Comparison of Pulsed and Continuous-Wave Deposition of Thin Films from Saturated Fluorocarbon/H_2 Inductively Coupled rf Plasmas

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Thin films are prepared by plasma polymerization using inductively coupled continuous-wave (CW) and variable duty cycle pulsed rf plasmas. The effects of hydrogen addition (0−97.5%) on thin films deposited from CW saturated fluorocarbon (CF_4 and C_2F_6) plasmas are examined. Variable duty cycle, pulsed C_2F_6 rf plasmas are employed for comparison to the CW results. Film properties are determined using Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). Deposition rates and contact angles are also measured for all films. Analysis using these techniques indicates a strong dependence of the bulk and surface structure on the hydrogen content of the feed in the CW systems. Significantly different film chemistry and deposition rates are observed in the pulsed systems. For the pulsed systems, film composition is dependent on duty cycle and relative pulse on and off times. Using an optimum duty cycle of 3% results in a less cross-linked fluorocarbon polymer, with primarily CF_2 species in the bulk film and CF_3 surface termination.

I. Introduction

Plasma polymerization has been extensively studied and is gaining recognition as an important process for the formation of entirely new kinds of materials.[1] One of the advantages to plasma polymerization is that many different starting materials can be used to produce thin films with a variety of properties. For example, continuous-wave (CW) fluorocarbon discharges have been examined by many research groups because of their dual ability to promote etching of various substrates[2,3] and to deposit fluorinated polymeric films.[4−8] With deposition, it has been shown that a fluorocarbon/hydrogen plasma can be used to deposit diamond-like carbon (DLC) films,[9,10] hydrogenated, fluorinated amorphous carbon films,[11−13] or amorphous fluorocarbon polymer films. Other workers have deposited diamond films from CF_4/H_2 mixtures[14] using both microwave[9] and inductively coupled rf plasmas operated at high pressures (5.0 Torr), substrate temperatures (∼850 °C), and powers (1−3 kW).[15] With microwave plasmas, diamond films are deposited from gas mixtures containing less than 40% CF_4, and the best quality films result from the lowest CF_4 concentration, 2.5%. With inductively coupled plasmas, diamond films with very little fluorine content are deposited from ∼8% CF_4 mixtures.[15] All these studies demonstrate that the composition of films deposited from fluorocarbon plasmas can be greatly changed by changing experimental conditions, fluorocarbon type, or amount of fluorocarbon in the plasma.

Previous research has utilized many different CW reactor designs,[21] plasma types,[16] and fluorocarbon feed gases.[17,18] d'Agostino and co-workers have performed the most complete study of these CW systems, using both gas-phase and surface diagnostics to examine film deposition. The work of this group has shown a number of general trends using saturated CW fluorocarbon/H_2 plasmas.[4−6,10,12] First, in pure saturated fluorocarbon

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plasmas, etching is the sole process that occurs,[4−6] a result of the high concentration of F atoms, a known etchant. Second, once deposition conditions are reached, at relatively high fluorocarbon concentrations, amorphous fluorocarbon polymer is deposited. At lower fluorocarbon concentrations, a hydrogenated, amorphous carbon film is deposited, designated as DLC.[11,19,20] Third, film deposition rates (DR) are maximized when the fluorocarbon to hydrogen ratio is near unity in the C_2F_6/H_2 system.[21]

Despite the extensive work with fluorocarbon/H_2 CW plasmas, there have been no studies of pulsed CF_4 and C_2F_6 plasmas. Furthermore, to our knowledge, there are no pulsed plasma studies of deposition systems with more than one feed gas. In the area of single-source pulsed plasmas, Savage, Timmons, and co-workers have pioneered the study of surface tailoring of plasma polymers. They have studied pure fluorocarbon precursors such as hexafluoropropylene oxide (C_3F_6O), perfluoropropylene (C_3F_6),[22,23] and perfluoro-2-butyltetrahydrofuran ($C_8F_{16}O$).[24] Yasuda and Hsu have also studied pulsed systems with a variety of hydrocarbons and two fluorocarbons, hexafluorobenzene (C_6F_6) and tetrafluoroethylene (C_2F_4).[25] In all these studies, the structure of plasma-polymerized films varies significantly with the type of rf duty cycle employed. For the fluorocarbon monomers, C_3F_6O and C_3F_6, a progressive decrease in the extent of polymer cross-linking with decreasing rf duty cycle is observed.[22] With both monomers, XPS spectra show an increase in CF_2 functionality as the duty cycle is lowered, indicating a less cross-linked film is deposited. A recent report on pulsed perfluorocyclohexane plasmas also showed some retention of monomer structure in the deposited films.[26]

Here, we report the use of both CW and variable duty cycle pulsed inductively coupled rf (13.56 MHz) plasmas to deposit films from saturated fluorocarbon/H_2 plasmas. This study concentrates on the comparison of films deposited from CW plasmas and pulsed plasmas and on the effect of hydrogen addition (0−97.5%) to the bulk and surface composition of the films deposited in CW plasmas. One goal of this work is to explore the use of pulsed plasma systems to deposit less cross-linked, poly(tetrafluoroethylene)-like polymeric films as these may be suitable for use as low-*k* interlevel dielectric (ILD) materials.[27] Furthermore, this is the first study to directly compare films deposited from CW and pulsed plasmas using mixed saturated fluorocarbon/H_2 feed gases.

Our films are characterized using FTIR spectroscopy, scanning electron microscopy (SEM), angle-dependent X-ray photoelectron spectroscopy (XPS), and contact angle measurements. We have also measured DRs for all systems. In the CW C_2F_6 system, we have performed a detailed study of the effects of substrate temperature and deposition time on deposition rate. Direct comparison of films deposited in the two CW systems (CF_4/H_2 and C_2F_6/H_2) shows similarities in both the surface and bulk composition. Comparison between the CW and pulsed C_2F_6 systems indicates films deposited from pulsed plasmas are less cross-linked. Spectroscopic characterization of the films reveals progressive differences in film composition with changes in the rf duty cycle.

II. Experimental Methods

All films were deposited in our home-built inductively coupled rf plasma reactor, described previously.[28] The chamber is pumped by either an Edwards two-stage rotary vane pump (2.3 L s^{-1}) for the CW experiments or an Alcatel 2012A (4.2 L s^{-1}) for the pulsed experiments. For the CW experiments, the applied power was kept at 40 W, with 2−5 W of reflected power. For the pulsed experiments, pulse power was kept at 300 W, with 0−5 W of reflected power. The pulse on time and duty cycle (defined as the ratio of pulse on time to pulse off time) was varied using the internal pulse generator of an RF Power Products RF5S power supply. For each deposition, a freshly pressed FTIR grade KBr (Aldrich) pellet and a silicon wafer (p-type, 1−0−0 crystallization orientation) with 40−60 Å of native oxide were used as substrates. These were placed on glass slides oriented parallel to gas flow in the coil region of the plasma chamber. CW deposition times ranged from 30 s to 120 min and are defined by when rf power was applied to the reactor. Pulsed deposition times range from 60 to 240 min and are defined by the total time the sample was exposed to both pulse on and off cycles.

To minimize possible contamination from previous depositions, the glass sleeves were cleaned regularly in a KOH solution. The sleeves were allowed to soak for ∼12 h and then were rinsed with deionized water and methanol and allowed to dry in an oven for several hours. UV/vis analysis of the sleeves before and after cleaning showed that removal of deposited material was complete. The reactor pieces were also cleaned using the same procedure.

Reactant gases C_2F_6 (Air Products, 99.96%), CF_4 (Matheson, 99.9%), and H_2 (General Air, 99.95%) were used without further purification. Gas flow was controlled through MKS mass flow controllers. All depositions were performed with fluorocarbon and hydrogen mixtures, with the fluorocarbon content of the plasma varying from 100% to 2.5%. The total gas flow was kept constant at 20 standard cubic centimeters per minute (sccm). The pressure in the chamber was monitored with a MKS Baratron capacitance manometer. The overall pressure was allowed to stabilize before initiating the discharge and was 300−350 mTorr for all depositions.

Substrates were removed from the plasma chamber for analysis. Transmission spectra for the KBr substrates were obtained with a Nicolet 5PC FTIR spectrometer for the CW samples (resolution of 2 cm^{-1} and averaging over 100 scans). A Nicolet Impact 410 spectrometer was used to obtain FTIR spectra for films from pulsed plasma experiments (resolution of 8 cm^{-1} and averaging over 100 scans). Spectra shown were corrected for residual carbon dioxide not purged from the FTIR spectrometer (absorbances at ∼2340 and 2360 cm^{-1}). Transmission spectra for the Si substrates was also performed using a Nicolet 760 FTIR spectrometer (resolution of 8 cm^{-1} and averaging over 100 scans).

Substrate temperatures were monitored using a k type thermocouple connected to an HH81 Omega temperature readout. For some of the experiments, a 3 cm × 5 cm × 0.5

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cm water cooled copper substrate holder was used. The H_2O flow rate was ~1.2 L/min. With this substrate holder, the substrate temperature reached an operating temperature of ~200 °C in less than 60 s. The temperature then remained constant at 200 °C for CW deposition times up to 60 min.

X-ray photoelectron spectroscopy (XPS) experiments were performed on the Washington Surface Science Instruments S-probe spectrometer. This system has a monochromatic Al Kα X-ray source ($h\nu = 1486.6$ eV), hemispherical analyzer, and resistive strip multichannel detector. A low energy (~5 eV) electron gun was used for charge neutralization on the nonconducting samples. The binding energy (BE) scales for the samples were referenced by setting the CH_x peak maxima in the C_{1s} spectra to 285.0 eV. The high-resolution C_{1s} spectra were acquired at an analyzer pass energy of 50 eV and an X-ray spot size of 1000 μm. XPS elemental compositions of samples were obtained using a pass energy of 150 eV. Angle-dependent XPS data were collected at nominal photoelectron takeoff angles of 0°, 55°, and 80°. The takeoff angle is defined as the angle between the surface normal and the axis of the analyzer lens system. To improve the depth resolution at each takeoff angle, the solid acceptance angle of the analyzer lens was decreased to 12° × 30° by placing an aperture over the analyzer lens.[29] As the angle is increased from 0° to 80° the sampling depth decreases from 90 to 15 Å.[30]

Film morphology for materials deposited on the silicon substrates was determined using a Philips 505 scanning electron microscope (SEM), with an accelerating voltage of 20 kV and a spot size of 20 nm. The films were sputtered with 10 nm of gold prior to SEM analysis.

