Macromolecules **2002,** *35,* 1967−1972

Fluorocarbon−Organosilicon Copolymer Synthesis by Hot Filament Chemical Vapor Deposition

Shashi K. Murthy[†] and Karen K. Gleason*[,‡]

Departments of Materials Science and Engineering and Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received July 20, 2001; Revised Manuscript Received December 3, 2001

ABSTRACT: Hot-filament chemical vapor deposition has been used to deposit copolymer thin films consisting of fluorocarbon and organosilicon groups from hexafluoropropylene oxide (HFPO) and hexamethylcyclotrisiloxane (D_3). This method offers an easy route to the production of such copolymers as the process does not require a solvent and can be performed in a single step. The presence of covalent bonds between the fluorocarbon and organosilicon moieties in the thin films has been confirmed by infrared spectroscopy; X-ray photoelectron spectroscopy (XPS); and solid-state ^{19}F, ^{13}C, and ^{29}Si nuclear magnetic resonance (NMR) spectroscopy. The film structure consists of chains with linear and cyclic siloxane groups and CF_2 groups as repeat units. Cross-linking and termination occur mainly via the siloxane units.

Introduction

Fluorocarbon and organosilicon thin films produced by chemical vapor deposition have a wide variety of applications, ranging from biocompatible coatings for medical implants[1−6] to low-κ dielectrics in integrated circuits.[7−13] Fluorocarbon films have been found to be biocompatible and to have low dielectric constants. Organosilicon films with cross-linked siloxane groups offer the advantage of superior thermal stability [relative to linear poly(dimethylsiloxane)].[14] Further, they adhere well to silicon substrates by means of covalent bonds formed with the native oxide on the silicon surface.[15] A fluorocarbon−organosilicon copolymer film therefore has the potential to incorporate the desirable attributes of each class of material into a single film.

Silicone or fluorocarbon homopolymers can be coated onto surfaces by a number of techniques such as spin-on coating, casting, or chemical vapor deposition. An important advantage of chemical vapor deposition (CVD) is the ability to create copolymers that are difficult to synthesize by bulk or solution techniques, such as fluorocarbon−organosilicon copolymers. Organosilicon polymers having fluorocarbon pendant groups of the form $CH_2CH_2(CF_2)_xCF_3$ as well as polymers having short fluorocarbon segments attached to siloxane chains have been synthesized by solution chemistry techniques.[16−19] CVD offers an easier route to the production of these polymers as the process does not involve a solvent and can be performed in a single step.

Among the different CVD techniques available, hot-filament CVD (HFCVD, also known as pyrolytic or hot-wire CVD) is unique in several respects. First, HFCVD does not require the generation of a plasma, thereby avoiding defects in the growing film produced by UV irradiation and ion bombardment. In addition, films produced by HFCVD have better-defined chemical structures because there are fewer reaction pathways than in the less-selective plasma-enhanced CVD method. Further, HFCVD has been shown to produce films that have low degrees of cross-linking.[20] Co-deposition of fluorocarbon and organosilicon precursors has been performed using plasma-enhanced CVD methods,[21−23] but the resulting films had complex structures without clearly defined spectroscopic features.

HFCVD has been used to deposit fluorocarbon films that are spectroscopically similar to poly(tetrafluoroethylene) (PTFE),[20] as well as organosilicon films that consist of linear and cyclic siloxane repeat units.[24] The precursors used in these investigations were hexafluoropropylene oxide (HFPO) and hexamethylcyclotrisiloxane (D_3), respectively. The primary propagating unit in the fluorocarbon films was difluorocarbene, generated by the pyrolysis of HFPO. In the case of the organosilicon films, the decomposition of D_3 was postulated to occur in two ways: by the breakdown of the rings into dimethylsilanone and by methyl abstraction from the six-membered ring structure, giving rise to the linear and cyclic repeat units, respectively.

This paper describes the deposition of fluorocarbon−organosilicon copolymer thin films by HFCVD from HFPO and D_3. The copolymer films have well-resolved bonding environments, and extensive spectroscopic characterization confirms the presence of covalent bonds between CF_2 groups and siloxane-based polymeric units in the film.

Experimental Section

Depositions were performed in a custom-built vacuum chamber on to silicon wafer substrates. The pressure within the chamber was controlled by a butterfly valve connected to an MKS type 252 exhaust valve controller. Substrates were placed on a stage maintained at a low temperature (15 ± 5 °C) by the circulation of chilled water through internal coils. Precursor breakdown was achieved by means of a resistively heated 0.038-cm-diameter Nichrome wire (80% nickel, 20% chromium; Omega Engineering). The frame holding the filament wire was equipped with springs to compensate for thermal expansion of the wire upon heating. The distance between the filament wire and the substrate was 1.4 cm. The filament temperature was measured by a 2.2-μm infrared pyrometer. The spectral emissivity was estimated to be 0.85 on the basis of direct-contact thermocouple experiments.

