Contents lists available at ScienceDirect



International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms



Thermal decomposition of tetramethylsilane and tetramethylgermane by flash pyrolysis vacuum ultraviolet photoionization time-of-flight mass spectrometry

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Jessy M. Lemieux, Jingsong Zhang*

Department of Chemistry, University of California, Riverside, CA 92521, USA

ARTICLE INFO

Article history: Received 29 July 2014 Received in revised form 10 September 2014 Accepted 10 September 2014 Available online 19 September 2014

Keywords: Tetramethylsilane Tetramethylgermane Thermal decomposition Pyrolysis Photoionization Mass spectrometry

ABSTRACT

Thermal decomposition of tetramethylsilane (TMS) and tetramethylgermane (TMG) was studied on a short time scale of 20-100 µs using flash pyrolysis vacuum ultraviolet single-photon ionization time-offlight mass spectrometry (VUV-SPI-TOFMS). Primary decomposition of TMS and TMG occurred via loss of a methyl radical to form \bullet Si(CH₃)₃ and \bullet Ge(CH₃)₃, respectively. Both the \bullet Si(CH₃)₃ and \bullet Ge(CH₃)₃ radicals underwent secondary loss of a second methyl radical to form :Si(CH₃)₂ and :Ge(CH₃)₂, respectively. A previously unobserved secondary decomposition process in TMS involving loss of H atom from *Si(CH₃)₃ followed by elimination of H₂ to form SiC₃H₈, SiC₃H₆, and SiC₃H₄ was also identified. Sequential loss of the third and fourth methyl radical with significant formation of Ge and Ge₂ was observed in the TMG pyrolysis. Loss of a third methyl radical in the TMS pyrolysis was not significant, while Si and SiC products were possibly produced. Secondary reactions of methyl to form unsaturated $C_x H_y$ species, particularly in the TMG decomposition, were also observed.

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1. Introduction

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SiC is an interesting material due to its wide band gap which allows for high temperature, high frequency, and high power microelectronic applications. In addition SiC has a variety of attractive physical properties including high mechanical strength, wear resistance, and thermal stability. SiC thin films are generally produced via chemical vapor deposition (CVD) of SiH₄ and C₃H₈ precursors on Si substrate at temperatures above 1300 °C. However, this method has proven problematic due to the large difference in lattice constants and thermal expansion coefficients between Si and SiC [1]. Organosilanes such as tetramethylsilane (TMS) already contain a Si-C bond and generally decompose at relatively low temperatures, thus making them promising alternatives to the SiH₄/ C₃H₈ mixture. Indeed, precursors such as TMS have been successfully used to grow high quality SiC films by a variety of CVD techniques including plasma enhanced CVD, low pressure CVD, hot-wire catalytic CVD, and others [2-11], but further study is required in order to better control the SiC thin film properties.

Although the mechanism of SiC deposition from the TMS pyrolysis is not yet well understood, the gas phase pyrolysis of TMS has been previously examined using static cell [12], flow cell [13], "wall-less reactor" [14], and hot-wire catalytic [15–17] techniques. These studies suggest that TMS pyrolysis proceeds by first order reaction kinetics in which the initial cleavage of one Si-C bond is the rate determining step. Successive losses of the remaining methyl groups have been proposed to occur in succession [13,14].

$$Si(CH_3)_4 \rightarrow {}^{\bullet}Si(CH_3)_3 + CH_3 \tag{1}$$

$$^{\bullet}Si(CH_3)_3 \rightarrow :Si(CH_3)_2 + CH_3$$
(2)

E-mail address: jingsong.zhang@ucr.edu (J. Zhang).

 $:Si(CH_3)_2 \rightarrow SiCH_3 + CH_3$ (3)

The germanium analog of TMS, tetramethylgermane (TMG), also has found use in CVD processes particularly for deposition of GeC. The germanium carbide materials are not as well studied as silicon carbides but they are known to have several interesting properties that warrant further study of the CVD processes of GeC. These include tunable refractive index by varying germanium/ carbon ratios, and band gap tunability which may prove useful in photovoltaic applications.

$$SiCH_3 \rightarrow Si + CH_3$$
 (4)

