Formation of aminosilanes in the hot-wire chemical vapor deposition process using SiH_4 – NH_3 gas mixtures

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Dedicated to Professor Ted Sorensen on the occasion of his 75th birthday

Abstract
Vacuum ultraviolet laser single photon-ionization coupled with time-of-flight mass spectrometry has been used to detect the gas-phase reaction products from the HWCVD reactor with SiH_4 - NH_3 mixtures with various partial pressure ratios ranging from 1: 1 to 200 : 1 for NH_3 : SiH_4. The identity of the products depends strongly on the relative amounts of SiH_4 and NH_3 in the mixture. Low NH_3 content favors the production of disilane and trisilane. When the NH_3 content is high, the formation of aminosilanes becomes the primary pathway. The production of sufficient amount of NH_2 (or ND_2) radicals is found to play a key role in the competition between the two pathways. The formation of aminosilanes when using mixtures with an ammonia to silane pressure ratio greater than 49 : 1 is confirmed through the use of the isotopomer ND_3 in place of NH_3 in the gas mixtures. A stepwise amination reaction scheme, initiated by the reaction between the SiH_3 and NH_2 radicals, is responsible for the formation of aminosilanes. The effect of filament temperature on the formation of aminosilanes and di-/tri-silane has also been investigated.

Keywords: Aminosilane, hot-wire CVD, catalytic CVD, silicon nitride, vacuum ultraviolet laser single photon ionization

Introduction

Silicon nitride films have been extensively studied due to their applications as anti-reflection coatings and passivation layers in microelectronic devices.[1,2] Various chemical vapor deposition (CVD) techniques have been utilized for the deposition of silicon nitride thin films. These include thermal CVD,[3] plasma-enhanced CVD (PECVD),[2,4-6] and photo-assisted CVD.[7-9] Most commonly, mixtures of silane (SiH_4) and ammonia (NH_3) serve as the source gas for the

deposition. In the last two decades, the use of hot-wire CVD (HWCVD), also known as Catalytic CVD (Cat-CVD), to deposit silicon nitride (Si_xN_y) semiconductor thin films has attracted increasing interest[1,10] because of its ability to grow high quality films at low substrate temperatures while avoiding plasma-induced damages to the films. The technique of HWCVD involves the decomposition of a source gas on a heated metal filament to produce highly reactive radical species, which then react with each other, and with the abundant source gas molecules to generate film-growth precursor species. Ultimately, it is the abundance and identity of these growth precursors that dictates the properties of the resultant thin films. Despite the importance of understanding the gas-phase chemical processes in HWCVD, only recently has there been a focused effort in the literature to develop this understanding. Recent work by Umemoto *et al.* regarding the deposition chemistry of the NH_3-SiH_4 mixtures in the Cat-CVD processes has shown that the silyl (SiH_3) and amidogen (NH_2) radicals are the major deposition species for silicon nitride[11]. The suppression effect of SiH_4 presence in the mixtures on the NH_3 dissociation efficiency has also been demonstrated by several groups[12-14]. This is consistent with the fact that a high gas flow rate ratio of NH_3 to SiH_4 is typically needed under practical deposition conditions for silicon nitride films. However, very little is known about the formation of compounds containing direct silicon-nitrogen bond in the gas-phase in the HWCVD processes using NH_3-SiH_4 mixtures. In our study of examining the gas-phase chemical products of an NH_3-SiH_4 mixture with an NH_3 to SiH_4 partial pressure ratio of 100 : 1[15], the notable different intensity ratio of the peak at m/z = 92 to that at m/z = 62 from that assumed by pure SiH_4 samples and the observation of a peak at m/z = 76 has led us to conclude that tetraaminosilane, $Si(NH_2)_4$, is formed in the process with this mixture.

Aminosilane species have been proposed in previous studies to be very important film-growth precursors in PECVD[4] and photo-assisted CVD using excimer laser radiation at 193 nm[7]. Efforts have also been made to elucidate the mechanism of aminosilane formation in various CVD systems using mixtures of SiH_4 and NH_3. Theoretical calculation considering gas-phase reactions between SiH_4 and NH_3 revealed that silylamine, H_2N-SiH_3, the simplest aminosilane species, is the most favorable reaction product both thermodynamically and kinetically.[16] Koseki *et al.*[17] and O'Neal *et al.*[18] have shown that the insertion of silylene into N-H bond of NH_3 to form silylamine plays an important role in the pyrolysis process of the NH_3-SiH_4 mixture. In their study of silicon nitride film formation in a photo-assisted CVD involving the NH_3-SiH_4 mixture with a 185 nm radiation from a Hg lamp, Yoshimoto *et al.*[9] suggested that SiH_3 and NH_2 species, produced by the decomposition of NH_3 and SiH_4, reacted to form $SiNH_5$. Considering the fact that the formation of H_2N-SiH_3 was shown to be more thermodynamically and kinetically favourable compared to that of H_3N-SiH_2[16], it is reasonable to assign the identity of the $SiNH_5$ species which Yoshimoto observed to silylamine. Further evidence of the formation of silylamine and other silyated amines in the mercury-photosensitized reactions of SiH_4 and NH_3 was provided by Wu.[8]