The flow of HFPO gas (donated by DuPont) into the chamber was controlled by an MKS model 1295C mass flow controller

---

* Corresponding author. E-mail: kkg@mit.edu. Fax: (617) 253-6480.

[†] Department of Materials Science and Engineering.

[‡] Department of Chemical Engineering.

10.1021/ma011286a CCC: $22.00

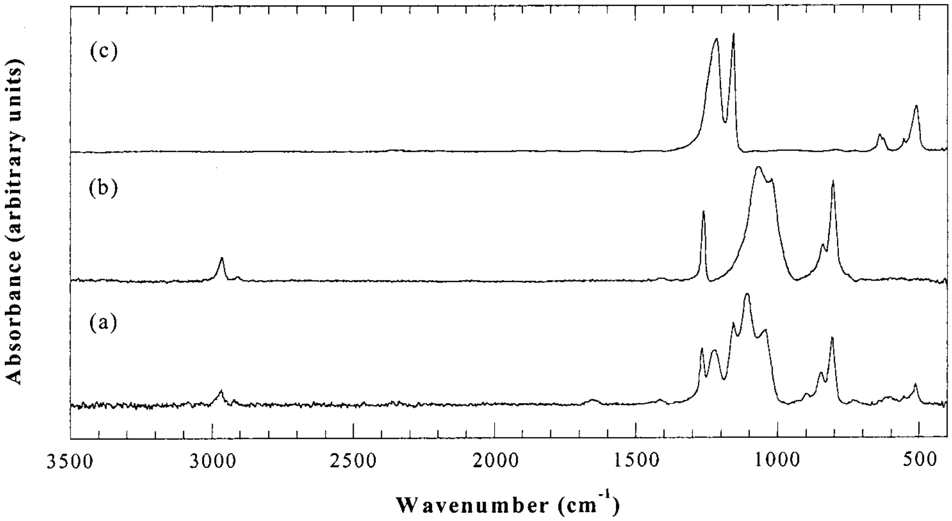

Figure 1. FTIR spectra of (a) copolymer, (b) silicone, and (c) fluorocarbon films, all deposited by HFCVD under the same conditions.

Table 1. Absorption Band Assignments for FTIR Spectra

assignment	copolymer (cm^{-1})	literature (cm^{-1})	ref
CF_2 rocking	514	516–520	37, 38
CF_2 wagging	610	650	39
Si–C stretching, CH_3 rocking in Si–Me_2	808	805	40
Si–C stretching, CH_3 rocking in Si–Me_3	848	845	40
Si–C stretching, CH_3 rocking in $Si(Me)_2(CF_2)$	899	N/A	N/A
Si–O–Si asymmetric stretching	1043, 1107	1050	40
CF_2 symmetric stretching	1155	1160	39
CF_2 asymmetric stretching	1223	1220	39
CH_3 symmetric bending in Si–Me_x	1265	1260	40
CH symmetric stretching in sp^3 CH_3	2913	2900	40
CH asymmetric stretching in sp^3 CH_3	2967	2960	40

(MFC). The silicone precursor, D_3 (Gelest) was vaporized in a stainless steel vessel that was heated to 90 ± 5 °C. The lines leading from the vessel to the vacuum chamber were maintained at 130 ± 5 °C. The flow of vapor from the vessel into the chamber was regulated by a needle valve.

Prior to the deposition of copolymer film, the filament wire was preconditioned by being heated at a constant voltage of 86.5 V and under a flow of HFPO into the reactor at 30 sccm for 20 min at a chamber pressure of 1 Torr. Following this treatment, the power to the filament was turned down over a 5-min span, and the chamber was pumped up to atmospheric pressure to facilitate cleaning and placement of a 4-in. wafer on the stage.

Depositions were performed at a filament temperature of 620 °C and a chamber pressure of 1 Torr. The precursor flow rates were 20 sccm for HFPO and 28 sccm for D_3. The duration of these depositions ranged between 10 and 30 min. The deposition rate, determined by profilometry, was approximately 250 Å/min.

Fourier transform infrared (FTIR) spectroscopy was performed on the deposited films using a Nicolet Magna 860 spectrometer in transmission mode. The spectra were baseline-corrected and normalized to a thickness of approximately 7000 Å. X-ray photoelectron spectroscopy (XPS) was carried out on a Kratos Axis Ultra spectrometer using a monochromatized aluminum K α source.

Solid-state NMR spectroscopy was performed on a home-built spectrometer comprising a 6.338 T Oxford superconducting magnet and a 3.2-mm Chemagnetics magic angle sample spinning (MAS) probe. For this analysis, approximately 14 mg of film was scraped off wafers from nine 30-min depositions and packed into a zirconia rotor of 11 mm^3 internal volume. Sample spinning at the magic angle of 54.7° was performed to mitigate spectral broadening due to strong homonuclear dipolar and anisotropic chemical shift effects. The sample spinning speeds were 5, 25, and 10 kHz for ^{29}Si, ^{19}F, and ^{13}C, respectively.

