Structural Correlation Study of Pulsed Plasma-Polymerized Fluorocarbon Solids by Two-Dimensional Wide-Line Separation NMR Spectroscopy

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Two-dimensional wide-line separation (WISE) NMR spectroscopy has been applied to obtain structural correlation in fluorocarbon films deposited via a pulsed plasma enhanced chemical vapor deposition. Films from two pulsed deposition conditions, 10/20 and 10/400 ms on/off times, were analyzed in detail. One-dimensional ^{19}F and ^{13}C NMR results agreed well with prior studies of these films using X-ray photoelectron spectroscopy, which showed greater CF_2 fractions with decreasing pulsed deposition duty cycle. ^{13}C CPMAS studies, in addition, distinguished between unsaturated and saturated fluorocarbon species in these films. However, $^{19}F-^{13}C$ WISE allowed further differentiation of fluorocarbon moieties by the difference in nearest-neighbor connectivity. The 10/20 film showed a prevalence of at least two inequivalent CF_3 species. A weak presence of unsaturated $=CF-$ species was also detected. No specific CF_2 moiety was resolved, which was attributed to significant chemical shift dispersion and heterogeneity in CF_2 bonding environment. In contrast, the 10/400 film displayed an increased proportion of CF_2 species, predominantly as $-CF_2CF_2-$ and CF_3CF_2- groups, and less CF_3 termination, indicative of a structure approaching that of poly(tetrafluoroethylene). These observations support the hypothesis of a less aggressive deposition environment, inducing less cross-links and unsaturation and promoting linear chain propagation, with a longer pulse off-time during deposition. Spinning sideband patterns in the ^{19}F dimension of NMR spectra did not severely hinder spectral interpretation but instead offered a means of revealing motional differences in the fluorocarbon moieties.

Introduction

Plasma polymerization of fluorocarbon thin films[1−3] has been a subject of intense interest which is largely motivated by the desire to produce films having composition and properties that mimic those of bulk Teflon. Such properties as low coefficient of friction, low dielectric constant, good thermal stability, excellent chemical resistance, and durability offer great potential for this material to be adopted in a diverse array of applications such as biopassivation coatings[4,5] and low-*k* interlayer dielectric for integrated circuits.[6,7] However, Teflon is extremely difficult to process into thin films using typical polymer processing methods because of its high melt viscosity and poor solubility.[8] Thus, the ability to use plasma enhanced chemical vapor deposition (PECVD) as a solventless technique to produce films with properties approaching that of Teflon with the added control over film thickness is extremely attractive.

Traditionally, PECVD uses a continuous radio-frequency (rf) wave to excite the precursor gases. The resulting plasma contains ions, radicals, excited species, and neutrals from which solid coatings are deposited. X-ray photoelectron spectroscopy (XPS) of fluorocarbon films deposited in this manner showed they contain not only CF_2 species, but a significant amount of CF, CF_3, and quaternary carbon moieties. The CF and quaternary carbons suggest a high degree of cross-linking within the films.[9] This is attributed to the complex precursor decomposition reactions taking place within the plasma coupled with ion bombardment of the growing film.[10] The difficulty in controlling plasma chemistry and resulting film composition also reflects one of the main disadvantages of PECVD as a synthesis technique.

Greater compositional control can be achieved by pulsing the applied rf power, hence generating the plasma for only a short time interval (on-time) within each pulse cycle.[11,12] Pulsing

reduces both excessive gas-phase precursor fragmentation and ion bombardment of the film surface. Since the ions are relatively short-lived, the remaining longer-lived radicals and neutrals, which remain after the glow discharge is extinguished, continue to contribute to film growth during the off-time.[13] XPS studies revealed a significantly larger fraction of CF_2 groups can be incorporated into pulsed PECVD films, and the proportion of CF_2 species can be manipulated by changing the duty cycle (ratio of the on-time to the total cycle period).[11−13] This has generated interest in our laboratory to study the viability of using pulsed PECVD for biopassivation and interlayer dielectric coatings.[13−15]

Potentially, solid-state nuclear magnetic resonance (NMR) spectroscopy can advance the understanding of the complex nature of plasma polymers. Specifically, NMR provides details on the connectivity of the network, i.e., next-nearest neighbors, information that is not obtainable by XPS. Previous ^{19}F NMR studies of fluorocarbon films deposited by continuous PECVD gave limited spectral resolution even with 12.5 kHz magic angle spinning (MAS).[16] This was attributed to the heterogeneity of structural environments created by the complex plasma deposition mechanisms, which in turn gave rise to chemical shift dispersion. Trapped radicals and dangling bonds within the films may also cause appreciable line broadening effects through interactions of unpaired electrons with fluorine nuclei. ^{19}F NMR has also been used to study the effect of a fluorocarbon plasma on diamond powders.[17] High resolution in fluorine spectra can often be limited by large chemical shift anisotropy (CSA) and strong homonuclear dipolar couplings. Efforts in narrowing ^{19}F line widths through multiple pulse sequences[18,19] or high-speed MAS[20] or in combination, combined rotation and multiple pulse spectroscopy (CRAMPS),[16] have been made, but they often place excessive demands on spectrometer conditions and hardware; furthermore, not all the broadening effects may be entirely eliminated.

[13]C cross-polarization with magic angle spinning (CPMAS) studies of plasma-polymerized fluorocarbon films show a different perspective in spectral resolution limitation.[21,22] Isotropic chemical shifts of different fluorocarbon species, particularly CF_2 and CF_3 groups, are bundled close together, causing pronounced overlapping of individual peaks. This is further aggravated by chemical shift dispersion characteristic of these films and heteronuclear dipolar coupling effects between fluorine and carbon nuclei. However, ^{13}C spectra of these films were able to distinguish fluorocarbon groups with saturated and unsaturated bonds. Thus, to date, neither ^{19}F nor ^{13}C one-dimensional (1D) solid-state NMR studies have been able to provide much more structural information than is already obtainable from XPS results.

