to the trap faces that are perpendicular to the magnetic field. Ions of all mass-to-charge ratios are simultaneously and coherently excited into cyclotron orbits using a stored waveform [10,11] applied to two opposing trap faces which are parallel to the magnetic field. Following cyclotron excitation, the image currents induced on the two remaining faces of the trap are amplified, digitized, and Fourier analyzed to yield a mass spectrum.

The calculation of cross sections from the mass spectrum intensities requires knowledge of the gas densities, the electron beam current, and the number of ions produced. These calibration issues have been described previously [9,12]. The intensity ratios of the ions from TMA or TMG to Ar^+ give cross sections relative to those for argon ionization [13] since the pressure ratio of Ar to TMA or TMG is known. As a cross check, and for ion molecule kinetic analyses, the gas pressure is calibrated using a pulsed valve and a spinning rotor friction gauge (MKS Instruments model SRG2, Burlington, MA) with the vacuum chamber sealed off from the pumps. Electron current is collected on a Faraday cup and recorded with a digital oscilloscope after passage of the electron beam through the ion trap. The quantitative relationship between the image current and the number of ions is based on a lengthy, but elementary, solution of Maxwell's equations for the cubic ICR cell. This information is required to quantify both excitation of the ions and detection of the resulting image current [9].

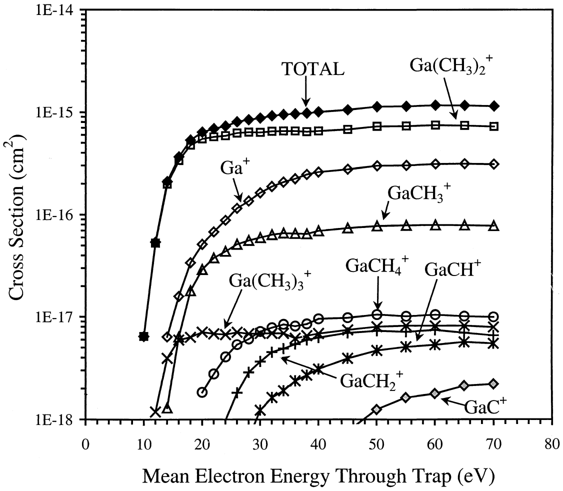

Fig. 1. Cross sections for ionization of $Ga(CH_3)_3$ by electron impact.

3. Results and discussion

Fig. 1 shows the electron impact ionization cross sections of TMG over an energy range of 10–70 eV. The total cross section reaches $1.2 \pm 0.1 \times 10^{-15}$ cm^2 at 70 eV. The ionization produces the molecular ion $Ga(CH_3)_3^+$ and seven fragment ions with cross sections above 10^{-18} cm^2, with the ion population dominated by $Ga(CH_3)_2^+$ in the energy range studied. The fragmentation is characterized by the loss of one or multiple CH_3 groups from the molecular ion. The less significant fragmentation channels involve the hydrogen atom rearrangement to form $GaCH_x^+$ ($x =$ 0–2, 4). Neutral fragment products of the dissociative ionization are generally difficult to deduce, but in the case of the ionization channel forming $Ga(CH_3)_2^+$, we feel it is reasonable to assume the neutral partner to be the CH_3 radical, resulting from the direct cleavage of a Ga–CH_3 bond in the molecular ion. Also, since the partial ionization cross section for $Ga(CH_3)_2^+$ comprises more than 60% of the total ionization cross

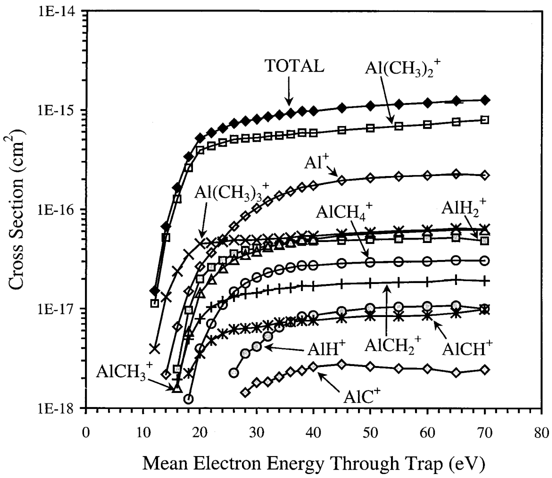

Fig. 2. Cross sections for ionization of Al$(CH_3)_3$ by electron impact.

section at all energies studied, we propose that the CH_3 radical is the major neutral product from the electron impact ionization of Ga$(CH_3)_3$. The formation of GaCH$_3^+$ or Ga$^+$, however, is less likely to be produced by means of successive loss of CH_3 units because the process is against the even-electron rule [14]; the first CH_3 loss from the molecular ion results in the even-electron ion Ga$(CH_3)_2^+$ which, according to the even-electron rule [14], can decompose only by loss of an even-electron molecule rather than the CH_3 radical. The formation of these two ions is more likely to be via the fragmentation with C rearrangement of Ga$(CH_3)_3^+$ and Ga$(CH_3)_2^+$, respectively, with the neutral loss likely to be an ethane molecule.

