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Oxidation of Fluorinated Amorphous Carbon (a-CF_x) Films

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Amorphous fluorinated carbon (a-CF_x) films have a variety of potential technological applications. In most such applications these films are exposed to air and undergo partial surface oxidation. X-ray photoemission spectroscopy has been used to study the oxidation of fresh a-CF_x films deposited by magnetron sputtering. The oxygen sticking coefficient measured by exposure to low pressures ($< 10^{-3}$ Torr) of oxygen at room temperature is on the order of $S \approx 10^{-6}$, indicating that the surfaces of these films are relatively inert to oxidation when compared with most metals. The X-ray photoemission spectra indicate that the initial stages of oxygen exposure ($< 10^7$ langmuirs) result in the preferential oxidation of the carbon atoms with zero or one fluorine atom, perhaps because these carbon atoms are more likely to be found in configurations with unsaturated double bonds and radicals than carbon atoms with two or three fluorine atoms. Exposure of the a-CF_x film to atmospheric pressures of air (effective exposure of 10^{12} langmuirs to O_2) results in lower levels of oxygen uptake than the low pressure exposures ($< 10^7$ langmuirs). It is suggested that this is the result of oxidative etching of the most reactive carbon atoms, leaving a relatively inert surface. Finally, low pressure exposures to air result in the adsorption of both nitrogen and oxygen onto the surface. Some of the nitrogen adsorbed on the surface at low pressures is in a reversibly adsorbed state in the sense that subsequent exposure to low pressures of O_2 results in the displacement of nitrogen by oxygen. Similarly, when an a-CF_x film oxidized in pure O_2 is exposed to low pressures of air, some of the adsorbed oxygen is displaced by nitrogen. It is suggested that these forms of nitrogen and oxygen are bound to free radical sites in the film.

1. Introduction

Amorphous fluorinated carbon (a-CF_x) films have potential application in many technologies. These include applications as overcoats on magnetic hard disks,[1-3] low friction and low stiction coatings,[4] control of surface wetting,[5,6] corrosion-resistant coatings,[7] and coatings for biomedical applications.[8,9] There are many issues that impact the performance of a-CF_x films in any application in which they are exposed to air or other environments. The oxidation of the a-CF_x film during exposure to air is one of the issues which requires study before these films are used in any applications in which their surface properties are of importance. Previous studies have shown that a-CF_x films are oxidized immediately after removal from vacuum.[10-12] However, the kinetics of oxidation and the compositional changes of the a-CF_x surface during oxidation have not been studied carefully. Understanding of the a-CF_x oxidation is important because oxidation impacts their thermal stability.

This paper focuses on the composition changes of a-CF_x films during oxidation and on the kinetics of the oxidation process. a-CF_x films contain carbon atoms with varying degrees of fluorination, each of which are easily distinguished using X-ray photoemission spectroscopy (XPS). The oxidation of the different components in the a-CF_x film was monitored during exposure to low pressures of oxygen or clean dry air under controlled conditions without prior exposure to ambient air. Fresh a-CF_x films were also exposed to air at atmospheric pressure to mimic the air exposure of overcoats that occurs during disk manufacturing and the air exposure that occurs in most applications of fluorinated carbon films. The results give direct insight into the oxidation processes that occur on the surface and the types of partially oxidized species that are formed during exposure to air or oxygen.

2. Experimental Section

All experiments were performed in an ultrahigh-vacuum (UHV) chamber with a base pressure of $< 10^{-9}$ Torr. This apparatus has been designed to allow deposition of thin films by magnetron sputtering followed by surface analysis without exposure to air. The a-CF_x films were prepared on Ni foils by dc magnetron sputtering (MAK130 VCFUHV dc magnetron sputter source, US Inc., 1.3 in. graphite target) using Ar and CF_4 gases. The surface of the Ni foil was cleaned by several cycles of Ar^+ sputtering followed by annealing to 950 K before deposition of the a-CF_x film.

Deposition of the a-CF_x film directly onto the Ni substrate leads to fluorination of the Ni substrate. Fluorination of the Ni was confirmed by the F 1s XP spectrum which revealed a peak due to Ni−F at a binding energy of 685.4 eV that is resolved from those due to fluorine bonded to carbon. To avoid the direct contact of the Ni substrate and the a-CF_x film, a carbon

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underlayer was deposited onto the Ni substrate before the deposition of a-CF_x film. The carbon underlayer was deposited with a dc power of 75 W at a substrate temperature of 800 K in pure Ar gas. This carbon underlayer was then heated to 900 K at a rate of 2 K/s. This carbon underlayer is probably graphite-like because it was deposited at high substrate temperature (800 K) and then annealed to 900 K. The thickness of this carbon underlayer was estimated to be about 50 Å based on the attenuation of the Ni substrate signal.

The conditions for deposition of the a-CF_x film were chosen to be similar to those used to deposit the a-CH_x films used as overcoats on magnetic data storage media. The a-CH_x films generated under these conditions exhibited Raman spectra similar to those of a-CH_x films used in commercial hard disk drives.[13−15] The dc power of the magnetron sputter source was set to be 75 W. a-CF_x films were then deposited under various conditions: substrate temperatures in the range 443−843 K, total CF_4 and Ar gas pressure of 5−12 mTorr, and 10−30% CF_4/(Ar + CF_4). The optimal a-CF_x film deposition condition was determined to be the one which generated an a-CF_x film having the highest F:C ratio. The a-CF_x films used for the studies reported in this paper were deposited using a dc power of 75 W at a substrate temperature of 443 K. The total pressure was maintained at 8 mTorr during the deposition process using a 20% CF_4/(Ar + CF_4) gas mixture. The a-CF_x film thickness was determined to be about 70 Å based on the attenuation of the Ni substrate signal.

