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Gas Phase Ion–Molecule Reactions in Mixtures of Silicon and Germanium Hydrides by Ion Trap Mass Spectrometry[†]

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The gas phase reactivity of CH_3GeH_3/SiH_4 and GeH_4/CH_3SiH_3 mixtures has been studied by ion trap mass spectrometry at 60 °C and 7.0 × 10^{-5} Torr helium pressure. Different reaction pathways have been identified, which are common to the two systems here investigated, but which occur at different extents. In both systems SiH_n^+ (n = 0–3) and GeH_n^+ (n = 0–3) ions show a high reactivity and their abundances decrease very quickly with the reaction time. In contrast, $GeCH_n^+$ (n = 3, 5) ions increase their abundances with reaction time, as they are also formed in ion–molecule processes, and transport most of the ion current in the CH_3GeH_3/SiH_4 mixture. Moreover, $SiCH_5^+$ ions show an analogous behavior in the GeH_4/CH_3SiH_3 system, being the base peak at 50-ms reaction time. Remarkable differences are observed in the formation of species containing new Ge–Si bonds. These are mainly formed by GeH_n^+ (n = 0–2) in the GeH_4/CH_3SiH_3 mixture and by both $Si_mH_n^+$ (m = 2, n = 2–4; m = 3, n = 4–6) and GeH_n^+ (n = 1, 2) in the CH_3GeH_3/SiH_4 one. Moreover, the abundances of ions containing silicon and germanium together show small differences and their abundances are very similar in the mixtures examined. The results have been compared with those of CH_3SiH_3 and of the GeH_4/SiH_4 mixture, for their relevance in photovoltaic technology.

Introduction

Hydrogenated amorphous compounds of elements of group 14 are promising in electronic and optoelectronic applications. Alloys with optical gaps smaller than a-Si:H, such as a-GeSi:H,[1,2] are of interest in photovoltaic devices since they improve the long-wavelength sensitivity, while alloys with gaps wider than a-Si:H, such as a-CSi:H,[3,4] allow the collection of the short-wavelength photons of the solar spectrum.

Tetrahedrally bonded ternary amorphous semiconductors, e.g. a-CGeSi:H, have been studied recently[5–7] with the aim to obtain wide-range light collectors. The techniques to prepare these materials are sputter assisted, laser assisted, or other way assisted plasma chemical vapor deposition (CVD), starting from gaseous mixtures containing volatile hydrides of carbon, germanium, and silicon. The relative abundance of each element in the solid depends on the molar fraction of the respective hydride in the gas mixture, but not in a direct way. Therefore it is of fundamental importance to find the relationship between the concentration of a gaseous reactant and its abundance in the final product.

In previous studies,[8–11] the interpretation of the mechanisms involved in X-ray assisted CVD of binary mixtures has been succesfully obtained by chemical ionization mass spectrometry, Fourier transform mass spectrometry, or ion trap mass spectrometry. In this paper we investigate by ion trap mass spectrometry the reaction mechanisms involved in the formation of species containing C, Ge, and Si, with the aim of finding the most efficient system. It has been previously observed[12] that the radiolytical production of a-CGe:H has a higher yield when the gaseous precursor is CH_3GeH_3 with respect to a CH_4/GeH_4 mixture. Therefore, we have considered the two binary mixtures CH_3GeH_3/SiH_4 and GeH_4/CH_3SiH_3 in which a methyl group is already bonded to a germyl or a silyl group.

Experimental Section

Germane[13] and methylgermane[14] were prepared as described in the literature. Silane and methylsilane were obtained commercially in high purity and were used as supplied.

All experiments were run on a Finnigan Mat ion trap mass spectrometer. The gas inlet system was modified in order to introduce simultaneously two reagent gases into the vacuum chamber through different lines and helium buffer gas through a third line. A Bayard Alpert ionization gauge was used to measure the pressures, which were corrected on the basis of the relative sensitivities of the ion gauge response with respect to nitrogen.[15,16] Helium buffer gas was generally admitted to the vacuum chamber at a pressure of 7.0 × 10^{-5} Torr. The

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Table I. Labels on the Main Reaction Pathways As Reported in Schemes I–VII

labels	reacting molecule	neutral loss
Sa	CH_3SiH_3	SiH_4
Sb	SiH_4 or CH_3SiH_3	SiH_2
Sc	SiH_4 or CH_3SiH_3	H_2
Sd	SiH_4 or CH_3SiH_3	
Si	SiH_4 or CH_3SiH_3	GeH_3
Ga	GeH_4 or CH_3GeH_3	SiH_4
Gc	GeH_4 or CH_3GeH_3	H_2
G_2c	GeH_4 or CH_3GeH_3	$2H_2$
Ge	GeH_4 or CH_3GeH_3	SiH_3
Gg	GeH_4 or CH_3GeH_3	CH_3SiH_3
Gh	CH_3GeH_3	GeH_4
Gi	GeH_4 or CH_3GeH_3	GeH_3
Gl	GeH_4 or CH_3GeH_3	GeH_2
Gm	GeH_4 or CH_3GeH_3	CH_4

temperature was maintained at 60 °C in order to avoid thermal decomposition. Ions were detected in the *m/z* 20–400 mass range.

The scan modes for ion–molecule reaction experiments both without and with mass selective storage have been previously described.[19] Ionization was performed by electron impact with electrons at about 70 eV energy and ionization time generally 1 ms. In the first kind of experiment, after the ionization event, reaction (time ranging from 0 to 100 ms) and acquisition took place. When isolation of ions was performed, ionization was followed by a reaction time suitable to maximize the abundance of ions to be stored. Isolation of the selected ion, its reactions with neutrals in the trap for convenient reaction times, and acquisition were the successive events.

