



Hot-Filament Chemical Vapor Deposition of Organosilicon Thin Films from Hexamethylcyclotrisiloxane and Octamethylcyclotetrasiloxane

Hilton G. Pryce Lewis,^z Thomas B. Casserly, and Karen K. Gleason*

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

A nonplasma technique, hot-filament chemical vapor deposition (HFCVD), is an alternative method for producing organosilicon films of novel structure. Films are deposited onto room-temperature substrates from the precursors hexamethylcyclotrisiloxane (D_3) and octamethylcyclotetrasiloxane (D_4) at high rates ($>1 \mu\text{m}/\text{min}$). Filament temperature can be used to control film structure, and the limited reaction pathways available via thermal decomposition make it possible to elucidate the chemistry of the growth process. During film growth, there appears to be competition between reaction pathways for the incorporation of cyclic and linear siloxane structures. For both D_3 and D_4 HFCVD films, infrared, Raman, and nuclear magnetic resonance spectroscopies indicate the incorporation of ring structures consisting of three siloxane units. The concentration of these structures increases as filament temperature is raised and is especially pronounced for films deposited from D_3 . In comparison, films grown from D_4 show a greater degree of incorporation of linear, unstrained structures over the range of filament temperatures studied. In contrast to plasma-deposited organosilicon films, cross-linking in HFCVD films occurs predominantly via silicon-silicon bonding and not from siloxane bonds with tertiary or quaternary silicon atoms.

© 2001 The Electrochemical Society. [DOI: 10.1149/1.1415723] All rights reserved.

Manuscript submitted March 12, 2001; revised manuscript received July 16, 2001. Available electronically November 2, 2001.

Organosilicon thin films produced by chemical vapor deposition (CVD) have attracted considerable interest in a wide variety of applications, ranging from biocompatible coatings for medical implants to permselective membranes.¹⁻⁹ In particular, organosilicon films are presently under consideration as low dielectric constant, or low- k , interlayer dielectric (ILD) candidates for future semiconductor processing. These materials, termed organosilicate glasses (OSGs), are typically carbon-doped oxides or siloxanes deposited by CVD or plasma-enhanced CVD (PECVD).¹⁰⁻¹² Research in this field has primarily focused on the use of PECVD for producing organosilicon films with desirable properties (see Wróbel and Wertheimer¹ for an extensive review).

A plasma-based deposition technique, however, has inherent deficiencies. Plasma polymers tend to show high dielectric loss as compared to conventional polymers, as well as an aging effect upon exposure to the atmosphere. It has been proposed that exposure of the growing film to UV irradiation and ion bombardment during the deposition process can result in the formation of trapped free radicals, or dangling bonds, in the film.¹³ These defect sites are then subject to oxidation upon exposure to the atmosphere. The effect of ion bombardment is also to increase the cross-link density in plasma films, which often results in brittle, inflexible films. Pulsed-PECVD is a technique that can be used to minimize plasma exposure during film growth. In this method, plasma excitation is modulated to alter the dynamics of competing deposition pathways, allowing for greater compositional control and lower cross-link density in the resulting films.¹³⁻¹⁷ Using pulsed-PECVD with the precursor hexamethylcyclotrisiloxane (D_3), we have demonstrated flexible, conformal coatings on nonplanar substrates suitable for implantation.³

Hot-filament chemical vapor deposition (HFCVD, also known as pyrolytic CVD) does not suffer from the UV irradiation and ion bombardment associated with plasma exposure. In addition, HFCVD allows for more control over precursor fragmentation pathways than PECVD. Thermal activation is limited to the gas phase and independent control of the substrate temperature can be exercised. Indeed, HFCVD using hexafluoropropylene oxide as the precursor gas has been shown to produce fluorocarbon films with low dangling bond density having a chemical structure which is spectroscopically similar to polytetrafluoroethylene (PTFE).^{17,18}

In this study, we consider the structure of films produced by

HFCVD using the precursors hexamethylcyclotrisiloxane, $[(\text{CH}_3)_2\text{SiO}]_3$, and octamethylcyclotetrasiloxane, $[(\text{CH}_3)_2\text{SiO}]_4$, commonly known as D_3 and D_4 . Previously, we demonstrated that polymeric thin films could be deposited from D_4 by HFCVD at rates of up to 2500 nm/min depending on filament temperature.¹⁹ In this work, we show that filament temperature (T_f) has a strong influence on composition for both D_3 and D_4 HFCVD films and postulate a structure for these novel films.

Experimental

Films were deposited on silicon wafer substrates in a custom-built vacuum chamber, which has been described previously.¹⁸ Thermal excitation was accomplished by resistively heating tantalum wire (0.5 mm diam) strung on a filament holder. Springs on the holder maintained wire tension to compensate for thermal expansion and prevent drooping. The filament wire was mounted in a parallel array designed to minimize thermal gradients between individual wires and offer uniform heating over an area the size of a wafer. The filament holder straddled a cooled stage on which a silicon wafer substrate was placed. A filament-to-substrate standoff of 1.3 cm was used. Pure precursor was vaporized in a heated vessel and delivered through a needle valve to maintain flow rates of approximately 14 sccm for D_3 and 11 sccm for D_4 . Pressure in the reactor was maintained at 300 mTorr by a butterfly valve. No diluent gas was used.

Filament temperature was measured using an $2.2 \mu\text{m}$ infrared pyrometer. For oxidized tantalum, a spectral emissivity of 0.20 was estimated from direct contact thermocouple measurements. Due to the difficulties of direct measurement at high temperatures, reported temperatures are probably accurate to $\pm 50^\circ\text{C}$. However, temperatures were consistent from run to run and there was little variation in power requirements for heating the wire. Substrate temperature was maintained below 60°C by back-side water cooling. Films were deposited on 100 mm diam p-type silicon (100) wafers at filament temperatures ranging from 800 to 1200°C . Deposition rates were monitored *in situ* using interferometry and checked using profilometry at the center of each wafer after deposition.

For film characterization, infrared spectroscopy was performed using a Nicolet Magna 860 Fourier transform infrared (FTIR) spectrometer operating in transmission mode. All spectra were normalized to a standard thickness of 150 nm and baseline corrected for purposes of comparison. Resonant Raman spectra were obtained using a Kaiser Optical Systems Hololab 5000R Modular Research Micro-Raman Spectrograph, with 785 nm laser line excitation and

* Electrochemical Society Active Member.

^z E-mail: hiltonpl@mit.edu

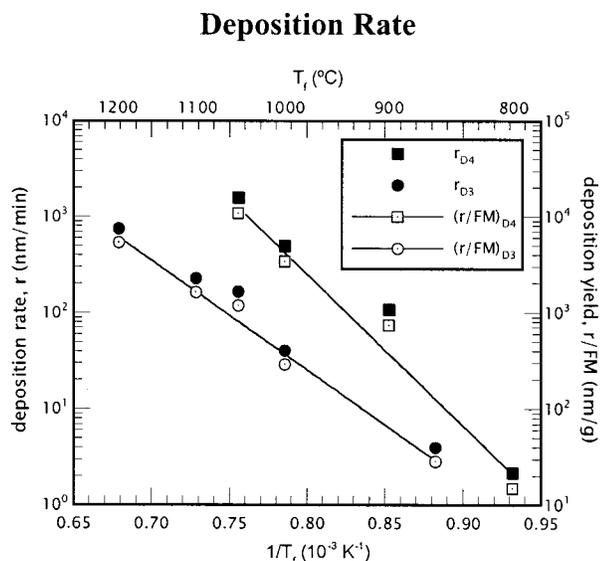


Figure 1. Arrhenius plot of D₃ and D₄ films produced by HFCVD: (■, ●) measured deposition rates, r (left axis), and (□, ○) thickness-based deposition yields, r/FM (right axis). Straight lines were fitted to the deposition yield data by regression.

15 mW power at the sampling stage under 50 times magnification. High-resolution solid-state nuclear magnetic resonance (NMR) spectra were acquired on a homebuilt NMR spectrometer²⁰ equipped with a 6.338 T Oxford superconducting magnet and a 3.2 mm Chemagnetics probe with spinning capabilities up to 25 kHz. Magic-angle spinning (MAS) and cross-polarization (CP) from the proton spin bath were used to resolve isotropic chemical shifts and reduce acquisition time. Approximately 10 mg of film was scraped off the wafer and packed into a zirconia rotor, which was spun at 7 kHz. 14,512 acquisitions were performed for signal averaging. A ¹H-²⁹Si CP time of 5 ms was chosen to maximize the overall signal intensity. Experiments confirmed that the contact time between the silicon and proton spin baths was sufficient to provide uniform ²⁹Si polarization. Indeed, a direct comparison of NMR spectra acquired with direct- and cross-polarization confirmed that CP spectra were quantitative. All NMR spectra were referenced to tetramethylsilane (TMS) and are plotted in parts per million. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos AXIS ULTRA spectrometer using a monochromatized aluminum K α source. Atomic force microscopy (AFM) was performed on a Digital Instruments Dimension 3000. Images were taken under tapping mode with a standard etched silicon tip.