The ionization cross sections of TMA displayed in Fig. 2 show similar features to TMG including the order of the relative magnitudes for the dissociation channels, except for the added channels forming AlH$_y^+$ ($y = 1, 2$). The total cross section reaches $1.3 \pm 0.1 \times 10^{-15}$ cm^2 at 70 eV. The existence of AlH$_y^+$ from TMA by electron impact and the fact that AlH$_2^+$ is also formed in Ar$^+$ reaction with TMA, as presented later, suggest that the formation of AlH$_y^+$ from TMA is thermodynamically favored compared to that of the hypothetical GaH$_y^+$ from TMG. The molecular ion is more significant in TMA (5% of the ion population at 70 eV) than in TMG (only 0.7% of the ion population at 70 eV). From both TMA and TMG, there are several ions containing only one C atom but varying numbers of H atoms, in particular, the numbers of H atoms less than that in a methyl group, i.e. GaCH$_x^+$ or AlCH$_x^+$ where $x = 0$–2. The analogies for other ions containing more than one C atom are absent or very insignificant. We consider this to imply a multiple bond between the metal and C atom in GaCH$_x^+$ or AlCH$_x^+$, which facilitates the removal of the H atom(s) from the methyl unit; in the ions containing two or more C atoms, Ga or Al that has the oxidation number of +3 and usually carries the positive charge cannot form a multiple bond to any of the C atoms.

The gas-phase reactions between some dominant ions (i.e. ionization cross sections $> 10^{-17}$ cm^2 at 70 eV) and their neutral parent molecules are summarized in Table 1. The reactant ions are generated by electron impact at 25 or 50 eV and no changes in their reactivities with the different incident electron energies are observed beyond the experimental error. All reactions observed can be grouped into three categories: forming M$^+$ (M = Ga or Al), M$(CH_3)_2^+$, or cluster ions. The cluster ions do not grow larger than molecules with two metal atoms under our experimental conditions (i.e. 10^{-7} Torr gas pressure and 1 s reaction time). The cluster ions $Al_2C_5H_{15}^+$ and $Al_2C_4H_{13}^+$ are not likely to have a metal–metal bond in their structures because that would make the oxidation number of the metal atom greater than +3. Possible structures for these ions are likely to have two-electron three-center bridging bonds, as shown in *1* and *2* in Scheme 1, respectively. Other ions with two metal atoms listed in Table 1 are also expected to have similar bridging bond structures.

The bridging bond structure may also be used to explain other reactions in Table 1. Take the reaction

Scheme 1.

Table 1
Ion–molecule reaction rate coefficients and branching ratios of selected ions that are produced with ionization cross sections greater than 10^{-17} cm^2 at 70 eV

		Product ion (M = Ga or Al)		
Reaction	Rate (10^{-10} cm^3 s^{-1})	M^+	$M(CH_3)_2^+$	Cluster ion
$Ga^+ + Ga(CH_3)_3$	no reaction	. . .	. . .	. . .
$GaCH_3^+ + Ga(CH_3)_3$	4.8 ± 0.5	66%	32%	$Ga_2(CH_3)_3^+$:2%
$Ga(CH_3)_2^+ + Ga(CH_3)_3$	no reaction	. . .	. . .	. . .
$Al^+ + Al(CH_3)_3$	no reaction	. . .	. . .	. . .
$AlH_2^+ + Al(CH_3)_3$	6.0 ± 0.5	0	100%	0
$AlCH_2^+ + Al(CH_3)_3$	3.7 ± 0.5	16%	71%	$Al_2C_3H_8^+$:13%
$AlCH_3^+ + Al(CH_3)_3$	2.1 ± 0.2	30%	67%	$Al_2(CH_3)_3^+$:3%
$AlCH_4^+ + Al(CH_3)_3$	5.4 ± 0.5	0	100%	0
$Al(CH_3)_2^+ + Al(CH_3)_3$	0.18 ± 0.02	0	0	$Al_2H(CH_3)_4^+$:100%
$Al(CH_3)_3^+ + Al(CH_3)_3$	4.6 ± 0.5	0	69%	$Al_2(CH_3)_5^+$:31%