Every time an rf or dc voltage is applied, a settling time is necessary, as well as a 4-ms stabilization time for the multiplier. Therefore, when the reaction time is set to zero, some time has passed from the formation of ions (ionization event) and it cannot be ruled out that ion–molecule reactions have already occurred to some extent.

Results

The gas phase ion–molecule reactions of the mixtures CH_3GeH_3/SiH_4 and GeH_4/CH_3SiH_3 have been examined by ion trap mass spectrometry (ITMS). The reaction mechanisms are complex, and the formation of ions having the same nominal mass, but different composition, is also possible. Results concerning GeH_4,[17] CH_3GeH_3,[10] SiH_4,[18] and CH_3SiH_3[19] have already been reported, as well as data on the GeH_4/SiH_4 mixture.[11]

The meanings of the labels in all schemes are given in Table I, in order to facilitate their reading.

Ion–Molecule Reactions in CH_3GeH_3/SiH_4 Mixtures. In Table II the relative abundances of the most significant ions in the mass spectra of the CH_3GeH_3 (4.0×10^{-7} Torr)/SiH_4 (4.0×10^{-7} Torr) mixture are reported, at reaction times from 0 to 50 ms. All abundances refer to the most abundant ion at any time here studied, which is $GeCH_5^+$ after a reaction time of 50 ms.

Several ionic families are present, which can be distinguished in primary ions of both reacting molecules, SiH_4 and CH_3GeH_3 (SiH_n^+, $n = 0$–3; GeH_n^+, $n = 0$–3; $GeCH_n^+$, $n = 1$–5), and secondary ions formed in ion–molecule reactions ($SiCH_n^+$, $n = 3, 5$; $Si_2H_n^+$, $n = 1$–4; $Si_3H_n^+$, $n = 5$–7; $GeC_2H_7^+$; $GeSiH_n^+$, $n = 2$–4; $GeSiCH_n^+$, $n = 4$–6; $GeSi_2H_5^+$; $Ge_2CH_n^+$, $n = 4$–6; $Ge_2C_2H_n^+$, $n = 6, 7$). The identification of all the ions reported in this table has been rather difficult because of the isotopic pattern of germanium and of the high variety of ionic species which give the same *m/z* ratio for different ions. Difficulties due to overlapping of ions containing different isotopes of germanium (i.e. ions at *m/z* 89 can be formulated as $^{76}GeCH^+$, $^{74}GeCH_3^+$, $^{73}GeCH_4^+$, and $^{72}GeCH_5^+$) were eliminated by easy calculations on the basis of the natural isotopic abundances of germanium. In the second case (i.e. *m/z* 101 can be formulated as both $^{70}GeC_2H_7^+$ and $^{70}GeSiH_3^+$) to separate the contributions of the two ions it has been necessary to perform experiments with selective ionic storage of the respective precursors.

Table II. Relative Abundances of Significant Ions in the IT Mass Spectra of the CH_3GeH_3/SiH_4[a] Mixture as a Function of the Reaction Time[b]

		reaction time (ms)					
m/z[c]	ions	0	10	20	30	40	50
28	Si^+	19.3	12.4	6.5	3.6	2.0	1.2
29	SiH^+	15.3	10.3	5.3	3.0	1.6	1.1
30	SiH_2^+	23.6	14.4	7.3	3.9	1.6	1.0
31	SiH_3^+	30.4	24.2	18.4	13.7	9.5	6.0
43	$SiCH_3^+$	1.4	1.6	1.7	1.5	1.3	1.0
45	$SiCH_5^+$	1.9	2.8	3.2	3.2	3.4	2.9
57	Si_2H^+	0.5	0.8	0.9	0.9	0.8	0.8
58	$Si_2H_2^+$	1.8	3.4	3.6	3.9	3.0	3.3
59	$Si_2H_3^+$	1.3	1.8	3.1	2.8	2.7	2.7
60	$Si_2H_4^+$	0.8	1.4	1.5	1.5	1.1	1.0
70	Ge^+	21.9	17.1	13.6	9.7	7.0	6.8
71	GeH^+	12.4	12.6	8.7	7.3	4.4	4.3
72	GeH_2^+	17.4	8.0	5.3	3.5	3.4	1.2
73	GeH_3^+	8.5	6.0	2.7	0.6		
83	$GeCH^+$	5.2	3.5	3.4	2.6	2.5	2.6
84	$GeCH_2^+$	10.6	8.3	7.8	5.9	5.8	5.7
85	$GeCH_3^+$	32.1	39.5	43.4	49.3	49.1	48.3
86	$GeCH_4^+$	27.2	25.0	23.6	22.1	21.4	18.6
87	$GeCH_5^+$	65.7	77.9	77.0	80.8	81.6	100
89	$Si_3H_5^+$	3.6	2.6	3.7	5.0	5.2	4.9
90	$Si_3H_6^+$	5.3	2.7	7.0	1.2	1.0	1.2
91	$Si_3H_7^+$	2.8	2.3	7.5	8.9	9.0	6.1
100	$GeSiH_2^+$	2.2	2.5	3.8	4.8	5.7	6.9
101	$GeC_2H_7^+$	1.3	2.6	2.5	4.7	7.2	7.8
101	$GeSiH_3^+$	5.1	7.7	9.9	13.4	15.3	16.5
102	$GeSiH_4^+$	2.1	2.4	2.5	2.9	3.5	3.4
114	$GeSiCH_4^+$	0.3	0.4	0.6	0.7	0.7	0.6
115	$GeSiCH_5^+$		0.1	0.2	0.3	0.4	0.3
116	$GeSiCH_6^+$		0.2	0.4	0.5	0.6	0.8
131	$GeSi_2H_5^+$		0.1	0.4	0.6	0.6	0.5
156	$Ge_2CH_4^+$	6.2	12.2	14.8	17.3	17.0	18.9
157	$Ge_2CH_5^+$	4.8	10.3	10.8	11.1	11.2	12.2
158	$Ge_2CH_6^+$		1.2	4.4	5.6	7.1	5.9
170	$Ge_2C_2H_6^+$	3.5	5.6	7.8	11.8	12.9	14.8
171	$Ge_2C_2H_7^+$	0.9	1.3	1.5	2.2	2.8	3.5

[a] The pressure of both CH_3GeH_3 and SiH_4 is 4.0×10^{-7} Torr, the total pressure is 7.0×10^{-5} Torr, and the temperature is 60 °C. [b] Data are reported as the sum of the abundances of the species containing all the isotopes of Ge and Si. [c] Masses are calculated on ^1H, ^{12}C, ^{70}Ge, and ^{28}Si.

