Macromolecules **1996,** *29,* 4220−4225

Pulsed Plasma Polymerization of Perfluorocyclohexane

A. M. Hynes, M. J. Shenton,[†] and J. P. S. Badyal[*]

Department of Chemistry, Science Laboratories, Durham University, Durham DH1 3LE, UK

Received November 27, 1995; Revised Manuscript Received March 20, 1996[⊗]

ABSTRACT: Pulsed versus continuous wave plasma polymerization of perfluorocyclohexane is compared as a function of duty cycle off-time, on-time, and peak power. The chemical composition of the deposited films has been determined by X-ray photoelectron spectroscopy (XPS). A greater retention of the chemical structure associated with the precursor molecule is found for the pulsed plasma polymerization experiments. This can be rationalized in terms of the relative perturbation of reactive species contained in the electrical discharge.

Introduction

Conventional polymerization of an organic monomer results in the synthesis of a polymer consisting of repeat units whose structure is closely related to the precursor species.[1] The precise nature of the polymer product depends on factors such as the catalyst employed, polymerization mechanism, reaction temperature, pressure, etc. Careful control of the reaction conditions can yield a polymer with the desired physicochemical properties. In more recent years, plasma polymerization has become an established technique for the dry deposition of thin polymeric films. It can be executed at ambient temperature and generates very little waste compared to more established wet chemical routes. This method is based upon the activation and reaction of a precursor molecule by a non-equilibrium electrical discharge.[2] For instance, plasma polymerization of perfluoromonomers can result in the deposition of films with very low surface energy;[3] these films find application as hydrophobic,[4,5] protective,[6,7] and biocompatible coatings.[3,8] Low-pressure electrical discharges are capable of generating a range of chemically reactive species from a wide variety of precursor molecules.[9] Ions, radicals, electrons, metastables, and photons contained within the glow discharge can all contribute toward the deposition of polymeric material over all surfaces in contact with the plasma. This initiation step is believed to be followed by propagation involving the reaction of gas phase free radicals or non-fragmented monomer with trapped free radical centers at the surface.[10] Termination occurs (as in conventional polymerization) by the combination of two reactive species to form a non-reactive moiety which may be subsequently incorporated back into the plasma polymerization reaction pathways.[2]

One of the major drawbacks of plasma polymerization is that the inherently complex nature of the glow discharge leads to a variety of functionalities being incorporated into the resultant polymeric layer. Variation in experimental parameters such as input power,[11] feed gas ratio, monomer pressure,[12,13] substrate temperature,[14] and substrate position[15] can help to control film composition. The input power can be altered either by changing the peak power in the continuous wave (CW) mode or by pulsing the ac voltage by using a signal generator.[16] Pulsing has several inherent advantages over continuous wave plasma polymerization.[17−19] Excessive heating of reactor walls and substrate is avoided due to reduced ion bombardment of the surfaces in contact with the plasma.[17] Also, any decay of short-lived excited species during the off portion of the duty cycle can help to attenuate both the VUV emission and the variety of species contributing to the overall plasma polymer structure. In addition, conventional polymerization reactions can occur during the off-time. The extent to which pulsing can be used to enhance desired chemical reaction pathways within an electrical discharge is not yet fully established.

Perfluorocyclohexane (PFCH), C_6F_{12}, is a fairly inert molecule,[20] which contains exclusively CF_2 linkages, and therefore is a potential candidate for the synthesis of a PTFE-like plasma polymer. Indeed, it has been previously demonstrated that low-power CW plasma polymerization of perfluorocyclohexane can yield cross-linked polymeric fluorocarbon films with a high fluorine content.[12] In this article, we compare the continuous wave and pulsed rf plasma polymerization of perfluorocyclohexane to explore to what extent further enhancement of chemical selectivity can be achieved by pulsing the electrical discharge. The resultant polymeric films have been characterized by X-ray photoelectron spectroscopy (XPS). Different CF_n environments ($n = 0-3$) can be easily distinguished by XPS because of the large C(1s) core level shifts associated with the various types of fluorinated carbon centers; furthermore, the inherent surface sensitivity of the technique (sampling depth: 2−10 atomic layers)[21] renders it suitable for the analysis of thin films.

