Influence of Substrate Material and Ion Bombardment on Plasma-Deposited Fluorocarbon Thin Films

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SYNOPSIS

The influence of substrate material and ion bombardment on fluorocarbon thin films deposited using a C_2F_6 glow discharge in an rf, parallel plate reactor was investigated. Monitoring of the plasma process by optical emission spectroscopy indicated that the dominant species in the glow discharge was CF_2. Studies of bulk polytetrafluoroethylene (PTFE) and plasma-polymerized fluorocarbon thin-film samples in an XPS system demonstrated that the formation of non-CF_2 species can be induced by ion bombardment of CF_2 molecules. Characterization of the deposited fluorocarbon films by XPS found that the F/C ratio and CF_x distribution ($0 < x < 3$) in the films were dependent on processing conditions. Fluorocarbon films deposited simultaneously onto Al, glass, steel, and PTFE substrates using a C_2F_6 plasma and a graphite sputter target had measurably different F/C ratios, with the F/C ratio of the films deposited onto the Al substrates consistently lower than the F/C ratios of the films deposited onto the other substrates. When a C_2F_6 plasma was used without a graphite target, the F/C ratio in the film was constant, but the CF_x distribution was different for each of the substrate materials. Analysis of the plasma-polymerized films by TEM revealed that localized growth of fluorocarbon particles occurred during the initial stages of deposition, consistent with an activated growth mechanism. Differences in the F/C ratio for films deposited onto the various substrate materials were attributed to the interaction of the fluorocarbon plasma with the exposed surface of the substrate prior to complete coverage by the polymeric film. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Fluorocarbon plasmas can be characterized by the competing reactions of fluorine etching and polymer deposition. Many of the mechanisms that occur during the etching process also occur during plasma polymerization.[1] Whether etching or polymerization is the dominant mechanism is determined by a number of processing parameters including substrate bias, reactor geometry, F/C ratio in the feed gas, and the addition of secondary gases. Deposition of polymeric films is favored the lower the F/C ratio in the monomer gas is, due to an increase in the relative density of CF_x species to F atoms in the glow discharge. Numerous studies on the effect of gas composition and processing conditions on the deposition of plasma-polymerized films have been reported.[2-6] Growth of the plasma-polymerized films has been described by an activated growth model (AGM) in which film deposition occurs only at specific polymer sites that have been "activated" by energy transfer from the plasma to the surface site, typically by ion bombardment.[7,8] The influence of ion bombardment on the growth mechanism of plasma-polymerized films has been apparent in several studies.[9-11]

Inherent in the early stages of every plasma-assisted deposition process is the interaction of the glow-discharge media with the substrate material. Although a significant amount of characterization of fluorocarbon plasmas has been conducted, relatively few studies have been done on the effect of

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substrate material on the deposition of plasma-polymerized thin films.[12–14] Results from these studies indicate that substrate material can significantly alter the final film composition and chemistry. In addition, the processing conditions favorable to polymer film deposition have been found to be a function of the substrate material. Measurable differences in film composition with substrate material is consistent with the AGM in that plasma–surface interactions during the initial stages of deposition dominate and establish the growth mechanism and characteristics of the film. In this study, variation of processing parameters and substrate material were used to investigate the role of plasma/surface interactions and ion bombardment on the deposition of fluorocarbon plasma polymer films.

EXPERIMENTAL

Deposition of fluorocarbon thin films was done in a rf, parallel plate sputter deposition system using both a consumable graphite target and a nonconsumable stainless-steel disk as the cathode material and hexafluoroethane (C_2F_6) as the monomer feed gas. Substrate materials were 1 mm-thick samples of Corning 7059 borosilicate glass, mechanically polished low carbon steel, cold-rolled aluminum foil, and polytetrafluoroethylene (PTFE). Processing parameters were held constant at a 5 sccm flow rate and 100 W of power during synthesis and the films were deposited for 1 h onto the four substrate materials simultaneously; details of the experimental setup have been previously reported.[13]

Characterization of the glow discharge was done using a PARC OMA III optical emission spectrometer, whereas film composition was measured on a Perkin-Elmer 5400 X-ray photoelectron spectroscopy (XPS) unit using MgKα radiation (1253.6 eV). Curve fitting of the C 1s spectra was done using a Gaussian–Lorentzian peak shape; goodness of fit was $\sim$ 1 for each spectrum. Transmission electron microscopy (TEM) samples were prepared by directly depositing fluorocarbon polymer onto holey carbon TEM support films. Analysis of the TEM specimen was done using a Philips 400T transmission electron microscope operated at 120 kV.