Kim et al. more recently suggested that the loss of the second methyl was the rate limiting step in TMS pyrolysis [1]. Recent hot filament dissociation vacuum-ultraviolet photoionization timeof-flight mass spectrometry (VUV-PI-TOFMS) experiments measured methyl as the primary product of catalytic TMS dissociation on heated tungsten wire [15,18]. Hydrogen abstraction by methyl and its pyrolysis complement from the parent may also be an important pathways [19]

$$Si(CH_3)_4 + CH_3 \rightarrow Si(CH_3)_3CH_2 + CH_4$$
(5)

$${}^{\bullet}Si(CH_3)_3 + {}^{\bullet}CH_3 \rightarrow Si(CH_3)_2CH_2 + CH_4$$
(6)

Toukabri et al. very recently measured the relative methyl production during hot-wire catalytic decomposition of tetramethylsilane, trimethylsilane, dimethylsilane, and methylsilane [17,20]. They found that TMS produced the least number of methyl radicals with the highest activation energy. Hot-wire catalytic studies at a time scale of seconds to minutes from the same group indicated abstraction of hydrogen atoms from trimethylsilane at the Si—H and the C—H bond locations to be the most prominent secondary decomposition process with the H abstraction from the Si atom being preferred [16].

Only two known studies of TMG pyrolysis exist. In the previously referenced "wall-less reactor" study [14], the mechanism of TMG pyrolysis was stated to be the same as that for TMS shown above. Smith and Patrick studied the TMG pyrolysis in 1983 using the Knudsen cell very low pressure pyrolysis (VLPP) technique and determined a Ge—C bond energy of 83 kcal mol⁻¹ but did not propose a mechanism for the TMG pyrolysis [21].

In this study, the flash pyrolysis vacuum ultraviolet single-photon ionization time-of-flight mass spectrometry (VUV-SPI-TOFMS) technique is used to study the thermal decomposition processes of TMS and TMG relevant to the SiC and GeC CVD. The previous mechanistic studies of the SiC CVD precursors were complicated by the recombination of reactive intermediates prior to detection, as well as fragmentation of pyrolysis products due to electron impact (EI) and multi-photon ionization (MPI). In this work, TMS and TMG are pyrolyzed on a short 20-100 µs time scale, much shorter than in the previous studies, minimizing secondary reactions and recombination of the pyrolysis products. A 10.45 eV "soft" VUV photoionization radiation source is used to ionize the pyrolysis products for detection by TOFMS, thereby minimizing photoionization fragmentation. This technique allows direct observation of initial thermal decomposition products and reactive intermediates, providing greater insight into the gas-phase processes involved in the CVD of SiC and GeC.

2. Experimental

The TMS and TMG pyrolysis experiments were conducted on a home-built vacuum ultraviolet (VUV) photoionization timeof-flight mass spectrometer (TOFMS) apparatus that has been previously described [22–24]. TMS (99.9%) and TMG (99%) were obtained from Sigma–Aldrich and used without further purification. Samples were diluted to approximately 1% concentration in helium carrier gas by passing helium through liquid TMS or TMG contained in glass bubblers immersed in cold temperature baths. A -41 °C acetonitrile/dry ice bath was used for TMS. TMG was held at -10 °C using a saturated NaCl solution with ice.

The diluted TMS and TMG samples were expanded into vacuum through a pulsed valve and a SiC tubular nozzle of inner diameter 1 mm that was heated to temperatures of approximately



Fig. 1. Stack plot of mass spectra of Si(CH₃)₄ (\sim 1%) in He at room temperature and pyrolysis temperatures 660 K to 1470 K. Mass spectra are offset for clarity.

600–1500 K by passing an electric current through two graphite electrodes press fitted on the SiC tube approximately 1 cm apart [22,25]. The temperature of the nozzle was monitored using an Omega (Type C) thermocouple attached to the outside of the nozzle and calibrated to the internal nozzle temperature. Products passed into the differentially pumped photoionization region and were ionized by 118 nm (10.45 eV) VUV radiation produced from frequency tripling of the 355 nm output of a Nd:YAG laser operating at 10 Hz and then accelerated by electric fields toward a multichannel plate detector. The resulting mass spectra were collected on a digital storage oscilloscope with typical 512 laser shots.

