

Mass spectrometric study of gas-phase chemistry in a hot-wire chemical vapor deposition reactor with tetramethylsilane

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Abstract

To understand the gas-phase chemistry in the processes of hot-wire chemical vapor deposition (HWCVD) with tetramethylsilane (TMS), the gas-phase products from the decomposition of TMS on a hot tungsten filament and the secondary gas-phase reactions in a HWCVD reactor have been studied using vacuum ultraviolet laser single photon ionization time-of-flight mass spectrometry. It is found that TMS decomposes on the filament to methyl and trimethylsilyl radicals. Subsequent reactions between these two primary radicals and with the parent molecule have resulted in the formation of alkyl-substituted silanes ($m/z = 102, 116, 146$) and silyl-substituted alkanes ($m/z = 160, 174, 188, 232, 246$). Small alkenes ($C_nH_{2n}, n \leq 4$) are produced at high filament temperatures ($T \geq 1800^\circ\text{C}$). The dominant pathways in the secondary gas-phase reactions are found to be the biradical combination reactions involving the alkylsilyl-substituted methyl radicals formed from the H abstraction reaction of either alkyl-substituted silane or silyl-substituted alkanes by methyl radicals. Silicon carbon (Si–C) bond is found to be the major bond connection in the gas-phase reaction products in mass regions higher than the parent mass. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane molecule ($m/z = 144$) is believed to be formed in the HWCVD reactor, implying the existence of the unsaturated silene intermediates.

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1. Introduction

Although tetramethylsilane (TMS) is more familiar to many chemists as an NMR standard, the volatile liquid's simple molecular structure can be exploited in the gas phase for chemical vapor deposition (CVD). TMS has been used for the preparation of silicon carbide (SiC) films by plasma enhanced CVD (PECVD) [1–3], low-pressure CVD (LPCVD) [4], rapid thermal CVD (RTCVD) [5], metalorganic CVD (MOCVD) [6,7], and hot-wire CVD (HWCVD) [8]. Among all these CVD methods, HWCVD [9], also referred to as catalytic CVD (Cat-CVD) [10], is a relatively new technique, yet has been demonstrated as one of the most promising techniques for producing device quality silicon-containing thin films needed for a wide range of applications in microelectronic devices, solar cells, automobiles, food-packaging, and biotechnology [11]. In this method, source gases are catalytically decomposed at a heated wire, usually

made of tungsten, at temperatures higher than 1200°C , producing gas phase film growth precursors. These species are then transported to the substrate placed near the heated wire, but kept at a relatively low temperature ($\sim 300^\circ\text{C}$), where thin film deposition occurs.

During the past two decades, HWCVD has been extensively studied. Numerous studies have indicated that the physical and chemical characteristics of the films are strongly dependent on the deposition conditions. However, a comprehensive deposition model for HWCVD has not yet been presented since the filament-related reactions both in the gas phase and on the film surface are unknown. A lot of effort has been made to understand the mechanism of thin film growth in HWCVD. The deposition of hydrogenated amorphous Si (a-Si:H) films from $\text{SiH}_4/(\text{H}_2)$ gases is the most studied process. It is found that HWCVD deposition of Si-based thin films involves the following three processes: (a) catalytic decomposition of source gases on a hot wire; (b) radical-molecule and radical–radical reactions in the gas phase; (c) surface reactions leading to film growth [12]. The gas-phase reactions play an important role in determining the film properties. It is therefore desirable to study the gas-

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phase chemistry in the processes of HWCVD. Although TMS has been used as a source gas in different CVD processes, the gas-phase chemistry involved in the processes is not well understood. The analysis of gas-phase chemical species generated from the thermal decomposition of TMS in the reactor during the growth process of SiC films by RTCVD [5] indicated that TMS dissociated into hydrogen, silicon atoms, and hydrocarbons such as CH₄, C₂H₂, and C₂H₄ at the growth temperatures of 1000–1100 °C and a growth pressure of 1×10^{-4} Torr. In their work on studying the gas-phase species from reactions of methylsilanes, including mono-, di-, tri- and tetra-methylsilane, on tungsten and rhenium filaments in the HWCVD process of silicon carbide films [13], Zaharias et al. detected methyl and Si atoms as the products from tetramethylsilane decomposition when the chamber pressure was 5×10^{-6} Torr. Typical deposition pressures for SiC films using HWCVD or PECVD with either gaseous mixtures of silane and hydrocarbons or single source precursors such as methylsilane range from 0.1 Torr to several Torr [2,3,14,15]. At these relatively high pressures, secondary gas-phase reactions between the primary radicals themselves and between the radicals and parent molecules become important. However, little is known about the nature of the secondary reactions and their products. The current study addresses this question by studying the gas-phase reaction products of hot wire decomposition of TMS in a HWCVD reactor under practical deposition pressures.

In this work, we have used vacuum ultraviolet (VUV) laser single photon ionization (SPI) coupled with time-of-flight (TOF) mass spectrometry (MS) to probe the gas-phase chemical species produced from both catalytic decomposition of TMS on a hot filament and secondary reactions. Non-resonant SPI using VUV wavelengths ($100 \text{ nm} \leq \lambda \leq 200 \text{ nm}$) is generally considered to be a soft ionization method [16–18]. Efficient ionization of the chemical species of interest can be achieved by this method with little or no fragmentation. The identification of molecular

species using this technique is thus made much simpler [19,20] than those using conventional ionization methods such as electron impact, fast atom bombardment, or multiphoton ionization. By using VUV SPI-TOF MS, we were able to detect various chemical species from the hot-wire decomposition of TMS. With the help from the experiments using the deuterated isotopomer, TMS-d12, the identities of the gas-phase species observed were elucidated, and their formation mechanism was discussed.

2. Experimental details

A schematic of the apparatus used to record the VUV laser/TOF mass spectra of TMS from a HWCVD reactor and/or from a hot filament is shown in Fig. 1(a). The apparatus consists mainly of an ionization laser source, a HWCVD source, and a linear TOF mass spectrometer (R.M. Jordan Co.). To detect the chemical species formed directly from the hot wire, the filament was placed in the main chamber with the TOF mass spectrometer. A schematic of the flange for this purpose is shown in Fig. 1(b). The base pressures in the main chamber and the flight tube were maintained at 1×10^{-7} Torr and 1×10^{-8} Torr, respectively, by a diffusion pump and a turbo pump. The operating pressure was $\sim 5 \times 10^{-6}$ Torr. In this experimental setup, a collision-free condition was maintained; therefore, the secondary gas-phase reactions were avoided. TMS (99.9+%, NMR grade, Sigma–Aldrich) and TMS-d12 (99%, CDN Isotopes) was degassed by several cycles of freeze-pump-thaw. The room-temperature vapor of TMS (or TMS-d12) was then diluted in He (ultra high purity, 99.995%, Praxair) to give a mixture. The resultant TMS/He mixture was then injected into the vacuum chamber using a mass flow controller (MFC) (MKS, type 1179A) with a flow rate of 0.8 sccm. The W filament (10 cm length, 0.5 mm diameter) was resistively heated by a DC power supply and its temperature was measured by a two-color pyrometer (Chino Works) through an IR-grade quartz window. To avoid inter-

