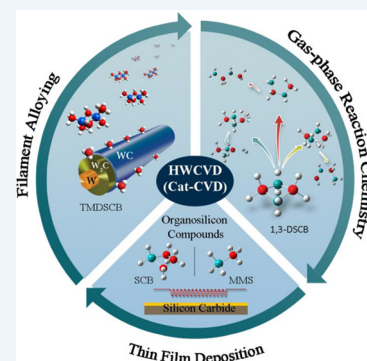# Hot Wire Chemical Vapor Deposition Chemistry in the Gas Phase and on the Catalyst Surface with Organosilicon Compounds

Yujun Shi*

Department of Chemistry, University of Calgary, Calgary, Alberta T2N 1N4, Canada

CONSPECTUS: Hot wire chemical vapor deposition (HWCVD), also referred to as catalytic CVD (Cat-CVD), has been used to produce Si-containing thin films, nano-materials, and functional polymer coatings that have found wide applications in micro-electronic and photovoltaic devices, in automobiles, and in biotechnology. The success of HWCVD is largely due to its various advantages, including high deposition rate, low substrate temperatures, lack of plasma-induced damage, and large-area uniformity. Film growth in HWCVD is induced by reactive species generated from primary decomposition on the metal wire or from secondary reactions in the gas phase. In order to achieve a rational and efficient optimization of the process, it is essential to identify the reactive species and to understand the chemical kinetics that govern the production of these precursor species for film growth.

In this Account, we report recent progress in unraveling the complex gas-phase reaction chemistry in the HWCVD growth of silicon carbide thin films using organosilicon compounds as single-source precursors. We have demonstrated that laser ionization mass spectrometry is a powerful diagnostic tool for studying the gas-phase reaction chemistry when combined with the methods of isotope labeling and chemical trapping. The four methyl-substituted silane molecules, belonging to open-chain alkylsilanes, dissociatively adsorb on W and Ta filaments to produce methyl radical and H_2 molecule. Under the typical deposition pressures, with increasing number of methyl substitution, the dominant chemistry occurring in the gas phase switches from silylene/silene reactions to free-radical short chain reactions. This change in dominant reaction intermediates from silylene/silene to methyl radicals explains the observation from thin film deposition that silicon carbide films become more C-rich with a decreasing number of Si−H bonds in the four precursor molecules. In the case of cyclic monosilacyclobutanes, we have shown that ring-opening reactions play a vital role in characterizing the reaction chemistry. On the other hand, exocyclic Si−H(CH$_3$) bond cleavages are more important in the less-puckered disilacyclobutane molecules. Metal filaments are essential in HWCVD since they serve as catalysts to decompose precursor gases to reactive species, which initiate gas-phase reaction chemistry and thin film growth. We discuss the structural changes in metal filaments when exposed to various precursor gases. Depending on the nature of the radical intermediates formed from the hot-wire decomposition and subsequent gas-phase reactions, metal silicides and carbides can be formed.

Overall, study of the gas-phase reaction chemistry in HWCVD provides important knowledge of the chemical species produced prior to their deposition on a substrate surface. This helps in identifying the major contributor to alloy formation on the filament itself and the film growth, and consequently, in determining the properties of the deposited films. An integrated knowledge of the gas-phase reaction chemistry, filament alloy formation, and thin film deposition is required for an efficient deposition of high-quality thin films and nanomaterials.

1. INTRODUCTION

Since its development in the late 1980s, the technique of hot wire chemical vapor deposition (HWCVD),[1] also known as catalytic CVD,[2] has received continuing research interest. Device-quality Si-containing thin films produced using HWCVD have been utilized in thin film silicon solar cells and large-area liquid crystal displays. New and innovative use of HWCVD continues to emerge for the deposition of metal oxide nanoparticles,[3] carbon nanotubes,[4] and functional polymer coatings.[5] HWCVD utilizes the catalytic ability of metal filaments (e.g., W or Ta) to decompose the source gases to radicals at high temperatures (≥1500 °C). This is followed by secondary radical−radical and radical−molecule reactions in the gas phase to produce the final mix of film growth precursors that react with the substrate at a relatively low temperature (150−300 °C), leading ultimately to thin film formation. The growth rate and properties of the

deposits depend strongly on the nature of the gas-phase growth precursors. Therefore, information on the gas-phase reaction chemistry, including the mechanisms and kinetics, is critical for understanding the HWCVD film growth process. Although extensive studies can be found on optimizing the process conditions and characterizing the properties of final deposits, far less is known about the source gas decomposition on hot filament and subsequent gas-phase reactions. The past two decades have seen an increasing effort to investigate the gas-phase reaction chemistry in HWCVD.[6−8] Most of the studies have focused on the deposition process of diamond coatings from hydrocarbons[6] or silicon films from SiH$_4$.[7,8] As a result, significant advancement
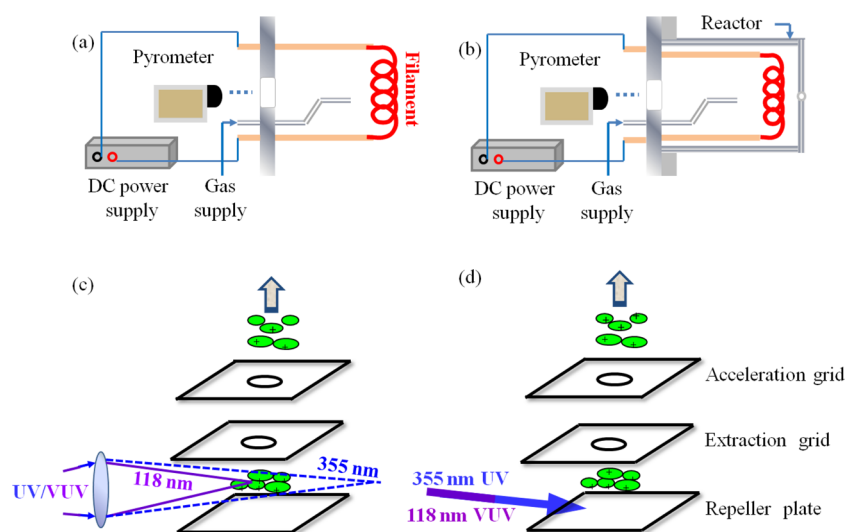
Figure 1. Schematic diagrams of (a) a collision-free setup to detect the primary decomposition products on metal filaments, (b) a HWCVD reactor setup for the detection of secondary gas-phase reaction products (Adapted with permission from ref 23. Copyright 2007 Elsevier), (c) 118 nm VUV SPI source; and (d) a dual LIEI/SPI ionization source (Adapted with permission from ref 15. Copyright 2007 Springer).

in the understanding of these processes has been achieved at the molecular level.

The deposition chemistry for the formation of silicon carbide ($Si_{1-x}C_x$), on the other hand, has received less attention. Most CVD growth of $Si_{1-x}C_x$ proceeds through the use of separate Si-(SiH_4, SiH_2Cl_2) and C-bearing (CH_4, C_3H_8) precursors. However, handling of pyrophoric and highly toxic silane and chlorosilane gases is difficult. The optimum composition of the mixture also varies with the deposition conditions. This situation has spurred interest in investigating alternative single-source precursors for $Si_{1-x}C_x$ deposition. Two types of organosilicon compounds, namely, open-chain alkylsilanes[9] and cyclic (di)-silacyclobutanes,[10] have been explored. The Si/C composition in the resultant $Si_{1-x}C_x$ films when using these single-source precursors is mainly controlled by the decomposition and reaction chemistry along with other deposition parameters. Much work remains to understand the reactions in the gas phase and on the filament/substrate surfaces for a complete understanding of the film growth mechanisms for silicon carbide and for a rational and efficient improvement of the process.

