Pulsed-PECVD Films from Hexamethylcyclotrisiloxane for Use as Insulating Biomaterials

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Thin films produced by plasma-enhanced chemical vapor deposition (PECVD) have potential application as conformal coatings on implantable devices with complex topologies and small dimensions. Coatings on such devices need to be biocompatible, insulating, and flexible enough to minimize static forces on the surrounding tissue. In this study, we describe the use of pulsed-PECVD to deposit thin films from hexamethylcyclotrisiloxane (D_3). Pulsed-PECVD is a method in which plasma excitation is modulated to favor deposition from neutral and radical species. Thin, conformal coatings were demonstrated on nonplanar substrates suitable for implantation, such as copper wires and neural probes. Coatings were resistant to prolonged immersion in warm saline solution, and wire coatings produced by pulsed-PECVD showed more flexibility than analogous coatings deposited by continuous-wave (CW) excitation. Using Fourier transform infrared spectroscopy, it was demonstrated that the mode of plasma excitation is important in determining film structure. Both CW and pulsed-PECVD showed evidence of cross-linking via ternary and quaternary silicon atoms bonded to more than two oxygen atoms. Methylene groups were observed only in CW films, and may constitute part of a carbon cross-linking unit of the form $Si(CH_2)_nSi$, where $n \geq 1$. Methylene was not detectable in the pulsed-PECVD films, suggesting that formation of carbon cross-links requires a longer plasma decomposition period. The presence of two distinct cross-linking structures in CW films leads to a highly networked structure and results in brittle coatings on thin wires. A higher proportion of terminal methyl groups was also observed in CW films, suggesting that pulsed-PECVD films may retain more precursor ring structure than CW films.

Introduction

Polymeric thin films produced by plasma-enhanced chemical vapor deposition (PECVD) offer several advantages over films produced by conventional polymerization. Thin, pinhole-free films that are highly coherent and adherent to a variety of substrates may be prepared from monomers not polymerizable by conventional means. Films are generally chemically inert, insoluble, mechanically tough, and thermally stable and have been used in a wide variety of electrical, optical, and biomedical applications and as permselective membranes and protective coatings.[1−11] In particular, plasma deposited films have potential application as conformal coatings on implantable devices with complex topologies and small dimensions, such as neurological electrodes.[12] Coatings on such devices need to be biocompatible, adherent, and flexible enough to minimize static forces on the surrounding tissue. The insulator should also have good dielectric properties and low permeability. In this work, we describe progress made toward a material that satisfies the foregoing properties.

Previous work has confirmed the suitability of PECVD organosilicon films for use as biomaterials. Chawla has investigated plasma-deposited films of hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane on Celgard-2400 and Silastic membranes and determined that the coatings reduced the adhesion of platelets both in vitro[6] and ex vivo with a canine model.[7] Ishikawa et al. examined coatings from a number of organosilicon precursors and found that the coatings reduced the adhesion of platelets on glass slides by 10−30%.[8] Hasirci investigated the deposition of hexamethyldisiloxane on activated charcoal by PECVD and found that the organosilicon coating significantly reduced damage to

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(1) Wróbel, A. M.; Wertheimer, M. R. In *Plasma Deposition, Treatment, and Etching of Polymers*; d'Agostino, R., Ed.; Academic Press: San Diego, 1990.
(2) Shi, F. F. *Surf. Coat. Technol.* **1996**, *82*, 1−15.
(3) Ogumi, Z.; Uchimoto, Y.; Takehara, Z. *J. Electrochem. Soc.* **1989**, *136*, 625−630.
(4) Kusabiraki, M. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1990**, *46*, 473−492.
(5) Tien, P. K.; Smolinsky, G.; Martin, R. J. *Appl. Opt.* **1972**, *11*, 637−642.
(6) Chawla, A. S. *Artif. Organs* **1979**, *3*, 92−96.
(7) Chawla, A. S. *Biomaterials* **1981**, *2*, 83−88.
(8) Ishikawa, Y.; Sasakawa, S.; Takase, M.; Iriyama, Y.; Osada, Y. *Makromol. Chem., Rapid Commun.* **1985**, *6*, 495−502.
(9) Hasirci, N. *J. Appl. Polym. Sci.* **1987**, *34*, 2457−2468.
(10) Cannon, J. G.; Dillon, R. O.; Bunshah, R. F.; Crandall, P. H.; Dymond, A. M. *J. Biomed. Mater. Res.* **1980**, *14*, 279−288.
(11) Matsuyama, H.; Kariya, A.; Teramoto, M. *J. Appl. Polym. Sci.* **1994**, *51*, 689−693.
(12) Nichols, M. F. *Crit. Rev. Biomed. Eng.* **1994**, *22*, 39−67.