Two-dimensional (2D) NMR spectroscopy offers a viable route for more definite structural correlation to be made in solids. Heteronuclear correlation (HETCOR) methods are well documented[23−25] and have been generously employed in the study of polymers[26] and polymer blends,[27,28] although most of the systems investigated were hydrocarbon polymers. A majority of HETCOR techniques require precise multiple pulse sequences during the evolution and mixing periods. Recently, attention has been given to a heteronuclear 2D experiment, wide-line separation spectroscopy (WISE), first suggested by Zumbulyadis.[29] This experiment is a 2D offshoot of the cross-polarization−dipolar decoupling technique commonly used in 1D ^{13}C studies of solids. The only modification involves placing a t_1 evolution period between the initial 90° excitation pulse and the subsequent spin lock period. WISE experiments have so far focused on detecting motional heterogeneity in polymeric materials.[30−33] The wider spread of chemical shift in the carbon dimension compared to the proton dimension allows the separation of proton sites with limited motion and having broad CSA patterns from fast-motion sites with isotropically narrowed peaks.

In this paper, we demonstrate the application of 2D [19]F−[13]C WISE spectroscopy to fluorocarbon solids, in particular to thin films deposited using the novel pulsed PECVD technique, in an attempt to obtain more substantial structural correlation of fluorocarbon moieties than is possible from corresponding 1D ^{19}F or ^{13}C spectra. An interesting contrast to the typical [1]H−[13]C WISE experiments is that the wider isotropic chemical shift span in the fluorine dimension is taken advantage of to resolve out the closely spaced carbon shifts. Because isotropic chemical shift dispersion is inherent in plasma-polymerized films, a 2D heteronuclear experiment, like WISE, is particularly useful in enabling more concrete spectral assignments. The ease in implementing the WISE experiment with fewer demands on spectrometer conditions and with comparable sensitivity to that of normal CPMAS experiments also makes this 2D method a more attractive one for the study of plasma-polymerized films where sample size is usually a constraining factor.

Experimental Section

Fluorocarbon films were deposited onto 4 in. diameter silicon wafers by a pulsed radio-frequency (13.56 MHz) plasma enhanced chemical vapor deposition (PECVD) technique using hexafluoropropylene oxide (C_3F_6O) (PCR Inc.) as the precursor material. Details of the deposition method and reaction conditions are described elsewhere.[15] Each film was scraped off from the substrate using a razor blade and ground to a fine powder for subsequent NMR analysis.

Static broad-line ^{19}F NMR spectra were obtained for ∼20 mg samples from 5 μm thick films deposited at pulse cycles of 10/20, 10/50, 10/200, and 10/400 ms on/ms off times. Data

TABLE 1: Composition of 10/20 and 10/400 Films As Determined by XPS^a

% CF_x species	10/20	10/400
CF_3	19	15
CF_2	39	65
CF	23	10
C−CF	19	10

^{a} Limb, S. J.; Edell, D. J.; Gleason, E. F.; Gleason, K. K. Submitted for publication.
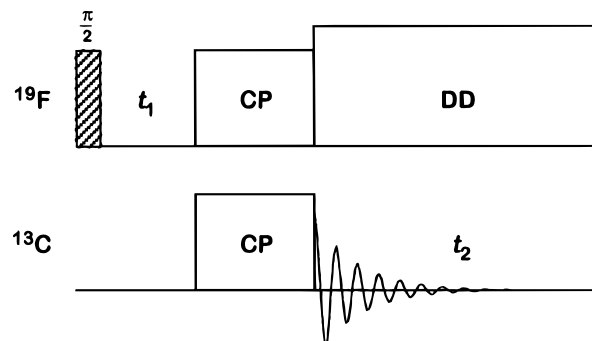

Figure 1. Pulse sequence for two-dimensional WISE NMR spectroscopy experiment.

acquisition was performed on a home-built solids probe and spectrometer[17] at a [19]F Larmor frequency of 280.8 MHz. The 90° pulse time and recycle delay were set at 2 μs and 2 s, respectively. Dwell time was 2 μs, corresponding to a spectral window of ±250 kHz. Static spectra were also acquired for a dispersion-polymerized powder of poly(tetrafluoroethylene) (PTFE) (Dupont, 98% crystallinity) and for one of its oligomers, perfluoroeicosane ($C_{20}F_{42}$) (Aldrich), as model compounds for comparison purposes. Both were used as received.

Static spectra from the pulsed plasma-polymerized films revealed the greatest line-shape differences between the 10/20 and 10/400 samples (see Results and Discussion). Previous XPS studies have also shown significant differences in CF_x composition between the 10/20 and 10/400 films (Table 1).[34] Thus, further NMR characterization concentrated on samples from these two extreme pulse conditions as well as the model compounds. In order to increase the sensitivity and signal-to-noise of the these experiments, larger sample sizes of ∼0.50 g representing 50 μm thick films were prepared for the 10/20 and 10/400 pulse cycles.

The experiments were performed on a home-built spectrometer at a [19]F Larmor frequency of 254.0 MHz using a Doty 7 mm double-resonance magic angle spinning (MAS) probe having negligible fluorine and carbon backgrounds. The spinning speed was maintained at 5 kHz. Direct fluorine observation was made with a 3.6 μs 90° pulse and a dwell time of 2 μs. An attempt was also made to increase resolution through the use of the SPEDA (single pulse excitation and delayed acquisition) technique.[35−37] Delay times before acquisition varied depending on the resolution that could be obtained. Experiments involving cross-polarization from fluorine to carbon were done using contact times between 750 μs and 3 ms that maximized the overall intensity of the spectra. Decoupling field strength during acquisition exceeded 70 kHz in all cases. [19]F and [13]C 90° pulse widths were both 3.6 μs. Dwell time and pulse delay were set at 20 μs and 5 s, respectively.

