

Adsorption of Fluorinated Ethers and Alcohols on Fresh and Oxidized Carbon Overcoats for Magnetic Data Storage

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Temperature programmed desorption has been used to study the desorption kinetics and desorption energies of perfluorodiethylether, $(CF_3CF_2)_2O$, and 2,2,2-trifluoroethanol, CF_3CH_2OH , adsorbed on fresh and oxidized hydrogenated amorphous carbon ($a-CH_x$) films. $(CF_3CF_2)_2O$ and CF_3CH_2OH serve as models for the ether backbone and hydroxyl end-groups of Fomblin Zdol, the lubricant most commonly used to lubricate the surfaces of amorphous carbon overcoats on magnetic data storage hard disks. Our measurements clearly reveal, for the first time, the effects of surface oxidation on the adsorption of fluorocarbon lubricants such as Fomblin Zdol on $a-CH_x$ films. Oxidation of the $a-CH_x$ surface increases the desorption energy of CF_3CH_2OH but has no observable impact on the desorption energy of $(CF_3CF_2)_2O$. These results support the suggestion that the alcohols interact with the surface via hydrogen bonding. From a practical perspective, these results imply that the oxidation of the fresh $a-CH_x$ film may serve as a means to control or tailor the $a-CH_x$ surface to optimize the properties of the lubricant–overcoat interface in hard disks.

1. Introduction

The hard disks used for magnetic data storage are typically protected from the environment and from contact with the read–write head by a thin hydrogenated or nitrogenated amorphous carbon film ($a-CH_x$ and $a-CN_x$, respectively) that is coated with a thin layer of perfluoropolyalkylether (PFPE) lubricant. The chemical interactions between the lubricant and the carbon overcoat dictate the tribological performance of the head–disk interface. The work described in this paper explores the fundamental chemical mechanisms by which the PFPE lubricants interact with the $a-CH_x$ overcoat and focuses on the effects of $a-CH_x$ overcoat oxidation on these interactions.

In the last stages of disk manufacturing, the $a-CH_x$ film is deposited on the disk surface by vacuum sputter deposition to a thickness of $<50 \text{ \AA}$. The disk is then removed from vacuum, and the PFPE lubricant is applied by dipping the disk into a solution of the lubricant and then withdrawing it at a constant rate to leave a $5\text{--}20 \text{ \AA}$ film of lubricant on the surface. The need to increase the density of data stored on the disk surfaces creates an increasing need to reduce the gap between the read–write head and the magnetic layer. This, in turn, requires increased tolerance on the specifications to which the $a-CH_x$ and the PFPE lubricant films are prepared.^{1–7} Currently, the lubricant dip-coating process is perhaps one of the most poorly characterized steps in disk manufacturing because it requires the removal of the disk from the vacuum environment in which it is made, and thus, there is exposure to air and air-borne contamination prior to application of the lubricant film. As a consequence, the $a-CH_x$ surface must become oxidized prior to lubricant deposition, but the effects of this surface oxidation have never been studied systematically.

Vapor-phase lubrication is one possible alternative technology for the deposition of lubricants onto the surfaces of hard disks without prior exposure of the $a-CH_x$ overcoat to air. In a vapor lubrication process, lubricant application to the surface would be integrated into the vacuum processing steps. Among its potential advantages are improved reproducibility to allow the preparation of lubricant films to higher tolerances, the elimination of solvents from the media production process, and the elimination of one of the disk handling steps needed in the current process. Vapor-phase lubrication will, however, change the nature of the interface between the $a-CH_x$ overcoat and the lubricant by eliminating the oxidation of the $a-CH_x$ overcoat surface prior to lubricant deposition. Thus, vapor lubrication may change some of the properties of the lubricant film and its interactions with the $a-CH_x$ overcoat. This must be understood in order to develop a vapor-phase lubrication process that mimics the desirable properties of the disk surface to as great an extent as possible.

The lubricant film on the disk surface must be very thin ($<20 \text{ \AA}$) and must have a number of properties to protect the disk surface from damage due to contact with the read–write head. The lubricant must have some component that is bonded to the surface of the disk to prevent it from flowing off the disk surface under the centrifugal and wind-shear forces that act on the film while the disk is spinning. At the same time, the lubricant must have some mobility to allow it to flow into regions of the surface that may have been depleted of lubricant during the head–disk contact. One of the most common perfluoropolyalkylether lubricants is Fomblin Zdol, which has a fluorinated ether backbone and hydroxyl end-groups.^{3,4} Fomblin Zdol has the molecular structure



$$\frac{x}{y} = \frac{2}{3} \text{ to } 1$$

Previous studies have shown that the ether backbone and hydroxyl end-groups of Fomblin Zdol bind to amorphous carbon films by different mechanisms. The ether backbone interacts with the $a-CH_x$ film via electron donation from the lone pairs on the oxygen atoms. The hydroxyl end-groups interact with the overcoat by hydrogen bonding. In addition, the lubricants interact with

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(1) Casiraghi, C.; Ferrari, A. C.; Ohr, R.; Chu, D.; Robertson, J. *Diamond Relat. Mater.* **2004**, *13* (4–8), 1416.