Experimental Section

Low-pressure plasma polymerization experiments were carried out in an electrodeless cylindrical glass reactor (internal diameter = 5 cm, volume = 490 cm^3) enclosed in a Faraday cage[15] (Figure 1). This was continuously pumped by a 33 dm^3 h^{-1} Edwards E2M2 mechanical rotary pump via a liquid nitrogen cold trap, yielding a base pressure of 2×10^{-3} mbar and a leak rate of better than 2.3×10^{-12} kg s^{-1} (calculated by assuming ideal gas behavior).[22] A 13.56 MHz rf generator was inductively coupled to the gas via an LC matching circuit and a copper coil (0.5 cm diameter, 10 turns) wound externally around the reaction chamber spanning 8−16 cm from the gas inlet. The substrate was positioned in the center of the copper coils. In the case of pulsed plasma polymerization experiments, a signal generator was attached to the rf power source, and a cathode ray oscilloscope was used to monitor the pulse duration, interval, and amplitude. The pulse rise and fall time was 100 ns. The peak power (P_p) delivered to the copper coil could be varied between 20 and 200 W, while on-times (t_{on}) and off-times (t_{off}) varied between 20−400 μs and 5−400 μs,

---

[*] Author to whom correspondence should be addressed.

[†] Present address: Chemistry Department, University of York, York, England.

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

S0024-9297(95)01747-5 CCC: $12.00

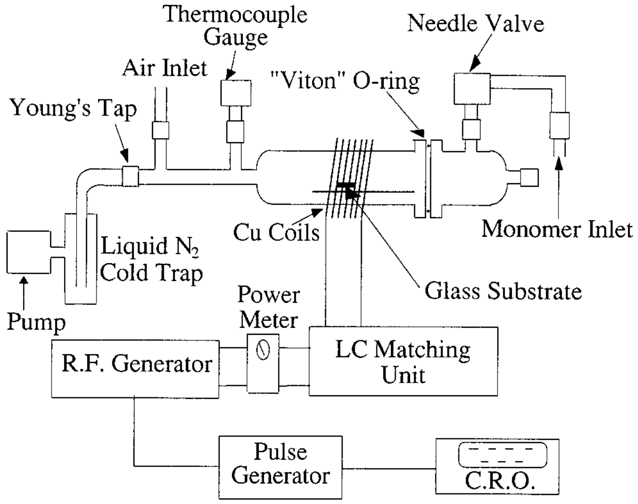

Figure 1. Experimental setup for pulsed and CW plasma polymerization.

respectively. The average power $\langle P\rangle$ delivered during pulsing was calculated using the following expression:[23]

$$\langle P\rangle = P_{\mathrm{p}}\frac{t_{\mathrm{on}}}{t_{\mathrm{on}} + t_{\mathrm{off}}} \tag{1}$$

Prior to each experiment, the reactor and glass slides were scrubbed with detergent, rinsed with isopropyl alcohol (IPA), oven-dried, and then cleaned with 50 W air plasma at a pressure of 0.2 mbar for 30 min. Then 0.2 mbar of perfluorocyclohexane (Fluorochem Ltd., 97% purity) was introduced into the reaction chamber via a fine needle valve at a flow rate of 1.6×10^{-7} kg s^{-1}. The reactor was purged with monomer for 2 min prior to igniting the glow discharge. Plasma polymerization was carried out for 10 min. Upon termination, the reaction zone was purged with perfluorocyclohexane for an additional 2 min and finally vented to air.

A Kratos ES200 X-ray photoelectron spectrometer with an un-monochromated X-ray source (Mg $K\alpha_{1,2}$ = 1253.6 eV) was used for chemical characterization of the deposited fluorocarbon films. Emitted core level electrons were collected at a 30° take-off angle from the substrate normal, with a concentric hemispherical analyzer (CHA) operating in fixed retardation ratio mode (FRR = 22:1). The spectrometer was calibrated with respect to the gold $4f_{7/2}$ peak at 83.8 eV (FWHM = 1.2 eV).[24] The absence of any silicon XPS features following plasma polymerization was taken as indicative of complete coverage of the glass substrate.