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platelets, erythrocytes, and leucocytes in sheep's blood.[9] Cannon et al. detailed the synthesis of a fine neurological electrode consisting of W-26 atom % Re wire 125 μm in diameter coated with plasma-polymerized hexamethyldisilazane. No in vivo biocompatibility and stability studies were reported, and some problems were experienced obtaining smooth pinhole-free coverage of the substrate.[10] More recently, Nichols reported the synthesis of a novel polymeric material, Plasmalene, as an hermetic coating on wire substrates. The polymer coatings were deposited by vacuum processes which included PECVD and thermal vapor deposition of methane and xylylene. Encapsulant coatings were deposited on 75 μm wire substrates and demonstrated good mechanical durability and low leakage currents.[13]

Unlike conventional polymers, plasma polymers do not consist of chains with a regular repeat unit but tend to form an irregular three-dimensional cross-linked network. UV irradiation and ion bombardment of the growing film can result in the formation of trapped free radicals, or dangling bonds, in the film.[14] Upon exposure to atmosphere, these dangling bonds can be oxidized, leading to concomitant changes in film structure and properties. The effect of ion bombardment is also to increase the cross-link density in plasma films, which often results in brittle, inflexible films. In an effort to reduce dangling bond concentrations and cross-linking, we have used pulsed-PECVD to deposit coatings from an organosilicon precursor. In this technique, electrical power is repeatedly pulsed on and off. During the on-time, both ions and reactive neutrals are produced in the gas phase. During the off-time, the ratio of neutrals to ions increases due to the shorter lifetimes of ions: film deposition from reactive neutrals will thus be favored and a decrease in ion bombardment is anticipated.[15−17] Fragmentation of the precursor gas is also expected to be less since it is exposed to a lower average electron energy, and the dynamics of competing reactions can be altered by varying on- and off-times. Indeed, investigation of pulsed-PECVD using fluorocarbon precursors has been shown to produce flexible, conformal PTFE-like films with reduced dangling bond concentration and lower cross-link density as compared to films obtained using continuous-wave (CW) excitation.[18−23] By contrast, only a few authors have documented the use of pulsed-PECVD with organosilicon precursors.[6,14,24]

(13) Nichols, M. F. *Biomed. Sci. Instrum.* **1993**, *29*, 77−86.
(14) Yasuda, H.; Hsu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 81−97.
(15) Bouchoule, A.; Ranson, P. *J. Vac. Sci. Technol. A* **1991**, *9*, 317−326.
(16) Hansen, S. G.; Luckman, G.; Colson, S. D. *Appl. Phys. Lett.* **1988**, *53*, 1588−1590.
(17) Kono, A.; Haverlag, M.; Kroesen, G. M. W.; de Hoog, F. J. *J. Appl. Phys.* **1991**, *70*, 2939−2946.
(18) Labelle, C. B.; Limb, S. J.; Gleason, K. K. *J. Appl. Phys.* **1997**, *82*, 1784−1787.
(19) Limb, S. J.; Lau, K. K. S.; Edell, D. J.; Gleason, E. F.; Gleason, K. K. *Plasmas Polym.* **1999**, *4*, 21.
(20) Lau, K. K. S.; Gleason, K. K. *J. Fluorine Chem.* **2000**, *104*, 119−126.
(21) Savage, C. R.; Timmons, R. B.; Lin, J. W. In *Advances in Chemistry Series*; American Chemical Society: Washington, DC, 1993; Vol. 236.
(22) Panchalingam, V.; Poon, B.; Huo, H.-H.; Savage, C. R.; Timmons, R. B.; Eberhart, R. C. *J. Biomater. Sci. Polym. Ed.* **1993**, *5*, 131−145.
(23) Mackie, N. M.; Dalleska, N. F.; Castner, D. G.; Fisher, E. R. *Chem. Mater.* **1997**, *9*, 349−362.

In the present study, PECVD was used to deposit coatings from the precursor hexamethylcyclotrisiloxane to assess their potential as insulating biomaterials. Films of different structure were obtained by varying the mode and timing of plasma excitation. By using pulsed-PECVD it was possible to optimize the flexibility of coatings produced on thin copper wires and produce films robust enough to withstand prolonged exposure to warm saline solution.

Experimental Section

A custom-built parallel-plate PECVD system was employed, with a powered upper electrode and a grounded lower electrode. For continuous-wave (CW) runs, 100 W of power was applied continuously for the duration of the run. Lower values of CW power were explored, but the resulting films suffered from incorporation of particulates most likely generated by the cracking and flaking of film deposited on the upper electrode during long deposition periods. This problem was not as severe for the shorter deposition periods used for the 100 W CW runs. For pulsed-PECVD runs, a peak RF power of 300 W was applied during on-time excitation. Power modulation was achieved using a pulse generator. On-times were varied from 10 to 100 ms and off-times from 0 to 600 ms to achieve duty cycles—defined as the fraction of total time during which power is applied—from 2.4% to 100%. Notation such as 10/100 will be used to denote the on/off timing for a pulsed plasma film.

During an initial screening period, films were deposited on planar substrates at duty cycles of 100%, 33%, 20%, 14%, 9%, and 3% and investigated by soak testing. For lower duty cycles, on/off timing was limited by the frequency range of the pulse generator, and low duty cycles are thus characterized by shorter on-times than higher duty cycles. For instance, an on-time of 10 ms was used for a duty cycle of 3%, while 100 ms was used for a duty cycle of 33%. As a bridging condition, and to allow comparison of the effect of on-time and off-time, three different pulse cycles of 100/600, 50/300, and 10/60 were used for a duty cycle of 14%. On the basis of these preliminary results, films were deposited on wire substrates at selected duty cycles of 100%, 33%, 14%, and 8%. Analyses were then performed on both planar and wire substrates. Deposition times ranged from 50 min (for CW and high duty cycles) to 75 min (for low duty cycles).