At zero reaction time, the most abundant species are the primary ions which transport 26.4% (SiH_n^+, $n = 0$–3), 17.9% (GeH_n^+, $n = 0$–3), and 42.0% ($GeCH_n^+$, $n = 1$–5) of the total ion current, respectively. Moreover, the current transported by ions containing both germanium and silicon is only 2.9% in these experimental conditions. The most abundant ionic species contain germanium and hydrogen, or germanium, carbon, and hydrogen (64.9% of the total ion current), while those containing silicon and hydrogen, or silicon, carbon, and hydrogen, are 32.2%. At intermediate reaction times (30 ms), the abundances of the primary ions decrease and the fractions of ionic current transported by SiH_n^+ and GeH_n^+ ($n = 0$–3) become 7.8% and 6.8%, respectively. When the reaction time is 50 ms, this effect is even more evident and the SiH_n^+ and GeH_n^+

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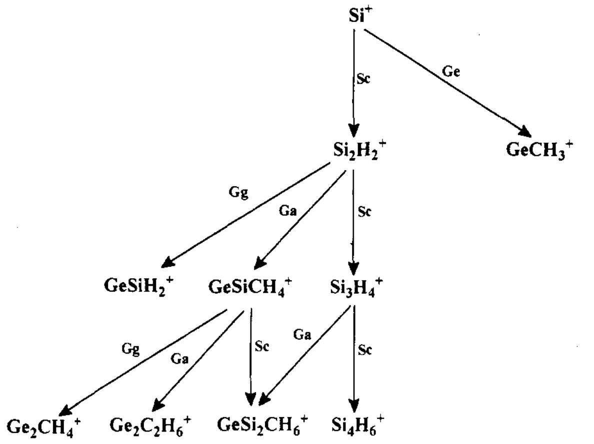
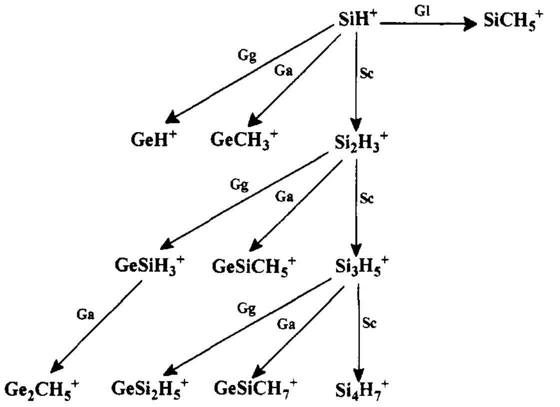
Scheme I. Reaction Mechanism of the Si^+ Ion in the CH_3GeH_3/SiH_4 Mixture



Scheme II. Reaction Mechanism of the SiH^+ Ion in the CH_3GeH_3/SiH_4 Mixture



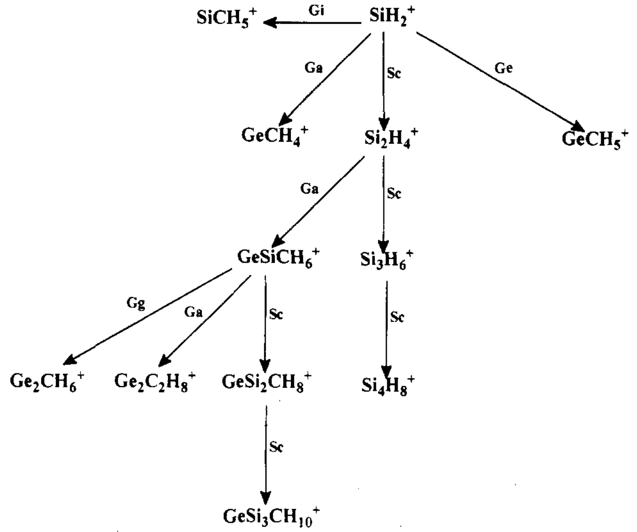
(n = 0–3) ionic families transport 3.0% and 4.0% of the total ion current, respectively. On the contrary, the abundances of the $GeCH_n^+$ (n = 1–5) ions increase at longer reaction times and they transport 51.7% and 56.0% of the total ion current after a reaction time of 30 and 50 ms, respectively. Actually, this behavior is due only to $GeCH_3^+$ and $GeCH_5^+$, whose abundances increase with the reaction time (Table II), indicating that they are formed not only by direct ionization but also in secondary processes.

It is worth noting that the total abundances of the ions containing silicon and hydrogen or silicon, carbon, and hydrogen decrease with increasing reaction time, being 32.2%, 17.1%, and 10.6% of the total ion current at 0-, 30-, and 50-ms reaction times, respectively. The opposite behavior is shown by the ionic species containing germanium and hydrogen or germanium, carbon, and hydrogen (64.9% at zero reaction time, 75.4% at 30 ms, and 80.1% at 50 ms) and by the ions which contain germanium, silicon, and hydrogen with and without carbon (2.9% at 0 ms, 7.5% at 30 ms, and 9.3% at 50 ms).