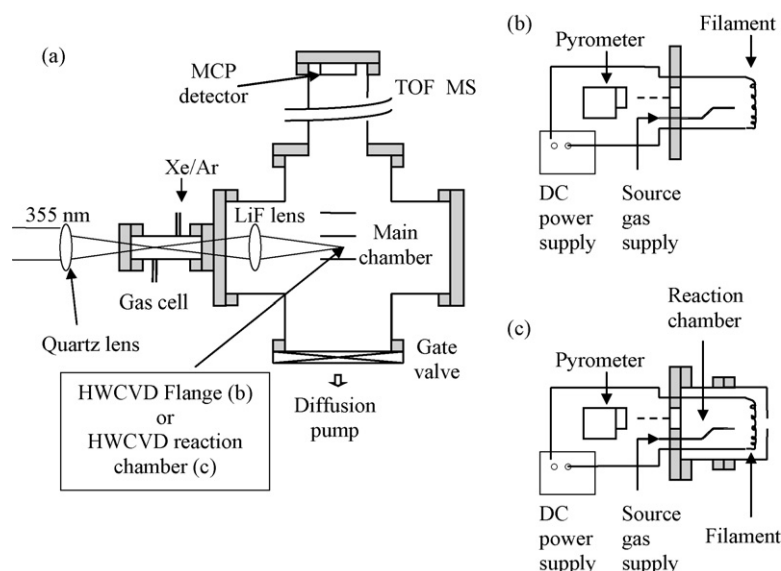


Fig. 1. Schematics of (a) the experimental setup for VUV SPI-TOF mass spectrometric measurements; (b) the HWCVD flange for detection of direct hot-wire decomposition products; (c) the HWCVD reaction chamber for detection of gas-phase reaction products.

ference to the electric fields in the ion optics of the TOF-MS from the hot W filament, a stainless steel shield with a hole in the center ($D=1.0$ cm) was mounted 3.5 cm in front of the W filament.

Chemical species produced from the hot wire decomposition of TMS were ionized by a VUV laser beam at 118 nm (10.5 eV) in a non-resonant single photon ionization process. The 118 nm radiation was generated in our lab by frequency tripling the 355 nm UV output from an Nd:YAG laser (Spectra-Physics, LAB-170-10) in a 10:1 Ar/Xe mixture [21,22]. The 355 nm laser output was attenuated by a combination of a half-wave plate and a Glan laser polarizer to maintain the output energy at 20 mJ/pulse. The laser was focused into a gas cell filled with 190 Torr of 10:1 Ar/Xe mixture. A lithium fluoride (LiF) lens was inserted into the optical path after the gas cell to separate the 118 nm wavelength from the fundamental 355 nm UV wavelength. The LiF lens was positioned so that the VUV beam was focused at the center of the ion source in the TOF mass spectrometer, while the UV beam was focused beyond this point. This minimizes the possibility of multiphoton effects from the residual 355 nm UV photon. Ions produced in the VUV single photon ionization process were mass dispersed in a 1 m-long linear TOF mass spectrometer and detected at the end of the flight tube with a microchannel plate (MCP) detector. Signals from the MCP detector were preamplified and displayed on a digital oscilloscope (Tektronics, TDS 3032B). The signals were averaged over 512 laser pulses before being saved into a computer using e-scope. The mass resolution of the TOF mass spectrometer is found to be ~ 350 .

For the detection of chemical products arising from the secondary gas-phase reactions, the filament was housed in a HWCVD reaction chamber. Fig. 1(c) shows a schematic of the reaction chamber. The pressure in the reactor was maintained at around 12 Torr using the MFC and was monitored by a capacitance manometer (MKS Baraton, type 626 A). This gives a partial pressure of TMS of 120 mTorr for a 1% TMS/He mixture. Gas-phase chemical species produced in the HWCVD reactor exited through a pinhole (0.15 mm diameter) into the main chamber, where they were ionized by the 10.5 eV (118 nm) VUV laser radiation and detected by the TOF mass spectrometer.

3. Results and discussions

The room-temperature VUV laser SPI TOF mass spectrum of TMS recorded when the filament is off is dominated by a fragment ion peak at $m/z=73$ ($(\text{CH}_3)_3\text{Si}^+$) and the parent ion peak at $m/z=88$. The peak intensity ratio of the fragment to the parent ion is 4.0:1. And the isotope peaks of the two ions originating from the ^{29}Si , ^{30}Si , and ^{13}C were observed at $m/z=74$, 75, 89, and 90. The predominance of the trimethylsilyl cation is due to the instability of the TMS ion and a low appearance potential of 10.2 eV of the $(\text{CH}_3)_3\text{Si}^+$ ion. This was discussed by McGinnis et al. [23] on the basis of the Jahn–Teller theorem. Aside from the trimethylsilyl ion, there are no other fragments observed in the mass spectrum taken when the filament is off. When there is no tripling medium, the Xe gas, in the gas cell for VUV generation, no ion signals were observed for TMS.

This indicates that VUV radiation is responsible for the ion signals observed and the contributions from multiphoton ionization (MPI) and photon-induced electron impact (EI) ionization by the fundamental UV radiation alone are negligible.

3.1. Decomposition of TMS on the W filament

From the experiments for the detection of chemical species under collision-free conditions, it was found that the peak intensity ratio of the trimethylsilyl ions to the parent ions when the filament was on was increased as compared to the ratio of 4.0:1 when the filament was off. The ratio generally keeps increasing with increased filament temperatures. This is shown in Fig. 2. At the same time, a peak at $m/z=15$ representing methyl radicals was seen to come out and increase in intensity with temperatures, as shown in Fig. 3. This indicates that TMS decomposed to trimethylsilyl and methyl radicals on the filament:



The production of methyl radicals shown in Eq. (1a) is generally accepted as the initial step in the thermal decomposition of all Group IV tetramethyl compounds [24]. The experimental observations from our experiment suggest that the primary decomposition products of TMS on a hot W filament also come from reaction (1a). According to Taylor and Milazzo [25] from their study on the pyrolysis of TMS using a wall-less reactor, TMS can dissociate in rapid succession, releasing one CH_3 radical at each step, i.e., after reaction (1a), the following reactions also occur:



In our experiment, the mass peaks at $m/z=58$, 43, and 28 were not observed. The ionization potential (IP) of Si is known to be

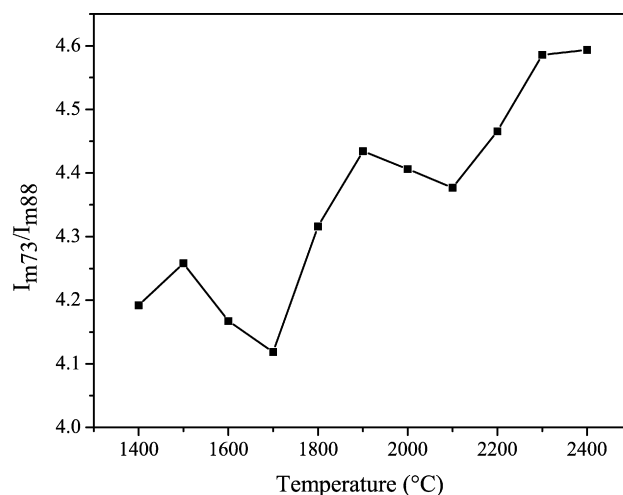


Fig. 2. The intensity ratio of mass peak at $m/z=73$ (trimethylsilyl) to that at $m/z=88$ (tetramethylsilane) at different filament temperatures at a chamber pressure of 5×10^{-6} Torr.

