Thin Solid Films xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Thin Solid Films

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

Role of free-radical chain reactions and silylene chemistry in using methyl-substituted silane molecules in hot-wire chemical vapor deposition

Yujun Shi

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

ARTICLE INFO

Article history:
Received 10 October 2016
Received in revised form 1 December 2016
Accepted 6 December 2016
Available online xxxx

Keywords:
Monommethylsilane
Dimethylsilane
Trimethylsilane
Tetramethylsilane
Chemical vapor deposition
Silicon carbide
Vacuum ultraviolet laser single-photon ionization
Mass spectrometry

ABSTRACT

The reaction chemistry of four methyl-substituted silane molecules, including monomethylsilane (MMS), dimethylsilane (DMS), trimethylsilane (TriMS), and tetramethylsilane (TMS), has been studied in the hot-wire (catalytic) chemical vapor deposition (HWCVD) process, both on heated tungsten or tantalum filaments and in the gas phase. The four molecules dissociate catalytically on hot W or Ta surfaces to form $\cdot CH_3$, $\cdot H$ and H_2. In a HWCVD reactor setup where the pressure is relatively high at 8–533 Pa, two reaction mechanisms involving silylene and free radical intermediate, respectively, operate with the four precursor gases. For MMS, its reaction chemistry is characterized by the exclusive involvement of methylsilylene intermediate. Reaction products when using DMS as a precursor gas come from silylene chemistry and free-radical chain reactions. Filament temperature and pressure affect strongly the competition between the two mechanisms. Specifically, silylene chemistry dominates at low temperatures of 1200–1300 °C and a low pressure of 16 Pa, and free-radical chain reactions take over at high temperatures and pressures. With the increasing methyl substitutions in TriMS and TMS, free-radical chain reactions become predominant. A clear transition in the operating reaction mechanism from silylene chemistry to free-radical chain reactions has been shown when the number of Si—CH_3 bonds increases in the methyl-substituted silane molecules.

© 2016 Published by Elsevier B.V.

1. Introduction

In methyl-substituted silane molecules, one or more Si—H bonds in SiH_4 are replaced by Si—CH_3 connections. They can be represented by a general formula of $SiH_x(CH_3)_{4-x}$ (x = 0–3), which includes monomethylsilane (MMS), dimethylsilane (DMS), trimethylsilane (TriMS), and tetramethylsilane (TMS). Due to the existing Si—C bond and tunable Si:C ratios in the methyl-substituted silane compounds, they have been used as single-source precursors for silicon carbide thin film deposition by the technique of hot-wire chemical vapor deposition (HWCVD), also known as catalytic CVD (Cat-CVD). Among the four molecules, MMS has been mostly widely used [1–7]. Research on silicon carbide deposition from DMS [7,8], TriMS [7,9], and TMS [7,9] by HWCVD have also been reported. The structures of the produced silicon carbide thin films range from amorphous, microcrystalline, polycrystalline, to highly crystalline. The observations are in good agreement with the conclusions drawn from many other studies that the structures and properties of the deposited thin films in HWCVD depend strongly on the type of precursor gases and the deposition conditions. It is generally accepted that three processes are important in understanding the thin film growth mechanism in HWCVD: (1) the primary decomposition of precursor gas on a heated metal filament surface to form reactive species such as radicals or diradicals; (2) the secondary chemical reactions in the gas phase between the reactive species and the abundant precursor gases; (3) reactions on the substrate surfaces at relatively low temperatures of 300–400 °C, leading to thin film growth.

Despite the wide use of methyl-substituted silanes in HWCVD and the extensive characterization of deposited silicon carbide film structures and properties, their decomposition chemistry on the hot metal filament surfaces and subsequent reactions in the gas phase have been much less studied. Zaharias and Bent studied the decomposition of MMS, DMS, TriMS, and TMS on heated tungsten and rhenium filaments in the temperature range of 1000–1950 °C at a pressure of 6.7×10^{-4} Pa [7]. Si radical was detected as the main product and $\cdot CH_3$ was also observed. The Bent group also employed in-situ multiple internal reflection-Fourier transform infrared spectroscopy to characterize the bonding in the amorphous hydrogenated silicon carbide (a-SiC:H) thin films grown using the methyl-substituted silane precursors in HWCVD [6,9]. Mixed silicon hydrides (SiH_n, n = 1–3) and methyl groups were present in the a-SiC:H films deposited.