Results

For each plasma polymer, the C(1s) XPS envelope was fitted using a Marquardt minimization computer program, which assumed a Gaussian peak shape with a fixed relative full width at half-maximum (FWHM).[25] The C(1s) XPS spectra were fitted using five different carbon functionalities:[12] $\underline{C}\mathrm{-CF}_n$ (286.6 eV), $\underline{C}\mathrm{F}$ (287.8 eV), $\underline{C}\mathrm{F-CF}_n$ (289.3 eV), $\underline{C}\mathrm{F}_2$ (291.2 eV), and $\underline{C}\mathrm{F}_3$ (293.3 eV). The $\underline{C}\mathrm{F}_3$ and $\underline{C}\mathrm{F}_2$ peaks could be assigned unambiguously, and therefore the dominant $\underline{C}\mathrm{F}_2$ peak was taken as a reference offset at 291.2 eV. Mg $K\alpha_{3,4}$ satellite peaks with different FWHM were also taken into consideration.[25] The Mg $K\alpha_{1,2}$ C(1s) FWHM were found to vary between 1.9 and 2.2 eV. The relative concentration of each carbon functionality was obtained by dividing the corresponding peak area by the total C(1s) envelope area. Figure 2 shows a typical C(1s) peak fit for a 5 W CW perfluorocyclohexane (PFCH) plasma polymer.

Continuous Wave Plasma Polymerization. The change in appearance of the C(1s) XPS spectra with increasing CW power is shown in Figure 3a. At higher powers, the deposited plasma polymer films exhibit very little variation in composition. At lower powers, however, the relative concentration of $\underline{C}\mathrm{F}_2$ functionality increases with decreasing power while the number of cross-linked ($\underline{C}\mathrm{-CF}_n$) carbon centers drops (Figure 3b). This suggests that the $\underline{C}\mathrm{F}_2$ content of the films could rise even further if the input power can be reduced. Below 1.5 W the CW plasma becomes unstable at the operating pressure of 0.2 mbar, so the electrical discharge was pulsed to sustain lower average powers.

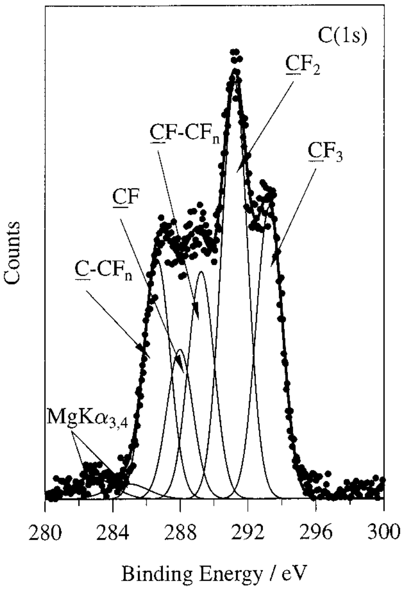

Figure 2. Typical peak-fitted C(1s) XPS spectrum (5 W CW plasma polymer).

Pulsed Plasma Polymerization. From eq 1, the average power delivered to the plasma is a function of three variables, viz., off-time, on-time, and peak power. The influence of each of these variables upon the composition of the deposited film was studied. Figure 4a shows the C(1s) XPS spectra of plasma polymer films obtained when the off-time was varied (with a fixed peak power of 20 W and an on-time of 20 μs). The $\underline{C}\mathrm{F}_2$ component increases relative to the cross-linked ($\underline{C}\mathrm{-CF}_n$) peak with rising off-times (i.e., decreasing average power). This trend was also observed for shorter on-times (with a fixed peak power of 20 W and an off-time of 250 μs) and lower peak powers (with a fixed on-time of 20 μs and off-time of 250 μs) (Figures 5 and 6, respectively). These results are consistent with the CW experiments, where decreasing average power was found to yield a higher $\underline{C}\mathrm{F}_2$ content and a lower level of cross-linked carbon, while the $\underline{C}\mathrm{F}_3$ contribution remains steady. Figure 7 compares the $\underline{C}\mathrm{F}_2$ content of the deposited plasma polymer films for all of the experiments. It can be concluded that, for the same average power, a pulsed glow discharge produces a film with higher $\underline{C}\mathrm{F}_2$ content than that obtained with a CW plasma at average powers below 7 W.