In 1990, Beach and Jasinski[7] reported a detailed study of the photochemistry of NH_3-SiH_4 mixtures induced by a 193 nm excimer laser radiation. Signals from all possible aminosilanes,

$SiH_x(NH_2)_{4-x}$ (x = 0-3), were observed using mass spectrometry. It was found that increasing the amount of ammonia in the gas mixture favored the production of aminosilanes over disilane and trisilane. Their proposed mechanism for the formation of aminosilanes constitutes the stepwise amination of $SiH_{3-x}(NH_2)_x$ (x = 0-3) as shown in Eqns. (1) to (3).

$$NH_2 + SiH_{3-x}(NH_2)_x \rightarrow \ H + SiH_{2-x}(NH_2)_{1+x} \ (x = 0\text{-}2) \qquad (1)$$
$$SiH_{2-x}(NH_2)_{1+x} + H \rightarrow SiH_{3-x}(NH_2)_{1+x} \ (x = 0\text{-}2) \qquad (2)$$
$$NH_2 + Si(NH_2)_3 \rightarrow \ Si(NH_2)_4 \qquad (3)$$
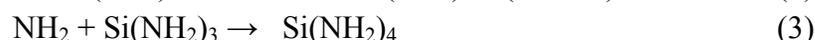
The above stepwise amination mechanism was supported by the work on the deposition chemistry for silicon nitride films from the NH_3-SiH_4 plasma reported by Smith *et al.*[4] in the same year. The gas-phase plasma chemistry was found to depend strongly on the radio-frequency (RF) power used to form the plasma. At low RF power, the dominant reaction pathway was the formation of disilane, which was attributed to the reaction of silyl radicals with each other and with silane, while ammonia acting as an inert diluent. At higher RF powers, the pathway leading to aminosilane formation became dominant. The existence of different growth regimes from NH_3-SiH_4 plasma deposition was later confirmed in an optical emission spectroscopic investigation[5]. Theoretical work has also been conducted to investigate the formation of aminosilanes. Kushner[19] showed that NH_2 is unreactive toward SiH_4, which supports the results from Beach and Jasinski, as well as their proposed mechanism.

  Though plasma CVD chemistry with NH_3-SiH_4 mixtures has been well studied, it is unclear if the same chemistry and mechanisms are taking place in the HWCVD process. Aminosilanes have been identified only recently in HWCVD,[15] and no detailed investigation into their formation mechanism has been presented. In this work, we present a more thorough discussion of the evidence in favor of the formation of aminosilane species in the HWCVD process using various SiH_4 and NH_3 gas mixtures with different partial pressure ratios to determine the experimental condition that favor their production. Results of our efforts to identify the mechanism of the aminosilane formation using deuterated ammonia (ND_3) are presented. Focus is also given on the issue if any of the radical products originating from NH_3 decomposition contribute to the formation of disilane and trisilane.

Experimental Details

Our previous experiments on detecting the reaction products from using NH_3-SiH_4 mixtures in a HWCVD reactor employed a time-of-flight mass spectrometer with an ionization source of co-existing laser induced electron impact ionization (LIEI) and a 118 nm vacuum ultraviolet (VUV) laser single-photon ionization (SPI),[14,15] i.e., the dual LIEI/SPI source. It has been shown that species with an ionization potential (I. P.) below 10.5 eV, such as Si_2H_6 and Si_3H_8, exhibit stronger peaks in the mass spectra recorded under pure VUV SPI mode, whereas the signals from

those with I.P. above 10.5 eV, e.g., H_2 and N_2, are enhanced with the dual LIEI/SPI mode. In this work, the signals from $Si_2H_6^+$, $Si_3H_8^+$ and $Si(NH_2)_4^+$ are of most interest to us. Although the I. P. of $Si(NH_2)_4$ is unknown, our experiment has shown that the signal from $Si(NH_2)_4^+$ has been enhanced by switching from the dual LIEI/SPI source to the pure SPI source, suggesting that its I. P. is below 10.5 eV. Therefore, for enhanced signals of $Si_2H_6^+$, $Si_3H_8^+$ and $Si(NH_2)_4^+$, the pure VUV SPI source coupled with TOF MS is employed in this work for the examination of aminosilane and disilane/trisilane formation.

The details of the experimental apparatus to record the VUV laser SPI / TOF mass spectra of the reaction products from a HWCVD reactor have been reported in our previous work.[20, 21] In brief, a HWCVD reactor, housing a heated tungsten filament, is incorporated by way of a 0.15 mm diameter pinhole into a high-vacuum ionization chamber for the TOF mass spectrometer (R. M. Jordan Inc.). The total pressures in the reactor are maintained at ~ 12 Torr using a mass flow controller (MFC), while those in the ionization chamber are ~ 4.0×10^{-6} Torr under working conditions. Gas-phase reaction products are continuously sampled through the pinhole, forming an effusive molecular beam. Sample molecules are ionized by a VUV photon of 10.5 eV (118 nm) in a single-photon ionization process. The 118 nm laser radiation was generated by frequency tripling the 355 nm UV output from an Nd:YAG laser (Spectra Physics, Lab 170-10). A lithium fluoride (LiF) lens was used to focus the 118 nm VUV light at the center of the ion source in the TOF MS. Ions extracted and dispersed into the 1-meter-long flight tube are detected by a microchannel plate (MCP) detector. Signals from the MCP detector are averaged over 512 laser shots before being saved to a computer for analysis. Mass spectra were collected for every minute over a ten-minute time span after turning on the filament. Filament temperatures ranged from 1500 – 2000 ºC and were monitored by a two-color pyrometer (Chino Works).

