Ionization of trimethylsilane, $(CH_3)_3SiH$

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Abstract

Cross sections for electron impact ionization of trimethylsilane from threshold to 70 eV have been measured using Fourier transform mass spectrometry. High resolution mass spectra show that the parent ion $Si(CH_3)_3H^+$ is not formed by electron impact. Only one of the 15 ions produced by dissociative ionization lacks a silicon atom. The total ionization cross section is 1.5×10^{-15} cm^2 at 70 eV. $(CH_3)_2SiH^+$ and $(CH_3)_3Si^+$ comprise over half of the ions produced by electron impact, but charge transfer reactions of $(CH_3)_2SiH^+$ and lighter ions yield $(CH_3)_3Si^+$ at pressure–time products in the 10^{-7} Torr s range. The implication of this ion chemistry is that ion fluxes to the walls of trimethylsilane plasmas are predominantly $(CH_3)_3Si^+$. (Int J Mass Spectrom 184 (1999) 83–88) © 1999 Elsevier Science B.V.

Keywords: Electron; Ion; Ionization; Reaction; Cross section

1. Introduction

The use of volatile silicon compounds for plasma enhanced chemical vapor deposition of semiconducting and insulative films requires their ionization by electron impact in plasmas. Although both silane (SiH_4) and tetramethylsilane ($(CH_3)_4Si$) are tetracoordinate molecules, their ion chemistries are quite different. Electron impact on SiH_4 produces a $^2T_2$ ion that is Jahn–Teller unstable and dissociates to SiH_3^+ and SiH_2^+; no parent SiH_4^+ is observed [1]. By contrast, a small yield of $(CH_3)_4Si^+$ is produced from tetramethylsilane [2]. Silane ion fragments polymerize with silane to give stable clusters with up to four silicon centers [3], but reactions of the ion fragments produced by dissociative ionization of tetramethylsilane with the parent gas do not lead to the ionic silicon polymerization [2].

Here we report measurements of the ionization cross sections and charge transfer reactions in trimethylsilane, a molecule that has both Si–H and Si–CH$_3$ bonding. This gas is a precursor for plasma enhanced chemical vapor deposition of amorphous silicon carbide films [4,5] and has applications for abrasion and chemically resistant coatings as well as semiconductor device elements.

2. Experimental

Trimethylsilane (99.99%, United Chemical Technologies, Inc.) gas is mixed with argon (99.999% Matheson Research Grade) with a ratio of 1:1 as determined by capacitance manometry. The mixture

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is admitted through a precision leak valve into a modified Extrel Fourier transform mass spectrometry (FTMS) system that has been described in detail elsewhere [6]. Ions are formed by electron impact in a cubic ion cyclotron resonance (ICR) trap cell (5 cm on a side) at pressures in the 10^{-7} Torr range. An electron gun (Kimball Physics ELG2, Wilton, NH) irradiates the trap for 6 ms with 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 [7,8] applied to two opposing trap faces that are parallel to the magnetic field. The excitation period is ~2 ms and the radius of ion cyclotron orbits after the excitation is ~0.5 cm. 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 data acquisition time is typically 2 ms.

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 [6]. The intensity ratios of the ions from $(CH_3)_3SiH$ to Ar^+ give cross sections relative to those for argon ionization since the $(CH_3)_3SiH:Ar$ 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 [6]. 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:

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

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

The monoisotopic mass spectral patterns were calculated using the isotope abundances for silicon: ^{28}Si (92.28%), ^{29}Si (4.67%), and ^{30}Si (3.05%), and for carbon: ^{12}C (98.9%) and ^{13}C (1.1%).

3. Results and discussion

Of the 15 ions produced by electron impact on trimethylsilane the $(CH_3)_2SiH^+$ and $(CH_3)_3Si^+$ together account for more than half of the total yield. Other fragments include $SiC_2H_x^+$ with $x = \{1,3,5,6\}$, $SiCH_y^+$ with $y = \{1-5\}$, and SiH_z^+ with $z = \{0,1,3\}$. Except for traces of CH_3^+ formed above 40 eV all of the ion fragments contain silicon. The cross sections are displayed in Fig. 1(a) and (b), with parameters for the fitted curves summarized in Table 1. The total ionization cross section at 70 eV is $5.1 \pm 0.5 \times 10^{-15}$ cm^2. Although cracking patterns of trimethylsilane at selected energies have been reported [9–11], this account is the first complete presentation of the energy-dependent partial ionization cross sections.

