

Electron stimulated decomposition of fluorocarbons on amorphous hydrogenated carbon ($a\text{-CH}_x$) overcoats used in data storage media

Yang Yun, Esteban Broitman and Andrew J. Gellman*

Department of Chemical Engineering, and Data Storage System Center, Carnegie Mellon University, Pittsburgh, PA 15213, USA

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The electron-induced surface chemistry of perfluoropolyalkylether (PFPE) lubricants on $a\text{-CH}_x$ films has been probed by studying the impact of free electrons on perfluorodiethylether, $(\text{CF}_3\text{CF}_2)_2\text{O}$, and 2,2,2-trifluoroethanol, $\text{CF}_3\text{CH}_2\text{OH}$, as models of the chemical functionality of PFPE lubricants such as Fomblin Zdol. Electron-stimulated decomposition of $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$ on fresh and oxidized $a\text{-CH}_x$ is observed when the sample is unbiased and in the presence of 70 eV free electrons. Electron-induced decomposition is indicated by the deposition of fluorine onto the surface of the $a\text{-CH}_x$ film following desorption of molecular $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$ by heating in front of a mass spectrometer. Biasing the sample to -80 V successfully eliminates the decomposition by preventing the impingement of electrons onto the surface. The electron-stimulated decomposition of PFPE lubricants may contribute to lubricant decomposition during normal drive operation.

KEY WORDS: magnetic data storage, fluorocarbons, polyethers, magnetic data disks (hard, floppy), lubricant degradation, carbon, graphite

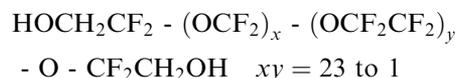
1. Introduction

In magnetic hard disk drives, the read–write head flies over the disk surface at a height of < 100 Å. To protect the magnetic media from damage caused by collisions with the read–write head, the magnetic media layer is covered by a thin hydrogenated or nitrogenated amorphous carbon film ($a\text{-CH}_x$ and $a\text{-CN}_x$, respectively) that is coated with a thin (< 20 Å) layer of perfluoropolyalkylether (PFPE) lubricant. The continual need to increase the density of data stored on disk surfaces creates an increasing need to reduce the gap between the read–write head and the magnetic layer, thus increasing the risk or frequency of contacts between the head and the disk surface. Maintaining adequate protection of the disk requires an understanding of the performance of the PFPE lubricant on the surfaces of amorphous carbon overcoats [1–7].

The decomposition of PFPE lubricants has been reported to form viscous products that attach to the head when the slider lands on the disk surface during stoppages of the drive [8,9]. PFPE decomposition has been proposed to arise from thermal or catalytic reaction mechanisms [8]. However, some experimental results have suggested that PFPE lubricant decomposition reactions due to triboelectrons are also a contributing decomposition mechanism [8,10–13].

When two solid surfaces come into sliding contact, tribocharging and the triboemission of electrons, photons, and ions can occur, generating a microplasma at the interface. These phenomena, i.e., triboemission, microplasma generation and tribocharging, are referred to as triboelectromagnetic phenomena [8,14], and could easily occur in magnetic hard disk drives [8,11,14–18]. In a disk drive, electric potentials of up to 0.1 V can be developed between the slider and the disk surface [13,19], indicating that some charge transport has occurred. As examples, Nakayama *et al.* observed triboelectromagnetic phenomena at two kinds of sliding solid–solid interfaces: $\text{Al}_2\text{O}_3/a\text{-CH}_x$ [20] and diamond/ $a\text{-CH}_x$ [14]. Triboelectromagnetic phenomena were also observed when the $a\text{-CH}_x$ film was coated with PFPE fluid [8,11,16].

The principle contribution of the work described in this paper is the study and understanding of the desorption and decomposition of fluorinated ethers and alcohols on fresh and oxidized $a\text{-CH}_x$ films in the presence and absence of free electrons. Perfluorodiethylether, $(\text{CF}_3\text{CF}_2)_2\text{O}$, and 2,2,2-trifluoroethanol, $\text{CF}_3\text{CH}_2\text{OH}$, were used as models for the chemical functionality in Fomblin Zdol, a common PFPE lubricant, which has fluorinated ether backbone and fluorinated hydroxyl end groups [3,4].