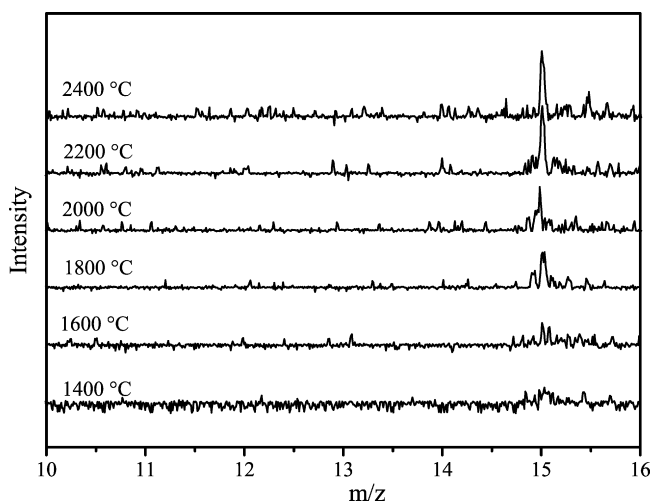
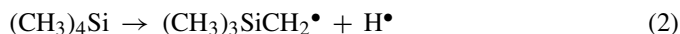


Fig. 3. 118 nm VUV SPI TOF mass spectra of TMS exposed to a W filament at different temperatures at a chamber pressure of 5×10^{-6} Torr.

8.15 eV, which is less than one VUV photon energy of 10.5 eV. The IP's of $(\text{CH}_3)_2\text{Si}$ and $(\text{CH}_3)\text{Si}$ are unknown, however, based on the known value of 7.03 eV for $(\text{CH}_3)_3\text{Si}$, those of $(\text{CH}_3)_2\text{Si}$ and $(\text{CH}_3)\text{Si}$ should not be higher than 10.5 eV. Therefore, the missing of the signals at $m/z=28$, 43 and 58 indicates that trimethylsilyl radicals did not further dissociate into smaller radicals on the W filament under our experimental conditions.

Aside from the Si–C bonds, C–H bonds also exist in TMS molecules. Since the bond dissociation energy of C–H ($D(\text{Me}_3\text{SiCH}_2\text{-H})=97$ kcal/mol [26]) is much higher than that of the Si–C ($D(\text{Me}_3\text{Si-Me})=79$ kcal/mol [27]), reaction (2) is less likely to occur as evidenced by the fact that a peak at $m/z=87$ representing trimethylsilylmethyl radical was not observed in the mass spectrum recorded under collision-free conditions:



3.2. Gas-phase reaction products from the HWCVD reactor

The chemical products from secondary gas-phase reactions between the primary decomposition products of TMS on the filament and the parent molecules were studied by monitoring the species exiting from a HWCVD reactor as described in Section 2. Mass spectra for filament temperatures ranging from 1300 °C to 1900 °C were recorded. For each temperature, a mass spectrum was collected every 5 min for 60 min. At temperatures higher than 1900 °C, the parent mass peak disappeared quickly after the filament was turned on. Fig. 4 shows the TOF mass spectra recorded for 12 Torr 1% TMS/He sample at different filament temperatures ranging from 1400 °C to 1700 °C. For comparison, the room-temperature mass spectrum is also shown. As shown in Fig. 4(a), the mass spectra when filament was on were still dominated by the parent ion peak and its fragment, trimethylsilyl ion. However, with increasing filament temperatures, the intensities of the parent mass peaks were decreased, indicating that the parent TMS molecules were decomposed on the filament and consumed in the secondary gas-phase reactions in the reactor. For example, after the filament was on for 30 min, the

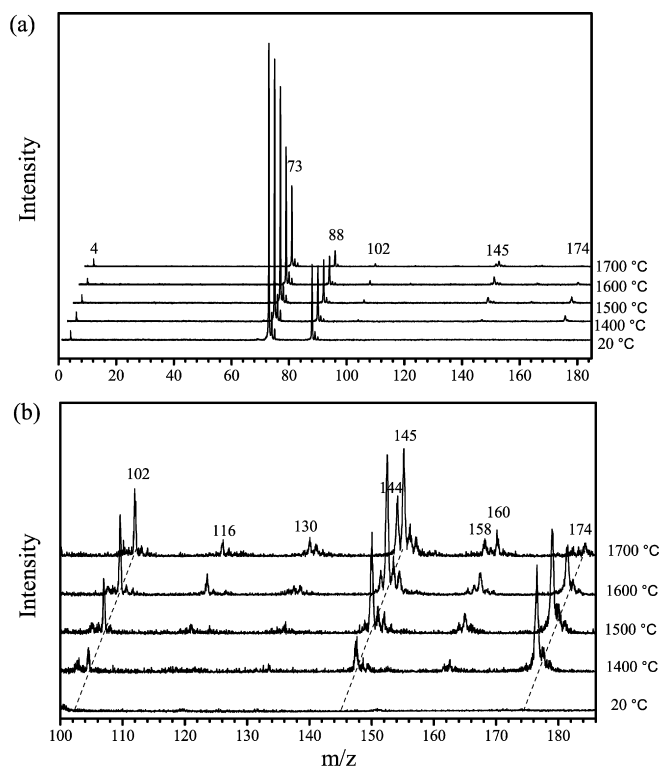


Fig. 4. (a) 118 nm VUV SPI TOF mass spectra of 12 Torr 1% TMS/He at filament temperatures between 1400 °C and 1700 °C. The spectrum at 20 °C is recorded when the filament is off. (b) Enlarged spectra in mass regions between 100 amu and 186 amu.

parent mass peak intensity was decreased by 21%, 33%, 57%, and 74%, respectively, at a filament temperature of 1400 °C, 1500 °C, 1600 °C, and 1700 °C as compared to the filament-off spectrum. The trimethylsilyl fragment peak at $m/z=73$ in Fig. 4(a) was also seen to decrease, however, the extent to which this peak was decreased was found to be less than that of the corresponding parent peak at $m/z=88$. The intensity ratios of this peak to that of the parent mass peak was calculated from all the spectra collected, and they were plotted against the filament-on time and filament temperatures for 1400 °C, 1600 °C, and 1800 °C, as shown in Fig. 5. It is clear that almost all the intensity ratios were above the filament-off ratio of 4.0:1, and the ratio also increased with filament-on time at all filament temperatures. As mentioned earlier, the decomposition of TMS on the hot filament also produces trimethylsilyl species. By comparing Fig. 5 with Fig. 2, the increase in the ratio in a HWCVD reactor was found to be greater. This suggests that in addition to the contribution of photofragmentation of the TMS parent ions and decomposition of TMS on the filament to the peak intensity at $m/z=73$, other sources were also responsible for it. This will be discussed later.