Fig. 2 shows high resolution spectra at masses where evidence of an undissociated molecular ion should be seen. The peaks near $m/e = 74$ and 75 are shown to arise from the naturally abundant isotopes of silicon and carbon, proving that the $Si(CH_3)_3H^+$ is not formed by electron impact. Based on our detection sensitivity, the cross section for producing the parent ion must be less than 2×10^{-18} cm^2. The observation of $Si(CH_3)_3H^+$ (50%) following Penning ionization by Ar* ($^3P_2$) [12] of trimethylsilane shows that this ion is thermodynamically stable; it is not formed by electron impact because of the short interaction time and unfavorable momentum considerations compared with Penning ionization.

Figs. 3(a)–(c) illustrates the fate of all ions produced by 50 eV electron impact as they are allowed to collide with neutral trimethylsilane. The trimethylsilyl cation, $Si(CH_3)_3^+$, is produced by hydride transfer reactions of all lighter ion fragments with $(CH_3)_4Si$. $Si(CH_3)_3^+$ reacts slowly ($k = 6 \times 10^{-12}$ cm^3 s^{-1})
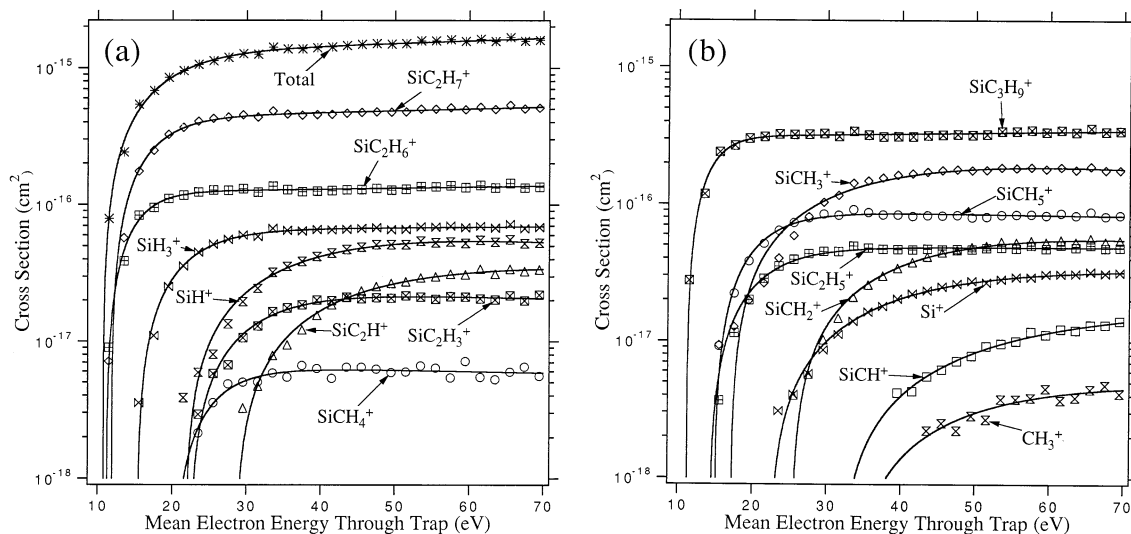
Fig. 1. (a) and (b) Cross sections (cm^2) for ionization of (CH$_3$)$_3$SiH by electron impact. Points represent experimental data, and solid lines are fits of the form described in the text.

with trimethylsilane to yield a cluster ion Si$_2$C$_6$H$_{19}^+$. This association reaction requires either emission of a photon or a vibrationally excited intermediate that survives at least for milliseconds to be collisionally stabilized at our experimental pressures.