Fluorocarbons are notoriously sensitive to electron-induced decomposition on surfaces [10,11]. The roles of temperature and free electrons in the decomposition of

*To whom correspondence should be addressed.
E-mail: ag4b@andrew.cmu.edu

small fluorinated ethers on metal and metal-oxide surfaces such as Ru [21], ZrO₂ [22], and Al₂O₃ [23,24], have been studied. It is noteworthy that 300 eV electrons have a high cross section for decomposition of (CF₂H)₂O on Al₂O₃ [11,24]. It is also suspected that electrons can affect PFPE lubricants on the carbon overcoats used in hard disk drive. Yates *et al.* [11] observed electron stimulated decomposition of Fomblin Zdol on carbon overcoats under exposure to low energy electrons (3–20 eV). They used commercial magnetic hard disk platters as the sample and thus carbon overcoats that had been oxidized by exposure to air prior to the deposition of the lubricant. In current hard disk manufacturing, the disk platter with its carbon overcoat is removed from vacuum environment in which the disk platter is made and exposed to ambient air prior to deposition of the PFPE lubricant [3,25,26]. Therefore the carbon overcoat is oxidized and contaminated by the ambient air before the deposition of the PFPE lubricant. The interaction of electrons with PFPE lubricant on “fresh” carbon overcoats has not been studied but is of importance in vapor phase lubrication technologies that would deposit lubricant onto fresh carbon overcoats [25].

The work reported in this paper is a study of electron-induced decomposition of fluorocarbons on both fresh and oxidized *a*-CH_x overcoats. It demonstrates a high probability of electron-induced decomposition and the fact that the decomposition reaction deposits fluorine onto the carbon surface. Both model compounds, (CF₃CF₂)₂O and CF₃CH₂OH, adsorb and desorb reversibly from the *a*-CH_x surface during heating but exhibit some signs of decomposition in the presence of 70 eV free electrons. The decomposition of (CF₃CF₂)₂O and CF₃CH₂OH on the surfaces of fresh and oxidized *a*-CH_x films is shown to be solely due to the electron stimulation under the conditions of these experiments. The results demonstrate that neither the fresh nor the oxidized *a*-CH_x films decompose small adsorbed fluorocarbons in the absence of free electrons. Consequently, the results support the notion that PFPE lubricants used on magnetic hard disks are inherently unstable in the presence of electrons.

2. Experimental

All experiments were performed in an ultra high vacuum (UHV) chamber with a base pressure of <10⁻⁹ Torr. The UHV chamber was designed and constructed for the express purpose of studying the surface chemistry of *a*-CH_x films *in situ*. The UHV chamber consists of two levels separated by a gate valve. The lower level is used for *a*-CH_x deposition and is pumped with a turbo pump. It is equipped with an Ar⁺ sputter gun for substrate cleaning and a DC magnetron sputter source (MAK130VCFUHV, 1.3” graphite

target, US Inc.) for *a*-CH_x film deposition. Gas flow controllers allow introduction of a mixture of Ar and CH₄ into the lower level at constant pressure during the sputter deposition process. When the sample is in the lower deposition level of the chamber, a seal isolates the two chambers to minimize contamination of the upper surface analysis level by the sputter gases. In addition, the lower level has one leak valve for introduction of air or O₂ for oxidation of the *a*-CH_x films.

The upper level of the UHV chamber is used for surface analysis of *a*-CH_x films prepared in the lower level and is pumped with a cryopump and a sublimation pump. It is equipped with an X-ray source (XR50, Specs), and a hemispherical electron energy analyzer (CLAM II, VG Scientific) which are used for X-ray photoelectron spectroscopy (XPS). The upper level is equipped with leak valves for introduction of gases or vapors such as (CF₃CF₂)₂O and CF₃CH₂OH. In addition, the upper level is equipped with a quadrupole mass spectrometer (Q200MS, Ametek) with an electron impact ionization energy of 70 eV which is used for temperature programmed desorption (TPD) studies of (CF₃CF₂)₂O and CF₃CH₂OH adsorbed on the surface of the *a*-CH_x film.