Results and Discussion

Deposition rate.—The measured deposition rate, r , and the thickness-based deposition yield, r/FM (where F is the volumetric flow rate, and M is the molecular weight of the precursor), are plotted in Arrhenius form in Fig. 1. The deposition yield expresses the deposition rate per unit mass of the precursor compound and allows the relative reactivities of D₃ and D₄ to be compared directly.²¹ As shown in Fig. 1, the deposition yield appears to follow an Arrhenius-type relationship as a function of filament temperature. The highest deposition rate observed was 1574 nm/min for D₄ at a filament temperature of 1050°C. No film deposition was detected at filament temperatures below 800°C with either precursor. At the higher filament temperatures, run times were limited to 1.5 min to produce thin films appropriate for subsequent characterization. These temperatures are consistent with other studies of the vacuum pyrolysis of D₄.²² Regression of the data in Fig. 1 yielded apparent activation energies of 218 ± 35 kJ/mol for D₃, and 301 ± 102 kJ/mol for D₄ (at a 90% confidence level).

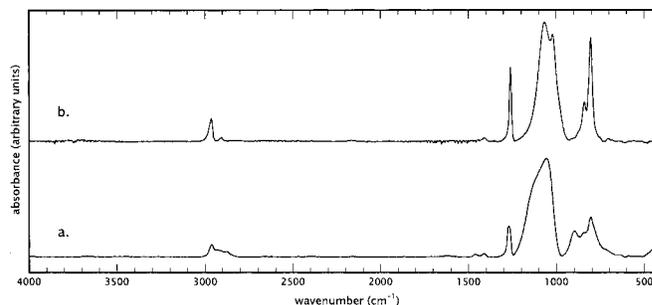


Figure 2. FTIR spectra of (a) D₃ PECVD film deposited under continuous-wave excitation and (b) D₃ HFCVD film deposited at 1000°C.

FTIR spectroscopy.—A comparison of the FTIR spectra of D₃ films deposited using HFCVD and continuous-wave excitation PECVD is shown in Fig. 2a and b. The spectra for the CW PECVD film (Fig. 2a) was taken from previous work by our group.³ Assignments have been made from the literature and are shown in Table I. Comparison of these spectra indicates that the HFCVD film differs structurally from the PECVD film. Only sp³-carbon bonding is observed in the HFCVD film, and no cross-linking of Type II, *i.e.*, via carbon cross-links, is evident.³ Carbon is thus preserved primarily as methyl, giving rise to the distinct pair of symmetric and asymmetric CH stretches²³⁻²⁵ at 2907 and 2964 cm⁻¹. The asymmetric stretching mode (ASM) of the siloxane group (SiOSi) shows two distinct bands for the HFCVD film, a characteristic observed in the IR signatures of polydimethylsiloxanes with chain lengths of more than two siloxane units or ring sizes of larger than eight units.^{26,27} Below 1000 cm⁻¹, absorption bands associated with SiMe₂ rocking and stretching are observed at 878 and 805 cm⁻¹, and those associated with SiMe₃ rocking near 840 cm⁻¹. Qualitatively, the PECVD film appears to have a higher SiMe₃/SiMe₂ ratio, suggesting that the HFCVD film may be less branched than its PECVD analog.³

FTIR spectra of films deposited at filament temperatures of 860, 1000, and 1200°C using D₃, and 800, 900, and 1000°C using D₄, are also shown (Fig. 3 and 4, respectively). The region around the ASM has been expanded for detail. Strong absorptions associated with SiMe₂ (805 cm⁻¹), methyl in SiMe_x (1412 cm⁻¹), and the ASM (1020-1075 cm⁻¹) are apparent. The band at about 880 cm⁻¹ observed in the low-filament-temperature D₄ film is usually associated with the symmetric CH₃ rocking mode in SiMe₂. The disappearance of this band at higher filament temperatures may be due to the conformational constraints present in a more highly networked structure. Similar effects in this infrared region have been observed in temperature-dependent spectroscopy studies of other organosilicon compounds.^{28,29}

Table I. FTIR assignments from the literature.

Wavenumber (cm ⁻¹)	Mode ^a	Comment	Ref.
2963-2965	$\nu_{\text{CH}}^{\text{A}}$	In sp ³ CH ₃	24, 25, 31, 36
2935	$\nu_{\text{CH}}^{\text{A}}$	In sp ³ CH ₂	24, 25
2907	$\nu_{\text{CH}}^{\text{S}}$	In sp ³ CH ₃	24, 25, 31, 36
2878	$\nu_{\text{CH}}^{\text{S}}$	In sp ³ CH ₂	24, 25
1463	$\delta_{\text{CH}_2}^{\text{A}}$		24, 25
1412	$\delta_{\text{CH}_3}^{\text{A}}$	In SiMe _x	24, 25, 27, 31, 36
1262	$\delta_{\text{CH}_3}^{\text{S}}$	In SiMe _x	25, 27, 30, 31, 36
1020-1075	$\nu_{\text{SiOSi}}^{\text{A}}$		24, 25, 27, 31, 36
878	$\rho_{\text{CH}_3}^{\text{S}}$	In SiMe ₂	25, 27, 30, 36
804-806	$\nu_{\text{Si-C}}^{\text{A}}, \rho_{\text{CH}_3}^{\text{A}}$	In SiMe ₂	25, 27, 30, 31, 36
839-845	$\rho_{\text{CH}_3}^{\text{A}}$	In SiMe ₃	25, 27, 30, 36

^a ν , δ , and ρ denote stretching, bending, and rocking modes, respectively; a and s denote asymmetric and symmetric vibrations.

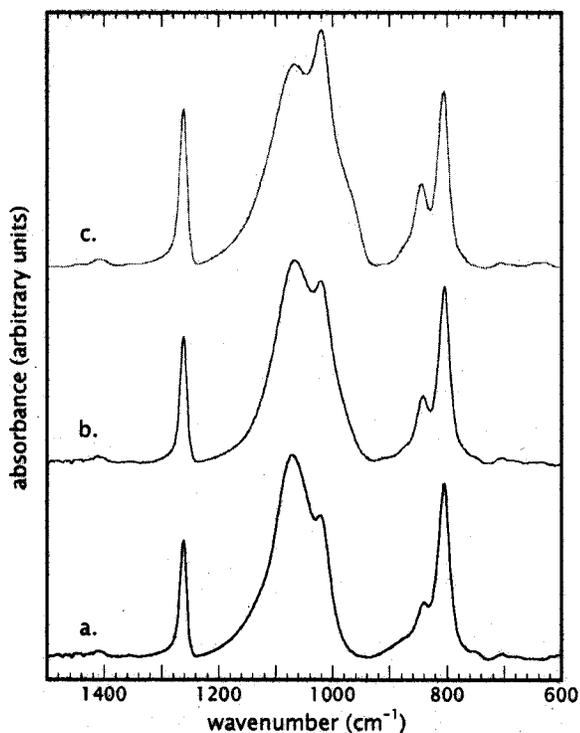


Figure 3. FTIR spectra of D_3 HFCVD films deposited at filament temperatures of (a) 860, (b) 1000, and (c) 1100°C.