The NH_3-SiH_4 source gas mixtures under study were prepared using pure NH_3 (99.999%, BOC Gases), 1% SiH_4 in He (BOC Gases), and ultra high purity He (99.995%, Praxair). Mixtures with various partial pressure ratios were prepared in a 2.25 L stainless steel sample cylinder before being introduced into the HWCVD reactor. The composition of the NH_3/SiH_4 gas mixtures studied in this work is listed in Table 1. To develop a more thorough understanding of the formation of aminosilane and disilane/trisilane, the isotopomer ND_3 (99.99%, Spectra Gases) was used to replace NH_3, and the same experiments were conducted using the same compositions as listed in Table 1.

Table 1. Composition of the $NH_3/SiH_4/He$ mixtures studied in this work

Mixtures[a] (P(NH$_3$) : P(SiH$_4$))	P(NH$_3$) (Torr)	P(SiH$_4$) (Torr)
200 : 1	660	3.3
100 : 1	1000	10
49 : 1	660	13.5
23 : 1	380	16.3
1 : 1	20	20

[a] All mixtures are balanced with He to a total pressure of 3 atm.

Results and Discussion

The gas-phase reaction chemistry of SiH_4 in the HWCVD processes has been well studied.[22, 23] The SiH_4 molecule decomposes on the hot tungsten filament to Si and H atoms, which then react with the ambient silane molecules to form the final mix of depositing precursors such as SiH_3 and Si_2H_{2y} (y = 1 - 3).[24-27] Our previous work has shown that the principal gas-phase reaction products when using SiH_4 as a source gas in a HWCVD reactor are Si_2H_6, Si_3H_8, and H_2.[14, 15] The intensity ratio of the peaks from disilane to trisilane was found to be 2.9 : 1. This is consistent with the work reported by Nakamura *et al.*,[28] who proposed a mechanism for the formation of the higher-order silanes, initiated by the recombination reactions between SiH_3 radicals. Therefore, the detection of Si_2H_6, Si_3H_8 and H_2 in our work using SiH_4 in the HWCVD reactor strongly suggests that SiH_3 radicals are being produced in the process. Our examination of the reaction chemistry of NH_3 in the HWCVD process has found that the major gas-phase products correspond to hydrogen and nitrogen.[14, 15] The deposition chemistry of ammonia in the HWCVD process has been well characterized by Umemoto *et al.*[29] They have identified H and NH_2 radicals as the primary decomposition products of NH_3 on the hot W filaments. Signals from H_2 and N_2 were also detected using mass spectrometry. It was proposed that the H_2 and N_2 are produced mainly as a result of chamber wall reactions involving the NH_2 radicals, with minor contributions from the gas-phase reactions also originating from the NH_2 radicals. The detection of the N_2 and H_2 species in our work indicates that NH_2 radicals are being formed in our system.

To investigate the gas-phase reaction chemistry of the mixtures of SiH_4 and NH_3 in the HWCVD processes, mixtures with the partial pressure ratio of NH_3 to SiH_4 ranging from 1 : 1 to 200 : 1 were prepared and the products from using each mixture in the HWCVD reactor were detected using the VUV SPI TOF mass spectrometer. Figure 1 shows the mass spectra from