Silicon wafer substrates were placed on the lower electrode, and the lower electrode temperature was maintained near ambient by cooling water. Coatings were produced on 3-mil copper wires (0.003 in. diameter), which were strung across an aluminum ring placed on the lower electrode. After deposition, film thickness was estimated from optical micrographs of wire cross-sections. Pressure in the reactor was maintained at 500 mTorr by a butterfly valve. The precursor used was hexamethylcyclotrisiloxane (D_3), a cyclic organosilicon compound consisting of three dimethylsiloxane (D) units of the form $-Si(CH_3)_2O-$. The precursor was vaporized in a heated vessel and delivered through a needle valve. The needle valve was calibrated by isolating the chamber from the vacuum pump and observing the pressure rise over time as the precursor flowed into the chamber. A precursor flow rate of 8 sccm was used for all runs. Argon was used as a diluent and the flow rate was maintained at approximately 40 sccm by a mass-flow controller.

To assess the insulation performance of coatings under conditions approximating that of the human body, films on silicon wafer substrates were subjected to soak testing. For each chosen condition, five identical samples were produced: four for bulk resistivity measurements and one for thickness measurements and film characterization. All five samples were deposited at the same time in the reactor. Once coated with

(24) Panchalingam, V.; Chen, X.; Savage, C. R.; Timmons, R. B.; Eberhart, R. C. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1994**, *54*, 123−141.

Table 1. Results of Wire Coatings on 3-mil Copper Wire Deposited from D_3 Using Pulsed-PECVD

duty cycle (%)	plasma excitation[a]	equivalent power (W)	thickness (μm)	deposition rate (Å·min^{-1})
100	CW	100	19	3800
33	100/200	100	25	4200
14	10/60	43	9	1800
	50/300	43	12	2400
	100/600	43	13	2600
8	50/600	23	6	790

[a] CW denotes continuous-wave excitation. 100/600 denotes 100-ms on time, 600-ms off time.

the PECVD film, silicone O-rings were glued to the surface of the silicon pieces to delineate an area of 0.28 cm^2 to be exposed to saline solution. Wires were attached to the backside of the silicon pieces using silver epoxy on a freshly scratched surface. All areas other than the test area were then coated with silicone to provide electrical isolation. The four samples for soak testing were then immersed in saline at the bottom of a test tube, heated to 80 °C, and plugged into the electrometer system. Current−voltage sweeps were run continuously from −5 to +5 V, relative to a platinum ball electrode. For film characterization, infrared spectroscopy was performed using a Nicolet Magna 860 FTIR spectrometer in transmission mode. All spectra were normalized to a standard thickness of 1500 Å.

Results and Discussion

A. Wire Coatings. Wire coatings were produced under CW excitation and at various duty cycles, and thickness was measured for each wire sample. Table 1 indicates that deposition rate depends strongly on duty cycle. Previously reported deposition rates for organosilicon films produced by RF PECVD are typically in the range 100−1100 Å·min^{-1}.[4−7,11,25,26] To test the flexibility of each coating, coated wires were twisted around a mandrel 750 μm in diameter and observed under an optical microscope. Wire coatings deposited at the duty cycles indicated in Table 1 (i.e. 100%, 33%, 14%, and 8%) were all examined for flexibility. Figure 1 shows the results of this testing for a CW coating and three coatings deposited at the same duty cycle of 14% but with different on- and off-times. Coatings deposited under continuous-wave excitation (Figure 1a) showed considerable cracking and flaking under tension, while coatings deposited at a lower duty cycle of 14% showed improved flexibility (Figure 1b−d). In particular, cracking and flaking was reduced as the on-time and off-time were increased, as illustrated by the good flexibility of the 100/600 film. Indeed, of all the coatings tested, only the coating deposited at 100/600 did not crack, despite being more than 50% thicker than the 50/600 film (a duty cycle of 8%). This suggested that, though thickness may be important in determining flexibility, the effect of pulsing plasma excitation is more significant. Coatings on wires were conformal, as illustrated by a cross-sectional ESEM of film deposited on a University of Michigan (UM) probe (Figure 2).

B. Soak Testing. Multiple samples of pulsed-PECVD films were placed under saline soak at 80 °C and the leakage current was monitored over time. Results to date (Table 2) indicate that many of the films still survive after nearly 1 year under soak. Films are robust and appear to adhere well to silicon surfaces. In particular, the 100/600 film that showed good flexibility has proved resistant to prolonged exposure to warm saline solution. Bulk resistivities for these films are lower than observed for high-quality silicones (typically 10^{16} Ω·cm) but are acceptable for our applications. Failure mode was determined by examination of failed films under an optical microscope. The failure mode observed for the pulsed-PECVD samples appeared to be defect inclusion, where a pinhole or particulate caused a loss in insulating characteristics, while the CW films failed primarily through cracking.