The sample substrate was a Ni foil, which could move between the two levels of the chamber on a manipulator that extends through the gate valve separating the two. The nickel foil substrate was machine-punched to produce an 11 mm diameter disk that was mounted onto the manipulator by two tantalum wires spot-welded to its rear face. The sample could be cooled by liquid nitrogen to 80 K and heated resistively to >1000 K. The temperature was measured by a chromel-alumel thermocouple spot-welded to the back of the sample.

The *a*-CH_x film deposition conditions were chosen to generate *a*-CH_x films which exhibited Raman spectra similar to those of *a*-CH_x films used commercially. The nickel foil substrate was cleaned by several cycles of Ar⁺ sputtering followed by annealing to 950 K before *a*-CH_x film deposition. Films were then deposited using a DC power of 75 W at a substrate temperature of 443 K. The total pressure was maintained at 8 m Torr during the deposition process using a 10% CH₄/(Ar + CH₄) gas mixture. These conditions were identified by producing films at a variety of different sputter powers, substrate temperatures, pressures, and CH₄ concentrations. Raman spectroscopy was performed by removing the sample from the UHV chamber.

The *a*-CH_x films were characterized by *in situ* XPS immediately after deposition. The XPS spectra were obtained using a 290 W Mg K_α (*hν* = 1253.6 eV) X-ray source. A pass energy of 50 eV was used for all measurements. All the XP spectra were collected by holding the sample at 300 K. The film thickness was determined to be about 70 Å based on the attenuation of the signal from the Ni substrate. The TPD of (CF₃CF₂)₂O and

CF₃CH₂OH on fresh *a*-CH_x films was then performed immediately after the XPS characterization. The air-exposed *a*-CH_x film was prepared by venting the chamber with one atmosphere of ambient air immediately after film deposition. The *a*-CH_x film was kept in atmospheric pressure air at room temperature for 1 h. The chamber was then evacuated to $<10^{-9}$ Torr in ~ 12 h for XPS and TPD measurements. The O₂-exposed *a*-CH_x film was prepared by introducing pure O₂ into the chamber immediately after film deposition. Exposure of the *a*-CH_x film surface to O₂ was conducted by positioning the *a*-CH_x film ~ 4 cm from the end of a stainless steel dosing tube attached to a leak valve. The *a*-CH_x film was exposed to 8×10^{-4} Torr of O₂ at 300 K for 2 h. The chamber was then evacuated to $<10^{-9}$ Torr in ~ 30 min for XPS and TPD measurements. The oxygen contents of the air-exposed *a*-CH_x film and the O₂-exposed *a*-CH_x film were $\sim 6\%$ and $\sim 20\%$, respectively. These are the saturation oxidation levels achievable by exposure to air and to O₂.

The adsorption of (CF₃CF₂)₂O and CF₃CH₂OH onto the fresh and oxidized *a*-CH_x surface was accomplished by leaking vapor into the UHV chamber while the sample was held at 80 K. The sample was biased at either 0 V or -80 V during adsorption and subsequent TPD experiments in order to explore the effects of electrons on the surface chemistry of the adsorbed fluorocarbons. During TPD, the *a*-CH_x film adsorbed with (CF₃CF₂)₂O and CF₃CH₂OH was positioned ~ 2 mm from the aperture of the mass spectrometer. Electrons emitted from the mass spectrometer filament hit the sample directly. The sample current was ~ 35 nA corresponding to an electron flux of 2×10^{-4} site⁻¹•s⁻¹, assuming a surface adsorption site density of 10^{15} cm⁻². The sample was exposed to electrons for a period on the order of 100 s during the TPD experiment, so the integrated electron flux on the sample was in the range 10^{-2} to 10^{-1} site⁻¹. The energy of electrons emitted from the mass spectrometer filament was ~ 70 eV. These electrons stimulate the decomposition of (CF₃CF₂)₂O and CF₃CH₂OH.