RESULTS AND DISCUSSION

As-deposited Films

Depositions that were conducted with the nonconsumable stainless-steel cathode more closely resembled a fluorinated residue on the surface of the substrate material than they did a deposited film, similar to the results of Iriyama and Yasuda.[3] The fluorinated films were easily removed by Scotch-tape peel testing and by rubbing the surface with a cotton swab. In contrast, depositions done using a graphite sputter target as the cathode material were qualitatively adherent using the same tests, had a measurable thickness of $\sim$ 100 nm, and could be reproducibly fabricated. The optical emission spectrum (OES) for each experimental condition was dominated by the ($\tilde{A}\,^1B_1 \rightarrow \tilde{X}\,^1A_1$) band of CF_2 vibronic transitions[15,16] (Fig. 1). However, an increase in intensity of specific transitions occurred when the graphite target was used and these peaks most closely matched the collision-free $A(0,0,0)$ transitions [Fig. 1(d)].[15]

Analysis of the C 1s and F 1s photoelectron spectra from the deposited films revealed significant differences in both the F/C ratio and the CF_x and F binding energy distribution for films deposited with and without a graphite target. In addition, substrate material affected the fluorocarbon chemistry of the films, especially the films deposited with the graphite target as the cathode material. Survey sweeps of the samples in the XPS after processing did not detect the underlying substrate materials for any of the samples, indicative of complete coverage of the substrate surface by the fluorocarbon films.

Presented in Figure 2 are the C 1s and F 1s spectra from fluorocarbon films on PTFE [Fig. 2(a) and (b)] and aluminum [Fig. 2(c) and (d)] substrates after plasma processing without a graphite target. The dominant CF_2 peak at 292 eV for the films on both substrates was consistent with the OES results that showed that glow discharge was predominantly difluorocarbene. The existence of non-CF_2 species in the films was also apparent; however, the carbon peak at 285 eV was very small for the film on PTFE but was equal in intensity to the CF_2 peak on the Al substrate. Adsorbed carbon (285 eV) on the surface of samples exposed to air during transfer from the deposition system to the XPS unit was not a factor in these results because the samples were exposed to air for the same amount of time (a few minutes) before characterization. The differences in the binding energy distribution was also evident in the F 1s spectra from the same samples. Whereas the fluorocarbon film on the PTFE substrate contained fluorine that was bound to carbon (690 eV), the fluorine atoms in the film on the Al substrate were both bound to carbon and unbound (686 eV). The peak at 686 eV could be interpreted as an Al—F complex, but no Al peak was detected during analysis