At the same time when the parent mass peaks decreased in intensities, three new mass peaks were observed at $m/z=102$, 145, and 174 in mass regions higher than the parent mass ($m/z=88$) in Fig. 4(a). The intensities of the three new mass peaks are weak as compared to the parent mass. For example, at 1500 °C, the peak intensity at $m/z=102$, 145, and 174 is 7%, 13%, and 14%, respectively, of the parent mass. From

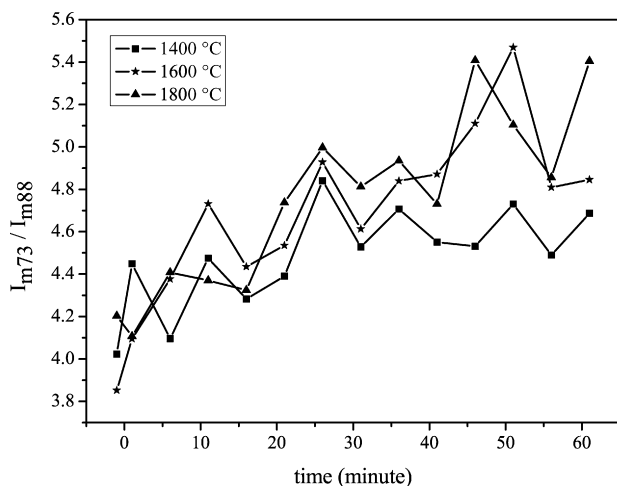


Fig. 5. The intensity ratio of mass peak at $m/z=73$ (trimethylsilyl) to that at $m/z=88$ (TMS) from 12 Torr 1% TMS/He in a HWCVD reactor vs. the filament-on time at filament temperatures of 1400 °C (■), 1600 °C (★), and 1800 °C (▲).

the enlarged picture shown in Fig. 4(b), weaker high mass peaks at $m/z=116$, 130, 131, 144, 158, 159, 160, and 172 were also observed. In order to assign these new mass peaks unambiguously, we have performed the same experiments using the deuterated isotopomer, tetramethylsilane- d_{12} . Fig. 6 shows the mass spectra of a 1% TMS- d_{12} /He sample recorded at a filament temperature of 1700 °C. The masses detected with TMS- d_{12} and their corresponding peaks using TMS were listed in Table 1. With the help from the TMS- d_{12} experiments, the elemental composition of the peaks observed for TMS from the HWCVD reactor when the filament was on can be deduced and this was also listed in Table 1. It is noted that in the mass spectra of TMS- d_{12} shown in Fig. 6, peaks with mass separation of 1 amu

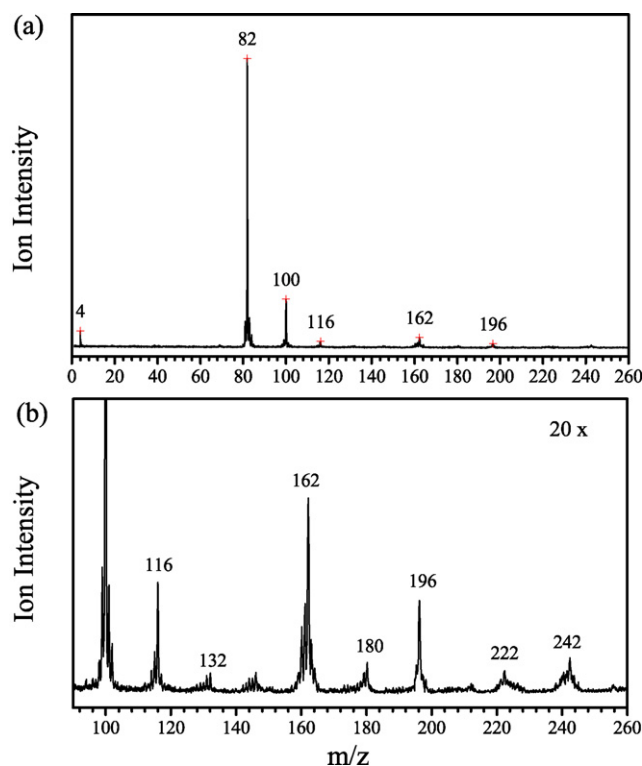


Fig. 6. (a) 118 nm VUV SPI TOF mass spectra of 12 Torr 1% TMS- d_{12} /He at a filament temperature of 1700 °C. (b) An enlarged picture of (a) in the mass regions between 90 amu and 260 amu (the peak at $m/z=100$ is overloaded).

were observed for all the main peaks, e.g., those at $m/z=116$, 132, 162, 180, and 196. From the room-temperature mass spectrum of TMS- d_{12} , the isotopic impurity of TMS- d_{11} ($m/z=99$) was found to be around 3%. However, the intensity ratio of the (M-1) peak to the M peak in Fig. 6 was more than what should

Table 1

The masses detected from both TMS and TMS- d_{12} in the HWCVD reactor and their assignments

Mass peaks (amu)		Assignments with TMS	
With TMS	With TMS- d_{12} ^a	Molecular formula	Molecular structure
28	32	C ₂ H ₄	CH ₂ =CH ₂
42	48	C ₃ H ₆	CH ₃ CH=CH ₂
56	64	C ₄ H ₈	CH ₃ CH ₂ CH=CH ₂
73	82	SiC ₃ H ₉	SiMe ₃ ^b
88	100	SiC ₄ H ₁₂	SiMe ₄
102	116	SiC ₅ H ₁₄	Me ₃ SiEt ^c
116	132	SiC ₆ H ₁₆	Me ₃ SiPr- n^d or Me ₂ SiEt ₂
130	144	Si ₂ C ₅ H ₁₄	Me ₂ SiCH ₂ SiMe ₂
131	146	Si ₂ C ₅ H ₁₅	Me ₃ SiSiMe ₂
145	162	Si ₂ C ₆ H ₁₇	Me ₃ SiCH ₂ SiMe ₂
160	180	Si ₂ C ₇ H ₂₀	Me ₃ SiCH ₂ SiMe ₃
174	196	Si ₂ C ₈ H ₂₂	Me ₃ SiCH ₂ CH ₂ SiMe ₃
188	212	Si ₂ C ₉ H ₂₄	Me ₃ SiCH ₂ CH ₂ SiMe ₂ Et
201	222	Si ₃ C ₈ H ₂₁	Me ₂ SiCH ₂ Si(Me)CH ₂ CH ₂ SiMe ₂
217	242	Si ₃ C ₉ H ₂₅	Me ₃ SiCH ₂ Si(Me ₂)CH ₂ SiMe ₂
232	n/a	Si ₃ C ₁₀ H ₂₈	Me ₃ SiCH ₂ Si(Me ₂)CH ₂ SiMe ₃
246	n/a	Si ₃ C ₁₁ H ₃₀	Me ₃ SiCH ₂ Si(Me ₂)CH ₂ CH ₂ SiMe ₃

^a d, deuterium.