Conventionally,^{25,27,30} the band around 845 cm^{-1} is assigned to an asymmetric CH_3 -rocking mode in SiMe_3 , with an accompanying symmetric CH_3 -rocking mode at 760 cm^{-1} . The SiMe_3 group is a chain or branch termination group that is associated with an M

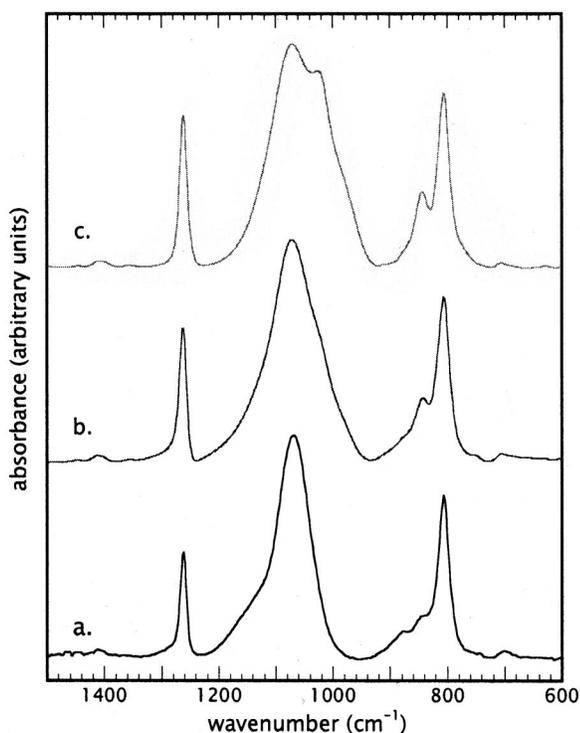


Figure 4. FTIR spectra of D_4 HFCVD films deposited at filament temperatures of (a) 800, (b) 900, and (c) 1000°C.

group in siloxanes,³ where M is the trimethylsiloxane unit (CH_3)₃SiO-. The relative intensities of the SiMe_2 and SiMe_3 bands depend on the length of chains in open-chain regions of the film structure, and the strength of the SiMe_3 band is an indication that chains are either short or highly branched.^{26,31} The $\text{SiMe}_3/\text{SiMe}_2$ ratio also increased only slightly as filament temperature was increased, suggesting that the chain length and branching was similar for both sets of films. Other data obtained for these films, particularly from NMR analysis, show only small quantities of M groups in the films, with the highest concentrations appearing in low-filament-temperature D_3 and high-filament-temperature D_4 films. This implies that short chain segments or branches of similar length are present in low concentrations in almost all the films produced.

Significant changes in the relative intensities of the bands of the ASM band are observed for both D_3 and D_4 films. The spectra of the D_3 film shows a doublet for all three filament temperatures, with the shoulder on the doublet switching from the low- to high-wavenumber side at higher filament temperatures (compare Fig. 3a and 3c). By contrast, the spectra of the D_4 film deposited at a filament temperature of 800°C (Fig. 4a) showed only a singlet, and the IR spectra resembled that of the precursor D_4 .^{26,27} Unlike D_4 , however, which is a liquid at room temperature, the film was solid and contiguous and came off the wafer in flakes when scraped with a razor. The D_4 film deposited at higher filament temperature showed behavior similar to that of the D_3 film. As filament temperature was increased, the low-wavenumber peak of the ASM doublet increased in intensity, exceeding that of the high-wavenumber peak above 1050°C (spectra not shown), as in the case of the D_3 film.

The ASM doublet of the film deposited from D_3 at a filament temperature of 1100°C (Fig. 3c) resembles that observed in FTIR analyses of other organosilicon PECVD films.^{3,25,32} Typically for these films, the low-wavenumber band was more intense than the high-wavenumber band. This ASM signature is also observed in spin-on methyl silsesquioxane (MSQ) films.³³ For bulk polydimethylsiloxane (PDMS), the intensities of these bands are approximately equal at room temperature.³⁴ To our knowledge, no IR spectra with an ASM doublet similar to that observed in Fig. 3a, 3b, and 3c have been reported for organosilicon films deposited by CVD from comparable precursors. The configuration of the ASM doublet is likely to be conformational in origin. For PDMS, the splitting of the doublet has been attributed to coupling between adjacent chain segments.³¹ In other work using Raman spectroscopy, the splitting of the symmetric SiOSi stretching mode has been correlated to the crystalline state of PDMS.³⁵

The intensity ratio of the two bands of the ASM doublet has been correlated with the length of chains or size of rings in the polymethylsiloxane network.²⁵⁻²⁷ In particular, for a series of linear and cyclic polymethylsiloxanes of increasing chain length or ring size, a doublet was observed in FTIR spectra only when chain lengths exceeded two siloxane units and ring size exceeded five siloxane units. The ASM singlet for D_3 was offset at 1020 cm^{-1} compared to larger ring structure. The band at 1020 cm^{-1} may thus be associated with an increasing proportion of six-membered D_3 -like rings in the film structure. This is in the same region as the low-wavenumber band of the ASM doublet in PDMS, however, making it difficult to differentiate between the presence of chains and bound D_3 rings using IR analysis.³¹

Raman spectroscopy.—Though some work has been done in characterizing pure organosilicon compounds using Raman spectroscopy, little has been reported on the use of Raman for characterizing more complex organosilicon materials, such as those produced by CVD. Figure 5 compares the Raman spectra of the pure compounds D_3 , D_4 , and PDMS with that of HFCVD films grown from D_3 and D_4 using high filament temperatures. Assignments in Table II have been made based on the literature.^{28,31,36,37} The symmetric siloxane stretching mode (SSM), which is weak in FTIR spectra, is strong in the Raman spectra. The position of the symmetric siloxane

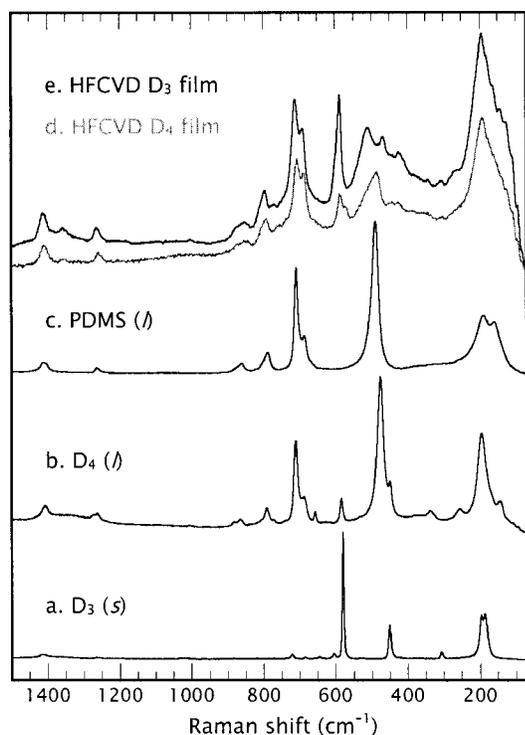


Figure 5. Micro-Raman spectra of (a) D_3 , (b) D_4 , (c) PDMS, and (d) D_4 HFCVD film deposited at a filament temperature of 1000°C , and (e) D_3 HFCVD film deposited at a filament temperature of 1100°C .

Raman band is shifted to higher wavenumbers for D_3 due to ring strain, and bands associated with ring deformation can be observed for both D_3 and D_4 .³¹ Raman spectroscopy is thus a sensitive probe for observing ring structure. Indeed, Raman spectroscopy is capable of identifying siloxane ring "defects" in SiO_2 films produced by sol-gel³⁸⁻⁴¹ and CVD processes.⁴² Raman spectra for these materials exhibit specific bands corresponding to ring structures comprised of different numbers of silicon atoms. In particular, Raman bands at 605 and 495 cm^{-1} in silica have been attributed to rings with three and four siloxane units, termed R_3 and R_4 , respectively.^{38,39,41,42}

As observed in Fig. 5, the Raman shift region of the HFCVD films from 400 to 600 cm^{-1} differs from that of the pure compounds. Both HFCVD films show a band in the range $586\text{--}590\text{ cm}^{-1}$ which is not observed in PDMS or other linear siloxane compounds.³¹ This is close to the band assigned to the SSM at 581

cm^{-1} in pure D_3 . During an experiment in which polarization of the Raman beam was changed from the parallel to the perpendicular mode, the band in the HFCVD film was also found to be polarized, which is consistent with results observed for the SSM in D_3 .^{31,37} This band may thus be evidence of a bound D_3 -like ring structure in the film. The $5\text{--}10\text{ cm}^{-1}$ shift from the position of this band in D_3 may be conformational in origin and a result of the strain of being locked into a seminetworked structure. Such shifts are possible, and Table III shows Raman assignments for the SSM mode in different chemical environments. In the highly networked environment of vitreous and chemical vapor-deposited silica, the characteristic vibrational mode of the six-membered planar ring of siloxane units, R_3 , has been observed at shifts as high as 608 cm^{-1} .^{38,40,43} By contrast, the SSM mode is typically observed from 581 to 587 cm^{-1} for unconstrained D_3 . The band at around 590 cm^{-1} for the HFCVD films falls between these extremes and is thus assigned to an oR_3 group. The term oR_n is derived from the R_n unit observed in silica and is intended to represent an organically substituted ring consisting of n siloxane units, which is bound into the film structure. By analogy, there may also be rings consisting of four siloxane units bound into the film structure (oR_4). Table III shows that the band at 485 cm^{-1} observed primarily for the D_4 HFCVD films falls between the SSM bands for D in PDMS, R_4 in silica, and unperturbed D_4 . This suggests that the band is associated with oR_4 groups and/or unstrained siloxane units in the film. The unstrained siloxane units may be present in linear structures or in ring structures larger than four units, and are designated as lD . The predominance of these groups in the D_4 films, particularly at low filament temperature, suggests that they are unique to the pyrolysis chemistry of D_4 and may be the four siloxane-unit ring analog, oR_4 .