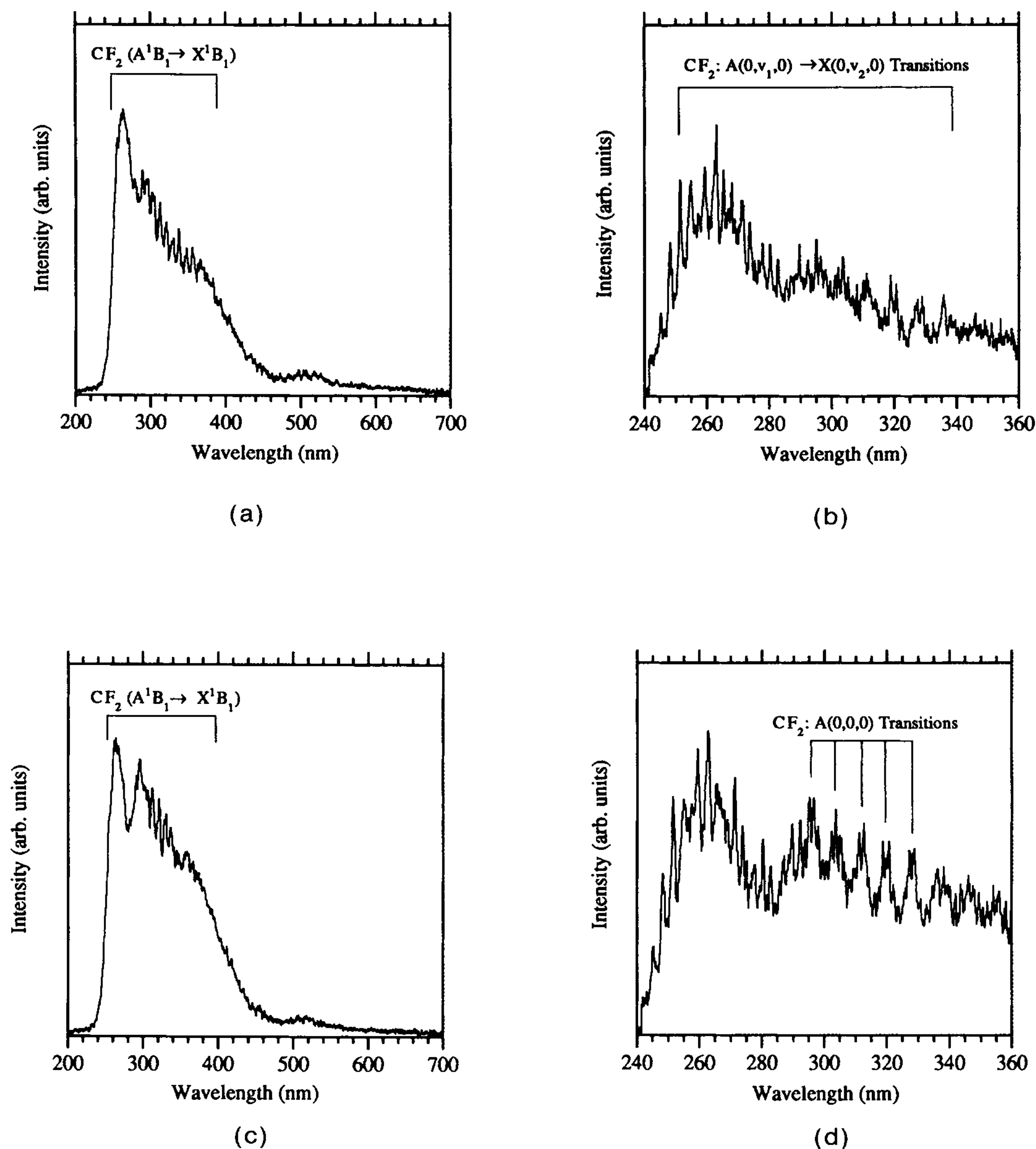

Figure 1 Optical emission spectra from C_2F_6 glow discharges (a, b) without and (c, d) with a graphite sputter target.

and, therefore, the peak at 686 eV was assigned to unbound or ionic fluorine. The results from the fluorocarbon films on steel and glass substrates were similar to the Al and PTFE data in that the dominant peaks of the XPS spectra were at 292 eV (CF_2) for C 1s photoelectrons and 690 eV (C—F) for F 1s photoelectrons, but the maximum intensity values at 285 eV (C) and 686 eV (F) were approximately half the intensity of the CF_2 and C—F peaks, respectively.

Determination of the F/C ratio for the films in Figure 2 was done by integrating the area under the curves and multiplying by the appropriate sensitivity factor for each element. All the films prepared without a graphite sputter target had a $F/C \approx 2$, in agreement with the OES data. As can be seen in Figure 2, the binding energy of the atoms in the films was measurably different on the substrates even though the stoichiometric ratio of the atoms was the same. These results were reproducible and suggested that substrate material affected the deposition and growth mechanism.

In contrast to the constant F/C ratio in the films deposited without a graphite target, the F/C ratio

