J. Phys. B: At. Mol. Opt. Phys. **32** (1999) 1639–1646. Printed in the UK PII: S0953-4075(99)96311-3

Ionization of tetraethylgermanium, $GeEt_4$

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Received 28 July 1998

Abstract. The ion chemistry in tetraethylgermanium ($GeEt_4$) has been examined by Fourier-transform mass spectrometry under single-collision conditions in the 10^{-7} torr pressure range. The cross sections for electron impact ionization of $GeEt_4$ are measured from threshold to 70 eV. The molecular ion and 15 fragment ions from the electron–molecule collision are observed with a total cross section of $3.5 \pm 0.4 \times 10^{-15}$ cm^2 at 70 eV. All fragment ions, except $GeC_6H_{15}^+$, are found to react readily with $GeEt_4$ to yield $GeC_6H_{15}^+$, with rate coefficients in the range of 2–5 $\times 10^{-10}$ cm^3 s^{-1}. Small yields of digermanium cluster ions are observed at higher reactant pressures.

1. Introduction

Amorphous materials can be divided into two categories based on their electronic structures and properties: amorphous semiconductors and amorphous dielectrics. The transition between the dielectric and semiconducting properties occurs as the preparation conditions for these materials change [1–5]. One such transition is described in recent studies of germanium:carbon films prepared by plasma deposition from alklylated germanes [6–15]. Gazicki and his co-workers [10–15] correlated the stoichiometry and bulk electrical properties of films deposited from tetraethylgermanium plasma with radio-frequency power levels. They link the transition from dielectric to semiconducting films to changes in the composition of the plasma. In spite of the previous research activities, and the fact that these germanium:carbon films are important elements of coatings and semiconductors, only limited information about the electron impact ionization of tetraethylgermanium has been reported, namely, the cracking patterns at 50 eV [16] and 70 eV [17]. In this paper we present measurements of the ionization cross sections of tetraethylgermanium ($GeEt_4$) for electron energies from threshold to 70 eV. Rate coefficients for the reactions of fragment ions and Ar^+ with neutral $GeEt_4$ are also reported.

2. Experimental

Tetraethylgermanium (99%, Aldrich) gas is mixed with argon (99.999% Matheson Research Grade) in a $GeEt_4$:Ar of 1:1.3, as determined by capacitance manometry. The mixture is admitted through a precision leak valve into a modified Extrel Fourier-transform mass spectrometry (FTMS) system which has been described in detail elsewhere [18]. Ions are formed by electron impact in a cubic ion cyclotron resonance (ICR) trap cell at pressures in the 10^{-7} torr range. An electron gun (Kimball Physics ELG2, Wilton, NH) irradiates the trap with

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0953-4075/99/071639+08$19.50

a few hundred picocoulombs of low-energy electrons. The motions of the ions are constrained radially by a superconducting solenoidal magnetic field (~ 2 T) 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 [19, 20] 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 analysed to yield a mass spectrum.

The calculation of cross sections from the mass spectrum intensities requires a knowledge of the gas densities, the electron beam current and the number of ions produced. These calibration issues have been described previously [18, 21]. The intensity ratios of the ions from $GeEt_4$ to Ar^+ give cross sections relative to those for argon ionization [22] since the $GeEt_4$:Ar pressure ratio is fixed.

The distribution of electron energies in the trap, based on the solution of Laplace's equation for the experimental geometry, is roughly Gaussian with a full width at half maximum of 0.5 eV due to the electrostatic trapping bias [18]. The mean energy of the irradiating electrons is accurate to ± 0.2 eV based on comparison of noble gas ionization thresholds with spectroscopic data. We fit the cross section data to an empirical functional form:

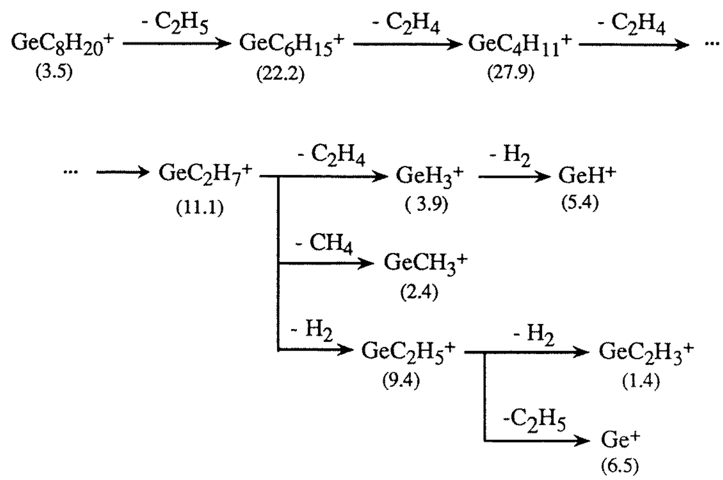
$$\sigma = A \tanh \frac{\pi(\varepsilon - T)}{\alpha} \mathrm{e}^{-k(\varepsilon - T)}$$

where σ is the cross section, ε is the electron energy, T is the appearance potential, A scales the amplitude, α quantifies $\mathrm{d}\sigma/\mathrm{d}\varepsilon$ near threshold and k characterizes behaviour at energies $\gg T$.

3. Results and discussion

Tetraethylgermanium ionization was first reported 30 years ago with cracking patterns at 50 and 70 eV [16, 17]. At these energies the most abundant ion is $GeC_4H_{11}^+$, with minimal but detectable concentrations of $Ge(C_2H_5)_4^+$. The present measurements confirm the cracking patterns at 50 and 70 eV and provide new data on dissociative ionization at other electron energies that are important for plasma processing. The calibration with Ar and the lack of mass dependence in the detection sensitivity of our FTMS instrument quantify the partial ionization cross sections for this molecule.

Of the 378 ion stoichiometries which might be formed on statistical grounds by ionization of $Ge(C_2H_5)_4$, only 15 are formed with cross sections greater than 2×10^{-18} cm^2. The most abundant ion fragments that contain Ge are illustrated in scheme 1 with relative yields at 70 eV shown in parentheses. The neutral fragments in the scheme are only our suggestions and no bonding arrangements are shown since these are not measured in our experiments. Ions containing no Ge atoms have lower intensities and include $C_3H_7^+$ (0.9%), $C_3H_5^+$ (0.1%), $C_2H_5^+$ (1.9%), $C_2H_4^+$ (0.2%), $C_2H_3^+$ (1.6%) and $C_2H_2^+$ (0.2%). These ion stoichiometries are based on exact mass measurements. The total ionization cross section at 70 eV is 13 times that of Ar, $3.5 \pm 0.4 \times 10^{-15}$ cm^2. More than 95% of the ions produced by electron impact contain the Ge atom. The cross sections for each dissociative ionization process are shown from threshold to 70 eV in figure 1, and the coefficients for our functional fit are summarized in table 1. The first three to emerge are the molecular ion $GeC_8H_{20}^+$ and the two largest fragment ions $GeC_6H_{15}^+$ and $GeC_4H_{11}^+$. $GeC_6H_{15}^+$ is the most abundant ion from threshold to 25 eV. Above 25 eV, $GeC_4H_{11}^+$ has the largest partial ionization cross section. Over 95% of the ionization is dissociative, so that the present data provide lower bounds for the total dissociation cross section of this molecule by electron impact. Note also that neutral fragments whose composition is not measured in these experiments are also produced by dissociative ionization.



Scheme 1.

Table 1. Fitting parameters for dissociative ionization cross sections of GeEt$_4$. Ions are listed in the order of decreasing mass. Also listed are the cross sections, σ, at 70 eV.