Schemes I–III report the reaction pathways of the SiH_4 primary ions Si^+, SiH^+, and SiH_2^+, respectively. The schemes were built in successive experiments in which every primary ion and every identified product ion was isolated and stored for variable reaction times. The number of reaction steps was limited by the loss of instrumental sensitivity at long reaction times.

When the neutral reagent is SiH_4, pathway **Sc** is the only process observed in this system, the leaving neutral species being a hydrogen molecule. This reaction mainly occurs for ions containing only silicon and hydrogen in self-condensation processes to form $Si_2H_n^+$ (n = 2–4), $Si_3H_n^+$ (n = 4–6), and $Si_4H_n^+$ (n = 6–8) in successive steps. Also $GeSiCH_n^+$ (n = 4, 6) ions react with silane to give the corresponding $GeSi_2CH_{n+2}$ ions and $GeSi_2CH_8^+$ also gives $GeSi_3CH_{10}^+$ through pathway **Sc**.

Scheme III. Reaction Mechanism of the SiH_2^+ Ion in the CH_3GeH_3/SiH_4 Mixture



In all other pathways the reacting neutral molecule is CH_3GeH_3 which mainly eliminates CH_3SiH_3 and SiH_4, in reactions **Gg** and **Ga**, respectively. A less frequent path involves the loss of a SiH_3 radical (pathway **Ge**) and is observed only for Si^+, which forms $GeCH_3^+$ in Scheme I, and for SiH_2^+, which forms $GeCH_5^+$ in Scheme III.

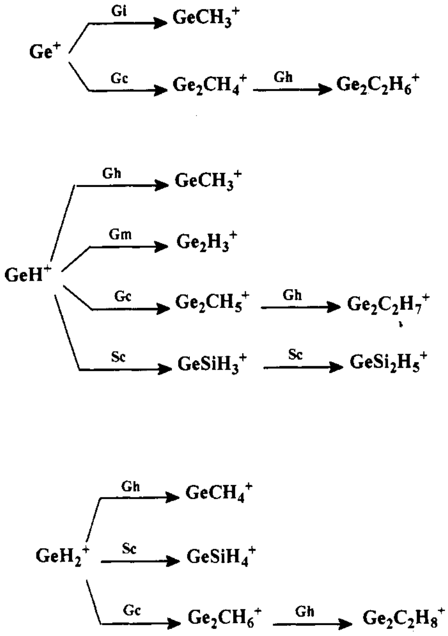
The reaction scheme of SiH_3^+ is not shown, as it reacts very slowly to give only three product ions: $Si_2H_5^+$ by reaction with SiH_4 and elimination of H_2; $SiCH_5^+$ and $GeCH_5^+$ by reaction with CH_3GeH_3 and elimination of GeH_4 and SiH_4, respectively.

Schemes I–III show a general behavior which consists of lowering the silicon content of the ions formed in successive ion–molecule reactions and agrees with the higher abundances of ions containing only carbon, germanium, and hydrogen at 50-ms reaction time, observed in Table II. Pathway **Sc** on $GeSiCH_4^+$ (Scheme I) and $GeSiCH_6^+$ (Scheme III) ions gives products with a higher content of silicon.

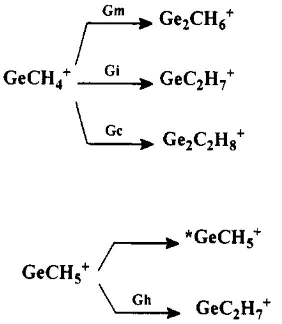
The reaction mechanisms of the primary ions deriving from methylgermane are reported in Schemes IV (Ge^+, GeH^+, and GeH_2^+) and V ($GeCH_4^+$ and $GeCH_5^+$). In order to avoid interference of ions having different formulas but the same nominal masses the following ions were isolated: $^{70}Ge^+$, $^{70}GeH^+$, $^{76}GeH_2^+$, $^{76}GeH_3^+$, $^{70}GeCH_3^+$, $^{76}GeCH_4^+$, and $^{76}GeCH_5^+$, even if they are reported without the mass number in the schemes and in the text. Both GeH_3^+ and $GeCH_3^+$ are not reported, as they are unreactive up to 100-ms reaction time. Only GeH^+ and GeH_2^+ react with silane through pathway **Sc** to give $GeSiH_3^+$ and $GeSiH_4^+$, respectively, by loss of a hydrogen molecule. All other reactions take place with CH_3GeH_3 as the neutral molecule with loss of a variety of neutral fragments: GeH_3 (**Gi**), GeH_4 (**Gh**), CH_4 (**Gm**), and H_2 (**Gc**). $^{76}GeCH_5^+$ gives isotopic scrambling with formation of $*GeCH_5^+$ ions, containing all the natural isotopes of germanium.

Ion–Molecule Reactions in GeH_4/CH_3SiH_3 Mixtures. Table III reports the relative abundances of the

Scheme IV. Reaction Mechanisms of the Ge^+, GeH^+, and GeH_2^+ Ions in the CH_3GeH_3/SiH_4 Mixture



Scheme V. Reaction Mechanisms of the $GeCH_4^+$ and $GeCH_5^+$ Ions in the CH_3GeH_3/SiH_4 Mixture



most significant ions in the ion trap mass spectra of a GeH_4 (4.0×10^{-7} Torr)/CH_3SiH_3 (4.0×10^{-7} Torr) mixture at 0-, 10-, 30-, 50-, and 100-ms reaction times. Again, all ionic abundances refer to the most abundant ion at any time here considered, i.e. $SiCH_5^+$ after 50 ms of reaction. A great number of ionic families are present, which are formed by direct ionization or in ion–molecule processes of both neutral molecules: SiH_n^+ (n = 0–3), $SiCH_n^+$ (n = 2–5), $SiC_2H_n^+$ (n = 6, 7), GeH_n^+ (n = 0–3), $Si_2CH_n^+$ (n = 4, 5), $GeCH_n^+$ (n = 3–5), $Si_2C_2H_n^+$ (n = 6–9, 11), $Si_2C_3H_n^+$ (n = 9, 11, 13), $GeSiCH_n^+$ (n = 4–6), $Si_3C_2H_9^+$, $GeSiC_2H_n^+$ (n = 6, 7), $Si_3C_3H_n^+$ (n = 10–13), and $Ge_2H_n^+$ (n = 2–4). In this table, some couples of ions have the same nominal mass, i.e. GeH_3^+ and $Si_2CH_5^+$ at m/z 73. Therefore, the formulas reported have been obtained by experiments of selective storage of ions and by calculations on the isotopic distributions of germanium and silicon.