^{29}Si NMR experiments were performed with proton cross-polarization (CP) and proton decoupling to enhance the signal and resolution from the low-natural-abundance ^{29}Si nuclei. The ^{1}H–^{29}Si CP time was 5 ms (as determined by contact-time experiments performed by Pryce Lewis et al.[24]), and the 90° pulse width was 1.3 μs. ^{29}Si spectra were also obtained with fluorine cross-polarization and fluorine decoupling. The purpose of this was to determine which silicon atoms were in close proximity (<10 Å) to fluorine-containing moieties. Contact time experiments indicated that a CP time of 5 ms was sufficient to maximize the signal intensity. The 90° pulse width for these measurements was 1.2 μs. ^{29}Si chemical shifts were externally referenced to tetramethylsilane.

^{19}F NMR spectra were obtained by direct polarization with a 90° pulse width of 1.2 μs. Chemical shifts were externally referenced to trichlorofluoromethane. ^{13}C spectra were obtained by direct polarization with proton decoupling, as well as direct polarization with fluorine decoupling. The 90° pulse width was 1.8 μs for both types of spectra. ^{13}C chemical shifts were externally referenced to tetramethylsilane.

Results and Discussion

Fourier Transform Infrared (FTIR) Spectroscopy. Figure 1 shows the FTIR spectrum of a copolymer film compared with the spectra of homopolymeric fluorocarbon and silicone films obtained from HFPO and D_3, respectively. Table 1 gives the absorption band assignments from the literature. All of the bands associated with the pure-fluorocarbon[20] and pure-silicone[24] films appear in the hybrid film, although slight shifts in position occur in some of the bands.

The FTIR bands in all three HFCVD films in Figure 1 are relatively narrow (fwhm of ~ 60 cm^{-1} or less), aiding in the resolution of specific chemical environments. For example, the symmetric (1155 cm^{-1}) and

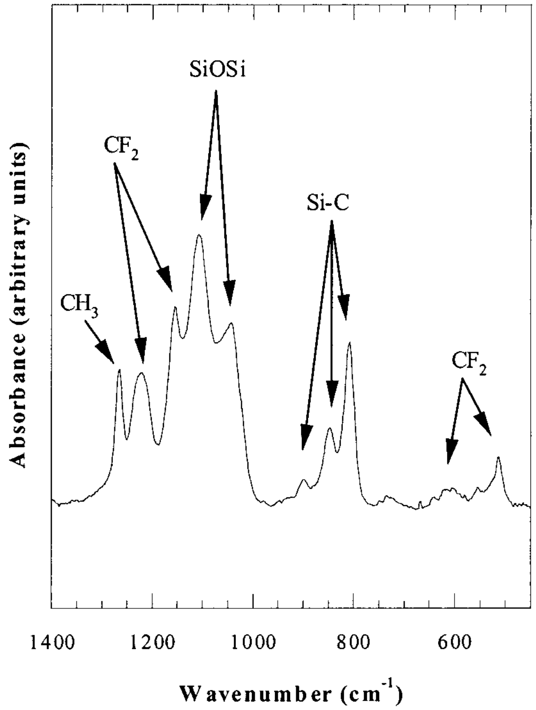

Figure 2. Low-wavenumber region from the FTIR spectrum of the copolymer film.

asymmetric (1223 cm^{-1}) CF_2 stretches can be clearly resolved in Figure 1c. In plasma-deposited films, there is typically only one broad band in the 1100−1500-cm^{-1} region[20] resulting from overlap of several types of C−F bonding environments. The narrowness of the FTIR bands thus indicates the structural simplicity of the HFCVD copolymer films.

The asymmetric stretching mode (ASM) of the siloxane (Si−O−Si) group is also easily resolved. The region around these bands in the copolymer spectrum is expanded for detail in Figure 2. The ASM appears as a doublet, as in the case of poly(dimethylsiloxane) chains with three or more siloxane units or ring structures of more than eight siloxane units.[25,26] Both peaks of this doublet in the copolymer film (1043 and 1107 cm^{-1}) are shifted toward higher wavenumbers relative to the pure-silicone film (1020 and 1068 cm^{-1}). No shift would be expected if the fluorocarbon and organosilicon moieties were simply depositing together as two independent phases. Also, it is known[27] that electronegative substituents on the silicon atom increase the Si−O stretching frequency. Hence, the shift of the ASM is consistent with copolymerization, where bonds are formed between silicon atoms and CF_2 groups.

Two other modes (rocking and wagging) of the CF_2 groups appear at 514 and 610 cm^{-1} in the copolymer spectrum. The band at 610 cm^{-1} is shifted relative to its position in the pure-fluorocarbon spectrum (620 cm^{-1}). This shift toward lower wavenumbers is consistent with the shift of the ASM in the opposite direction, an effect of the redistribution of electron density caused by copolymerization.