Static contact angles for water were measured using the sessile drop method with a contact angle goniometer (Ramé-Hart Model 100). Measurements were taken on both sides of water drops at ambient temperature, 30−40 s after 1 μL drops were applied to the surface and the needle tip removed from each drop. For each sample, six drops were placed at different locations on the surface of a 1000 Å thick film. Reported contact angles are the average of these measurements for three samples. Film thicknesses were obtained by masking a portion of the substrates during deposition and then measuring the resulting step height by profilometry (Tencor Alpha Step 100).

III. Results

A. Fourier Transform Infrared Spectroscopy. Infrared spectra provide useful information on the bulk structure of plasma-deposited films. For plasma polymerized fluorocarbon films, however, assignment of the IR bands is somewhat difficult due to the high degree of cross-linking and the amorphous nature of the films.[21] Furthermore, the IR absorption bands associated with CF_3 and CF_2 groups are difficult to differentiate in the infrared.[31] Table 1 lists the absorbance bands we observe for our films, along with the assignments we have adopted and their literature references. Unless otherwise noted, all FTIR spectra were collected from KBr substrates. For simplicity, we designate plasmas by their fluorocarbon feed content. For example, 70% C_2F_6 indicates a plasma containing 70% C_2F_6 and 30% H_2, as measured by mass flow rate.

C_2F_6 CW Plasmas. Figure 1a shows FTIR spectra of films deposited from C_2F_6/H_2 plasmas containing 70% and 50% C_2F_6. For these feed gas compositions, the IR absorption spectra contain the three characteristic absorbance bands associated with plasma-polymerized fluorocarbon polymers.[21] The most prominent feature is the strong absorbance band at 1100−1400 cm^{-1}, attributable to all CF_x ($x = 1-3$) stretching modes (Table 1). Assignment of the weaker absorbance band at 738 cm^{-1} is more difficult. It has been attributed to "amorphous" poly(tetrafluoroethylene) (PTFE);[13,21] to Si−F stretching resulting from the formation of a silicon fluoride compound as a consequence of silica ablation from the glass tube;[32,33] and to a CF_3 group, possibly $CF-CF_3$.[31] Most recently, Rabolt and co-workers have attributed it to the zone center CF_2 symmetric stretching vibration of the infinite chain PTFE.[34] The third characteristic IR band is the relatively weak absorbance at 1700−1850 cm^{-1} (Figure 1a), which we attribute to either the $-C{=}CF_2$ group or to the $-CF{=}CF_2$ group (Table 1).[31] Films deposited from C_2F_6/H_2 plasmas with fluorocarbon content up to 90% yield similar FTIR spectra. No film deposition is observed using 100% C_2F_6.[35] All films deposited from CW C_2F_6/H_2 mixtures are slightly yellow in color and are optically transparent. For films deposited from a 50% C_2F_6 plasma, there is a trace amount of hydrogen incorporation, indicated by the weak CH absorbance band at ~2900 cm^{-1}.

Figure 1b contains FTIR spectra for films deposited from 30%, 10%, and 2.5% C_2F_6 plasmas. For these films, the absorbance bands in the region between 1000 and 1600 cm^{-1} have become more well resolved, while the weak absorbance at ~740 cm^{-1} has disappeared.

Table 1. Absorbance Band Assignments for Films Deposited from CW and Pulsed Fluorocarbon/Hydrogen Plasmas

absorbance (cm^{-1})	assignment	ref
738	amorphous (PTFE)	13, 21
	Si−F stretch	33, 32
	CF_3, possibly $CF-CF_3$	31
	zone center CF_2 ν_{sym} stretch	34
~980	CF_3 vibration	21, 34, 41
1050	Si−O−C, Si−O−Si	39
1151	CF_2 ν_{sym} stretch	21
1217	CF_2 ν_{asym} stretch	21
1225	FHF deformation	36[a]
1100−1400	CF_x ($x = 1, 2, 3$)	8, 21, 31
1340	CF stretch	21, 34, 41
	axial CF_2 stretch	21, 34, 41
1384	CH_3 deformations	37
1437	CH_2, CH_3 deformations	37
1450	−C=C−, C−C stretch	37
1522	sp^2/sp^3 C−C stretch	37
	FHF asymmetric stretch	36[a]
1700−1850	$-C{=}CF_2$, $-CF{=}CF_2$	31
1833	$-CF{=}O$	17
2042	$-C{=}C{=}C-$	31
~2100	Si−H stretch	28
2954	olefinic sp^2 $-CH_2$ stretch	37
	sp^3 $-CH_3$ stretch	37
2925	sp^3 $-CH_2$	37
2870	sp^3 $-CH_2$ or $-CH_3$	37

[a] This is likely a result of formation of KHF_2 with the underlying KBr substrate.

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(35) This is true for the deposition conditions given in the experimental methods.

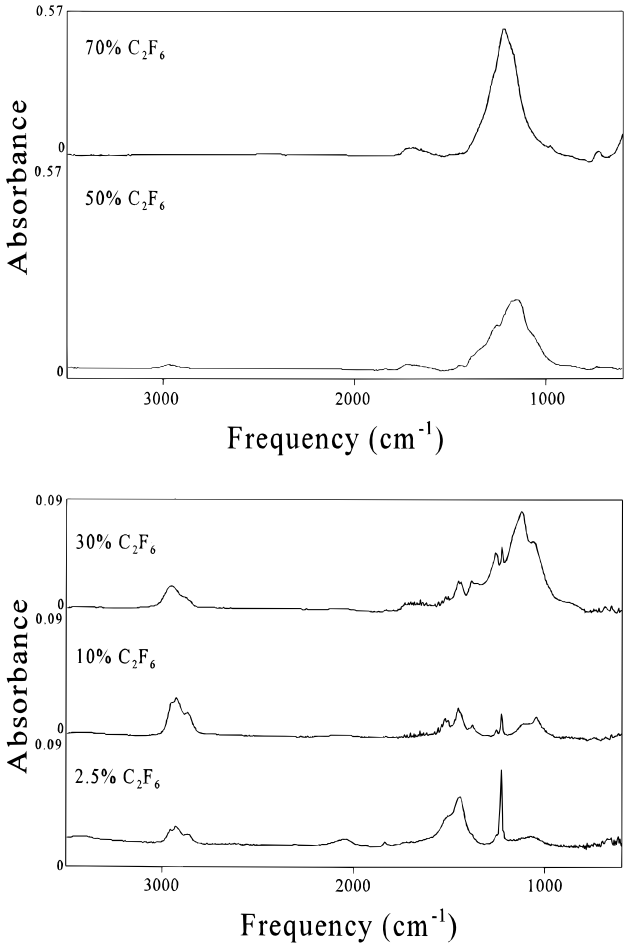

Figure 1. FTIR transmission spectra of films deposited on freshly pressed KBr pellets from C_2F_6/H_2 plasmas with (a, top) 70% and 50% C_2F_6 and with (b, bottom) 30%, 10%, and 2.5% C_2F_6. Deposition conditions are rf input power = 40 W; reactor pressure = 300−350 mTorr; deposition time = 60 min.

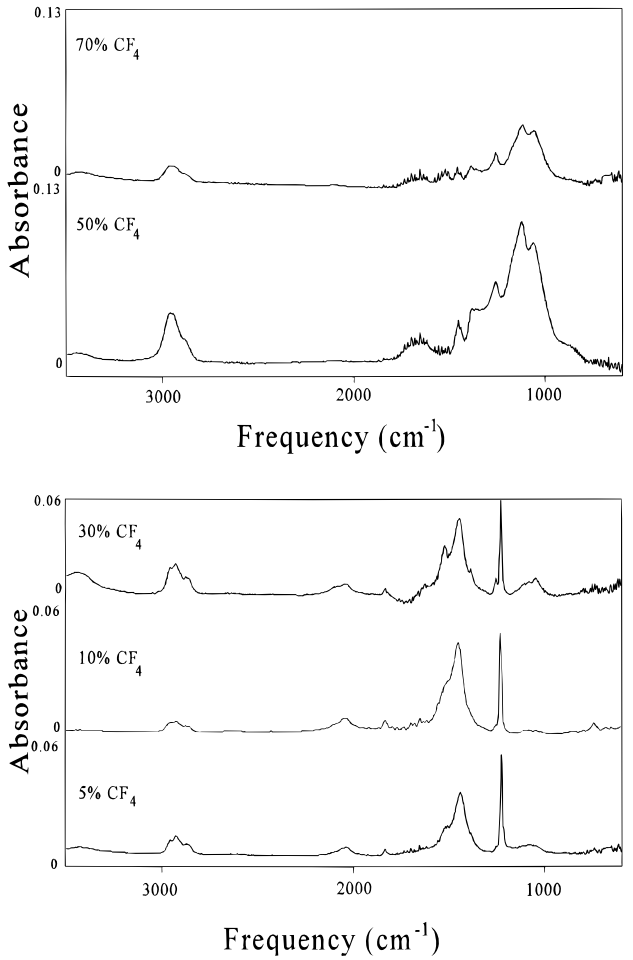

Figure 2. FTIR transmission spectra of films deposited on freshly pressed KBr pellets from CF_4/H_2 plasmas with (a, top) 70% and 50% CF_4 and with (b, bottom) 30%, 10%, and 5% CF_4. Deposition conditions are rf input power = 40 W; reactor pressure = 300−350 mTorr; deposition time = 60 min.

The spectrum for the film deposited from 30% C_2F_6 contains CF_x absorbance peaks (Table 1) and the weak $-C{=}CF_2/-CF{=}CF_2$ absorbance at ~1700 cm^{-1}. In contrast to the films deposited from 70% and 50% C_2F_6, films deposited from 30% C_2F_6 plasmas exhibit a significant absorbance band for the sp^2 and sp^3 CH stretches at 2960 and 2884 cm^{-1}, respectively. The presence of spectral features attributable to both CH and CF moieties indicates this material is a partially fluorinated hydrocarbon film, a-C:H,F.[13] The IR spectrum for the film deposited from 10% C_2F_6 shows a substantial decrease in the CF_x stretching band between 1100 and 1400 cm^{-1}. In addition, the C−H stretching band at ~2900 cm^{-1} has become better resolved and the CH_2 and CH_3 deformation modes at 1437 and 1384 cm^{-1} are present in this film.