Two-dimensional WISE experiments[30] were performed using the pulse sequence in Figure 1 on the 10/20 and 10/400 samples, PTFE powder, and perfluoroeicosane. Quadrature detection was achieved in the ω_1 dimension by shifting the phase of the excitation pulse in the fluorine channel by 90°. Hypercomplex

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data sets were generated with 256 complex data points and 20 μs dwell time in the t_2 dimension for t_1 increments ranging between 64 and 128 and a t_1 dwell time of 4 μs. Zero filling was applied before Fourier transformation of both dimensions, and exponential broadening of 50−250 Hz was required in the t_2 dimension.

All NMR spectra were obtained at room temperature and were appropriately referenced to CFCl$_3$ for fluorine chemical shifts and TMS for carbon chemical shifts.

Results and Discussion

Surface Morphology. Differences in macroscopic surface texture of as-deposited pulsed PECVD fluorocarbon films already offer an insight into the structural modifications brought about by changing the duty cycle of rf pulsing during deposition. For the thicker (∼50 μm) films, deposition at the 10/20 pulsing condition produced a brittle film in which severe crazing is observed. The 10/400 film, however, gave a smooth and continuous surface coverage, and free-standing films can be peeled off. These observations agree well with the greater flexibility seen in fluorocarbon coatings of wire loops deposited at increased pulse off-times.[14] The decrease in film brittleness with a decrease in duty cycle is attributed to a reduced constraining of the cross-linked network inherent in plasma-polymerized films.

1D ^{19}F NMR Characterization. Figure 2 shows the ^{19}F broad-line NMR spectra of PTFE and pulsed PECVD films. For PTFE, while the homonuclear ^{19}F dipolar broadening effect[38] is large, the appearance of an asymmetric line shape suggests a comparable anisotropy effect from the −CF$_2$CF$_2$− CSA having a width of ∼137 ppm.[18] Perfluoroeicosane, in addition, shows a feature at −83 ppm arising from a significant presence of CF$_3$ end groups. With a strong fluorine CSA effect and a larger isotropic chemical shift range, even static spectra are able to reveal changes in the fluorine environment of pulsed PECVD films with changes in pulsing conditions during deposition. The 10/20 sample gives a dominant feature centered at −65 ppm and a smaller one at −200 ppm. On increasing the off-period while keeping the pulse on-time at 10 ms, spectra of the resulting films show the appearance of a third peak at −128 ppm whose position corresponds closely to the major resonant feature in PTFE. Less noticeable but still perceptible is a gradual upfield shift of the feature from −65 ppm for the 10/20 film to −75 ppm for the 10/400 film. Because spectral differences observed between the 10/20 and 10/400 films are the greatest, further NMR experiments and their corresponding results discussed hereafter have concentrated on samples deposited from these two extreme pulsing conditions.

In an attempt to improve spectral resolution, MAS spectra were acquired (Figure 3). Significant sideband patterns are seen for PTFE and perfluoroeicosane. Both show a dominant resonant peak at −123 ppm, which is where the isotropic shift for −**CF$_2$**CF$_2$− groups is located (Table 2). The latter also shows another relatively intense peak at −83 ppm which cannot be assigned solely as a refocused sideband but being close to the **CF$_3$**CF$_2$− resonance can be a result of an overlap of a −**CF$_2$**CF$_2$− sideband with the isotropic **CF$_3$**CF$_2$− resonance. The appearance of spinning sideband patterns at a relatively low spinning speed of 5 kHz supports the idea of an appreciable fluorine CSA effect comparable to the dipolar coupling effect. The MAS spectra of 10/20 and 10/400 samples offer no significant resolution enhancement over corresponding static spectra with residual broad components which have not been averaged by MAS. Thus, SPEDA[35,36] was attempted as a way to remove these broad features.
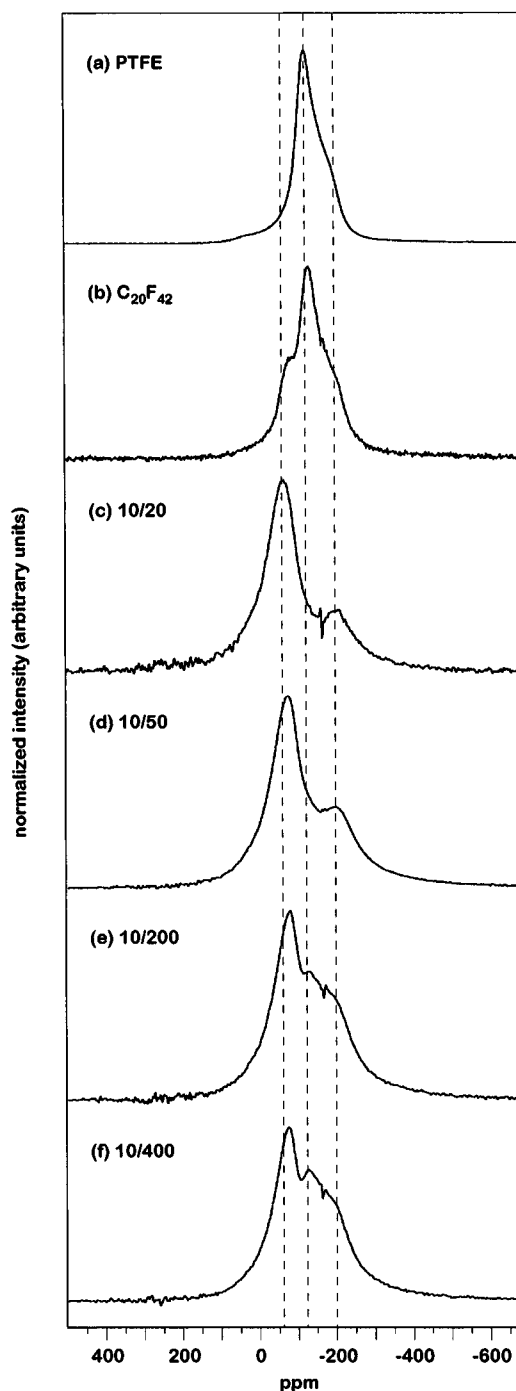

Figure 2. ^{19}F static NMR spectra of (a) PTFE (64 transients, 2048 points), (b) perfluoroeicosane (8 transients, 2048 points), and fluorocarbon films deposited under pulsing conditions of (c) 10/20, (d) 10/50, (e) 10/200, and (f) 10/400 ms on/ms off times (1024 transients, 2048 points).