In the pure-silicone film, Si−C stretching bands appear at 808 and 848 cm^{-1}. The copolymer spectrum contains both of these bands, as well as a third band at 899 cm^{-1}. The Si−C stretching mode is dependent on the vibrations of the substituents on the silicon atom.[28] Hence, it is likely that the band at 899 cm^{-1} is due to the Si−C stretching mode of a siloxane moiety that has both methyl and CF_2 substituents bonded to silicon.

Table 2. XPS Survey Scan Data

binding energy (eV)	element	atomic concentration (%)
101	Si (2p)	13.55
283	C (1s)	30.70
531	O (1s)	15.33
576	Cr (2p)	0.48
687	F (1s)	38.42
859	Ni (2p)	1.53

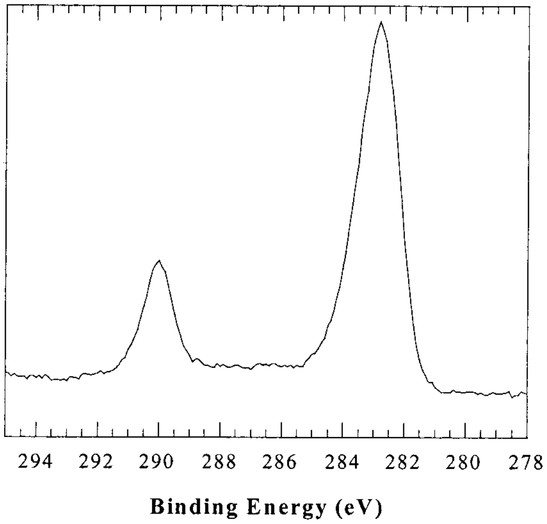

Figure 3. Carbon (1s) high-resolution scan of the HFCVD copolymer film showing CF_2 and CH_3 peaks.

The bands at 2913 and 2967 cm^{-1} represent the symmetric and asymmetric stretching modes of the CH bond in sp^3 CH_3, respectively. The absence of sp^3 CH_2 bands indicates that there is no cross-linking through methylene bridges.

X-ray Photoelectron Spectroscopy. Table 2 summarizes atomic composition data obtained from a survey scan. The Si/O ratio is approximately 1:1.13. The high-resolution Si (2p) scan (not shown) contains a single peak with no apparent shoulders. The line width of this peak is slightly larger than that for a film deposited under the same conditions using D_3 only. Hence, whereas the Si/O ratio suggests that the silicon atoms in the copolymer film are almost entirely in the +2 oxidation state, the line width of the Si (2p) peak indicates the possibility of a small concentration of different oxidation states.

A C 1s high-resolution scan (Figure 3) indicates the presence of only two types of carbon moieties, CF_2 and CH_3. The respective assignments at 290.0 and 282.8 eV were made using data obtained from pure-fluorocarbon and pure-silicone films. The assumption that most of the carbon present is in the form of either CF_2 or CH_3 will greatly simplify the process of making peak assignments in the NMR spectra.

The XPS survey scan also detected small amounts of nickel and chromium in the film (<1.5 atom %). Because no copolymer film was produced with a tantalum filament of equivalent diameter under the same conditions, this observation suggests that Nichrome plays a catalytic role in the process.

Solid-State Nuclear Magnetic Resonance Spectroscopy. The ^{19}F NMR spectrum of the copolymer film is shown in Figure 4, with spinning sidebands labeled

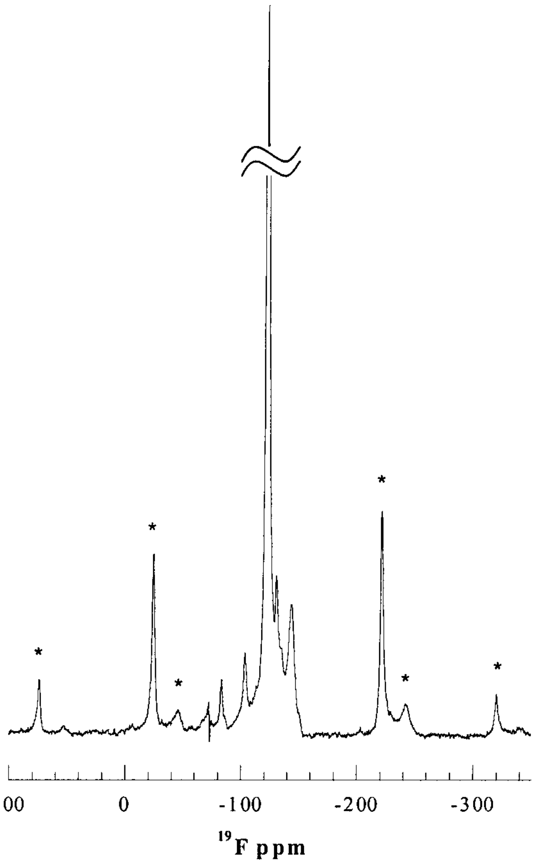

Figure 4. Solid-state ^{19}F NMR spectrum of the HFCVD copolymer film. The feature at −72 ppm is a spectrometer artifact.