The GeH_n^+ (n = 0–3) and $SiCH_n^+$ (n = 2–5) primary ions of GeH_4 and CH_3SiH_3 and the fragment ions SiH_n^+ (n = 0–3) together transport 85.7% of the total ion current at zero reaction time. As reactions proceed, their abundances continuously decrease and they transport 51.7% and 38.4% of the total ion current at 50- and 100-ms reaction times, respectively. Among these ions, $SiCH_5^+$ shows a different trend, as its abundance increases up to 50-ms reaction time. This behavior suggests that ion–molecule processes give a contribution to the formation of the primary ion $SiCH_5^+$.

Table III. Relative Abundances of Significant Ions in the IT Mass Spectra of the GeH_4/CH_3SiH_3[a] Mixture as a Function of the Reaction Time[b]

		reaction time (ms)				
m/z[c]	ions	0	10	30	50	100
28	Si^+	16.9	9.8	2.8	0.9	
29	SiH^+	6.1	3.1	1.1	0.2	
30	SiH_2^+	3.6	2.0	2.7	0.2	
31	SiH_3^+	2.9	0.8	0.3	0.2	
42	$SiCH_2^+$	8.7	6.7	3.3	1.5	0.5
43	$SiCH_3^+$	28.8	25.8	21.2	15.6	7.1
44	$SiCH_4^+$	29.1	18.7	9.9	6.1	2.6
45	$SiCH_5^+$	67.8	85.3	99.6	100	83.0
58	$SiC_2H_6^+$	1.7	1.5	1.6	1.5	1.3
59	$SiC_2H_7^+$	5.5	10.5	19.8	26.9	40.2
70	Ge^+	18.8	16.0	2.7	5.6	2.5
71	GeH^+	13.4	10.6	7.2	5.9	2.5
72	GeH_2^+	16.9	9.7	4.1	2.3	
72	$Si_2CH_4^+$	0.5	1.4	1.8	1.7	0.3
73	GeH_3^+	20.7	17.8	9.1	5.8	0.7
73	$Si_2CH_5^+$	1.0	1.1	1.7	0.8	1.3
85	$GeCH_3^+$	3.4	4.1	6.0	7.2	7.4
86	$GeCH_4^+$	2.7	3.3	5.8	6.0	6.6
86	$Si_2C_2H_6^+$	0.9	2.0	2.1	1.9	0.8
87	$GeCH_5^+$	4.1	6.6	9.1	10.0	15.6
87	$Si_2C_2H_7^+$	0.5	1.1	1.7	1.9	1.3
88	$Si_2C_2H_8^+$	1.2	2.0	2.1	2.1	2.6
89	$Si_2C_2H_9^+$		0.3	0.6	1.5	1.2
91	$Si_2C_2H_{11}^+$			0.8	1.5	1.6
101	$Si_2C_3H_9^+$		0.4	0.7	1.0	1.1
103	$Si_2C_3H_{11}^+$	0.4	0.6	0.9	1.1	1.0
105	$Si_2C_3H_{13}^+$	1.4	1.6	2.1	2.6	3.9
114	$GeSiCH_4^+$	2.8	4.8	6.3	5.7	4.0
115	$GeSiCH_5^+$	2.9	5.1	7.3	8.1	6.9
116	$GeSiCH_6^+$	1.3	2.7	4.4	5.7	3.4
117	$Si_3C_2H_9^+$		0.1	0.2	0.3	0.5
128	$GeSiC_2H_6^+$		1.0	1.0	1.1	1.3
129	$GeSiC_2H_7^+$		0.5	2.3	2.5	4.3
130	$Si_3C_3H_{10}^+$	0.3	0.8	1.9	2.8	2.7
131	$Si_3C_3H_{11}^+$	0.2	0.9	2.0	3.0	4.7
132	$Si_3C_3H_{12}^+$	0.4	1.0	1.8	2.2	2.5
133	$Si_3C_3H_{13}$	0.3	0.6	1.3	2.1	2.4
142	$Ge_2H_2^+$	5.1	10.2	15.2	18.2	20.4
143	$Ge_2H_3^+$		2.8	6.3	8.1	10.6
144	$Ge_2H_4^+$	2.4	3.4	4.1	7.2	8.5

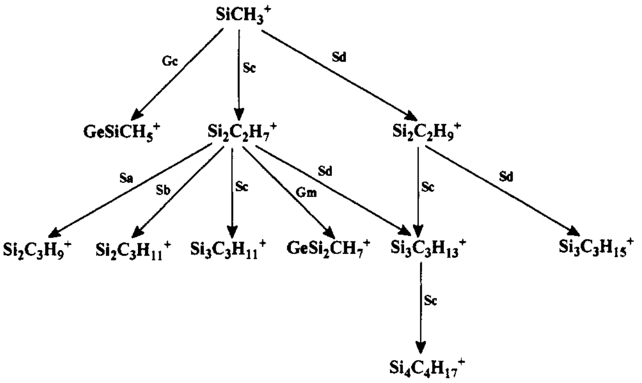
[a] The pressure of both GeH_4 and CH_3SiH_3 is 4.0×10^{-7} Torr, the total pressure is 7.0×10^{-5} Torr, and the temperature is 60 °C. [b] Data are reported as the sum of the abundances of the species containing all the isotopes of Ge and Si. [c] Masses are calculated on ^1H, ^{12}C, ^{70}Ge, and ^{28}Si.