using different NH_3-SiH_4 mixtures in the HWCVD reactor at a filament temperature of 1500 °C. For comparison, the mass spectrum of 1% SiH_4 in He mixture is also shown in Figure 1.
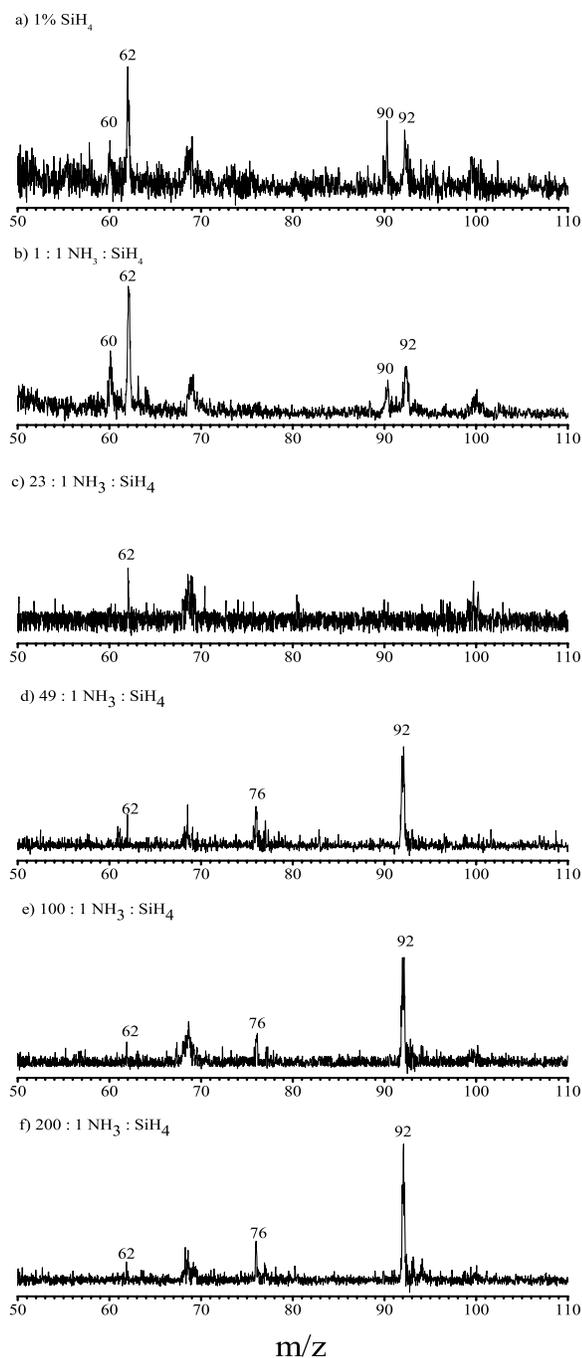
Figure 1. The 118 nm VUV laser SPI / TOF mass spectra of 12 Torr of (a) 1% SiH_4 / He; (b) 1 : 1; (c) 23 : 1; (d) 49 : 1; (e) 100 : 1; and (f) 200 : 1 NH_3 : SiH_4 in He mixture in the mass region of 50 – 110 amu at a filament temperature of 1500 °C.

For the 1 : 1 NH_3 : SiH_4 mixture, the production of disilane (m/z = 62) and trisilane (m/z = 92) was unaffected by the addition of NH_3. The intensity ratio of the peak at m/z = 62 to that at m/z = 92 was nearly identical to the ratio observed using only SiH_4. Signals in the mass region above 50 amu from the 23 : 1 NH_3 : SiH_4 mixture were generally very weak, however, the signals at m/z = 62 still dominated and that at m/z = 92 was not visible. Increasing the amount of NH_3 in the mixture further caused a significant change in the relative intensities of the two mass peaks at m/z = 62 and 92 in the spectra. For the 49 : 1 NH_3 : SiH_4 mixture, the peak at m/z = 92 became stronger than that at m/z = 62, as shown in Figure 1d). At the same time, a peak at m/z = 76 was observed with this mixture. The behavior from the more NH_3-enriched mixtures, i.e., the 100 : 1 and 200 : 1 NH_3 : SiH_4 mixtures, was very similar to those of the 49 : 1 NH_3 : SiH_4 mixture. As previously described, the study of 1% SiH_4 in He mixture revealed that the peak at m/z = 62 ($Si_2H_6^+$) was always stronger than the peak at m/z = 92 ($Si_3H_8^+$). When considering the characteristic ratio of the peak at m/z = 62 to that at m/z = 92 of 2.9 : 1 for 1% SiH_4 and the weak intensities of the peak at m/z = 62 for the 49 : 1, 100 : 1 and 200 : 1 NH_3 : SiH_4 mixtures, it is clear that the contribution of trisilane to the m/z = 92 peak intensities in Figures 1d) – 1f) is negligible. This suggests that the majority of the intensity at m/z = 92 in Figures 1d) – 1f) must originate from a new species, which was proposed to be tetraaminosilane, $Si(NH_2)_4$, in our previous work.[15] The peak at m/z = 76 was not consistently observed in our previous work due to the weak nature of this signal from using the dual SPI/LIEI source. When using the pure SPI source in this work, the signal intensity for the peaks at m/z = 92 and 76 is enhanced. It is found that the m/z = 76 peak almost always accompanies the observation of that at m/z = 92. The intensity ratio for the peak at m/z = 92 to the one at m/z = 76 ranges from 2.4 to 8.7, depending on the source mixture composition and filament temperature. Both Smith *et al.*[4] and Beach *et al.*[7] observed the peak at m/z = 76 in their work, which was assigned to be $Si(NH_2)_3^+$. Smith *et al.* attributed this peak to be from either triaminosilane ($SiH(NH_2)_3^+$) losing a H atom or tetraaminosilane ($Si(NH_2)_4^+$) losing an NH_2 fragment, whereas Beach *et al.* assigned it to be the M-1 peak from the triaminosilane parent ion. When examining the intensity of the m/z = 77 peak observed in this work, it was found to vary from 15.5 % to 119% of the intensity of the m/z = 76 peak. This is much larger than the 6.2% intensity expected from the (M+1) isotope contribution from the m/z = 76 peak. Therefore, triaminosilane, $SiH(NH_2)_3^+$, might contribute to the peak intensity at m/z = 77 observed in this work and the $Si(NH_2)_3^+$ peak observed could be the fragment ion of both triaminosilane and tetraaminosilane parent ions.