Table 3. Chemical Shift Assignments for the ^{19}F NMR Spectrum

chemical shift (ppm)	structure	% area	ref
−83.6	$CF_3{*}CF_2$	1.65	41−47
−104.5	$CF_2{*}O$	2.97	48
−123.4	$CF_2CF_2{*}CF_2$	70.30	41−47
−128.0	$CF_3CF_2{*}CF_2$	0.08	41−47
−131.1	$CF_2CF_2{*}Si$	6.27	29
−135.3	$CF_3CF_2{*}Si$	1.10	29
−144.4	$SiCF_2{*}Si$	17.63	29

by asterisks. The remaining seven peaks represent resolved isotropic chemical shifts for fluorine. The chemical shift assignments are listed in Table 3. ^{19}F spectra of homopolymeric fluorocarbon films deposited by the same technique[20] show three peaks: $CF_2CF_2{*}CF_2$ at −123 ppm, $CF_3CF_2{*}CF_2$ at −128 ppm, and $CF_3{*}CF_2$ around −84 ppm. All three of these peaks are present in Figure 4.

The assignments for the peaks at −131.1, −135.3, and −144.4 ppm are based on chemical shifts reported for various Si−CF_2 environments in perfluoro(alkylsilanes) by Sharp et al.[29] It is postulated that these peaks correspond to $CF_2CF_2{*}Si$, $CF_3CF_2{*}Si$, and $SiCF_2{*}Si$, respectively. The sidebands that appear at −46 and −243 ppm are associated with the $SiCF_2{*}Si$ peak, indicating a broad chemical shift tensor and a lack of mobility of the fluorine atoms in this environment. The ^{19}F spectrum also indicates the presence of a small number of CF_2O linkages (−104.5 ppm). These linkages could form as a result of the copolymerization of CF_2 units and linear siloxane chains.

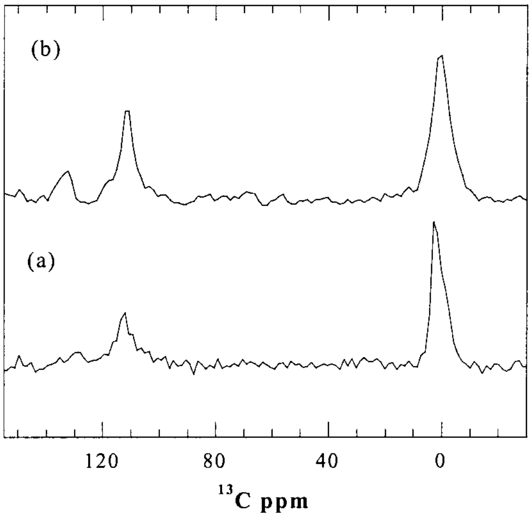

Figure 5. Solid-state ^{13}C NMR spectra of the HFCVD copolymer film obtained with (a) ^{1}H and (b) ^{19}F decoupling.

Table 4. Chemical Shift Assignments for the ^{13}C NMR Spectra

peak	chemical shift (ppm)	structure	% area
i	0	CH_3	62.0
ii	112	CF_2	29.4
iii	119	CF_3	1.1
iv	131	$Si{-}CF_2{-}Si$	7.5

The presence of Si−CF_3 linkages was ruled out on the basis of ^{19}F and ^{19}Si NMR experiments performed on a model compound [$CF_3{-}Si{-}(CH_3)_3$]. The observed ^{19}F and ^{29}Si shifts for this compound were −27.8 and −36.2 ppm, respectively.

Figure 5 shows the ^{13}C NMR spectra obtained with ^{1}H and ^{19}F decoupling. Chemical shift assignments for these spectra are summarized in Table 4. Assignments for peaks i−iii are taken from the literature.[30−34] In these spectra, the CH_3 and CF_2 peaks are the most intense; hence, the NMR analysis of the bulk film is in qualitative agreement with the surface analysis by C (1s) high-resolution XPS (Figure 3). As expected, the CH_3 peak is narrowest in the proton-decoupled spectrum, whereas the CF_2 and CF_3 peaks are narrowest in the fluorine-decoupled spectrum. There is a small amount of CF_3, evidenced by the presence of a shoulder on the peak at 118.6 ppm.

Given the appreciable content of $SiCF_2{*}Si$ in the ^{19}F spectrum, it seems likely that this moiety would also appear in the ^{13}C spectra. The peak at 131 ppm narrows considerably under fluorine decoupling and is therefore postulated to represent the $SiCF_2Si$ moiety. This hypothesis was tested by performing the calculation described below.