In this Account, we review recent progress in the investigation of gas-phase reaction chemistry in the HWCVD process for the formation of $Si_{1-x}C_x$ thin films with single-source organosilicon precursors. Due to space limitation, this Account is mainly focused on the work carried out in our laboratory. The development of various laser ionization methods to be used in tandem with time-of-flight (TOF) mass spectrometry (MS) as a diagnostic tool to unravel the complex gas-phase chemistry in HWCVD is described first. Then, the gas-phase reaction chemistry when open-chain alkylsilanes and cyclic (di)silacyclobutanes are used as single-source precursors is discussed. Correlation with results from thin film characterization sheds light on the significance of identifying the gas-phase chemical species formed prior to their deposition on the substrate. Metal filaments play a central role in HWCVD in controlling the final mix of gas-phase film growth precursors, and consequently the film properties. Lastly, formation of metal silicides and carbides on filament surfaces upon their exposure to various precursor molecules is discussed.

2. LASER IONIZATION MASS SPECTROMETRY FOR DIAGNOSING HWCVD REACTION CHEMISTRY

Laser ionization mass spectrometry has been used to study the products formed from primary decomposition of open-chain alkylsilanes and cyclic (di)silacyclobutanes on a heated metal filament and from subsequent secondary reactions in the gas phase. To detect the nascent products formed from the primary decomposition, a collision-free setup (Figure 1a) is used where a resistively heated metal filament (W or Ta) is placed directly in the main chamber housing a TOF mass spectrometer under an operating pressure of 1×10^{-5} Torr. To allow for the detection of the products from secondary gas-phase reactions important under the typical deposition pressures (0.1−10 Torr), a cylindrical HWCVD reactor (Figure 1b) is employed to house the filament and to provide appropriate sample pressures.

The main diagnostic tool to probe the chemical species formed from both the collision-free setup and the HWCVD reactor is single photon ionization (SPI) with a vacuum ultraviolet (VUV) wavelength of 118 nm coupled with TOF MS. The electron ionization by hot filaments is confirmed to be nonexistent. The 118 nm radiation (10.5 eV) is generated by frequency tripling the 355 nm UV light in a Xe/Ar gaseous mixture. A lithium fluoride lens is placed to focus the 118 nm light at the center of the ionization region (Figure 1c). VUV SPI is generally considered a "soft" ionization method.[11,12] Its ability to provide less convoluted mass spectra and to detect multiple species at one time has proved to be advantageous for analysis of complex reaction systems such as pyrolysis[13] and CVD[14] processes. However, the 118 nm SPI cannot be used in identifying species with ionization energy (IE) higher than 10.5 eV. To detect these species, for example, H_2 and N_2, a complementary dual ionization source incorporating both VUV SPI and a laser-induced electron ionization (LIEI) mode has been developed.[15] In this source, the electron pulses are generated by directing an unfocused laser beam containing both 355 and 118 nm radiation to the repeller plate in TOF MS (Figure 1d). The photoelectrons then gain energy in the electric field between the repeller and extraction plate to ionize the molecules, achieving LIEI. The coexistence of the 10.5 eV SPI and LIEI allows for simultaneous observation of molecular ions having high IEs by the incorporation of LIEI and
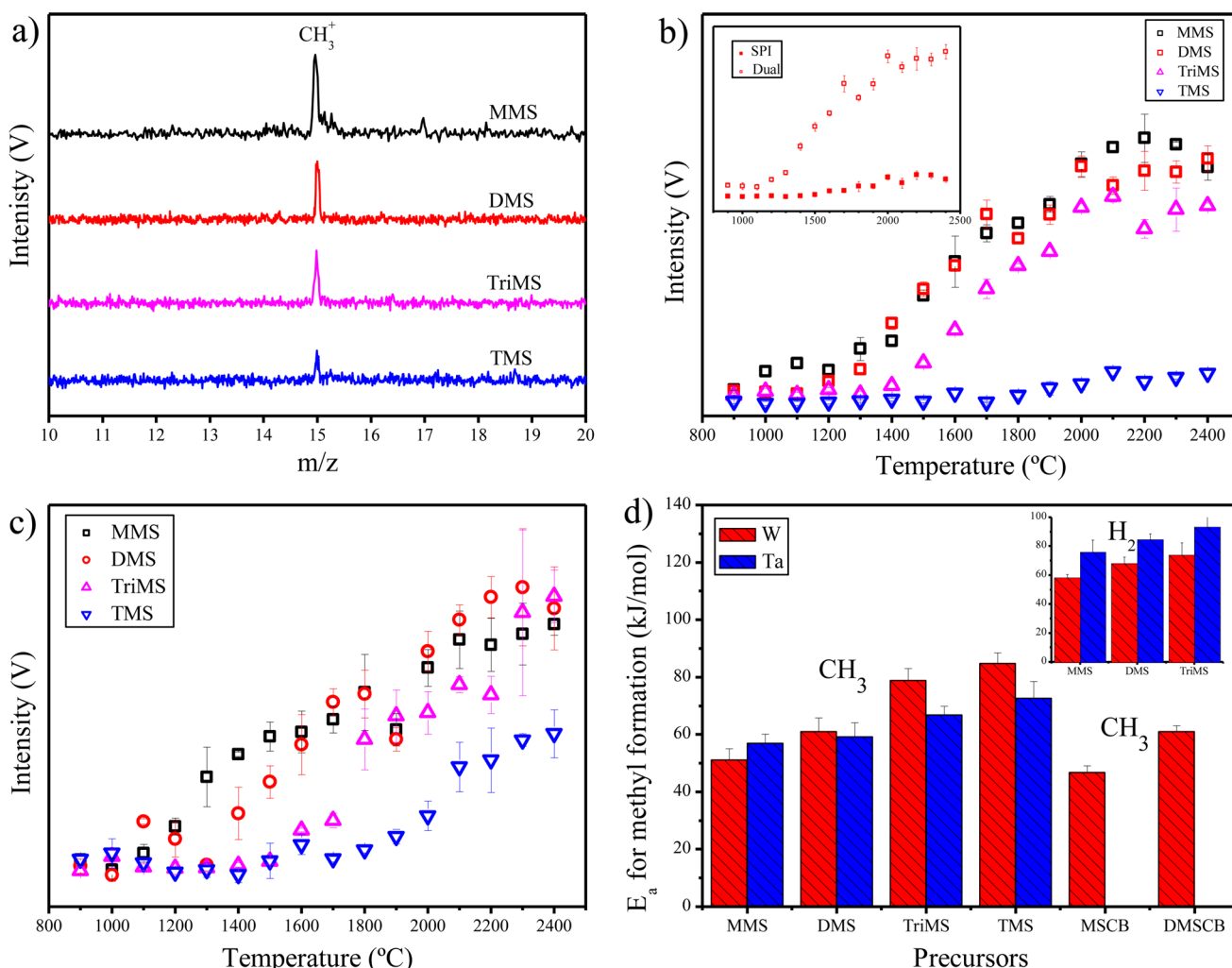
Figure 2. (a) SPI mass spectra (10.5 eV) in the m/z region of 10−20 at 2100 °C, (b) the temperature profile of normalized intensity H_2 molecule using SPI/LIEI (inset, comparison of the H_2 intensity from DMS sample using the two ionization modes), (c) methyl radical using SPI (Reproduced with permission from ref 17. Copyright 2013 American Chemical Society), and (d) the activation energies for $^\bullet CH_3$ and H_2 formation for MMS, DMS, TriMS, and TMS.

those with IE < 10.5 eV to have enhanced intensities due to SPI. By identification of the nature of the products from both the primary decomposition and secondary gas-phase reactions, mechanistic details of the gas-phase reactions involved in HWCVD have been obtained. The reaction kinetics have also been studied by monitoring the product distributions at different deposition parameters, including reaction time, filament temperature, and gas pressure.