Ion	A (cm^2)	k (eV^{-1})	α (eV)	T (eV)	σ at 70 eV (10^{-16} cm^2)
$GeC_8H_{20}^+$	8.9×10^{-17}	-5.8×10^{-3}	15	10.4	1.2
$GeC_6H_{15}^+$	6.1×10^{-16}	-4.6×10^{-3}	22	10.7	7.8
$GeC_4H_{11}^+$	9.2×10^{-16}	-1.2×10^{-3}	49	11.9	9.8
$GeC_2H_7^+$	4.6×10^{-16}	3.1×10^{-3}	74	16.8	3.9
$GeC_2H_5^+$	4.7×10^{-16}	5.2×10^{-3}	88	22.2	3.3
$GeC_2H_3^+$	4.2×10^{-17}	-6.1×10^{-3}	50	37.7	0.50
$GeCH_3^+$	6.0×10^{-17}	-7.1×10^{-3}	33	26.7	0.83
GeH_3^+	1.4×10^{-16}	-2.7×10^{-3}	91	22.5	1.4
GeH^+	1.8×10^{-16}	-2.9×10^{-3}	95	22.2	1.9
Ge^+	1.7×10^{-16}	-9.1×10^{-3}	96	23.1	2.3
$C_3H_7^+$	2.5×10^{-17}	-4.5×10^{-3}	35	15.6	0.31
$C_3H_5^+$	1.2×10^{-17}	2.0×10^{-2}	110	31.7	0.04
$C_2H_5^+$	6.8×10^{-17}	-4.0×10^{-3}	93	24.8	0.68
$C_2H_4^+$	1.4×10^{-17}	1.7×10^{-2}	108	33.2	0.09
$C_2H_3^+$	4.9×10^{-17}	-1.7×10^{-2}	101	26.3	0.90
$C_2H_2^+$	3.8×10^{-17}	1.9×10^{-2}	267	38.9	0.08

We track the reactions of ion fragments with GeEt$_4$ by introducing a delay between the ion formation at 50 eV and ion cyclotron excitation and detection, as shown in figure 2. Using double-resonance techniques† we have found that Ar^+ reacts with GeEt$_4$ to form $GeC_6H_{15}^+$ (70%), $GeC_2H_7^+$ (22%) and $C_3H_7^+$ (8%) with branching ratios shown in parentheses. $GeC_6H_{15}^+$ is unreactive for products of $Ge(C_2H_5)_4$ pressure and times of less than 10^{-7} torr s. All other fragment ions react rapidly with GeEt$_4$ to form $GeC_6H_{15}^+$ on this collisional time scale. Table 2 summarizes our measured bimolecular reaction rate coefficients. The reaction rates

† For a review of the double-resonance technique in FTMS, see [23].