In the ^{19}F spectrum, the contribution of fluorine atoms to the $SiCF_2Si$ (peak area/2) was divided by the sum of the contributions from all of the fluorine atoms [(sum of all CF_2 peak areas)/2 + (CF_3 peak area)/3]. From the ^{13}C spectrum, the peak area of $SiCF_2Si$ was divided by the total area occupied by fluorocarbon groups (peaks ii−iv). The resulting values are in agreement (within 10%), supporting the respective assignments in the ^{19}F and ^{13}C spectra. These assignments are further substantiated by the ^{19}F and ^{13}C NMR data reported for a related molecule ($FMe_2Si{-}CF_2{-}SiMe_2F$) by Fritz and Bauer.[35] However, this type of linkage does not account for all of the CF_2 groups in the film as the ^{19}F NMR

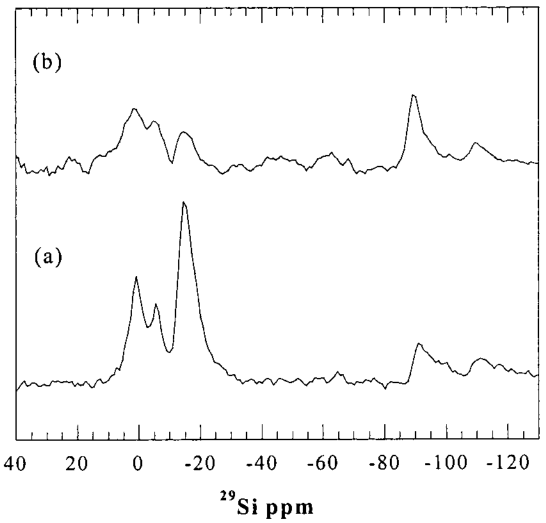

Figure 6. Solid-state ^{29}Si NMR spectra of the HFCVD copolymer film obtained with (a) ^{1}H and (b) ^{19}F cross-polarization and decoupling.

Table 5. Chemical Shift Assignments for the ^{29}Si NMR Spectra

chemical shift (ppm)	structure
0	$(CH_3)_2Si(O)(CF_2)$
−6.4	*o*-R_3
−15.5	$(O)_2Si(CH_3)_2$
−92.0	$(O)_2Si(CF_2)_2$
−112.0	$(O)_3Si(CF_2)$

spectrum indicates that a significant fraction of the CF_2 groups is linked to other fluorocarbon groups. The possibility of having CF_2 chains that are not linked to any organosilicon moiety cannot be ruled out.

The ^{29}Si NMR spectra obtained with ^{1}H and ^{19}F cross-polarization and dipolar decoupling (CP/DD) are shown in Figure 6, with the peak assignments listed in Table 5. Although the CP/DD method increases sensitivity, the peak areas do not yield quantitative concentrations. This is in contrast to the ^{19}F and ^{13}C NMR spectra, which were obtained by direct polarization. The limited amount of film available precluded the use of direct polarization for ^{29}Si NMR spectroscopy.

The narrowing effect of ^{1}H decoupling is greatest for the peaks at 0, −6.4, and −15.5 ppm, indicating that these silicon environments are in the vicinity of hydrogen. The most intense of these peaks (−15.5 ppm) is assigned to the D unit [$(O)_2Si(CH_3)_2$] assuming a small shift relative to its −19-ppm position in spectra of films deposited from pure D_3.[24] This downfield shift is attributed to the effect of electronegative CF_2 groups bonded to neighboring siloxane groups and is consistent with the shifts observed in the FTIR spectrum of the copolymer (Figure 1c). Assuming a similar downfield shift, the peak at −6.4 ppm is assigned to the *o*-R_3 environment in the copolymer film.

o-R_3 represents a ring structure of three siloxane units that is bound to the film structure by Si−Si bonds. The presence of these groups is attributed to a reaction pathway involving abstraction of one or more methyl groups in D_3 with retention of the ring structure.[24] The absence of peaks at −9 and −19 ppm suggests that all of the siloxane ring structures have some degree of fluorocarbon substitution.

The peak at 0 ppm is assigned to linear siloxane units with two methyl groups and one CF_2 unit bonded to each silicon atom. The proposed bonding to CF_2 is consistent with the 0 ppm peak being the most prominent of the three peaks in this portion of the ^{19}F cross-polarized and decoupled spectrum (Figure 6b). Also, because the CF_2 group is less electronegative than oxygen, this moiety must lie between the M group (Me_3SiO, typically observed at +6 ppm[36]) and the D group (−15.5 ppm). The combination of one CF_2 group and one oxygen atom would, however, cause the silicon atom to appear as Si^{+2} in the XPS spectrum. The FTIR band at 899 cm^{-1} is probably due to the Si−C stretching mode in this moiety.