Ions formed in ion–molecule reactions follow two different trends. In fact, the abundances of the $Si_2CH_n^+$ (n = 4, 5), $Si_2C_2H_n^+$ (n = 6, 7, 9), and $GeSiCH_n^+$ (n = 4–6) ions increase, reach a maximum at 30- or 50-ms reaction time, and then decrease again. In contrast, the ionic abundances of $SiC_2H_7^+$, $GeCH_n^+$ (n = 3–5), $Si_2C_3H_n^+$ (n = 9, 11, 13), $Si_3C_3H_n^+$ (n = 10–13), and $Ge_2H_n^+$ (n = 2–4) continuously increase up to 100-ms reaction time.

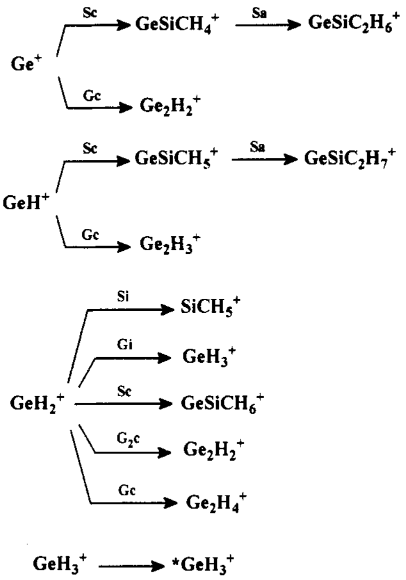
In Scheme VI the reaction pathways of $SiCH_3^+$ are reported. The reaction sequences of the other primary ions containing silicon are not reported, as they give only the self-condensation reactions already described.[19] Most of the reactions which are displayed in Scheme VI for the GeH_4/CH_3SiH_3 mixture are self-condensation processes of methylsilane. Moreover, two ions react with neutral GeH_4 to form species containing germanium, silicon, and carbon together: $GeSiCH_5^+$ from $SiCH_3^+$, and $GeSi_2CH_7^+$ from $Si_2C_2H_7^+$.

Scheme VII shows the reaction patterns of the GeH_n^+ (n = 0–3) primary ions of GeH_4. In a first reaction step, the GeH_n^+ (n = 0–2) ions react with CH_3SiH_3 molecules

Scheme VI. Reaction Mechanism of the $SiCH_3^+$ Ion in the GeH_4/CH_3SiH_3 Mixture



Scheme VII. Reaction Mechanisms of the Ge^+, GeH^+, GeH_2^+, and GeH_3^+ Ions in the GeH_4/CH_3SiH_3 Mixture



by elimination of a hydrogen molecule (pathway **Sc**) to give the $GeSiCH_n^+$ (n = 4–6) ions. Alternatively, the same GeH_n^+ (n = 0–2) species react with GeH_4, yielding $Ge_2H_n^+$ (n = 2–4) ions by loss of H_2 (pathway **Gc**). $Ge_2H_2^+$ is also formed from GeH_2^+, eliminating two hydrogen molecules (pathway $\mathbf{G_2c}$). At their turn, the $GeSiCH_n^+$ (n = 4, 5) ions generate $GeSiC_2H_n^+$ (n = 6, 7) by reaction with neutral methylsilane and elimination of SiH_4 (pathway **Sa**). A different reaction pathway is followed by GeH_2^+ ions, which react with both CH_3SiH_3 (pathway **Si**) and GeH_4 (pathway **Gi**) by loss of a GeH_3 radical to form $SiCH_5^+$ and GeH_3^+, respectively. Finally, GeH_3^+ gives isotopic scrambling leading to the $^*GeH_3^+$ ions containing all natural isotopes of germanium.

GeH_4/SiH_4 Mixture. This system has been studied previously, and both reaction schemes and variations of ionic abundances with reaction time have already been published.[11] However, as the pressures of the reagent gases were different from those used in this study, results cannot be compared directly. Therefore, the relative abundances of significant ions in the ion trap mass spectra of the GeH_4 (4.0×10^{-7} Torr)/SiH_4 (4.0×10^{-7} Torr) mixture are reported in Table IV.

Discussion

In the CH_3GeH_3/SiH_4 system the $GeCH_n^+$ (n = 3–5) species show a very low reactivity and the reactive collisions involve silicon containing ions or GeH_n^+ (n = 0–2) fragment ions. A comparison can be drawn with the GeH_4/SiH_4 system, in which interesting reactions are given by $Si_2H_n^+$ (n = 2–5) and GeH_4 leading to $GeSiH_n^+$ (n = 2–5) and $Ge_2H_n^+$ (n = 2–5) ions in two successive substitution processes of silicon by germanium atoms.[11] Similar reaction sequences are observed in the CH_3GeH_3/SiH_4 system, even if the pattern is more complicated than in the previous mixture. In fact, in Scheme I, $Si_2H_2^+$ is reported to give $GeSiH_2^+$ and $GeSiCH_4^+$ in parallel reactions with elimination of CH_3SiH_3 and SiH_4, respectively. Successive substitution processes of silicon with germanium occur from $GeSiCH_4^+$ to $Ge_2CH_4^+$ (– CH_3SiH_3) and $Ge_2C_2H_6^+$ (– SiH_4). Similar substitution processes of silicon with germanium atoms are also observed for $Si_2H_3^+$ and for $Si_2H_4^+$, as reported in Schemes II and III. Moreover, $GeSiH_3^+$ and $GeSiH_4^+$ ions are formed also from GeH^+ and GeH_2^+, respectively, reacting with neutral SiH_4 (Scheme IV), through the same processes previously reported for the GeH_4/SiH_4 system.