Perfluorodiethylether [(CF₃CF₂)₂O, Strem Chemicals, 90%] and 2,2,2-trifluoroethanol [CF₃CH₂OH, TCI-G.R.] were each placed in glass vials attached to the leak valve. High vapor pressure contaminants were removed by several freeze-pump-thaw cycles and the vapor purity was then checked with mass spectrometry. Exposure of the sample surface to each adsorbate was conducted by positioning the *a*-CH_x sample held at 80 K directly in front of a stainless steel dosing tube attached to the leak valve and then opening the leak valve to introduce vapor into the chamber. After adsorption of the vapor, the *a*-CH_x sample was positioned ~ 2 mm from the aperture of the mass spectrometer. TPD spectra were obtained by heating the sample at a constant rate of 2 K/s while monitoring the

desorbing species with the mass spectrometer. In order to prevent any irreversible damage to the *a*-CH_x film during heating, the upper temperature was limited to 320 K during the TPD. This is well below the temperature of 443 K at which the *a*-CH_x film was deposited. The TPD spectra were highly reproducible indicating that the *a*-CH_x film surface was unchanged by adsorption and desorption of (CF₃CF₂)₂O and CF₃CH₂OH.

3. Results

3.1. Thermal decomposition of fresh *a*-CH_x films

Prior to the study of the adsorption of (CF₃CF₂)₂O and CF₃CH₂OH on the *a*-CH_x film surface, the thermal decomposition of fresh *a*-CH_x films was studied. The *a*-CH_x films were heated from 95 K to 950 K at a constant rate of 2 K/s while monitoring the desorbing species with the mass spectrometer immediately after the film deposition and XPS characterization. Figure 1 shows the temperature programmed decomposition spectra of a fresh *a*-CH_x film obtained by monitoring the signals at $m/q = 2$ (H₂⁺), 15 (CH₃⁺), 16 (CH₄⁺), 29 (C₂H₅⁺), and 30 (C₂H₆⁺). It appears that the decomposed *a*-CH_x releases hydrogen and hydrocarbons simultaneously. The decomposition becomes rapid at temperatures greater than 700 K and reaches a maximum rate at ~ 860 K. The small peaks at temperatures below 200 K in the spectra of $m/q = 16$, 29, and 30 arise from desorption of ambient hydrocarbon gases adsorbed on the surface of the *a*-CH_x film after film deposition. During the TPD of (CF₃CF₂)₂O and CF₃CH₂OH described below, the upper temperature was limited to 320 K, far below the onset of *a*-CH_x decomposition. Thus the *a*-CH_x films are unchanged during the TPD of (CF₃CF₂)₂O and CF₃CH₂OH.

3.2. Molecular adsorption and desorption of fluorocarbons on fresh and oxidized *a*-CH_x films

The surface chemistry of Fomblin Zdol lubricant on *a*-CH_x films was probed by the adsorption of (CF₃CF₂)₂O and CF₃CH₂OH as models for the fluoroether backbone and the hydroxyl end groups of Fomblin Zdol, respectively. The surface chemistry of *a*-CH_x films is complicated by the fact that they are chemically heterogeneous. The surfaces expose carbon atoms with different hybridization (*sp*² and *sp*³) and different degrees of hydrogenation [27–29]. The heterogeneity of the adsorption sites on fresh and oxidized *a*-CH_x is revealed by the TPD spectra of (CF₃CF₂)₂O and CF₃CH₂OH on *a*-CH_x films. As the example, figure 2 illustrates the TPD spectra of (CF₃CF₂)₂O adsorbed on a fresh *a*-CH_x film, at coverages of