There is still a debate about the precise origin of line width narrowing and the validity of spectral assignments in the SPEDA experiment. The memory effect seems to play an important role in spin relaxation,[37] and it has been suggested that the acquisition delay filters out the immobile components within the solid, allowing the remaining small fraction of species undergoing isotropic motion to be detected.[39] It has also been proposed that the broad signal acquired without delay is composed of numerous overlapping peaks representing a range of transition frequencies and SPEDA simply removes most of these peaks.[40] Thus, it is uncertain whether SPEDA yields true isotropic shifts, and since SPEDA does not eliminate spinning sidebands, this further complicates spectral interpretation.
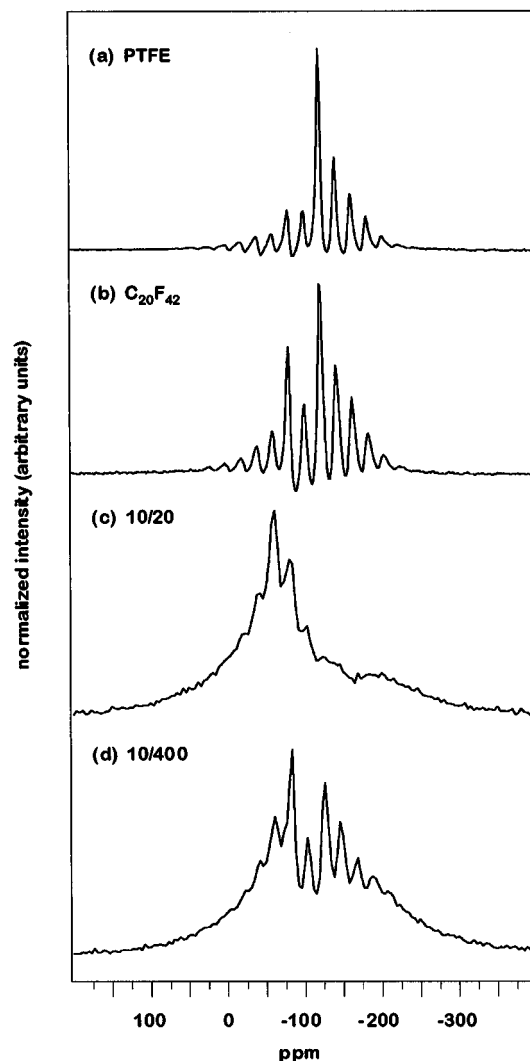
Figure 3. ^{19}F MAS NMR spectra of (a) PTFE (4 transients, 1024 points), (b) perfluoroeicosane (4 transients, 1024 points), (c) 10/20 film (16 transients, 512 points), and (d) 10/400 film (16 transients, 512 points).
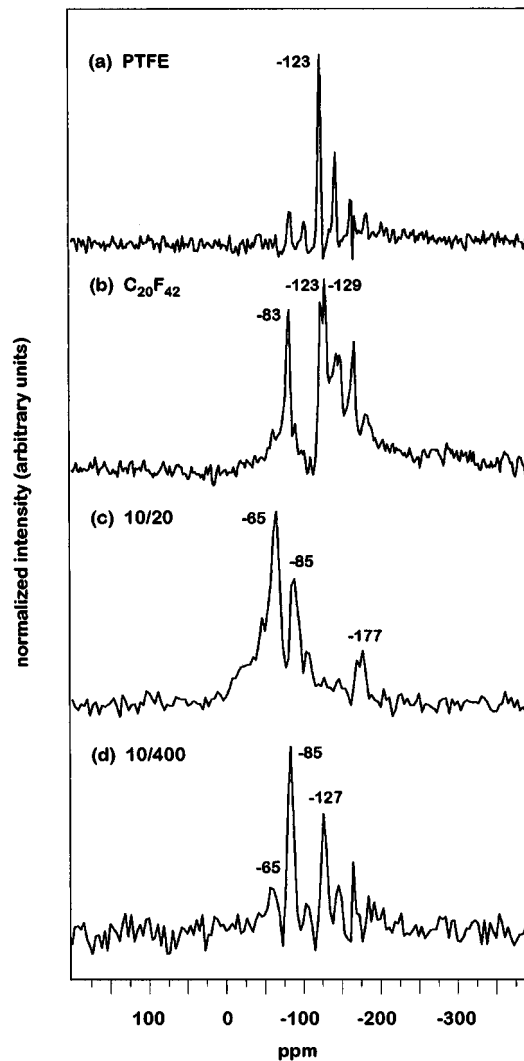

Figure 4. ^{19}F SPEDA NMR spectra of (a) PTFE (256 transients, 1024 points, 1 ms delay), (b) perfluoroeicosane (256 transients, 1024 points, 800 μs delay), (c) 10/20 film (256 transients, 512 points, 200 μs delay), and (d) 10/400 film (1024 transients, 512 points, 600 μs delay). Spinning speed at 5 kHz.