Most of the remaining ion kinetics can be summarized by the overall methide and hydride transfer reactions:

$$R^+ + (CH_3)_3SiH \rightarrow SiC_2H_7^+ + (RCH_3) \tag{1}$$

$$R^+ + (CH_3)_3SiH \rightarrow SiC_3H_9^+ + (RH) \tag{2}$$

with branching ratios summarized for each applicable R in Table 2. The SiH$^+$ ion also produces SiCH$_3^+$ with a 15% branching ratio, and the yield of CH$_3^+$ from dissociative ionization was too small to quantify its reactions.

Table 1
Fitting parameters for dissociative ionization cross sections; ions are listed in the order of the decreasing intensities at 70 eV that are shown in the last column

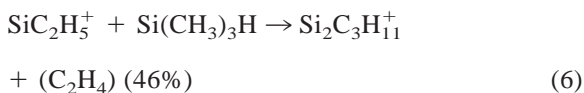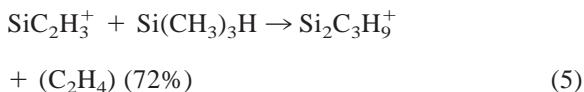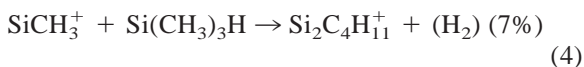| Ion	A (cm^2)	k (eV^{-1})	α (eV)	T (eV)	σ at 70 eV $(10^{-16}$ cm^2)
SiC$_2$H$_7^+$	4.3×10^{-18}	-3.2×10^{-3}	26	11.9	5.1
SiC$_3$H$_9^+$	3.1×10^{-18}	-1.9×10^{-3}	15	11.2	3.5
SiCH$_3^+$	2.8×10^{-16}	6.9×10^{-3}	87	17.2	1.8
SiC$_2$H$_6^+$	1.2×10^{-18}	-1.8×10^{-3}	19	11.2	1.3
SiCH$_5^+$	8.9×10^{-17}	1.4×10^{-3}	29	15.0	0.83
SiH$_3^+$	6.5×10^{-17}	-9.9×10^{-4}	32	15.4	0.68
SiCH$_2^+$	8.5×10^{-17}	7.6×10^{-3}	91	25.4	0.54
SiH$^+$	8.1×10^{-17}	7.6×10^{-3}	83	21.8	0.53
SiC$_2$H$_5^+$	4.9×10^{-18}	2.0×10^{-4}	33	14.3	0.48
SiC$_2$H$^+$	4.4×10^{-17}	4.2×10^{-3}	86	28.5	0.34
Si$^+$	3.8×10^{-17}	2.2×10^{-3}	86	22.4	0.32
SiC$_2$H$_3^+$	2.4×10^{-18}	3.1×10^{-3}	43	22.4	0.22
SiCH$^+$	1.5×10^{-17}	-3.1×10^{-3}	96	31.8	0.14
SiCH$_4^+$	6.6×10^{-17}	2.3×10^{-3}	28	20.2	0.06
CH$_3^+$	8.0×10^{-18}	8.8×10^{-3}	114	33.4	0.04
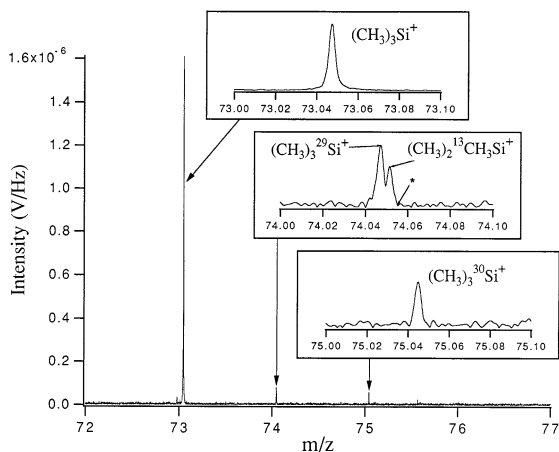
Fig. 2. High resolution mass spectrum of $(CH_3)_3SiH$ acquired at 30 eV. It shows the absence of the molecular ion, $(CH_3)_3SiH^+$, which has the mass-to-charge ratio position marked by asterisks in the inset.