3. Results

3.1. Tetramethylsilane pyrolysis

Pyrolysis of TMS was examined at temperatures of 660, 910, 1060, 1200, 1300, 1390, and 1470 K. The pyrolysis mass spectra up



Fig. 2. Enlarged stack plot of mass spectra for pyrolysis of Si(CH₃)₄ (\sim 1%) in He at pyrolysis temperatures 1060–1470 K to more clearly show product peaks. Mass spectra are offset for clarity. The insert plots the CH₃ radical peaks at *m*/*z* 15.

to 1470 K, along with a room temperature mass spectrum, are plotted in Figs. 1 and 2, showing the parent TMS and the major products of the TMS pyrolysis. At room temperature, peaks were observed at m/z 88 and 73 which correspond to the parent TMS peak and the (CH₃)₃Si⁺ trimethylsilyl cation, respectively (Fig. 1). The trimethylsilyl ion fragment was the main peak in the room temperature spectrum appearing in a 3.8:1 ratio relative to the parent peak. As the appearance energy of (CH₃)₃Si⁺ from TMS is 10.2 eV [26], the 10.45 eV photoionization radiation is sufficiently energetic to photoionize and fragment a significant fraction of the TMS molecules. Silicon isotope peaks of TMS and (CH₃)₃Si⁺ due to ²⁹Si. ³⁰Si were also observed at m/z=89, 90 and m/z=74, 75, respectively. The relative abundances of ²⁸Si, ²⁹Si, and ³⁰Si are 0.9223, 0.0467, and 0.031, respectively. The pyrolysis temperature was increased incrementally to 660, 910, and 1060 K, but no thermal decomposition was observed at these temperatures (Fig. 1).

As shown in Fig. 2, at pyrolysis temperature 1200 K a small peak appeared at m/z = 15 indicating production of the methyl radical. The co-production of the ${}^{\circ}Si(CH_3)_3$ radical resulted in a simultaneous decrease in intensity of the m/z 88 parent peak and increase in the intensity of the m/z 73 peak, although the contribution of the ${}^{\circ}Si(CH_3)_3$ radical to the m/z 73 peak was somewhat obscured by the presence of the large photoionization cation fragment peak (CH₃)₃Si⁺ at the same mass (Fig. 1). The primary methyl production was accompanied by a drop in the intensity of the TMS peak relative to the intensity of the (CH₃)₃Si⁺ peak, or an increase of the intensity ratio of m/z 73 versus m/z 88, as shown in Fig. 3. These data clearly indicate cleavage of the Si—C bond as the initial step of TMS thermal decomposition, as shown in Reaction (1), in agreement with the previous studies [13,14]

The intensity of the methyl peak continued to grow as the nozzle temperature was increased to 1300 K. The size of the TMS parent again declined relative to that of the $(CH_3)_3Si^+$ peak indicating further methyl loss from the parent (Figs. 1–3). A very small peak at m/z 58 appeared indicating beginning of subsequent methyl loss from the $^{\circ}Si(CH_3)_3$ radical in Reaction (2), as seen in Fig. 2.

At 1390 K, increased amount of methyl was produced at m/z 15 (Fig. 2). In addition, loss of multiple hydrogen atoms from Si(CH₃)₃ occured as evidenced by the appearance of peaks at m/z 72, 70, and 68. The peak at m/z 58 increased significantly, showing clear evidence of the :Si(CH₃)₂ production, from the subsequent methyl loss from the •Si(CH₃)₃ radical in Reaction (2). Small peaks at m/z



Fig. 3. Ratio of the peak intensities of m/z 73 for $(CH_3)_3Si^{**}$ ion versus Si $(CH_3)_4$ parent peak. The trend shows the onset of thermal decomposition of TMS at approximately 1100 K.

54 and 56 appeared to indicate H₂ elimination from:Si(CH₃)₂. New peaks also appeared at m/z 42 and 44 and a very small peak at m/z 43 which could correspond to *Si(CH₃). The relatively small peak of Si(CH₃) observed suggests that further loss of methyl from :Si (CH₃)₂, reaction (3), is less prevalent in the TMS decomposition than its previous analogs, reactions (1) and (2), different from the previously proposed mechanisms [13,14]. Instead there appeared to be production of SiCH₂ at m/z 42 possibly from elimination of methane from *Si(CH₃)₂ after isomerization, although loss of H atom from the small amount of *Si(CH₃) may also contribute.

$$^{\bullet}Si(CH_3)_2 \rightarrow SiCH_2 + CH_4 \tag{7}$$

A peak at m/z = 28 was also observed which could correspond to the bare ²⁸Si atom, whose ionization energy (IE) is 8.1 eV. Alternatively, m/z 28 peak could be due to ethylene (as a reaction product from the methyl radical), although ethylene is not easily ionized in this experiment due to its high IE of 10.51 eV. Also, the m/zz 42–44 peaks could be due to C₃H_{6–8} (possible reaction products of CH₃).