To confirm the assignments of $Si(NH_2)_4^+$ and $Si(NH_2)_3^+$, respectively, to the peak at m/z = 92 and 76 for the 49 : 1, 100 : 1 and 200 : 1 NH_3 : SiH_4 mixtures, the same experiments were repeated using an isotropically labelled source gas, ND_3, in place of NH_3 in the gas mixtures. Figure 2 shows the mass spectra in the mass region of 50 – 110 amu for a 100 : 1 mixture of ND_3 : SiH_4 and a 100 : 1 NH_3 : SiH_4 mixture, respectively, at a filament temperature of 1800 ºC.
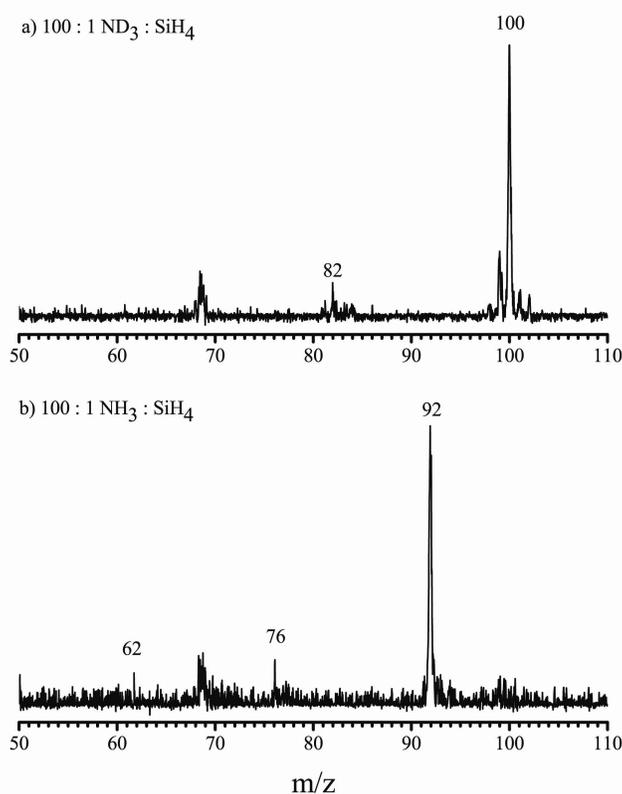
Figure 2. The 118 nm VUV laser SPI / TOF mass spectra of 12 Torr of (a) 100 : 1 ND_3 : SiH_4; and (b) 100 : 1 NH_3 : SiH_4 in He mixture in the mass region of 50 – 110 amu at a filament temperature of 1800 °C.

The $Si(NH_2)_4^+$ peak at m/z = 92 is completely absent in the spectrum obtained using ND_3. At the same time, by using ND_3, the peak at m/z = 100 demonstrates a strong increase in intensity when the filament is turned on. Clearly, the m/z = 92 peak is shifted to m/z = 100 when NH_3 is replaced by ND_3. This corresponds to the identification of the peak at m/z = 100 as $Si(ND_2)_4^+$, which confirms our assignment of the m/z = 92 peak as $Si(NH_2)_4^+$. Simultaneously, the m/z = 76 peak observed with NH_3 shifts to m/z = 82 when ND_3 is used instead, indicating that the peak at m/z = 82 is from $Si(ND_2)_3^+$, confirming our assignment of the m/z = 76 peak with NH_3 to $Si(NH_2)_3^+$. It is noted that in the mass spectra shown in Figure 2a) with the 100 : 1 ND_3 : SiH_4 mixture, peaks with mass separation of 1 amu from the two main peaks at m/z = 82 and 100 were also observed, but relatively weakly, indicating some isotope scrambling for the two peaks. This is attributed to the ND_2H isotope impurities in the ND_3 source gas, which was confirmed from the existence of a mass peak at m/z = 19 in our room-temperature mass spectrum of the 50% ND_3 gas sample. If the parent triaminosilane peak, $SiH(NH_2)_3^+$, contributed to the peak intensity at m/z = 77, the peak should be shifted to m/z = 83 or 84 upon replacing the NH_3 with ND_3 isotopomer. These two mass peaks are the isotope peaks of the $Si(ND_2)_3^+$ at m/z = 82. However, the intensities of the m/z = 83 and 84 peaks were found to be 19% – 83% and 18% – 118%,

respectively, of the intensity of the m/z = 82 peak. This suggests that triaminosilane is likely formed in the system. Our experiment using ND_3 to replace NH_3 in the 100:1 NH_3:SiH_4 mixture clearly demonstrates that the peaks at m/z = 76 and 92 originate from the $Si(NH_2)_3^+$ and $Si(NH_2)_4^+$ species, and more importantly, all the H atoms in the two species come from the NH_3 component in the mixture. This is consistent with the stepwise amination mechanism proposed by both Beach *et al.*[7] and Smith *et al.*[4] As represented by Eqn. (1) with x = 0, the reaction between SiH_3 and NH_2 to form SiH_2NH_2 constitutes the first step in the stepwise mechanism. The discussions at the beginning of this section have clarified that the two radical reactants in this first step, i.e., NH_2 and SiH_3, are being produced in the HWCVD reactor using the two components in the mixture separately. Therefore, the formation of tetraaminosilane in our HWCVD reactor with the NH_3/SiH_4 mixtures is possible through the stepwise amination mechanism represented by Eqns. (1) – (3).