Double resonance experiments allowed the isolation of channels for the production in small yield of disilicon cations $Si_2C_4H_{11}^+$, $Si_2C_3H_9^+$, $Si_2C_3H_{11}^+$, and $Si_2C_6H_{19}^+$ with branching ratios shown below in parentheses. These following reactions are in addition to reaction (1) and (2)
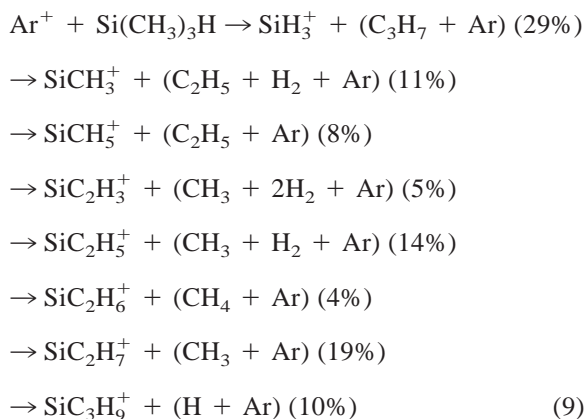
$$Si^+ + Si(CH_3)_3H \rightarrow Si_2C_3H_9^+ + H \ (27\%) \qquad (3)$$

$$SiCH_3^+ + Si(CH_3)_3H \rightarrow Si_2C_4H_{11}^+ + (H_2) \ (7\%) \tag{4}$$

$$SiC_2H_3^+ + Si(CH_3)_3H \rightarrow Si_2C_3H_9^+$$
$$+ (C_2H_4) \ (72\%) \tag{5}$$

$$SiC_2H_5^+ + Si(CH_3)_3H \rightarrow Si_2C_3H_{11}^+$$
$$+ (C_2H_4) \ (46\%) \tag{6}$$

$$SiC_3H_9^+ + Si(CH_3)_3H \rightarrow Si_2C_6H_{19}^+ \ (100\%) \tag{7}$$
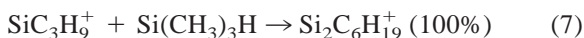
and are quantified in Table 2. Among the products of these dimerization reactions only $Si_2C_3H_{11}^+$ undergoes further reaction with trimethylsilane:

$$Si_2C_3H_{11}^+ + Si(CH_3)_3H \rightarrow Si_2C_4H_{13}^+ + (SiC_2H_8) \tag{8}$$
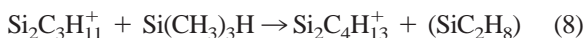
The other disilicon alkylcations react only with background moisture to produce oxygen-containing disilicon cations. This behavior lies between the clustering of silane, which proceed to tetra-silicon ions before slowing, and tetramethylsilane, which exhibits no cationic polymerization.

Since argon is commonly used as a diluent in plasma processing we have also measured the reaction of Ar^+ with trimethylsilane with products and branching ratios shown in

$$Ar^+ + Si(CH_3)_3H \rightarrow SiH_3^+ + (C_3H_7 + Ar) \ (29\%)$$

$$\rightarrow SiCH_3^+ + (C_2H_5 + H_2 + Ar) \ (11\%)$$

$$\rightarrow SiCH_5^+ + (C_2H_5 + Ar) \ (8\%)$$

$$\rightarrow SiC_2H_3^+ + (CH_3 + 2H_2 + Ar) \ (5\%)$$

$$\rightarrow SiC_2H_5^+ + (CH_3 + H_2 + Ar) \ (14\%)$$

$$\rightarrow SiC_2H_6^+ + (CH_4 + Ar) \ (4\%)$$

$$\rightarrow SiC_2H_7^+ + (CH_3 + Ar) \ (19\%)$$

$$\rightarrow SiC_3H_9^+ + (H + Ar) \ (10\%) \tag{9}$$

We have repeated the ion kinetic studies for ions produced by electron impact at 20, 35, and 70 eV to probe for chemistry driven by ions with vibrational, electronic, or rotational excitation. As summarized in Table 2, all reaction rates reported here are independent of the electron energy with which the reactant ions are formed. If internally excited ions are produced at elevated electron energies they are neither more nor less reactive than their counterparts formed at lower electron energies.