Considering the typically high deposition pressures in HWCVD, ranging from a couple of hundred milliTorr to several Torr [1,2,8,10],

E-mail address: shiy@ucalgary.ca.

http://dx.doi.org/10.1016/j.tsf.2016.12.007
0040-6090/© 2016 Published by Elsevier B.V.

Please cite this article as: Y. Shi, Role of free-radical chain reactions and silylene chemistry in using methyl-substituted silane molecules in hot-wire chemical vapo..., Thin Solid Films (2016), http://dx.doi.org/10.1016/j.tsf.2016.12.007

ARTICLE IN PRESS

our research laboratory has recently investigated the primary decomposition of four methyl-substituted silane molecules on heated tungsten and tantalum wire surfaces under collision-free conditions at a low pressure of 6.7×10^{-4} to 1.3×10^{-3} Pa [11–13], and also the gas-phase reaction chemistry [14–17] at relatively high pressures of 8 Pa to 533 Pa. This paper provides an overview of our research on the decomposition chemistry of MMS, DMS, TriMS, and TMS in the HWCVD processes to shed light on the effect of methyl substitution on the reaction chemistry both on the hot metal surfaces and in the gas phase. Formation of methyl radical and H_2 molecule from the hot-wire decomposition of the four precursor molecules will be discussed briefly. At elevated pressures of 8 Pa to 533 Pa, two main reaction mechanisms, i.e., free-radical chain reactions and reactions involving silylenes (:SiR_1R_2, $R_1, R_2 = H, CH_3$) and silenes ($H_2C = SiR_1R_2$), dominate the secondary reactions in the gas phase. It should be noted that the ground states of methyl-substituted silylenes are singlet with no unpaired electrons. The effect of precursor gas pressure and filament temperature on the competition between the two reaction mechanisms with the four methyl-substituted silane molecules will also be discussed.

2. Experimental methods

The diagnostic tool for studying the decomposition chemistry of the four methyl-substituted silane molecules on the hot metal surfaces and in the gas phase is laser ionization mass spectrometry. Two laser ionization sources, including single-photon ionization (SPI) with a vacuum ultraviolet (VUV) wavelength of 118 nm [18] and a dual SPI/LIEI ionization source incorporating both VUV SPI and a laser induced electron ionization (LIEI) [19] were used. Details of the experimental apparatus for the laser ionization time-of-flight (TOF) mass spectrometer coupled with the HWCVD sources have been described elsewhere [11,12,17]. Briefly, the products formed from the primary decomposition of MMS, DMS, TriMS, and TMS on heated W and Ta filaments were detected using a collision-free HWCVD source operating at a pressure of 6.7×10^{-4} to 1.3×10^{-3} Pa. The gas-phase reaction chemistry at relatively high pressures of 8 to 533 Pa for the precursor gases was studied using a HWCVD reactor, which is connected to the TOF mass spectrometer via a 0.15 mm pinhole. The methods of isotope labeling and chemical trapping were employed to help understand the reaction mechanism. The ionization laser source at 118 nm was generated in a nonlinear third harmonic process using the 355 nm UV output from an Nd:YAG laser in a 10:1 Ar:Xe gas mixture contained in a gas cell. All chemicals, including MMS (Gelest, 99.9%), DMS (ABCR, 97%), TriMS (Voltaix, 99.99%), and TMS (Sigma-Aldrich, 99.9 +%) were used as received.