(2) Ferrari, A. C. *Surf. Coat. Technol.* **2004**, *180–181*, 190.

(3) Hsu, S. M. *Tribol. Int.* **2004**, *37* (7), 537.

(4) Sinha, S. K.; Kawaguchi, M.; Kato, T.; Kennedy, F. E. *Tribol. Int.* **2003**, *36* (4–6), 217.

(5) Tan, A. H.; Chang, J. K. *Diamond Relat. Mater.* **2005**, *14* (2), 226.

(6) Yamamoto, T.; Hyodo, H. *Tribol. Int.* **2003**, *36* (4–6), 483.

(7) Zhu, H.; Bogy, D. B. *Tribol. Int.* **2004**, *37* (2), 193.

the surface via van der Waals attractions. These are the interactions that give the current lubricants their desirable balance of properties on the surface.^{8–14} As mentioned, in current disk fabrication, the surface of the *a*-CH_x overcoat is exposed to air prior to application of the lubricant by dip-coating. Thus, the PFPE lubricant is interacting with a surface that is partially oxidized. In a vapor lubrication process, the lubricant film might be applied to a *a*-CH_x film that has not been oxidized, and this will undoubtedly have an impact on the properties of the surface and its interaction with the lubricant. To avoid this might require that the disk surface be partially oxidized under controlled conditions before vapor lubrication. Development of a vapor lubrication process requires that one understand the effects of *a*-CH_x surface oxidation on its interaction with the lubricant and understand the oxidation kinetics of fresh *a*-CH_x overcoats.

The principle contribution of the work described in this paper is the study and understanding of the effects of *a*-CH_x surface oxidation on the adsorption of fluorinated ethers and alcohols. Past work has used perfluorodiethyl ether, (CF₃CF₂)₂O, as a model for the ether linkage in the backbone of Fomblin lubricants and 2,2,2-trifluoroethanol, CF₃CH₂OH, as a model for the hydroxyl end-groups in Fomblin Zdol.^{8–11,15} In this work the effect of surface oxidation on the bonding of PFPE lubricant to *a*-CH_x films has been studied by comparing the desorption energies, Δ*E*_{des}, of (CF₃CF₂)₂O and CF₃CH₂OH on fresh *a*-CH_x films with those on air-exposed *a*-CH_x films and O₂-exposed *a*-CH_x films. The desorption energy of CF₃CH₂OH is dependent on the degree of oxidation of the surface, while the interaction of (CF₃CF₂)₂O with *a*-CH_x is independent of its degree of oxidation. The fact that the desorption energy of CF₃CH₂OH increases with oxidation of the surface is consistent with CF₃-CH₂OH interacting with the surface via hydrogen bonding.^{8–14} The results support the possibility of using surface oxidation to control the bonding and properties of lubricants such as Fomblin Zdol on the *a*-CH_x surface. These fundamental studies help to probe the bonding mechanism of perfluoropolyalkylether lubricants with *a*-CH_x film surfaces and also provide the types of insights needed to help design a vapor-phase lubrication process for disk surfaces.

2. Experimental Procedures

All experiments were performed in an ultrahigh vacuum (UHV) chamber with a base pressure of <10⁻⁹ Torr. The UHV chamber was designed and constructed with the express purpose of studying the vapor-phase lubrication 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⁺ ion sputter gun for substrate cleaning, a DC magnetron sputter source (MAK130VCFUHV, 1.3" graphite target, US Inc.) for *a*-CH_x film deposition, and one leak valve for the introduction of air or O₂ for oxidation of the *a*-CH_x films. In addition, it is equipped with gas flow controllers to allow introduction of a mixture of Ar and CH₄ into the lower level at constant pressure during the sputter deposition process.

The upper level of the UHV chamber is used for surface analysis of films prepared in the lower level and is pumped with a cryo pump and 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). In addition, the upper level is equipped with a quadrupole mass spectrometer (Q200MS, Ametek) for temperature programmed desorption (TPD) studies of (CF₃CF₂)₂O or CF₃CH₂OH adsorbed on the surface of the *a*-CH_x film.