TABLE 2: ^{19}**F Isotropic Chemical Shift Data for Various Fluorocarbon Groups**

CF_x species	^{19}F chemical shift $\sigma_{iso,F}$ (ppm from CFCl$_3$)
$-CF_2\mathbf{CF_3}$	-83^a
$-CF(\mathbf{CF_3})_2$	-75^c
$-C(\mathbf{CF_3})_3$	-60^a
$-\mathbf{CF_2}CF_2-$	-123^a
$-\mathbf{CF_2}CF_3$	-128^a
$=\mathbf{CF_2}$ or branched $\mathbf{CF_2}$	-100 to $-120^{b,c}$
$-\mathbf{CF}\langle$	-170 to -190^c

[a] Harris, R. K.; Jackson, P. *Chem. Rev.* **1991**, *91*, 1427. [b] Dec, S. F.; Wind, R. A.; Maciel, G. E. *Macromolecules* **1987**, *20*, 2754. [c] Katoh, E.; Sugimoto, H.; Kita, Y.; Ando, I. *J. Mol. Struct.* **1995**, *355*, 21.

Hence, we did not attempt any spectral assignment. However, a qualitative comparison of spectral peaks to ^{19}F chemical shift ranges of various fluorocarbon groups reported in literature (Table 2) is still insightful.

Figure 4 shows the SPEDA results. PTFE gives its characteristic sideband pattern though at a much lower sensitivity. Perfluoroeicosane offers a more interesting spectrum with not only peaks at $-\mathbf{CF_2}CF_2-$ and $\mathbf{CF_3}CF_2-$ positions but also a peak (-129 ppm) near the $CF_3\mathbf{CF_2}-$ resonance. The 10/20 SPEDA spectrum gives two peaks at -65 and -85 ppm which lie within the CF$_3$ chemical shift range, suggesting the existence

of distinct CF$_3$ groups differentiated by different nearest neighbors to them. The smaller peak at -177 ppm may be from CF species. In contrast, the corresponding 10/400 spectrum shows a sharply reduced downfield peak (-65 ppm) intensity with an increase in intensity of the -85 ppm resonance, which implies a particular CF$_3$ species may preferentially be formed as the pulse deposition off-period is increased. There is also the emergence of a peak at -127 ppm close to CF$_2$ resonance shifts. The features discussed so far in both the 10/20 and 10/400 spectra are believed to be isotropic resonances because their positions did not change when we conducted the experiments at a lower spinning speed of 3.5−3.8 kHz (spectra not shown). However, although SPEDA provides considerable line width narrowing, it fails to capture all the isotropic resonances that would be expected from these films if we were to compare these results with corresponding XPS data (Table 1). We can only surmise these discrepancies arise perhaps from the sensitivity degradation inherent in SPEDA, or the breadth of the CSA together with limited quantities of these unresolved fluorocarbon moieties may spread the signal out and lower the intensities to unobservable levels, or the unresolved species reside predominantly within the relatively immobile component of the solid which may presumably have been filtered out by SPEDA.
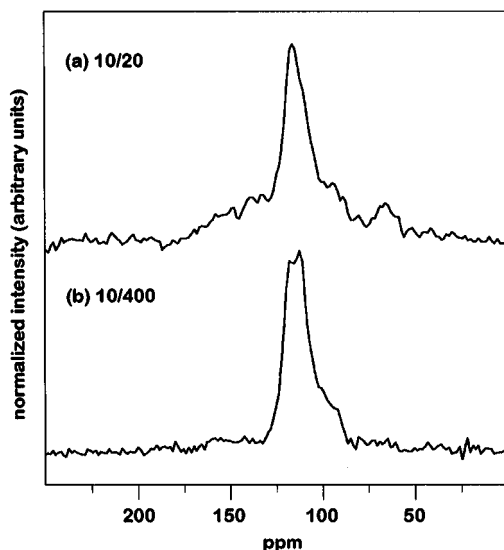
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Figure 5. ^{13}C CPMAS NMR spectra of (a) 10/20 film (1024 transients, 512 points, 1 ms mixing) and (b) 10/400 film (1024 transients, 512 points, 750 μs mixing) at 5 kHz spinning speed.

TABLE 3: ^{13}C Isotropic Chemical Shift Data for Various Fluorocarbon Groups

CF$_x$ species	^{13}C chemical shift[a] $\sigma_{iso,C}$ (ppm from TMS)
$-CF_3$	118
$-CF_2-$	112
$=CF_2$	150$-$160
$-CF\langle$	100
$=CF-$	130$-$160
$\rangle C\langle$	70
$=C\langle$	140$-$150

[a] Kaplan, S.; Dilks, A. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* **1984**, *38*, 105 and references therein.

1D ^{13}C NMR Characterization. Figure 5 shows the spectra of ^{13}C nuclei cross-polarized from ^{19}F nuclei of the 10/20 and 10/400 samples. Unlike its fluorine counterparts, ^{13}C environments of fluorocarbon species display relatively weak chemical shift anisotropies which are spun out at a modest 5 kHz spinning speed. Unfortunately, high-resolution spectra are still precluded because the ^{13}C isotropic chemical shift range of fluorocarbon groups is not as extended as in hydrocarbons, and furthermore chemical shift dispersion due to sample disorder contributes to additional line broadening. However, spectral differences in films deposited at different pulsing conditions are nevertheless noticeable.

The 10/20 spectrum (Figure 5a) is similar to the one obtained by Kaplan and Dilks for a fluorocarbon film deposited using a continuous plasma and a tetrafluoroethylene gas source.[21] A variety of carbon species, both saturated and unsaturated, are observed and can be coarsely assigned based on published chemical shifts (Table 3). On increasing the deposition off-time (Figure 5b), unsaturation (>120 ppm) in the film is dramatically reduced as are quaternary carbon sites at 70 ppm. However, unlike their corresponding ^{19}F SPEDA spectra, the 10/400 ^{13}C CPMAS spectrum reveals the lingering presence of CF species ($\sim$100 ppm) while the 10/20 spectrum shows a noticeable presence of CF$_2$ species.