Discussion

Continuous Wave Plasma Polymerization. $\underline{C}\mathrm{F}_3$ and $\underline{C}\mathrm{F}_2$ functionalities account for up to 65% of the total C(1s) envelope in the CW plasma polymerization of PFCH, which is consistent with previously reported studies in the 1−100 W power range.[12] The amount of

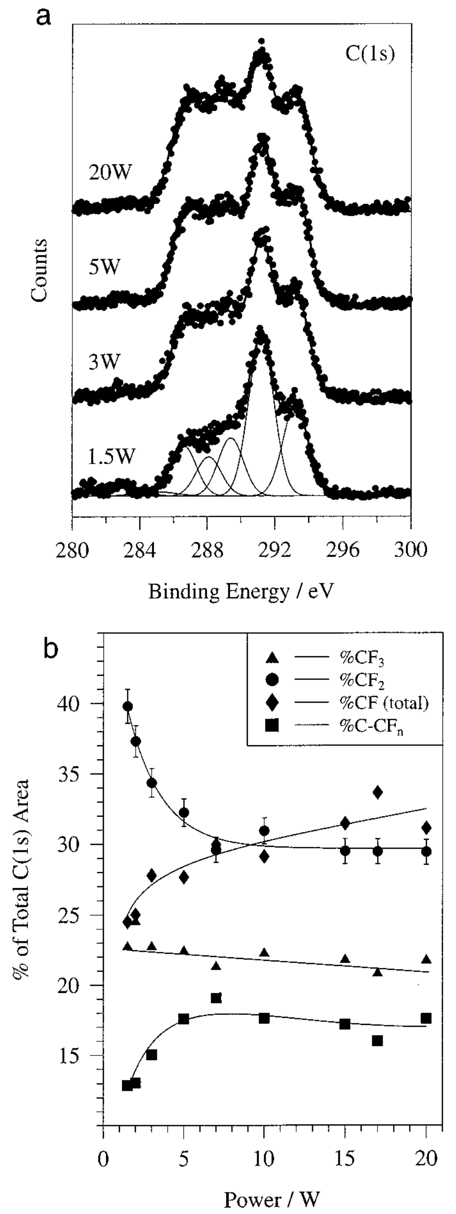

Figure 3. (a) C(1s) XPS spectra for CW experiments. (b) Variation in fluorinated functionalities with power for CW experiments.

cross-linking in the plasma polymer is dependent upon the *W*/*FM* parameter[2] (where *W* is the discharge wattage, *F* is the flow rate in moles/minute, and *M* is the molecular mass of the gas). In the present study, both *F* and *M* are constants and therefore the degree of cross-linking ($\underline{C}-CF_n$) can be directly correlated to the input power (Figure 3b).

A variety of reactions can potentially occur during plasma polymerization. These can be subdivided into collision-induced reactions (e.g., electron impact dissociation, polymerization in the gas phase, and ion bombardment at the gas–substrate interface) and radiation-induced reactions (e.g., unimolecular excitation and dissociation, along with radiative degradation of the growing polymer network). The effect of power level on each of these types of reaction is considered below.

The input power influences the average electron energy $\langle \epsilon \rangle$, the population of the high-energy tail of the electron energy distribution, and the density of excited species present in the plasma.[26] Any reactions that involve electrons from the high-energy tail of the electron energy distribution will be affected by the drop in the number of high-energy electrons with decreasing input power.[27] One such reaction is the ionization of PFCH, which has an activation energy of approximately 13 eV.[12] A smaller fraction of PFCH molecules will be expected to undergo dissociation via electron collision ionization at lower input powers, resulting in more nonfragmented PFCH molecules impinging upon the substrate. Such a rise in PFCH flux incident upon the surface will lead to a greater $\underline{C}F_2$ content in the resultant plasma polymer network.