X-ray photoemission spectroscopy (XPS) was used to study the thickness, composition, and chemical states of the a-CF_x films. The a-CF_x film was characterized by *in situ* XPS immediately after deposition and without exposure to ambient air. The XP spectra were obtained using a Specs 290 W Mg Kα ($h\nu$ = 1253.6 eV) X-ray source and a VG Scientific CLAM II hemispherical analyzer. A pass energy of 50 eV was used for all the measurements.

The oxidation of a-CF_x films in low pressure ($< 10^{-3}$ Torr) O_2 and in clean air (H_2O < 2 ppm, total hydrocarbon < 0.1 ppm, CO and CO_2 < 1 ppm) was performed by introducing gas into the chamber immediately after film deposition. For low pressure oxidation, the a-CF_x film was positioned ~4 cm from the end of a stainless steel dosing tube that was attached to a leak valve. The leak valve was used to introduce gas into the chamber at a predetermined pressure ($< 10^{-3}$ Torr) with the a-CF_x held at 300 K. Unless specifically mentioned, the ionization pressure gauge was turned off after the gas pressure stabilized to eliminate the influence of electrons and excited species created by the ionization pressure gauge. Following oxidation, the chamber was evacuated to 10^{-9} Torr in ~30 min for XPS analysis.

The oxidation of a-CF_x film in high pressure (1 atm) air was conducted by venting the UHV chamber with air immediately after film deposition. The a-CF_x film was kept in air at room temperature for 1 h. The chamber was then evacuated to $< 10^{-9}$ Torr in ~12 h for XPS measurements. Both ambient air and clean air (H_2O < 2 ppm, total hydrocarbon < 0.1 ppm, CO and CO_2 < 1 ppm) were used to perform the high pressure air oxidation. No significant difference was observed between the a-CF_x exposed to 1 atm of ambient air and the a-CF_x exposed to 1 atm of clean air.

3. Results

3.1. Composition of Freshly Deposited *a*-CF_x Films. The quality of a-CH_x films is often characterized by the ratio of carbon atoms in sp^2 and sp^3 hybridizations as determined from UV Raman spectroscopy.[16,17] As in the case of a-CH_x films, the chemical compositions of freshly deposited a-CF_x films are complex in the sense that the carbon atoms exist in an array of chemically distinct states. The chemical composition of fresh a-CF_x films was investigated with XPS which provides much greater insight into the composition of these films than it does into the composition of a-CH_x films. The dotted lines in Figure 1 are the XP spectra of the C 1s, O 1s, and F 1s levels of the fresh a-CF_x film. The features appearing at 285.2, 287.2, 290.0, and 292.2 eV are assigned to emission of C 1s photoelectrons from carbon atoms bonded to different numbers of fluorine atoms: 0 (C), 1 (CF), 2 (CF_2), and 3 (CF_3), respectively. This assignment is based on comparison with the XP spectra of multilayer films of CF_3CH_2OH, $CF_3CF_2CH_2I$, $CH_3C{=}OCH_3$, and CH_3CH_2COOH adsorbed on the surface of the a-CF_x film. Such spectra have also been obtained during other studies of a-CF_x films and given the same assignment.[9,18] Fitting of the features in the C 1s spectrum suggests that the ratios of the concentrations of C:CF:CF_2:CF_3 are 51:29:16:4. This corresponds to a total F:C ratio of 0.7. The F 1s spectrum shows a single peak and the spectrum taken in the region 528−540 eV reveals that the freshly deposited a-CF_x film is free of oxygen.

The a-CF_x films deposited under various conditions reveal that the F:C ratio is more sensitive to the substrate temperature and to the CF_4/(Ar + CF_4) ratio than it is to the total pressure of CF_4 and Ar. When the CF_4/(Ar + CF_4) ratio is in the range 10−20% and the dc power, substrate temperature, and total pressure are 75 W, 443 K, and 8 mTorr, respectively, the F:C ratio of the resulting a-CF_x film ranges from 0.7 to 0.8. However, when the CF_4/(Ar + CF_4) reaches 30%, no a-CF_x film is obtained at all. This suggests that high fluorine content in the gas phase results in etching of the film at a rate equal to its deposition rate and, thus, no net accumulation of a-CF_x on the substrate. Films deposited at substrate temperatures in the range 443−843 K clearly show a monotonic decrease in the F:C ratio with increasing substrate temperature. When the substrate temperature is 843 K and the dc power, total pressure, and CF_4/(Ar + CF_4) are 75 W, 8 mTorr, and 20%, respectively, the F:C ratio is only 0.2. For the a-CF_x films deposited at total pressures varying from 5 to 12 mTorr with the dc power, substrate temperature, and CF_4/(Ar + CF_4) at 75 W, 443 K, and 20%, respectively, the variation in the F:C ratio is less than 10%.