However, remarkable differences in the reactivity of CH_3GeH_3 and GeH_4 toward SiH_4 can be seen. In the CH_3GeH_3/SiH_4 system, $GeSiCH_n^+$ (n = 4, 6) ions react also with silane to give $GeSi_2CH_{n+2}$ (n = 4, 6) ions, as reported in Schemes I and III. Analogous processes have not been observed in the GeH_4/SiH_4 mixture.

In the GeH_4/CH_3SiH_3 system ions containing germanium and silicon together are formed mainly by GeH_n^+ (n = 0–2). All the SiH_n^+ (n = 0–3) and $SiCH_n^+$ (n = 2, 4, 5) species react only with CH_3SiH_3 through the processes observed in self-condensation.[19] $SiCH_3^+$ reacts with both CH_3SiH_3 and GeH_4 through a Gc pathway (Scheme VI) to give a minor contribution to the abundance of $GeSiCH_5^+$, which is mainly formed from GeH^+ through a **Sc** pathway. The same reaction path leads to the other Ge–Si ionic species from Ge^+ and GeH_2^+ (Scheme VII).

In order to check the effect of the relative concentrations of the two reactants on the formation of ions containing both germanium and silicon, some experiments have been performed at different GeH_4/CH_3SiH_3 ratios of partial pressures. Namely, GeH_4/CH_3SiH_3 1:1, 3:1, and 6:1 mixtures have been studied and the results have been compared. The main difference concerns the ionic abundances of the $GeSiCH_n^+$ (n = 4–6) and $Ge_2H_n^+$ (n = 2–4) ionic species. In fact, $GeSiCH_n^+$ (n = 4–6) ions at 30-ms reaction time transport 6.6%, 2.4%, and 0.9% of the total ion current in the 1:1, 3:1, and 6:1 mixtures, respectively. At the same reaction time and in the corresponding mixtures, $Ge_2H_n^+$ (n = 2–4) ions transport a fraction of the total ion current which is 9.3%, 27.4%, and 46.8%, respectively. The decrease of abundances of the ions containing Ge and Si at decreasing relative content of CH_3SiH_3 is in agreement with the main formation pathway observed for the $GeSiCH_n^+$ (n = 4–6) species, which involves GeH_n^+ (n = 0–2) ions and CH_3SiH_3 molecules. A parallel competitive process concerns formation of $Ge_2H_n^+$ (n = 2–4) ions again from GeH_n^+ (n = 0–2) reacting with neutral GeH_4. In this case, the increase of dimer ion abundances is in agreement with the increase of GeH_4 content in the three mixtures.

In the CH_3GeH_3/SiH_4 system, the SiH_n^+ (n = 0–3) ions display the usual reaction pattern due to self-condensation

Table IV. Relative Abundances of Significant Ions in the IT Mass Spectra of GeH$_4$/SiH$_4$[a] as a Function of the Reaction Time[b]

		reaction time (ms)							
m/z[c]	ions	0	10	20	30	40	50	75	100
28	Si^+	25.8	17.1	11.6	8.5	6.6	5.5	3.2	2.5
29	SiH^+	14.9	9.8	5.9	3.5	2.2	1.5	0.6	
30	SiH_2^+	43.4	23.5	13.3	7.8	4.3	2.9	0.9	
31	SiH_3^+	54.6	41.9	32.7	25.3	17.7	13.0	5.7	3.2
58	$Si_2H_2^+$	3.4	4.4	5.1	5.2	4.9	4.5	4.1	3.1
59	$Si_2H_3^+$	2.0	3.0	3.3	3.2	3.3	2.8	2.7	2.5
60	$Si_2H_4^+$	4.6	8.1	9.7	8.7	8.5	8.2	5.9	3.7
61	$Si_2H_5^+$	0.4	0.4	0.6	0.7	0.6	0.6	0.4	
70	Ge^+	25.8	19.5	20.5	17.6	15.8	14.7	11.5	8.2
71	GeH^+	14.1	13.3	10.8	9.6	9.0	7.5	5.0	2.8
72	GeH_2^+	39.2	34.9	27.8	21.3	17.3	14.8	8.8	6.6
73	GeH_3^+	71.3	80.7	86.3	92.4	94.8	95.2	100	97.1
88	$Si_3H_4^+$			0.5	0.7	0.7	0.6	0.4	0.4
89	$Si_3H_5^+$		0.6	0.9	1.1	1.3	1.0	0.6	0.5
90	$Si_3H_6^+$				0.3	0.3	0.4		
91	$Si_3H_7^+$				0.2	0.3	0.3		
100	$GeSiH_2^+$	1.5	3.2	3.6	4.3	3.7	3.9	3.0	2.9
101	$GeSiH_3^+$	3.3	3.2	4.1	4.2	4.1	3.9	3.6	3.0
102	$GeSiH_4^+$	3.6	7.3	10.1	11.5	11.7	10.6	9.2	8.9
118	$Si_4H_6^+$					0.2	0.2	0.4	0.5
119	$Si_4H_7^+$				0.3	0.4	0.4	0.6	0.7
129	$GeSi_2H_3^+$			0.4	0.9	1.5	1.3	1.1	1.2
142	$Ge_2H_2^+$	11.1	14.8	22.6	27.5	27.2	32.0	37.3	41.1
143	$Ge_2H_3^+$	7.0	8.5	10.3	13.7	14.6	15.4	14.7	17.1
144	$Ge_2H_4^+$	7.7	10.1	13.4	16.0	17.8	19.1	21.6	26.5

[a] The pressure of both GeH$_4$ and SiH$_4$ is 4.0×10^{-7} Torr, the total pressure is 7.0×10^{-5} Torr, and the temperature is 60 °C. [b] Data are reported as the sum of the abundances of the species containing all the isotopes of Si. [c] Mass are calculated on ^1H, ^{12}C, ^{70}Ge, and ^{28}Si.

processes. Moreover, all of them react with CH_3GeH_3 to give the $GeCH_n^+$ ($n = 3–5$) ionic family, by elimination of a SiH_3 radical (Si^+ and SiH_2^+) or a SiH_4 molecule (SiH^+) (Schemes I–III).