In the theoretical simulations of the gas-phase processes in the rare gas-silane-ammonia plasma system, Kushner showed that the production of NH_2 in sufficient densities from NH_3, Eqn. (4), is the rate-limiting step in producing the aminosilanes.[19]

$$NH_3 \rightarrow NH_2 + H \qquad\qquad (4)$$

Results from reports by several groups[2, 5, 6] have provided clear support to the argument that NH_2 radical abundance is the key determinant in the formation of tetraaminosilane in the NH_3-SiH_4 plasma systems. This also explains the clear trend in the change of the intensity ratios of the peak at m/z = 62 to that at m/z = 92 for the mixtures of 200 : 1, 100 : 1, 49 : 1, 23 : 1 and 1 : 1 NH_3 : SiH_4 content, as illustrated in Figure 1. When ammonia is present in equal proportion to silane, aminosilane production is not observed and the intensity ratio of the peak at m/z = 62 to that at m/z = 92 is virtually identical to that observed when ammonia is absent. This indicates that the formation of disilane and trisilane is still predominant in the 1:1 NH_3:SiH_4 mixture. When the ammonia content is 49 times that of the silane content in the mixture, the production of tetraaminosilane becomes so significant that the peak at m/z = 92 is actually much stronger than the peak at m/z = 62. The production of tetraaminosilane is more pronounced as the proportion of ammonia increases, as evidenced by the increase in the intensity ratio of the peak at m/z = 92 to that at m/z = 62 in the 49 : 1 to 200 : 1 NH_3 : SiH_4 mixtures. These results are consistent with the proposed formation mechanism, whereby production of NH_2 radicals from NH_3 decomposition acts as the limiting factor in aminosilane formation. As shown in our previous work regarding the interplay of the NH_3 and SiH_4 components in the gas-phase reaction chemistry in HWCVD, by raising the amount of NH_3 in the mixtures, the decomposition efficiency of NH_3 increases[14]. This, in turn, results in the production of more NH_2 radicals and consequently more tetraaminosilane will form. Beach and Jasinski noted in their work of photochemistry from the 193 nm laser photolysis of SiH_4-NH_3 mixtures that increasing the ratio of ammonia to silane in the mixture favors production of the higher aminosilanes at the expense of disilane and trisilane formation. They observed that disilane production dominates the

product spectra for the 1 : 1 and 10 : 1 NH_3 : SiH_4 mixtures, and its formation was not quenched even at a 49 : 1 NH_3 : SiH_4 ratio. This is good agreement with our observations; although not dominant, the disilane signals were present with a mixture having a 49 : 1 NH_3 : SiH_4 ratio, as shown in Figure 1d). In our experiments, the disilane signals were observable even at an ammonia to silane ratio of 200 : 1. It appears that there is an active competition between the two reaction pathways. Formation of disilane and trisilane dominates unless there is a great excess of NH_3 molecules, at which time aminosilane production becomes the dominant pathway.

   Figure 3 shows the mass spectra from using different ND_3-SiH_4 mixtures in the HWCVD reactor at a filament temperature of 1500 °C.
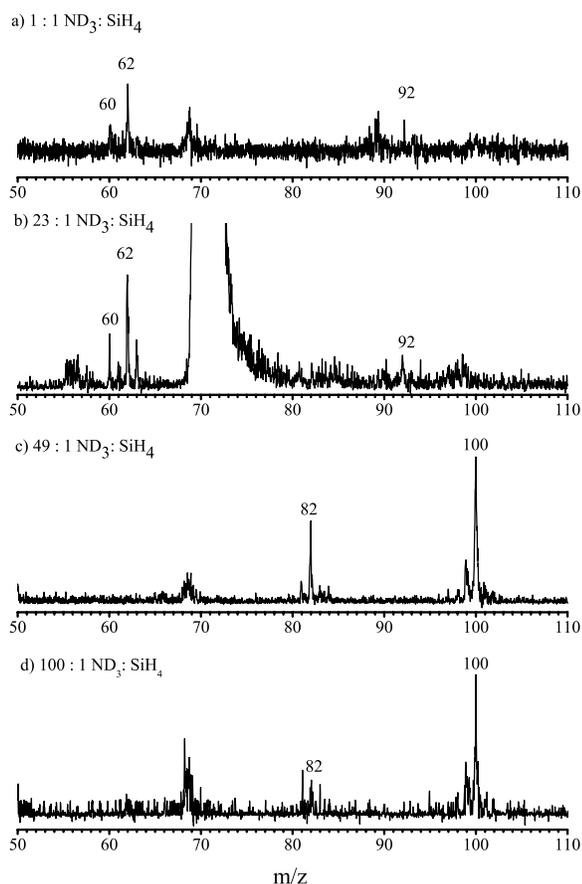
Figure 3. The 118 nm VUV laser SPI / TOF mass spectra of 12 Torr of (a) 1 : 1; (c) 23 : 1 ND_3 : SiH_4; (d) 49 : 1; and (e) 100 :1 ND_3 : SiH_4 in He mixture in the mass region of 50 – 110 amu at a filament temperature of 1500 °C.