The Raman spectra of the HFCVD films also show a low-intensity band at 425 cm^{-1} not observed in any of the pure compounds. No assignment could be found for this band in the literature, but it is in the region associated with a silicon-silicon stretching mode.⁴⁴ The Si-Si stretch gives a strong Raman band at $400\text{--}405\text{ cm}^{-1}$ for hexamethyldisilane and is highly sensitive to silicon substituents. For polar substituents, shifts can be large. For example, the Si-Si stretching mode for $\text{FMe}_2\text{SiSiMe}_2\text{F}$ has been reported at 433 cm^{-1} , a shift of 30 cm^{-1} from the unsubstituted disilane.⁴⁵ Hence, this band is tentatively assigned to an Si-Si bond in the film structure.

Figures 6 and 7 show the effect of filament temperature as probed by Raman spectroscopy. The spectra of the films deposited from D_3 (Fig. 6) show an increasing intensity of the bands from oR_3 units and Si-Si bonds as filament temperature is increased, and the D_3 film deposited at 1100°C shows significant ring incorporation. FTIR spectra for these films show a similar increase in intensity in

Table II. Raman assignments from the literature.

Raman shift (cm^{-1})	Mode ^a	Comment	Ref.
1410	$\delta_{\text{CH}_3}^{\text{A}}$		23, 28, 36
1260-1265	$\delta_{\text{CH}_3}^{\text{S}}$		23, 28, 36
795	$\nu_{\text{SiC}}^{\text{A}}$	In SiC_2	23, 28, 36, 37
707-712	$\nu_{\text{SiC}}^{\text{S}}$	In SiC_2	23, 28, 36, 37
690	$\rho_{\text{CH}_3}^{\text{A}}$		23, 28, 37
581	$\nu_{\text{SiOSi}}^{\text{S}}$	In D_3	31, 37, 72
489	$\nu_{\text{SiOSi}}^{\text{S}}$	In PDMS	23, 36
476	$\nu_{\text{SiOSi}}^{\text{S}}$ and/or ring deformation	In D_4	23, 37
450	Ring deformation	In D_3 and D_4	23, 37
424-426	Possible Si-Si stretch		44
190-194	$\delta_{\text{SiC}}^{\text{S}}$	In SiC_2	31, 37
160	$\delta_{\text{SiC}}^{\text{S}}$ and twist	In PDMS	31
145	$\delta_{\text{SiC}}^{\text{S}}$	In D_4	31

^a ν , δ , and ρ denote stretching, bending, and rocking modes, respectively, a and s denote asymmetric and symmetric vibrations.

Table III. Raman SSM assignments for various chemical environments.

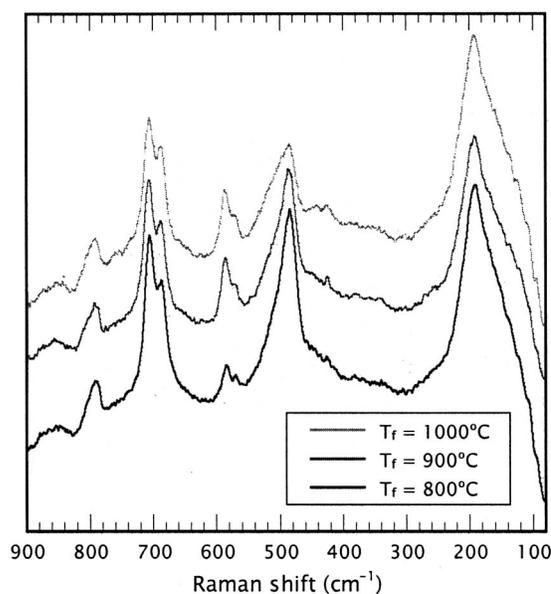
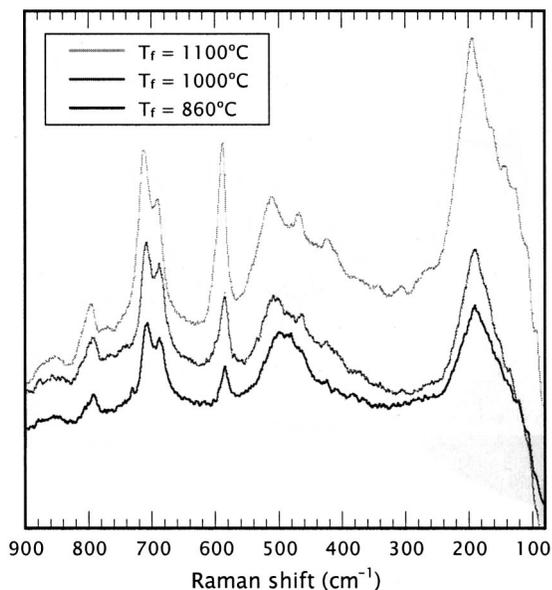
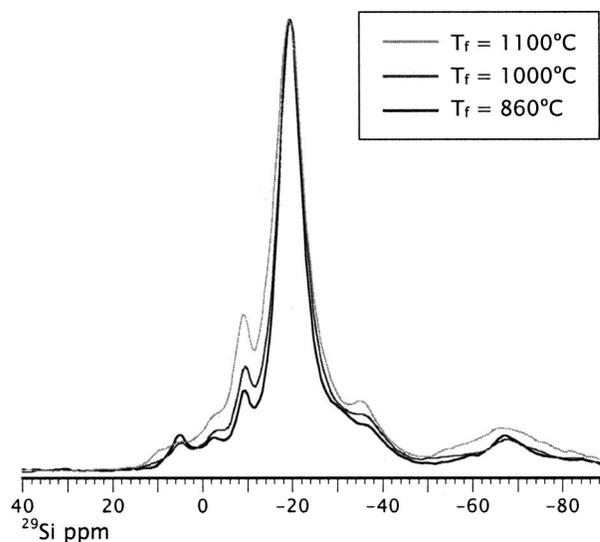
Symbol	Raman shift (cm^{-1})	Comment	Ref.
R_3	600-608	In vitreous and/or CVD silica	38-42
oR_3	586-590	In D_3 and D_4 HFCVD films	
D_3	581-587	In D_3	31, 37, 72
D	489-497	In PDMS	23, 36
R_4	490-495	In vitreous and/or CVD silica	38-42
oR_4 and/or /D	485	In D_3 and D_4 HFCVD films	
D_4	475-480	In D_4	23, 28, 36, 37

the low-wavenumber band of the ASM doublet (see Fig. 3), suggesting that this band at 1020 cm^{-1} is indeed associated with three siloxane-unit ring structures. By contrast, the spectra of the films deposited from D_4 (Fig. 7) show a strong band at 485 cm^{-1} , assigned to the presence of oR_4 and/or unstrained D units. A slight increase in oR_3 incorporation is observed as T_f increases, but this band does not dominate as it does in the spectra of the D_3 films (Fig. 6). Hence, the D_3 and D_4 films differ structurally at high filament temperatures, despite the similarities in structures suggested by FTIR.

Nuclear magnetic resonance (NMR) spectroscopy.—The ^{29}Si CP-MAS NMR spectra obtained for the D_3 and D_4 HFCVD films are shown in Fig. 8 and 9. Typical chemical shifts reported in the literature for organosilicon CVD films are included in Table IV.^{20,32,46-49} As suggested by the data in this table, films deposited by other CVD methods commonly show a wide variety of bonding environments, including the presence of M, D, T, and Q groups as well as their hydrogenated analogs.^{32,49,50} By contrast, only two primary peaks were observed in these HFCVD films.