Further decreasing the fluorocarbon content of the feed to 2.5% C_2F_6 changes the composition of the film (Figure 1b). The most striking feature of the FTIR spectrum for this film is the sharp absorption band at 1225 cm^{-1}. While the sharpness of this feature is unusual for a solid-state IR spectrum, we believe it to be an FHF deformation as a result of formation of fluoride salts such as KHF_2.[36] This band is not present in FTIR spectra of films deposited on Si substrates but has been observed in films deposited from a 70:30 CH_4/CF_4 gas mixture[33] and in films deposited from CF_4/NH_3 mixtures.[16] In addition to the sharp absorbance band, there is a broad band in the 1400−1600 cm^{-1} region (Table 1).[37] The C−H stretching absorbance band at ~2900 cm^{-1} is fairly well resolved (Figure 1b). The absorbance bands at 2954, 2925, and 2870 cm^{-1} are assigned to C−H stretches based on the assignments of Dischler[37] (Table 1), indicating the presence of both sp^3 and sp^2 hybridized carbons. Thus, we characterize the amorphous, hydrogenated carbon film deposited from a 2.5% C_2F_6 plasma as DLC.

CF_4 CW Plasmas. Figure 2a shows FTIR spectra for films deposited from CF_4/H_2 plasmas with 70% and 50% CF_4, while Figure 2b has FTIR spectra for films deposited from 30%, 10%, and 5% CF_4 plasmas. All films deposited from CF_4 plasmas exhibit spectral features attributable to C−H stretching modes at ~2900 cm^{-1}, indicative of incorporated hydrogen. In addition, films deposited from CF_4 gas mixtures have a broad absorption band at ~3500 cm^{-1}, attributable to O−H stretching from adsorbed water. If the CF_4 content of the plasma is increased to greater than 70%, no film is

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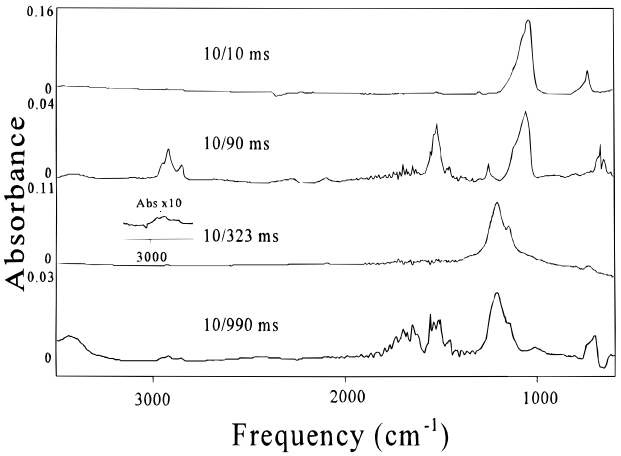

Figure 3. FTIR transmission spectra of films deposited on freshly pressed KBr pellets from pulsed 90% C_2F_6 plasmas using the first timing sequence. The pulse on time was kept constant at 10 ms, and the pulse off time was varied from 10 to 990 ms. The inset shows the C−H stretching region for the 10/323 pulse sequence magnified by a factor of 10.

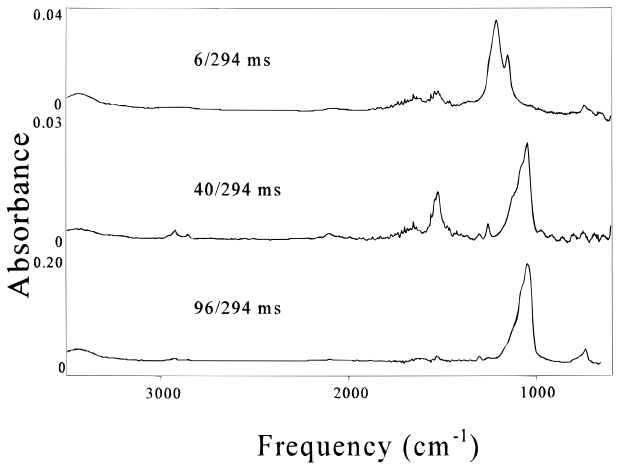

Figure 4. FTIR transmission spectra of films deposited on freshly pressed KBr pellets from pulsed 90% C_2F_6 plasmas using the second timing sequence. Pulse off time was kept constant at 294 ms and pulse on times of 6, 40, and 96 ms were used.

deposited. All films deposited from CW CF_4/H_2 plasmas are slightly yellow in color and are optically transparent.

The spectral features for films deposited from 70% and 50% CF_4 (Figure 2a) are similar to those deposited from 30% C_2F_6 (Figure 1b) and we have assigned corresponding peaks similarly (Table 1). On the basis of these assignments and on the similarity between these films and those deposited from 30% C_2F_6, we characterize these films as a-C:H,F.[13] Decreasing the CF_4 content of the feed to 30% simplifies the FTIR spectrum for the deposited films (Figure 2b). It is clear from the spectra for films deposited from 10% and 5% CF_4 plasmas that continuing to decrease the CF_4 content of the feed gas does not dramatically alter film composition. The spectra for these films are very similar to those for films deposited from a 2.5% C_2F_6 plasmas (Figure 1b). Thus, we characterize these films as DLC.

C_2F_6 Pulsed Plasmas. The effect of variation in rf duty cycle (ratio of pulse on time to total time) on films deposited from a 90% C_2F_6 plasma was examined, keeping all other reaction variables constant. Two timing sequences were employed: a sequence of constant on time and variable off time and a sequence with constant off time and variable on time. In addition, depositions at a fixed duty cycle of 3% but varying the on−off pulse widths were also performed. Depositions at all pulse sequences were replicated multiple times, with excellent reproducibility in the bulk film analysis.

Figure 3 shows FTIR spectra of films deposited from pulsed 90% C_2F_6 plasmas, using a constant on time of 10 ms and a variable off time (10−990 ms).[38] The film deposited from the 10/10 ms pulse is dominated by an absorbance band at 1050 cm^{-1}, which is attributed to Si−O−C and linear Si−O−Si groups (Table 1). We believe this is a result of F atoms etching the glass reactor. The only other absorbance peak in the spectrum is found at 736 cm^{-1}. Although this absorbance band has been assigned to a variety of functional groups, we attribute it to an SiF stretching mode (Table 1) based on the incorporation of silicon in our films.

Increasing the pulse off time changes the film composition considerably (Figure 3). At 90 ms off time, the SiO absorbance (∼1050 cm^{-1}) broadens and decreases slightly, and a small absorbance peak appears at 1254 cm^{-1}. This is attributed to CF_x groups as before. Evidence of hydrocarbon incorporation is also seen with strong absorbance bands at ∼2900 cm^{-1}. The absorbance band observed at 1522 cm^{-1} can be attributed to either a mixed sp^2/sp^3 C−C stretch,[37] or to the FHF asymmetric stretching vibration.[36] Further increasing the off time to 323 ms produces a film that has only two absorbance bands at 1217 and 1151 cm^{-1}. These are the CF_2 ν_{asym} and ν_{sym} modes, respectively.[17] The separation of these two absorbance bands indicates the bulk polymer film has a lower degree of cross-linking than amorphous fluorocarbon polymer films deposited from CW plasmas. There is negligible hydrocarbon incorporation. In addition, these films are visibly white and opaque, an indicator of crystallinity as with bulk PTFE.

Further increasing the off time to 990 ms dos not appreciably change the bulk film composition (Figure 3). Spectra of films deposited with a 240 ms off time indicate the bulk film composition is clearly intermediate between films deposited with 90 and 323 ms off times. The spectra for films deposited with an off time of 490 are similar to those obtained with off times of 323 and 990 ms.

Figure 4 shows FTIR spectra of films deposited from pulsed 90% C_2F_6 plasmas using the second timing sequence, a constant 294 ms off time and a variable pulse on time. On times of 6, 40, and 96 ms are shown in Figure 4. At 6 ms on time the strongest absorbance peaks are at 1217 and 1151 cm^{-1}, attributed to the CF_2 ν_{asym} and ν_{sym} modes, respectively. Increasing the on time to 40 ms essentially eliminates the CF_2 peaks in the FTIR spectrum (Figure 4) and increases the SiO absorbance band at 1045 cm^{-1}. An intermediate pulse on time of 22 ms shows a film similar to that deposited at 6 ms on time. Further increasing the on time to 96 ms shows only the SiO absorbance band at 1050 cm^{-1}. Some films show a negligible contribution from C−H

(38) Because of the large variability in film thicknesses for the pulsed experiments, the FTIR spectra are shown with full scale absorption, rather than on the same absorption scale. Note that films deposited from pulsed plasmas are considerably thinner than those deposited in the CW systems.

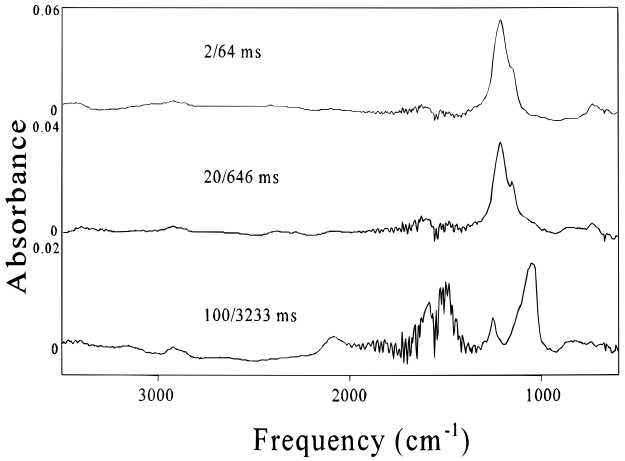

Figure 5. FTIR transmission spectra for films deposited with a constant duty cycle of 3%. The pulse on and off times are varied from 2/64 to 100/3233.

stretching modes at ~2900 and ~1400 cm^{-1} and from Si−H at ~2100 cm^{-1}.[28]

Given the results from the two timing sequence sets of experiments, we find that short on times (~15 ms) and 300−500 ms off times yield less cross-linked fluorocarbon polymer films. This corresponds to a duty cycle of 3−5%. A third set of experiments was performed wherein the duty cycle remained constant at 3%, and the pulse on and off times were varied. From the FTIR spectra for films deposited in this set of experiments (Figure 5), there is little change in film structure up to a pulse ratio of 20/646 ms. Increasing the on and off times to 100/3233 ms, however, results in a very different film (Figure 5). Here, the dominant feature in the FTIR spectrum is the broad SiO absorbance band at 1050 cm^{-1}.[39] Thus, we believe that under these conditions, etching becomes the dominant process in the plasma.