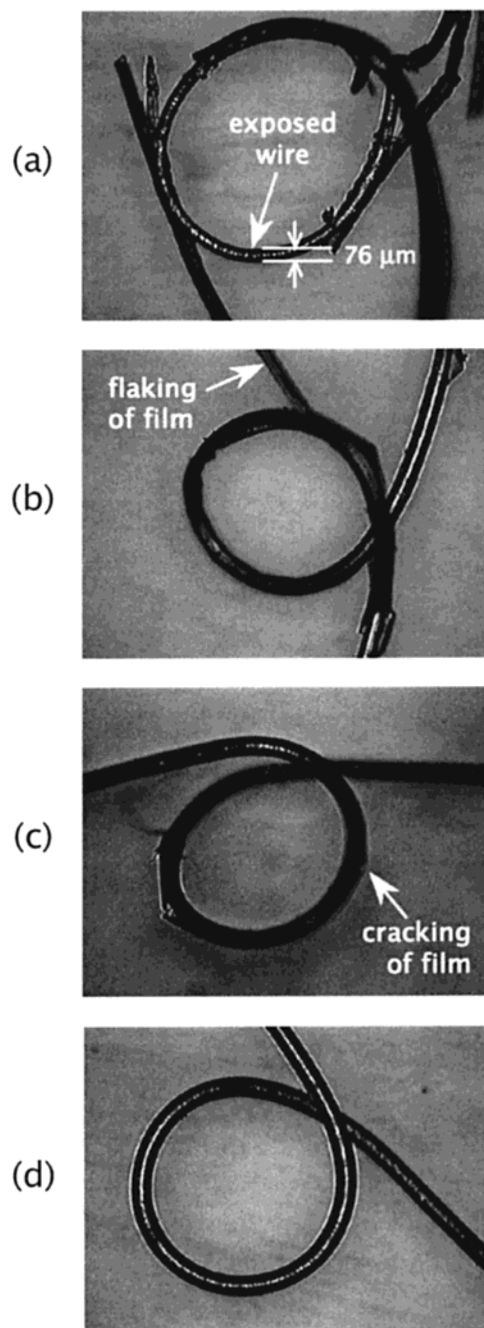

Figure 1. Optical micrographs showing 750 μm loops of 3-mil copper wire coated with D_3 pulsed-PECVD film at (a) CW, (b) 10/60, (c) 50/300, and (d) 100/600. Film thickness is (a) 19 μm, (b) 9 μm, (c) 12 μm, and (d) 13 μm. Film deposited at 100/600 shows the most flexibility.

C. Film Structure. The FTIR spectrum of a 100/600 film is compared to that of the bulk polymer poly(dimethylsiloxane) (PDMS) in Figure 3. Major assignments have been made in Table 3 based on the

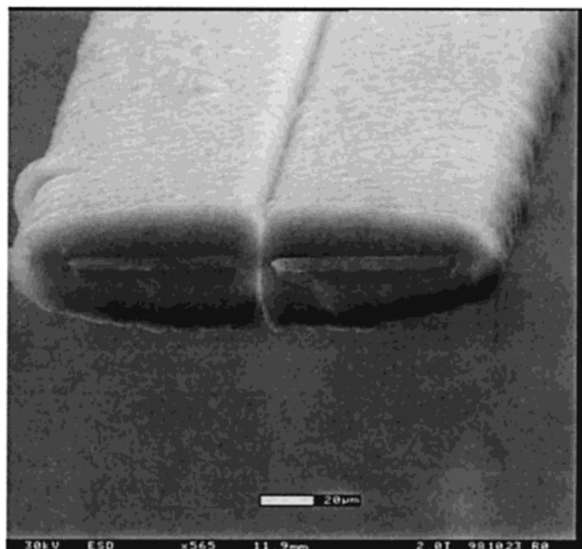

Figure 2. Coating on a University of Michigan probe deposited at 50/300, showing conformity of coating. Film is 20 μm at the thickest point.

Table 2. Results of Saline-Soak Testing of Pulsed-PECVD Films Deposited under a Variety of Pulse Conditions

duty cycle (%)	plasma excitation	no. of samples tested	years under soak	survival rate (%)	average resistivity[a] (Ω cm)
100	CW	8	1.23	88	4.5×10^{12}
	CW	4	0.90	100	3.3×10^{13}
33	100/200	4	0.90	75	2.3×10^{13}
20	100/400	8	1.23	75	1.6×10^{13}
	100/400	8	0.90	100	4.7×10^{13}
14	10/60	8	0.90	75	5.8×10^{13}
	50/300	4	0.73	75	2.9×10^{13}
	100/600	4	0.90	100	4.7×10^{13}
9	10/100	8	1.23	88	4.6×10^{13}
	10/100	4	0.90	100	2.0×10^{14}
3	10/250[b]	4	0.90	50	9.1×10^{12}
			average	84	4.6×10^{13}

[a] Error in resistivity for each sample over time was small, typically less than 5%. [b] The 10/250 film was considerably thinner than other samples tested, which may account for its poor soak performance.