3. GAS-PHASE REACTION CHEMISTRY WITH OPEN-CHAIN ALKYLSILANES

3.1. Primary Decomposition on Heated Metal Filament Surfaces

The simplest organosilicon compounds containing direct Si−C bonds are methyl-substituted silanes. These molecules, including monomethylsilane (MMS), dimethylsilane (DMS), trimethylsilane (TriMS), and tetramethylsilane (TMS), have been used as single-source precursors in HWCVD for the preparation of $Si_{1−x}C_x$ films.[9,16] When we examine the primary decomposition of the four precursor molecules on a W or Ta filament under the collision-free conditions, the common pathways are found to be the formation of methyl radical (Figure 2a) and hydrogen

molecule (Figure 2b, inset).[17] The H_2 peak has a weak intensity when observed using SPI due to its high IE of 15.4 eV but can be significantly enhanced when LIEI is used in conjunction with SPI. For all four molecules, the methyl radical and H_2 peak intensity increases with filament temperature to around 2000−2100 °C and saturates beyond it (Figure 2b,c). This signifies a transition in the rate-limiting step from surface reactions at low temperatures to mass transport at higher temperatures. The same behavior was observed in the Si atom formation during the hot-wire decomposition of SiH_4[18,19] and methyl-substituted silanes.[20] Among the four molecules, TMS produces the least amount of $^\bullet CH_3$, whereas the amount produced by TriMS, DMS, and MMS is similar (Figure 2c). This is counterintuitive from the perspective that the $^\bullet CH_3$ amount would be higher as the number of methyl groups in the precursor molecule increases. The determined activation energies (E_a) for the formation of $^\bullet CH_3$ and H_2 on W and Ta for MMS, DMS, TriMS, and TMS (Figure 2d) show a clear trend of increase with increasing number of methyl substitutions. The same trend is observed for the formation of Si from the same four molecules.[20] Overall, the E_a values for forming H_2 (58.2−93.4 kJ·mol$^{−1}$) from the dissociation of MMS, DMS, and TriMS fall in a similar range to those for the $^\bullet CH_3$ formation (51.1−78.8 kJ·mol$^{−1}$) from the same

three molecules. This indicates that the rate-limiting step in forming both species is the same. Also, it is noted that the E_a values for the formation of $^{\bullet}CH_3$ and H_2 are significantly lower than their respective Si−CH$_3$ and Si−H bond dissociation energies for MMS, DMS, TriMS, and TMS (368.6−377.8 kJ· mol^{-1}[21]). Therefore, the formation of $^{\bullet}CH_3$ and H_2 from the decomposition of methyl-substituted silanes on W and Ta filaments is a catalytic process. This is in good agreement with previous studies on hot-filament decomposition of SiH$_4$[19,22] and alkylsilanes.[20]

A dissociative adsorption mechanism (Figure 3) has been proposed for the hot-filament decomposition of methyl-substituted
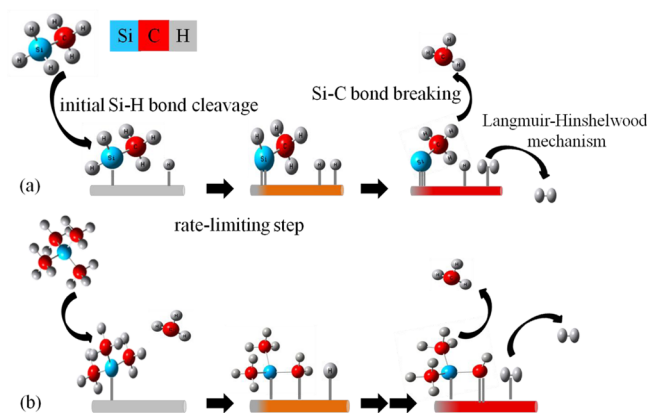

Figure 3. Formation of $^{\bullet}CH_3$ and H_2 by the dissociative adsorption of (a) MMS and (b) TMS on a W or Ta surface.

silane molecules.[17] The dissociation of MMS, DMS, and TriMS is initiated by the Si−H bond cleavage, leading to the formation of methyl-substituted silyl/silylene/silylyne and H adsorbates. The initial Si−H bond rupture is followed by Si−CH$_3$ bond breaking to form methyl radicals. The formation of H$_2$ follows the Langmuir−Hinshelwood mechanism, where two adsorbed H atoms recombine on metal surfaces to form H$_2$, which rapidly desorbs. Considering that formation of H$_2$ and $^{\bullet}CH_3$ has the same rate-limiting step, the initiation step by Si−H bond cleavages involved in the formation of both species should be rate limiting. TMS does not contain any Si−H bonds; therefore, it becomes less susceptible to decomposition on heated metal filaments, leading to the highest activation energy as determined. This also explains why TMS produces the least amount of $^{\bullet}CH_3$ even though it has the greatest number of methyl substituents. The dissociation of TMS to form $^{\bullet}CH_3$ and H$_2$ proceeds via the cleavage of Si−CH$_3$ and C−H bonds (Figure 3b).

3.2. Secondary Reactions in the Gas Phase

When an increased pressure of 0.12 Torr TMS is used in the reactor, the dominant pathways in the secondary gas-phase
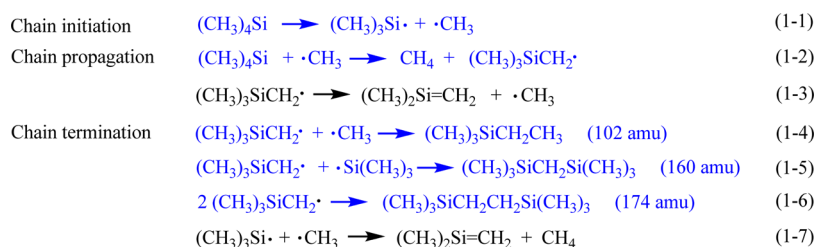
reactions are found to be short chain reactions.[23] The radical formation in the primary decomposition initiates the chain reaction, followed by a propagation step of the H abstraction reaction by $^{\bullet}CH_3$ from the parent TMS. Finally, the radical recombination reactions in the termination step are responsible for most of the stable products detected (Scheme 1). Two categories of major products are found: alkyl-substituted silanes such as ethyltrimethylsilane (102 amu); silyl-substituted alkanes such as bis(trimethylsilyl)methane (160 amu) and bis-(trimethylsilyl)ethane (174 amu) (Figure 4a). An increase in the filament temperature ($T \geq 1600\ ^{\circ}$C) leads to the formation of 1,1,3,3-tetramethyl-1,3-disilacyclobutane (TMDSCB, 144 amu) originating from the dimerization of the unstable 1,1-dimethylsilene ($(CH_3)_2Si{=}CH_2$) intermediate.