approximately 0.2–1 monolayer. The sample was biased at -80 V during adsorption and desorption in order to repel stray electrons coming from the ionizer of the mass spectrometer. The spectra in figure 2 were obtained by monitoring the signal at $m/q = 69$ (CF_3^+) and were accompanied by spectra for $m/q = 50$ (CF_2^+) and 31 (CF^+). At low submonolayer coverages there is a single desorption peak. As the coverage of $(\text{CF}_3\text{CF}_2)_2\text{O}$ is increased, the peak desorption temperature decreases monotonically and the peak broadens. This behavior has been observed many times in studies of the adsorption of these compounds from various types of amorphous carbon films and is attributed to the heterogeneity of the surface [30,31]. As a consequence of the heterogeneity of the $a\text{-CH}_x$ surfaces, there is no clear resolution of the monolayer, and multilayer desorption features which would be resolved on homogeneous single crystalline surfaces [32,33]. At submonolayer coverages of $(\text{CF}_3\text{CF}_2)_2\text{O}$, the peak desorption temperature decreases monotonically with increasing coverage until the coverage reaches one monolayer and further exposure results in multilayer adsorption. The area under the TPD spectra was used as the measure of the coverage. The monolayer TPD spectrum was chosen to be the one with the minimum peak desorption temperature and its area was used to define the monolayer coverage. Similar spectra (not shown) were obtained for $\text{CF}_3\text{CH}_2\text{OH}$

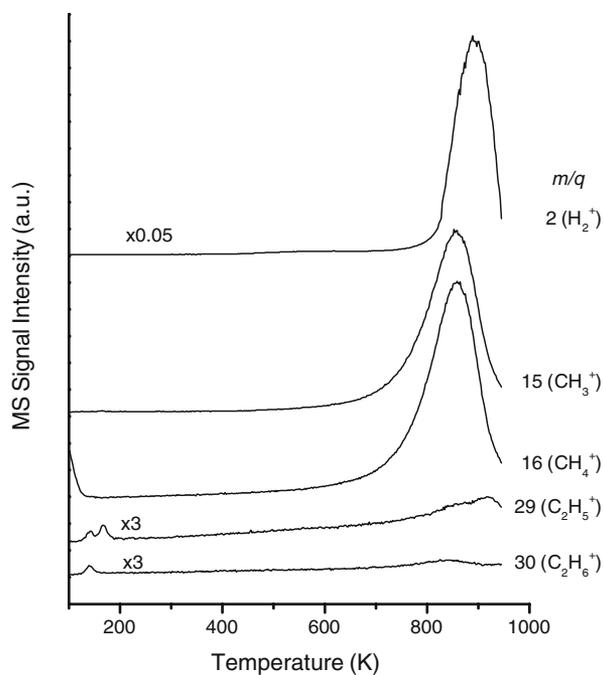


Figure 1. Temperature programmed decomposition spectra of fresh $a\text{-CH}_x$ obtained by heating at a constant rate of 2 K/s. Rapid decomposition starts at ~ 700 K much higher than the upper limit temperature of 320 K used in the following TPD of $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$. The small desorption features below 200 K observed at $m/q = 16, 29,$ and 30 arise from hydrocarbon gases adsorbed on film surface immediately after film deposition.