Although standard CPMAS spectra do not yield quantitation of each species, a relative comparison of the 10/20 and 10/400 spectra is permissible. Thus, the increase in the amount of CF$_2$ moieties with the simultaneous decrease in CF and quaternary carbon fractions with a longer deposition off-time indicates a

less cross-linked and less disordered film being formed on increasing the off-period during pulsed deposition.

Cross-polarization kinetics also suggest the 10/400 film contains more fluorinated fluorocarbon groups compared to the 10/20 film. Contact times used to maximize the overall intensity of the 10/20 and 10/400 CPMAS spectra were 1 ms and 750 μs, respectively. Different fluorocarbon moieties have different cross-polarization rates, with less fluorinated species requiring a longer time for polarization transfer by virtue of having fewer C$-$F bonds. Thus, it is reasonable to say that the longer mixing time for the 10/20 sample implies more CF groups, or alternatively fewer CF$_2$ and CF$_3$ groups are present compared to the 10/400 sample. Because the 10/20 film contains a significant CF$_3$ fraction, as evidenced by both XPS and ^{13}C CPMAS results, it is more likely that the difference in contact times is due to more CF$_2$ and fewer CF groups seen in the 10/400 film.

It is also interesting to note that the mixing times are much shorter for the pulsed PECVD films compared to the model compounds (^{13}C CPMAS spectra not shown). Both PTFE and perfluoroeicosane require 3 ms contacts to maximize total spectral intensity, contact times which are also used to perform the spin lock during the WISE experiments. Since spectral maxima in CPMAS experiments arise from a transition of cross-polarization dynamics from one dominated by ^{19}F$-$^{13}C spin transfer to one dominated by $T_{1\rho}$ relaxation, the times to reach maxima reflect this transition.[41] Thus, the difference observed in cross-polarization times between the model compounds and the films implies a faster $T_{1\rho}$ relaxation and a slower spin transfer rate of the latter. A faster relaxation decay may be a result of interactions of fluorine nuclei with unpaired electrons inherent in these films. Spin transfer kinetics as mentioned may be rate limited by CF species.

2D ^{19}F$-$^{13}C WISE Experiments. Even though the trends seen from 1D ^{19}F and ^{13}C NMR results match well with those from XPS data, 1D NMR characterization has not been able to provide significantly more structural information on plasma-polymerized films. This is mainly due to the questionability of spectral assignments in ^{19}F SPEDA spectra and the limited resolution offered by ^{19}F MAS and ^{13}C CPMAS spectra.

2D WISE spectroscopy is demonstrated below as a tool that yields more information on bonding environments, in particular, to next-nearest neighbors of the various fluorocarbon moieties. It should be stressed that we have used WISE simply as an avenue for seeking more substantial structural correlation and have not used this technique to specifically identify motional heterogeneity, as is the common application of WISE.[30$-$33]

Figure 6 displays the 2D WISE contour plots of PTFE, perfluoroeicosane, 10/20, and 10/400 films. It should be noted that all the spectra are plotted on the same scale for both frequency domains, except for the 10/20 plot which is accommodated on a wider shift range for both axes. As expected, PTFE (Figure 6a) produces a spinning sideband pattern in the ^{19}F dimension which is correlated with a single ^{13}C resonance. This corresponds to linear $-CF_2CF_2-$ groups having isotropic shifts of $-$123 and 112 ppm in their ^{19}F and ^{13}C domains, respectively. Refer to Tables 1 and 2 for respective isotropic ^{19}F and ^{13}C chemical shift values of various fluorocarbon moieties. The fluorine spinning sideband pattern spans a width of about 120 ppm. This value agrees well with the CSA width for CF$_2$ groups which are static (Table 4), and understandably, CF$_2$ moieties within a predominantly crystalline (98%) PTFE lattice should not undergo any significant motional averaging at room temperature.
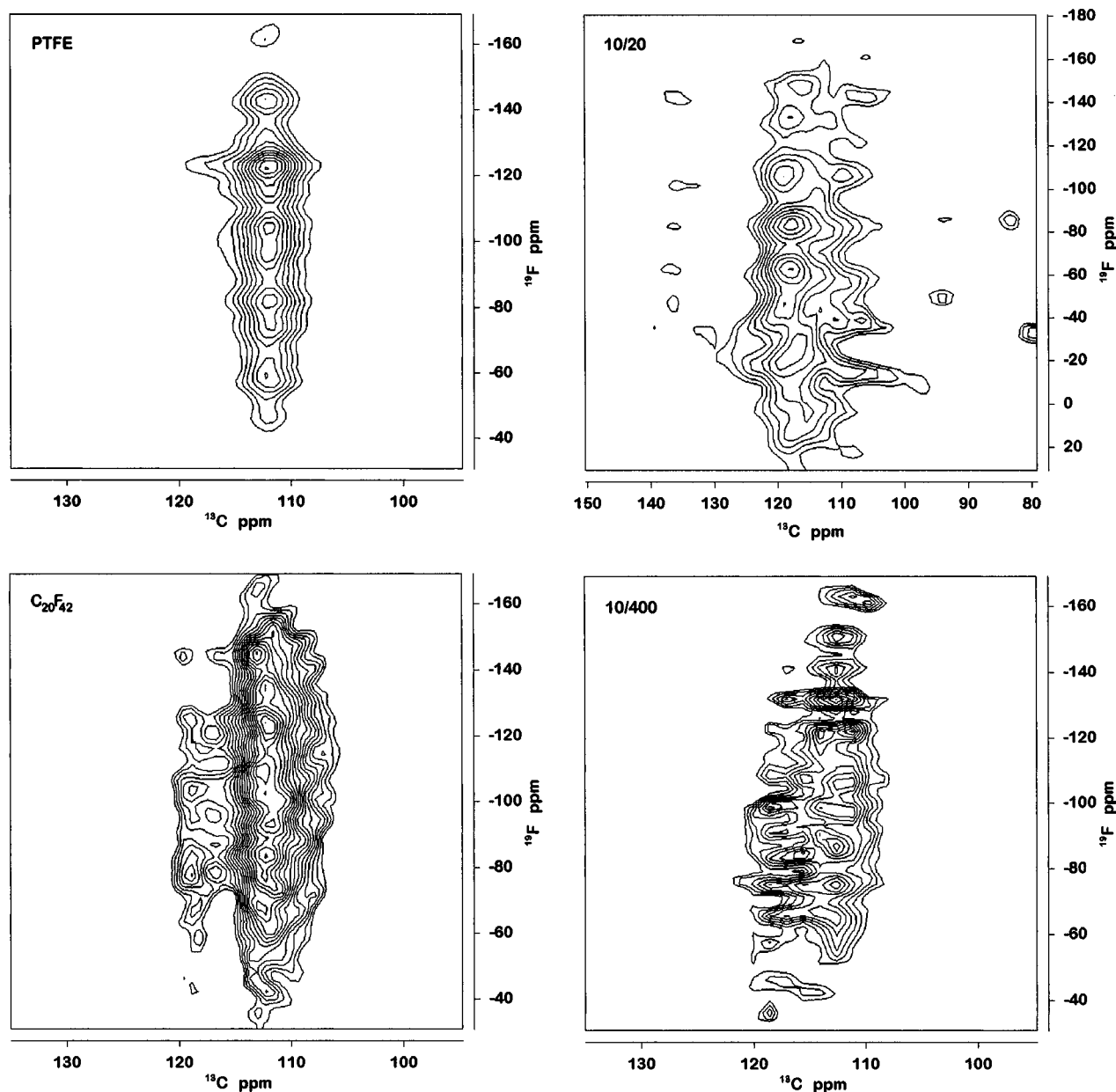
Figure 6. 2D $^{19}F-^{13}C$ WISE NMR spectra of (a) PTFE (64 transients, 1024 × 512, 3 ms mixing), (b) perfluoroeicosane (64 transients, 1024 × 512, 3 ms mixing), (c) 10/20 film (304 transients, 1024 × 256, 1 ms mixing), and (d) 10/400 film (128 transients; 1024 × 512; 750 µs mixing). Spinning speed at 5 kHz.