literature.[26−31] The spectrum for the pulsed-PECVD film bears some resemblance to that obtained previously for PECVD films from organosilicon precursors.[26] Of particular note is the strong doublet centered around 1090 cm^{-1}, identified as the asymmetric stretching mode (ASM) of a polymeric siloxane backbone. The ratio of the two peaks of this doublet has been correlated with the length of chains or size of rings in the polymethylsiloxane network.[26,32] 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 eight siloxane units. Hence, the films produced by pulsed-PECVD show some polymeric character.[32] Strong absorptions are observed near 800 and 850 cm^{-1} and have been assigned to dimethyl- and trimethyl-substituted silicon atoms. The strong band at 1263 cm^{-1} represents the bending mode for a silicon-bonded methyl group. Absorptions correlated to CH_x groups are observed at higher wavenumbers. For this sample, only sp^3-hybridized carbon bonding is observed. Comparison of the FTIR spectra reveals that plasma excitation timing can strongly influence film structure. Films deposited at duty cycles of 100% (CW), 14% (100/600), and 2.4% (10/400) show the most variation both in the silicon-correlated and carbon-correlated regions (Figures 4 and 5). The spectra of films deposited at duty cycles ranging from 33% to 8% bore a close resemblance to that of the 100/600 film. Of particular note is the 100/200 film, which was deposited at the same equivalent power as the CW film (100 W), where equivalent power is obtained by multiplying duty cycle by peak power. The FTIR spectrum of the 100/200 film (not shown) resembles that of the 100/600 film rather than that of the CW film. Thus, the difference in structure between CW and pulsed-PECVD films is attributed to the effect of pulsing rather than that of equivalent power.

In the region from 600 to 1500 cm^{-1} (Figure 4), the spectrum of the CW film shows a shift to higher wavenumbers for the ASM and an increase in the intensity of the peak at 900 cm^{-1}. The peak at 900 cm^{-1} is in the region usually assigned to the stretching and bending modes for $SiMe_2$. Typically, this peak has been reported at lower wavenumbers than observed here, as for instance in the work of Rau et al,[26] who observed the peak at 885 cm^{-1}. It is odd that an increase in intensity for this peak is coupled with a reduction in intensity for the peak also associated with $SiMe_2$ at 803 cm^{-1} for the CW film, although this may be due to steric effects. Since no literature was found to suggest any other assignment, the $SiMe_2$ assignment is thus made tentatively. A band of low intensity at 780 cm^{-1} is more pronounced for the CW film and corresponds to $SiMe_1$ stretching. This suggests the presence of silicon atoms which may be involved in cross-linking and/or branching. We have identified two categories of cross-links and/

Table 3. FTIR Assignments from the Literature

wavenumber (cm−1)	mode[a]	comment	refs
2964−2967	ν^A_{CH}	in sp^3 CH_3	26, 28, 30
2933	ν^A_{CH}	in sp^3 CH_2	26, 30
2907−2909	ν^S_{CH}	in sp^3 CH_3	26, 28, 30
2878	ν^S_{CH}	in sp^3 CH_2	26, 30
1463	$\delta^A_{CH_2}$		26, 30
1413	$\delta^A_{CH_3}$	in $SiMe_x$	26, 28, 30, 31
1263	$\delta^S_{CH_3}$	in $SiMe_x$	26, 28, 29, 31
1028−1120	ν^A_{SiOSi}		26, 28, 30, 31
895	ν_{SiC}, ρ_{CH_3}	in $SiMe_2$	26, 28, 29, 31
803	ν_{SiC}, ρ_{CH_3}	in $SiMe_2$	26, 28, 29, 31
845−850	ν_{SiC}, ρ_{CH_3}	in $SiMe_3$	26, 28, 29, 31
760	ν_{SiC}, ρ_{CH_3}	in $SiMe_3$	26, 28, 29, 31
780	ν_{SiC}	in SiMe	26, 29

[a] ν, δ, and ρ denote stretching, bending, and rocking modes respectively; A and S denote asymmetric and symmetric vibrations.

(25) Vasile, M. J.; Smolinsky, G. *J. Electrochem. Soc.* **1972**, *119*, 451−455.
(26) Rau, C.; Kulisch, W. *Thin Solid Films* **1994**, *249*, 28−37.
(27) Anderson, D. R. In *Analysis of Silicones*; Smith, A. L., Ed.; Wiley: New York, 1974; Vol. 41.
(28) Kriegsmann, H. *Advances in Molecular Spectroscopy: Proceedings of the IVth International Meeting on Molecular Spectroscopy*, Bologna and Rome, Italy, 1962; p 1000−1014.
(29) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*, 2nd ed.; John Wiley & Sons: New York, 1958.
(30) McNamara, K. M.; Williams, B. E.; Gleason, K. K.; Scruggs, B. E. *J. Appl. Phys.* **1994**, *76*, 2466−2472.
(31) Richards, R. E.; Thompson, H. W. *J. Chem. Soc.* **1949**, 124−132.
(32) Wright, N.; Hunter, M. J. *J. Am. Chem. Soc.* **1947**, *69*, 803−809.

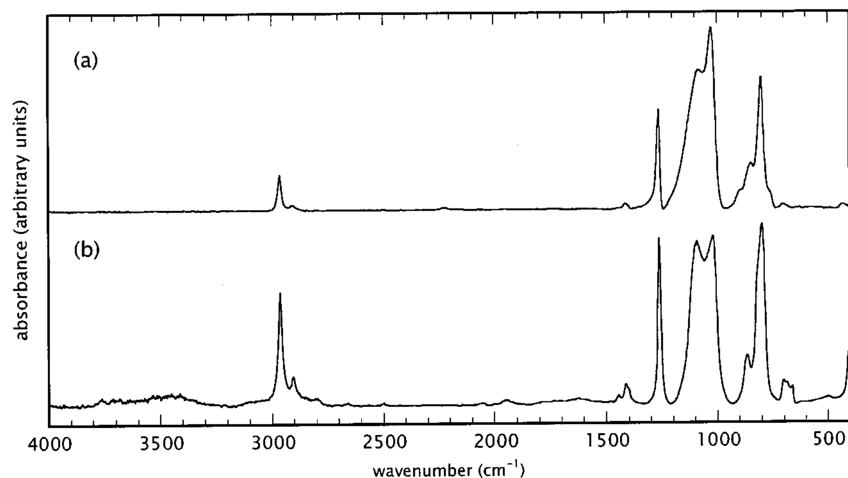

Figure 3. FTIR spectra of (a) pulsed-PECVD film deposited at 100/600, and (b) PDMS secondary standard. Absorption spectra of pulsed-PECVD film has been normalized to a standard thickness of 1500 Å.