The peak at −92.0 ppm is most enhanced by ^{19}F cross-polarization and decoupling, indicating that CF_2 and silicon are in close proximity. This peak is assigned to the $(O)_2Si(CF_2)_2$ moiety, as the large number of fluorine atoms would cause such an enhancement. The assignment is supported by the reported position of the $(SiO)_4Si^*$ (commonly known as “Q”) moiety in the literature (−105 to −110 ppm).[36] Replacing two of the oxygen atoms with less-electronegative CF_2 groups would cause a downfield shift. The peak at −112.0 ppm is believed to be due to the $(O)_3Si(CF_2)$ moiety, which bears a closer resemblance to the Q group. The peak is sharper in the ^{19}F cross-polarized spectrum, indicating that it must be proximate to a fluorocarbon group. The oxidation state of silicon in $(O)_3Si(CF_2)$ is +3, and the intensity of the peak indicates that only a very small amount is present. This is probably why it is not easily resolved in the Si(2p) high-resolution scan.

Film Structure. The repeat units in the copolymer film consist of fluorocarbon units, siloxane units, and the linkages between them. Spectroscopic data indicate that the fluorocarbon content of the films is almost entirely in the form of CF_2 and that siloxane D units are present in both linear and cyclic form. There are four distinct types of copolymer linkages. The Si−CF_2-Si linkage can be present between siloxane rings or between rings and linear siloxane groups. The $(CH_3)_2$-$Si(CF_2)(O)$ link is linear and could act as a junction between linear siloxane segments and fluorocarbon units. $(O)_2Si(CF_2)_2$ units are branch points and can be present in siloxane rings or in linear chains. The $(O)_3Si$-(CF_2) unit, which is present in low concentrations, is a cross-linking group. The presence of these different copolymer linkages suggests that the copolymer is random.

All of the siloxane rings in the film have some degree of CF_2 substitution, and hence, the rings can also be considered as cross-linking groups and branch points. As there is no evidence of tertiary carbon, cross-linking and branching occur entirely via these siloxane moieties.

Chain termination takes place primarily with siloxane rings (Si−Si bonding between the repeat unit and the terminating ring). Termination could also occur by means of CF_3CF_2Si or $CF_3CF_2CF_2$, but the concentration of these linkages is small.

Conclusions

Fluorocarbon−organosilicon copolymer thin films can by synthesized by hot-filament CVD from HFPO and D_3. Spectroscopic data (from XPS and FTIR and solid-state NMR spectroscopies) indicate the presence of covalent bonds between the fluorocarbon and siloxane repeat units. The data also allow for the identification of different copolymer linkages. The film structure consists of chains with linear and cyclic siloxane groups and CF_2 groups as repeat units. Cross-linking and termination occur mainly via the siloxane units.

Acknowledgment. We gratefully acknowledge the support of the NIH under Contract NO1-NS-9-2323. In addition, this work made use of MRSEC Shared Facilities supported by the NSF under Award DMR-9400334. We also thank Bradley D. Olsen for preparing samples for NMR analysis. B. D. Olsen was supported by the Paul E. Gray Fund for undergraduate research at MIT.