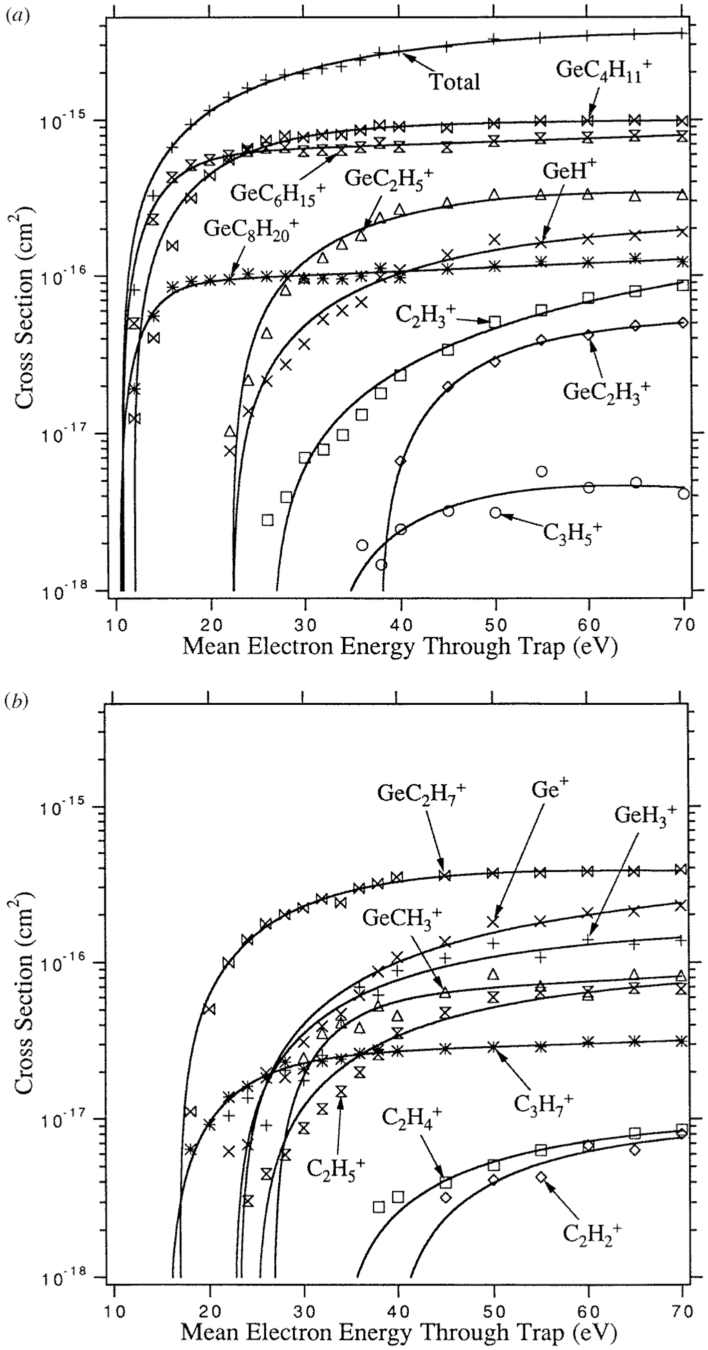


Figure 1. Cross sections (cm^2) for ionization of $GeEt_4$ by electron impact. Points represent experimental data, and full curves are fits of the equation described in the text.

are identical to within 10% experimental uncertainty when the electron energy with which the reactant ions are formed is 20, 35 or 50 eV. If products of dissociative ionization are produced