The sample was a Ni foil substrate coated with the *a*-CH_x film and could move between the two levels on a manipulator that extends through the gate valve, when it is open. 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. The nickel foil substrate was machine-punched to produce an 11 mm diameter disk that was mounted to 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 that 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 mTorr during the deposition process using a 10% CH₄/(Ar + CH₄) gas mixture. Raman spectroscopy was performed by removing the sample from the UHV chamber. The final deposition conditions were identified by producing films at a variety of different pressures, sputter source powers, CH₄ concentrations, and substrate temperatures. The conditions chosen were those that yielded *a*-CH_x films with Raman spectra closest to those of *a*-CH_x films produced for commercial use.

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. The film thickness was determined to be about 70 Å based on the attenuation of the signal from the Ni substrate. 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 air at room temperature for 1 h. The chamber was then evacuated to <10⁻⁹ Torr for ~12 h for XPS and TPD measurements. The *a*-CH_x surfaces were also modified by low pressure exposure to pure O₂ rather than air. The O₂-exposed *a*-CH_x film was prepared by introducing 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 directly in front of a stainless steel dosing tube that was attached to a leak valve. The distance between the *a*-CH_x film and the end of the dosing tube was approximately 4 cm. 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 for ~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 ~6 and ~20%, respectively. The air-exposed surface and O₂-exposed surface were then used as substrates for subsequent TPD studies of (CF₃CF₂)₂O or CF₃CH₂OH.

The adsorption of (CF₃CF₂)₂O or CF₃CH₂OH onto the *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 to -80 V to avoid adsorbate decomposition by ambient electrons. Perfluorodiethylether [(CF₃CF₂)₂O, Strem Chemical, 90%] and 2,2,2-trifluoroethanol [CF₃CH₂OH, TCI-G.R.] were each placed in a glass vial 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. To prevent any irreversible damage to the *a*-CH_x film during heating, the upper temperature was limited to 320 K in the TPD experiments, well below the temperature at which the

(8) Lei, R. Z.; Gellman, A. J. *Langmuir* **2000**, *16* (16), 6628–6635.

(9) Lei, R. Z.; Gellman, A. J. *Langmuir* **2001**, *17* (20), 6240–6247.

(10) Shukla, N.; Gellman, A. J. *J. Vac. Sci. Technol., A* **2000**, *18* (5), 2319.

(11) Shukla, N.; Gellman, A. J.; Gui, J. *Langmuir* **2000**, *16* (16), 6562–6568.

(12) Zhang, B.; Nakajima, A. *Microsyst. Technol.* **2005**, *2005* (11), 875–880.

(13) Khurshudov, A.; Waltman, R. J. *Tribol. Lett.* **2001**, *11* (3–4), 143.

(14) Waltman, R. J.; Khurshudov, A. G. *Tribol. Lett.* **2002**, *13* (3), 197.

(15) Shukla, N.; Gui, J.; Gellman, A. J. *Langmuir* **2001**, *17* (8), 2395–2401.

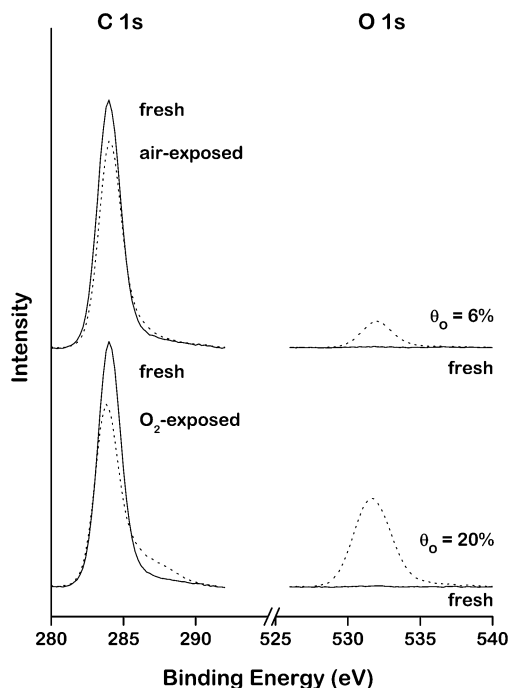


Figure 1. C 1s and O 1s XPS spectra of $a\text{-CH}_x$ films obtained immediately after deposition and after exposure to air (1 atm ambient air for 1 h) and O_2 (8×10^{-4} Torr for 2 h) at room temperature. The high binding energy shoulder on the C 1s peak reveals the presence of oxidized carbon species (CO_x). Exposure to air and O_2 results in oxidation of the $a\text{-CH}_x$ film to $\sim 6\%$ and $\sim 20\%$ oxygen content, respectively.

