

Spectroscopic Investigation of the Synthesis of Thin Silicon Nitride Films on Silicon Single-Crystal Wafers via Ammonia-Assisted Pyrolysis of Organosilicon Polymers

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Thin layers of α -Si₃N₄ were synthesized by the pyrolysis of thin films of poly(methylsilane) (PMS) and poly(dimethylsilane) (PDMS) spin-coated on silicon single-crystal wafers and via deposition of the volatile species resulting from the thermal cracking of the bulk precursor in the presence of ammonia. The process was monitored by FT-IR spectroscopy. The reaction between NH₃ and PMS begins at 200 °C with the slow production of a slightly cross-linked product involving Si₃N knots. Extensive amination of PMS occurs on pyrolysis at 300 °C, under 5–10 Torr NH₃ overpressure. The product exhibits IR bands characteristic of both a silazane and an aminosilane species, which are presumably formed by Si–H and N–H heterodehydrocoupling. Between 200 and 450 °C, this cross dehydrocoupling reaction competes very effectively with the Kumada rearrangement. Significant loss of carbon occurs from the resulting poly(carbosilazane) between 500 and 600 °C. Prolonged curing under NH₃ at 300 °C, to remove all Si–H groups and to give a densely cross-linked polysilazane, suppresses the Kumada rearrangement, and negligible carbon loss occurs on raising the pyrolysis temperature to 700 °C. Although the main product is still α -Si₃N₄, there is an increased amount of residual carbon.

Introduction

Important applications of monolithic Si₃N₄ involve the formation of films or coatings such as (i) membranes for X-ray masks used in synchrotron radiation lithography,^{1,2} (ii) thin dielectric layers in metal–nitride–oxide–semiconductor (MNOS) and nonvolatile memory devices,³ (iii) inversion layers in solar cells,⁴ and (iv) the gate dielectric in bulk and thin film transistors (TFTs).⁵ For these electronic applications, Si₃N₄ is obtained via chemical vapor deposition (CVD).⁶ The processing of plastic polymeric precursors can be adapted easily to the production of coatings and membranes, but specific requirements have to be met for the synthesis of electronic-grade layers, with respect to purity, homogeneity, and thickness control. The use of organosilicon precursors that already contain the framework of the ceramic material opens the possibility for lower processing temperatures, an essential factor in minimizing interlayer outdiffusion, mismatches with the substrate

thermal expansion coefficient, and temperature-induced changes in the shape of crystallinity of the substrate.⁷

Polysilazanes, poly(carbosilanes) (PCS), and polysilanes are being used in the production of silicon nitride. The main focus is on polysilazanes, because they already contain the nitrogen required for Si₃N₄ formation.⁸ Considerable information has been published on the thermal cross-linking, thermal decomposition, and pyrolysis of different polysilazanes under inert atmospheres.^{9–17} For example, pyrolysis of poly(hydridochlorosilazanes) under an inert atmosphere leads to retention of the nitrogen from the silazane group, while the facile cross-linking of the Si–H function results in

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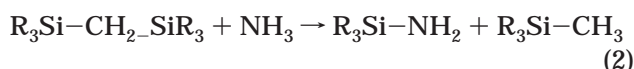
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increased ceramic yields of the carbonitride product.¹⁸ Intimate mixtures of Si₃N₄/SiC nanosized powders have been produced by pyrolysis of polysilazane/poly(carbosilane) mixtures, and the initial Si–N and Si–C bonds in the precursor were retained.¹⁹ As a general rule, carbon removal from the organic substituents on silicon is not complete and SiC/Si₃N₄ mixtures are usually obtained. To minimize the amount of residual carbon, pyrolyses have been performed under ammonia, and silicon nitride and oxynitrides have been produced from carbon-containing precursors.^{20–23} Because the Si–N bond is stronger than is the Si–C bond ($D_{\text{Si-N}} = 420$ kJ/mol and $D_{\text{Si-C}} = 370$ kJ/mol),²⁴ carbon/nitrogen exchange is favored thermodynamically at high temperatures. The mechanism of the exchange reactions involving cleavage of Si–C bonds is not clear. The alkyl (aryl) substituents on silicon are usually regarded as nonlabile groups in typical bench chemical reactions,^{25,26} but the situation changes at the higher temperatures used for pyrolyses. In an ammonia atmosphere, a cleavage reaction can occur (eq 1), whereas exchange of the methylene bridges in poly(carbosilane) can result from the reaction shown in eq 2.²⁷



Amination of poly(carbosilanes) was reported in 1985.²⁸ Seyferth's group²⁹ has used polysilazanes for pyrolyses under N₂, N₂/H₂, or NH₃, while monitoring the C/N ratio in the final materials. Pyrolysis of ethylsilazane in ammonia led to almost complete removal of carbon from the silicon nitride product.³⁰ Silicon nitride containing less than 2% carbon has been synthesized from a vinylic polysilane precursor.³¹