3.2. Low Pressure ($< 10^{-3}$ Torr) Oxidation of *a*-CF_x Films in O_2. Oxidation of the surfaces of a-CF_x films occurs rapidly on exposure to air and influences the surface properties of the film. In order to study the oxidation kinetics and the evolution of the film structure during oxidation, we have exposed the surface of fresh a-CF_x films to low pressures ($< 10^{-3}$ Torr) of pure O_2 while using XPS to monitor the uptake of oxygen and the evolution of the different chemical states of the carbon atoms in the film. The XP spectra were obtained starting with fresh a-CF_x films without prior exposure to ambient air. One of the attractive features of studying the a-CF_x films is that the ability of XPS to resolve structure in the C 1s feature provides insight into the details of the oxidation process that cannot be obtained easily from XPS studies of the oxidation of a-CH_x films.[13,15,19]

The evolution of the chemical composition of the a-CF_x film is revealed by the C 1s XP spectra obtained during the course of the oxidation. Room temperature exposure of an a-CF_x film to O_2 at a pressure of 4×10^{-4} Torr results in the adsorption of oxygen onto the surface (Figure 1). The overall intensity of the C 1s feature is attenuated by ~10% during oxidation; however, the

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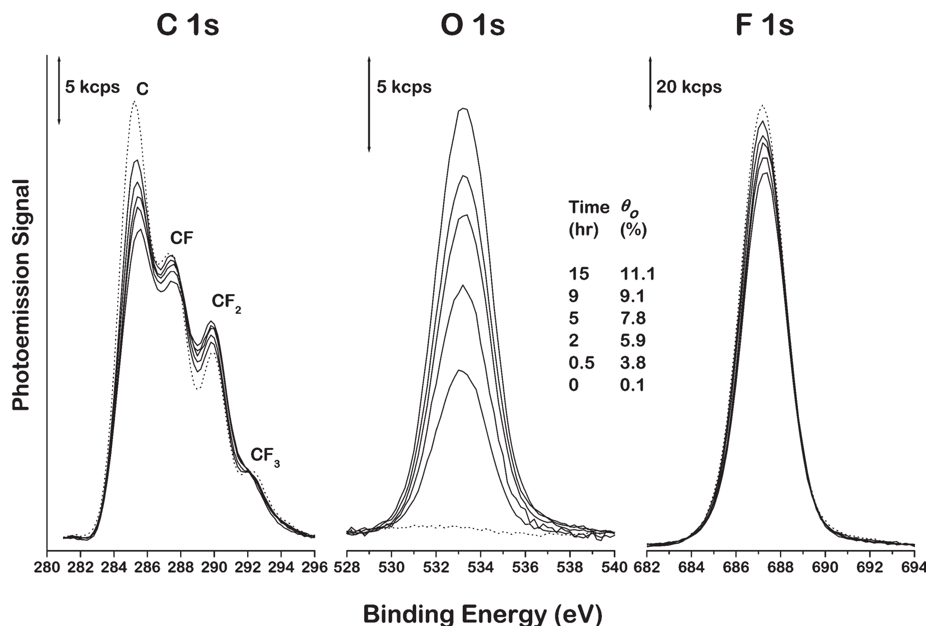

Figure 1. Time evolution of the C 1s, F 1s, and O 1s XP spectra of an a-CF_x film exposed to pure O_2. The freshly deposited a-CF_x film was exposed to pure O_2 at a pressure of 4×10^{-4} Torr and a temperature of 300 K. The C 1s spectra of the fresh a-CF_x film (dotted line) are resolved into components arising from C, CF, CF_2, and CF_3 groups. The C 1s XP spectra obtained during exposure to pure O_2 (solid lines) show a decrease of peaks assigned to C and CF and an increase of the peak assigned to CF_2, indicating the oxidation of C and CF into CFO and COO. The F 1s signal is attenuated as a result of shielding by oxygen on the a-CF_x film surface. The O 1s XP spectra were used to calculate the oxygen content (θ_O) on the film surface.

more interesting observation is that the relative intensities of the features associated with C, CF, CF_2, and CF_3 species also change. This indicates that there is a net change in the oxidation states of the carbon atoms at the surface of the a-CF_x film. The C 1s XPS features assigned to C and CF species attenuate, indicating that C and CF are the major components of the film that are being oxidized. In contrast, the feature associated with CF_2 species increases in intensity, indicating that the carbon atoms at the surface are becoming more highly oxidized. The feature associated with the CF_3 groups is not sufficiently well resolved to allow any definitive statement regarding its evolution during oxidation. The net observation is that the changes in the C 1s feature of the a-CF_x film are consistent with a net increase in the oxidation state of the surface atoms. This is consistent with XPS studies of the oxidation of a-CH_x films which reveal the appearance of high binding energy features during the course of oxidation.[13-15,19] In the case of the a-CF_x film, the changes can be resolved into the changes in the concentrations of the different components of the film.

The uptake of oxygen onto the a-CF_x film surface is revealed by the O 1s XP spectra shown in Figure 1. The O 1s signal increases very rapidly for low exposure times and then approaches its saturation value. The oxygen content (θ_O) was calculated by the following equation

$$\theta_O = \frac{A_O/0.71}{A_O/0.71 + A_C/0.30 + A_F/1.0} \times 100\%$$

where A_O, A_C, and A_F are the integrated areas under the O 1s, C 1s, and F 1s XP spectra. The XPS sensitivity factors for the O 1s, C 1s, and F 1s signals are 0.71, 0.30, and 1.0, respectively.[20] This gives a rough estimate of the oxygen content of the film because it does not attempt to account for the attenuation of the C 1s and the F 1s signals by the adsorbed oxygen. Figure 1 reveals that the attenuation of the C 1s and F 1s intensities are about 10% and 16%, respectively. After an exposure of 15 h (2×10^7 langmuirs), the θ_O of the a-CF_x film approaches its saturation value of 11%.