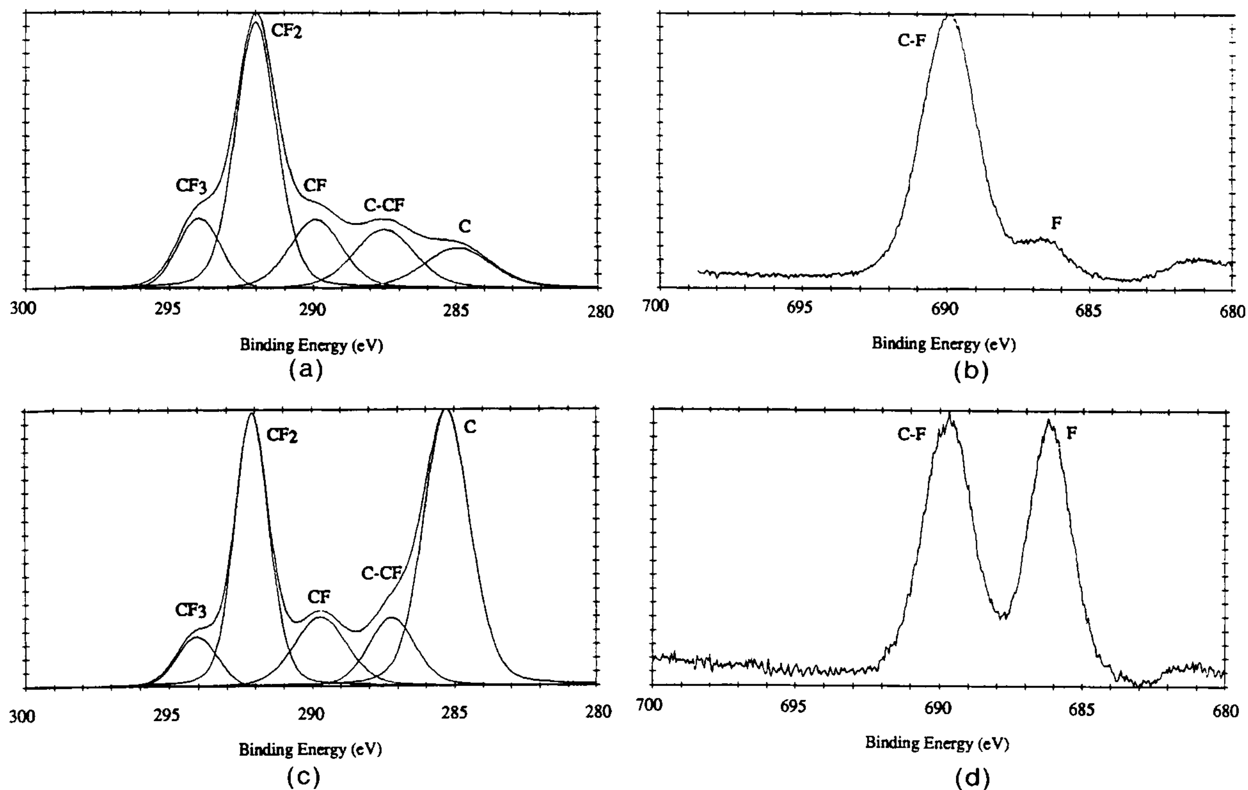

Figure 2 XPS spectra from fluorocarbon films deposited without a sputter target: (a) C 1s and (b) F 1s on a PTFE substrate; (c) C 1s and (d) F 1s on aluminum.