References and Notes

(1) Noort, R. v.; Black, M. M. In *Biocompatibility of Clinical Implant Materials*; Williams, D. F., Ed.; CRC Press: Boca Raton, FL, 1981; Vol. 2, p 79.
(2) Chawla, A. S. *Artif. Organs* **1979**, *3*, 92.
(3) Chawla, A. S. *Biomaterials* **1981**, *2*, 83.
(4) Ocumpaugh, D. E.; Lee, H. L. In *Biomedical Polymers*; Rembaum, A., Shen, M., Eds.; Marcel Dekker: New York, 1971; p 101.
(5) Thomson, L. A.; Law, F. C.; James, K. H.; Rushton, N. *Biomaterials* **1991**, *12*, 781.
(6) Guidoin, R.; Chakfe, N.; Maurel, S.; How, T.; Batt, M.; Marois, M.; Gosselin, C. *Biomaterials* **1993**, *14*, 678.
(7) Moore, J. A.; Lang, C.-I. In *Fluoropolymers*; Hougham, G., Cassidy, P., Johns, K., Eds.; Kluwer Academic/Plenum Publishers: New York, 1999; Vol. 1, p 273.
(8) Hougham, G.; Tesoro, G.; Viehbeck, A. *Macromolecules* **1996**, *29*, 3453.
(9) Lau, K. K. S.; Gleason, K. K. *Mater. Res. Soc. Symp. Proc.* **1999**, *544*, 209.
(10) Rosenmayer, T.; Huey, W. *Mater. Res. Soc. Symp. Proc.* **1996**, *427*, 463.
(11) Peters, L. *Semicond. Int.* **2000**, *23*, 108.
(12) Loboda, M. J. *Microelectron. Eng.* **2000**, *50*, 15.
(13) Grill, A.; Patel, V. *J. Appl. Phys.* **1999**, *85*, 3314.
(14) Michalczyk, M. J.; Farneth, W. E.; Vega, A. J. *Chem. Mater.* **1993**, *5*, 1687.
(15) Wróbel, A. M.; Wertheimer, M. R. In *Plasma Deposition, Treatment, and Etching of Polymers*; d'Agostino, R., Ed.; Academic Press: New York, 1990; p 234.
(16) Owen, M. J.; Kobayashi, H. *Macromol. Symp.* **1994**, *82*, 115.
(17) Owen, M. J. In *Block Copolymers Science and Technology*; Meier, D. J., Ed.; MMI Press: Midland, MI, 1983; p 129.
(18) Doeff, M. M.; Lindner, E. *Macromolecules* **1989**, *22*, 2951.
(19) Chen, G. J.; Tamborski, C. *J. Organomet. Chem.* **1985**, *293*, 313.
(20) Limb, S. J.; Lau, K. K. S.; Edell, D. J.; Gleason, E. F.; Gleason, K. K. *Plasmas Polym.* **1999**, *4*, 21.
(21) Sakata, J.; Yamamoto, M.; Tajima, I. *J. Polym. Sci. A* **1988**, *26*, 1721.
(22) Shirafuji, T.; Miyazaki, Y.; Nakagami, Y.; Hayashi, Y.; Nishino, S. *Jpn. J. Appl. Phys.* **1999**, *38* (7B), 4520.
(23) Kim, D. S.; Lee, Y. H.; Park, N. *Appl. Phys. Lett.* **1996**, *69*, 2776.
(24) Pryce Lewis, H. G.; Casserly, T. B.; Gleason, K. K. *J. Electrochem. Soc.* **2001**, *148* (12), F212.
(25) Richards, R. E.; Thompson, H. W. *J. Chem. Soc.* **1949**, *124*.
(26) Wright, N.; Hunter, M. J. *J. Am. Chem. Soc.* **1947**, *69*, 803.
(27) Lin-Vien, D.; Colthup, N.; Fatteley, W. G.; Grasselli, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press: New York, 1991; p 258.
(28) Matsurra, H.; Ohno, K.; Sato, T.; Murata, H. *J. Mol. Struct.* **1979**, *52*, 13.
(29) Sharp, K. G.; Li, S.; Johannesen, R. B. *Inorg. Chem.* **1976**, *15*, 2295.
(30) Ovenall, D. W.; Chang, J. J. *J. Magn. Reson.* **1977**, *25*, 361.
(31) Kaplan, S.; Dilks, A. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1984**, *38*, 105.
(32) Mallouk, T.; Hawkins, B. L.; Conrad, M. P.; Zilm, K.; Maciel, G. E.; Bartlett, N. *Philos. Trans. R. Soc. London A* **1985**, *314*, 179.
(33) Schwerk, U.; Engelke, F.; Kleber, R.; Michel, D. *Thin Solid Films* **1993**, *230*, 102.
(34) Hagaman, E. W.; Murray, D. K.; Cul, G. D. D. *Energy Fuels* **1998**, *12*, 399.
(35) Fritz, G.; Bauer, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 730.
(36) Marsmann, H. In *NMR: Oxygen-17 and Silicon-29*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: New York, 1981; p 65.
(37) Moynihan, R. E. *J. Am. Chem. Soc.* **1959**, *81*, 1045.
(38) Liang, C. Y.; Krimm, S. *J. Chem. Phys.* **1956**, *25*, 563.
(39) d'Agostino, R.; Cramarossa, F.; Fracassi, F.; Illuzzi, F. In *Plasma Deposition, Treatment, and Etching of Polymers*; d'Agostino, R., Ed.; Academic Press: New York, 1990; p 95.
(40) Rau, C.; Kulisch, W. *Thin Solid Films* **1998**, *249*, 28.
(41) Emsley, J. W.; Phillips, L. *Prog. NMR Spectrosc.* **1971**, *7*, 1.
(42) Dec, S. F.; Wind, R. A.; Maciel, G. E. *Macromolecules* **1987**, *20*, 2754.
(43) English, A. D.; Garza, O. T. *Macromolecules* **1979**, *12*, 351.
(44) Harris, R. K.; Jackson, P. *Chem. Rev.* **1991**, *91*, 1427.
(45) Kitoh, H.; Muroyama, M.; Sasaki, M.; Iwasawa, M. *Jpn. J. Appl. Phys.* **1996**, *35* (2B), 1464.
(46) Tonelli, C.; Tortelli, V. *J. Fluorine Chem.* **1994**, *67*, 125.
(47) Tortelli, V.; Tonelli, C.; Corvaja, C. *J. Fluorine Chem.* **1993**, *60*, 165.
(48) Banks, R. E. *Fluorocarbons and their Derivatives*, 2nd ed.; MacDonald Technical and Scientific: London, 1970; p 237.

MA011286A