At pyrolysis temperatures of 1470 K, significant loss of hydrogen from Si(CH₃)₃, :Si(CH₃)₂, and SiCH₂ was observed. The peaks m/z 70 and 68 increased significantly, indicating increased hydrogen loss from •Si(CH₃)₃. A small decrease in intensity of the m/z 58 peak,:Si(CH₃)₂, was accompanied by increases in m/z 54 and 56 peaks, indicating that a significant fraction of the :Si(CH₃)₂ radicals isomerized and underwent one and two sequential H₂ elimination reactions. Increase of the m/z = 42 peak, SiCH₂, was also observed along with the appearance of a peak at m/z 40 possibly due to SiC. Increased amounts of bare Si and/or ethylene at m/z = 28 were also produced. Alternatively, the m/z 40–44 peaks could be due to the hydrocarbon species C₃H_{4–8}.

Throughout all the temperatures, no mass peaks were observed in the range of m/z=83-87, indicating that primary loss of hydrogen from the TMS parent was an negligible dissociation channel, or bimolecular reactions of H-atom abstraction from the parent, such as Reaction (5), were insignificant in the current experiment, likely due to the much shorter reaction time scale. Also, no additional products larger than the parent were formed in secondary reactions in the short time scale of our experiment.

3.2. Tetramethylgermane pyrolysis

Mass spectra for pyrolysis of Ge(CH₃)₄ (~1%) in He at pyrolysis temperatures from 930 K to 1570 K as well as at room temperature are shown in Figs. 4 and 5. Photoionization fragmentation was more prevalent in the TMG pyrolysis mass spectra than in those for TMS due to the weaker Ge—C bond. The largest series of peaks in the room temperature spectrum was due to photoionization fragment Ge(CH₃)₃⁺ (Fig.4). This species is indicated by the series of peaks at *m*/*z* 115,117, 118, 119, and 121 due to germanium isotopes ⁷⁰Ge, ⁷²Ge, ⁷³Ge, ⁷⁴Ge, and ⁷⁶Ge, with natural abundances of 0.2123, 0.2766, 0.0733, 0.3594, and 0.0744, respectively. A series of small peaks at *m*/*z* 130, 132, 133, 134, and 136 were from the parent, TMG, with much lower intensity due to extensive photoionization fragmentation of TMG. There was a very small peak around *m*/*z* 74 in the room temperature spectrum (Fig. 5), which was from the photoionization fragmentation of TMG.

As shown in the expanded view of the pyrolysis products in Fig. 5, the onset of the pyrolysis was observed around 1060 K, where a m/z 15 peak appeared corresponding to methyl radical loss from TMG, similar to that of TMS in Reaction (1). The peak at m/z 74 was still due to the photoionization fragmentation of TMG. As the pyrolysis temperature was raised to 1170 K, the methyl peak at m/z 15 increased indicating further thermal decomposition of TMG with the loss of methyl radicals. The expected growth of the

•Ge(CH₃)₃ radical peak from TMG decomposition was likely obscured by the large photoionization fragment peak (Fig. 4).

At 1220 K increased methyl production continued as the m/z 15 peak increased in intensity by a factor of 3. New pyrolysis products, small peaks appeared at m/z 100, 102, 103 and 104 with the familiar Ge isotope profile indicating secondary loss of methyl from $Ge(CH_3)_3$ to form $Ge(CH_3)_2$. No mass peaks due to H losses from $Ge(CH_3)_3$ were observed (Fig. 4), different from $Ge(CH_3)_3$. A group of smaller peaks near m/z 89 corresponded to $GeCH_3$ indicating continued Ge—C bond homolysis. A new peak at m/z 72 appeared due to the Ge atom. There was a minor product at 1220 K at m/z 56, which was possibly C_4H_8 produced from secondary reactions of the methyl radicals.