On first inspection the Ar^+ reaction would complicate the composition of ion fluxes in trimethylsilane plasmas. However, each of the ion products in reaction (9) reacts rapidly according to reactions (1) and (2) so that the ion composition is largely $Si(CH_3)_3^+$ at pressures and residence times used in plasma processing. We have previously found identical film stoichiometries, SiC_3, using Auger electron spectroscopy of films produced in trimethylsilane and tetramethylsilane plasmas [13], as would be expected for ionic deposits from these two gases since each delivers $Si(CH_3)_3^+$ ions to the surface [14]. The ionic mechanism was further supported, in the earlier study, with film thickness modification by a magnetic field. In sum, the power and pressures of trimethylsilane and
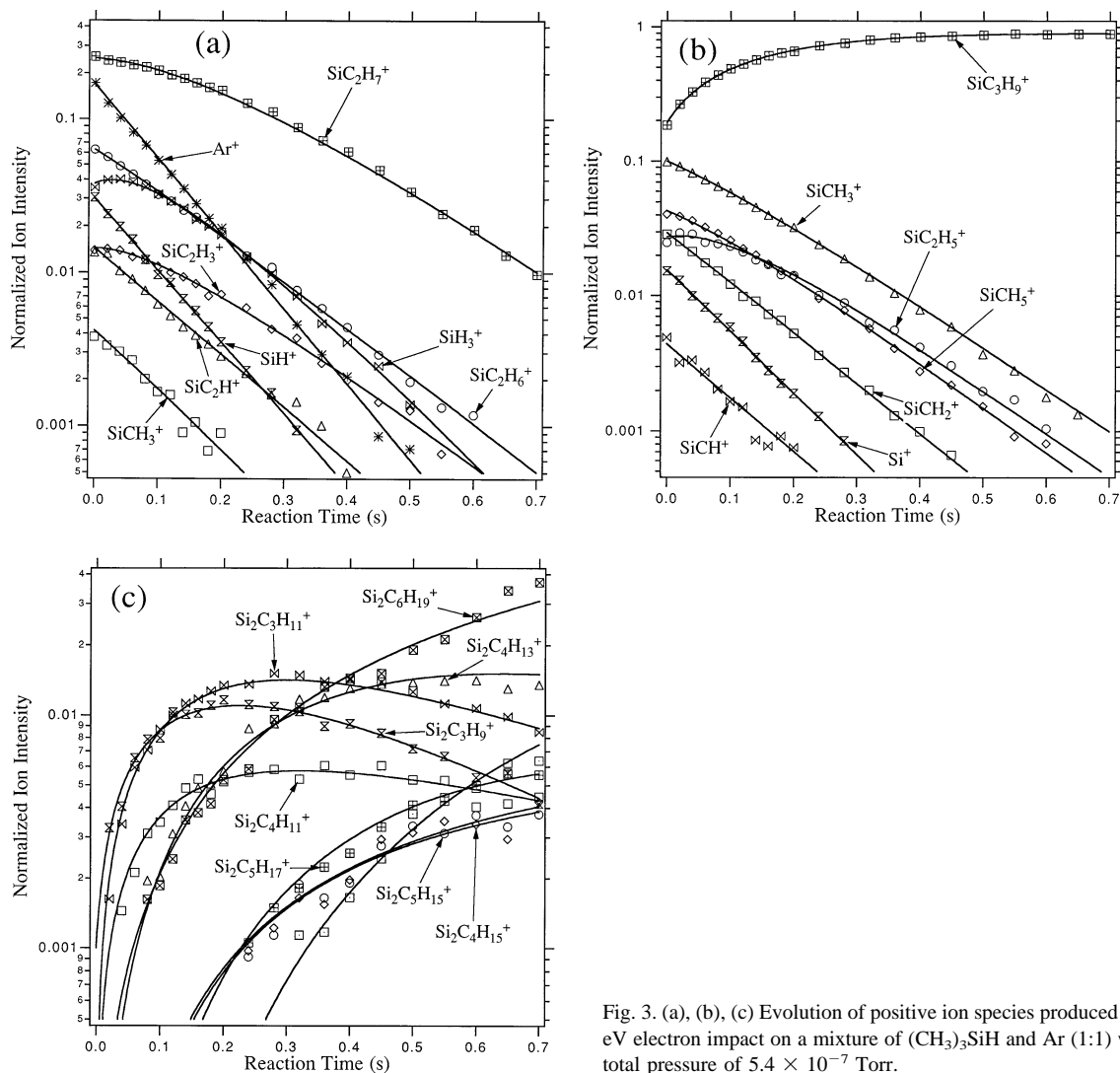
Fig. 3. (a), (b), (c) Evolution of positive ion species produced by 50 eV electron impact on a mixture of $(CH_3)_3SiH$ and Ar (1:1) with a total pressure of 5.4×10^{-7} Torr.