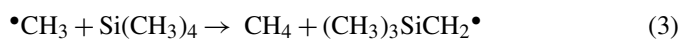
^b Me, CH₃.

^c Et, CH₃CH₂.

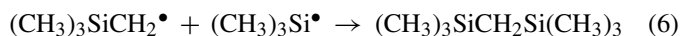
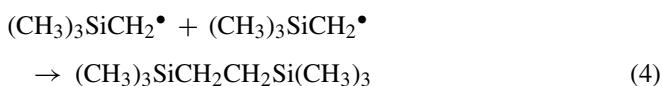
^d n-Pr, CH₃CH₂CH₂.

be expected from the isotopic impurity. The reason is that the same tungsten filament was used with TMS before, causing the contamination from TMS when the filament was turned on. This was confirmed by comparing with the mass spectra of TMS-d12 using a brand new W filament.

From Table 1, it is clear that all of the new mass peaks at $m/z > 88$ belong to hydrogenated silicon carbon clusters. They were believed to be the products from the secondary gas-phase reactions. As indicated previously, the primary decomposition reaction (1a) of TMS on the filament produced CH_3 and trimethylsilyl radicals. In our HWCVD reactor, secondary reactions of these radicals with the parent TMS molecule are likely to occur. It has long been known that methyl radicals can react with TMS by abstracting hydrogen atoms from it [26,28]. This leads to the formation of methane and trimethylsilylmethyl radical, $(\text{CH}_3)_3\text{SiCH}_2^\bullet$, as shown in the following equation:

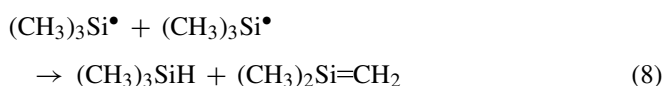
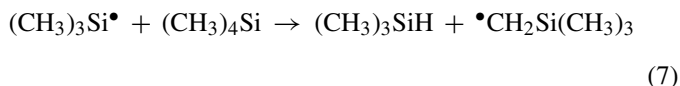


This can then be followed by several biradical combination reactions shown below:



The products of the above three reactions, i.e., 1,2-bis(trimethylsilyl)ethane at $m/z = 174$, ethyltrimethylsilane at $m/z = 102$, and bis(trimethylsilyl)methane at $m/z = 160$, were observed experimentally. The elemental compositions of these three peaks match those determined from the test with the TMS-d12 isotopomer as listed in Table 1. This suggests that the hydrogen abstraction reaction of TMS by methyl radicals occurred in the HWCVD reactor. However, it should be noted that signals from methane, the other product from Eq. (3), was not observed in our mass spectra. This is due to the high IP of 12.6 eV for this molecule, which is greater than the energy (10.5 eV) of the ionization VUV photons. Similar to the parent TMS molecule, the peak at $m/z = 174$, $m/z = 160$, and $m/z = 102$ can lose one methyl group upon ionization by VUV radiation. This leads to the observation of the peaks at $m/z = 159$, 145, and 87, respectively, in the mass spectra. The photofragment mass peak at $m/z = 145$ was found to be around 4.9 times as strong as its parent mass peak at $m/z = 160$. This makes the peak at $m/z = 145$ one of the three dominant high mass peaks, whereas the peak at $m/z = 160$ is relatively weak. Upon losing two methyl groups, bis(trimethylsilyl)methane ion could fragment to give a peak at $m/z = 130$. This was indeed observed in our experiment and the mass shift of this peak when using TMS-d12 shows that this mass species did contain two silicon atoms. The fragment peaks at $m/z = 159$ and 87 were found to be weaker than their corresponding parent mass peak at $m/z = 174$ and 102. The peak intensity ratios of $m/z = 159$ to $m/z = 174$ and of $m/z = 87$ to $m/z = 102$ were found to be 0.28 and 0.31, respectively.

In the previous studies [24,29] of TMS pyrolysis, trimethylsilane ($m/z = 74$) was observed as one of the products. In our mass spectra, the trimethylsilyl peak at $m/z = 73$ was always dominant, and its isotope peaks were present at $m/z = 74$ and 75. Examination of the peak intensity ratio of $m/z = 74$ to $m/z = 73$ revealed that it did not change after the filament was turned on and the ratio remained constant with increasing filament on time and filament temperatures. Therefore, it is believed that trimethylsilane was not produced in the HWCVD reactor with TMS. This implies that the following two reactions do not occur in our experiment:



However, hexamethyldisilane (HMDS, $m/z = 146$), the product of the recombination of trimethylsilyl radicals, was produced in the HWCVD reactor:

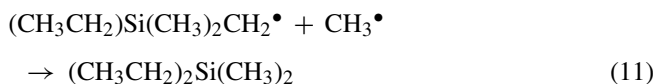
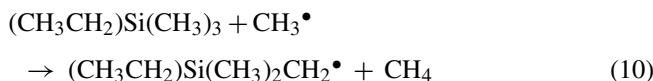


The peak at $m/z = 146$ is overlapping with one of the isotope peaks of the photofragment at $m/z = 145$ from the bis(trimethylsilyl)methane ion. The contribution from ^{29}Si and ^{13}C isotopes in the $m/z = 145$ ($(\text{CH}_3)_3\text{SiCH}_2\text{Si}(\text{CH}_3)_2$) species to the peak intensity at $m/z = 146$ amounts to 16.8% of the $m/z = 145$ peak intensity. However, the peak intensity ratio of $m/z = 146$ to $m/z = 145$ in our experiments was found to range from 22.1% to 32.2% depending on the temperatures. The formation of HMDS should be responsible for part of the peak intensity at $m/z = 146$. Upon photoionization by the 118 nm VUV laser radiation, HMDS produces two fragment peaks at $m/z = 131$ and $m/z = 73$. This was confirmed in our study by recording a room-temperature VUV TOF mass spectrum of HMDS. The peaks at $m/z = 131$ and 73 were found to be 3.8% and 15.3%, respectively, of its parent ion. According to this, the weak peak at $m/z = 131$ ($(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_2$) observed in Fig. 4(b) was believed to come from the photofragmentation of HMDS ion. The mass shift of 15 for this peak upon using TMS-d12 confirmed this assignment. And the observation of the weak peak at $m/z = 131$ is a strong indication that HMDS has been produced in the reactor.