The uptake of oxygen by the fresh a-CF_x and a-CH_x films during low pressure exposure to O_2 is qualitatively similar. Figure 2 shows the uptake curves on both films during exposure to O_2 at pressures in the range $10^{-6}-10^{-3}$ Torr. An ion gauge was used to determine the pressure as O_2 was being introduced into the chamber but was then turned off immediately afterward to avoid the influence of electrons, ions, or excited state neutrals emitted from the ion gauge. In prior work studying the oxidation of a-CH_x films, it was discovered and reported that the oxidation kinetics are sensitive to the ions and free electrons that are generated by the ion gauge used to measure O_2 pressure.[13-15] The same effect was observed when using a-CF_x films, and so the uptake curves reported in Figure 2 were all obtained with the ion gauge on for only 30 s every 30 min. This was determined to be sufficiently short that it did not influence the oxidation of the surface. The uptake of oxygen onto the a-CH_x films is more rapid than on the a-CF_x films, and the saturation oxidation level after exposures of up to 15 h is always somewhat greater on the a-CH_x films than on the a-CF_x films. It seems, however, that the saturation oxidation values are pressure dependent and are lower at lower pressures. This may, however, be due to limitations on the total exposure times that were used at low pressures. Saturation requires up to 600 min at an O_2 pressure of 6×10^{-4} Torr. At 10^{-5} Torr the same exposure would require 600 h. At an O_2 pressure of 10^{-4} Torr, it takes $\sim 10^4$ s for the a-CF_x and a-CH_x oxidation to approach saturation. This indicates that the dissociative sticking coefficient for O_2 on a-CF_x is $S \approx 10^{-6}$. This is a rough estimate, and it is important to bear in mind that the dissociative sticking coefficient is quite likely to vary significantly with oxygen coverage as the a-CF_x and a-CH_x surfaces are quite heterogeneous. Although a sticking coefficient on the order of $S \approx 10^{-6}$ is much lower than the dissociative oxygen sticking

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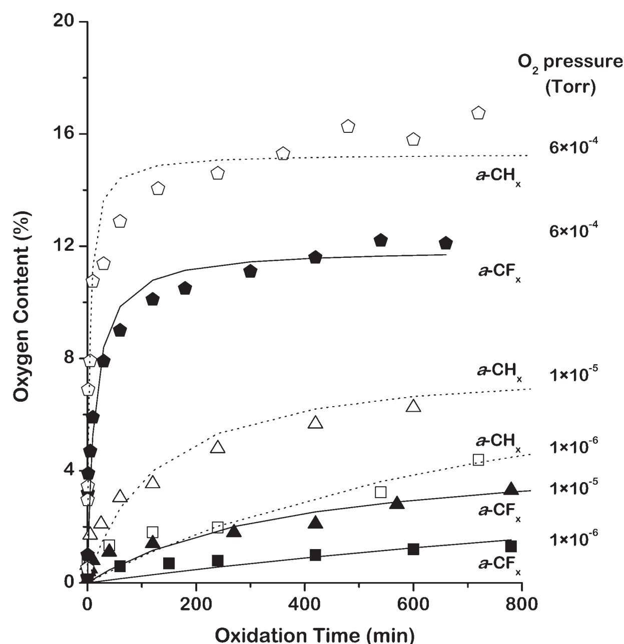

Figure 2. θ_O on the *a*-CF_x film and *a*-CH_x film surfaces as a function of oxidation time. The uptake curves (solid symbols for *a*-CF_x) were measured at O_2 pressures varying from 1×10^{-6} to 6×10^{-4} Torr with the *a*-CF_x film held at 300 K. The uptake of oxygen on the *a*-CH_x film (open symbols) under the same experimental conditions is shown for comparison. The solid lines and dashed lines are the fits of a Langmuir−Hinshelwood adsorption model to data. The ion pressure gauge was used initially to reach the desired pressure and was then shut off.

coefficient on most metal surfaces, it is important to point out that this would lead to saturation of the surface with oxygen in a period of a few milliseconds during exposure to atmospheric pressure air.

The oxygen uptake curves in Figure 2 were fit (solid and dashed lines) with a model derived from Langmuir−Hinshelwood kinetics.[21,22] This model has been used in a prior study of the oxidation of *a*-CH_x films and includes two steps: the reversible molecular adsorption of O_2 and the irreversible dissociation of O_2 into adsorbed O atoms.[15] The two physical quantities used in the model are the equilibrium constant, *K*, for first-order, reversible adsorption of molecular O_2 onto empty sites and the rate constant, *k*, for second-order dissociation onto pairs of empty oxidation sites. Consistently, the values of *K* obtained from fitting to the uptake curves in Figure 2 fall in the range 10^3−10^4 $Torr^{-1}$, and the values of *k* are in the range 10^{-8}−10^{-7} s^{-1}. A simple Langmurian model of oxygen uptake on *a*-CF_x and *a*-CH_x films ignores the fact that their surfaces are heterogeneous and thus expose sites with a variety of different values of *K* and *k*. As a result, one cannot expect the fits of such a model to the data to be perfect. In fact, it is quite interesting to see that the fits in Figure 2 are as good as they are.