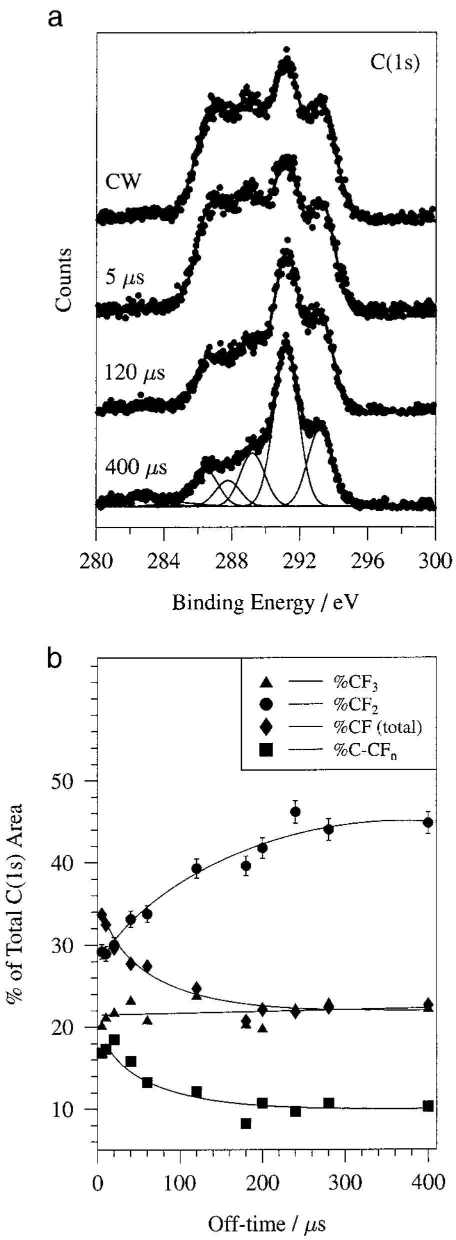

Figure 4. (a) XPS spectra for pulsed experiments with variation in off-time (peak power = 20 W, on-time = 20 μs). (b) Variation in fluorinated functionalities with off-time for pulsing experiments (peak power = 20 W, on-time = 20 μs).

The type and relative abundance of CF_n radicals contained in the glow discharge can also influence the composition of the plasma polymer deposit.[28,29] The difluorocarbene radical, CF_2, is relatively stable with respect to other types of CF_n radical. It has been shown to be a major constituent of and an important precursor to polymer formation in fluorocarbon plasmas.[11,30] Depletion of CF_2 species from fluorocarbon plasmas can occur via electron collision processes to liberate a fluorine

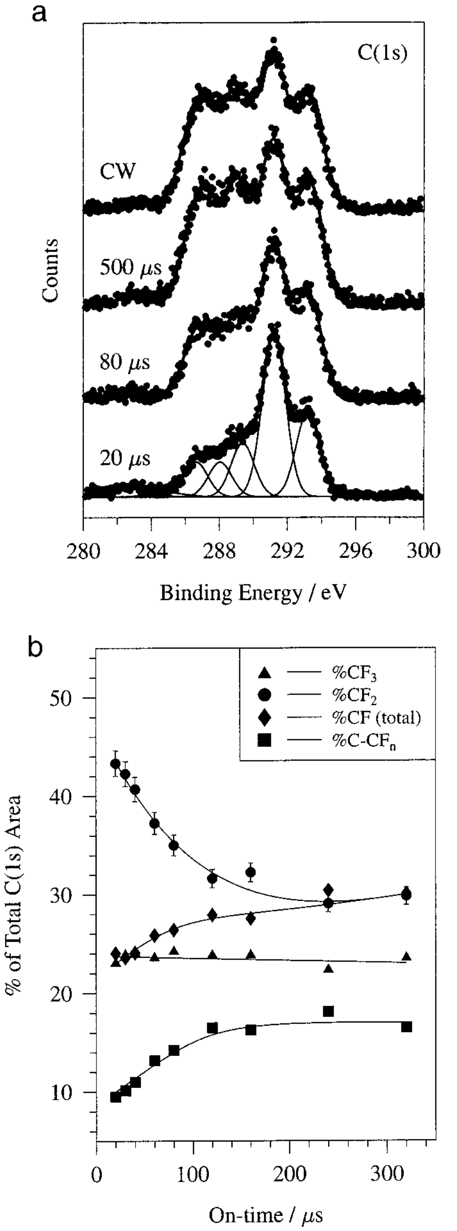

Figure 5. (a) XPS spectra from pulsed experiments with variation in on-time (peak power = 20 W, off-time = 250 μs). (b) Variation in fluorinated functionalities with on-time for pulsing experiments (peak power = 20 W, off-time = 250 μs).

atom as follows:[31]

$$CF_2 + e^- \rightarrow CF + F + e^- \qquad (2)$$

This reaction has an electron energy threshold of 6.1 eV. Since 6.1 eV is greater than the average electron energy within the plasma (typically about 2 eV),[27] one would also expect a drop in the number of CF_2 species lost through this particular process with a corresponding increase in the $\underline{C}F_2$ content of the plasma polymer layer.