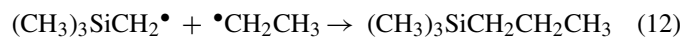
Similar to HMDS, other products such as ethyltrimethylsilane, bis(trimethylsilyl)methane, and 1,2-bis(trimethylsilyl)ethane from the secondary gas-phase reactions contain the trimethylsilyl group, and it is possible that they will produce a trimethylsilyl ion with $m/z = 73$ upon VUV laser ionization. This is believed to be the main reason for the increased intensity ratios of the peak at $m/z = 73$ to that at $m/z = 88$ observed when the filament was on in a HWCVD reactor, as discussed earlier.

From Table 1, it is apparent that the peak at $m/z = 116$ contains only one Si atom, the mass difference between this peak and the ethyltrimethylsilane peak at $m/z = 102$ is 14, representing a CH_2 group. This mass peak could be produced in a similar

reaction scheme to the formation of ethyltrimethylsilane. Specifically, the methyl radical in the reactor could abstract a H atom from ethyltrimethylsilane, producing an ethyldimethylsilylmethyl radical, $(\text{CH}_3\text{CH}_2)\text{Si}(\text{CH}_3)_2\text{CH}_2^\bullet$, which then combines with the methyl radical to give diethyldimethylsilane with $m/z = 116$:



Another possible mechanism for the formation of the peak at $m/z = 116$ is from the combination of the $(\text{CH}_3)_3\text{SiCH}_2^\bullet$ produced from Eq. (3) with ethyl radicals to yield *n*-propyltrimethylsilane, i.e.:



However, our current experimental setup cannot distinguish between the two isomers, i.e., diethyldimethylsilane and propyltrimethylsilane. The ethyl radicals could originate from the reaction series initiated by the recombination of CH_3 radicals as shown in the following equations:

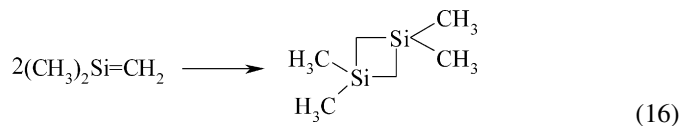


These three reactions will be discussed in detail later.

In the study of trimethylsilane pyrolysis by Davidson and Lambert [30], 1,3-dimethyl-1,3-disilacyclobutane with $m/z = 116$ was identified as one of the products. However, this product contains two Si atoms. The experiments using TMS-d12 has clearly demonstrated that this compound has not been formed in the HWCVD reactor with TMS. This supports the observation that trimethylsilane was not produced in the reactor. Similar reactions to those shown in Eqs. (10)–(12) could also apply to *n*-propyltrimethylsilane or dimethyldiethylsilane to yield other alkyl-substituted monosilane compounds, however, all the mass peaks beyond the one at $m/z = 116$ were shown to contain more than one silicon atoms. Therefore, no other monosilane species than ethyltrimethylsilane and diethyldimethylsilane/*n*-propyltrimethylsilane were produced in the HWCVD reactor under our experimental condition.

It is well known that olefins are formed in radical chain reactions, i.e., the Rice–Herzfeld mechanism, for the pyrolysis of hydrocarbons [31]. However, whether or not the same mechanism can apply to the pyrolysis of organosilanes is a question. This is mainly due to the inability to synthesize any stable compounds containing silicon–carbon double bonds. Silene ($\text{CH}_2=\text{SiH}_2$), an unsaturated compound containing a silicon–carbon double bond, is considered to be short-lived and unstable [32]. Maier et al. [33] found that silene was

stable only under argon matrix isolation at 10 K and it dimerized to 1,3-disilacyclobutane upon thawing of the matrix at 35 K. In a study of thermal decomposition of 1,1-dimethyl-1-silacyclobutane [34], although kinetic evidence supports the existence of an unstable intermediate, 1,1-dimethyl-1-silene, the only products detected are ethene and 1,1,3,3-tetramethyl-1,3-disilacyclobutane. 1,1-Dimethylsilene, an analog of silene, was found to undergo similar dimerization reactions to yield 1,1,3,3-tetramethyl-1,3-disilacyclobutane:



Our study of the hot wire decomposition of silacyclobutane [35] also showed that silene ($\text{H}_2\text{Si}=\text{CH}_2$) was produced, supported by the observation of its dimer signal, 1,3-disilacyclobutane. For the pyrolysis of TMS, 1,1,3,3-tetramethyl-1,3-disilacyclobutane ($m/z = 144$) [24,29] were previously observed as a product from the analysis by gas chromatography (GC) or GC–MS. This compound was thought to be formed from the dimerization of the $(\text{CH}_3)_2\text{Si}=\text{CH}_2$ intermediates, produced from TMS pyrolysis.

In our experiment with TMS in the HWCVD reactor, a mass peak at $m/z = 144$ came out strongly at higher filament temperatures together with two other peaks at $m/z = 158$ and 172, as shown in Fig. 7. As indicated in previous studies, the peak at $m/z = 144$ is most likely a disilacyclobutane compound formed from dimerization of $(\text{CH}_3)_2\text{Si}=\text{CH}_2$. A mass peak at $m/z = 160$ was observed with TMS-d12, indicating a mass shift of 16 amu for the peak at $m/z = 144$ with TMS. This confirmed that this species contained two silicon atoms and agreed with the assignment of this peak to 1,1,3,3-tetramethyl-1,3-disilacyclobutane. Possible reactions to produce $(\text{CH}_3)_2\text{Si}=\text{CH}_2$ involve the trimethylsilylmethyl or trimethylsilyl radicals:

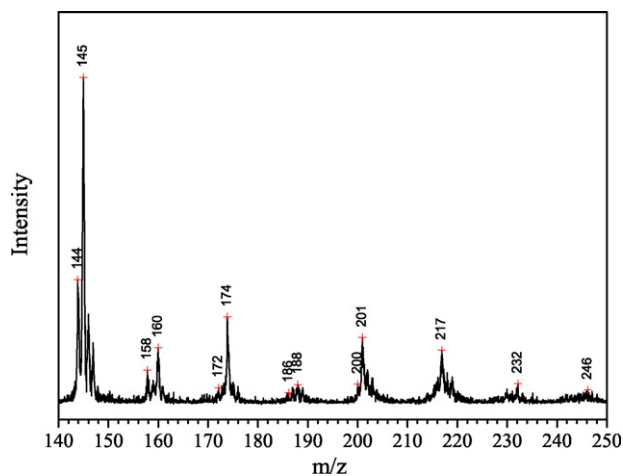
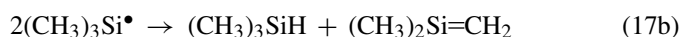
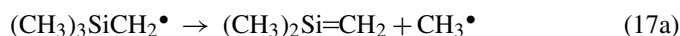
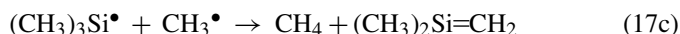


Fig. 7. One hundred and eighteen nanometer VUV SPI TOF mass spectrum of 12 Torr 1% TMS/He sample at a filament temperature of 1700 °C in the mass regions between 140 amu and 250 amu.