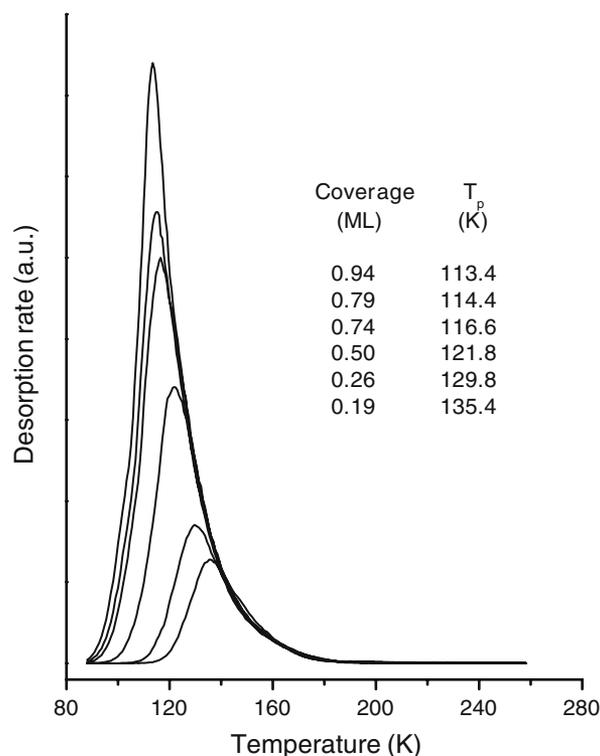


Figure 2. TPD spectra of $(\text{CF}_3\text{CF}_2)_2\text{O}$ from the surface of a fresh $a\text{-CH}_x$ film. The initial coverages varied in the range of approximately 0.2–1 monolayer (ML). At coverages below 1 ML the peak desorption temperatures decrease with increasing coverage, reflecting the heterogeneity of the $a\text{-CH}_x$ surface. The TPD spectra shown were collected using a heating rate of 2 K/s while monitoring the signal at $m/q = 69$ (CF_3^+) for $(\text{CF}_3\text{CF}_2)_2\text{O}$. Additional spectra were obtained by monitoring the signals at $m/q = 50$ (CF_2^+) and $m/q = 31$ (CF^+) and indicate that $(\text{CF}_3\text{CF}_2)_2\text{O}$ desorbs molecularly. The sample was biased at -80 V to repel ambient electrons. The TPD spectra of $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$ on fresh and oxidized $a\text{-CH}_x$ are all qualitatively similar.

desorption but by monitoring the signals at m/q ratios of 31 (CF^+), 69 (CF_3^+), and 29 (COH^+). The primary point is that adsorption and desorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$ was reversible on the fresh $a\text{-CH}_x$ film biased at -80 V.

TPD of $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$ on air-oxidized and O_2 -oxidized $a\text{-CH}_x$ films were also conducted to investigate the adsorption of Fomblin Zdol on oxidized $a\text{-CH}_x$ surfaces. In the current disk fabrication process, the disks are removed from the vacuum environment in which they are fabricated and dipped into a solution of the PFPE lubricant. As a consequence of the removal from vacuum, the surface of the $a\text{-CH}_x$ is exposed to air prior to application of the lubricant [26]. Exposure of $a\text{-CH}_x$ films to air or O_2 generates partially oxidized carbon species such as C–O–C, C–OH, and C=O on the $a\text{-CH}_x$ surface [34,35]. In our experiments using oxidized $a\text{-CH}_x$ surfaces either air or O_2 was introduced into the chamber immediately after $a\text{-CH}_x$ film preparation and prior to $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$ adsorption. The

air-exposed film was prepared by exposing the $a\text{-CH}_x$ film to one atmosphere of ambient air for 1 h at room temperature. The O_2 -exposed $a\text{-CH}_x$ film was prepared by exposing the $a\text{-CH}_x$ film to 8×10^{-4} Torr of pure O_2 for 2 h at room temperature to saturate the $a\text{-CH}_x$ film with oxygen. The chamber was then evacuated to $< 10^{-9}$ Torr for adsorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$ or $\text{CF}_3\text{CH}_2\text{OH}$ and subsequent TPD measurements. Again, the sample was biased at -80 V to eliminate the effects of ambient electrons. The TPD spectra of $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$ adsorbed on air-exposed $a\text{-CH}_x$ films and O_2 -exposed $a\text{-CH}_x$ films are qualitatively similar to one another and they are qualitatively similar to those on the fresh $a\text{-CH}_x$ film. A detailed discussion of the oxidation kinetics [36] and of the effects of oxidation on $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$ adsorption are to be published elsewhere [25]. The primary point is that the adsorption and desorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$ was reversible on the O_2 and air oxidized $a\text{-CH}_x$ films biased at -80 V.