The major peak at -19 ppm is assigned to the D unit, $(\text{SiO})_2\text{Si}^*(\text{CH}_3)_2$.^{32,46,48,49} The chemical shift for this moiety depends on the conformation of the siloxane chain, typically varying from -22 ppm for PDMS to -10 ppm for D_3 (due to ring strain). The lack of a doublet for this resonance analogous to that observed in FTIR is probably due to the longer time scales used for signal averaging in NMR. The closest assignment for the peak at -9 ppm suggested by the literature was for $\text{M}^{\text{H}} [(\text{SiO})\text{Si}^*(\text{H})(\text{CH}_3)_2]$, which is typically reported at -6 ppm .^{47,49} However, there is little

evidence of Si-H bonding (usually observed near 2140 cm^{-1}) in FTIR spectra of the HFCVD films. Since the Si-H stretching vibration has a high oscillator strength,⁵¹ even low concentrations of this

**Figure 7.** Micro-Raman spectra of D_4 HFCVD films deposited at filament temperatures of 800, 900, and 1000°C .**Figure 6.** Micro-Raman spectra of D_3 HFCVD films deposited at filament temperatures of 860, 1000, and 1100°C .**Figure 8.** ^{29}Si solid-state CP-MAS NMR spectra of D_3 HFCVD film deposited at filament temperatures of 860, 1000, and 1100°C .

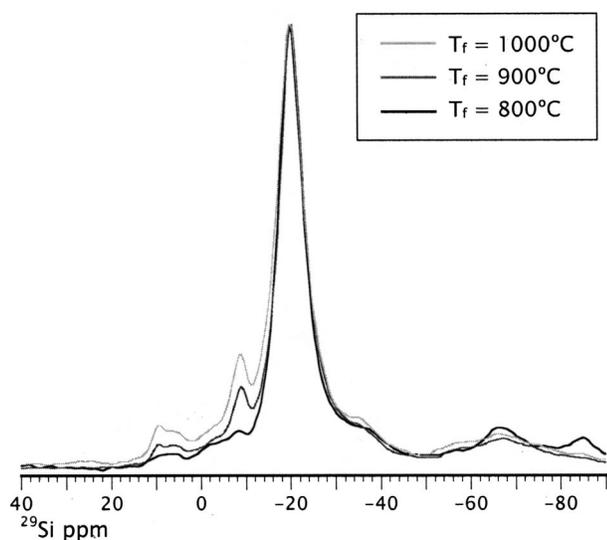


Figure 9. ^{29}Si solid-state CP-MAS NMR spectra of D_4 HFCVD film deposited at filament temperatures of 800, 900, and 1000°C.

Table IV. ^{29}Si NMR structures and chemical shifts commonly observed in organosilicon CVD films.

Symbol	Structure	Chemical shift (ppm)	Ref.
M	$(\text{SiO})\text{Si}^*(\text{CH}_3)_3$	+6	32, 49, 52, 73
M^{H}	$(\text{SiO})\text{Si}^*(\text{H})(\text{CH}_3)_2$	-6	47, 49, 52
D	$(\text{SiO})_2\text{Si}^*(\text{CH}_3)_2$	-10 in D_3 -20 in D_4 -22 in PDMS	32, 46, 48, 49, 52
D^{H}	$(\text{SiO})_2\text{Si}^*(\text{H})(\text{CH}_3)$	-34 to -37	46, 47, 49, 52, 74
T	$(\text{SiO})_3\text{Si}^*(\text{CH}_3)$	-67	32, 46, 49, 52
T^{H}	$(\text{SiO})_3\text{Si}^*(\text{H})$	-84	20, 47
Q	$(\text{SiO})_4\text{Si}^*$	-105 to -110	32, 46, 48, 49, 52

moiety should yield a visible peak in the FTIR spectra. Furthermore, CP contact time experiments produced no change in the relative intensities of the major peaks at -9 and -19 ppm. It is anticipated that silicon directly bonded to hydrogen would increase the CP rate. Thus, the peak at -9 ppm is not indicative of an M^{H} structure. As suggested by Raman spectroscopy, this peak is assigned rather to the presence of σR_3 ring structures in the film. This assignment is close to the reported shift of -10 ppm for the D unit in the strained molecule D_3 .^{46,48,52} The major peak at -19 ppm is then associated with σR_4 and/or unstrained siloxane units. The shift of +3 ppm from an unstrained D group suggests that this unit may be primarily present in the form of a ring structure rather than a linear chain.⁴⁸

For both the D_3 and D_4 films, the peak at -9 ppm increases in intensity as filament temperature increases (see Fig. 8 and 9). While this peak is present in the spectra of the D_3 films over the whole range of filament temperatures, it is of very low intensity in the spectra of the D_4 film deposited at a filament temperature of 800°C. This is consistent with Raman data, which shows very little σR_3 in this film. The M peak at 5-6 ppm is also more intense in the D_3 film deposited at filament temperature of 860°C than in its 1100°C counterpart. Since M is more likely to be associated with linear structures in the film, a lower M content at high filament temperatures is consistent with the higher content of ring structures suggested by Raman spectroscopy. The NMR spectra of both D_3 and D_4 films show a low and constant concentration of T groups, and almost no Q

group. T and Q groups are conventional cross-linking and/or branching groups in organosilicon materials and are observed in significant concentrations in the films produced using PECVD.^{3,32,49,50} The absence of these groups suggests that cross-linking in the film must be associated with some other bonding structure. Based upon the evidence of Si-Si bonding observed in Raman spectroscopy, it is postulated that cross-linking in these films occurs preferentially via this bonding.

X-ray photoelectron spectroscopy.—Elemental ratios obtained using X-ray photoelectron spectroscopy (XPS) analysis are reported in Table V. The highest O:Si ratio is 1.23 for the D_4 film deposited at a filament temperature of 800°C. The higher O:Si ratio for this film is consistent with ^{29}Si NMR data indicating a greater concentration of T groups.

A C:Si ratio of less than 2.0 indicates that all films are deficient in carbon as compared to the precursor molecules. C 1s high-resolution scans confirm that carbon is present exclusively as methyl. The methyl content appears to depend on filament temperature, with a significant loss of methyl at high filament temperatures for both D_3 and D_4 films. In all but one film, Si 2p high-resolution scans showed no evidence of silicon oxidation states other than 2+, confirming that very little T and Q is present in the films. For the D_3 film deposited at a filament temperature of 1100°C, the Si2p and C 1s high-resolution scans show slight shouldering on the main peaks. One source for this shouldering may be the slight increase in T group concentration observed in ^{29}Si NMR (Fig. 8). However, this is inconsistent with the low O/Si ratio reported for this film, and similar shouldering is not observed in the D_4 film deposited at filament temperature of 800°C, which shows a greater O/Si ratio. More likely, the shouldering is a shift associated with Si-Si bonding that becomes visible when the concentration of this moiety is high. The origin of the shouldering in the C 1s scan is uncertain but is unlikely to originate from carbonyl or methylene moieties in the films, as these would be visible using other spectroscopic techniques (e.g., FTIR).

Atomic force microscopy.—AFM indicated that the films were very smooth. A typical micrograph is shown in Fig. 10, in this case for a D_4 film deposited at a filament temperature of 900°C. Root-mean-square (rms) roughnesses for all films were of the order of 1.0 nm. The rms roughness of the silicon substrate was 0.53 nm.⁵³ This in contrast to fluorocarbon films deposited using HFCVD, which often show greater roughness and characteristic morphology.⁵⁴ This morphology is possible due to the lack of ion and electron bombardment, which tends to cause densification and damage to the growing film during PECVD. The smoothness of our films deposited using a similar HFCVD process suggests that there is efficient packing on the molecular level in the organosilicon films.

Chemical reactions.—Possible pathways for the production of film growth species under thermal excitation are shown in Scheme 1. Reactions 1-3 describe the molecular rearrangement of D_4 to produce D_3 and the intermediate species dimethylsilanone (D_1 , $\text{Me}_2\text{Si}=\text{O}$), methyl abstraction from the ring to produce a radical ring species, and ring-opening to produce a linear diradical group, respectively. Reactions 4-6 are analogous pathways for D_3 .

Table V. XPS elemental ratios for HFCVD films from D_3 and D_4 .