Nitrogen concentrations in the doping range of 10¹⁵–10¹⁸ atoms/cm³ have been produced in thin SiC films synthesized from PMS under a low partial pres-

sure of NH₃.^{32,33} In this case, the Kumada rearrangement may follow a specific pathway induced by the facile heterolytic thermal dissociation of the Si–H bond; i.e., silylene insertion is favored over a radical mechanism such as that proposed for poly(dimethylsilane).^{34,35} The reactivity of the Si–H bond in PMS toward NH₃ leads to dehydrocoupling occurring at 10 atm combined pressure of NH₃ and methylsilane. The resulting poly(methylaminosilane) affords a mixture of SiC and Si₃N₄ after pyrolysis under nitrogen.³⁶ The rearrangement of PMS into PCS at 200–450 °C makes PMS a good precursor to Si₃N₄, since PCS has been reported to form silicon nitride by reactive pyrolysis under NH₃.³⁷

Experimental Section

PMS was prepared as described in detail previously,³⁸ viz., sodium dehalocoupling of methylchlorosilane and the removal of residual chlorine by reaction with LiAlH₄. Polymerization of the Wurtz-coupled prepolymer with DMZ was followed by subsequent pyrolysis of the resulting polymers as bulk samples and as thin films deposited on [100]-oriented Czochralski-silicon single-crystal wafers doped with boron and with resistivities of 0.1–10 Ω cm. Scanning electron microscopy (SEM) and ESCA (electron dispersive X-ray analysis, EDX, and X-ray photoelectron spectroscopy, XPS) were used in characterizing the thin films. The use of milligram-scale samples (as thin coatings) for the ceramic films provided a more reliable approach to the analysis of equilibrium states since diffusion-limited processes in the bulk materials (such as solvent evaporation,³⁹ diffusion to the reaction center in the solid, or outdiffusion of the gaseous products formed during pyrolysis) were minimized. In addition, better resolution of the bands was obtained when the samples were analyzed by IR spectroscopy. The pyrolyses were performed in a quartz tube placed in a Lindberg single-zone programmable furnace equipped with a Eurotherm PID temperature controller working up to 1100 °C and providing an accuracy of ±1 °C at 1000 °C. Purified NH₃ from Matheson was passed immediately prior to use through a column (1.5 m in length, 3 in. in diameter) of KOH and a mixture of molecular sieves 3–4 at flow rates of 10–200 mL/min. Pure NH₃ or mixtures of UHP Ar/NH₃ were used as flowing gas phases during the pyrolyses. FT-IR spectra were recorded on a Bruker IFS-48 spectrometer equipped with a microscope, DTGS detector, and a Sony Trinitron PVM 1340 color monitor for spectral display. TGA/DTA analyses were performed on a Seiko 200 instrument.

Results and Discussion

Reactions in the Range of Room Temperature to 300 °C. At room temperature, no reaction was observed between NH₃ and spin-coated films of PMS on any of the tested substrates. Since some comparatively low-temperature reactions had been previously observed

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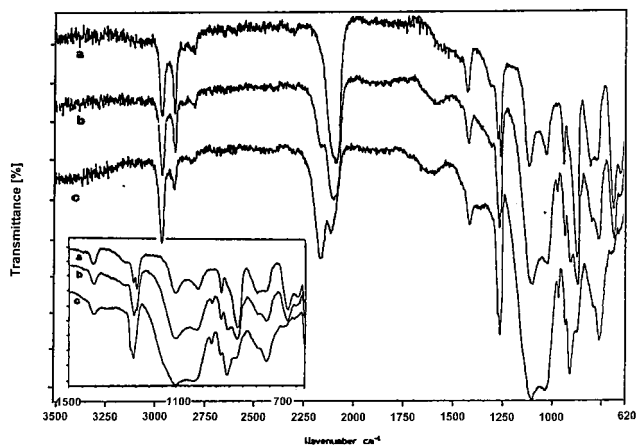


Figure 1. FT-IR spectra of a thin film of PMS exposed to NH_3 at 150°C after oxidation at room-temperature for (a) 2 min, (b) 3 min, and (c) 10 min (see inset for expanded region $1500\text{--}620\text{ cm}^{-1}$). Note changes in spectra a–c for the $\delta_{\text{as}}(\text{Si-CH}_3)$ ($1270\text{--}1240\text{ cm}^{-1}$), O-Si-C (967 cm^{-1}), $\nu(\text{Si-N})$ (870 cm^{-1}), and $\nu(\text{Si-C})$ (796 cm^{-1}) vibrations.

for a vinylic system,³¹ further analysis was performed in search of any hidden effects such as the formation of small amounts of Si_3N cross-link sites. The IR spectra exhibit essentially the same features as those obtained in an earlier study of the oxidation of the starting polymer.⁴⁰ The growth in the intensity of the band around 1000 cm^{-1} ($\nu_{\text{as}}(\text{Si-O-Si})$) suggests a major reaction involving the formation of siloxane. The broadness and band splitting is characteristic for polymer species, while the maximum intensity at 1106 cm^{-1} is associated with mobility of the chain on the silicon substrate. This results in predominantly absorption of the oxygen bridges in the polymer onto interstitial sites at the silicon surface. The emergence of the band at 908 cm^{-1} ($\nu_{\text{as}}(\text{Si-O-Si})$) is related to the same reaction involving the formation of siloxane. The broadness and band splitting is characteristic for polymer species, while the maximum intensity at 1106 cm^{-1} is associated with mobility of the chain on the silicon substrate. This results in a predominant adsorption of the oxygen bridges present in the polymer onto interstitial sites at the silicon surface. The emergence of the band at 908 cm^{-1} ($\delta(\text{Si-O})$), and especially that at 967 cm^{-1} ($\delta(\text{O-Si-C})$), which appears at higher degrees of oxidations, confirms this observation. The interpretation of the IR spectra led us to believe that there is no reaction at room temperature between the PMS and ammonia and it may well be the vinyl functionality that created the difference observed in ref 31.