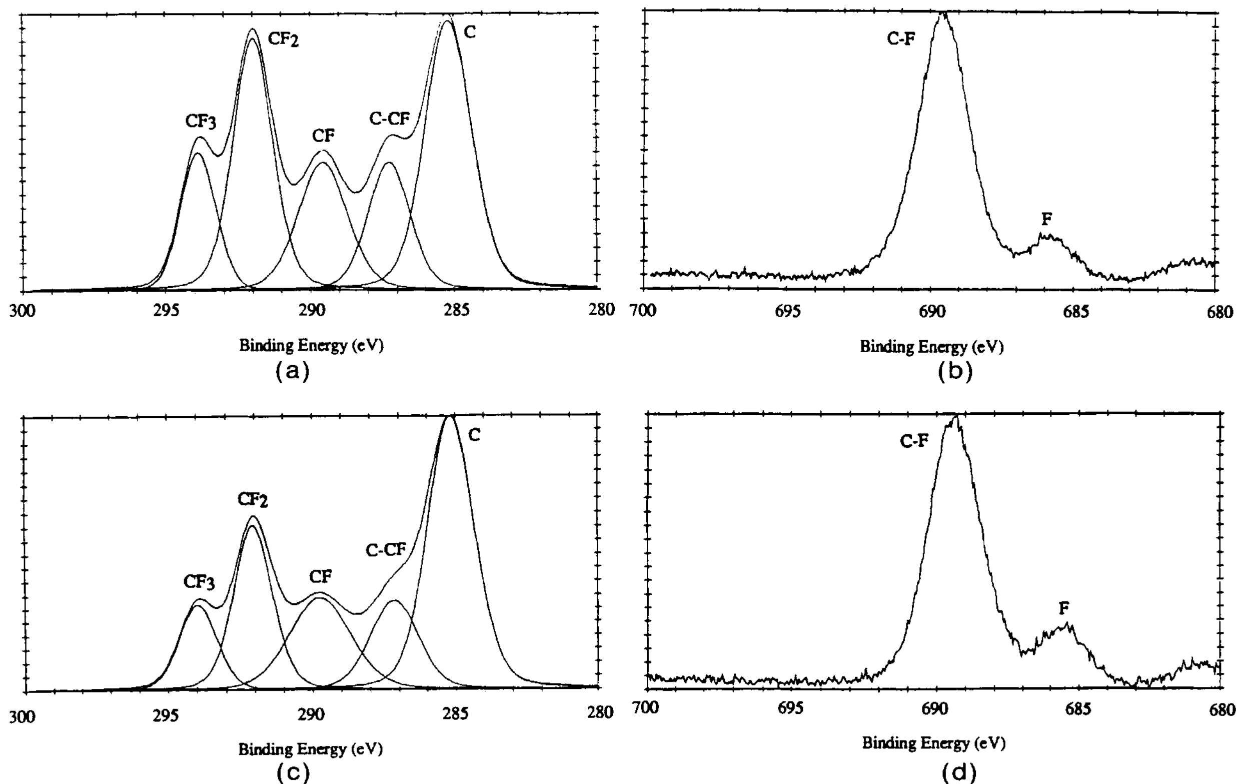

Figure 3 XPS spectra from fluorocarbon films deposited with a graphite sputter target: (a) C 1s and (b) F 1s on a PTFE substrate; (c) C 1s and (d) F 1s on aluminum.

in the films fabricated with a graphite target was influenced by the substrate material even though the films were ~ 100 nm thick and the underlying substrate material was not detected during XPS analysis. Fluorocarbon films deposited onto glass, PTFE, and steel substrates had a F/C ratio that was consistently between 1.4 and 1.7, whereas the F/C ratio of the films deposited at the same time onto Al foil substrates was between 1.1 and 1.2. A lower F/C ratio and pronounced C 1s peak at 285 eV for the films deposited using a graphite sputter target was expected due to physical sputtering of the carbon target. Carbon and fluorine 1s spectra from films deposited using a C_2F_6 plasma and a graphite target on PTFE and Al substrates are presented in Figure 3. The lower F/C ratio in the as-deposited films on Al substrates can be explained by the dominant C 1s peak at 285 eV [Fig. 3(c)]. Intensity of the 285 eV carbon peak on the other three substrates, including PTFE [Fig. 3(a)], was approximately equal in value to the CF_2 peak at 292 eV. The CF_3, CF, and C—CF peaks in Figure 3 are more readily resolved and have an increase in signal intensity compared to same peaks in Figure 2. An increase in the amount of carbon–fluorine bonding in the graphite/C_2F_6 deposited films can also been seen in the F 1s spectra in Figure 3(b) and (d). Fluorine atoms in the as-deposited films were in a C—F binding energy state (690 eV) with very little unbound fluorine (686 eV). The addition of carbon to the plasma significantly increased the amount of non-CF_2 species and reduced the concentration of the fluoride ion in the deposited films.

The reproducibility of the results presented in Figure 3 indicated that the chemistry and composition of plasma-polymerized fluorocarbon films were a function of substrate material. However, the underlying substrate material was never detected during XPS analysis, which measures the top ~ 5 nm of the sample. Therefore, the influence of substrate material on film composition and chemistry was evident at distances an order of magnitude away from the film/substrate interface. In an attempt to try to explain this phenomenon, plasma deposition of fluorocarbon films using a C_2F_6/graphite configuration was done onto electron transparent, TEM holey carbon support films in order to look at the initial stages of film formation and growth. Figure 4 is a bright-field TEM micrograph of fluorocarbon particles after 10 min of deposition. It is evident from the micrograph that discrete fluorocarbon particles are present during the initial stages of film growth, indicative of preferred nucleation and growth sites and consistent with an activated growth model. Also apparent from the micrograph in Figure 4 was the exposed surface of the underlying substrate