3.3. High Pressure (1 atm) Oxidation of *a*-CF_x Films in Air. Currently, hard disk manufacturing involves the removal of carbon-coated disks from the vacuum deposition apparatus in which they are fabricated and subsequent lubrication by dip-coating. Removal of the disk from vacuum and exposure to ambient air results in the immediate oxidation of the exposed surface of the amorphous carbon film.[10−12] In addition to ~80% nitrogen and ~20% oxygen, ambient air contains water vapor and possible contaminants that might influence the oxidation of the *a*-CF_x film in ways that would not have been captured by our study of its oxidation in pure O_2. In order to decouple the effects of high pressure exposure from the possible effects of the contaminants in ambient air, the *a*-CF_x film was exposed to atmospheric pressures of both ambient air and clean air for 1 h at 300 K. Oxidation in atmospheric pressure air is too fast to allow study of the oxidation kinetics by XPS, but the possible differences between *a*-CF_x oxidation in ambient air and pure O_2 can be explored by obtaining XP spectra before and after exposure of the *a*-CF_x film to atmosphere. Figure 3 shows the C 1s, F 1s, O 1s, and N 1s XP spectra of an *a*-CF_x film taken before and after exposure to clean air at atmospheric pressure for 1 h (equivalent to a 5×10^{11} langmuir exposure to O_2). A subsequent exposure to 1 atm of clean air for 15 h indicated that 1 h was sufficient to ensure saturation of the oxygen uptake. An equivalent exposure of a fresh *a*-CF_x film to ambient air at a pressure of 1 atm produced a surface with a similar composition to that obtained using clean air, indicating that the contaminants in ambient air do not have a significant influence on the oxidation of the *a*-CF_x surface.

Atmospheric pressure exposure of the *a*-CF_x film to clean air resulted in some of the changes expected on the basis of our study of *a*-CF_x oxidation in low pressure pure O_2. The C 1s feature shows a decrease in the intensity of the features assigned to the C and CF groups and an increase in the intensity of the feature assigned to the CF_2 group (Figure 3). The most surprising observation is that the saturation value of θ_O is only 2.8%, in spite of the fact that the effective exposure to O_2 in clean air at a pressure of 1 atm was more than 10^4 times higher than the low pressure exposure to pure O_2 (Figure 1). After low pressure O_2 exposure (4×10^{-4} Torr for 15 h) the oxidation of the *a*-CF_x film reached θ_O = 11%. The results of high pressure oxidation in ambient laboratory air containing carbon dioxide, hydrocarbons, and water vapor (data not shown) were very similar to those of atmospheric pressure oxidation in clean air. Atmospheric pressure exposures of the *a*-CF_x film to ambient air for 1 h resulted in oxygen contents of 2.8−3.2%, again much lower than the saturation values of θ_O observed on *a*-CF_x films exposed to pure O_2 at low pressure. The low level of *a*-CF_x oxidation observed in atmospheric pressure air is not related to the presence of contaminants or water vapor in the ambient air.

3.4. Low Pressure ($< 10^{-3}$ Torr) Oxidation of *a*-CF_x Films in Air. In order to begin to understand the differences between *a*-CF_x oxidation in low pressure O_2 ($< 10^{-3}$ Torr) and high pressure air (1 atm), *a*-CF_x was exposed to low pressures of clean air at 300 K. Figure 4 shows the evolutions of the C 1s, N 1s, O 1s, and F 1s XP spectra of a fresh *a*-CF_x exposed to 6×10^{-4} Torr of clean air. After a 10 h exposure to low pressure air, the oxidation level reached a value of θ_O = 6.5%. The effective exposure to O_2 (4×10^6 langmuirs) after 10 h exposure to 6×10^{-4} Torr clean air is roughly equal to the exposure to pure O_2 at 4×10^{-4} Torr for 2 h (3×10^6 langmuirs) which resulted in an oxidation level of θ_O = 5.9%. In other words, the low pressure exposure to clean air resulted in the degree of *a*-CF_x oxidation that one would expect for oxidation in pure O_2 at an equivalent partial pressure. The important point is that exposure to a low pressure of clean air results in a significantly higher level of *a*-CF_x oxidation than exposure to atmospheric pressure clean air.

Another unexpected result of the low pressure exposure of *a*-CF_x to clean air is the observation of nitrogen adsorption. The nitrogen content, θ_N, in Figure 4 clearly reveals the increasing concentration of adsorbed nitrogen atoms on the *a*-CF_x film