3. Results and discussion

3.1. Formation of methyl radical and H_2 molecule by the hot-wire decomposition of methyl-substituted silane molecules

When detecting the chemical species produced from the primary decomposition of the four methyl-substituted silane molecules on heated W and Ta filaments, new peaks at *m/z* 2 and 15, representing H_2 and $\cdot CH_3$ appeared in the TOF mass spectra when the filament was turned on. The temperature dependence of the evolution of both H_2 and $\cdot CH_3$ follows an Arrhenius behavior. The activation energies for the formation of H_2 and $\cdot CH_3$ on the two filaments of W and Ta [12,13] are listed in Table 1. These activation energies are significantly lower than the bond dissociation energies of Si—CH_3 and Si—H in the same molecules (also listed in Table 1 for comparison). Therefore, it is demonstrated that the decomposition of the four methyl-substituted silane molecules on W and Ta filaments is a catalytic process. The activation energy data in Table 1 also shows that the values increase with increasing number of methyl substitution in the molecules. The activation energy for H_2 formation from TMS has not been obtained due to the low H_2 intensities produced from TMS. The use of a Ta filament results in the activation energies similar to those for W, suggesting that the formation of $\cdot CH_3$ and H_2 follows the same mechanism on both filaments. More importantly, it is noted that the determined activation energy values of 51.1–78.8 $kJ \cdot mol^{-1}$ for the formation of $\cdot CH_3$ are in a similar range to those for the H_2 formation at 58.2–93.4 $kJ \cdot mol^{-1}$, which indicates the same rate-limiting step in forming the two species. For MMS, DMS, and TriMS, the dissociation is activated by the rate-limiting Si—H bond cleavage on the W and Ta surfaces, forming methyl-substituted silyl/silylene/silylyne and H adsorbates [11–13]. As the filament temperature is increased, Si—CH_3 bond breaks to form the CH_3 radicals. Two adsorbed H atoms on metal surfaces may recombine to produce H_2 observed in the gas phase. The lack of Si—H bond in TMS leads to the highest activation energy barrier as determined. The dissociation of TMS on W and Ta surfaces occurs by the cleavage of both Si—CH_3 and C—H bonds. Our results are in agreement with the observations by Lee et al. [9] that TriMS and MMS are more reactive than TMS in forming the a-SiC:H films.

3.2. Role of silylene/silene chemistry and free-radical chain reactions in the secondary gas-phase chemistry with methyl-substituted silane molecules

The secondary gas-phase reaction chemistry with the four methyl-substituted silane molecules was studied using the HWCVD reactor setup at increased pressures ranging from 8 to 533 Pa. Table 2 summarizes the main reaction products observed using our VUV SPI laser ionization mass spectrometric diagnostic tool when 8–64 Pa of MMS, DMS, TriMS and TMS were used on both W and Ta filaments. The secondary gas-phase reaction chemistry of MMS is characterized by the reactions involving exclusively the methylsilylene intermediate, :$SiH(CH_3)$. At all filament temperatures from 1100 to 1800 °C, two major products of 1,2-dimethyldisilane (DMDS, 90 amu) and 1,3-disilacylcobutane (DSCB, 88 amu) were observed. This can be seen in a representative mass spectrum of 64 Pa of MMS at 1300 °C, shown in Fig. 1a). Using the isotope labeling with CH_3SiD_3 (MMS-d_3) and trapping of silylene using 1,3-butadiene [14], it is demonstrated that the insertion of methylsilylene, :$SiH(CH_3)$, into the Si—H bond of MMS (H—$Si(CH_3)_3$) is responsible for the formation of DMDS (Eq. (1)), whereas DSCB is formed by the dimerization of methylsilylene (Eq. (2)).

$$(CH_3)HSi: + CH_3SiH_3 \rightarrow CH_3SiH_2SiH_2CH_3 \text{ (DMDS)} \quad (1)$$

Table 1
The activation energies (E_a) for the formation of H_2 and CH_3 on heated W and Ta from four methyl-substituted silane molecules and a comparison of the bond dissociation energy (BDE) of Si—C and Si—H in the same molecules.

Molecule	E_a (CH_3)[a] ($kJ \cdot mol^{-1}$)		BDE (Si-CH_3)[b]	E_a (H_2)[c] ($kJ \cdot mol^{-1}$)		BDE (Si—H)[b]
	W	Ta	($kJ \cdot mol^{-1}$)	W	Ta	($kJ \cdot mol^{-1}$)
H_3SiCH_3 (MMS)	51.1 ± 4.0	57.3 ± 5.0	369.0	58.2 ± 2.2	75.9 ± 8.5	374.9
$H_2Si(CH_3)_2$ (DMS)	61.0 ± 4.9	59.2 ± 5.0	369.4	68.0 ± 4.5	84.5 ± 4.0	374.0
$HSi(CH_3)_3$ (TriMS)	78.8 ± 4.2	66.8 ± 3.1	368.6	74.0 ± 8.4	93.4 ± 7.2	377.8
$Si(CH_3)_4$ (TMS)	84.7 ± 4.0	72.7 ± 6.0	374.0			

[a] Ref. [12].
[b] Ref. [25].
[c] Ref. [13].

Please cite this article as: Y. Shi, Role of free-radical chain reactions and silylene chemistry in using methyl-substituted silane molecules in hot-wire chemical vapo..., Thin Solid Films (2016), http://dx.doi.org/10.1016/j.tsf.2016.12.007

Download English Version:

https://daneshyari.com/en/article/5465967

Download Persian Version:

https://daneshyari.com/article/5465967

Daneshyari.com