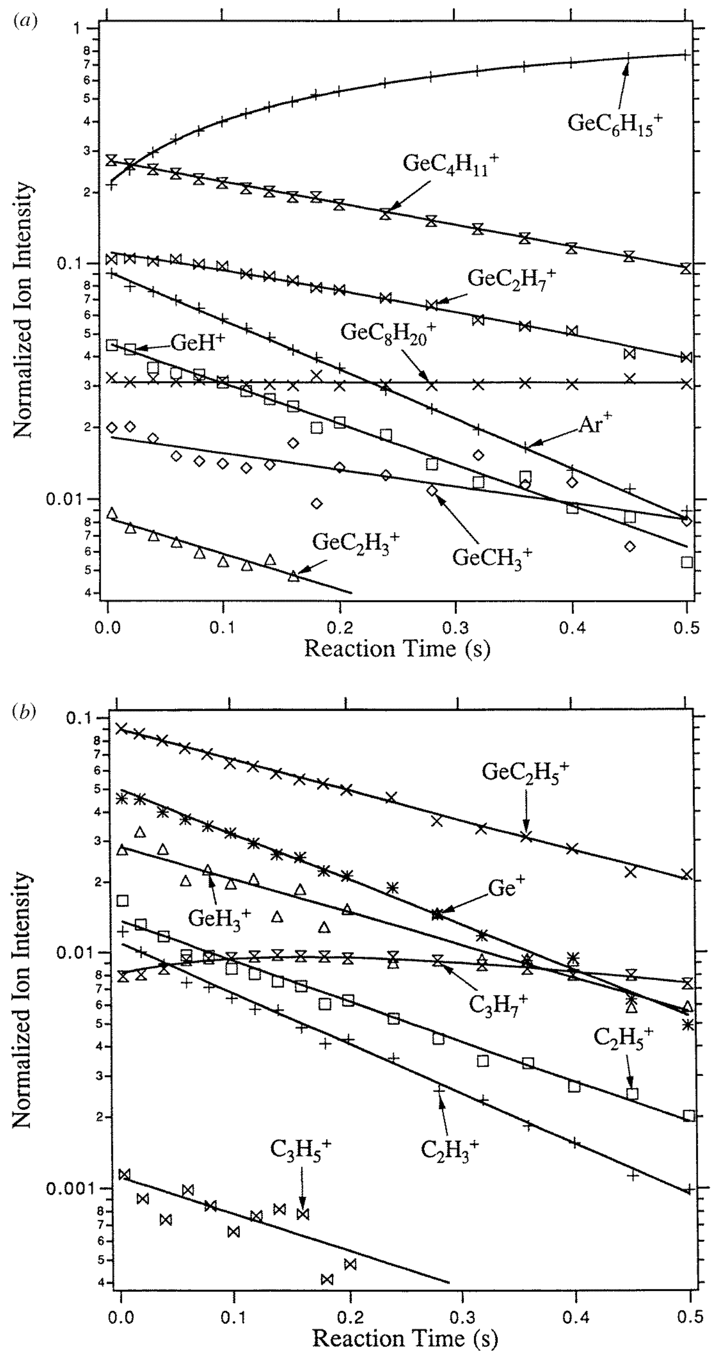


Figure 2. Time evolution of positive ion species produced by 50 eV electron impact at a mixture of $GeEt_4$ and Ar (1:1.3) with a total pressure of 6.8×10^{-7} torr. Points represent experimental data, and full curves are fits of a kinetic model which gives the reaction rate coefficients presented in table 2.

Table 2. Ion–molecule reaction rate coefficients in units of 10^{-10} cm^3 s^{-1}, measured in three separate experiments, 1–3, in which the primary ions are formed by electron impact at 20, 35 and 50 eV, respectively.

	Reaction rate coefficients		
Reactant ion	Experiment 1	Experiment 2	Experiment 3
$GeC_4H_{11}^+$	2.3 ± 0.2	2.4 ± 0.2	2.2 ± 0.2
$GeC_2H_7^+$	2.7 ± 0.3	2.6 ± 0.3	2.7 ± 0.3
$GeC_2H_5^+$	—	3.0 ± 0.3	3.1 ± 0.3
$GeC_2H_3^+$	—	—	3.6 ± 0.4
$GeCH_3^+$	—	1.7 ± 0.2	1.7 ± 0.2
GeH_3^+	—	3.5 ± 0.4	3.3 ± 0.4
GeH^+	—	4.1 ± 0.4	4.2 ± 0.4
Ge^+	—	4.6 ± 0.5	4.6 ± 0.5
$C_3H_7^+$	1.8 ± 0.2	1.8 ± 0.2	1.7 ± 0.2
$C_3H_5^+$	—	—	3.7 ± 0.4
$C_2H_5^+$	—	4.2 ± 0.4	4.1 ± 0.4
$C_2H_4^+$ [a]			
$C_2H_3^+$	—	5.2 ± 0.5	5.1 ± 0.5
$C_2H_2^+$ [a]			
Ar^+	5.2 ± 0.5	5.1 ± 0.5	5.0 ± 0.5

[a] Values for these ions are not available because of their intensities being too low to permit reliable measurements.

with extra internal energy as the electron energy is increased they do not have enhanced or reduced reactivity with the parent gas. Division of the reaction rates by the square root of the reduced mass reveals that the probability of reaction per Langevin collision is constant to within 25% for all ions except $GeCH_3^+$ and $C_3H_7^+$.