3.3. Electron-stimulated decomposition of PFPE model molecules

The electron-stimulated decomposition of PFPE lubricant on fresh and oxidized $a\text{-CH}_x$ surfaces was investigated through the adsorption and desorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$ in the presence or absence of ambient electrons. With the sample grounded with respect to the UHV chamber there are always electrons incident on the surface from sources such as the ionizer of the mass spectrometer and the filament of the ionization pressure gauge. The current measured with the sample in front of the mass spectrometer was ~ 35 nA, yielding a flux of $\sim 2 \times 10^{-4}$ electrons per site (surface atom) calculated assuming a density of 10^{15} atoms $\cdot\text{cm}^{-2}$. Biasing the sample at -80 V with respect to the chamber eliminates the impingement of low energy electrons onto the surface. The surface of the $a\text{-CH}_x$ film was analyzed using XPS after the adsorption and desorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$ with the sample held at either 0 V or -80 V. Figure 3 shows the F 1s spectra obtained from the surface following the adsorption and desorption of 0.1, 0.3, and 0.5 monolayers of $(\text{CF}_3\text{CF}_2)_2\text{O}$ with the sample at 0 V. The spectra revealed the deposition of 0.7, 1.2, and 2.1% fluorine onto the surface resulting from the electron-stimulated decomposed $(\text{CF}_3\text{CF}_2)_2\text{O}$. The fluorine content (θ_F) on the $a\text{-CH}_x$ surface was calculated from the areas under the C 1s and F 1s XP spectra. The areas were then scaled by the sensitivity factors for carbon (0.3) and fluorine (1.0) to give

$$\theta_F = \frac{A_F/1.0}{A_C/0.3 + A_F/1.0} \times 100\%$$

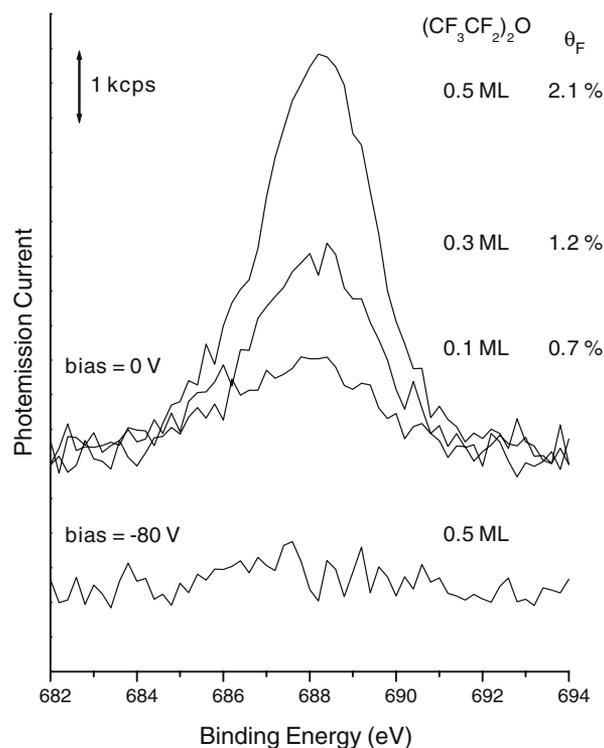


Figure 3. F 1s XP spectra of a fresh $a\text{-CH}_x$ film obtained immediately after adsorption and desorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$. Adsorption of 0.1, 0.3, and 0.5 ML of $(\text{CF}_3\text{CF}_2)_2\text{O}$ on the unbiased (0 V) fresh $a\text{-CH}_x$ film followed by TPD in front of the mass spectrometer resulted in the deposition of 0.7%, 1.2%, and 2.1% of fluorine. The appearance and accumulation of fluorine on the surface of the unbiased $a\text{-CH}_x$ film reveals the decomposition of $(\text{CF}_3\text{CF}_2)_2\text{O}$. Also shown is the F 1s XP spectrum of a fresh $a\text{-CH}_x$ film biased at -80 V immediately after adsorption and desorption of 0.5 ML $(\text{CF}_3\text{CF}_2)_2\text{O}$. There is no detectable deposition of fluorine onto the surface of the biased film. The electrons emitted from the ionizer of the mass spectrometer must induce the decomposition on the unbiased sample.

where A_C is the integrated area of the C 1s XP spectrum and A_F is the integrated area of the F 1s XP spectrum.

The decomposition of $(\text{CF}_3\text{CF}_2)_2\text{O}$ is due to electrons emitted from the ionizer of the mass spectrometer. A similar experiment was performed with the sample biased at -80 V with respect to the chamber. Figure 3 shows the F 1s XP spectrum of a fresh $a\text{-CH}_x$ film after the adsorption and subsequent desorption of 0.5 monolayers of $(\text{CF}_3\text{CF}_2)_2\text{O}$. The absence of fluorine indicates completely reversible, molecular desorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$.