In an effort to understand the competition between deposition and etching in the pulsed plasma systems, we have examined the influence of substrate location on the resulting film composition. Substrates were placed at various distances from the coil region of the plasma reactor and a 90% C_2F_6 plasma was ignited using a 50% duty cycle (10/10). This pulse sequence was chosen because it resulted in deposition of SiO_2, indicating a predominantly etching system. In general, FTIR analysis of substrates placed closest to the coil was identical with that shown in Figure 3. Films deposited on substrates placed 25 cm downstream from the coil region were primarily fluorocarbon polymer, similar to that obtained with a pulse sequence of 10/990, Figure 3. Note, however, that the DR on the downstream substrates was considerably less than that observed directly in the coil using the 10/990 pulse sequence. Thus, etching occurs closer to the coil and deposition dominates downstream.

B. Deposition Rates. Deposition rates for both CW and pulsed systems are shown in Figure 6. Rates for films deposited for 60 min from CW C_2F_6/H_2 and CF_4/H_2 plasmas are shown in Figure 6a. These should be considered as average DRs for the entire deposition period. For the same gas ratios, the C_2F_6/H_2 mixtures

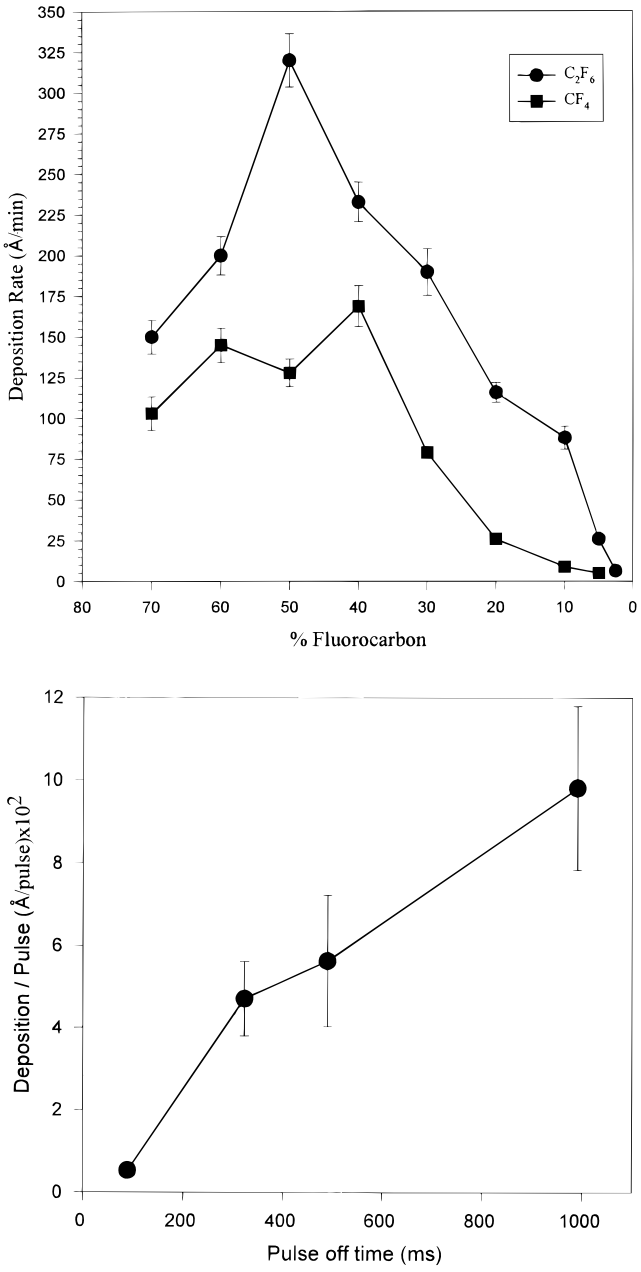

Figure 6. (a, top) Deposition rates for films deposited for 60 min from CW C_2F_6/H_2 (closed circles) and CF_4/H_2 (open squares) plasmas. All films were deposited with an rf input power of 40 W and a reactor pressure of 300−350 mTorr. (b, bottom) Film deposition rates per complete cycle for fluorocarbon polymer films deposited at a constant plasma on time of 10 ms and plasma off times ranging from 90 to 990 ms. All depositions were performed at 300 W peak power. Values are averages of three independent depositions. Errors bars indicate standard deviations of the average values and lines serve to aid the reader's eye.

have higher DRs than the CF_4/H_2 feeds. The maximum DR of 320 ± 16 Å/min occurs for 50% C_2F_6. At lower fluorocarbon content, DRs for both the C_2F_6 and CF_4 plasmas drop significantly. At the highest fluorocarbon concentration, the decrease in DR is presumably due to increased etching by F atoms.

Deposition rates for the pulsed plasma systems are much harder to measure. Because of the varying duty cycle pulsed discharges employ, plotting deposition rates per unit time is relatively meaningless. Furthermore, the predominate process occurring in the plasma appears to shift from deposition to etching as the pulse

(39) Conley, R. T. In *Infrared Spectroscopy*; Allyn & Bacon: Boston, 1966; Mukherjee, S. P.; Evans, P. E. *Thin Solid Films* **1972**, *14*, 105.

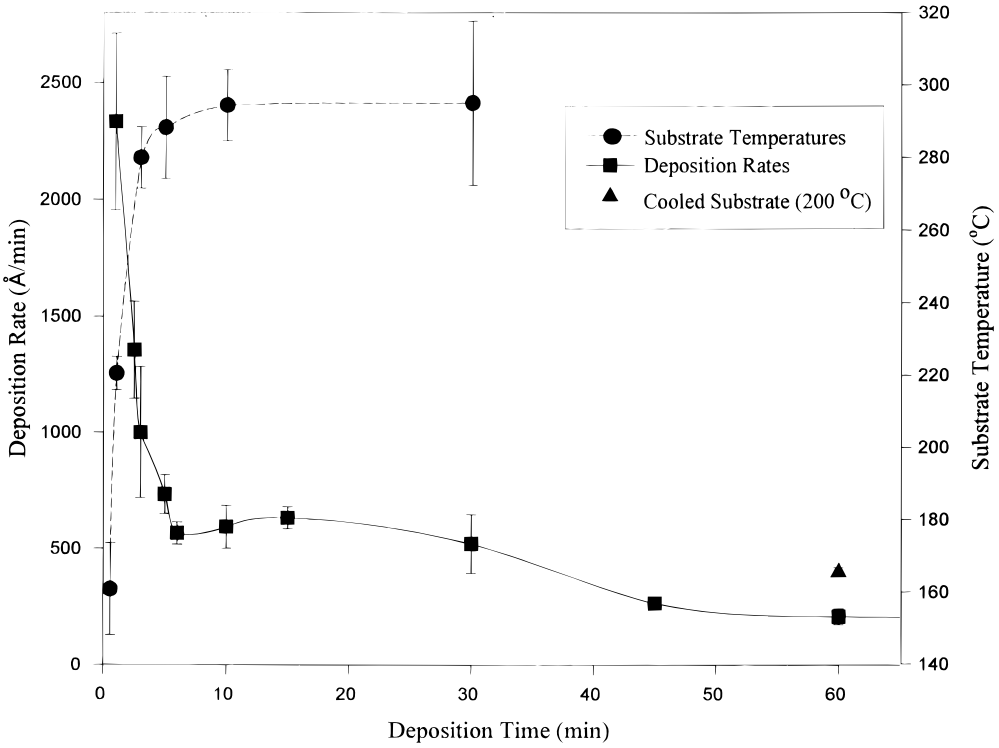

Figure 7. Dependence of deposition rate on deposition time and ambient temperature using a 70% C_2F_6 plasma. The left-hand vertical axis shows the deposition rate as a function of time (closed squares). The right-hand vertical axis indicates the ambient substrate temperature for the indicated times (closed circles). Error bars are one standard deviation on the measurements. Also shown is the deposition rate for a 60 min deposition using the cooled substrate holder (closed triangle). The lines serve to aid the reader's eye.

sequences change. DRs are, therefore, plotted as deposition per pulse vs pulse off times for depositions carried out at a constant on time of 10 ms and peak power of 300 W (Figure 6b). As shown in this figure, there is a steady increase in film DR per pulse cycle as the plasma off time is increased. This demonstrates film formation is occurring during plasma off periods, which has been observed previously for different monomers.[22,40]

To explore the effect of deposition time and substrate temperature on the CW DR, a series of timed experiments were performed using a 70% C_2F_6 plasma (Figure 7). At the shortest deposition time (1 min), the average DR is very high, ~2300 Å/min. At longer deposition times, this rate decreases dramatically, leveling off to ~500 Å/min at deposition times between 5 and 30 min. At longer times, the average DR has decreased to only ~200 Å/min. Also shown in Figure 7 are the corresponding substrate temperatures, indicating the ambient temperature reached during these timed experiments. The substrate temperature increases rapidly from 160 °C at 30 s to 295 °C in 6 min. The temperature then remains constant at ~300 °C for deposition times up to 60 min. Thus, there is a clear correlation between substrate temperature and deposition rate. As the deposition time increases, the substrate temperature increases, and the deposition rate decreases.