A series of IR spectra were measured on 50 mg samples, which were kept at 150°C for 2.5 h under a flow of NH_3 (100 N mL/min) and subsequently subjected to slow oxidation at room temperature (Figure 1). Some minor changes compared to the oxidation of the “green” polymer were detected for this series, e.g., in the $1500\text{--}700\text{ cm}^{-1}$ range (inset Figure 1) for the material exposed to NH_3 at 150°C . The changes include the appearance of new, but low intensity, bands in the $1000\text{--}750\text{ cm}^{-1}$ region. In addition, the $\delta_{\text{as}}(\text{Si-CH}_3)$ band at 1247 cm^{-1} exhibits two significant differences compared to the IR

spectra of PMS pyrolyzed in an inert atmosphere at 150°C and that of the unoxidized polymer at room temperature. First, instead of the expected split for the $\delta_{\text{as}}(\text{CH}_3)$ band,⁴¹ a new band develops at 1270 cm^{-1} . This new band may be assigned to the presence of (N)Si- CH_3 groups, based on a similar shift toward higher wavenumbers that is usually observed in the case of substituents with electron-withdrawing properties. Second, the ratio of the intensities of the $\nu_{\text{s}}/\nu_{\text{as}}(\text{C-H})$ stretches of the methyl groups at 2897 and 2965 cm^{-1} has an abnormally low value for siloxane species. Moreover, the intensity (normalized with respect to the $\nu_{\text{as}}(\text{C-H})$ band) of the SiH_2 deformation at 930 cm^{-1} is reduced at the completion of the oxidation process, while the bands at 796 and 870 cm^{-1} , which appear during the reaction of PMS with NH_3 , disappear during the oxidation cycle. These last effects are associated with oxidation or hydrolysis of Si-N bonds, which lead to the disappearance of the $\nu_{\text{as}}(\text{N-Si-N})$ and the out-of-phase $\nu(\text{C-Si-N})$ modes, respectively. The N-Si-N groups result from $=\text{Si}(\text{NH}_2)_2$ groups formed by amination of terminal SiH_2 groups in the precursor. All these changes can be explained by a slow coupling reaction between the Si-H, or SiH_2 bonds, and the N-H bonds, to give (N)Si- CH_2X ($\text{X} = \text{H}, \text{SiR}_3$) groups. The change in the C-H bond polarity associated with the presence of the electronegative nitrogen attached to silicon is probably responsible for the decrease in the intensity of the symmetric C-H stretch. This was previously observed during oxygen insertion into the silicon backbone of PMS.⁴⁰ The extent of the coupling reaction presently observed at 150°C is still very small compared to the dehydrocoupling reaction detected at higher temperature between the Si-H and N-H bonds in vinylpolysilazane ($-\text{SiViH-NH-}$) or ($-\text{SiMeH-NH-}$)_n precursors, where Vi represents a vinyl group.⁴²

Pyrolysis of PMS at 200°C for 20 h led to the development of a strong band at 1000 cm^{-1} instead of a $\nu(\text{Si-N})$ mode near 950 cm^{-1} (Figure 2). This new band is assigned to a mixed Si-O-N phase, as suggested by the FT-IR data obtained for thin films of Si/O/N alloys⁴³ and for the oxidized thin film samples of PMS.⁴⁰ This assignment is supported by the following observations: (a) The development of the band at 1000 cm^{-1} is associated with a decrease in the growth of the Si-O-Si band at $1100\text{--}1050\text{ cm}^{-1}$ band and with a reduction in the final intensity of the Si-O-Si band. (b) There is a decrease of the 967 cm^{-1} band, which is characteristic of a high degree of oxidation of PMS. (c) There is a shift of the $\delta_{\text{s}}(\text{Si-CH}_3)$ absorption from 1250 to 1270 cm^{-1} (see above). These changes can be attributed to a diminished concentration of O-Si-O groups, compared to that observed in oxidized PMS, and to a substantial concentration of N-Si-O groups.

The lability of the Si-N bond toward oxidation and hydrolysis during the CVD formation of “soft-vacuum” silicon (oxy)nitride layers usually led to a higher oxygen content in the coating.⁴⁴ This type of contamination is

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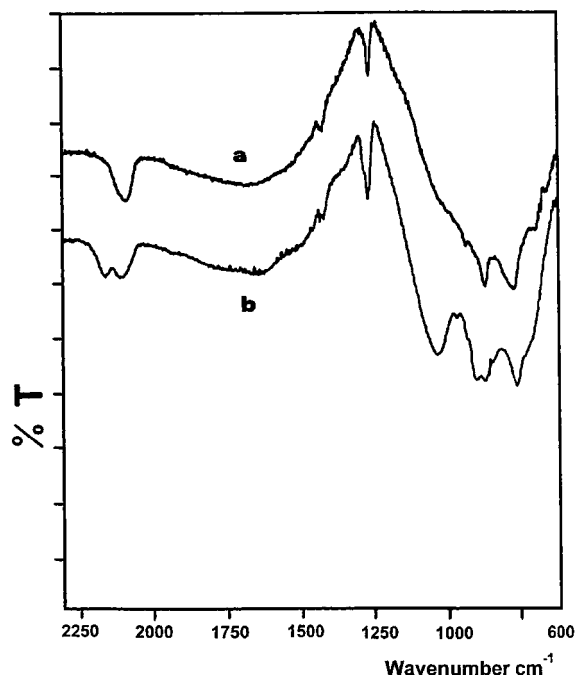