It is of interest to note that the relative number of $\underline{C}F_3$ functionalities contained in the deposited PFCH plasma polymer films remains fairly constant with respect to CW power level. CF_3 species can be produced in the gas phase both through unimolecular rearrangements (as evidenced by mass spectrometry)[32] and through ion–molecule collisions.[33] On the surface, ion bombardment of the fluorocarbon polymer also results in the generation of CF_3 functionalities.[34] CF_3 moieties can

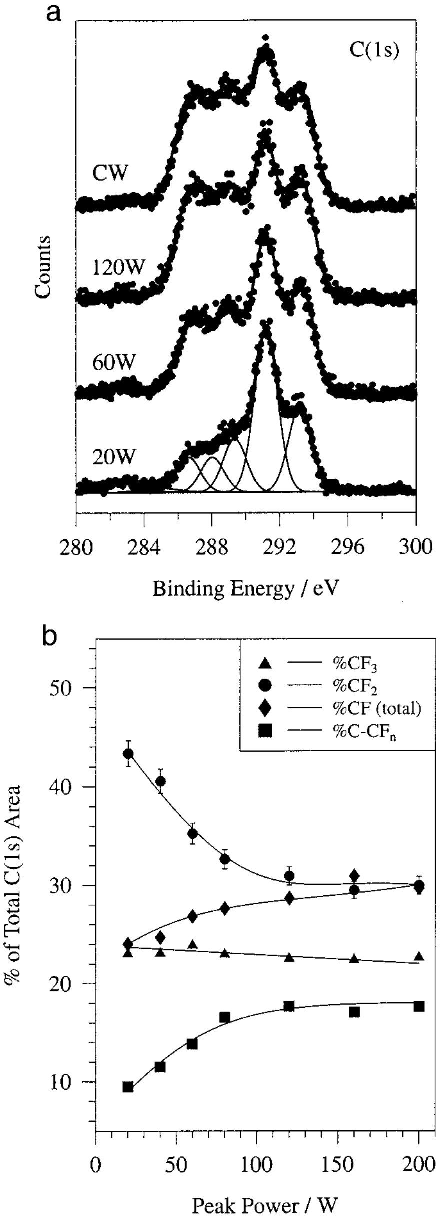

Figure 6. (a) XPS spectra from pulsed experiments with variation in peak power (on-time = 20 μs, off-time = 250 μs). (b) % area versus peak power for pulsing experiments (on-time = 20 μs, off-time = 250 μs).

be removed from the plasma through reactions of the following type:

$$CF_3 + e^- \rightarrow CF_2 + e^- + F \qquad (3)$$

Electron collision dissociation of CF_3 yields CF_2 and fluorine, which requires electrons of 2.2 eV energy. Since this is fairly close in magnitude to the average electron energy within the glow region (typically about 2 eV), the number of electrons at these energies will be relatively unperturbed by variations in the input power supplied to the electrical discharge. Even at low powers there should be an ample supply of 2.2 eV electrons for this reaction to proceed.[35]

Another consequence of the drop in high-energy electrons at lower powers is a decrease in the number and energy of electrons able to traverse the plasma sheath, thereby leading to an attenuation in the level of ion and electron bombardment of the growing film to result in less cross-linking at lower CW powers. Excited

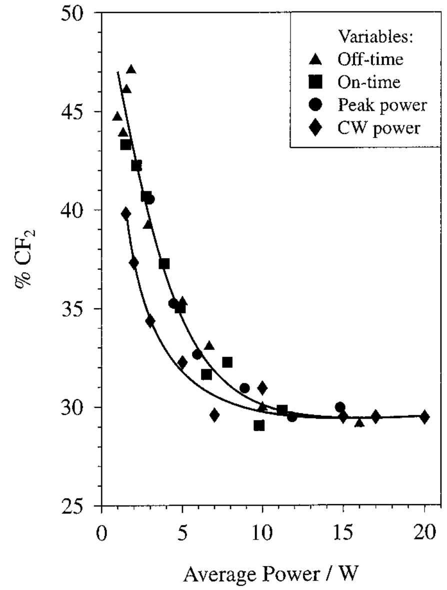

Figure 7. Variation in CF_2 functionalities with average power for pulsed and CW experiments.

species within plasmas emit photons with energies between 3 and 40 eV.[35] For instance, UV radiation of this kind has been shown to cause cross-linking of poly(ethylene) surfaces.[36] A reduction in power will attenuate the VUV flux incident upon the growing plasma polymer film, which in turn will produce less cross-linking.

