Control of Surface Film Composition and Orientation with Downstream PECVD of Hexafluoropropylene Oxide

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Introduction. Poly(tetrafluoroethylene) (PTFE) films have many applications due to their biocompatibility, flexibility, and low dielectric constants.[1,2] As a result, much research has been aimed at obtaining PTFE-like polymer films using plasma polymerization methods. Continuous wave (CW) plasma polymerization using saturated fluorocarbons, however, generates amorphous, highly cross-linked films with low F/C ratios.[3] One method for controlling the composition of fluorocarbon films is to pulse the plasma power, thus increasing functionality and reducing cross-linking in the deposited materials.[4,5] Alternatively, downstream CW deposition of fluorocarbon films also results in increased fluorine incorporation, low cross-linking, and unique film structures.[6,7]

Hexafluoropropylene oxide (HFPO) is a good fluorocarbon precursor for obtaining high F/C ratio polymers.[8] Recently, Gleason and co-workers used a parallel plate plasma reactor to deposit fluorocarbon films from CW and pulsed HFPO plasmas.[8,9] Under CW conditions, amorphous fluorocarbon films with a distribution of CF_x species were deposited at rf powers of 25, 50, and 140 W. Similar films were deposited at all powers. In contrast, under optimal pulsed conditions (0.5% duty cycle, 280 W peak power) highly flexible films[10] with up to 70% CF_2 were deposited. No analyses for surface orientation or short-range geometric structure were reported.

Savage, Timmons, and Lin (STL) have also studied CW and pulsed HFPO plasmas.[4,11] Using a cylindrical Pyrex glass reactor, no net film deposition was observed in a 300 W CW plasma. Under pulsed conditions (1% duty cycle, 300 W peak power), however, films similar in composition to those produced by Gleason and co-workers[8,9] were deposited. These films had F/C ratios of 1.9−2.1, and the X-ray photoelectron spectroscopy (XPS) data confirm the dominant film functionality was CF_2 with small contributions from CF_3.[4,11,12] No film orientation or structure analysis was performed on these films.

Castner et al. performed extensive surface analyses of films deposited from a C_2F_4 glow discharge, with substrates placed both directly in the visible glow and downstream from the glow.[7] Their detailed characterization of the surface stoichiometric composition (XPS analysis) and film orientation [polarized near edge X-ray absorption fine structure (NEXAFS) spectroscopy] showed that films deposited within the glow were highly amorphous with random orientation. In contrast, films deposited downstream from the glow contained ~90% CF_2 groups, aligned in CF_3-terminated chains perpendicular to the substrate. For comparison, commercial PTFE comprises CF_2 chains oriented parallel to the surface plane.

Here, we describe downstream deposition of fluorocarbon films (28 cm) in a CW HFPO plasma. All films were analyzed with Fourier transform infrared spectroscopy (FTIR), angle-dependent XPS, and NEXAFS to provide bulk and surface composition as well as chain orientation information. Our films have high CF_2 content (~80%) and are highly oriented, with polymer chains aligned normal to the substrate.

Experimental Methods. All films were deposited on 300 K substrates in our home-built inductively coupled rf plasma reactor,[13] with the downstream section lengthened to 36 cm. Applied rf power was varied (13−60 W), and the monomer flow rate was 10 sccm. For each deposition, a KBr pellet and a silicon wafer (p-type, 110) with 40−60 Å of native oxide were used as substrates placed 28 cm downstream from the last rf coil. Monomer flow was allowed to stabilize at 185 mTorr before applying rf power. Deposition time was 30 min.[14]

Transmission FTIR spectral analysis was performed ex situ using a Nicolet Magna 760 FTIR spectrometer (8 cm^{-1} resolution, averaging 128 scans). Spectra shown are corrected for residual carbon dioxide not purged from the FTIR spectrometer (absorbances at 2340 and 2360 cm^{-1}). XPS analyses were performed on a Surface Science Instruments S-probe spectrometer located at the

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[14] Film thickness of ~125 Å were measured using a Dektak I profilometer, yielding a deposition rate of ~2 Å/min.

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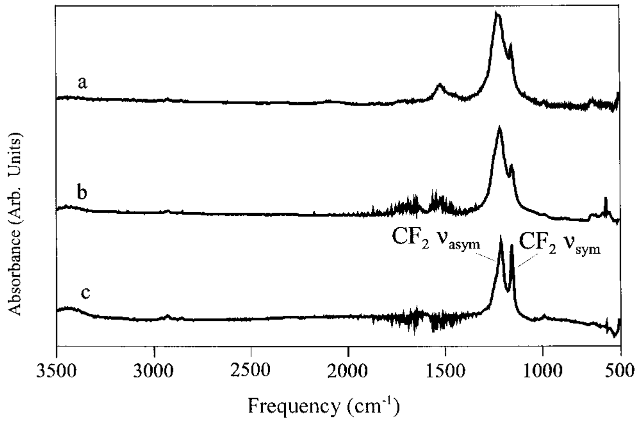

Figure 1. FTIR transmission spectra of films deposited on freshly pressed KBr pellets 28 cm downstream from HFPO plasmas at three different applied rf powers: (a) 60 W, (b) 30 W, and (c) 13 W. Pressure was 185 mTorr in all systems.