Figure 2. FT-IR spectra of PMS following reaction with NH_3 at 200 °C for 20 h. Note the split of $\delta_s(\text{Si}-\text{CH}_3)$ mode at 1270 cm^{-1} indicating formation of $(\text{N})\text{Si}-\text{CH}_3$ groups and leading to a weaker absorption at 967 cm^{-1} . The broad band at 1000 cm^{-1} is assigned to a SiO_xN_y product.

partly due to the higher activation energy for the nitridation reaction compared to oxygen incorporation at temperatures below 300 °C.⁴⁵ It is also known that the lability of the Si-N bond in polymeric precursors toward traces of moisture is responsible for oxygen incorporation into the polymer and, ultimately, oxygen contamination of the pyrolysis products.⁴⁶ This effect is a considerable limitation to the use of the low-temperature reaction of PMS with NH_3 as a cross-linking process of the polymer. The presence of adventitious oxygen in the samples reacted at temperatures below 300 °C could not be avoided, and results similar to those obtained during CV deposition of silicon nitride were observed. In the CVD process, the temperature of the substrate was increased to 350 °C in order to counter the oxidation.

Reactions in the 300–700 °C Range. A major change in the reaction of PMS with NH_3 occurs above 300 °C, as evidenced by the appearance of a characteristic N-H absorption in the FT-IR spectrum at 3397 cm^{-1} and the DTA/TGA scans (Figure 3). DTA (Figure 3b) reveals an exothermic process between 300 and 400 °C during the pyrolysis under NH_3 , which is not present in the pyrolysis under an inert atmosphere; and the TGA measurements show that a different pathway occurs under NH_3 compared to pyrolysis under Ar (Figures 3a and 4, respectively). A major weight loss occurs in the TGA curves when the reaction is performed under NH_3 at 300–400 °C, and an unusual increase in weight is observed in the 600–700 °C temperature range (Figure 3a). A strong IR absorption due to ν_{NH} appeared at 3397 cm^{-1} in the FT-IR spectrum at 300 °C, substantiating the occurrence of an amination

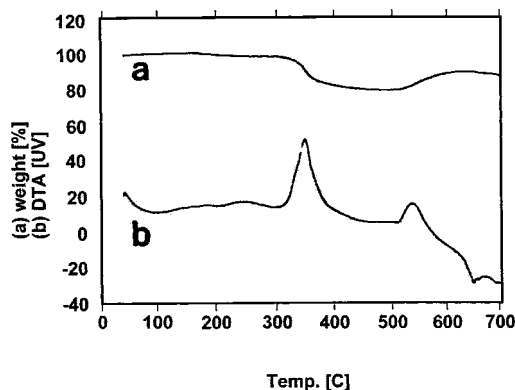


Figure 3. (a) TGA and (b) DTA data for the PMS precursor during reactive pyrolysis under NH_3 .

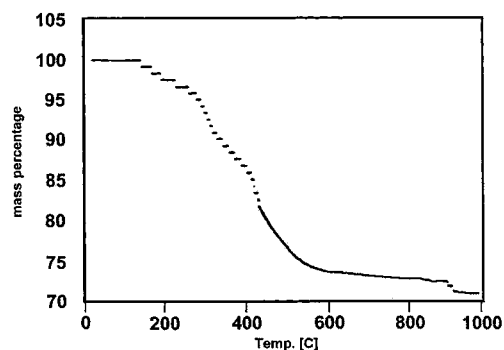


Figure 4. TGA analysis of the PMS precursor during pyrolysis under the inert (N_2) atmosphere.

process leading to the formation of silazane rather than aminosilane species.⁴⁷ The formation of Si_3N cross-link sites by NH_3 curing at low temperature was found to inhibit the rearrangement of PMS to PCS. A sample of PMS exposed to NH_3 for 10 h at 300 °C (heating rate 2 °C/min) showed no IR evidence of Si-H bonds.⁴⁹ Pyrolysis of this sample up to 1100 °C was monitored by IR spectroscopy (Figure 5), and the lack of absorption at 1356 cm^{-1} over the whole temperature range indicates no formation of PCS via the Kumada rearrangement. Instead, a strong broad IR absorption between 1200 and 900 cm^{-1} was observed (Figure 6), assigned to a Si-O-N-containing material. Residual hydrogen appears to be bonded mainly as NH_x groups. This is different from the usual absorption observed at 840 cm^{-1} in CVD-deposited layers, characteristic of a distorted trigonal site for nitrogen in the Si_3N_4 lattice.^{50,51} The presence of the oxidized material is due, probably, to some hydrolysis during the extended low-temperature reaction with NH_3 . The 1200 cm^{-1} band is assigned to the presence of a silicon oxycarbide component.

A bulk sample processed similarly exhibited the ^{29}Si MAS NMR spectrum showing resonances for Si_3N_4 (–50 ppm) and SiON impurity (–100 ppm, around 3% of the total amount).