Using a temperature-controlled substrate holder, however, indicates that there may be an additional reason for the observed drop in DR with deposition time. With our water-cooled substrate holder, we have the ability to maintain substrate temperatures at lower than ambient. When the substrate temperature is kept constant at ~200 °C, we observe an average DR of only ~400 Å/min for 60 min depositions (Figure 7). For comparison, a 60 min deposition results in an ambient substrate temperature of 300 °C and an average DR of 210 ± 20 Å/min. Alternately, a 1 min deposition results in an ambient substrate temperature of 220 °C and an average DR of 2300 ± 290 Å/min. Thus, the observed decrease in deposition rate appears to depend on both substrate temperature and deposition time.

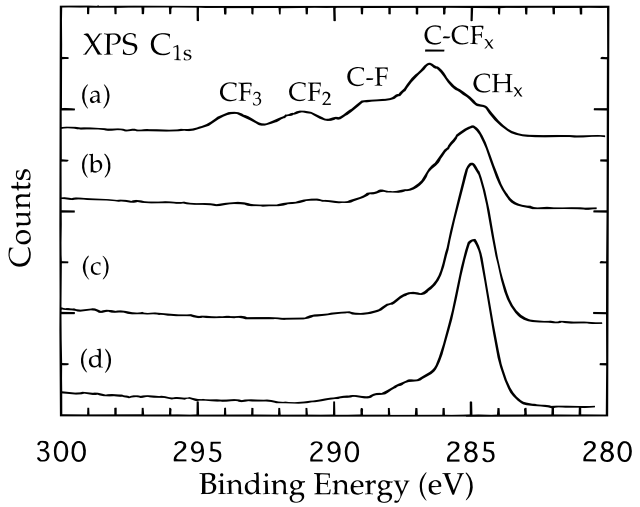

Figure 8. XPS C_{1s} spectra from films deposited using (a) a 50% C_2F_6 plasma, (b) a 50% CF_4 plasma, (c) a 10% C_2F_6 plasma, and (d) a 10% CF_4 plasma at a photoelectron take-off angle of 80° from the surface normal.

C. X-ray Photoelectron Spectroscopy Analysis. *C_2F_6 and CF_4 CW Plasmas.* XPS analysis was performed on films deposited on glass substrates from 50% and 10% CW fluorocarbon plasmas. Angle-resolved XPS

(40) Chen, X.; Rajeshwar, K.; Timmons, R. B.; Chen, J-J.; Chyan, O. M. R. *Chem. Mater.* **1996**, *8*, 1067−1077.

Table 2. Atomic Stoichiometry and C_{1s} Contributions for Films Deposited from C_2F_6/H_2 Plasmas[a]

		atom %				stoichiometry ratio[c]		C_{1s} contribution %				
% C_2F_6	angle θ[b]	C	F	O	Si	F/C	C/O	−CH	−*C*−CF	−CF	$-CF_2$	$-CF_3$
10	0	80.7	9.5	9.8		0.1	8.3	73.9	18.9	7.3		
10	55	81.7	10.6	7.8		0.1	10.5					
10	80	80.8	12.8	6.4		0.2	12.7	80.7	15.8	3.5		
50	0	56.1	40.3	2.9	0.8	0.7	19.5	19.1	32.8	22.4	16.1	9.6
50	55	57.3	38.2	3.1	1.4	0.7	18.4					
50	80	56.2	37.1	3.9	2.7	0.7	14.3	18.3	38.6	21.7	11.9	9.6

[a] Taken from high-resolution, angle-resolved XPS data. [b] Photoelectron takeoff angle, measured with respect to the surface normal. [c] Calculated from the atomic percentage at each analysis depth.

Table 3. Atomic Stoichiometry and C_{1s} Contributions for Films Deposited from CF_4/H_2 Plasmas[a]

		atom %				stoichiometry ratio[c]		C_{1s} contribution %				
% CF_4	angle θ[b]	C	F	O	Si	F/C	C/O	−CH	−*C*−CF	−CF	$-CF_2$	$-CF_3$
10	0	79.7	8.0	12.4		0.1	6.4	76.6	16.2	7.1		
10	55	81.6	8.3	10.1		0.1	8.1					
10	80	82.1	8.4	9.5		0.1	8.7	81.6	14	4.4		
50	0	65.8	21.5	9.1	3.7	0.3	7.3	70.2	20.7	7.7	1.2	
50	55	65.2	17.8	10.3	6.7	0.3	6.3					
50	80	59.7	11.4	15.3	13.7	0.2	3.9	58.6	23.2	12.7	4.7	0.8

[a] Taken from high-resolution, angle-resolved XPS data. [b] Photoelectron takeoff angle, measured with respect to the surface normal. [c] Calculated from the atomic percentage at each analysis depth.

C_{1s} spectra for films deposited from 50% and 10% C_2F_6 plasmas taken at an 80° takeoff angle are shown in Figure 8a,c. Analysis shows that the experimental curves can be fit using a series of peaks assigned to $-CF_3$ (BE = 294.0 eV), $-CF_2$ (BE = 292.1 eV), −CF (BE = 289.5 eV), −*C*−CF (BE = 287.3 eV) and −CH (BE = 285 eV) groups on the basis of literature data.[21] The XPS C_{1s} spectra indicate the surface composition of the film deposited from 50% C_2F_6 (Figure 8a) is heterogeneous with $-CF_3$, $-CF_2$, −CF, and −CH groups present. Furthermore, the film composition does not change significantly as a function of analysis depth. The relative abundance of −*C*−CF and other fluorocarbon species indicates that this film is highly cross-linked.[5]

In contrast, the XPS C_{1s} spectra of a film deposited from a 10% C_2F_6 plasma (Figure 8c) is predominantly composed of CH species and contains relatively small amounts of CF_x groups. Indeed, the only distinguishable fluorocarbon groups are the −CCF and the −CF moieties. In addition, the CF_x groups have a reduced concentration near the surface. This clearly indicates this film can not be considered purely as a fluorocarbon polymer but is better described as a-C:H,F.

Angle-resolved XPS C_{1s} spectra for films deposited from 50% and 10% CF_4 plasmas are shown in Figures 8b,d, respectively. Although we observe the same trend in film composition in going from 50% to 10% CF_4, the composition of the film deposited from 50% CF_4 is very different from that deposited using a 50% C_2F_6 plasma with the primary C_{1s} peak resulting from a −CH moiety. The relative intensities of the −CF and $-CF_2$ species in the film are smaller than those observed in the film deposited from 50% C_2F_6. In addition, $-CF_3$ groups are only present near the surface in the film deposited from 50% CF_4 (Figure 8b). The spectrum for the film deposited from a 10% CF_4 plasma (Figure 8d) looks remarkably similar to that obtained from the film deposited from a 10% C_2F_6 plasma (Figure 8c). Again, we do not observe a high number of CF_x species in this film, indicating it is an a-C:H,F film.

The relative abundances of carbon components, as determined by XPS analysis, for films deposited from 50% and 10% C_2F_6 plasmas are reported in Table 2. Similar analyses for films deposited from 50% and 10% CF_4 are reported in Table 3. Carbon, fluorine, and oxygen were present in all samples. The presence of oxygen in our samples may be attributed to the quenching of radicals in the films by reaction with oxygen when exposed to atmosphere.[41]

The F/C stoichiometry of the films is also reported in Tables 2 and 3. These values were obtained from the ratio of the total integrated intensities of the C_{1s} and F_{1s} levels. Films deposited from 10% fluorocarbon plasmas have low fluorine content, yielding F/C ratios of ∼0.1 for the films deposited from CF_4 and ∼0.15 for those deposited from C_2F_6. In contrast, films deposited from 50% fluorocarbon plasmas have higher fluorine content, with F/C ratios of ∼0.7 for films deposited from C_2F_6 and of ∼0.13 for those deposited from CF_4.

Silicon was present in the films deposited from 50% fluorocarbon plasmas. This may result from the presence of a fluorosilicon compound formed by ablation of the glass reactor. As noted above, at high fluorocarbon content, we observe an IR absorbance band at ∼740 cm^{-1}, which can be attributed to a Si−F stretching mode. As the fluorocarbon content of the plasmas decreases, we no longer observe this band in the IR and there is no silicon observed in the XPS analysis. This is consistent with a contamination produced by the etching effect of a high F atom concentration. Thus, this seems a reasonable explanation for the presence of Si in films deposited from 50% fluorocarbon plasmas, but not in the films deposited from 10% fluorocarbon plasmas.[42]

C_2F_6 Pulsed Plasmas. XPS C_{1s} spectra for films deposited from pulsed 90% C_2F_6 plasmas with pulse

(41) Giegengack, H.; Hinze, D. *Phys. Status Solidi A* **1971**, *8*, 513−520.

(42) An alternate explanation for the presence of Si in our samples is silicone contamination. Si is not detected in the Washington XPS system on films deposited from other glass wall reactors unless the film is thinner than the XPS sampling depth. In those cases, the Si signal is from the underlying substrate. Castner, D. G.; Lewis, K. B., Jr.; Fischer, D. A.; Ratner, B. D.; Gland, J. L. *Langmuir* **1993**, *9*, 537−542.

Table 4. Atomic Stoichiometry and C_{1s} Contributions for Films Deposited from 90/10 C_2F_6/H_2 Pulsed Plasmas[a]

		atom %					stoichiometry ratio[b]		C_{1s} contribution %				
pulse on time (ms)	pulse off time (ms)	C	F	O	Si	Na	F/C	C/O	−CH	−*C*−CF	−CF	$-CF_2$	$-CF_3$
2	18	24.2	40.6	10.2	15.7	9.4	1.68	2.37	27.5	25.1	19.6	15.7	12.0
10	240	31.5	54.4	4.3		7.1	1.73	7.33	12.9	18.7	17.6	37.1	13.7
10	323	34.7	64.4	0.9			1.85	38.6	1.0	15.9	12.6	55.0	15.5
10	990	39.9	59.0	1.1			1.47	36.3	3.0	22.0	20.3	37.4	17.4

[a] All data taken with a photoelectron takeoff angle of 55°, measured with respect to the surface normal. [b] Taken from high-resolution, angle-resolved XPS data.