TABLE 4: ^{19}F Chemical Shift Anisotropy Widths for Various Fluorocarbon Groups

CF_x species	^{19}F CSA[a] $\Delta\sigma_F$ (ppm)
CF_3 (static)	150
CF_3 (motionally narrowed)	75
CF_2 (static)	120-140
CF_2 (motionally narrowed)	50-100
CF	100

[a] Scruggs, B. E.; Gleason, K. K. *J. Phys. Chem.* **1993**, *97*, 9187 and references therein.

Compared with PTFE, perfluoroeicosane (Figure 6b) shows a more interesting contour plot. The $-CF_2CF_2-$ groups (^{19}F, −123 ppm; ^{13}C, 112 ppm) show their characteristic spinning sideband pattern analogous to that for PTFE, although it is more difficult to identify. The reason for the decreased resolution is the presence of a second sideband pattern at the same ^{13}C chemical shift. This is attributed to the $-CF_2CF_3$ resonance (^{19}F, −128 ppm; ^{13}C, 112 ppm), which has a somewhat narrower

CSA width of 100 ppm. The CF_3 resonance (^{19}F, −83 ppm; ^{13}C, 118 ppm) for the $-CF_2CF_3$ group is also resolved, and it exhibits an apparent CSA width of approximately 100 ppm. Thus, CF_3 end groups in perfluoroeicosane are experiencing partial motional averaging, neither fully static ($\Delta\sigma_F = 150$ ppm) nor completely motionally averaged ($\Delta\sigma_F = 75$ ppm). This greater mobility is in turn imparted to CF_2 groups attached to these chain ends, since the sideband expanse for the $-CF_2CF_3$ resonance lies within the range of CSA widths expected for motionally narrowed CF_2 groups.

The 10/20 WISE spectrum (Figure 6c) shows more complex spectral features and spreads over a wider chemical shift range in both ^{19}F and ^{13}C dimensions compared to the WISE spectra for the model compounds. The increase in the fluorine chemical shift range is due to the highly intense CF_3 sideband pattern extending across a total of 180 ppm. However, as shown in Table 4, CSA widths for CF_3 groups are typically up to only 150 ppm. So the wider width observed most likely means there is more than one sideband pattern present, representing CF_3

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species with different ^{19}F isotropic chemical shifts but having similar ^{13}C isotropic chemical shifts. Partial overlap of the different sideband patterns causes the total pattern to extend over an extremely wide range. The two intense peaks at ^{19}F chemical shifts of about -80 and -70 ppm further support the heterogeneity in CF$_3$ sites since it is unlikely that a sideband pattern for a single site will show two dominant peaks. The increase in the carbon chemical shift range in the 10/20 spectrum is due to the presence of weakly resolved unsaturated $=$CF$-$ groups at 136 ppm ^{13}C chemical shift, which is farther downfield than CF$_2$ and CF$_3$ sites. Its spinning sideband pattern has a width of 100 ppm and corresponds closely to the typical CSA width for CF species.

Although the 10/20 film also contains $-$CF$\langle$, $=$CF$_2$, $=$C$\langle$, and $\rangle$C$\langle$ groups as evidenced in its ^{13}C CPMAS spectrum (Figure 5a), they are not seen in the WISE plot. The quaternary carbons are not observed because they are not correlated to any fluorine site in the ^{19}F$-$^{13}C WISE experiment, but it is unclear why $-$CF$\langle$ and $=$CF$_2$ moieties are not resolved. One plausible reason could be the lack of sensitivity inherent in the smaller fractions of these groups as well as due to differences in cross-polarization efficiencies during the spin lock period. Since we have placed the fluorine frequency to match that of the $-$CF$_2$CF$_2$$-$ resonance, fluorocarbon groups having resonances farther away will suffer additional intensity losses. CF$_2$ species are clearly present at their ^{13}C chemical shift position, but the more dominant CF$_3$ features seem to occlude CF$_2$ sideband patterns from being picked out. This poor resolution points to a substantial irregularity in the CF$_2$ bonding environment containing perhaps highly branched CF$_2$ units which have a dispersion of isotropic chemical shifts, thus causing severe broadening in the peaks.