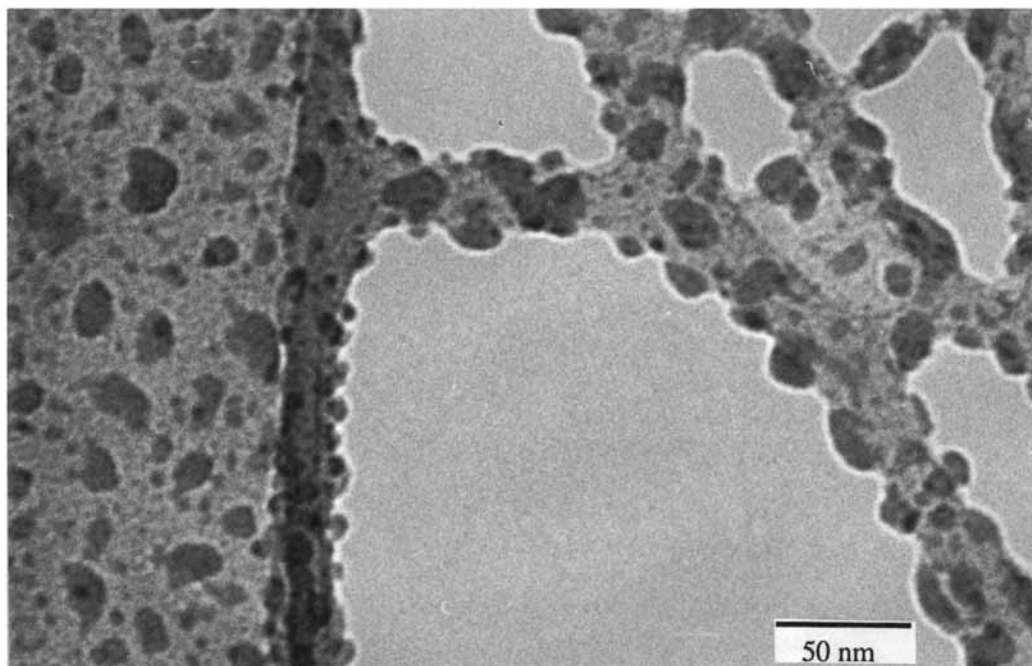

Figure 4 Bright-field TEM micrograph of fluorocarbon particles on a holey carbon support film during the initial stages of deposition.

material. The three-dimensional, island growth pattern of the fluorocarbon film leaves significant areas of the substrate material in contact with the plasma for a relatively long period of time. These plasma/surface interactions continue until the fluorocarbon particles completely cover the substrate surface. This study did not determine the critical thickness for complete coverage of the substrate surface, but it was believed to be on the order of several hundred angstroms.

Exposure of the surface of the substrate material to the fluorocarbon plasma for an extended period of time provides some explanation to the influence of substrate material on the composition and chemistry of plasma-polymerized fluorocarbon thin films. As long as the substrate is exposed to the plasma, plasma/substrate interactions will occur. Materials that readily react with the glow-discharge species will be either etched or form fluoride or carbide compounds, whereas substrates that are relatively unreactive with the plasma will have fluorocarbon products that are determined by the plasma composition and processing parameters. In the present study, the lower F/C ratio for plasma-polymerized films on aluminum substrates can be attributed to the loss of fluorine by formation of aluminum fluoride compounds, which, although not as volatile as aluminum chloride compounds formed during standard aluminum plasma etching processes, have been reported for aluminum electrodes exposed to C_2F_6 glow discharges.[3] The depletion of fluorine from the depositing film results in the lower F/C ratio and increase in the C 1s peak at 285 eV [Fig. 3(c)].

Ion Bombardment

Optical emission spectra from the fluorocarbon plasmas in this study indicated that the glow-discharge composition was predominantly CF_2. Fluorocarbon species in the film, however, had measurable quantities of non-CF_2 species, including CF_3, CF, and C—CF. It has already been demonstrated that the growth of the films was consistent with an activated growth model. Assuming that the concentration of non-CF_2 species in the gas phase was small compared to the concentration of CF_2, then the formation of CF_3, CF, and C—CF occurred at the active polymer growth sites on the substrate and not in the gas phase. Typically, activation of the polymer surface is by energy transfer from the plasma by electron or ion collision processes.

To determine the effect of ion bombardment on fluorocarbon materials, Ar ion sputtering of PTFE substrates and plasma-polymerized fluorocarbon films deposited using the C_2F_6/graphite arrangement was conducted in the XPS system. Polytetrafluoroethylene is a crystalline fluoropolymer with a simple repeat unit of difluorocarbene (—CF_2—). The C 1s and F 1s spectra from a sample prior to Ar sputtering is presented in Figure 5(a) and (b), respectively. Figure 5(a) and (b) presents data taken from a sample that was not chemically cleaned before analysis; as a result, it contains a C peak at 285 eV associated with adsorbed carbon on the surface of sample. (The 285 eV peak was not present on PTFE samples that were cleaned before XPS characterization.) In the as-received state, the PTFE sample had carbon and fluorine binding energies associated with CF_2 (292 eV) and C—F (690 eV) bonding. After argon sputtering, the binding energy of the carbon atoms in the specimen were distributed over a range of energies (284–295 eV), whereas the binding energy of the fluorine atoms remained at 690 eV [Fig. 5(c) and (d)], in agreement with other studies on the effect of charged particles on fluorocarbon polymers.[17,18] The 285 eV carbon signal was significantly reduced, verifying that the C peak in Figure 5(a) was adsorbed carbon on the surface. In addition, the F/C ratio in the PTFE sample went from 2.25 (ideal F/C ratio = 2) before sputtering to 1.53 after sputtering, but all the fluorine in the sample was still bonded to carbon. Therefore, fluorine atoms were removed from the surface of the sample during Ar sputtering. The bond rearrangement and defluorination of the PTFE sample clearly demonstrated that the formation of non-CF_2 molecules from CF_2 repeat units was possible by ion bombardment.