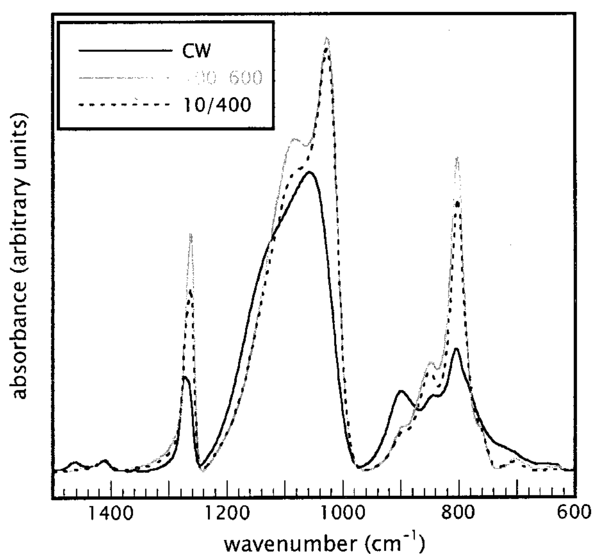

Figure 4. FTIR spectral region from 600 to 1500 cm^{-1} for CW, 100/600, and 10/400 films. Respective duty cycles are 100%, 14%, and 2.4%.

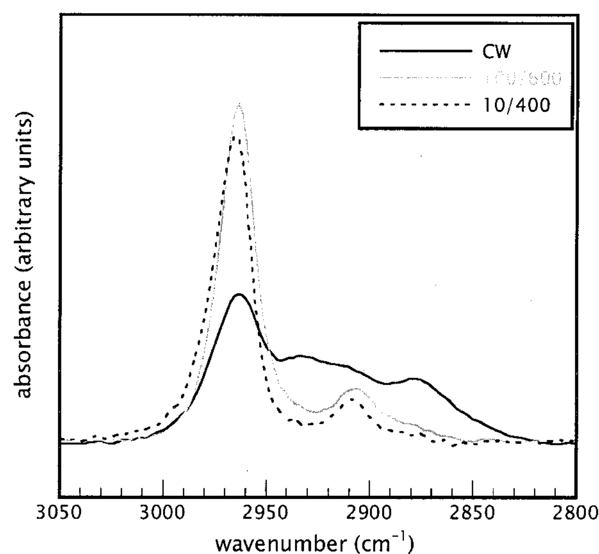

Figure 5. FTIR spectral region from 3050 to 2800 cm^{-1} for CW, 100/600, and 10/400 films, showing CH_x correlated absorptions.

or branches: type I, which consists of siloxane side chains originating from nodes where silicon is attached to more than two oxygen atoms; and type II, which consists of carbon side chains originating from methylene-substituted multioxygen nodes. These categories are illustrated structurally in Figure 6. Here, M, D, T, and Q represent silicon atoms with increasing numbers of oxygen substituents, and DCH_2, $D(CH_2)_2$, and TCH_2 represent D and T groups with methylene substituents. Note that Figure 6 is not intended to be a rigorous summary of the silicon bonding environments present in our PECVD films. Indeed, hydrogen-substituted versions of M through Q (typically referred to as MH, DH, etc.) have been observed in ^{29}Si solid-state NMR analysis of these films, and other structural variations are possible.

Both CW and pulsed-PECVD films show a lower methyl content than PDMS (compare parts a and b of Figure 3). This confirms, as does the hardness of the films, that cross-linking groups are present in the films. Indeed, T and Q groups have been clearly observed in PECVD organosilicon films by other workers[33] and in our own laboratory using solid-state ^{29}Si NMR spectroscopy. Cross-links of type I are thus present in both CW and pulsed-PECVD films. In the CW film, absorptions associated with methylene groups are observed at 2933 and 2878 cm^{-1} (Figure 5). This is consistent with an absorption of low intensity at 1463 cm^{-1}, also attributed to the presence of the methylene group, as well as the lower relative intensity of the methyl band at 1263 cm^{-1} for the CW film. Additional analyses on several of these films, including XPS and solid-state ^{29}Si NMR, have indicated that pulsed-PECVD films are more oxidized than their CW counterparts and contain more T and Q groups. For instance, a 10/60 film analyzed using ^{29}Si SSNMR showed 0.6% more T groups and 3.2% more Q groups than a CW film. Considering the enhanced flexibility observed in pulsed-PECVD films, this suggests that methylene is present in CW films primarily in the form of carbon cross-links rather than as carbon side chains. These carbon cross-links are of type II and originate from DCH_2, $D(CH_2)_2$, and TCH_2 nodes. Whether methylene is bonded as $SiCH_2Si$ or Si-

(33) Tajima, I.; Yamamoto, M. *J. Polym. Sci., A, Polym. Chem.* **1987**, *25*, 1737–1744.