When the pyrolysis temperature was raised to 1340 K, m/z15 grew significantly indicating further methyl loss from TMG and its fragments. Peaks at m/z 100, 102, 103, and 104 doubled in size relative to those at 1220 K as a result of further secondary loss of methyl from Ge(CH₃)₃. A series of peaks were observed in the region of m/z 84–91. The m/z 84 peak was due to 70 GeCH₂. ⁷¹Ge does not occur naturally so m/z 85 exclusively represented ⁷¹GeCH₃. The fraction of •GeCH₃ relative to GeCH₂ can be judged by the ratio of these peak intensities which was approximately 6 to 5. The rest of the series m/z 86–91 were due to a mixture of GeCH₂ and •GeCH₃, exhibiting the loss of CH₄ from:Ge(CH₃)₂ or H atom from •GeCH₃ to form GeCH₂ and the loss of CH₃ radical from :Ge (CH₃)₂ to form GeCH₃. Significant formation of the Ge atoms began as demonstrated by the peaks at m/z 70, 72, 73, 74, and 75 in Fig. 5 bearing the Ge isotope mass profile. A series of less resolved peaks in the m/z 140–150 region also appeared indicating combination of Ge atoms to form Ge₂, as well as the formation of Ge₂H_x. The m/z56 peak increased in intensity indicating increased C₄H₈ production. C_3H_6 and C_3H_4 were also observed as peaks at m/z 40 and 42. A peak at m/z 28 appeared due to ethylene with m/z 29, ${}^{\circ}C_{2}H_{5}$, also observed.

At 1540 K, the m/z 15 peak decreased in intensity by about 50% indicating the consumption of the methyl radicals in secondary reactions. Production of Ge and Ge₂ increased by about 5 times at 1570 K resulting in a sharp increase of intensity at peaks in the m/z 70–75 and m/z 140–148 mass regions. No peaks appeared at m/z



Fig. 4. Stack plot of mass spectra for pyrolysis of $Ge(CH_3)_4$ (\sim 1%) in He at room temperature and pyrolysis temperatures 930 K to 1570 K. Mass spectra are offset for clarity.

100 through 104 indicating that: $Ge(CH_3)_2$ was completely depleted by methyl loss reactions at 1570 K, as was the •GeCH₃ product of this reaction, as H atom loss resulted in the disappearance of peaks at m/z 85, 87, and 89. Aforementioned peaks at m/z 28, 40, and 42 also grew significantly as C_2H_4 and C_3H_4 were likely the products of the methyl secondary reactions. The C_4H_8 peak at m/z56 dropped sharply in intensity from 1340 K to 1570 K due to H_2 elimination to form C_4H_4 and C_4H_6 , as indicated by the appearance of the peaks at m/z 52 and 54.

4. Discussion

The observed TMS pyrolysis products and proposed decomposition pathways are summarized in Scheme 1. At temperatures of 1060 K and below, no significant TMS pyrolysis was observed. The increase of the m/z 73 peak relative to the parent above 1060 K and the growth of the m/z 58 peak at 1390 K, corresponding to the 'Si $(CH_3)_3$ and $:Si(CH_3)_2$ product, respectively, indicate the importance of the loss of the first and second methyl group from the parent as the reaction pathway in the early stages of TMS decomposition, as also indicated by the methyl production giving rise to a significant m/z 15 peak. Loss of H atom from the parent was not observed, and this is expected due to the larger C—H bond dissociation energy of 97 kcal mol⁻¹ versus 79 kcal mol⁻¹ for the Si—C bond [27,28]. It has been suggested that abstraction of H atom from TMS by methyl is a significant secondary process [27,29]. However, this was not observed in this study, probably due to the short reaction time $(<100 \,\mu s)$, thus minimizing the secondary reactions.

Loss of 1, 3, and 5H atoms from the ${}^{\circ}Si(CH_3)_3$ radical, which has not been previously suggested in the literature, was observed in this study to be competitive with the loss of a second methyl radical as evidenced by the significant peaks at m/z 68 and 70, as well as a left hand shoulder to the m/z 73, ${}^{\circ}Si(CH_3)_3$, peak which



Fig. 5. Stack plot of mass spectra for pyrolysis of $Ge(CH_3)_4$ (~1%) in He at room temperature and pyrolysis temperatures 800 K to 1570 K enlarged to more clearly show product peaks. Mass spectra are offset for clarity. The large $Ge(CH_3)_3^+$ peaks are not plotted here.



Scheme 1. Decomposition of TMS including example mechanism for H₂ elimination from *Si(CH₃)₃ via isomerization to a linear structure prior to H₂ elimination.

was likely a poorly resolved m/z 72 peak. These peaks were due to loss of a single H atom from ${}^{\circ}Si(CH_3)_3$, followed by successive H_2 elimination reactions. However, the formation of these compounds would require isomerization of ${}^{\circ}Si(CH_3)_3$. A mechanism via a linear structure is shown in Scheme 1 as an example.