The WISE spectrum (Figure 6d) for the 10/400 film is comparatively less complex than the one for the 10/20 film, showing similarities instead with the spectra for the model compounds, particularly perfluoroeicosane (Figure 6b). CF$_3$ resonances are less pronounced in the 10/400 film. The two distinct spinning sideband patterns, each extending 100 ppm, which are identifiable imply at least two different CF$_3$ groups having different nearest neighbors are present. Since the most intense peaks are at ^{19}F chemical shifts of about -80 and -70 ppm, we may conjecture that these are roughly the positions of the isotropic peaks for the two spinning sideband patterns, the former probably arising from $-$CF$_2$**CF$_3$** species and the latter from $-$CF(**CF$_3$**)$_2$ groups. CF$_2$ resonances are also well resolved, and again two spinning sideband patterns are observed, each having their most prominent peaks at ^{19}F shifts of -123 and -130 ppm, corresponding perhaps to $-$**CF$_2$**CF$_2$$-$ and $-$**CF$_2$**CF$_3$ groups, respectively. The widths of their patterns also support these spectral interpretations. The former has a width of 120 ppm and agrees with the value obtained for $-$**CF$_2$**CF$_2$$-$ species in perfluoroeicosane while the latter with a width of 80 ppm is slightly narrower than the 100 ppm width for $-$**CF$_2$**CF$_3$ groups in perfluoroeicosane. But the fact that CF$_2$ moieties in $-$**CF$_2$**CF$_3$ groups are found to be more mobile than in $-$**CF$_2$**CF$_2$$-$ groups remains unchanged. The lack of any resolved $-$CF$\langle$ resonances, even though ^{13}C CPMAS results indicate otherwise, can be, as mentioned previously, attributed to the decrease in sensitivity in detecting these species.

The 2D WISE experiments provide clear evidence of the drastic structural changes induced by changes in the pulse deposition off-time. Increasing the deposition off-time, all else remaining unchanged, yields films having a greater CF$_2$ content with fewer double bonds and branch or cross-linking junctions. What is significant from the NMR results is that the CF$_2$ groups

are in an increasingly more homogeneous structure consisting of more linear fluorocarbon $-$CF$_2$CF$_2$$-$ units. The weakening of the CF$_3$ sideband patterns also imply fewer termination groups. Thus, the overall film structure approaches that of bulk PTFE when film deposition is performed using a lower duty cycle pulsed plasma discharge. Because ions generated during glow discharge are short-lived while CF$_2$ radicals persist longer over the off-period, more ordered film growth involving CF$_2$ radical polymerization with less ion-induced surface damage is favored.[13]

Even though the WISE experiments do not remove complex spinning sideband patterns in the ^{19}F dimension, in many cases they are sufficiently sensitive in providing nearest-neighbor information on fluorocarbon moieties that XPS does not reveal. The presence of anisotropy information, instead, provides an advantage for us to distinguish motional differences in various fluorocarbon entities indirectly, albeit on a coarser scale of sensitivity, and as a way to confirm the presence or absence of certain fluorocarbon groups.

Conclusion

We have applied solid-state NMR spectroscopy and in particular 2D ^{19}F$-$^{13}C WISE spectroscopy to the study of plasma-polymerized films deposited using a pulsed plasma enhanced chemical vapor deposition technique with hexafluoropropylene as the precursor gas source. Unlike the more common application of WISE to the study of motional heterogeneity in polymeric materials, WISE was used specifically in this case to obtain structural correlations in these fluorocarbon thin films.

1D ^{19}F and ^{13}C NMR results did not offer substantially more compositional information than is obtainable from XPS.[34] ^{13}C CPMAS spectra, however, did show the existence of double-bonded fluorocarbon groups as well as quaternary carbons within films deposited at higher duty cycles but, like XPS, no nearest-neighbor information is derivable. 2D WISE, on the other hand, revealed significant differences between films deposited at different pulse off-times, not only in terms of the various fluorocarbon moieties present but also in the structural connectivities of these groups to their nearest neighbors. With an increase in pulse off-time, we see a corresponding decrease in the structural complexity of the films based on our WISE results. There is a predominance of $-$CF$_2$CF$_2$$-$ linear chain content as opposed to heterogeneity in CF$_2$ bonding environments seen for films at higher duty cycles. CF$_3$ groups are less prominent, which alludes to less premature chain termination. Fewer CF units and less unsaturation imply less cross-linking and branching. Thus, a lower pulse duty cycle during deposition favors formation of film structures approaching that of straight-chain PTFE.

Although dynamics is not our focus in this study, we are able to identify motional differences in the various fluorocarbon species by comparing the breadth of their spinning sideband patterns in the ^{19}F dimension with typical CSA widths. NMR reveals a large anisotropy for the $-$CF$_2$CF$_2$$-$ group, showing it is relatively static. On the other hand, a CF$_2$ species nearest to a CF$_3$ group, i.e., CF$_3$CF$_2$$-$, is more mobile, the increased mobility arising from the motional averaging experienced by the CF$_3$ group.

Although it is widely recognized that fast spinning probes ($>$15 kHz) are almost necessary for high-resolution NMR studies of solids containing fluorine,[42] 2D ^{19}F$-$^{13}C WISE spectroscopy offers a surprisingly worthy compromise between hardware requirements and spectral resolution needed for structural correlation.

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