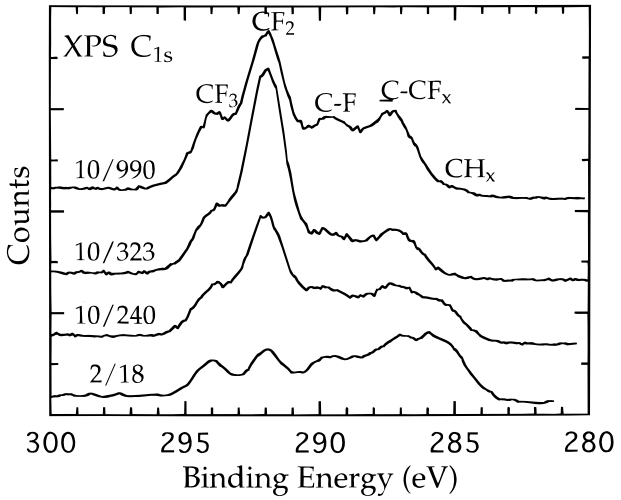

Figure 9. XPS C_{1s} spectra from films deposited using a pulsed 90% C_2F_6 plasma with a pulse power of 300 W. Pulse duty cycles were 2/18, 10/240, 10/323, and 10/990. All spectra were taken at a photoelectron take-off angle of 55° from the surface normal.

cycles of 2/18, 10/240, 10/323, and 10/990 ms are shown in Figure 9. Spectra are fit to the same series of peaks used for the CW films. These results indicate the surface composition changes markedly with duty cycle. The dominate peak at 292 eV in the spectra for films deposited with 10/240, 10/323, and 10/990 pulse cycles is indicative of a CF_2 bonding environment. The relative abundance of $-CF_2$ over other −CF functionalities maximizes at a duty cycle of 10/323. The film deposited from a 10/323 pulsed plasma has a small amount of $-C-$CF (287 eV) and CF (289.5 eV) compared to CF_2. This indicates that these films are not highly cross-linked and that the surface structure is approaching that of a linear polymer. In contrast, the XPS C_{1s} spectra of the film deposited from a 2/18 pulse comprises mainly −CH and $-C-$CF species. This indicates that the surface of this film is highly cross-linked a-C:H,F.

The relative abundance of carbon components are reported in Table 4 along with the F/C and C/O ratios in the films deposited from pulsed plasmas. The latter values were obtained from the ratio of the total integrated intensities of the C_{1s} and F_{1s} levels. Carbon, fluorine, and oxygen were present in all samples. Films deposited using pulsed duty cycles of 10/240, 10/323, and 10/990 all have a high fluorine content. The film deposited from a 10/323 pulsed plasma has the maximum F/C ratio of 1.85, approaching that of PTFE. The maximum C/O ratio observed also occurs with this film (Table 4).

The film deposited from 2/18 pulse sequence has a significantly different elemental composition with large amounts of silicon, sodium, and oxygen present. This surface composition compares well with the bulk composition of films deposited from 10% duty cycles (Figure 3). These analyses support the conclusion that we are etching the glass reactor and incorporating the ablated products in our films. Silicon was absent from all other samples examined by XPS.

D. Scanning Electron Microscopy. SEM results for films deposited from 50% C_2F_6, 50% CF_4, 10% C_2F_6, 10% CF_4, and 2.5% C_2F_6 plasmas are shown in Figure 10. The micrographs indicate that all of our films are pinhole-free and amorphous, even at high magnifications. There are some differences in the film morphologies, however. The surface of films deposited from 50% C_2F_6 is very smooth (Figure 10a), while the films deposited from a 50% CF_4 plasma (Figure 10b) have a more interesting surface morphology, with small ∼0.5 μm nodules dispersed on the surface.

As the fluorocarbon content of the plasmas decreases, the surface of films deposited becomes rougher as can be seen with films deposited from a 10% C_2F_6 plasma (Figure 10c). The rough, pebbly appearance of this film is similar to that of an amorphous hydrogenated carbon film deposited from CH_4/H_2 mixtures.[43] The surfaces of films deposited from 10% CF_4 plasmas are slightly smoother (Figure 10d), but a surface roughness persists. Films deposited from 2.5% C_2F_6 plasmas (Figure 10e) exhibit very rough surfaces, with a grainy appearance at high magnifications. Hence, as the bulk film structure changes from fluorocarbon polymer to a-C:H,F, to DLC the surface roughness of the films increases. SEM analysis of films produced in pulsed plasmas (90% C_2F_6, 3% duty cycle) indicates these films are also pinhole free, similar to the films produced with CW plasmas at high fluorocarbon feed. At the highest magnifications, there are also some small striations in the film surface.

E. Contact Angle and Adhesion. Contact angle measurements are a sensitive means of probing surface composition and were measured for all films studied. Contact angles were measured for thin films (∼1000 Å thick) deposited from both C_2F_6/H_2 and CF_4/H_2 CW plasmas as well as for films deposited from 90% C_2F_6 pulsed plasmas. Results of the measurements for the CW films, as a function of fluorocarbon content in the plasma, are shown in Figure 11 along with linear regression fits to the data.[44] For films deposited from C_2F_6 CW plasmas, the contact angle increases linearly with increasing fluorocarbon content in the feed, suggesting a direct correlation with the C_2F_6 content and hydrophobicity. The same trend is observed with the

(43) Nakayama, M.; Tsuyoshi, A.; Shibahara, M.; Maruyama, K.; Kamata, K. *J. Vac. Sci. Technol. A* **1995**, *13*, 195−199.

(44) These fits do not include the measurements for films deposited at the lowest fluorocarbon content for each system, i.e., 2.5% for C_2F_6 and 5% for CF_4. The correlation coefficient (R^2) values for these fits are 0.885 and 0.641 for the C_2F_6 and CF_4 systems, respectively.

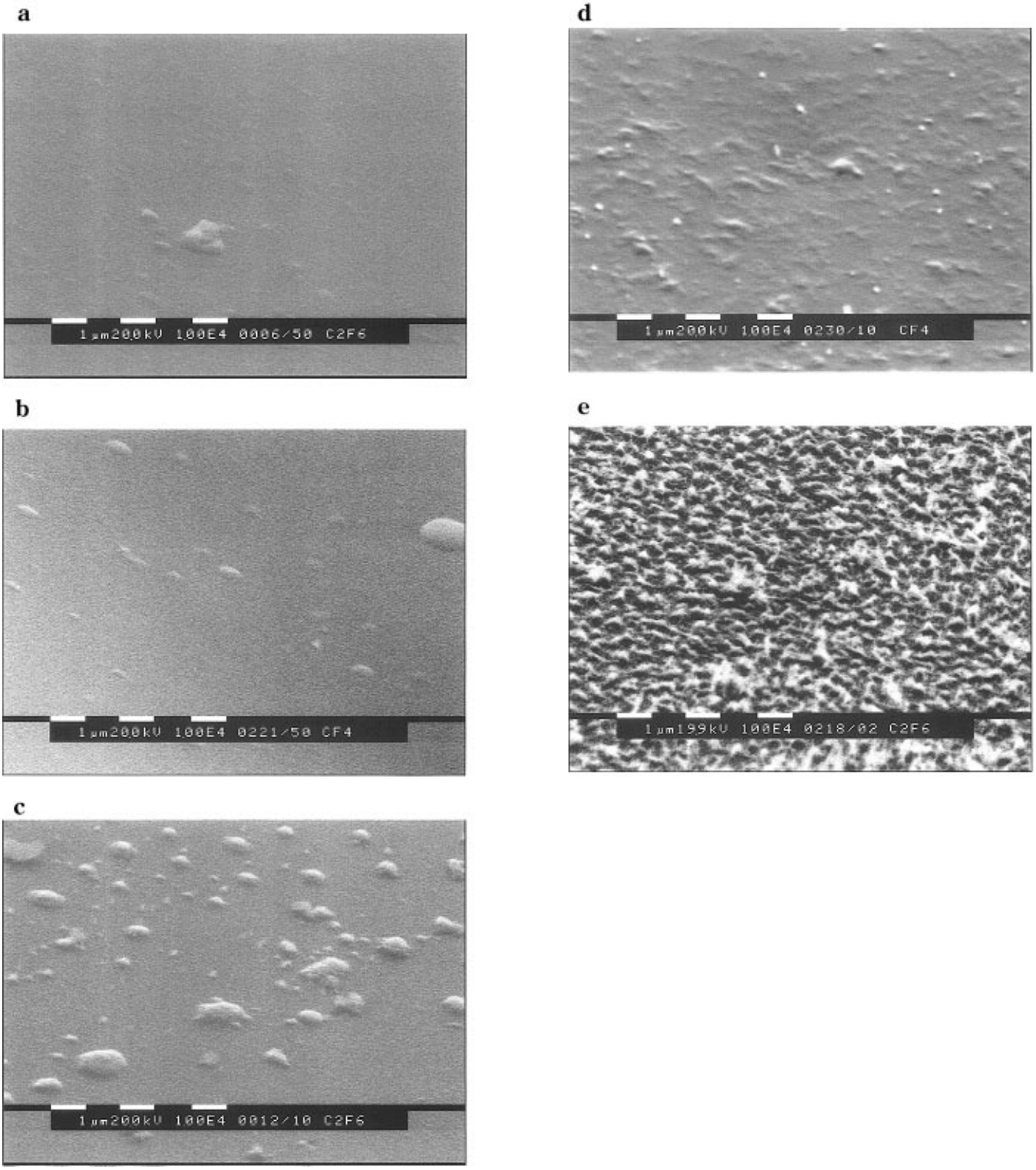

Figure 10. Scanning electron micrographs of films deposited for 60 min from fluorocarbon/hydrogen CW plasmas with an applied power of 40 W. All films are shown with the same magnification (×10 000): (a) 50% C_2F_6; (b) 50% CF_4; (c) 10% C_2F_6; (d) 10% CF_4; (e) 2.5% C_2F_6.

films deposited from CF_4 CW plasmas, although it is not as pronounced.