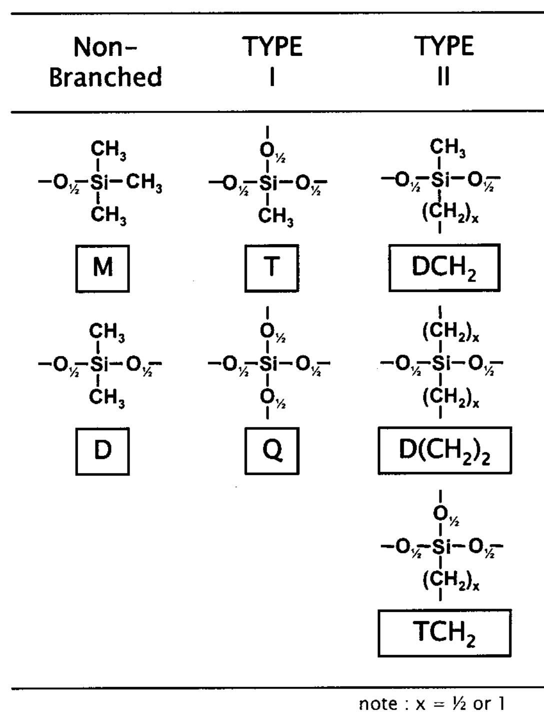

Figure 6. Possible cross-linking and/or branching nodes present in PECVD films. Nonbranching M and D groups are shown for reference. Nodes of type I involve only oxygen, while nodes of type II involve both oxygen atoms and methylene groups.

$(CH_2)_2Si$ is uncertain. Previous workers have argued that even a small absorption at 1360 cm^{-1} is evidence of the former, but no assignment has been made in this work.[26] The lack of methylene cross-linking groups in pulsed-PECVD films suggests that there may be more pathways available for incorporation of oxygen during pulsed excitation than during CW excitation. With just a single type of cross-linking group, reasonable mechanical flexibility can still be retained.

The intensities of both the $SiMe_3$ absorptions (at 845 cm^{-1}) and the $SiMe_2$ absorptions (at 803 cm^{-1}) are lower in the CW film than in the pulsed-PECVD films. However, the ratio of the intensities of $SiMe_3$ to $SiMe_2$ is higher for the CW film than for the pulsed-PECVD films. This suggests that there are more terminal groups per polymeric siloxane (or D) unit in the CW film. Two main differences in structure are postulated to account for this. First, polymeric segments in the CW film may be shorter on average than those in the pulsed-PECVD film. These segments could be main chains or side chain branches attached to a main chain. Second, since ring structures preclude the possibility of $SiMe_3$ groups, the CW film may have less ring structure overall than the pulsed-PECVD films. A more highly branched structure in CW films would also be consistent with an increase in the ratio of endgroups to backbone groups. The poor flexibility of CW coatings, however, suggests that these films are highly networked, rather than highly branched.

Mechanisms of plasma polymerization have been considered by various authors, notably Wróbel et al.,[1] who provide a good overview of plasma-polymerized organosilicon materials. They argue that the dominant mode of precursor fragmentation is methyl abstraction and that the active species in polymerization are primarily ionic in nature. In particular, an ionic mechanism for the ring expansion of D_3 during oligomerization is proposed.[34,35]

Scheme 1. Reaction Pathways for the Production of Polymerization Precursors from D_3

1.	$D_3 \leftrightarrow D_2 + D_1$	*decomposition*
2.	$D_3 \rightarrow Me\bullet + Me_5O_3Si_3\bullet$	*methyl abstraction*
3.	$D_3 \rightarrow l\text{-}D_3$	*ring opening*

The thermal decomposition of cyclosiloxanes has also been investigated.[36-38] Davidson and Thompson, in particular, considered the pyrolysis of D_4 and estimated kinetic parameters for some proposed decomposition pathways. On the basis of their work, we have identified possible reaction pathways for the production of polymerization precursors from the decomposition of D_3, as shown in Scheme 1. D_1 in reaction 3 is the intermediate dimethylsilanone, $Me_2Si{=}O$. It is a potential film growth species that could lead to structures analogous to linear PDMS chains. The abstraction of a methyl group from D_3, as represented by reaction 2, may take place via electron impact and may result in a ionic silicon species rather than the radical species proposed for thermal decomposition. The presence of ionic silicon species in plasmas has been predicted and confirmed by other workers.[39-42] Mass spectrometry has been used to directly sample the reaction species from an RF plasma consisting of a mixture of vinyltrimethylsilane (VTMS) and argon. The distribution of ionic and neutral products indicated that successive dissociation and ionization of VTMS by low-energy electron impact was the dominant mode of energy transfer at high pressures (>0.5 Torr).[42,43] These results suggest that ion and radical chemistries may both be important in organosilicon plasmas.[1,34]