$a\text{-CH}_x$ film was deposited or at which it would begin to undergo decomposition. The TPD spectra were highly reproducible, indicating that the $a\text{-CH}_x$ film surface was unchanged by repeated adsorption and desorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$.

After TPD of $(\text{CF}_3\text{CF}_2)_2\text{O}$ or $\text{CF}_3\text{CH}_2\text{OH}$, the $a\text{-CH}_x$ film surface was examined by XPS to determine whether any residual fluorine was left on the surface as a result of decomposition. Fluorine did appear on the surface when the sample was held at ground potential during the TPD experiment. This is due to partial decomposition of the fluorocarbons by electrons emitted by the ionizer of the mass spectrometer and by the ion pressure gauge. This decomposition was eliminated by biasing the sample to -80 V during the experiments. Once the sample was biased, adsorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$ was completely reversible, and both desorbed completely during heating.

3. Results

3.1. In Situ Study of $a\text{-CH}_x$ Film Oxidation. Prior to the study of the adsorption and desorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$ or $\text{CF}_3\text{-CH}_2\text{OH}$ from fresh and oxidized $a\text{-CH}_x$ films, oxidation of the $a\text{-CH}_x$ films was studied during exposure to O_2 or air. The details of that study and of the kinetics of $a\text{-CH}_x$ oxidation are to be published elsewhere.¹⁶ The surface composition of the $a\text{-CH}_x$ films was determined in situ by XPS immediately before and after oxidation. Figure 1 shows the C 1s and O 1s XPS spectra of two fresh $a\text{-CH}_x$ films. No oxygen was observed on the fresh $a\text{-CH}_x$ films, indicating that the oxygen concentration was less than 0.5%.

For the purposes of this work, we have used $a\text{-CH}_x$ surfaces saturated with oxygen by exposure to O_2 at low pressures (8×10^{-4} Torr) or to air at atmospheric pressure. Figure 1 shows the C 1s XPS spectra of $a\text{-CH}_x$ after exposure to air (1 atm ambient air for 1 h at 300 K) or to O_2 (8×10^{-4} Torr for 2 h at 300 K).

Exposure to air or O_2 results in the formation of oxidized carbonaceous species such as C-OH , C-O-C , and C=O on the $a\text{-CH}_x$ film surface.¹⁷⁻¹⁹ The oxidation of the carbon is revealed by the appearance of the high binding energy shoulder at 285–290 eV in the C 1s spectra. The O 1s photoemission spectra also reveal the presence of oxygen on the $a\text{-CH}_x$ film surface and can be used to quantify the oxygen concentration of the film. The oxygen content, θ_{O} , was calculated using

$$\theta_{\text{O}} = \frac{A_{\text{O}}/0.71}{A_{\text{O}}/0.71 + A_{\text{C}}/0.30} \times 100\%$$

where A_{O} and A_{C} are the integrated areas under the O 1s and C 1s XPS peaks, respectively. The 1 atm air exposure results in an oxygen coverage of $\theta_{\text{O}} = 6.0 \pm 0.5\%$ on the $a\text{-CH}_x$ surfaces, while the low pressure O_2 exposure (8×10^{-4} Torr, 2 h) leads to an oxygen content of $\theta_{\text{O}} = 20.0 \pm 0.5\%$. The low level of oxygen uptake is observed whether we expose the surface to clean, dry air or ambient laboratory air, so it is not associated with contaminants or water vapor. It is surprising that the exposure of the $a\text{-CH}_x$ films to low pressures ($< 10^{-3}$ Torr) of O_2 leads to a higher oxygen content than the exposure to 1 atm of air. To try to eliminate the possible role of air-borne contaminants, the $a\text{-CH}_x$ film was also exposed to 1 atm of clean air ($\text{H}_2\text{O} < 2$ ppm, total hydrocarbon < 0.1 ppm, CO and $\text{CO}_2 < 1$ ppm) at room temperature for 1 h. The oxygen coverage of the $a\text{-CH}_x$ exposed to clean air was $\theta_{\text{O}} = 5\%$, still much lower than the oxygen coverage after exposure to low O_2 pressures. This cannot be explained in the framework of any simple adsorption model, all of which would predict that the oxygen content should increase monotonically with oxygen pressure. Nonetheless, this has been observed repeatedly during exposure to high pressure air or low pressure O_2 under a variety of conditions.¹⁶ The result suggests that during the exposure to high pressures of air, some of the most easily oxidized surface carbon atoms are fully oxidized to species such as carbon dioxide that desorb from the surface. This then removes some of the oxygen adsorbed during the initial uptake and leaves a surface that is inert to further oxidation.