Repeating the Ar sputtering experiment for plasma-polymerized films resulted in similar data. As depicted in Figure 6(a) and (b), the C 1s and F 1s photoelectron spectra from an as-deposited plasma-polymerized film on a steel substrate closely matched the fluorocarbon films in Figure 3. After ion bombardment, the C 1s spectrum no longer had clearly definable CF_x peaks and the binding energy of the peaks assigned in Figure 6(c) are shifted to lower values. The F 1s spectra from the film after sputtering [Fig. 6(d)] indicated that an increase in the amount of unbound fluorine (686 eV) occurred during the ion bombardment. The change in the F/C ratio for the film before, 1.50, and after, 1.32, sputtering was significantly less than was the change for the bulk PTFE sample.

A smaller change in the F/C ratio for plasma-polymerized films after ion bombardment compared to the change for bulk PTFE can be attributed to the differences in the structure of the fluoropoly-

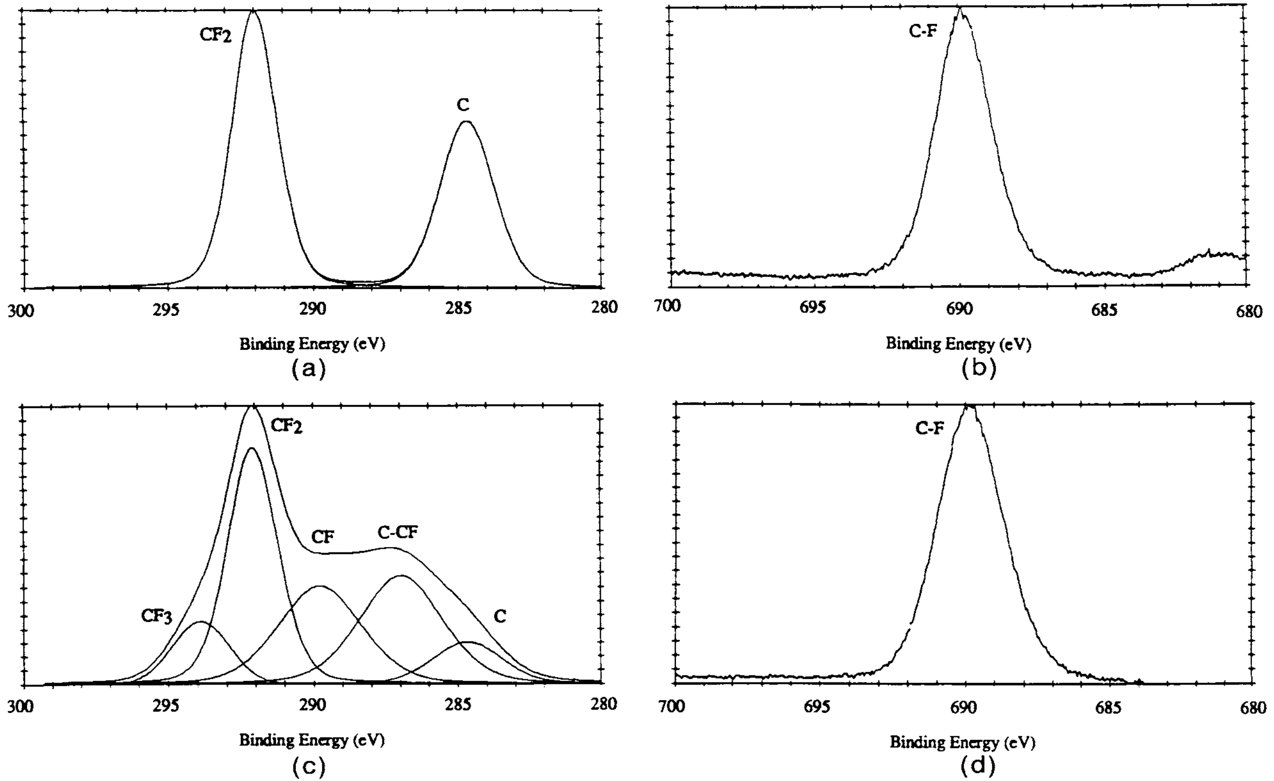

Figure 5 (a) C 1s and (b) F 1s XPS spectra from a bulk PTFE substrate before ion bombardment; (c) C 1s and (d) F 1s XPS spectra from the same sample after Ar sputtering.