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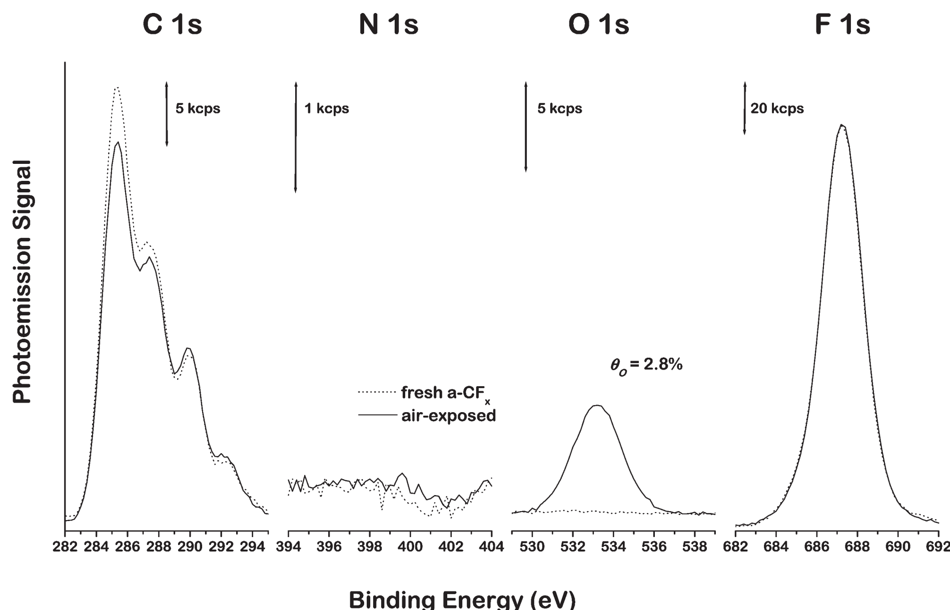

Figure 3. C 1s, N 1s, O 1s, and F 1s XP spectra of a fresh a-CF$_x$ film (dashed line) and the same film after atmospheric pressure exposure to clean air at 300 K (solid line). Atmospheric exposure to air results in the same qualitative changes in the C 1s feature as low pressure exposure to pure O_2. The saturation oxygen content, however, is $\theta_O = 2.8\%$, which is significantly less than that observed during the low pressure ($< 10^{-3}$ Torr) exposure to pure O_2 ($\theta_O = 11\%$).

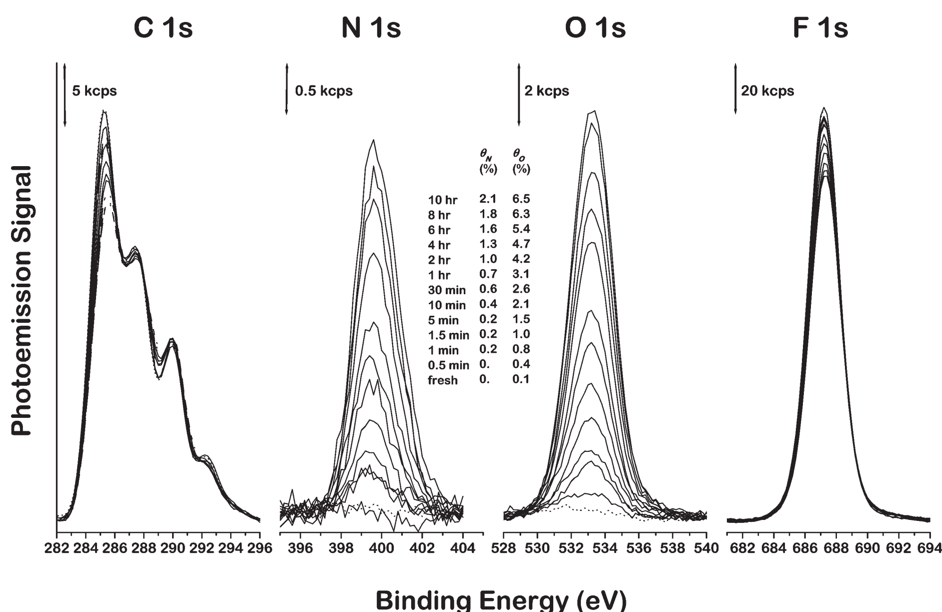

Figure 4. Evolution of the C 1s, N 1s, O 1s, and F 1s XP spectra of a-CF$_x$ film during low pressure (6×10^{-4} Torr) exposure to clean air at 300 K. Both nitrogen and oxygen were observed on the a-CF$_x$ film surface and increased with exposure. The θ_O increased to 6.5%, significantly higher than the θ_O observed after atmospheric pressure exposure to air.

surface during the exposure to clean air at 6×10^{-4} Torr. The nitrogen content, θ_N, was calculated using

$$\theta_N = \frac{A_N/0.48}{A_N/0.48 + A_O/0.71 + A_C/0.30 + A_F/1.0} \times 100\%$$

where A_N, A_O, A_C, and A_F are the integrated areas under the N 1s, O 1s, C 1s, and F 1s XPS peaks, respectively. After 10 h the θ_N reached 2.1%. In contrast, there was no adsorbed nitrogen observed after the atmospheric pressure exposure to clean air (Figure 3).