   Clearly, the mixtures with lower ND_3 content, such as those of the 1 : 1 and 23 : 1 ND_3 : SiH_4 mixtures, show predominantly the formation of disilane (m/z = 62) and trisilane (m/z = 92), with no observation of the peaks from $Si(ND_2)_3^+$ (m/z = 82) and $Si(ND_2)_4^+$ (m/z = 100). For the 23 : 1

ND_3 : SiH_4 mixture, a strong and broad peak centered at m/z = 70 was observed in the mass spectra recorded at different temperatures. This peak is overloaded in Figure 3b) and is always accompanied by relatively weaker but broad peaks at m/z = 28 and 56. The intensities of these peaks decay very quickly with increasing filament-on time for each temperature run. They could be from the Si/Si_2 or Si_xN_y species, but their true identities and how they are formed need a more detailed investigation. As shown in Figures 3c) and 3d), the formation of tetraaminosilane, represented by the peaks at m/z = 82 and 100, takes over for the mixtures with higher NH_3 content (the 49 : 1 and 100 : 1 ND_3:SiH_4). The change in the reaction chemistry from the formation of disilane and trisilane to that of the aminosilane with increasing NH_3 content in the mixture is further confirmed.

Additional support for the formation of tetraaminosilane in the HWCVD processes with NH_3-SiH_4 mixtures was gained by examining the behavior of the peaks at m/z = 62, 92 (using NH_3) and at m/z = 82, 100 (using ND_3) as a function of the filament temperature. As shown in Figure 4, the peak intensities at m/z = 62 and 92 from the 1 : 1 NH_3 : SiH_4 mixture decreased with increasing filament temperature.
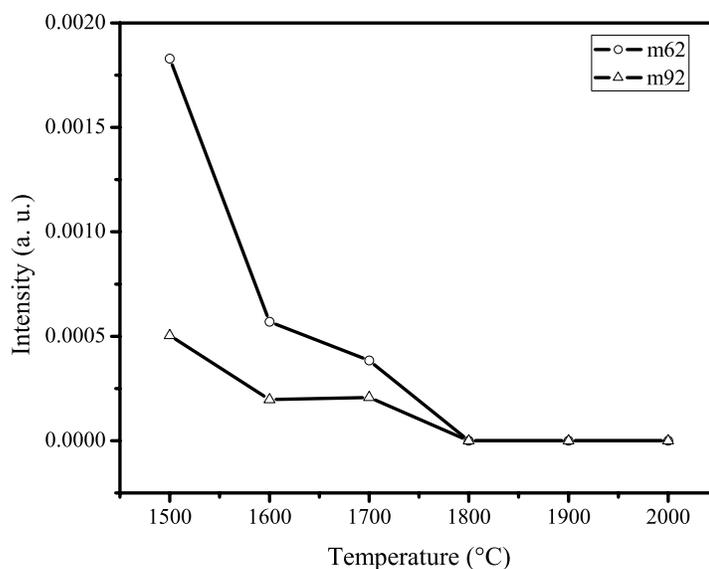
Figure 4. The distribution of the peak intensities at m/z = 62 and m/z = 92 for the 1 : 1 NH_3 : SiH_4 mixture versus the filament temperature.

For the 100 : 1 NH_3 : SiH_4 mixture, the intensity of the peak at m/z = 92 first increased with temperature and reached a maximum at 1800 °C. This is shown in Figure 5a). The intensity distribution for the peak at m/z = 62 from the 100 : 1 NH_3:SiH_4 mixture is too weak to be plotted. The difference in the intensity distribution with filament temperature for the same peak at m/z = 92 with different mixtures is due to the fact that it is from different origins. As has been

discussed before, this peak from the 1 : 1 NH_3 : SiH_4 mixture corresponds to trisilane, characteristic of silane chemistry, and the same mass peak from the 100 : 1 NH_3 : SiH_4 mixture is predominantly from tetraaminosilane. Not surprisingly, as illustrated in Figure 5b), the temperature distribution for the peak at m/z = 100 representing $Si(ND_2)_4^+$ from the 100 : 1 ND_3 : SiH_4 mixture shows similar behavior to that of the one at m/z = 92 ($Si(NH_2)_4^+$) from the 100 : 1 NH_3:SiH_4 mixture. The existence of an optimum filament temperature for the formation of aminosilane is a result of the balance for the opposite behavior of the NH_2 and SiH_3 radicals, the two initial reactants, with filament temperature.