of $Al(CH_3)_3^+ + Al(CH_3)_3$ producing $Al(CH_3)_2^+$ as an example. If proceeding through a charge transfer mechanism this reaction would be endothermic, because the net reaction will be a dissociation reaction: $Al(CH_3)_3^+ \rightarrow Al(CH_3)_2^+ + CH_3$, which is apparently endothermic. One might argue that the reaction we observe involves excited reactant ions, but this would mean that about 69% of $Al(CH_3)_3^+$ were in the excited states, as we observed in experiments that essentially all of the $Al(CH_3)_3^+$ reacted, and that 69% of them produced $Al(CH_3)_2^+$. The sequence and efficiency are considered highly improbable. Furthermore, the kinetic data of $M(CH_3)_3^+$ do not show biexponential decay and changing the buffer gas pressure makes no statistically meaningful changes in the reaction rate and the product branching ratios. Therefore we propose an alternate mechanism: with initial formation of a bridging bond structure by $Al(CH_3)_3^+$ and $Al(CH_3)_3$, there is C atom rearrangement to form a stable hydrocarbon species (e.g. C_2H_6), and after the removal of this species, the cleavage of the bridging bonds generates the product ion $Al(CH_3)_2^+$. It may be noteworthy to point out the absence of any observed reactivity for Ga^+ or Al^+. For transition metal ions, it has been reported that the bare and ligated metal ions have dramatic differences in their reactivities with organic and organometallic compounds [15]. The unreactivity of Ga^+ or Al^+ toward their parent molecules may be explained by (1) their closed shell electronic configuration, and/or (2) the lack of the capability of forming an intermediate structure similar to *1* or *2* that has two bridging bonds.

Since argon is commonly used as the diluent in PECVD, the argon ion reactions with TMA and TMG were also studied. Ar^+ reacts with $Al(CH_3)_3$ to yield Al^+ (19%), AlH_2^+ (8%), $AlCH_2^+$ (4%), $AlCH_3^+$ (25%), $AlCH_4^+$ (7%), and $Al(CH_3)_2^+$ (37%) at a rate coefficient of $5.9 \pm 0.5 \times 10^{-10}$ cm^3 s^{-1}, and with $Ga(CH_3)_3$, to yield Ga^+ (42%), $GaCH_3^+$ (13%), $GaCH_4^+$ (1%), and $Ga(CH_3)_2^+$ (44%) at a rate coefficient of $4.7 \pm 0.5 \times 10^{-10}$ cm^3 s^{-1}. The product ions from these reactions undergo secondary reactions with their parent gases as described in Table 1, resulting in the dimethyl metal ion $M(CH_3)_2^+$ and the bare metal ion M^+ as the final major ions.

4. Conclusion

Electron impact ionization of TMA and TMG, with total cross sections of $1.3 \pm 0.1 \times 10^{-15}$ and $1.2 \pm 0.1 \times 10^{-15}$ cm^2 at 70 eV, respectively, yields similar ionic populations including the molecular ions and dominant dimethyl metal ions. The small difference of the two compounds is the added ionization channels in TMA to form AlH_y^+ ($y = 1, 2$) and the more significant molecular ion in TMA than in TMG (5% versus 0.7%, respectively, of the ion population at 70 eV). The major neutral product of the dissociative ionization is believed to be the CH_3 radical. The gas-phase reactions of selected intense ions generated from the electron impact ionization are studied. Except $M(CH_3)_2^+$ and M^+ that are basically unreactive, all of the ions studied react readily with their parent molecules producing mainly $M(CH_3)_2^+$ and M^+, and certain cluster ions that have two metal atoms, with rate coefficients $k \sim (2\text{–}6) \times 10^{-10}$ cm^3 s^{-1}. $Al(CH_3)_2^+$ slowly undergoes clustering reaction with TMA at a rate of $\sim 0.18 \pm 0.02 \times 10^{-10}$ cm^3 s^{-1}. Ar^+ reacts with TMA and TMG with rate coefficients of 5.9 and $4.7 \pm 0.5 \times 10^{-10}$ cm^3 s^{-1}, respectively, generating mainly $M(CH_3)_2^+$. In summary, $M(CH_3)_2^+$ and M^+ are likely to be the most and second most dominant ionic species found in the gas phase of a typical plasma using TMA or TMG gas.

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