Study of TriMS chemistry reveals the effect of the Si−H bond.[24] The two major products of TriMS are TMS and hexamethyldisilane (HMDS, 146 amu) and are formed from the short chain reactions (Scheme 2), which still dominate the reaction chemistry at all temperatures tested at 900−2000 °C (Figure 4b). A relatively stronger signal from TMDSCB is observed, indicating the formation of more 1,1-dimethylsilene. Therefore, with the introduction of a Si−H bond in TriMS, the reactive silene intermediates start to play a more active, although still minor, role.

This role is further enhanced when DMS is used as a precursor. Both free-radical short chain reactions and those involving silylene/silene intermediates are important in characterizing the reaction chemistry with DMS.[25] The competition between the two types of reactions depends strongly on filament temperature and reaction time. At 1100−1200 °C and short time, the formation of 1,1,2,2-tetramethyldisilane (TMDS, 118 amu), produced by the insertion of dimethylsilylene (:Si(CH$_3$)$_2$) into the Si−H bond in DMS, predominates (Figure 4c). Another major product, 1,3-dimethyl-1,3-disilacyclobutane (DMDSCB, 116 amu), is formed at low temperatures from the dimerization of either 1-methylsilene or dimethylsilylene (Scheme 3a). Therefore, reactions involving silylene/silene intermediates rule at low filament temperature and short reaction time. This is quite different from the observations with TMS and TriMS where silene intermediates only make a minor contribution at $T \geq 1600$ °C. Free-radical reactions, which dominate the reaction chemistry with TMS and TriMS at all temperatures, only become important at high temperatures when DMS is used. This is represented by the dominant formation of TriMS at 1500−1600 °C.

The involvement of silylene intermediates is more accentuated as the number of Si−H bond in the precursor gas is further increased. The gas-phase reaction chemistry of MMS involves exclusively silylene intermediates.[26] The two major Si-containing products, 1,2-dimethyldisilane (DMDS, 90 amu) and 1,3-disilacyclobutane (DSCB, 88 amu), both originate from the methylsilylene (:SiH(CH$_3$)) intermediate (Scheme 3b, Figure 4d). Free radical and silene species do not play a role. Therefore, a

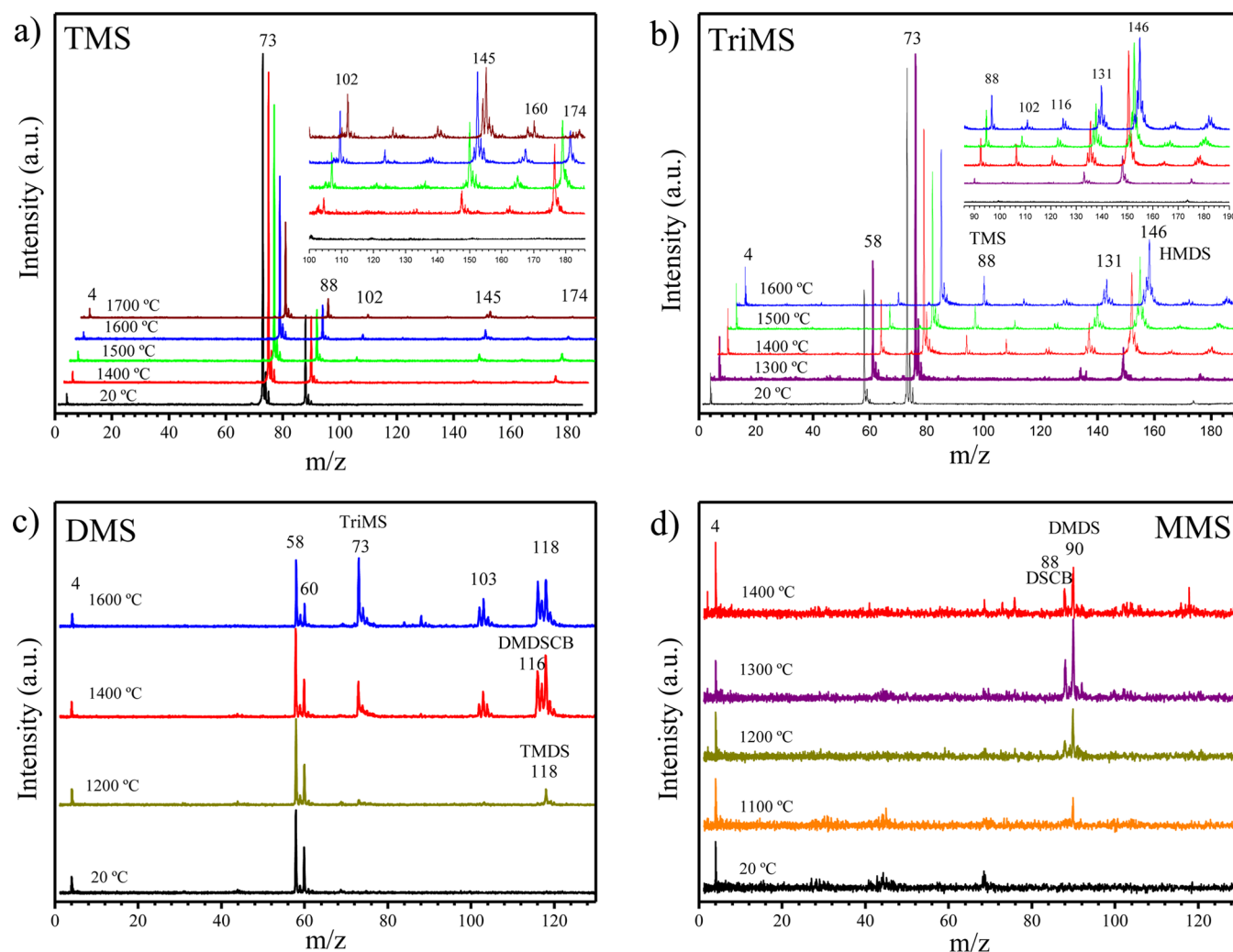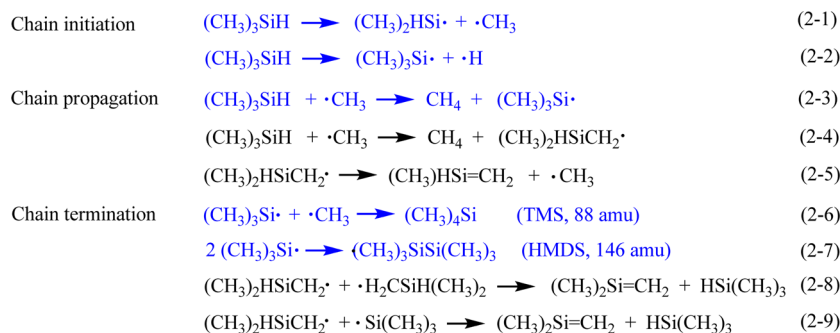## Scheme 1. Short Chain Reactions of Tetramethylsilane