The chemical state of the oxygen and the nitrogen in the a-CF$_x$ films after exposure to O_2 or air is not clear. One would expect that they are adsorbed as dissociated atomic species irreversibly bound to the surface by the formation of covalent bonds with the carbon. However, there is some evidence that this is not completely correct. We have observed that some fraction of the oxygen and the nitrogen in the films can be displaced under low pressure exposures to O_2 and air. Figure 5A reveals the displacement of nitrogen from an air-exposed surface during subsequent exposure to pure O_2. The displacement experiment started by using an a-CF$_x$ film having $\theta_O = 7.2\%$ and $\theta_N = 4.6\%$ on its surface prepared by exposing a fresh a-CF$_x$ film to low pressure clean air at 300 K. The film was then exposed to O_2 at 6×10^{-4} Torr and 300 K. During the low pressure O_2 exposure, the value of θ_O increased monotonically from 7.2% and saturates at 9.8% after 210 min. Simultaneously, the value of θ_N decreased

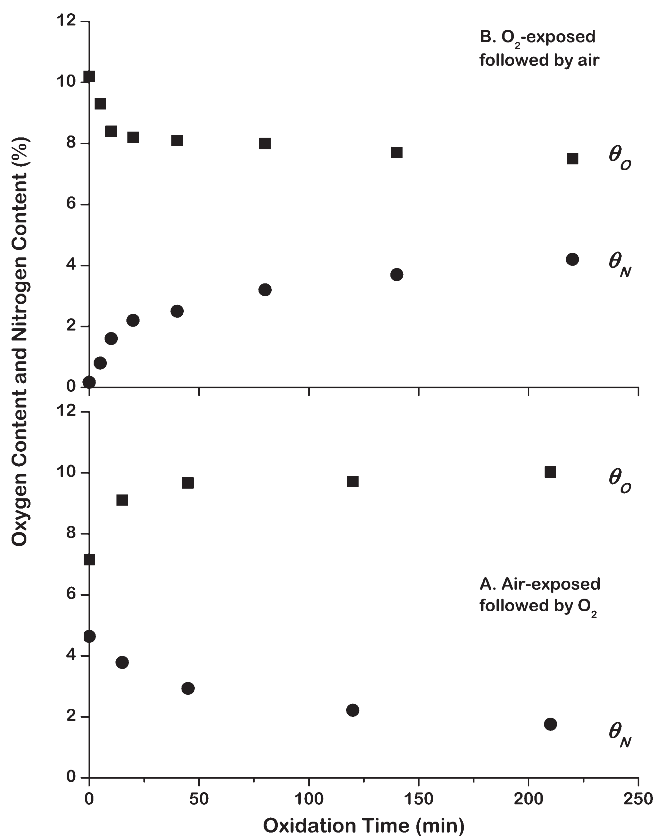

Figure 5. Changes of θ_O and θ_N on (A) an air-exposed surface during exposure to O_2 and (B) an O_2-exposed surface during exposure to air. The initial exposures of the surfaces were sufficient to saturate the two with oxygen. Subsequent exposures were performed at 6×10^{-4} Torr of O_2 at 300 K. On the surface initially exposed to air (A), subsequent exposure to pure O_2 results in the displacement of nitrogen by oxygen. On the surface initially exposed to pure O_2 (B), subsequent exposure to air results in the displacement of oxygen by nitrogen.

monotonically from 4.6% to 1.4%. Similarly, some fraction of the oxygen on an *a*-CF_x film exposed to pure O_2 can also be replaced by nitrogen during subsequent exposure to air (Figure 5B). This displacement experiment started by using an *a*-CF_x film having θ_O = 10.2% following exposure to low pressure O_2 at 300 K. During subsequent exposure to clean air at 6×10^{-4} Torr and 300 K, the value of θ_O decreases monotonically from 10.2% to 7.6%. Simultaneously, the value of θ_N increased monotonically and saturated at 4.2% after 220 min. The reversible displacement of oxygen and nitrogen suggests that some fraction might be adsorbed in a molecular state but with heats of adsorption that are sufficiently high that they are stable in vacuum at 300 K. The displacement also indicates that *a*-CF_x films exposed to low pressure O_2 or air are still active for further oxidation.

In summary, the results of our study of the oxidation of *a*-CF_x films by low pressure O_2 and air reveal two anomalies. During low pressure exposures to clean air, the *a*-CF_x films incorporate measurable amounts (> 2%) of nitrogen. However, nitrogen is not observed following exposure of the *a*-CF_x films to clean air at high pressure. The most surprising observation has been that the exposure of the *a*-CF_x films to low pressures (< 10^{-3} Torr) of either air or O_2 leads to a higher value of θ_O than atmospheric pressure exposure to air. This cannot be explained in the framework of any simple adsorption model, any of which would predict that the θ_O should increase monotonically with oxygen exposure.

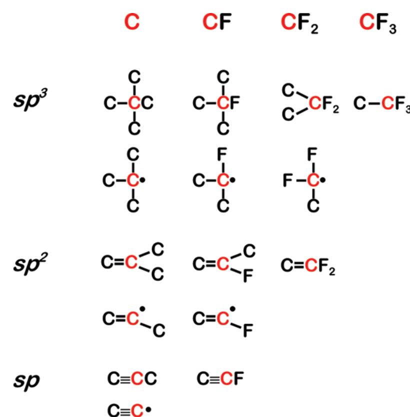

Figure 6. Possible carbon atom configurations in *a*-CF_x films. The unsaturated carbon−carbon bonds and free radicals are primarily associated with C and CF groups which are prone to oxidation. These are the species that disappear during exposure to oxygen.