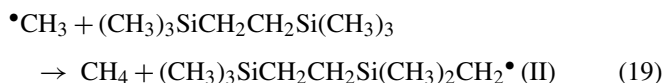
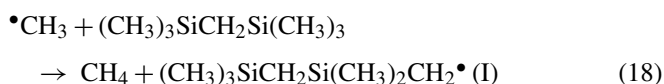


Since trimethylsilane signals were not observed in our experiment, the disproportionation reaction (17b) is not likely to be responsible for the formation of the $(\text{CH}_3)_2\text{Si}=\text{CH}_2$ intermediate. The other two reactions (17a) and (17c) should account for it. Therefore, the detection of mass peaks at $m/z=144$ in our experiments implies the existence of 1,1-dimethyl-1-silene, an unstable intermediate containing Si–C double bonds, in the reactor.

In the study of the pyrolysis of trimethylsilane by Davidson and Lambert [30], two silene intermediates, 1-methyl-1-silene and $(\text{CH}_3)_2\text{Si}=\text{CH}_2$, were thought to be produced, which gave rise to three different methyl-substituted disilacyclobutane products by cycloaddition reactions. Based on this, it is believed that the two other peaks with $m/z=158$ and 172 coming out together with the one at $m/z=144$ should also be alkyl-substituted disilacyclobutane molecules. It is known from the discussions above that three other alkyl substituted monosilane compounds, namely ethyltrimethylsilane ($m/z=102$), *n*-propyltrimethylsilane or dimethyldiethylsilane ($m/z=116$), were produced in the secondary gas-phase reactions in the HWCVD reactor using TMS. Similar to the parent TMS molecule and trimethylsilane, it is possible that these monosilane compounds also produce other silene intermediates than the $(\text{CH}_3)_2\text{Si}=\text{CH}_2$ from TMS. For example, for ethyltrimethylsilane molecule, the H abstraction reaction by the methyl radicals could produce $(\text{CH}_3\text{CH}_2)\text{Si}(\text{CH}_3)_2\text{CH}_2$ or $(\text{CH}_3)_3\text{SiCHCH}_3$ radicals. This is followed by similar reactions to (17a) and (17c), leading to the formation of $(\text{CH}_3)_2\text{Si}=\text{CH}_2$, 1,1,2-trimethyl-1-silene ($(\text{CH}_3)_2\text{Si}=\text{CHCH}_3$), and 1-methyl-1-ethyl-1-silene ($(\text{CH}_3)(\text{CH}_3\text{CH}_2)\text{Si}=\text{CH}_2$). The cycloaddition reactions between these silene compounds could produce different alkyl-substituted disilacyclobutane molecules with $m/z=158$ and 172 . However, no structural assignments for these two mass peaks can be made from our current experiment. Further work is needed to provide support for assigning these two peaks to disilacyclobutane ring compounds.

Further reactions of the chemical species produced from secondary gas-phase reactions make the gas-phase chemistry in the reactor very complicated, at the same time producing more species, such as those observed at $m/z=201$, 217 , 232 , and 246 as shown in Fig. 7. The mass shift for the two relatively strong peak at $m/z=201$ and 217 when using TMS- d_{12} was found to be 21 and 25, indicating that these two species have 21 and 25 H atoms, respectively. Therefore, their molecular formulae were believed to be $\text{Si}_3\text{C}_8\text{H}_{21}$ and $\text{Si}_3\text{C}_9\text{H}_{25}$, respectively, suggesting that the two species contained three silicon atoms. According to the mechanisms described above, the dominant reaction channels all involve the trimethylsilylmethyl radical ($(\text{CH}_3)_3\text{SiCH}_2^\bullet$, $m/z=87$) produced mainly from the H abstraction reaction of tetramethylsilane by the methyl radicals. The two silyl-substituted alkanes containing two silicon atoms, bis(trimethylsilyl)methane and 1,2-bis(trimethylsilyl)ethane, resulting from secondary gas-phase reactions, could undergo similar H abstraction reaction

by CH_3 radicals, and they are shown in the following equations:



This can be followed by several biradical reactions between I ($m/z=159$)/II ($m/z=173$) and trimethylsilyl ($m/z=73$)/trimethylsilylmethyl ($m/z=87$) to give molecules with three silicon atoms. These include those with $(\text{CH}_3)_3\text{SiCH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{Si}(\text{CH}_3)_3$ ($m/z=232$), $(\text{CH}_3)_3\text{SiCH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$ ($m/z=246$), and $(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{Si}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{Si}(\text{CH}_3)_3$ ($m/z=260$). From Fig. 7, very weak peaks at $m/z=232$ and 246 were indeed observed. Similar to tetramethylsilane, bis(trimethylsilyl)methane and 1,2-bis(trimethylsilyl)ethane, these two molecules tend to lose one or more methyl groups upon ionization by the 118 nm VUV laser radiation, and this leads to the observation of the relatively stronger signals observed at $m/z=201$ and 217 , originating from the masses at $m/z=246$ and 232 , respectively. The molecular formulae deriving from this are consistent with those obtained from the isotope labeling experiments. It should be noted that the peaks at $m/z=231$ and 216 from the photoionization of the molecule with $m/z=246$ were also observed, albeit weakly.

The intensity distribution curves of the parent mass peak at $m/z=88$ and its photofragment peak at $m/z=73$ versus filament on time at a filament temperature of 1700°C are shown in Fig. 8(a), whereas those for the three dominant high mass peaks observed, namely the ethyltrimethylsilane at $m/z=102$, the peak at $m/z=145$ originating from bis(trimethylsilyl)methane at $m/z=160$ (also shown), and 1,2-bis(trimethylsilyl)ethane at $m/z=174$, are shown in Fig. 8(b). It is clear that the intensity of the parent molecules keeps decreasing with increased filament-on time, characteristic of the behavior for the reactant molecule in a complex reaction scheme. The intensities of the mass peaks at $m/z=102$, 160 , and 174 rise to their respective maxima, and then fall down. This suggests that these molecules act as both a product and a reactant, consistent with the reaction mechanisms proposed. For example, the bis(trimethylsilyl)ethane molecule was produced through reaction (4), but it also led to the formation of the weak high-mass peaks at $m/z=246$ by reaction (19) followed by biradical combination reactions with trimethylsilyl radicals. All these have led to the conclusion that the gas-phase chemistry of tetramethylsilane in the HWCVD reactor is complex in nature.