tetramethylsilane plasmas can be tuned to deliver ion fluxes with the same composition to a substrate. This has practical value since liquid tetramethylsilane is less expensive and easier to handle than trimethylsilane gas.

4. Conclusion

Electron impact ionization of trimethylsilane produces no $Si(CH_3)_3H^+$. Dissociative ionization produces 15 ionic fragments, only one of which lacks a silicon atom, with a total cross section of $1.5 \pm 0.5 \times 10^{-15}$ cm^2 at 70 eV. Over half of the ion yield is comprised of $Si(CH_3)_3^+$ and $SiH(CH_3)_2^+$. Although produced in higher yield by electron impact, Si-H(CH_3)_2^+$ reacts rapidly with trimethylsilane to produce $Si(CH_3)_3^+$. Lighter ions react rapidly to form $Si(CH_3)_3^+$ and $SiH(CH_3)_2^+$, so that trimethylsilane plasmas produce $Si(CH_3)_3^+$ at the expense of other ion species. Cationic polymerization yields ions with only two silicon atoms; no trisilicon cations were formed. The stability of the parent molecular ion and the

Table 2
Branching ratios of reactions (1) and (2) for selected reactant ions (see the text); also listed are the rate coefficients measured with reactant ions formed by dissociative ionization at different electron energies

		Branching ratios [a]		Reaction rate coefficients			
m/z	Ion	rxn.1	rxn.2	20 eV [b]	35 eV [b]	50 eV [b]	70 eV [b]
28	Si^{+c}	35	38	$\cdots$	10.7	10.7	10.5
29	SiH^{+d}	41	44	$\cdots$	10.9	10.9	10.6
31	SiH_3^+	72	28	10.6	10.6	10.6	10.3
41	$SiCH^+$	53	47	$\cdots$	9.3	9.3	9.4
42	$SiCH_2^+$	44	56	$\cdots$	8.8	8.8	8.6
43	$SiCH_3^{+c}$	23	70	7.5	7.5	7.4	7.3
44	$SiCH_4^+$	52	48	$\cdots$	10.1	10.1	9.9
45	$SiCH_5^+$	67	33	8.1	8.1	8.1	8.0
53	SiC_2H^+	17	83	$\cdots$	8.1	8.1	8.5
55	$SiC_2H_3^{+c}$	15	13	$\cdots$	7.3	7.1	7.1
57	$SiC_2H_5^{+c}$	25	29	7.9	7.9	7.8	7.8
58	$SiC_2H_6^+$	17	83	7.3	7.3	7.3	7.1
59	$SiC_2H_7^+$		100	6.9	6.9	6.9	6.2
73	$SiC_3H_9^{+e}$			0.06	0.06	0.06	0.06
103	$Si_2C_3H_{11}^{+e}$			2.1	2.1	1.9	1.9

[a] Branching ratios of reactions (1) and (2), respectively, for the selected ions. See the text.
[b] Electron energies at which the reactant ions are formed.
[c] Si^+, $SiCH_3^+$, $SiCH_3^+$, and $SiC_2H_5^+$ also undergo clustering reactions (3)–(6), respectively.
[d] SiH^+ also produces $SiCH_3^+$ with a 15% branching ratio.
[e] $SiC_3H_9^+$ and $Si_2C_3H_{11}^+$ undergo reactions (7) and (8), respectively.

extent of cationic polymerization of trimethylsilane lie between those for silane and tetramethylsilane.

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