FT-IR spectroscopy also revealed for the product of pyrolysis at 700 °C (Figure 5d) an additional broad band

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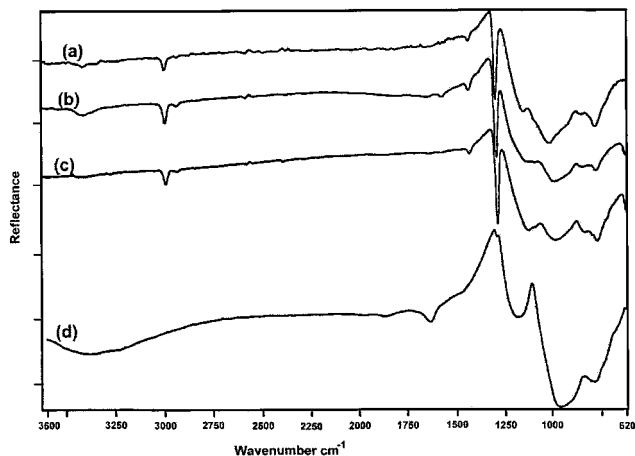


Figure 5. FT-IR spectra of thin films of PMS cross-linked via Si_3N sites produced by reaction with NH_3 at $300\text{ }^\circ\text{C}$ and annealed in NH_3 at (a) 500 , (b) 700 , (c) 900 , and (d) $1100\text{ }^\circ\text{C}$. Note that the reaction excludes the Kumada rearrangement; the band at 1270 cm^{-1} disappears simultaneously with the $\nu(\text{C}-\text{H})$ bands of the methyl groups and $\delta_{\text{as}}(\text{Si}-\text{CH}_3)$ at $700\text{ }^\circ\text{C}$. In spectrum d, the absorption below 1000 cm^{-1} is assigned to $\nu(\text{Si}-\text{N})$, while the 800 cm^{-1} band is attributed to $\nu(\text{SiC})$.

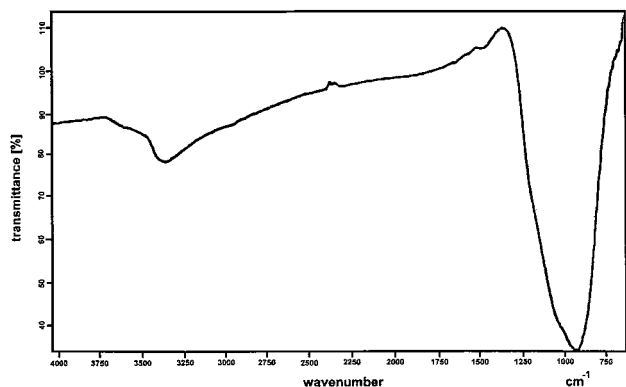


Figure 6. FT-IR spectrum of a silicon nitride layer spin-coated on a silicon wafer. Residual $\text{N}-\text{H}$ bonds are indicated by the band at 3400 cm^{-1} .

centered at 1200 cm^{-1} and a band due to residual $\text{Si}-\text{C}$ bonds at 788 cm^{-1} . The presence of $\text{Si}-\text{C}$ is not evident in the ^{29}Si MAS NMR spectrum of a bulk sample.

Reactions in the $700\text{--}1100\text{ }^\circ\text{C}$ Range. A deposition experiment involving the transport of the volatile species formed by thermal cracking of PMS during pyrolysis (polymer-assisted vapor deposition, PA-VD) was performed on a silicon substrate held at ca. $500\text{--}600\text{ }^\circ\text{C}$. The IR spectrum of this sample, which exhibits a band at 835 cm^{-1} , is more characteristic of silicon nitride produced by CVD using SiH_4 and NH_3 than that obtained from polymeric precursors (Figure 7). A good adhesion of the film to the substrate was noted. This can be related to the formation of an intermediate silazane species, since hexamethyldisilazane is one of the most used adhesion promoters on silicon and silica substrates.⁵² The EDX spectrum of the film revealed the presence of adventitious oxygen and the carbon content was estimated to be less than 1% (Figure 8). In addition, XPS data (Figure 9) revealed some details on the nature of the residual carbon, consistent with a cyano environment. It should be mentioned that when a similar

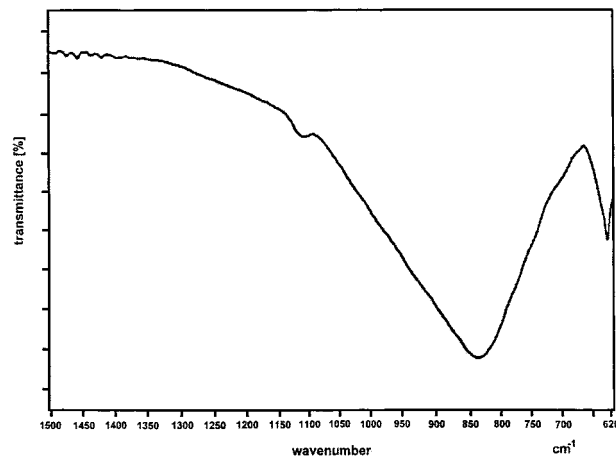


Figure 7. FT-IR spectrum of a CP-VD Si_3N_4 layer at $1100\text{ }^\circ\text{C}$, with substrate temperature approximately $600\text{ }^\circ\text{C}$.