University of Washington, described elsewhere.[15] Binding energy (BE) scales for the samples were referenced by setting the CF_2 peak maxima in the C_{1s} spectra to 292.0 eV.[15] High-resolution C_{1s} spectra were acquired at an analyzer pass energy of 25 eV and an X-ray spot size of 1000 μm and were fit using Gaussian functions with fwhm of 1.3−1.5 eV. XPS elemental compositions were obtained using a pass energy of 150 eV. Photoelectron takeoff angles of 0°, 55°, and 80° were used.[16]

NEXAFS analysis was performed at the National Synchrotron Light Source at Brookhaven National Laboratory using beamline U7A. The 600 *l*/mm grating monochromator was calibrated using the graphite $C_{1s} \rightarrow \pi^*$ transition (285.35 eV) and had a fwhm of ~0.15 eV resolution at the carbon K edge. Photoelectrons and Auger electrons were collected with a negatively biased channeltron to obtain partial electron yield (PEY) spectra. These spectra were normalized by using the PEY from a 90% transmission grid which was gold coated in situ and positioned in the incoming X-ray beam. The incidence angle is defined as the angle between the incident X-ray beam and the sample surface.

Results and Discussion. FTIR spectra in Figure 1 show the dependence of film composition on applied rf power. The spectrum of the film deposited at the highest power (60 W) shows features that are consistent with amorphous, cross-linked fluorocarbon films.[3] The CF_x ($x = 1-3$) symmetric and asymmetric stretches appear as a broad band at ~1250 cm^{-1}.[3,6,17] The other absorption peak observed at 1629 cm^{-1} corresponds to $C{=}CF_x$ vibrations.[17] The coalescence of the CF_x vibration bands and the presence of unsaturated moieties indicate that the bulk structure of these films is highly cross-linked and amorphous. In contrast, lower applied rf powers produce films with only two absorbance bands at 1155 and 1209 cm^{-1}, corresponding to the CF_2 symmetric and asymmetric stretches, respectively.[3,4] The $C{=}CF_x$ absorbance is virtually eliminated from the IR spectra, suggesting there is little cross-linking and unsaturation in these films. This indicates that a much higher degree of order exists in films deposited downstream at low rf powers.[18] Such film characteristics are most likely caused by lower ion densities and less energetic ions impacting the film surface.[19]

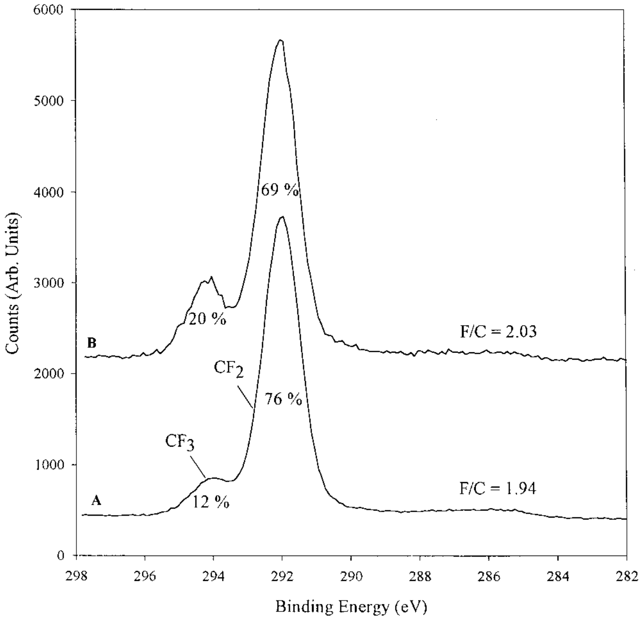

Figure 2. XPS C_{1s} spectra from films deposited using a 23 W HFPO CW plasma 28 cm downstream from the plasma glow. Spectra were taken with photoelectron takeoff angles of (a) 0° and (b) 80°. The F/C atom ratios determined from the C_{1s} peak areas at each takeoff angle are also provided.

XPS analysis further characterizes films deposited downstream in our reactor. Figure 2 shows XPS C_{1s} spectra (takeoff angles of 0° and 80°) for films deposited 28 cm downstream at 23 W. Peaks assignable to CF_2 and CF_3 moieties at 292 and 294 eV, respectively, are observed. Peak-fitting results of the data acquired at a takeoff angle of 0° (sampling depth ~100 Å) reveal that the CF_2 content is 76%, while the CF_3 content is 12%.[20] The remaining spectral area can be assigned to CF_x species where $x < 2$. As the takeoff angle is increased to 80° (sampling depth ~20 Å), the relative intensity of the CF_3 peak increases significantly. This indicates that the CF_3 groups are present primarily at the outer surface of the film.