As shown before, the intensities of disilane and trisilane formed from SiH_3 radicals showed a decrease with increasing filament temperature. The decrease of the SiH_3^+ signal intensity with temperature has also been demonstrated by Tange *et al.*[27] Umemoto *et al.*[29] has shown that the NH_2 radical intensity grows with filament temperature, and this is confirmed in our previous work with 50% NH_3 in the HWCVD reactor.[14]
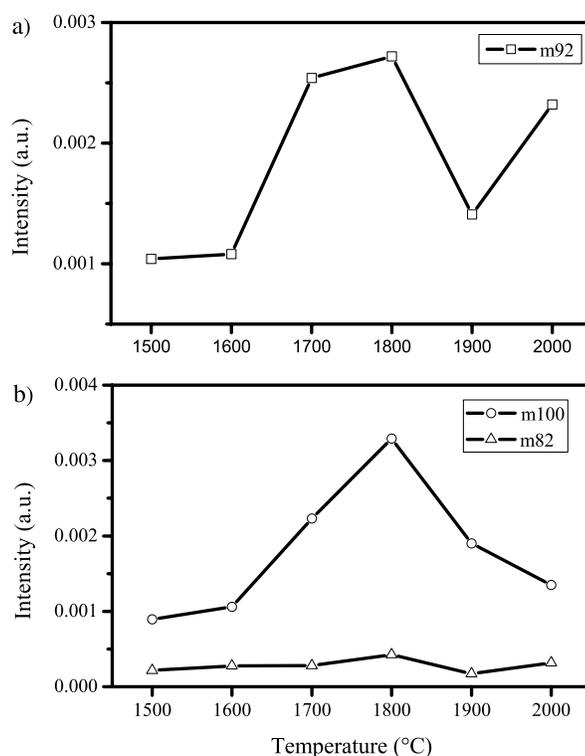
Figure 5. The distribution of the peak intensities at (a) m/z = 92 for the 100 : 1 NH_3: SiH_4 mixture; and (b) m/z = 82 and 100 for the 100 : 1 ND_3: SiH_4 mixture versus the filament temperature

An important question to be addressed in studying the gas-phase reaction chemistry of SiH_4-NH_3 mixtures in HWCVD is whether or not there is any cross-talk between SiH_4 and NH_3 molecules and their respective filament decomposition products during the formation of disilane and trisilane. Based on the fact that these two species are observed even when NH_3 is absent, it is believed that the H atoms in disilane and trisilane originate from SiH_4 molecule itself. If this is true, then even with ND_3 replacing NH_3 in the source gas mixtures, the disilane and trisilane species should still appear at m/z = 62 and 92, rather than be shifted to m/z = 62 + m (m = 0 − 6) and 92 + n (n = 0 − 8), respectively. Examination of the mass spectra of 1 : 1 and 23 : 1 ND_3 : SiH_4 mixture in Figure 3 shows that this is indeed the case. This clearly demonstrates that the disilane and trisilane production from silane or silane-ammonia mixtures occurs without interference or interaction with ammonia.

Conclusions

Gas-phase reaction products from the HWCVD reactor with SiH_4-NH_3 mixtures of various partial pressure ratios ranging from 1 : 1 to 200 : 1 for NH_3 : SiH_4 have been examined using VUV SPI / TOF mass spectrometry. When the two components are present in equal amount, the formation of disilane and trisilane dominates. The two mass peaks appear in approximately the same amounts when compared with those for the 1% SiH_4 in He sample. Increasing the amount of ammonia in the mixture causes a shift in the reaction pathway from disilane and trisilane production toward aminosilane formation. When NH_3 is present in a 49 : 1 ratio to SiH_4, aminosilane dominates in the reaction products. The identities of the $Si(NH_2)_4^+$ and $Si(NH_2)_3^+$ were confirmed by examining the products from mixtures with the isotopmer ND_3 replacing the NH_3 component. Using isotopically labeled ND_3, it has also been shown that the H-atoms in the aminosilane species come solely from NH_3. This is consistent with the formation mechanism of aminosilanes by way of stepwise amination reactions between SiH_3 radicals originating from SiH_4 decomposition and NH_2 radicals from NH_3 decomposition. No interference or interaction with ammonia is found in the formation of disilane and trisilane.

The production of sufficient amount of NH_2 (or ND_2) radicals plays a key role in the competition between the two pathways. Insufficient NH_2 densities will result in the formation of disilane and trisilane species, since the SiH_3 radicals produced from SiH_4 decomposition will react with each other, rather than with the NH_2. High NH_2 densities favor aminosilane formation. The presence of SiH_4 suppresses NH_3 decomposition, and the suppression extent is reduced when the NH_3 content is high. Therefore, it is necessary to have a large excess of NH_3 in the gas mixture to ensure good decomposition efficiency and NH_2 production to promote aminosilane formation. The optimum filament temperature for aminosilane formation is found to be 1700 to 1800 °C, whereas low filament temperatures favor the formation of disilane and trisilane. It should be possible to select experimental conditions that maximize formation of

either aminosilanes or di-/tri-silane species through adjustment of the source gas composition and the filament temperature.

Acknowledgements

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