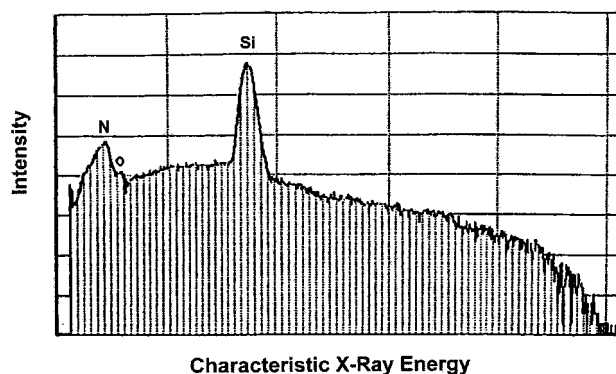


Figure 8. EDX analysis of the ceramic layer synthesized from spin-coated PMS.

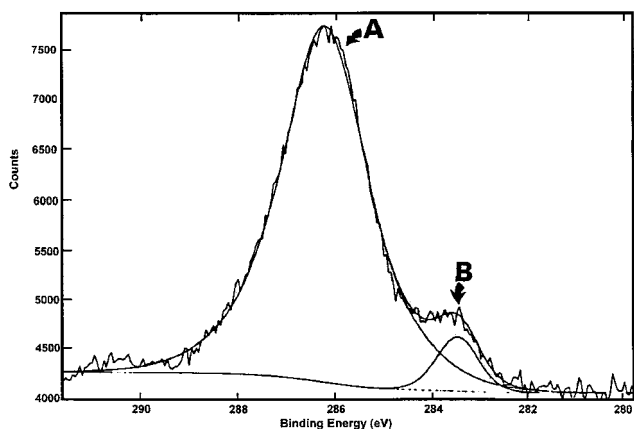


Figure 9. C_{1s} XPS analysis of the ceramic layer consistent with a cyano environment for the residual carbon. (The noise is due to the minimal amount of residual carbon in the sample.)

experimental setup was used earlier for the synthesis of SiC layers, the concentration of oxygen was significantly lower.³⁵ This difference could be the result of the higher sensitivity of the $\text{Si}-\text{N}$ bonds toward oxidation and hydrolysis.

The utility of silicon wafers as IR windows for monitoring the complex chemical processes involved in the pyrolysis of PMS under NH_3 is revealed in the high resolution obtained for the FT-IR spectrum of a spin-coated layer annealed at $400\text{ }^\circ\text{C}$ (Figure 10). The frequency range $1100\text{--}1000\text{ cm}^{-1}$ would be the most affected since this region will contain overlapping bands

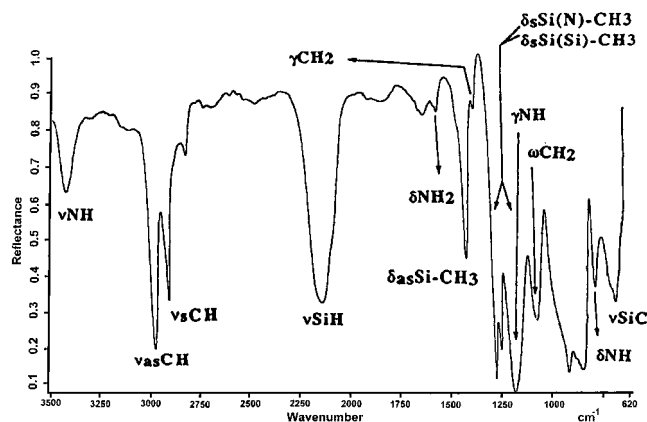


Figure 10. High-resolution FT-IR spectrum of the mixture of species produced during the pyrolysis of spin-coated PMS at 400 °C under NH_3 .

due to $\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$, $\nu_{\text{as}}(\text{Si}-\text{N})$, and $\omega(\text{Si}-\text{CH}_2-\text{Si})$ modes.

Some uncertainty exists in the literature concerning the assignment of the bands in the 1400–1000 cm^{-1} region. For instance, a band at 1050 cm^{-1} has been attributed to both the scissoring mode of a CH_2 group in a carbosilane unit^{53–56} and to $\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$.⁵⁷ The position of the $\gamma(\text{CH}_2)$ mode in this region is based on the assignment of a similar mode in $\text{H}_3\text{SiCH}_2\text{SiH}_3$ at 1370 cm^{-1} .⁵⁸ Also, the band at ca. 1050 cm^{-1} has been attributed to the methylene wagging vibration.

The IR spectrum in Figure 10 exhibits bands suggesting that the intermediate product of the pyrolysis at 400 °C is a carbosilazane. The simultaneous presence of the bands at 3396, 1179, and 778 cm^{-1} strongly supports the predominance of a silazane species over an aminosilane; the presence of a small amount of the latter is responsible for the weak (NH_2) absorption at 1544 cm^{-1} . In the 2000 cm^{-1} region, the $\text{Si}-\text{H}$ band appears at 2131 cm^{-1} , shifted from 2075 cm^{-1} in the starting material. This band shift indicates the conversion of most of the $\text{Si}-\text{Si}(\text{H})\text{R}-\text{Si}$ groups in the backbone into $\text{N}-\text{Si}(\text{H})\text{R}-\text{N}$ units. The high intensity of the $\text{Si}-\text{H}$ band after amination may be explained in two ways: (a) While the $\text{Si}-\text{H}$ groups undergo amination, the Kumada rearrangement generates new $\text{Si}-\text{H}$ groups. (b) NH_3 reacts mainly with the $\text{Si}-\text{Si}$ bonds and not with the $\text{Si}-\text{H}$ bonds. The last process would explain the increased weight loss observed in the TGA measurements. The increased mass transport through the gas phase may be responsible for the high deposition rates of ceramics on colder substrates during the CP-VD process under these conditions.