In some plasma deposition processes, high substrate temperatures are required to encourage surface reactions and achieve good quality films.[37] A lower substrate temperature gives rise to greater adsorption of non-fragmented precursor molecules onto the substrate.[14,38] A drop in substrate temperature at lower powers should reduce the number of reactions occurring at the surface, especially positive enthalpy change reactions (e.g., chemical bond cleavage).

Pulsed Plasma Polymerization. For average powers below 7 W, pulsing of the PFCH glow discharge produces a plasma polymer network with a greater $\underline{C}F_2$ content and less cross-linked ($\underline{C}-CF_n$) carbon than those found for corresponding CW experiments. One possible explanation for the drop in cross-linking during pulsing could be the lower substrate temperature, since a significant advantage of pulsing the fluorocarbon glow discharge is that extensive heating of the reactor walls and substrate can be avoided.[39] The plasma sheath voltage decays rapidly, leading to a time-averaged reduction in the number and energy of positive ions bombarding the surface; hence, the substrate experiences less heating. Previous XPS studies have shown that ion bombardment of plasma-polymerized fluorocarbon films results in a rise in cross-linked carbon centers at the expense of $\underline{C}F_3$ and $\underline{C}F_2$ functionalities.[34] Therefore, a drop in ion bombardment of the growing plasma polymer layer will lead to a smaller amount of cross-linking. It has also been reported that VUV emission from pulsed discharges is less intense than that from CW discharges;[16] this should further reduce the activation of the substrate, again resulting in a decrease in cross-linking. The cumulative effect of lower substrate temperature, ion bombardment, and VUV irradiation during pulsed plasma polymerization is manifested in a narrower distribution of electronic environments [C(1s) FWHMs] with decreasing power (Figure 8).

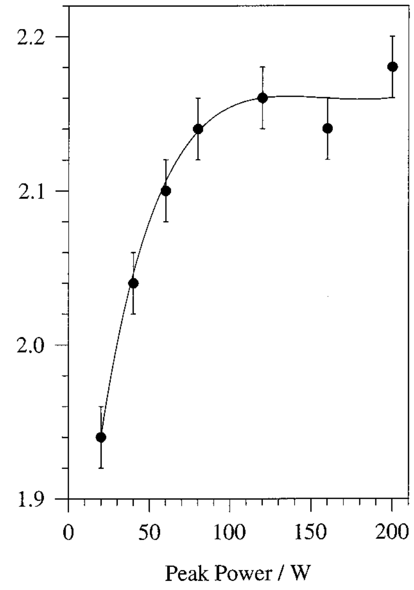

Figure 8. FWHM of C(1s) component peaks versus peak power (on-time = 20 μs, off-time = 250 μs).

Conclusions

A comparison of continuous versus pulsed plasma polymerization of perfluorocyclohexane has demonstrated that there is a greater retention of CF_2 functionalities from the precursor molecule into the growing film during pulsing in conjunction with a drop in cross-linking.

Acknowledgment. A.M.H. and M.J.S. thank the CEC and Du Pont, respectively, for financial support during the course of this work.