Chain initiation	$(CH_3)_4Si \longrightarrow (CH_3)_3Si\cdot + \cdot CH_3$	(1-1)
Chain propagation	$(CH_3)_4Si + \cdot CH_3 \longrightarrow CH_4 + (CH_3)_3SiCH_2\cdot$	(1-2)
	$(CH_3)_3SiCH_2\cdot \longrightarrow (CH_3)_2Si{=}CH_2 + \cdot CH_3$	(1-3)
Chain termination	$(CH_3)_3SiCH_2\cdot + \cdot CH_3 \longrightarrow (CH_3)_3SiCH_2CH_3$ (102 amu)	(1-4)
	$(CH_3)_3SiCH_2\cdot + \cdot Si(CH_3)_3 \longrightarrow (CH_3)_3SiCH_2Si(CH_3)_3$ (160 amu)	(1-5)
	$2\ (CH_3)_3SiCH_2\cdot \longrightarrow (CH_3)_3SiCH_2CH_2Si(CH_3)_3$ (174 amu)	(1-6)
	$(CH_3)_3Si\cdot + \cdot CH_3 \longrightarrow (CH_3)_2Si{=}CH_2 + CH_4$	(1-7)

Figure 4. SPI mass spectra (10.5 eV) of (a) 0.12 Torr TMS (inset: enlarged spectra in the *m/z* region of 100−190. Adapted with permission from ref 23. Copyright 2007 Elsevier). (b) 0.12 Torr TriMS (inset: enlarged spectra in the *m/z* region of 80−190. Adapted with permission from ref 24. Copyright 2011 American Chemical Society), (c) 0.12 Torr DMS (Adapted from ref 25 with permission from the PCCP Owner Societies), and (d) 0.48 Torr MMS at various filament temperatures (Adapted with permission from ref 26. Copyright 2014 American Chemical Society).

Scheme 2. Short Chain Reactions of Trimethylsilane

| Chain initiation | $(CH_3)_3SiH \longrightarrow (CH_3)_2HSi\cdot + \cdot CH_3$ | (2-1) |
	$(CH_3)_3SiH \longrightarrow (CH_3)_3Si\cdot + \cdot H$	(2-2)
Chain propagation	$(CH_3)_3SiH + \cdot CH_3 \longrightarrow CH_4 + (CH_3)_3Si\cdot$	(2-3)
	$(CH_3)_3SiH + \cdot CH_3 \longrightarrow CH_4 + (CH_3)_2HSiCH_2\cdot$	(2-4)
	$(CH_3)_2HSiCH_2\cdot \longrightarrow (CH_3)HSi=CH_2 + \cdot CH_3$	(2-5)
Chain termination	$(CH_3)_3Si\cdot + \cdot CH_3 \longrightarrow (CH_3)_4Si$ (TMS, 88 amu)	(2-6)
	$2(CH_3)_3Si\cdot \longrightarrow (CH_3)_3SiSi(CH_3)_3$ (HMDS, 146 amu)	(2-7)
	$(CH_3)_2HSiCH_2\cdot + \cdot H_2CSiH(CH_3)_2 \longrightarrow (CH_3)_2Si=CH_2 + HSi(CH_3)_3$	(2-8)
	$(CH_3)_2HSiCH_2\cdot + \cdot Si(CH_3)_3 \longrightarrow (CH_3)_2Si=CH_2 + HSi(CH_3)_3$	(2-9)

switch in the prevailing chemistry from free-radical short chain reactions to silylene insertion/dimerization reactions occurs as the number of Si−H bonds increases in the four methyl-substituted silane molecules.

3.3. Correlation of Gas-phase Chemistry with Deposited Film Structures

To correlate the gas-phase reaction chemistry with the final film structures, examination of the film structures deposited when

these methyl-substituted silane molecules are used is required. Lee et al. carried out a spectroscopy study of the bonding in amorphous hydrogenated silicon carbide (a-SiC:H) films grown by HWCVD using pure MMS.[9] They have found that the films grown have a methylated polysilane character, which is net-worked through Si atoms with the C present in the intact CH_3 groups. This has led them to conclude that the a-SiC:H growth occurs primarily by Si−H bond cleavage in MMS, which points

Scheme 3. Reactions Involving Silylenes and Silenes When (a) Dimethylsilane and (b) Monomethylsilane Are Used
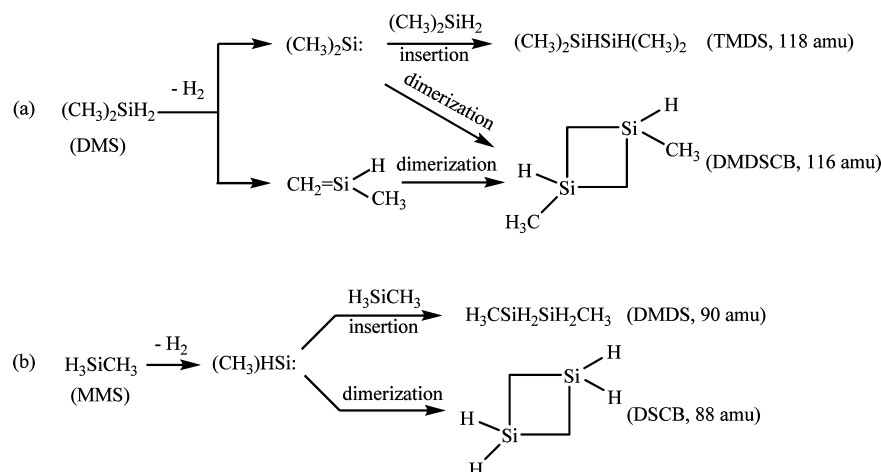
to the possible presence of silyl or silylene species. Our work on the gas-phase reaction chemistry of MMS has provided clear evidence of the existence of methylsilylene diradical and its dominant presence. This provides support for their argument that silyl radical production is not as important. A study comparing the structures of a-SiC:H films grown by HWCVD using three different precursors of MMS, TriMS, and TMS has shown that the extent of Si−C and C−H bond rupture during the film growth is increased in TriMS compared with that in MMS.[16] TMS is found to be much less reactive than TriMS and MMS in forming the a-SiC:H films. The major pathway to film growth when using TMS is the less favorable C−H bond cleavage. These results are in good agreement with our studies on the gas-phase reaction chemistry showing that the dominant chemistry for TMS and TriMS involves short free-radical chain reactions, where •CH₃ produced via Si−C breakage abstracts a H atom from the C−H bonds in TriMS and TMS. The study on the a-SiC:H film structure grown using the four precursors (TMS, TriMS, DMS, MMS) clearly demonstrates that the grown film becomes less Si-rich as the number of Si−H bonds is decreased.[20] This should be related to the change in the dominant intermediates produced in the gas phase from silylene/silene species to methyl radicals when moving from MMS to TMS. Overall, it can be concluded that study of the HWCVD reaction chemistry provides important knowledge of the gas-phase species produced prior to their deposition on a substrate. This helps in identifying the major contributor to the film growth, and consequently, in determining the properties of the deposited films.

4. GAS-PHASE REACTION CHEMISTRY WITH CYCLIC MONO- OR DI-SILACYCLOBUTANES

Four-membered-ring mono- and di-silacyclobutanes are a class of strained cyclic organosilicon compounds. The high ring strain energy and the ability of these molecules to produce reactive silene and silylene species upon thermal activation[27] have made them excellent choices as single-source precursors for the CVD growth of Si₁₋ₓCₓ.[10,20] Our laboratory has recently studied the decomposition of several mono- and di-silacyclobutane molecules on a hot metal filament and the secondary gas-phase reaction chemistry. The structures of these molecules along with their full names and abbreviations are shown in Figure 5.