3.2. Electron Induced Decomposition of Perfluoropolyalkylether Model Compounds. Fluorocarbons are notoriously sensitive to electron induced decomposition on surfaces.²⁰⁻²² Prior to performing extensive adsorption and desorption studies, it was necessary to determine the extent to which the fluorocarbons were likely to decompose on the surface as a result of electrons emanating from the ionizer of the mass spectrometer or from the ion gauge used to measure the pressure in the UHV chamber. Initially, the adsorption and desorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$ was studied on the surface of an $a\text{-CH}_x$ film that was grounded or unbiased with respect to the chamber. Adsorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$ onto the $a\text{-CH}_x$ surface was accomplished by leaking $(\text{CF}_3\text{CF}_2)_2\text{O}$ vapor into the UHV chamber while the $a\text{-CH}_x$ film was held at ~ 80 K. After adsorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$, the $a\text{-CH}_x$ sample was positioned ~ 2 mm from the aperture of the mass spectrometer. The desorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$ was conducted by heating the sample to 260 K at a constant rate of 2 K/s while monitoring the

(17) Filik, J.; May, P. W.; Pearce, S. R. J.; Wild, R. K.; Hallam, K. R. *Diamond Relat. Mater.* **2003**, *12*, 974.

(18) Haasz, A. A.; Chiu, S.; Pierre, J. E.; Gudimenko, Y. I. *J. Vac. Sci. Technol., A* **1996**, *14* (1), 184.

(19) Kian Ping Loh, X. N. X.; Yang, S. W.; Zheng, J. C. *J. Phys. Chem. B* **2002**, *106*, 5230.

(20) Nakayama, K. *Surf. Coat. Technol.* **2004**, *188-189*, 599.

(21) Jong-Liang, L.; Bhatia, C. S.; Yates, John, T., Jr. *J. Vac. Sci. Technol., A* **1995**, *13* (2), 163-168.

(22) Jong-Liang, L.; Yates, John, T., Jr. *J. Vac. Sci. Technol., A* **1995**, *13* (4), 1867-1871.

(16) Gellman, A. J.; Yun, Y. *Proceedings of World Tribology Congress III 2005*, WTC2005-63165.

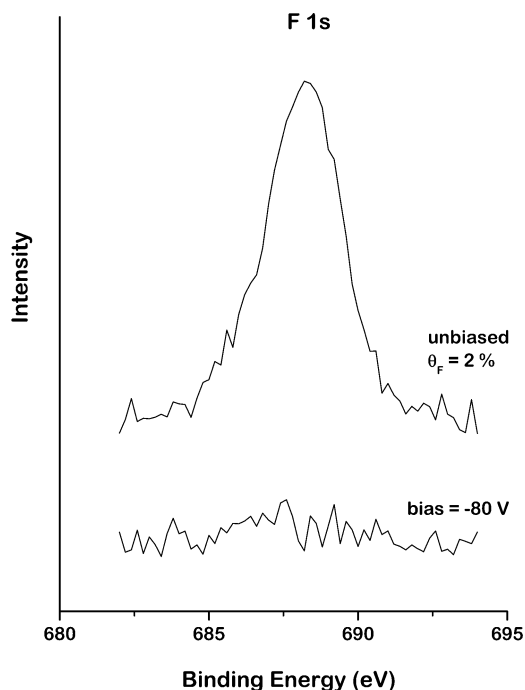


Figure 2. F 1s XPS spectra of $a\text{-CH}_x$ obtained immediately after TPD of $(\text{CF}_3\text{CF}_2)_2\text{O}$. The appearance of $\sim 2\%$ fluorine on the surface of the unbiased sample ($a\text{-CH}_x$ is grounded) indicates decomposition of $(\text{CF}_3\text{CF}_2)_2\text{O}$. The lack of fluorine on the surface following adsorption and desorption from a surface biased at -80 V indicates complete and reversible adsorption and desorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$. The decomposition on the unbiased sample must be induced by ambient electrons coming from the ionizer of the mass spectrometer and from the ion pressure gauge.