Although the ion ensemble produced by electron impact in a plasma depends on the distribution of electron energies in the discharge, $GeC_4H_{11}^+$ and $GeC_6H_{15}^+$ generally dominate the ion distribution because of their low thresholds and large cross sections. However, relaxation of the ion ensemble by charge transfer collisions occurs at pressure–time products in the 10^{-7} torr s range, increasing the proportion of $GeC_6H_{15}^+$ at the expense of all of the more extensively dissociated fragment ions. This chemistry is strikingly similar to our earlier observations on the isoelectronic $Si(CH_3)_4$ molecule, where charge transfer from lighter ions and Ar^+ leads to $Si(CH_3)_3^+$.

Gazicki and co-workers [15] have examined the effluent of a 70 mtorr radio-frequency plasma containing 1.5% $GeEt_4$ in argon using quadrupole mass spectrometry. Their mass spectra at 70 eV show no parent ion in the m/e 183–193 range and a ratio of $GeC_6H_{15}^+$ to $GeC_4H_{11}^+$ of over 20 at the lowest (7 W) plasma power. The absence of the parent ion may be due to a mislabelling of the mass scale in their figure 4. If we assume that all of the $GeC_4H_{11}^+$ comes from dissociative ionization of $GeEt_4$ then the precursor is at least 95% dissociated by their 7 W plasma.

Gazicki and his co-workers have also observed powder products in a separate study on $GeEt_4$ plasmas [24]. They rationalize the observed binary-particle size distribution by suggesting two different growth mechanisms. Inspired by clustering studies of silicon hydride cations in silane plasmas [25, 26] we probed the reactions of $GeC_6H_{15}^+$ and $GeC_8H_{20}^+$ with neutral $GeEt_4$ at pressure–time products of up to 5×10^{-6} torr s. Two Ge dimer ions, $Ge_2C_6H_{17}^+$ and $Ge_2C_8H_{21}^+$, were slowly formed (reaction rates $<10^{-12}$ cm^3 s^{-1}). This result implies that cationic polymerization of neutral $GeEt_4$ is not responsible for dust production. Ion–radical, radical–radical, anion–radical and anion–molecule collisions remain candidates for cluster formation. We do not observe negative ions from dissociative attachment to GeC_8H_{20}, but anions may be formed by electron attachment to neutral radicals that are produced in the plasmas.

4. Summary

Electron impact ionization of $GeEt_4$ produces the molecular ion $GeC_8H_{20}^+$ and 15 ionic fragments with a total cross section of $3.5 \pm 0.4 \times 10^{-15}$ cm^2 at 70 eV. Most of the fragment ions contain Ge, with less than 5% yield of hydrocarbon ions. Below 25 eV, $GeC_6H_{15}^+$ is the most abundant ion, while above 25 eV $GeC_4H_{11}^+$ has the largest partial ionization cross section. Smaller fragment ions undergo rapid reactions with $GeEt_4$ to form $GeC_6H_{15}^+$, with rate coefficients in the range of 2–5 $\times 10^{-10}$ cm^3 s^{-1}. $GeC_6H_{15}^+$ reacts with $GeEt_4$ to produce $Ge_2C_6H_{17}^+$ and $Ge_2C_8H_{21}^+$ at rates of less than 10^{-12} cm^3 s^{-1}. The reaction rates are independent of the electron energy with which the reactant ions are formed. Ar^+ reacts with $GeEt_4$ with a rate coefficient of 5.1×10^{-10} cm^3 s^{-1}, producing $GeC_6H_{15}^+$ with smaller yields of $GeC_2H_7^+$ and $C_3H_7^+$. Taken together, the cross sections and rate data imply that $GeC_6H_{15}^+$ dominates the ion flux to surfaces under many plasma conditions.

Acknowledgment

The authors wish to thank the Air Force Office of Scientific Research for financial support.

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