Precursor	T_f (°C)	O/Si	C/Si
D_3	860	1.19	1.63
	1000	1.14	1.42
	1100	1.12	1.38
D_4	800	1.23	1.86
	900	1.10	1.44
	1000	1.12	1.34

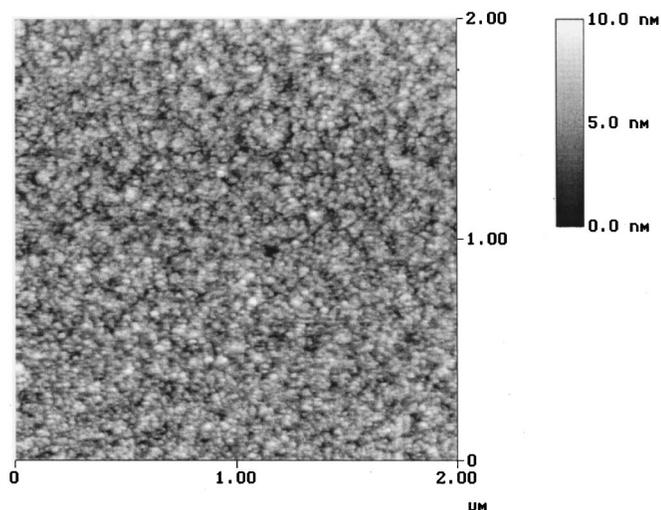


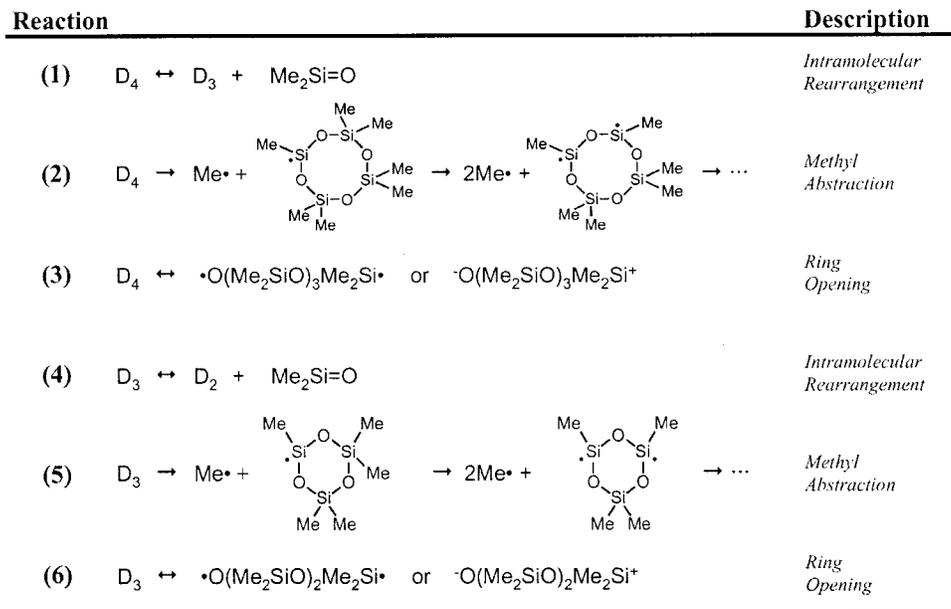
Figure 10. Atomic force micrograph of D_4 HFCVD film deposited at a filament temperature of 900°C . RMS roughness over image area is 1.1 nm. RMS roughness of bare silicon is 0.53 nm.

Previous studies have investigated the gas-phase pyrolysis of D_3 and D_4 over a temperature range from 400 to 1100°C and a pressure range from 10^{-4} to 1.0 Torr.^{22,55-58} For the pyrolysis of D_4 , the only products observed were D_3 and D_5 , with the rate of formation of D_5 decreasing rapidly above 2% decomposition until D_3 was the only product at high conversions.^{57,58} The formation of the intermediate D_1 was postulated to explain the observed results, and the presence of D_5 explained by recombination of D_1 with D_4 . Other authors have postulated the existence of D_1 ,^{56,59,60} and evidence for its existence has been collected in matrix IR studies of the vacuum pyrolysis of D_4 .²² In the latter study, temperatures from 900 to 1050°C were used, closer to those used in our work, and significant conversion of D_4 to D_3 was also noted at these higher temperatures. D_1 may result from the intramolecular rearrangement of D_4 at high temperatures, and similar thermal rearrangements have been observed in other dimethylsiloxanes. It has been suggested that these involve the for-

mation of a bicyclic transition state, accounting for the predominant cleavage of the Si-O bond over the weaker Si-C bond.^{22,56,60-64}

D_1 may be a growth precursor for the organosilicon films, with a polymerization mechanism analogous to that postulated for the diradical difluorocarbene (CF_2) during HFCVD of fluorocarbon films.⁶⁵ Indeed, heterogeneous loss of D_1 has been postulated to account for discrepancies in the mass balance in previous pyrolysis studies of D_4 .⁵⁸ For the early stages of this pyrolysis ($<4\%$ decomposition), an activation energy of 301 ± 6.3 kJ/mol was reported for Reaction 1.⁵⁸ This is close to the apparent activation energy of 301 ± 102 kJ/mol estimated from the kinetic data in Fig. 1 for D_4 , and suggests that Reaction 1 may be the predominant pathway for the pyrolysis of D_4 at low filament temperatures. It is illuminating to apply the reported rate law to our CVD system. At low filament temperatures (e.g., 800°C), where the conversion of D_4 is likely to be less than 4% and 569°C may be representative of the gas-phase temperatures some distance from the filament, the conversion of D_4 using this rate law is calculated to be 0.3%. Assuming a film density²⁵ of 1.3 g/cm³, the production of D_1 could yield film growth at a rate of 10.8 nm/min on a 4 in. wafer. By comparison, the measured deposition rate at 800°C was 2.2 nm/min. At higher filament temperatures (above 1000°C), the conversion of D_4 exceeds 4% and the rate law no longer applies. Hence, film growth by D_1 generated via Reaction 1 is possible, and could lead to a linear siloxane backbone structure. This may explain the higher C/Si ratio in XPS and the lack of ASM doublet structure in FTIR for the D_4 film deposited at a filament temperature of 800°C .

In contrast to D_4 , the pyrolysis of D_3 is not expected to yield significant quantities of D_1 . The D_2 ring is highly unstable^{60,66} and the elimination of D_1 from D_3 as shown in Reaction 4 is known to be highly endothermic.^{58,62} The lack of this pathway for producing growth species may explain the lower deposition yields observed for D_3 , despite the molecule's planar strained conformation and typically high reactivity in heterolytic reactions. Instead, the rupture of the silicon-methyl bond via Reaction 5 is likely to predominate. In preliminary studies, Davidson and Thompson⁵⁸ reported on the kinetics of this reaction for the loss of one methyl group between 578 and 662°C . Calculations at 662°C analogous to those performed for Reaction 1 showed that a loss of one methyl group from D_3 via Reaction 5 could account for a conversion of 0.6% of the precursor,



Scheme 1. Reaction pathways for the production of polymerization precursor species in D_3 and D_4 HFCVD.

and could yield film growth at a rate of 76.2 nm/min. If only one methyl group were lost per D_3 molecule, the oR_3 ring structure could be incorporated into the film as a terminal group. Additional methyl abstraction processes may also occur after the initial loss, resulting in incorporation of the oR_3 structure as a polymeric (loss of two methyl groups) or networked unit (loss of three methyl groups). Incorporation requires bonding of the oR_3 group to another oR_3 group and/or a D_1 unit, and, in the absence of free oxygen, involves a silicon-silicon bond. This may be the origin of the assigned silicon-silicon group observed in Raman spectroscopy. By similar reasoning, methyl abstraction from D_4 , as shown in Reaction 2, and subsequent incorporation of the oR_4 group is possible. However, no kinetic data has been found for Reaction 2.

Ring-opening is also possible for both D_3 and D_4 , as illustrated in Reactions 3 and 6. However, direct homolytic cleavage of the Si-O bond in cyclosiloxanes to produce diradicals of the form $\cdot SiMe_2(OSiMe_2)_nO\cdot$ is unlikely.^{60,62} Free radical polymerization of diradical species produced by Reactions 3 and 6 is thus improbable. Ionic polymerization also seems unlikely in an HFCVD environment, where ions are expected to be short-lived. Such pathways are more likely in a plasma environment, where ionic species formed from the ring-opening of cyclic dimethylsiloxanes have been postulated to explain growth mechanisms in organosilicon PECVD from similar precursors.^{1,67-69} Furthermore, if the ring-opening reaction were the primary contributor to the production of film growth species, it is anticipated that greater ring strain in D_3 would be reflected in higher growth yields for that precursor. Instead, Fig. 1 shows that deposition yields for D_4 are consistently higher than for D_3 . For comparison, ring strains of 10.5 kJ/mol for D_3 and 1.00 kJ/mol for D_4 have been reported.⁶⁶ Hence, polymerization of linear species produced via Reactions 3 and 6 does not appear to be a dominant mode of film growth.