desorbing species with the mass spectrometer. The desorption rate dropped back to almost zero at ~ 200 K, indicating the completion of molecular desorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$. The $a\text{-CH}_x$ film was then held at 300 K to obtain an XP spectrum to determine whether $(\text{CF}_3\text{CF}_2)_2\text{O}$ had desorbed completely or decomposed to deposit some fluorine on the surface. Figure 2 shows the F 1s spectrum obtained from the surface following desorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$ and clearly reveals the presence of residual fluorine on the unbiased sample, indicating that some decomposition occurred during the process of adsorption and desorption. The exposure of $(\text{CF}_3\text{CF}_2)_2\text{O}$ was ~ 0.4 L, which generated a coverage of ~ 0.5 monolayers as determined by the analysis described in the next section. The $a\text{-CH}_x$ film composition contains $\sim 2\%$ fluorine following $(\text{CF}_3\text{CF}_2)_2\text{O}$ desorption. The decomposition of $(\text{CF}_3\text{CF}_2)_2\text{O}$ is caused by ambient electrons emitted from the filaments of the mass spectrometer and ion pressure gauge and can be prevented by negative biasing of the sample. Similar experiments were performed using both $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{-CH}_2\text{OH}$ but with the sample biased at -80 V with respect to the chamber. Figure 2 shows the F 1s XPS spectrum of the $a\text{-CH}_x$ film after desorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$ with the sample biased at -80 V. The absence of residual fluorine indicates completely reversible molecular desorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$. Biasing the sample by -80 V prevents stray electrons from hitting the sample surface and inducing decomposition of the adsorbed fluorocarbons. All subsequent measurements of fluorocarbon adsorption and desorption were made with the sample biased at -80 V.

3.3. Fluorocarbon Desorption from Fresh and Oxidized $a\text{-CH}_x$. It is known that the surfaces of the $a\text{-CH}_x$ films are chemically heterogeneous. The surfaces expose carbon atoms with different hybridization (sp^2 and sp^3) and different degrees of hydrogenation.^{23–25} Exposure to air and O_2 further complicates

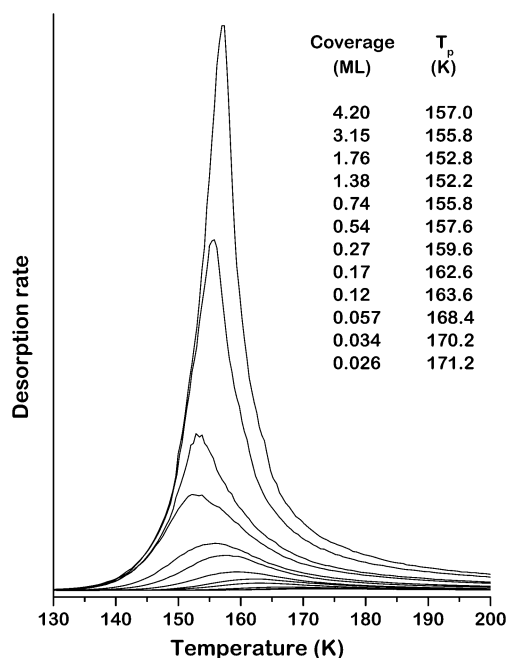


Figure 3. TPD spectra of $\text{CF}_3\text{CH}_2\text{OH}$ from the surface of a fresh $a\text{-CH}_x$ film with initial coverages varying from $\sim 2\%$ of a monolayer to >1 monolayer (ML). At coverages below 1 ML, the peak desorption temperatures decrease with increasing coverage, reflecting the heterogeneity 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 $m/q = 31$ for $\text{CF}_3\text{CH}_2\text{OH}$. Additional spectra were obtained by monitoring the signals at $m/q = 69$ (CF_3^+) and $m/q = 29$ (COH^+) and indicate that $\text{CF}_3\text{CH}_2\text{OH}$ desorbs molecularly. The TPD spectra of $\text{CF}_3\text{CH}_2\text{OH}$ on air-exposed $a\text{-CH}_x$ and O_2 -exposed $a\text{-CH}_x$ are qualitatively similar to these.

the surface composition by generating partially oxidized carbon species such as C-O-C , C-OH , and C=O on the $a\text{-CH}_x$ surfaces.^{17–19} The oxidation of the surface must influence its interaction with adsorbed species, but it is not clear to what extent or in what way. The presence or absence of oxygen at the surface of the $a\text{-CH}_x$ film must influence the interactions of PFPE lubricants with the surfaces and thus give rise to differences in performance of lubricants applied by dip-coating following air exposure and lubricants applied from the vapor phase in a vacuum.