In addition to determining the bulk and surface composition of these films, it is important to probe the alignment and orientation of the CF_2 chains. Information about the orientation, electronic structure, and short-range geometric structure can be obtained from polarized NEXAFS data. NEXAFS spectra taken at 90° and 20° angles of incidence are shown in Figure 3. Transitions to F−C σ^* orbitals (292 and 298 eV) are most intense when the X-ray beam is normal to the sample surface, while the transition to the C−C σ^* orbitals (295 eV) is strongest at a glancing angle of incidence. These changes in absorption intensities in-

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(15) Capps, N. E.; Mackie, N. M.; Fisher, E. R. *J. Appl. Phys.* **1998**, *84*, 4736−4743.

(16) The takeoff angle is defined as the angle between the surface normal and the axis of the analyzer lens.

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(18) None of the films displayed significant C−H or O−H vibration bands in the FTIR spectrum.

(19) Lieberman, M. A.; Lichtenberg, A. J. *Principles of Plasma Discharges and Materials Processing;* John Wiley and Sons: New York, 1994.

(20) In all films the amount of oxygen (atom %) was <1%.

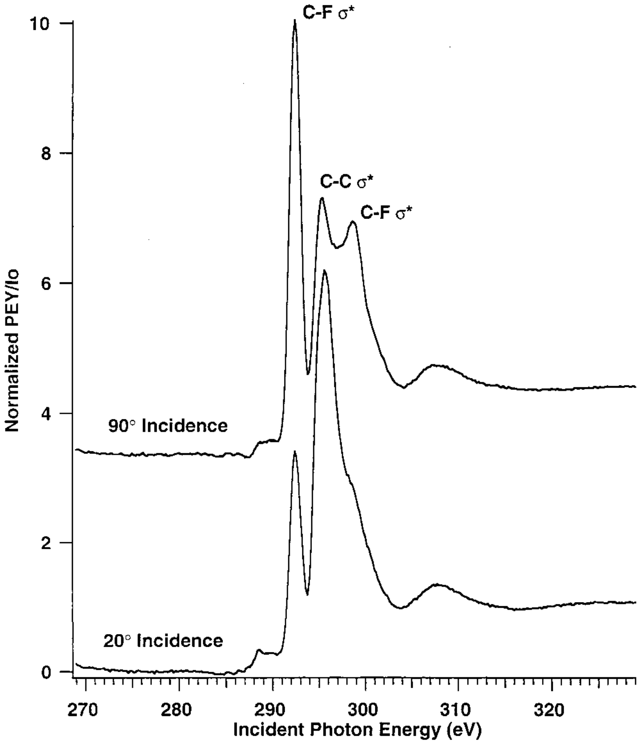

Figure 3. Carbon K-edge normalized partial electron yield NEXAFS spectra of a film deposited 28 cm downstream from the HFPO plasma (23 W) at 90° and 20° angles of incidence.

dicate that the films deposited downstream in our CW HFPO plasma comprise highly oriented CF_2 chains aligned normal to the underlying substrate.[7]

As noted above, films produced in CW plasmas are usually amorphous, contain C−C double bonds, and have F/C ratios < 2.0 (typically ∼1.6). The observation of a highly oriented film with a F/C of ∼2 deposited from a CW plasma is quite unusual. Moreover, the orientation of these materials is unlike that of commercial PTFE.[7] On the basis of polarized NEXAFS data, Castner et al. reported that PTFE contains CF_2 chains parallel to the substrate surface. They also reported that films deposited downstream from a C_2F_4 plasma show a CF_2 chain orientation normal to the substrate, similar to what we observe here. In contrast, films with a CF_2 chain parallel to the substrate have been reported for downstream deposition from a C_2F_6 plasma.[21]

It is also interesting to compare our films with those deposited previously in CW HFPO plasmas by STL[4,11] and by Gleason and co-workers.[8,9] As noted above, STL observe no net film deposition under CW conditions in their reactor. This is likely the result of the relatively high applied powers (300 W) used, although no power dependence is reported. In contrast, Gleason and co-workers deposit amorphous films under CW conditions with rf powers of 25−140 W.[8,9] In both studies, substrates were placed directly in the plasma glow. Our films have a higher CF_2 content than those obtained by Gleason and co-workers, but are similar to those deposited downstream from a C_2F_4 plasma by Castner and co-workers.[7] Thus, the differences between our films and those of STL and of Gleason and co-workers are likely the result of differences in reactor geometries, monomer pressure, applied rf power, and substrate position relative to the plasma glow.

In conclusion, we have shown that films deposited downstream from a low power CW HFPO plasma contain oriented CF_2 chains terminated with CF_3 groups. This is the third report of an oriented film being produced by an rf plasma deposition process,[7,21] but only the second time where chains in the film were perpendicular to the substrate. Additional studies of these films are currently underway, including comparison of films produced under pulsed plasma conditions and with different plasma parameters as well as exploring deposition mechanism issues.[22]

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