The presence of methylene bridges, confirming an ongoing Kumada rearrangement, is indicated by the CH_2 scissoring mode at 1356 cm^{-1} .⁵⁹ The rather sharp

Table 1. Proposed Assignments for the Observed Absorption Bands in the FT-IR Spectrum of Polycarbosilazane

| band posn (cm^{-1}) | assgnt | band posn (cm^{-1}) | assgnt |
|--------------------------------|---|--------------------------------|---|
| 3396 | $\nu(\text{NH})$ (in plane) | 1244 | $\delta_{\text{s}}(\text{Si}(\text{Si})-\text{CH}_3)^b$ |
| 2966 | $\nu_{\text{as}}(\text{CH})$ | 1179 | $\gamma(\text{NH})$ (out of plane) |
| 2888 | $\nu_{\text{s}}(\text{CH})$ | 1048 | $\omega(\text{CH}_2)$ |
| 2131 | $\nu(\text{SiH})$ | 916 | $\nu(\text{Si}\ddot{\text{N}}_{\text{p}}\ddot{\text{N}}\text{Si})$ (N planar) |
| 1554 | $\delta(\text{NH}_2)^a$ | 836 | $\nu(\text{Si}\ddot{\text{N}}_{\text{tr}}-\text{Si})$ (N pyramidal) |
| 1410 | $\delta_{\text{as}}(\text{Si}\ddot{\text{N}}\text{CH}_3)$ | 778 | $\gamma(\text{NH})$ (in plane) |
| 1351 | $\gamma(\text{CH}_2)$ bridges | 678 | $\nu(\text{Si}-\text{C})$ |
| 1270 | $\delta_{\text{s}}(\text{Si}(\text{N})-\text{CH}_3)^b$ | | |

^a Four deformation vibrations are expected for NH_2 . $\delta(\text{NH}_2)$ represents the deformation of the $\text{H}-\text{N}-\text{H}$ angle; ω , τ , and ρ are related to the SiNH angle. ^b Assignments based on comparison with the spectrum of the product of oxidation of PMS presented in ref 40.

absorption at 1048 cm^{-1} is assigned to the methylene wagging mode (CH_2), confirming an advanced stage of the Kumada rearrangement. Siloxanes have strong, broad absorptions in this region, but the bands are generally not as sharp as $\text{Si}-\text{CH}_2-\text{Si}$ and can be easily recognized, since they are much stronger, in which case the presence of $\text{Si}-\text{CH}_2-\text{Si}$ groups can be overlooked. The lower intensity for the CH_2 mode compared to that observed in the FT-IR spectrum of PMS-derived PCS at the same temperature indicates that the Kumada rearrangement occurs to a lesser extent in the presence of NH_3 . This is most likely due to competition between the formation of $\text{Si}-\text{CH}_2-\text{Si}$ and $\text{Si}-\text{NH}-\text{Si}/\text{Si}_3\text{N}$ groups.

The symmetric deformations of the $(\text{Si})\text{Si}-\text{CH}_3$ and $(\text{N})\text{Si}-\text{CH}_3$ groups are observed at 1244 and 1275 cm^{-1} , respectively. It should be mentioned that the absence of absorption bands at 2160, 1260, and 1100 cm^{-1} associated with $(\text{O})\text{Si}-\text{H}$, $(\text{O})\text{Si}-\text{CH}_3$, and $\text{Si}-\text{O}-\text{Si}$ groups respectively, indicates negligible oxidation of the backbone in this sample. The bands at 916 and 835 cm^{-1} are assigned to the trigonal-planar and distorted-pyramidal N geometries, respectively. Bulk samples of composite SiC_xN_y powders with low N-content have been shown to contain N atoms dissolved in the SiC lattice as both the tetrahedral form, bonded to four Si atoms, and the trigonal form, bonded to three Si atoms.⁶⁰ It is observed that the main $\nu(\text{Si}-\text{N})$ asymmetric IR band for Si_3N_4 produced by CVD can be deconvoluted into four best-fit $\nu(\text{Si}-\text{N})$ Gaussian components, the two most intense being located around 840 and 940 cm^{-1} .^{44,61} Finally, the band at 678 cm^{-1} is associated with $\text{Si}-\text{C}$ bonds. All of the proposed assignments are listed in Table 1.