Growth of the D_3 and D_4 HFCVD films is thus believed to occur mainly through the combination of growth precursors generated via Reactions 1, 2, and 5. For D_4 , there is competition between the generation of D_1 via Reaction 1 and the generation of oR_3 groups from methyl abstraction in Reaction 2. Since Reaction 1 produces D_3 , there is an additional pathway for the incorporation of oR_3 groups generated via Reaction 5. At low filament temperatures, Reaction 1 may dominate, resulting in film growth primarily from D_1 species. At higher filament temperatures, however, evidence of oR_3 incorporation suggests that Reaction 5 starts to compete. For D_3 , Reaction 5 is the predominant source of potential growth precursors in the form of oR_3 structures. However, it does not appear to be the only source, as all films from D_3 show some evidence of incorporation of oR_4 and/or ID units in the film structure. Pyrolysis studies of D_3 have shown evidence of appreciable concentrations of D_4 in the pyrolyzate, and it was found that the concentration of D_4 in the pyrolyzate decreased as pyrolysis temperature increased.^{55,56} At low filament temperatures, where D_4 concentrations are higher, there is probably a significant contribution of Reaction 1 to the chemistry. At higher temperatures, where D_3 concentrations are high, Reaction 1 is probably less favorable and D_4 reacts preferentially via the methyl abstraction process in Reaction 2. This may explain the shift observed in the Raman band assigned to oR_4 and/or ID as filament temperature increases (Fig. 6). For the 860°C film, this band is centered close to 495 cm^{-1} but shifts to about 505 cm^{-1} for filament temperatures above 1000°C. There also appears to be a new band that appears near 465 cm^{-1} above this temperature. Most likely, the band centered around 495 cm^{-1} is indicative of a linear siloxane unit derived from the polymerization of D_1 . The two bands that appear at higher temperature are indicative of an oR_4 unit (at 505 cm^{-1}) and a larger structure such as oR_5 (at 465 cm^{-1}). The five-membered siloxane ring, oR_5 , could originate from D_5 via methyl abstraction processes analogous to those in Reactions 2 and 5.

It is thus postulated that growth of the D_3 HFCVD film occurs in two distinct regimes: at low filament temperatures, there is growth primarily from linear polymeric units (ID) and by the incorporation of rings consisting of three siloxane units (oR_3); at high filament temperatures, there is growth primarily from three- and higher membered siloxane rings (oR_3 , oR_4 , oR_5 , and higher). This growth model is consistent with previous studies of D_3 pyrolysis, in which it was observed that as temperature increased, the composition of the pyrolyzate changed from a linear polymeric mixture of molecular weight 1810 to a mixture of cyclic components consisting mainly of D_3 , D_4 , and D_5 .⁵⁵

Film structure.—The physical properties of the D_3 and D_4 HFCVD films show evidence of cross-linking. In particular, as-deposited films are found to be insoluble in common solvents and form visible flakes when scraped off the wafer. In contrast, a poly-methylsiloxane polymer with a composition of 30% T and 70% D groups, corresponding to C:Si = 1.70, is a liquid at ambient conditions, and more cross-linked polymethylsiloxanes remain resinous up to a composition of about 90% T and 10% D groups, corresponding to C:Si = 1.10.⁶⁶ The HFCVD films show higher C:Si values between 1.90 and 1.30 but are coherent, hard, and show no evidence of tackiness. Qualitatively, films deposited at higher filament temperatures are observed to be harder than those deposited at lower filament temperatures, suggesting higher cross-link densities. However, the concentration of T and Q groups observed in NMR even at high filament temperatures is not sufficient to explain the lack of resinous character in the films. Some other type of cross-linking group must be present.

Spectroscopic evidence suggests that this networking occurs via silicon-silicon bonding which may originate during film growth from ring structures that have lost methyl groups, as illustrated in Reactions 2 and 5 in Scheme 1. These reactions produce cyclic structural units capable of silicon-silicon bonding. Ring structures are then “tiled” into the film structure and observed as the moieties oR_3 and oR_4 . Analogous silicon-silicon bonding of cyclic structures has been observed in radiation-induced cross-linking of D_4 ,⁷⁰ and occurrences of Si-Si bonding have also been reported for other organosilicon materials, including siloxane polymers and hexamethyldisiloxane.⁷¹ Raman data confirm that for both D_3 and D_4 films, there is a simultaneous increase in intensity for bands assigned to oR_3 and silicon-silicon bonding as filament temperature is raised. Reactions 2 and 5 thus appear to be the dominant pathway for silicon-silicon bonding.

Increased cross-link density by silicon-silicon bonding is expected to occur at the expense of methyl groups. This is confirmed by XPS data from Table V, which show a decrease in methyl content as filament temperature is increased, with little corresponding change in oxygen content. From the data, it is possible to speculate on the average number of silicon-silicon bonds per structural unit. To form part of a polymeric chain, at least two methyl abstraction events are required per structural unit. For the case where only three-membered siloxane rings are incorporated, data from Table V correspond to an average loss of 2.0 methyl groups per ring. For the case where only four-membered rings are incorporated, these data correspond to an average loss of 2.6 methyl groups per ring. A loss of at least three methyl groups per ring is necessary to produce a networked structure. The data are thus consistent with incorporation of both oR_3 and oR_4 units in HFCVD films.

Conclusions

HFCVD is a technique capable of producing smooth organosilicon thin films of unique structure at high deposition rates. Filament temperature can be used for controlling the film structure. During the growth process, there appears to be competition between pathways for the incorporation of three-membered and higher order siloxane ring structures, and pathways for the incorporation of linear structures in the films. For both D_3 and D_4 , there is greater incorpo-

ration of ring structures consisting of three siloxane units (oR_3) as filament temperature is increased. The incorporation of these structures is more pronounced for films grown from D_3 . The D_3 films also show evidence of higher order ring structures such as oR_4 and oR_5 at high filament temperatures. By contrast, D_4 films show a greater degree of incorporation of linear, unstrained structures (ID) over the range of filament temperatures studied. Ring structures are generated from methyl abstraction processes and are incorporated into the structure via silicon-silicon bonds. In contrast to organosilicon films produced by plasma processing, cross-linking via silicon-silicon bonding appears to predominate over that from siloxane bonds containing tertiary or quaternary silicon atoms.

Acknowledgments

We gratefully acknowledge the support of the NIH under contract NO1-NS-9-2323, and the NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing in funding this work. This work also made use of the MRSEC Shared Facilities supported by the National Science Foundation under award no. DMR-9400334 and NSF Laser Facility grant no. 9708265-CHE.

Massachusetts Institute of Technology assisted in meeting the publication costs of this article.