The adsorption of PFPE lubricant on $a\text{-CH}_x$ films was emulated by the adsorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$ or $\text{CF}_3\text{CH}_2\text{OH}$ as models for the fluoroether backbone and the hydroxyl end-groups, respectively. The heterogeneity of the bonding of PFPE lubricants with $a\text{-CH}_x$ films is revealed by the TPD spectra of $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$ on fresh $a\text{-CH}_x$ films, air-exposed $a\text{-CH}_x$ films, and $a\text{-CH}_x$ films exposed to O_2 . Figure 3 illustrates the TPD spectra of $\text{CF}_3\text{CH}_2\text{OH}$ adsorbed on the fresh $a\text{-CH}_x$ film, at coverages ranging from $\sim 2\%$ of a monolayer to greater than one monolayer. The spectra illustrated in Figure 3 were obtained by monitoring the signal at $m/q = 31$ and were accompanied by spectra for $m/q = 29$ and 69. Similar spectra were obtained for $(\text{CF}_3\text{CF}_2)_2\text{O}$ desorption but by monitoring the signals at m/q ratios of 69 (CF_3^+), 50 (CF_2^+), and 31 (CF^+). The TPD spectra of $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$ adsorbed on fresh $a\text{-CH}_x$ films, air-exposed $a\text{-CH}_x$ films, and O_2 -exposed $a\text{-CH}_x$ films are all qualitatively similar. At low submonolayer coverages, there is a single desorption peak. As the coverage of the adsorbate is increased, the peak desorption temperature decreases monotonically.

(23) Gao, G. T.; Mikulski, P. T.; Chateaufneuf, G. M.; Harrison, J. A. *J. Phys. Chem. B* **2003**, *107* (40), 11082.

(24) Lamperti, A.; Ossi, P. M. *Appl. Surf. Sci.* **2003**, *205* (1–4), 113.

(25) Li Hong, Z.; Hao, G.; Jian Ping, W. *J. Appl. Phys.* **2002**, *92* (6), 2962.

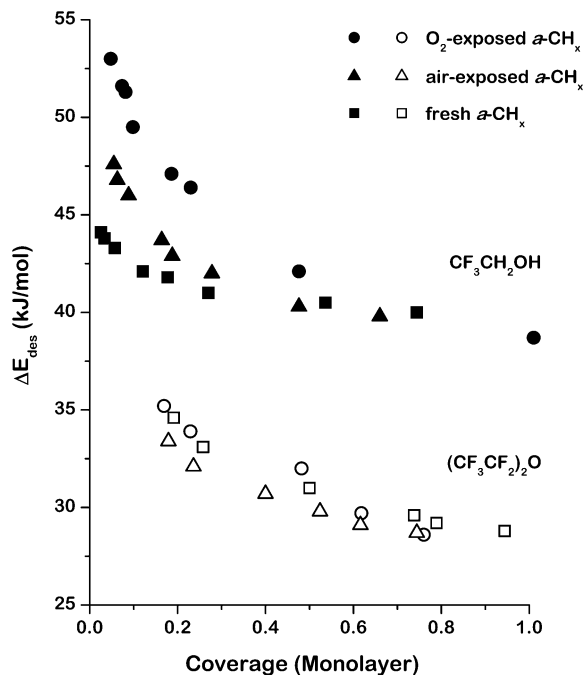


Figure 4. Desorption energies are plotted as a function of adsorbate coverage for $\text{CF}_3\text{CH}_2\text{OH}$ on fresh (■), air-exposed (▲), and O_2 -exposed (●) $a\text{-CH}_x$ films and for $(\text{CF}_3\text{CF}_2)_2\text{O}$ adsorbed on fresh (□), air-exposed (△), and O_2 -exposed (○) $a\text{-CH}_x$ films. The desorption energies all decrease monotonically with increasing coverage, reflecting the heterogeneity of the $a\text{-CH}_x$ surface. The desorption energy of $(\text{CF}_3\text{CF}_2)_2\text{O}$ is insensitive to the oxidation of $a\text{-CH}_x$, either by air or O_2 . The desorption energy of $\text{CF}_3\text{CH}_2\text{OH}$ is, however, sensitive to surface oxidation. The coverages were estimated using the areas under the $\text{CF}_3\text{CH}_2\text{OH}$ and $(\text{CF}_3\text{CF}_2)_2\text{O}$ monolayer desorption spectra. The monolayer desorption spectrum was chosen to be the one whose peak temperature reaches the minimum.

cally, and the peak broadens. At multilayer coverages, the peaks take a shape characteristic of desorption with zero-order kinetics with peak temperatures that begin to increase with coverage and low temperature leading edges that overlap one another. This behavior has been observed many times in studies of the desorption of these compounds from various types of amorphous carbon films and is attributed to the heterogeneity of the surface.^{8,9,26}

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 as is commonly observed on homogeneous single crystalline surfaces.^{27,28} The peak desorption temperature decreases monotonically with increasing coverage until the onset of multilayer desorption. The area under the TPD spectra was used as a measure of the coverage. As a consequence of the surface heterogeneity, however, the coverage of the adsorbed layer is difficult to calibrate because it is not possible to determine the coverage corresponding to one monolayer. Thus, the area under the monolayer TPD spectrum was estimated to be the area under the peak with the minimum peak desorption temperature.