In their pyrolysis experiments, Davidson and Thompson observed reaction 2 to be much faster than reaction 1. The Si−O bond in cyclosiloxanes has been found to be exclusively stable to homolytic cleavage, and the ring-opening of D_3 to form the biradical $\bullet Me_2Si(OSiMe_2)_2O\bullet$ by reaction 3 unlikely.[44] The radical or ion produced by reaction 2 may thus be of some importance in plasma polymerization. Its existence suggests that film growth may involve the incorporation of oligomeric cyclic groups in addition to linear chains. It is interesting to speculate that the right-hand peak of the ASM near 1020 cm^{-1} may be due to the presence of bound six-membered

(34) Wróbel, A. M.; Kryszewski, M.; Gazicki, M. *J. Macromol. Sci.—Chem.* **1983**, *A20*, 583−618.
(35) Kryszewski, M.; Wróbel, A. M.; Tyczkowski, J. *Am. Chem. Soc., Plasma Polym.* **1979**, *108*, 220−236.
(36) Davidson, I. M. T.; Thompson, J. F. *Chem. Commun.* **1971**, 251−252.
(37) Davidson, I. M. T.; Thompson, J. F. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 2260−2265.
(38) Gusel'nikov, L. E.; Nametkin, N. S.; Islamov, T. K.; Sobtsov, A. A.; Vdovin, V. M. *Izvest. Akad. Nauk SSSR, Ser. Khimi.* **1971**, *20*, 84−89.
(39) Hays, A. K. *Plasma Processing;* The Electrochemical Society: Denver, CO, 1981; p 75−81.
(40) Hays, A. K. *Thin Solid Films* **1981**, *84*, 401−407.
(41) Smolinsky, G.; Vasile, M. J. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 147−158.
(42) Vasile, M. J.; Smolinsky, G. *Int. J. Mass Spectrom. Ion Phys.* **1974**, *13*, 381−393.
(43) Vasile, M. J.; Smolinsky, G. *Int. J. Mass Spectrom. Ion Phys.* **1973**, *12*, 133−146.
(44) Voronkov, M. G. *J. Organomet. Chem.* **1998**, *557*, 143−155.

D_3-like rings within the film. In a series of IR spectra of cyclic polymethylsiloxanes from D_3 up to D_8, Wright et al. observed that the ASM consisted of a single peak for ring structures smaller than D_5. This peak was offset at 1020 cm^{-1} for D_3 due to higher ring strain. By this reasoning, the FTIR data indicate that films of lower duty cycle incorporate a higher proportion of six-membered D_3-like rings into their structure. Specifically, the FTIR spectrum for the 10/400 film in Figure 1 bears a closer resemblance to that of the precursor than the 100/600 film. The FTIR spectrum for high molecular-weight PDMS (Figure 3b), however, does show an ASM doublet with a peak close to 1020 cm^{-1}, making it difficult to differentiate between the presence of long chains and bound D_3 rings.[32] To form a network of rings, at least two methyl abstraction events are required per precursor molecule. In previous work, we have investigated films deposited from D_4 using pyrolytic CVD. From elemental analysis, we observed that 1.9 methyl groups were lost per D_4 molecule, offering strong evidence for the incorporation of precursor-like rings into the film structure.[45] For PECVD films, the destructive nature of the plasma means that both linear and ring structures are likely to coexist even for films deposited at low duty-cycle films. It is not yet clear whether the characterization techniques available to us are capable of separating these different structural forms.

Conclusions

Pulsed-PECVD of D_3 offers a means of producing thin, conformal, and insulating coatings at reasonable rates with adequate resistance to prolonged immersion in warm saline solution. Deposition was demonstrated on nonplanar substrates suitable for implantation, such as copper wires and neural probes. Wire coatings produced by pulsed-PECVD show more flexibility than CW coatings.

Both CW and pulsed-PECVD show evidence of cross-linking via T and Q groups. The carbon in pulsed-PECVD films is predominately bonded as CH_3, indicating retention of methyl groups from the D_3 precursor. By contrast, both CH_3 and CH_2 groups are observed in CW films. These methylene units, when bonded to D, T, or Q groups, constitute a cross-linking node we have designated as type II. Type II cross-links are characterized by carbon bridges of the form $Si(CH_2)_nSi$ ($n \geq 1$). The presence of cross-linking groups of both types I and II in CW films leads to a highly networked structure and results in brittle coatings on thin wires. Methylene was not detectable in the pulsed-PECVD films, suggesting that formation of type II cross-links requires a longer plasma decomposition period.

Endgroups and side chain terminations of the form $SiMe_3$ are prevalent in the CW film, indicating short chains and/or highly branched structures. In the pulsed-PECVD film, $SiMe_2$ is the predominate mode of methyl incorporation, consistent with enhanced retention of the precursor structure under conditions where plasma fragmentation processes are limited. Films with primarily $SiMe_2$ bonding must be either long linear siloxane chains and/or networks of interconnected ring structures. Polymerization of dimethylsilanone is one mechanism which could result in the growth of long linear chains. Six-membered D_3 rings and larger may be present in films produced by pulsed-PECVD, where neutral chemistry is more likely to compete with ionic chemistry and precursor fragmentation is expected to be less. This could explain the higher proportion of terminal methyl groups observed in FTIR of CW films, since these groups do not appear in siloxane ring structures.

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(45) Kwan, M. C.; Gleason, K. K. *CVD* **1997**, *3*, 299−301.