References and Notes

(1) Cowie, J. M. G. *Polymers: Chemistry and Physics of Modern Materials*, 2nd ed.; Blackie: Glasgow, 1991.
(2) Yasuda, H. *Plasma Polymerization*; Academic Press: Orlando, FL, 1985.
(3) Clarotti, G.; Aoumar, A. A. B.; Schué, F.; Sledz, J.; Geckeler, K. E.; Flösch, D.; Orsetti, A. *Makromol. Chem.* **1991,** *192*, 2581.
(4) Kohoma, M.; Okazaki, S.; Uchama, H. Patent No. JP 06 41755, February 1994.
(5) Iriyama, Y.; Yasuda, T.; Cho, D. L.; Yasuda, H. *J. Appl. Polym. Sci.* **1990,** *39*, 249.
(6) O'Kane, D. F.; Rice, D. W. *J. Macromol. Sci., Chem.* **1976,** *A10*, 567.
(7) Sato, K.; Omae, S.; Kojima, K.; Hashimoto, T.; Koinuma, H. *Jpn. J. Appl. Phys.* **1988,** *27*, L2088.
(8) Clarotti, G.; Schue, F.; Sledz, J.; Geckeler, K. E.; Göpel, W.; Orsetti, A. *J. Membr. Sci.* **1991,** *61*, 289.
(9) Biederman, H.; Osada, Y. *Adv. Polym. Sci.* **1990**, *95*, 57.
(10) Bell, A. T. *Top. Curr. Chem.* **1980**, *94*, 43.
(11) d'Agostino, R. D.; Favia, P.; Fracassi, F. *J. Polym. Sci., Polym. Chem. Ed.* **1990,** *28*, 3387.
(12) Clark, D. T.; Shuttleworth, D. *J. Polym. Sci., Polym. Chem. Ed.* **1980,** *18*, 27.
(13) d'Agostino, R.; Cramarossa, F.; Illuzzi, F. *J. Appl. Phys.* **1987,** *61*, 2754.
(14) Ratner, B. D.; Lopez, G. P. *J. Polym. Sci., Polym. Chem. Ed.* **1992,** *30*, 2415.
(15) Shard, A. G.; Munro, H. S.; Badyal, J. P. S. *Polym. Comm.* **1991,** *32*, 152.
(16) Yasuda, H.; Hsu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1977,** *15*, 81.
(17) Llewellyn, I.; Rimmer, N. *Thin Solid Films* **1990,** *191*, 135.
(18) Savage, C. R.; Timmons, R. B.; Lin, J. W. *Chem. Mater.* **1991**, *3*, 575.
(19) Ryan, M. E.; Hynes, A. M.; Badyal, J. P. S. *Chem. Mater.* **1996**, *8*, 37.
(20) Chambers, R. D. *Fluorine in Organic Chemistry*; Wiley & Sons: London, 1973.

(21) Christie, A. B. In *Methods of Surface Analysis: Techniques & Applications*; Wells, J. M., Ed.; Cambridge University Press: Cambridge, UK, 1989.
(22) Ehrlich, C. D.; Basford, J. A. *J. Vac. Sci. Technol.* **1992,** *A10*, 1.
(23) Nakajima, K.; Bell, A. T.; Shen, M. *J. Polym. Sci., Polym. Chem. Ed.* **1979,** *23*, 2627.
(24) Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. *Handbook of X-Ray Photoelectron Spectroscopy*; Perkin-Elmer Corporation, 1978.
(25) Wells, R. K.; Ryan, M. E.; Badyal, J. P. S. *J. Phys. Chem.* **1993,** *97*, 12879.
(26) McTaggart, F. K. *Plasma Chemistry in Electrical Discharges*; Elsevier Publishing Company: London, 1967.
(27) Grill, A. *Cold Plasmas in Materials Technology*; IEEE Press: Piscataway, NJ, 1994.
(28) Takahashi, K.; Hari, M.; Kishimoto, S.; Goto, T. *Jpn. J. Appl. Phys.* **1994,** *33*, 4181.
(29) d'Agostino, R. D.; Cramarossa, F.; Fracassi, F.; Desimoni, E.; Sabbatini, L.; Zambonin, P. G.; Caporiccio, G. *Thin Solid Films* **1986,** *143*, 163.
(30) Millard, M. M.; Kay, E. *J. Electrochem. Soc.* **1982**, 160.
(31) Bretagne, J.; Epaillard, F.; Ricard, A. *J. Polym. Sci., Polym. Chem. Ed.* **1992,** *30*, 323.
(32) Budzikiewiz, H.; Djerassi, C.; Williams, D. H. *Mass Spectrometry of Organic Compounds*, Holden-Day Inc.: San Francisco, 1967.
(33) Lias, S. G. In *Fluorine-Containing Free Radicals*, Root, J. W., Ed.; ACS Symposium Series; American Chemical Society: Washington, D.C., 1978.
(34) O'Keefe, M. J.; Rigsbee, J. M. *J. Appl. Polym. Sci.* **1994,** *53*, 1631.
(35) Clark, D. T.; Dilks, A.; Shuttleworth, D. in *Polymer Surfaces*; Clark, D. T., Feast, W. J., Eds.; Wiley & Sons: Bath, 1978.
(36) Hudis, M.; Prescot, L. E. *Polym. Lett.* **1972**, *10*, 179.
(37) Sherman, A. *Chemical Vapor Deposition for Microelectronics*; Noyes Publications: Park Ridge, NJ, 1990.
(38) Ratner, B. D.; Lopez, G. P. *Langmuir* **1991,** *7*, 766.
(39) Scarsbrook, G.; Llewellyn, I. P.; Ojha, S. M.; Heinecke, R. A. *Vacuum* **1988**, 627.

MA951747Q