Among the three monosilacyclobutane molecules, DMSCB holds a unique place in the history of organosilicon chemistry. The discovery in 1967 that DMSCB pyrolysis is a clean
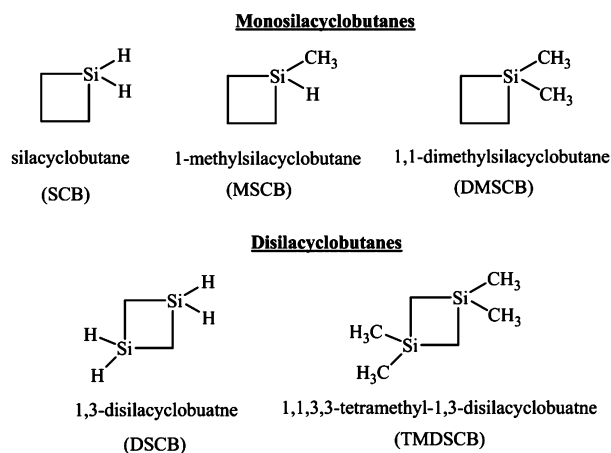

Figure 5. Structures of monosilacyclobutane and disilacyclobutane molecules.

cycloreversion reaction to form ethene and a transient 1,1-dimethylsilene intermediate marks the first observation of an unsaturated silene species.[27] Our examination of the decomposition of DMSCB in the presence of a W or Ta filament found that, aside from the well-known cycloreversion reaction, two other decomposition routes existed to form methyl radical and propene molecule.[28] The same three pathways were observed for MSCB (Scheme 4).[29] For SCB, only ethene and propene were formed.[30] The ring strain in MSCB and DMSCB reduces the activation energy for •CH₃ formation compared with the corresponding methyl-substituted silanes, that is, TriMS and TMS (Figure 2d).

Study of formation mechanisms for ethene and propene using the deuteriated isotopomers revealed some important results. When 1,1-bis(trideuteromethyl)silacyclobutane (DMSCB-d₆) was used to replace DMSCB, significant H/D scrambling was observed for ethene and propene, with a mass shift of up to two and four, respectively (Figure 6a).[28] These H/D scrambling patterns provide unambiguous support for a stepwise mechanism (Scheme 4) for the formation of both propene and ethene, initiated by the cleavage of ring Si−C and C−C bonds, respectively, to produce diradical intermediates. This agrees with our theoretical calculations on DMSCB and those by Gordon et al.[31] on SCB. The amount of ethene produced is much higher than that of propene. Therefore, it has been proven for the first time that an initial ring C−C bond cleavage in DMSCB to form ethene

Scheme 4. Primary Decomposition Pathways of 1-Methylsilacyclobutane
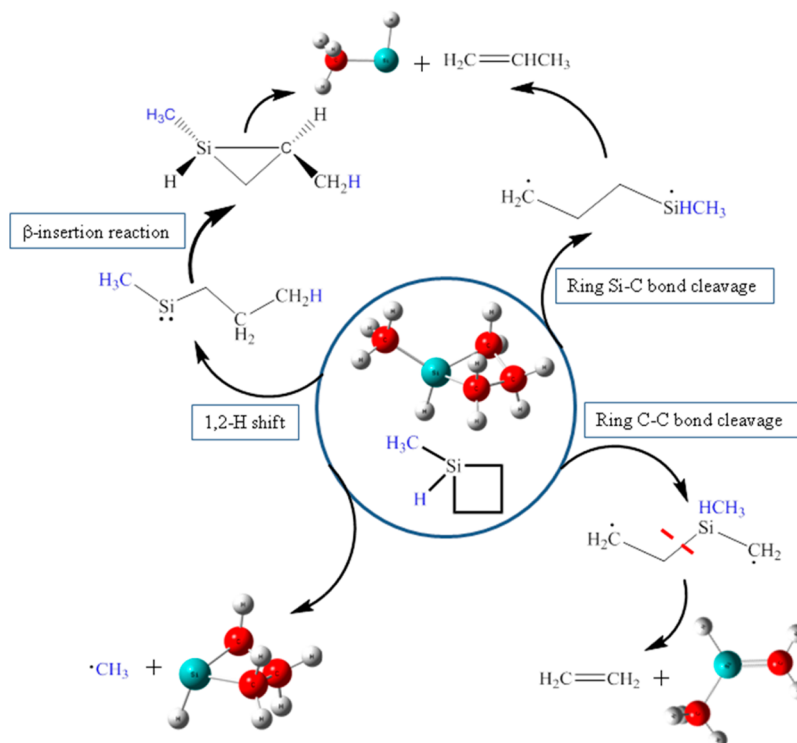
predominates over a ring Si−C bond cleavage to form propene. Experiments with 1-deuterio-1-methylsilacyclobutane (MSCB-d_1, Figure 6b)[29] and 1,1-dideuterio-1-silacyclobutane (SCB-d_2, Figure 6c)[30] revealed no H/D scrambling for ethene, whereas propene was deuteriated in varying amounts. The observation of deuteriated propene provides clear evidence for the existence of a path initiated by a 1,2-H(D) shift from Si to C (Scheme 4) for the propene formation. This agrees well with the results from the previous pyrolysis study.[32] Of the three molecules, SCB produced the greatest amount of propene, whereas DMSCB produced the least, suggesting that the existence of Si−H bonds favors propene formation.

Compared with the open-chain alkylsilanes, it is not surprising to find that ring-opening reactions play a significant role in the dissociation of monosilacyclobutanes. This is also reflected in the secondary gas-phase reaction chemistry assumed by these molecules. The predominant product when DMSCB is used in the reactor is TMDSCB (Figure 6a), which originates from the cyclodimerization of 1,1-dimethylsilene (eq 3).[28]

(3)
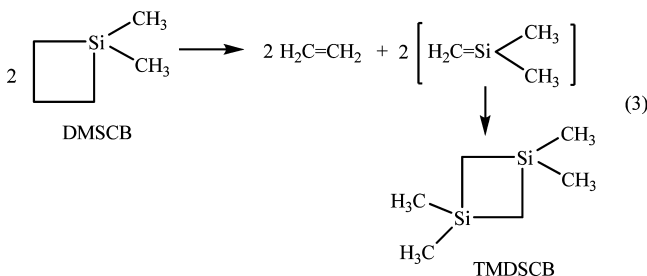
The gas-phase chemistry of MSCB, containing both Si−H and Si−CH$_3$ bonds, is more balanced with a competition between a free-radical chain reaction and silene cyclodimerization.[29] For SCB, insertion and π-type addition reactions of various silylene intermediates predominate.[30] Another distinct difference when comparing the reaction chemistry of SCB with that of DMSCB is that significantly more 1,1-dimethylsilene dimers are produced with DMSCB than silene dimers from SCB (Figure 6). Considering that (dimethyl)silene is the concomitant product of ethene from cycloreversion, the observed difference is consistent with the conclusion that DMSCB favors the formation of ethene and SCB favors propene formation.