It has also been proposed in the previous studies that the :Si $(CH_3)_2$ radical could lose a third methyl radical to form SiCH₃. However, in this study this pathway was observed to be less competitive compared with other decomposition pathways of:Si $(CH_3)_2$, such as sequential H₂ loss that formed a significant amount of SiC₂H₄ and SiC₂H₂ (peaks at *m*/*z* 56 and 54) and CH₄ loss to the product peak at *m*/*z* 42. These two new product channels have not been previously reported in the literature either. *Ab initio* calculations by Wu et al. have identified silacyclopropenylidene as the most stable SiC₂H₂ isomer [30], suggesting that H₂ elimination could occur through a cyclic intermediate (Scheme 1). Finally, the SiC and Si products could have been observed at the highest temperatures.

The pyrolysis of TMG was initiated with a methyl radical loss to form Ge(CH₃)₃, in a manner similar to that of the TMS pyrolysis. The Ge(CH₃)₃ radical also underwent a sequential loss of methyl radical to form :Ge(CH₃)₂, as in the TMS pyrolysis. However, no sequential H loss of the $Ge(CH_3)_3$ and $:Ge(CH_3)_2$ radicals were observed, different from the TMS pyrolysis. Instead, due to the fact that the Ge-C bond is weaker than the Si-C bond, loss of a third methyl radical from the:Ge(CH₃)₂ radical to GeCH₃ was clearly observed in the TMG pyrolysis, while this did not occur to a significant extent in the TMS pyrolysis under the same conditions. Furthermore, loss of the last methyl from GeCH₃ and thus production of the bare Ge atoms became significant at the highest temperatures (1340-1570 K), also different from TMS. Due to the significant production of the Ge atoms, the formation of the Ge₂ dimer was also observed to occur noticeably. The pyrolysis of TMG, due the weaker Ge–C bond, mainly proceeded with the simple mechanism of sequential loss of the methyl radicals all way to the final product of the bare Ge atoms.

The remainder of the decomposition chemistry was complicated by the secondary reactions of the methyl radical. These are more easily interpreted using the pyrolysis spectra of TMG for two reasons: (i) the weaker Ge–C bond is more easily cleaved leading to grater relative methyl production and thus higher rates of secondary reactions, and (ii) larger masses for product fragments that contain Ge, making Ge fragments less likely to have the same mass as small hydrocarbon products produced by methyl secondary reactions. The production of C₂H₄ dominated the secondary reactions with C_2H_5 also appearing. Notably, m/z29 due to C₂H₅, and other significant hydrocarbon peaks such as m/z 56, C₄H₈, were not significant in the TMS pyrolysis spectra. Thus, it can be concluded that secondary formation of hydrocarbon products was relatively low in the TMS pyrolysis conducted on the time scale of this experiment. C₂H₄ and larger unsaturated hydrocarbon products, such as C₃H₆, were possibly due to recombination of radicals and rapid hydrogen elimination according to the well established Rice-Herzfeld mechanism as indicated below [31].

•CH₃ + •CH₃→
$$C_2H_6$$

•CH₃₊ C_2H_6 → CH₄₊ C_2H_5
•CH₃₊ + C_2H_5 → C₃H₈ → C₃H₆ + H₂

5. Conclusion

Pyrolysis of Si(CH₃)₄ (TMS) and Ge(CH₃)₄ (TMG) was performed. Direct and secondary pyrolysis products produced on the 20 to 100 μ s time scale were directly observed. The primary thermal decomposition process for both TMS and TMG was cleavage of the Si—C and Ge—C bonds to form Si(CH₃)₃ and Ge(CH₃)₃, respectively. Secondary loss of a second methyl radical was also observed in both processes. A previously unobserved secondary decomposition process involving loss of H atom from Si(CH₃)₃ followed by elimination of H₂ to form SiC₃H₈, SiC₃H₆, and SiC₃H₄, likely involving isomerization to a linear or cyclic arrangement, was also observed. Sequential loss of the third methyl and fourth methyl with significant formation of Ge and Ge₂ was observed in the pyrolysis of TMG. Loss of a third methyl radical from TMS was not significant in the 20–100 μ s time scale at the 910 K to 1540 K temperatures reached in this experiment. However Si and SiC were possibly observed, perhaps due to elimination of methane from:Si (CH₃)₂ and subsequent H losses. Secondary reactions of methyl to form unsaturated C_xH_y species, particularly in the TMG decomposition, were also observed.

Acknowledgement

This work is supported by the National Science Foundation (CHE-1214157).

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