Nitridation of Poly(carbosilane). A PCS film on a silicon substrate was prepared by the thermal rearrangement of PMS under Ar (heating rate of 3 °C/min) up to 450 °C, with a residence time of 90 min at 450 °C. Ammonia was then introduced into the system, and the reaction with NH_3 at 450 °C was carried out until the IR spectrum showed the absence of the $\text{Si}-\text{H}$ band at 2100 cm^{-1} . The spectra of the initial PCS and the resulting ammonolysis product are shown in Figure 11. The presence of the antisymmetric N–H stretch, the lower frequencies of the $\delta_{\text{s}}(\text{N}-\text{H})$ band, and the band

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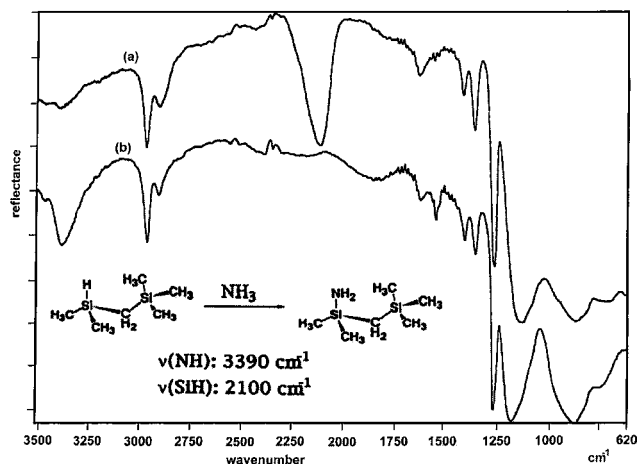


Figure 11. FT-IR spectra of (a) initial PCS and (b) the product of the reaction of PCS with NH_3 . Note the disappearance of the $\nu(\text{Si-H})$ band in PCS at 2100 cm^{-1} , via a heterodehydrocoupling reaction with N-H bonds and formation of aminosilane (3400 cm^{-1}).

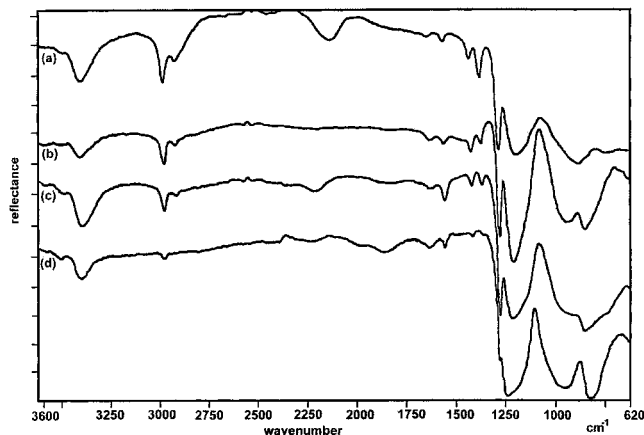


Figure 12. FT-IR spectra showing (a, b) consumption of Si-H bonds by Si-H/N-H coupling in poly(carbosilazane) formed by PMS pyrolysis under NH_3 at $500\text{ }^\circ\text{C}$ and (c, d) ongoing Kumada rearrangement of PCSZ at $500\text{ }^\circ\text{C}$ under Ar.

at 1549 cm^{-1} due to NH_2 in the product all indicate formation of aminosilane in large amounts. Further pyrolysis of this product led to the spectra shown in Figure 12. A sample of PCS was completely aminated by prolonged reaction with NH_3 at $400\text{ }^\circ\text{C}$, until the IR spectrum showed the absence of the Si-H band at 2100

cm^{-1} (Figure 12b). Further pyrolysis of this product led to the spectra shown in Figure 12c,d. From the new "precursor" (Figure 12b), Si-H bonds are reformed via Kumada rearrangement, as shown by the reappearance of the 2100 cm^{-1} absorption in Figure 12c. A decrease in the intensity of the $\gamma(\text{CH}_2)$ mode at 1350 cm^{-1} is initially accompanied by an increase in the intensity of the broad absorption at 940 cm^{-1} (Figure 12c), followed by a redistribution of intensity between the two bands at 940 and 840 cm^{-1} (Figure 12d). Another interesting feature is the merging of the $\delta_s(\text{Si(N)-CH}_3)$ mode at 1270 cm^{-1} with the broad band shifting from 1200 to 1250 cm^{-1} ; this convergence illustrates the difficulty in assigning the different vibrational modes in this region.

Conclusions

PMS containing catalytic amounts of DMZ reacts with NH_3 to produce amorphous Si_3N_4 after pyrolysis at $1100\text{ }^\circ\text{C}$. Low-temperature NH_3 curing is restricted by the unexpectedly low reactivity of PMS toward NH_3 below $300\text{ }^\circ\text{C}$. The main reaction at lower temperatures involves formation of a carbosilazane species, followed by thermal cracking of the methyl substituents on silicon. Carbon loss occurs at higher temperatures, mainly from the poly(carbosilane) and carbosilazane species present at these temperatures. On the basis of IR spectroscopic data, products free of C-H are formed at $600\text{ }^\circ\text{C}$ [for poly(carbosilanes) and carbosilazane] and $700\text{ }^\circ\text{C}$ (cross-linked silazane). The Kumada rearrangement is inhibited by the extensive formation of Si_3N knots when the PMS sample is heated under an NH_3 atmosphere at $200\text{ }^\circ\text{C}$. The residual carbon is mostly in the form of cyano groups in the Si_3N_4 layers produced by pyrolysis of spin-coated films of PMS at $1100\text{ }^\circ\text{C}$. The PA-VD process exhibited low deposition rates, and contamination with oxygen could not be completely avoided.

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