4. Discussion

Oxidation of an *a*-CF_x film results in changes in chemical structure of the film. Some insight into this process can be obtained by analyzing the possible carbon atom configurations in *a*-CF_x. Figure 6 lists the possible carbon atom configurations in fresh *a*-CF_x films; 15 possibilities are sorted into four columns according to the number of fluorine atoms bonded to the carbon atom and three rows for its possible hybridization into sp^3, sp^2, or sp electronic configurations. The C 1s XP spectra can be effectively related to the four columns as they distinguish carbon atoms by the numbers of attached fluorine atoms. One might expect that carbon atoms in double bonded configurations, triple bond configurations, and free radical configurations are more readily oxidized than carbon atoms in saturated configurations. These carbon atoms serve as the active reaction sites for oxidation and they concentrate in the C and CF components. As a consequence, C and CF components are the components that are oxidized during exposure to O_2.

Oxidation of the carbon atoms in the *a*-CF_x films results in the formation of species with increased C 1s binding energies. The feature at ~290.0 eV in the C 1s XP spectra of Figures 1 and 4 grows because of the formation of CFO (carbon atoms bonded with one oxygen atom and one fluorine atom) and COO (carbon atoms bonded with two oxygen atoms). Oxidation converts C and CF components of the films into CO (carbon atoms bonded with one oxygen atom), CFO, and COO. Furthermore, CO components may be oxidized into COO contributing to the increase in intensity of the feature at ~290.0 eV in the C 1s XP spectra. Thus, the XP spectra provide some insight into the components of the *a*-CF_x films that are most readily oxidized. Presumably, the same insights hold for oxidation of a-CH_x films, although this cannot be discerned from their XPS spectra because the different components in the a-CH_x films cannot be resolved as easily as in the *a*-CF_x films.

After low pressure exposures of the *a*-CF_x films to air or O_2, some fraction of the adsorbed oxygen and nitrogen is in a reversibly adsorbed state. Some fraction of the oxygen can be reversibly displaced by nitrogen during exposure to air and some of the nitrogen can be displaced by oxygen during exposure to pure O_2. It is rather surprising that nitrogen is adsorbed on these films in vacuum at room temperature. Similarly, it is also quite surprising that some of the oxygen can be reversibly displaced by nitrogen because this suggests that their heats of adsorption are comparable. One possibility is that the reversibly adsorbed components are bound to the free radical sites as N_2 and as O_2.

Although this is a difficult proposition to test experimentally, it is consistent with the observations and the reversibility of their adsorption.

The data presented here clearly indicate that there are some substantial differences between the process of a-CF_x oxidation at high and low pressures (exposures) of oxygen (or air). This observation is consistent with previously reported observations made during the oxidation of a-CH_x films. The results suggest that during exposure to high pressures of air some of the most easily oxidized carbon atoms are fully oxidized to gaseous species such as carbon dioxide and desorb from the surface. In essence, this changes the surface composition during the oxidation process by etching away various components. The partial pressure of O_2 in 1 atm air is ~150 Torr. Exposure to 1 atm of air results in an O_2 exposure that is at least 10^5 higher than the O_2 exposure resulting from low pressure ($< 10^{-3}$ Torr) air or O_2 exposures for the same time period. Such a high O_2 exposure could "etch" the a-CF_x film surface and reduce the oxygen content. In other words, for low exposure the oxygen content can rise to a level of ~10%, but significantly higher O_2 exposures reduce the surface oxygen content by removing some of the partially oxidized species and leaving a surface that is passivated against further oxidation. As a consequence, the concentration of partially oxidized carbon atoms in the a-CF_x film must first grow and then decrease during atmospheric exposure. Unfortunately, this process is too fast to be observed in the type of experiment done in this work. The "etching" is probably also happening in low pressures ($< 10^{-3}$ Torr) of air or O_2 but at a very slow rate.

The model proposed above for etching of the a-CF_x surface during atmospheric pressure exposure to air can also be used to explain the absence of nitrogen on the a-CF_x films exposed to atmospheric pressure air. The nitrogen molecules bonded either to carbon atoms or to oxygen atoms probably desorb from the surface during "etching". On a-CF_x films exposed to low pressure air, the adsorbed nitrogen survives because "etching" is probably much slower than nitrogen adsorption.

5. Conclusions

Exposure of freshly deposited a-CF_x films either to pure O_2 or to air results in the partial oxidation of their surfaces. Carbon atoms in these films are distinguished by their degree of fluorination as determined using XPS. The different components in the a-CF_x film exhibit different oxidation reactivity. C and CF appear to be the major components being oxidized in air or O_2, probably because unsaturated carbon−carbon bonds and carbon radicals concentrate on the C and CF components. Their oxidation results in the formation of COO species and CFO at the surface.

Study of the oxidation of a-CF_x in low pressures of either pure O_2 or air reveals that some of the adsorbed oxygen can be reversibly displaced by nitrogen and vice versa. This indicates that some component of the oxidized surface is quite labile and suggests that not all the adsorbed oxygen and nitrogen forms covalent bonds with the surface.

The oxidation of the a-CF_x films in atmospheric pressures of air with effective O_2 exposures of ~10^{12} langmuirs results in a lower level of oxygen uptake than oxidation at low pressures ($< 10^{-3}$ Torr) with effective exposures of 10^7 langmuirs. This surprising result suggests that some of the most easily oxidized surface carbon atoms are probably fully oxidized to gaseous species such as carbon dioxide which desorb from the surface. This "etching" effect becomes significant when the a-CF_x films are exposed to atmospheric pressures of air and leaves a surface that is passivated with respect to further oxidation and thus has a lower residual oxygen content than the surface exposed to air or O_2 at low pressures.

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