Similar experiments were performed with $\text{CF}_3\text{CH}_2\text{OH}$ and also revealed the deposition of some fluorine onto the fresh and oxidized $a\text{-CH}_x$ film surfaces during adsorption and desorption of $\text{CF}_3\text{CH}_2\text{OH}$ with the sample held at 0 V. There was no fluorine deposition during adsorption and desorption with the sample at -80 V. Biasing the sample by -80 V prevents stray electrons from hitting the sample surface and inducing decomposition of the adsorbed fluorocarbons.

4. Discussion

Freshly deposited $a\text{-CH}_x$ films have unsaturated carbon-carbon double bonds [27–29] and unpaired electrons localized in carbon dangling bonds [37] at the film surface. Air-exposed $a\text{-CH}_x$ films have partially oxidized species such as C–O–C, C–OH, and C=O at the surface [34,35]. Our results show that none of these species cause the decomposition of either $(\text{CF}_3\text{CF}_2)_2\text{O}$ or $\text{CF}_3\text{CH}_2\text{OH}$ at temperatures in the range 80–200 K indicating that the $a\text{-CH}_x$ overcoats on magnetic hard disks are chemically inert to the PFPE lubricant in this temperature range. On the other hand, electron stimulated decomposition of $(\text{CF}_3\text{CF}_2)_2\text{O}$ or $\text{CF}_3\text{CH}_2\text{OH}$ on $a\text{-CH}_x$ overcoats was clearly observed under impingement of free electrons emitted from the mass spectrometer with energies of 70 eV.

Possible electron-stimulated decomposition mechanisms include dissociative molecular ionization and dissociative electron attachment to the parent molecule [10,11]. Yates *et al.* [11] observed evidence of both mechanisms occurring in the decomposition of Fomblin Zdol on hard disks surfaces. The electrons causing the decomposition of $(\text{CF}_3\text{CF}_2)_2\text{O}$ or $\text{CF}_3\text{CH}_2\text{OH}$ in this paper come from the mass spectrometer with ionization energies of 70 eV. At this energy the decomposition is probably dominated by molecular ionization. The decomposition of fluorocarbon is very efficient. Yates *et al.* estimate a cross section of $\sim 10^{-16}$ cm². In our experiment we estimate the cumulative electron flux to be in the range 10^{-2} to 10^{-1} per site (cross section of 10^{-17} – 10^{-16} cm²) and we observe a yield of fluorine atoms of $\sim 10^{-2}$ remaining on the surface. It is not known how many fluorine atoms might be deposited onto the surface as a result of the decomposition of one $(\text{CF}_3\text{CF}_2)_2\text{O}$ molecule. Nonetheless, these numbers indicate that the decomposition per electron could be as high as 10%, roughly consistent with the estimates of Yates *et al.* [11].

Our results show that negatively biasing the sample successfully eliminates the electron-stimulated fluorocarbon decomposition by preventing electrons from hitting the sample surface. This suggests that preventing triboelectromagnetic phenomena in an operating disk drive will help to increase lubricant lifetime.

5. Conclusions

Fresh $a\text{-CH}_x$ films and $a\text{-CH}_x$ films oxidized by either O₂ or ambient air, are both chemically inert to decomposition of $(\text{CF}_3\text{CF}_2)_2\text{O}$ or $\text{CF}_3\text{CH}_2\text{OH}$. Both adsorb molecularly at low temperatures and desorb reversibly during heating. Both molecules are, however, sensitive to electrons, which induce decomposition and the deposition of fluorine onto the surface of the $a\text{-CH}_x$ films. This electron-stimulated decomposition can be avoided by a negative bias of the sample preventing the

impingement of ambient electrons. These results imply that the electron stimulated decomposition of fluorocarbon lubricants on hard disk surfaces can occur and may contribute to fluorocarbon lubricant decomposition.

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