Similar processes have been previously observed in the GeH$_4$/SiH$_4$ mixture,[11] in which SiH_n^+ ($n = 0–3$) ions react with neutral GeH$_4$ to form GeH_n^+ ($n = 0–3$) species, whose heats of formation are reported in the literature.[21,22,24] For reactions 1, always exothermic, the enthalpies have been

$$SiH_n^+ + GeH_4 \rightarrow GeH_n^+ + SiH_4 \qquad (1)$$

calculated for $n = 0$, $\Delta H^0_r = -37$ kcal/mol, for $n = 1$, $\Delta H^0_r = -34 \pm 1$ kcal/mol, for $n = 2$, $\Delta H^0_r = -65 \pm 1$ kcal/mol, and for $n = 3$, $\Delta H^0_r = -14 \pm 1$ kcal/mol.

On the basis of the occurrence of reactions 1, which are exothermic for all SiH_n^+ ($n = 0–3$) ions, it could be suggested that also process 2, observed in the GeH$_4$/CH$_3$SiH$_3$ system, and the general reactions 3, which have been observed in the CH$_3$GeH$_3$/SiH$_4$ mixture, are thermodynamically favored. The lack of heats of formation of the $GeCH_n^+$ ($n = 3–5$) ions prevents us from calculating the enthalpies of the last reactions (3). In contrast, the heats of formation of all the species involved in reaction 2 are reported in the literature.[20,23,24] The calculated enthalpy is positive by about 13 kcal/mol with an uncertainty of almost 10 kcal/mol, which can be considered as thermoneutral.

$$GeH_2^+ + CH_3SiH_3 \rightarrow SiCH_5^+ + GeH_3 \qquad (2)$$

$$SiH_n^+ \ (n = 0–3) \rightarrow GeCH_n^+ \ (n = 3–5) \qquad (3)$$

The exothermicity of reactions 1 and the related suggestions are in agreement with the variation of the abundances of the GeH_n^+ ($n = 0–3$), SiH_n^+ ($n = 0–3$), $GeCH_n^+$ ($n = 3–5$), and $SiCH_n^+$ ($n = 3–5$) ions, in the different systems here studied, with reaction time. In fact, when SiH_n^+ ($n = 0–3$) ions react with GeH$_4$ or CH$_3$GeH$_3$ (reactions 1 and 3), the abundances of the primary ions SiH_n^+ decrease very sharply. Under the same experimental conditions they are 41.6% and 8.9% of the total ion current at 0- and 50-ms reaction time, respectively, in the GeH$_4$/SiH$_4$ mixture (Table IV) and 26.4% and 3.1% at 0- and 50-ms reaction time, respectively, in the CH$_3$GeH$_3$/SiH$_4$ mixture.

In contrast, primary ions from CH$_3$SiH$_3$ behave in a different way with GeH$_4$ (reaction 2), as they only slightly decrease from 0- (59.7% of the total ion current) to 50-ms (44.2%) reaction time.

An opposite behavior is shown by the corresponding ions containing germanium, GeH_n^+ ($n = 0–3$) and $GeCH_n^+$ ($n = 3–5$). In the GeH$_4$/SiH$_4$ and CH$_3$GeH$_3$/SiH$_4$ mixtures, the abundances of the two ionic families GeH_n^+ ($n = 0–3$) and $GeCH_n^+$ ($n = 3–5$) are rather constant, changing from 45.1% to 51.6% and from 59.9% to 58.6%, respectively, in the first 50 ms of reaction. In the system GeH$_4$/CH$_3$SiH$_3$, the abundances of GeH_n^+ ($n = 0–3$) species decrease from 25.4% of the total ion current at zero reaction time to 6.9% at 50 ms.

Considering the abundances of secondary ions formed in condensation processes, very different behaviors are shown by the systems examined. At 50-ms reaction time, ions which do not contain germanium atoms transport 7.4%, 7.8%, and 20.6% of the total ion current in the GeH$_4$/SiH$_4$, CH$_3$GeH$_3$/SiH$_4$, and GeH$_4$/CH$_3$SiH$_3$ mixtures, respectively. At the same time of reaction, ions which do not contain silicon atoms transport 26.4%, 20.8%, and

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20.1% of the total ion current in the three systems, respectively.

A more steady behavior is displayed by these systems considering ions containing germanium and silicon together. In fact, their abundances at 50-ms reaction time range from a minimum of 7.7% of the total ion current in the GeH_4/SiH_4 mixture to a maximum of 9.3% in the CH_3GeH_3/SiH_4 system. In contrast, ions containing carbon, germanium, and silicon together behave very differently, as they transport 0.5% and 8.3% of the total ion current in the CH_3GeH_3/SiH_4 and GeH_4/CH_3SiH_3 mixtures, respectively. Therefore, it seems that the mixtures containing the methylated hydrides of germanium or silicon give a slightly better yield in terms of ions containing two different atoms (Ge, Si) and hydrogen. However, it must also be considered that the methyl derivatives are synthesized starting from the corresponding hydrides and that the yield of this preparation does not exceed 70%. Moreover, only the GeH_4/CH_3SiH_3 system forms appreciable amounts of ions containing the three atomic species, C, Ge, and Si, with hydrogen.

In conclusion, the best ionic contribution for the preparation of a-GeSi:H materials seems to be given by the simplest system, i.e. the GeH_4/SiH_4 mixture, while for the preparation of materials containing germanium, silicon, and carbon together, the highest yields are obtained in the GeH_4/CH_3SiH_3 system.

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