It is interesting to note that although the reactions in the HWCVD reactor with TMS are complex, the dominant reactions pathways are the biradical combination reactions involving the alkylsilyl substituted methyl radicals formed from the H abstraction reaction of either alkyl-substituted silane or silyl-substituted alkanes. Almost all the stable silicon-containing products detected from the reactor in our experiment, includ-

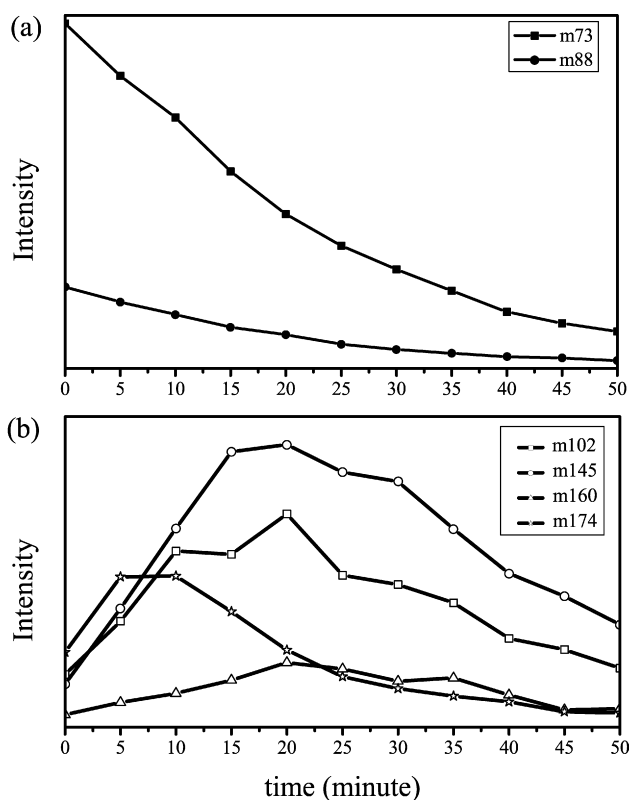


Fig. 8. The plot of the intensities of the peaks at (a) $m/z=73$ and 88 , and (b) $m/z=102$, 145 , 160 , and 174 vs. filament-on time at a filament temperature of 1700°C .

ing those with $m/z=102$, 116 , 160 , 174 , 188 , 232 , and 246 , are formed by this pathway. The molecular structures of all the peaks detected are listed in Table 1. It can be seen that the major bond connection when forming high mass peaks in the gas phase comes from the Si–C bond. The only exception is the formation of HMDS containing Si–Si bond and its corresponding photofragment peak at $m/z=131$. This is not surprising since Si–Si bond ($D(\text{Me}_3\text{Si}-\text{SiMe}_3)=69\text{ kcal/mol}$ [27]) is much weaker than Si–C bond. Consequently, it is expected that silicon carbide films formed from HWCVD using TMS should have a polycarbosilane structure, assuming the reactions on the substrate surface follow similar pathways. In the study of the microstructures of silicon carbide films grown from HWCVD at different substrate temperatures using mono- and tri-methylsilane as source gases [34], it was indicated that using a source gas with a high C:Si ratio such as trimethylsilane has led to a polycarbosilane structure characterized by a backbone containing both silicon and carbon, whereas a SiC film with a polymethylsilane character that is networked through the Si atoms was formed by using monomethylsilane at low substrate temperatures. Although the film microstructure using TMS was not reported, the mechanism proposed in this study for the formation of gas-phase silicon–carbon clusters is in trend with the previous study [36].

In the previous study of TMS pyrolysis by Taylor and Milazzo [25], ethene and propene were also observed as the products. The recombination reaction between methyl radicals followed by CH_3 insertion into C_2H_6 and subsequent decomposition of

C_2H_5 shown in Eqs. (13)–(15) were proposed to be responsible for the formation of ethene. In our experiment, weak signals at $m/z=28$, 42 , and 56 were only observed at high filament temperatures of 1800°C and 1900°C . The isotope labeling experiment confirmed that they correspond to ethene (C_2H_4), propene (C_3H_6), and butene (C_4H_8) (Table 1). Since methyl radicals were produced from the direct decomposition of TMS on a hot W filament under collision-free conditions, the ethene products observed in our experiments were believed to be from the secondary reactions of CH_3 radicals proposed by Taylor and Milazzo (Eqs. (13)–(15)). Similar sequences of reactions initiated by the recombination of CH_3 and C_2H_5 yielded the propene products observed:



And the following three reactions could account for the formation of butene:



In the previous study [25], although C_2H_4 was the dominant hydrocarbon product, other hydrocarbon gases such as CH_4 and C_2H_6 were also observed. However, no alkane products were observed in our experiments. This might be due to the fact that their IP's are above 10.5 eV . It should also be noted that the propene peaks were always stronger than the ethene peaks observed in our experiment. A propene/ethene peak intensity ratio observed in the mass spectra can range from 1.1:1 to 4.3:1. To account for the difference in the ionization cross-section of propene and ethene, we have prepared a mixture of equal pressure of ethene and propene diluted in helium and examined the intensities of the mass peaks at $m/z=28$ and 42 . The intensity ratio of the two peaks at 42 and 28 amu was found to be 36:1, indicating a much greater ionization cross-section for propene. Therefore, although ethene signal was weaker, it was favored over propene as a hydrocarbon product from the secondary gas-phase reactions, in agreement with the previous study [25]. The ethene/propene product ratio in our experiment could range from 32.7:1 to 8.4:1.

4. Conclusions

The chemical species formed from both direct decomposition of tetramethylsilane on a hot tungsten filament and secondary gas-phase reactions in a HWCVD reactor were diagnosed by 118 nm VUV laser single photon ionization coupled with TOF mass spectrometry. The initial primary products from the filament were methyl and trimethylsilyl radicals. Under pressures of 0.06 – 0.12 Torr , further reactions between the primary methyl radicals resulted in the formation of small alkenes including ethene, propene, and butene. Hexamethyldisilane was produced

from the recombination of primary trimethylsilyl radicals. This gives the only detected product that has a Si–Si bond. Secondary gas-phase reactions between the primary radicals and the parent TMS molecule lead to the formation of the high-mass alkyl-substituted silanes and silyl-substituted alkanes. Examples of the former type are ethyltrimethylsilane ($m/z = 102$), *n*-propyltrimethylsilane or dimethyldiethylsilane ($m/z = 116$). The mass peaks observed at $m/z = 160, 174, 188, 232,$ and 246 represent the latter. Although the secondary gas-phase reactions are complex in nature, the dominant reaction pathways are found to be the formation of alkylsilyl substituted methyl radicals from the H abstraction reaction of either alkyl-substituted silane or silyl-substituted alkanes by methyl radicals followed by the biradical combination reactions. It was found that the major bond connection when forming high-mass peaks in the gas phase comes from the Si–C bond. This is in good agreement with previous studies showing that a source gas with a high C:Si ratio would lead to a thin film with a polycarbosilane structure. 1,1,3,3-Tetramethyl-1,3-disilacyclobutane molecule was believed to be observed at $m/z = 144$, which resulted from the dimerization of 1,1-dimethyl-1-silene. This provides strong implication that the unsaturated silene molecules were produced in the HWCVD reactor.

Acknowledgements

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