Films deposited from the highest fluorocarbon content CW plasmas, are hydrophobic (contact angles of 91−101°). It is known that CF_3 moieties contribute to the hydrophobicity of fluorinated films,[13] indicating that our films are likely terminated by CF_2 and CF_3 groups. The C_{1s} contributions for the films deposited from 50% fluorocarbon plasmas, Tables 2 and 3 validate this, showing a large fraction of C−CF, CF, CF_2, and CF_3 groups at the surface. For comparison, we measured the contact angle of Teflon tape to be 113.7 ± 1.2° and the contact angle of water on polytetrafluoroethylene films is 109 ± 2°.[45] For films deposited from ≤5% CW fluorocarbon plasmas, we measure contact angles of

(45) Kiaei, D.; Hoffman, A. S.; Horbett, T. A. *J. Biomater. Sci. Polymer Ed.* **1992**, *4*, 35−44.

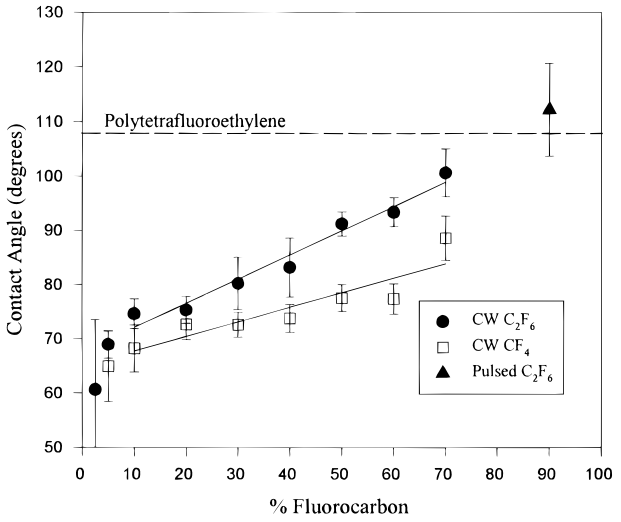

Figure 11. Relation of contact angle and fluorocarbon content in the feed gas for films deposited from CW C_2F_6 and CF_4 plasmas. Closed circles are data for C_2F_6 CW plasmas and open squares are data for CF_4 CW plasmas. Solid lines represent a linear regression fit to the data (excluding the 2.5% C_2F_6 point and the 5% CF_4 point), with slopes of 0.43 for the C_2F_6 data and of 0.25 for the CF_4 data. The contact angle for films deposited from 90% C_2F_6 pulsed plasmas with a 3% duty cycle is also plotted (closed triangle). For comparison, the contact angle for bulk poly(tetrafluoroethylene) (PTFE) is plotted as a dashed line.

∼45−65°, indicative of hydrophilic, wettable surfaces. This is likely due to a much lower fluorine content, as evidenced by the FTIR and C_{1s} spectra.

The average contact angle for films deposited from a 90% C_2F_6 pulsed plasma with a 3% duty cycle, and a peak power of 300 W is also shown in Figure 11. These films have a very high contact angle of ∼111°. This is higher than the contact angle measured for PTFE, also shown in Figure 11, possibly with CF_3 surface termination, as indicated in Table 4.

As a final analysis of the films deposited from both CW and pulsed plasmas, we performed the standard tape test.[46] All of our films do not significantly delaminate over long periods of time. Under the tape test conditions, however, films deposited from 70% and 50% CW C_2F_6 plasmas did not adhere well to either the glass slides or the Si substrates. Indeed, these films were completely removed from all substrates during the test. In contrast, fluorocarbon polymer films deposited from the pulsed systems adhered well to the underlying substrates, both silicon wafers and glass slides. This is true for films deposited from 10/90, 10/323, 10/990, 4/396, 12/400, 2/66, and 20/666 pulse cycles, with no discernible differences between films deposited at different duty cycles. The tape test was not performed on films considered to be the result of reactor etching.

F. Comparison of Pulsed and CW Plasmas. To directly compare films deposited from our pulsed plasmas to those deposited from CW plasmas, equivalent powers must be determined. We define equivalent power as

$$\text{equivalent power} = \left(\frac{t_{on}}{t_{on} + t_{off}}\right)(W) \qquad (1)$$

(46) Jacobsson, R. *Thin Solid Films* **1976**, *34*, 191−199.

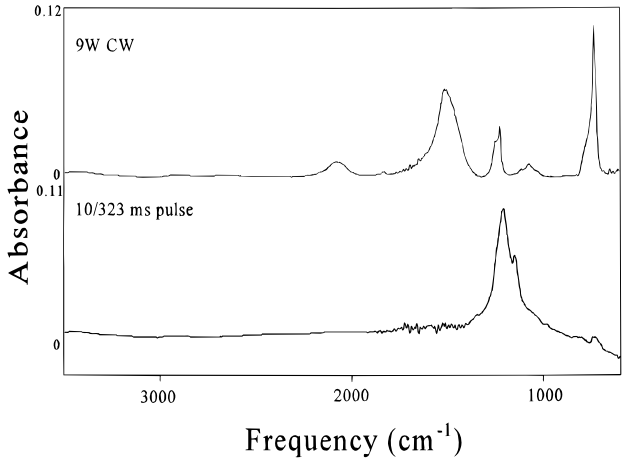

Figure 12. Comparison of the FTIR absorbance spectra of a film obtained from a 90% C_2F_6 plasma at 9 W CW with that deposited from a 10/323, 300 W (9 W equivalent) pulsed power.

where t_{on} and t_{off} are plasma on and off times, respectively, and W is the rf power during the on time. For this comparison we used a pulse sequence of 10/323 ms at 300 W, yielding an equivalent CW power of 9 W.[24]

Variations in film composition with changes from CW to equivalent power pulsed plasmas is nicely illustrated in the FTIR spectra of films deposited from 90% C_2F_6 plasmas (Figure 12). Clearly, the bulk structure of these two films are very different. The FTIR of the CW film has a strong absorbance band at 738 cm^{-1}, attributed to Si−F or CF_3 (Table 1); a small SiO absorbance at ∼1050 cm^{-1}; CF_x stretching bands at ∼1250 cm^{-1}; and a strong absorbance due to C−C stretching at 1520 cm^{-1}. The absorbance peak at 2020 cm^{-1} is attributed to cumulative double bonds (Table 1). The DR for a CW 90% C_2F_6 plasma is very slow, ∼1.1 Å/min, presumably because of the competing deposition and etching processes at this feed gas composition.

In contrast to the CW film, the FTIR spectrum for a film deposited from a pulsed plasma with equivalent power is considerably different (Figure 12). With the pulsed system, the only appreciable absorbance band observed is due to the CF_2 ν_{asym} and ν_{sym} modes. In the CW films, these stretching modes are not well defined and there are clearly contributions from other CF_x species. XPS C_{1s} spectra of films deposited under CW and optimal pulsed conditions (10/323) indicate the same film composition at the surface as seen in the bulk. The pulsed films are dominated by CF_2 groups, while the CW films are completely amorphous with multiple CF_x species throughout the film. This direct spectroscopic (both FTIR and XPS) comparison highlights the significantly different film chemistries evolving from CW and pulsed systems.

IV. Discussion

CW Plasmas. CW plasmas containing mixtures of a saturated fluorocarbon and hydrogen have been studied extensively. Our results for the bulk structure of films deposited from different feed gas compositions for both C_2F_6/H_2 plasmas and CF_4/H_2 plasmas are generally consistent with those of previous researchers. We note that different feed gas compositions in the two systems result in similar films. For example, in the

C_2F_6 system, the highest fluorocarbon plasmas deposit films exhibiting only characteristics of fluorocarbon polymer, with no hydrogen incorporation. As the C_2F_6 content decreases, we observe spectral features attributable to both CF_x and CH_x moieties. In the CF_4 system, however, we observe both CF and CH moieties at all feed gas compositions. Likewise, DLC films are deposited from 2.5% C_2F_6 and 10% CF_4 plasmas. This is likely a result of the F/C ratio of the feed gas which has a strong effect on both DR and film properties.[21] Furthermore, addition of hydrogen to the plasma serves to scavenge F atoms and effectively decreases the F/C ratio such that film deposition occurs.

Our results for the CF_4/H_2 systems compare favorably with previous work,[4,13,47] with no major discrepancies. Although our results for the C_2F_6/H_2 systems also agree favorably with the previous results of d'Agostino and co-workers[4−6,10,21] and with Masuoka and Yasuda,[32] there is one minor discrepancy with the work of d'Agostino. The changes in bulk film composition from fluorocarbon polymer to a-C:H,F to DLC occur at different fluorocarbon content. Our results indicate that fluorocarbon polymer is deposited with >50% C_2F_6 in the feed, a-C:H,F is deposited between 10 and 50% C_2F_6 and DLC is deposited at lower C_2F_6 content. d'Agostino and co-workers obtain hydrogenated polymer films with <5% C_2F_6 in the feed and fluorinated polymer films when the C_2F_6 content is >12%.[10] It is possible, however, that their films do incorporate small amounts of hydrogen in the bulk film at 12−20% C_2F_6. This is not, however, clear from the data presented.

Deposition Rate and Substrate Temperature. In the CW C_2F_6/H_2 systems, we find a maximum DR of 320 ± 16 Å/min at 50% C_2F_6 (Figure 6) for films deposited for 60 min. This is nearly identical with the results of Masuoka and Yasuda, who found a maximum rate of 275 Å/min at 50% C_2F_6.[32] d'Agostino and co-workers also found the maximum DR occurred at ∼60% C_2F_6. Their values, however, were significantly different, with average DRs of ∼1400 Å/min for substrates at 40 °C and ∼1000 Å/min for substrates at 100 °C.[6] While the location of the maximum, 60% C_2F_6, agrees well with our data, our DR is 3−4 times smaller than that found by d'Agostino.[21]

Our data in Figure 7 suggest the discrepancy between our results and those of d'Agostino may be the result of different deposition times and subsequently different substrate temperatures. Although a negative apparent activation energy effect has been alluded to in previous studies,[21] no complete study of DR, substrate temperature, and deposition time has been performed until now. Our data also suggest a correlation with deposition time and substrate temperature. The controlled substrate temperature studies show an increase in substrate temperature can not completely account for the observed decrease in DR. Thus, the deposition rate appears to be controlled by *both* substrate temperature and deposition time. The time dependence of Figure 7 may account for some of the discrepancies between our DRs and those of previous studies. It is, however, difficult to directly compare these results as many of the previous studies do not report deposition times and/or ambient substrate temperatures.[48]

In the CF_4 systems, we do not observe deposition until the H_2 concentration is above 30%. The maximum DR of ∼170 Å/min occurs at 60% H_2 (40% CF_4). Seth and Babu found essentially the same DR maximum, 193 Å/min, occurred at 50% CF_4.[13] Our results also agree with Inagaki and co-workers, who found the DR from CF_4/CH_4 systems reaches a maximum at ∼50% CF_4.[33] Our results do not, however, agree with those of d'Agostino, who found DRs in the CF_4/H_2 systems decrease monotonically with increasing H_2 dilution, and indicate a *maximum* DR at 90% CF_4.[4] We believe some of these discrepancies may be explained by the substrate temperature and deposition time effects observed in the C_2F_6 system.