Disilacyclobutanes are much less puckered with lower strain energy than their monosilacyclobutane analogues.[33] Furthermore, cycloreversion of DSCB to produce two silene molecules is more endothermic (75.6 kcal·mol^{-1})[34] than the corresponding reaction of SCB to form ethene/silene (42.0 kcal·mol^{-1}).[31] This leads to a less dominant contribution of DSCB cycloreversion in its decomposition and secondary reaction chemistry. DSCB decomposes on W and Ta filaments to produce H$_2$ molecules. Its secondary gas-phase reactions are characterized by the dominance of 1,3-disilacyclobut-1-ylidene formation via H$_2$ elimination and the insertion of the cyclic silylene into the Si−H bonds in DSCB (eq 4).

For TMDSCB where all four Si−H bonds in DSCB are replaced with Si−CH$_3$ connections, interestingly, a short free-radical chain reaction consisting of the H abstraction reaction and biradical recombination reactions is the main mechanism operating in a reactor setup.[35] A common discovery in the decomposition/reaction chemistry of DSCB and TMDSCB is that exocyclic bond cleavages play a vital role. This is quite different from the behavior of the monosilacyclobutanes where ring-opening reactions are more important.

5. SURFACE CHEMISTRY ON THE CATALYST: FILAMENT AGING

Metal filaments serve as catalysts in HWCVD to decompose the precursor gas to produce reactive species, which initiate the gas-phase reaction chemistry. These reactive species also react with the metal itself, causing structural changes in the filament.
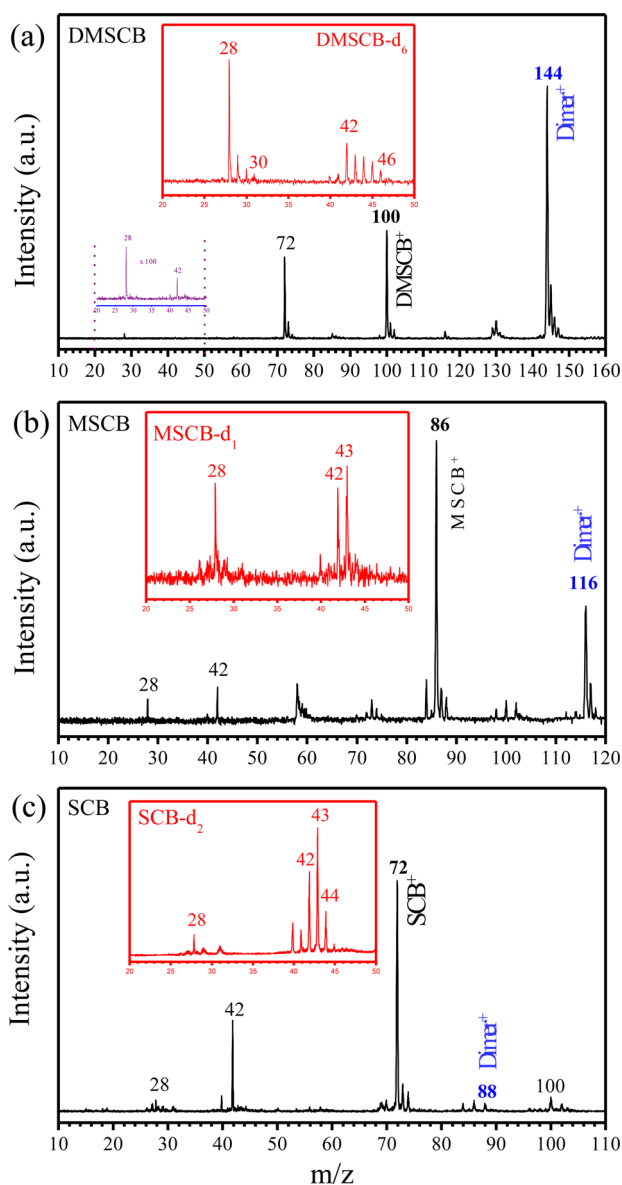
Figure 6. SPI Mass spectra (10.5 eV) of (a) 0.48 Torr DMSCB (inset: DMSCB-d_6), (b) 0.48 Torr MSCB (inset: MSCB-d_1), and (c) 0.12 Torr SCB (inset: SCB-d_2) at a filament temperature of 1200 °C.

Formation of metal silicides during Si film deposition[19,36,37] and metal carbides in the formation of diamond[38] and carbon nanotube[39] has been reported. Filament alloying shortens the filament lifetime, changes its catalytic ability, and causes contamination in the deposited films. These cause a process known as filament aging, which is detrimental to the HWCVD process. To develop a more efficient and controllable deposition process, an understanding of the filament alloying process is desirable.

The structural changes of metal filaments in Si film deposition using SiH_4 have been studied most extensively. A common observation is the growth of a silicide layer on filament surfaces.[19,36,37,40]
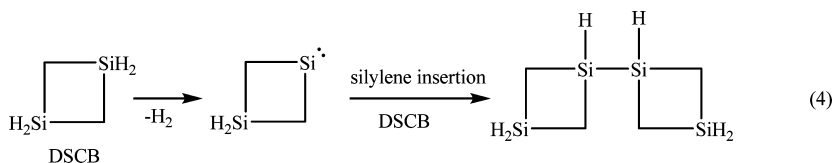
Two phases of silicide, Si-rich MSi_2 and Si-deficient M_5Si_3 (M = W, Ta), can be formed depending on the deposition time[36] and filament temperature.[37] Our group has demonstrated the formation of WSi_2 on the filament surface and a clear phase conversion to W_5Si_3 with increasing depth toward the center (Figure 7a).[40] Study of the depth profile of Si content at various deposition time shows that Si released from the $WSi_2 \rightarrow W_5Si_3$ conversion migrates to the filament center up to its solubility limit of 4% and the excessive Si reacts with W to form W_5Si_3, the only phase observed at longer times. The parabolic rate law determined (Figure 7b) provides strong support for a diffusion-controlled process. The temperature dependence of the silicide layer thickness (Figure 7c) is an illustration of the competition between the silicide formation at low temperatures and Si evaporation at high temperatures.

Much less research has been devoted to investigating filament aging in $Si_{1-x}C_x$ formation using either a SiH_4/hydrocarbon mixture or a single-source gas. When W filaments were exposed to SCB, only silicides (WSi_2/W_5Si_3) were formed.[41] However, with TMDSCB, only C and W signals were observed.[42,43] Based on the C content, graphite as well as both phases of carbides (WC and W_2C) were formed. The sharp difference in the nature of W alloys formed when using SCB and TMDSCB originates from their different gas-phase reaction chemistry.[44] As described previously, reactions involving the silylene species are the prevailing pathways in the gas phase with SCB. For TMDSCB, methyl is the dominant radical intermediate. This explains why only tungsten carbides are formed although TMDSCB itself contain Si. The comparison of the filament alloying processes with these two molecules clearly demonstrates that the nature of the radical intermediates formed from the hot-wire decomposition and subsequent reactions in the gas phase play important roles in determining the type of alloys formed on the filament.