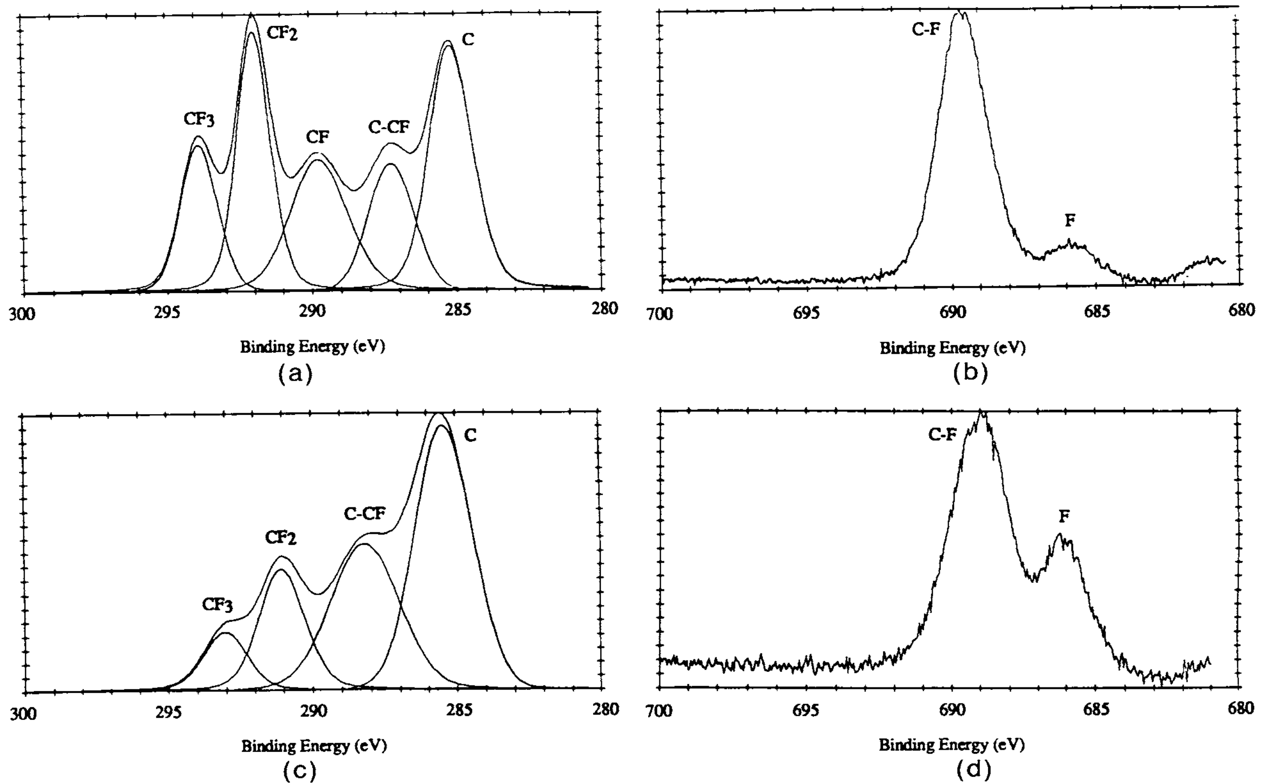

Figure 6 (a) C 1s and (b) F 1s XPS spectra from an as-deposited fluorocarbon thin film on a steel substrate before ion bombardment; (c) C 1s and (d) F 1s XPS spectra from the same sample after Ar sputtering.

mers. Whereas PTFE is a crystalline polymer with a simple repeat unit, carbon backbone, and no cross-linking, plasma-polymerized fluorocarbons are amorphous, highly cross-linked structures without a characteristic repeat unit. Ion bombardment of the PTFE causes cross-linking and defluorination to occur, whereas bombardment of the plasma-polymerized material breaks C—F bonds but results in a higher concentration of unbound C and F and not defluorination.

CONCLUSIONS

The influence of substrate material and ion bombardment on plasma-polymerized fluorocarbon films was investigated. Substrate materials that react with the fluorocarbon plasma, such as aluminum, have a different film composition and chemistry than that of unreactive substrates. Fluorocarbon films deposited onto aluminum substrates had significantly higher percentages of unbound C and F than did films deposited onto glass, PTFE, and steel substrates. Localized, three-dimensional nucleation and growth of fluorocarbon particles that occurs during deposition allows for substrate surface/plasma interactions to take place until the polymeric film completely covers the substrate surface. The plasma/surface interactions alter the film composition by affecting the relative fluorocarbon etching and polymerization rates and are consistent with an activated growth mechanism. Ion bombardment of the growing polymer particles during deposition can be used to explain the formation of CF_x species from CF_2 molecules as well as shifts toward lower F/C ratio values.

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