Pulsed C_2F_6 Plasmas. The film composition in the pulsed systems changes significantly from that deposited with CW plasmas. Our data for 90% C_2F_6 pulsed plasmas show a definite film structure dependance on the pulse cycle and duration. At short pulse off times (<290 ms) the dominant process in the plasma appears to be etching, as evidenced by the presence of SiF and SiO moieties in the deposited film (Figure 4). At longer off times (≥323 ms), the deposited film shows characteristics of a fluorocarbon polymer with little crosslinking, high CF_2 content, and little contribution from hydrocarbon species. These results compare favorably to those of Savage, Timmons, and co-workers, who also observe an increase in the CF_2 content at low duty cycles (<10%) for C_3F_6O, C_3F_6, and $C_2F_{16}O$.[37,38] Changing the pulse on time converts the plasma character from deposition to etching at long on times (>24 ms). These effects are possibly the result of increased fragmentation of the fluorocarbon source with longer plasma on times. Pulse on time dependence is also evident at a constant 3% duty cycle. Here, deposition occurs at pulse sequences up to 20/646 ms, but we see evidence of etching at longer on times.

As shown in Figure 12, comparison can be made between films deposited from a 90% C_2F_6 pulsed plasma (300 W, 3% duty cycle) and films deposited from an equivalent power (9 W) CW plasma. The dominant process in the CW plasma under these conditions is etching, as shown by the presence of SiO in the film with only a small contribution from fluorocarbon polymer. Films deposited from the pulsed system, however, have no SiO species and contain a large fraction of CF_2, as shown by the FTIR and XPS analyses.

We can also compare fluorocarbon polymer films deposited from the optimum CW conditions (70% C_2F_6, 40 W), shown in Figure 1a, and films deposited from a pulsed 90% C_2F_6, (3% duty cycle, 300 W), shown in Figure 12. The bulk structure of the CW film is amorphous, containing multiple CF_x species. In addition, the XPS C_{1s} spectra indicate a high level of crosslinking exists in these films. In contrast, the FTIR and XPS C_{1s} spectra of the pulsed film indicates primarily CF_2 species, with little contribution from CF and CF_3 moieties. This indicates a less crosslinked film is deposited and that a high level of controllability may be achieved using pulsed plasmas. This "molecular selectivity" has also been observed for films deposited from pulsed C_3F_6O,[22] allyl alcohol,[49] and allyl amine.[50]

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(48) Other possible sources of the discrepancy may be reactor pressure, pumping speed, or monomer flow rate.

Another important difference between films deposited from CW and pulsed plasmas is their adhesion to the underlying substrates. All of our films deposited from pulsed C_2F_6 plasmas adhere well to both silicon wafers and glass slides, while the CW films do not. This may arise from the amorphous, highly cross-linked nature of the CW films. In the pulsed systems, there is no duty cycle dependence to the adhesion of the films. Recent results of Rinsch et al. for pulsed plasma polymerization of allyl alcohol indicated that films deposited at lower duty cycles were significantly less adherent than films deposited at higher duty cycles.[49] This difference may be a result of the higher levels of oxygen in their films.

Deposition Mechanism. While the mechanism for film deposition from pulsed systems is not clear, it deserves some comment here. There are two issues to be considered. First is the effect of radical species in the plasma. With the unsaturated fluorocarbon sources C_6F_6 and C_2F_4, Yasuda and Hsu have shown CW plasmas generate more radicals than can be consumed in the deposition of a polymer film.[25] The excess gaseous free radicals can then be trapped in the growing film. In contrast, pulsed plasma conditions can be modified to generate radicals during the on period and consume them in the off period, thereby trapping fewer radicals in the film.[25]

In our CW systems, creation of excess fluorine radicals at high fluorocarbon feed ratios (i.e., 90% C_2F_6) establishes an etching environment. This leads to ablation of the glass reactor and the incorporation of SiF and SiO moieties in our films. Deposition of etch products has been seen previously in saturated fluorocarbon plasmas containing little or no H_2.[51] Furthermore, etching studies have shown a fluorocarbon adlayer is formed during fluorocarbon etching of SiO_2.[52] Using a low duty cycle pulsed plasma with a high fluorocarbon content creates a better balance between production and consumption of free radicals. Thus, deposition becomes the dominant process, and we observe creation of a less crosslinked fluorocarbon film. Because there are fewer excess free radicals, this film also presumably contains fewer dangling bonds.[53] On the basis of this work and the previous work of Timmons and co-workers,[22,49] we believe that the chemistry occurring during the plasma off times is highly selective. Here, film formation may be the result of polymerization of primarily CF_2 radicals during plasma off times. The reaction between fluorine atoms and hydrogen must also be fairly efficient during off times as we do not observe significant amounts of hydrogen incorporation in films grown under the "optimal" duty cycle conditions.[54]

In addition to balancing the production and consumption of free radicals, the production of charged species capable of promoting etching and deposition must be considered. Although CF_x radicals are thought to be the primary film precursors in CW plasmas, ion bombardment is believed to be an integral factor in the deposition mechanism, namely the source of "activated" polymer sites.[21] Gas-phase CF_x radicals can then add to the growing polymer at one of these activated sites. In the pulsed systems, the effect of ion bombardment is diminished because the concentration of ions decays rapidly during the plasma off times.[24,49] This decrease in ionic activation may produce fewer polymerization sites in the growing polymer film, thereby leading to a less cross-linked film. This is supported by the observation that films deposited in the coil, where ions are more prevalent are significantly different from those deposited downstream from the coil. Films deposited in the coil region under "etching" conditions contain Si−O and Si−F moieties, while downstream films do not. Although etching does dominate under some pulsed conditions, it can be controlled by establishing the proper duty cycle. With high duty cycle pulsed plasmas, the ions do not have enough time to decay before the next pulse creates more ions. Both the low duty cycle pulsed plasmas and the downstream depositions limit the films exposure to ions, leading to a less crosslinked material. Clearly, to create good quality films, the balance between ions and radicals must be maintained such that deposition dominates without ion exposure to the growing film. Because of the complexity of the plasma system, however, it is difficult to give a detailed mechanistic picture of the film deposition process in either the CW or pulsed systems.

Implications for Future Applications. The ability to deposit strongly adherent films with high CF_2 content may be important for technological applications of these materials. Low dielectric constant films are needed for use as interlevel dielectrics (ILD) in the microelectronics industry. Plasma-deposited fluorocarbon films are expected to have properties similar to bulk PTFE, including high chemical and thermal stability, low wettability, and low dielectric constants.[29] The major drawbacks to films deposited from CW plasmas, however, is their high degree of cross-linking and F/C ratios $\ll$2.0 due to a distribution of CF_x species. The results from our pulsed studies indicate we are able to deposit a less cross-linked film with a comparable CF_2 fraction to bulk PTFE and a very high contact angle. Films with similar properties have recently been reported using thermal decomposition of hexafluoropropylene oxide.[53]

We have performed preliminary experiments to measure the electrical properties of our films. Dc conductivity measurements indicate an upper limit to the conductivity of our films of 5.6×10^{-6} S cm^{-1}. Ellipsometry measurements of the films deposited from a 90% C_2F_6 10/323 pulsed plasma yield a refractive index of 1.32.[55] Using Maxwell's relation, $n = (k_e)^{1/2}$, where n is the refractive index and k_e is the static dielectric constant,[56] we calculate our best films to have a dielectric constant of $\geq$1.7. Although Maxwell's relation is not always valid, it does offer a lower limit to the dielectric constant of our films. For comparison, commercial PTFE has a refractive index of 1.38[57] and a dielectric constant of

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2.0−2.1.[1] Thus, our films may be useful for coating applications where low wettability, high flexibility and strong adhesion is desired. Further characterization of pulsed systems for the deposition of fluoropolymers as ILD materials is indicated.

There is one final point to be made about the plasma systems studied here. There is some environmental concern over the use of fully fluorinated gases because of their potential role in global warming.[58] Indeed, C_2F_6 is estimated to have 12 500 times the global warming potential of carbon dioxide.[59] Yet, it is still used extensively in the microelectronics industry for etching and cleaning purposes. One possible solution is the use of hydrofluorocarbon (HFC)-125, a more easily decomposed gas. In addition, there is a gas recovery unit currently being developed that would remove C_2F_6 from the waste stream of plasma processing systems.[59] In an effort to address these concerns, we are currently exploring pulsed plasma systems for deposition of polymeric materials with good electrical and mechanical properties using alternate hydrocarbon and fluorocarbon systems.[60]

V. Conclusions

We have deposited a variety of films from CW and pulsed rf plasmas using mixtures of saturated fluorocarbons (C_2F_6 and CF_4) and hydrogen. Bulk and surface composition of films deposited from saturated fluorocarbon CW inductively coupled rf plasmas change substantially with addition of H_2. The results presented here are consistent with those of previous studies, indicating that the composition of films deposited from saturated fluorocarbon/hydrogen plasmas is not strongly dependent on reactor type. Comparison of films deposited from CW and variable duty cycle pulsed 90% C_2F_6 plasmas demonstrates we have better control of bulk and surface film properties with the pulsed systems. An optimum duty cycle of 3% is found for the C_2F_6/H_2 system. At this duty cycle, with relatively short on times, a PTFE-type fluorocarbon polymer (primarily CF_2 species) is deposited. These results demonstrate the utility of pulsed plasmas for controlled deposition of new materials that may be used as ILD materials.

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