According to the depth profile of C content (Figure 7d) for filaments exposed to TMDSCB at different temperatures (1000−2000 °C),[42] both graphite and WC formed on the surface are converted to the W_2C phase when moving into the filament interior. A rise in filament temperature significantly increases the W_2C layer thickness (Figure 7e). This is in contrast with the behavior assumed by silicides whose thickness shows an exponential decay with increasing temperature due to Si evaporation from the surface. Therefore, C evaporation from W filament surface is not significant at $T \leq 2000$ °C. More importantly, a pure W_2C or WC layer can be formed by tuning the deposition parameters. The resistance measurements and XRD analysis suggest that W filaments are fully carburized to form crystalline W_2C with a growth rate of 4.4 μm/min after 1−2 h exposure to TMDSCB at 2400 °C. Further exposure leads to the formation of the C-rich crystalline WC on the outside layer (Figure 7f).[43] The significance of this work is that what has been a process causing problematic filament aging could be used for deposition of tungsten carbides that have found many applications in heterogeneous catalysis.[45]

6. SUMMARY AND OUTLOOK

The chemistry underlying HWCVD is complex and multifaceted. In this Account, we have discussed the use of laser ionization
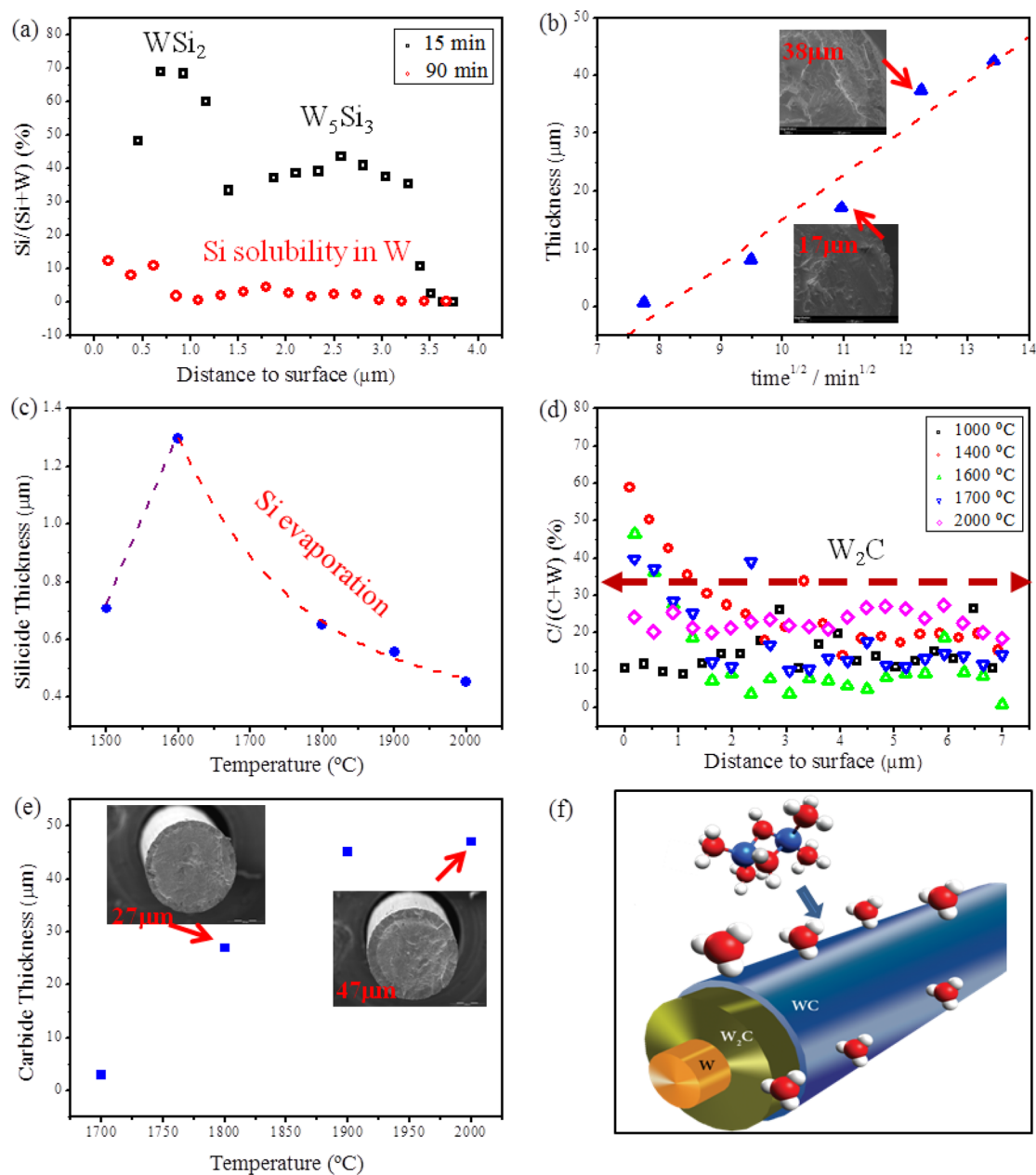

(4)

Figure 7. (a) The depth profile of Si content for aged filaments prepared using 0.1 Torr SiH$_4$. (b) The time distribution of silicide thickness at 1500 °C showing a parabolic growth law. Inset: SEM images showing the silicide layer. (c) The temperature distribution of silicide thickness. Panels a–c reproduced with permission from ref 40. Copyright 2011 Elsevier. (d) The depth profile of C content for aged filament prepared using 0.12 Torr TMDSCB. (e) The temperature distribution of carbide thickness. Inset: SEM images showing the carbide layer. (f) A schematic showing the formation of W$_2$C/WC layer on a W filament. Panels d–f reproduced with permission from refs 42 and 43. Copyright 2009 and 2013 American Chemical Society.

mass spectrometry as a powerful diagnostic tool in unraveling the complex reaction chemistry in HWCVD growth of Si$_{1-x}$C$_x$ using either open-chain alkylsilanes or cyclic mono- and di-silacyclobutane as single-source precursors. Our study of methyl-substituted silanes has shown that there is a transition in dominant reaction chemistry from silylene/silene reactions to free-radical short chain reactions with increasing number of methyl substitution. This is responsible for the observed change from Si-rich to C-rich in the deposited Si$_{1-x}$C$_x$ films as the number of Si–H bonds decreases in the four precursor molecules. Ring-opening reactions play an important role with monosilacyclobutanes, whereas disilacyclobutanes show different behavior ruled by exocylic bond cleavage. Finally, knowledge of metal silicide/carbide formation, Si/C diffusion, and Si/C

evaporation is needed to understand the filament aging process in HWCVD.

Although progress has been made in achieving a molecular-level understanding of chemical processes in HWCVD, potential challenges still exist. For instance, cyclic (di)silacyclobutanes are promising precursor molecules for the HWCVD growth of Si$_{1-x}$C$_x$ materials due to their proven ability to decompose at relatively low temperatures to produce silylene intermediates with high sticking coefficients toward the substrate surface. However, actual deposition studies using these precursors remain to be performed. This will help provide insights into the deposition process by correlation with the study on gas-phase reaction chemistry. In addition, a detailed kinetic study on the secondary gas-phase reactions important under typical deposition pressures

in HWCVD is needed for the development of a comprehensive deposition model. Further and stimulating research in this field will help achieve a rational and efficient optimization of the process

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: shiy@ucalgary.ca.

Notes
The authors declare no competing financial interest.

Biography
Yujun Shi received her B.S. and M.S. from Soochow University (Suzhou, China). After completion of her Ph.D. at the University of Western Ontario (London, Ontario), she performed postdoctoral work at the National Research Council of Canada in Ottawa on an NSERC Visiting Fellowship. She is now an associate professor in the Department of Chemistry at the University of Calgary. Her research interest involves understanding the chemical vapor deposition chemistry at a molecular level, development of laser analytical techniques, and application of laser dewetting methods for metal nanoparticle formation.

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