References

1. A. M. Wróbel and M. R. Wertheimer, in *Plasma Deposition, Treatment, and Etching of Polymers*, R. d'Agostino, Editor, p. 163, Academic Press, San Diego, CA (1990).
2. F. F. Shi, *Surf. Coat. Technol.*, **82**, 1 (1996).
3. H. G. Pryce Lewis, D. J. Edell, and K. K. Gleason, *Chem. Mater.*, **12**, 3488 (2000).
4. A. S. Chawla, *Biomaterials*, **2**, 83 (1981).
5. Z. Ogumi, Y. Uchimoto, and Z. Takehara, *J. Electrochem. Soc.*, **136**, 625 (1989).
6. M. Kusabiraki, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **46**, 473 (1990).
7. P. K. Tien, G. Smolinsky, and R. J. Martin, *Appl. Opt.*, **11**, 637 (1972).
8. Y. Ishikawa, S. Sasakawa, M. Takase, Y. Iriyama, and Y. Osada, *Makromol. Chem., Rapid Commun.*, **6**, 495 (1985).
9. H. Matsuyama, A. Kariya, and M. Teramoto, *J. Appl. Polym. Sci.*, **51**, 689 (1994).
10. L. Peters, *Semicond. Int.*, **23**, 108 (2000).
11. M. J. Loboda, *Microelectron. Eng.*, **50**, 15 (2000).
12. A. Grill and V. Patel, *J. Appl. Phys.*, **85**, 3314 (1999).
13. H. Yasuda and T. Hsu, *J. Polym. Sci., Polym. Chem. Ed.*, **15**, 81 (1977).
14. C. R. Savage, R. B. Timmons, and J. W. Lin, *Adv. Chem. Ser.*, **236**, 745 (1993).
15. N. M. Mackie, N. F. Dalleska, D. G. Castner, and E. R. Fisher, *Chem. Mater.*, **9**, 349 (1997).
16. C. B. Labelle, S. M. Karecki, L. R. Reif, and K. K. Gleason, *J. Vac. Sci. Technol. A*, **17**, 3419 (1999).
17. K. K. S. Lau and K. K. Gleason, *J. Fluorine Chem.*, **104**, 119 (2000).
18. S. J. Limb, K. K. S. Lau, D. J. Edell, E. F. Gleason, and K. K. Gleason, *Plasmas Polym.*, **4**, 21 (1999).
19. M. C. Kwan and K. K. Gleason, *Chem. Vap. Deposition*, **3**, 299 (1997).
20. W. K. Chang, M. Y. Liao, and K. K. Gleason, *J. Phys. Chem.*, **100**, 19653 (1996).
21. A. M. Wróbel, S. Wickramanayaka, Y. Nakanishi, Y. Fukuda, and Y. Hatanaka, *Chem. Mater.*, **7**, 1403 (1995).
22. V. N. Khabashesku, Z. A. Kerzina, A. K. Maltsev, and O. M. Nefedov, *J. Organomet. Chem.*, **364**, 301 (1989).
23. A. L. Smith, *Spectrochim. Acta*, **16**, 87 (1960).
24. K. M. McNamara, B. E. Williams, K. K. Gleason, and B. E. Scruggs, *J. Appl. Phys.*, **76**, 2466 (1994).
25. C. Rau and W. Kulisch, *Thin Solid Films*, **249**, 28 (1994).
26. N. Wright and M. J. Hunter, *J. Am. Chem. Soc.*, **69**, 803 (1947).
27. R. E. Richards and H. W. Thompson, *J. Chem. Soc.*, **1949**, 124.
28. T. Alvik and J. Dale, *Acta Chem. Scand.*, **25**, 2142 (1971).
29. G. G. Kirei and M. P. Lisitsa, *Opt. Spectrosc.*, **12**, 403 (1962).
30. L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, 2nd ed., p. 334, John Wiley & Sons, Inc., New York (1958).
31. A. L. Smith and D. R. Anderson, *Appl. Spectrosc.*, **38**, 822 (1984).
32. I. Tajima and M. Yamamoto, *J. Polym. Sci., Part A: Polym. Chem.*, **25**, 1737 (1987).
33. A. T. Kohl, R. Mimna, R. Shick, L. Rhodes, Z. L. Wang, and P. A. Kohl, *Electrochem. Solid-State Lett.*, **2**, 77 (1999).
34. M. C. Kwan, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA (1997).
35. M. Soutzidou, A. Panas, and K. Viras, *J. Polym. Sci., Part B: Polym. Phys.*, **36**, 2805 (1998).
36. H. Kriegsmann, in *Advances in Molecular Spectroscopy; Proceedings*, A. Mangini, Editor, Vol. 3, p. 1000, Pergamon Press, New York (1962).
37. G. Fogarasi, H. Hacker, V. Hoffmann, and S. Dobos, *Spectrochim. Acta*, **30A**, 629 (1974).
38. F. L. Galeener, *J. Non-Cryst. Solids*, **49**, 53 (1982).
39. C. A. M. Mulder, R. K. Janssen, P. Bachmann, and D. Leers, *J. Non-Cryst. Solids*, **72**, 243 (1985).
40. C. J. Brinker, D. R. Tallant, E. P. Roth, and C. S. Ashley, *J. Non-Cryst. Solids*, **82**, 117 (1986).
41. B. Humbert, A. Burneau, J. P. Gallas, and J. C. Lavalley, *J. Non-Cryst. Solids*, **143**, 75 (1992).
42. T. Nakano, N. Mura, and A. Tsuzumitani, *Jpn. J. Appl. Phys., Part 2*, **34**, L1064 (1995).
43. C. A. M. Mulder and A. A. J. M. Damen, *J. Non-Cryst. Solids*, **93**, 387 (1987).
44. U. G. Stolberg and H. P. Fritz, *Z. Anorg. Allg. Chem.*, **330**, 1 (1964).
45. M. Hayashi, *Nippon Kagaku Kaishi*, **78**, 1472 (1957).
46. R. K. Harris, J. D. Kennedy, and W. McFarlane, in *NMR and the Periodic Table*, R. K. Harris and B. E. Mann, Editors, p. 309, Academic Press, New York (1978).
47. E. A. Williams, in *Annual Reports on NMR Spectroscopy*, G. A. Webb, Editor, p. 235, Academic Press, London (1983).
48. D. J. Burton, R. K. Harris, K. Dodgson, C. J. Pellow, and J. A. Semlyen, *Polym. Commun.*, **24**, 278 (1983).
49. R. A. Assink, A. K. Hays, R. W. Bild, and B. L. Hawkins, *J. Vac. Sci. Technol. A*, **3**, 2629 (1985).
50. S. Roualdes, N. Hovnanian, A. van der Lee, J. Sanchez, and J. Durand, *J. Phys. IV*, **9**, 1147 (1999).
51. D. R. Anderson, in *Analysis of Silicones*, A. L. Smith, Editor, 41, p. 407, Wiley, New York (1974).
52. H. Marsmann, in *NMR: Oxygen-17 and Silicon-29*, P. Diehl, E. Fluck, and R. Kosfeld, Editors, Vol. 17, p. 65, Springer-Verlag, New York (1981).
53. C. B. Labelle and K. K. Gleason, *J. Appl. Polym. Sci.*, **74**, 2439 (1999).
54. K. K. S. Lau, J. A. Caulfield, and K. K. Gleason, *Chem. Mater.*, **12**, 3032 (2000).
55. M. Sobolevskii, I. Skorokhodov, V. Ditsent, L. Sobolevskaya, and G. Moiseyeva, *Vysokomol. Soedin., Ser. A*, **12**, 2714 (1970).
56. L. E. Gusef'nikov, N. S. Nametkin, T. K. Islamov, A. A. Soltsov, and V. M. Vdovin, *Izv. Akad. Nauk. SSR, Ser. Khim.*, **20**, 84 (1971).
57. I. M. T. Davidson and J. F. Thompson, *J. Chem. Soc., Chem. Commun.*, **1971**, 251.
58. I. M. T. Davidson and J. F. Thompson, *J. Chem. Soc., Faraday Trans. 1*, **71**, 2260 (1975).
59. G. Raabe and J. Michl, *Chem. Rev.*, **85**, 419 (1985).
60. M. G. Voronkov, *J. Organomet. Chem.*, **557**, 143 (1998).
61. T. Howard Thomas and T. C. Kendrick, *J. Polym. Sci., Part A-2*, **7**, 537 (1969).
62. L. E. Gusef'nikov and N. S. Nametkin, *Chem. Rev.*, **79**, 529 (1979).
63. N. Grassie and I. G. MacFarlane, *Eur. Polym. J.*, **14**, 875 (1978).
64. D. J. Bannister and J. A. Semlyen, *Polymer*, **22**, 377 (1981).
65. K. K. S. Lau, K. K. Gleason, and B. L. Trout, *J. Chem. Phys.*, **113**, 4103 (2000).
66. W. Noll, *Chemistry and Technology of Silicones*, 2nd ed., Academic Press, New York (1968).
67. A. M. Wróbel, M. Kryszewski, and M. Gazicki, *J. Macromol. Sci., Chem.*, **A20**, 583 (1983).
68. P. Favia, R. d'Agostino, and F. Fracassi, *Pure Appl. Chem.*, **66**, 1373 (1994).
69. G. Smolinsky and M. J. Vasile, *Int. J. Mass Spectrom. Ion Phys.*, **12**, 147 (1973).
70. S. W. Kantor and R. C. Osthoff, U.S. Pat. 2,793,222 (1957).
71. R. A. Shaw, in *International Symposium on Organosilicon Chemistry*, p. 297, Butterworths, London (1966).
72. D. M. Adams and W. S. Fernando, *J. Chem. Soc. Dalton Trans.*, **4**, 410 (1973).
73. R. K. Harris and B. J. Kimber, *J. Organomet. Chem.*, **70**, 43 (1974).
74. H.-G. Horn and H. C. Marsmann, *Makromol. Chem.*, **162**, 255 (1972).