3.4. Effects of $a\text{-CH}_x$ Oxidation on Fluorocarbon Adsorption. In the final steps of their production, magnetic data storage hard disks coated with $a\text{-CH}_x$ films are removed from the vacuum, unavoidably exposed to air, and then dipped into a solution of PFPE lubricant. Exposure to ambient air results in the immediate oxidation of the $a\text{-CH}_x$ film and, therefore, the generation of oxidized carbon species such as C-OH , C-O-C , and C=O on

the $a\text{-CH}_x$ film surfaces. The effect of oxidation on the bonding of the PFPE lubricant with the $a\text{-CH}_x$ films has been studied by examining the effect of surface oxidation on the adsorption and desorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$. The interaction of the PFPE lubricant with oxidized $a\text{-CH}_x$ films was quantified by using TPD spectra to estimate the desorption energies, ΔE_{des} , of $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$ on both fresh and oxidized $a\text{-CH}_x$ surfaces. The ΔE_{des} values of $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$ as a function of coverage were estimated from the peak desorption temperatures, T_p , using Redhead's equation

$$\frac{\Delta E_{\text{des}}}{RT_p^2} = \frac{\nu}{\beta} \exp\left(\frac{-\Delta E_{\text{des}}}{RT_p}\right)$$

with a pre-exponential factor of $\nu = 10^{13} \text{ s}^{-1}$ and a heating rate of $\beta = 2 \text{ K/s}$.^{29,30} The peak desorption temperatures measured in TPD experiments are reproducible to within $\pm 2 \text{ K}$ and thus propagate random errors of roughly $\pm 2\%$ into the estimated ΔE_{des} as indicated by the scatter in the values of ΔE_{des} plotted in Figure 4. Because the intent of this investigation is to compare the ΔE_{des} molecules on fresh, air-exposed, and O_2 -exposed $a\text{-CH}_x$ films, systematic errors introduced by the assumed magnitude of the desorption pre-exponent are not important.

The values of the desorption energies, ΔE_{des} , of $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$ as functions of coverage on the fresh, air-exposed, and O_2 -exposed $a\text{-CH}_x$ films are plotted in Figure 4. As expected, based on the coverage dependence of the peak desorption temperatures, the values of ΔE_{des} decrease smoothly and monotonically with increasing coverage on all surfaces. This has been observed in several previous studies of the desorption of these compounds from similar surfaces.^{8,9,26} The second feature that is clearly revealed by Figure 4 is that the ΔE_{des} of $\text{CF}_3\text{-CH}_2\text{OH}$ is higher than that of $(\text{CF}_3\text{CF}_2)_2\text{O}$. Again, this is consistent with all prior observations.^{8,9,26} The unique feature revealed by the data in Figure 4 is the effect of surface oxidation on the bonding of the fluorocarbons to the surface. In the case of $(\text{CF}_3\text{-CF}_2)_2\text{O}$, oxidation of the surface has only a negligible effect on the values of ΔE_{des} . In the case of $\text{CF}_3\text{CH}_2\text{OH}$, however, it is obvious that oxidation of the surfaces increases the value of ΔE_{des} at coverages below one-half monolayer. It is also clear that the increase in ΔE_{des} is greatest for the more heavily oxidized, O_2 -exposed $a\text{-CH}_x$ surface.

4. Discussion

Prior studies of the adsorption of $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$ on amorphous carbon ($a\text{-C}$) films have used $a\text{-CH}_x$, $a\text{-CN}_x$, and diamond-like carbon films that have been provided by commercial manufacturers of data storage disks. Those studies lead to the suggestion that the ethers bond to the surfaces through donation of lone pair electrons from the oxygen atoms while the alcohols adsorb via hydrogen bonding. However, all were performed on surfaces that had been exposed to air and thus were partially oxidized. They have not provided any insight into the bonding of PFPE lubricants to the fresh $a\text{-CH}_x$ surfaces that would be used in a vapor-phase lubrication process.^{8,9,31-34}

(29) Redhead, P. A. *Vacuum* **1962**, *12* (4), 203.

(30) Zhdanov, V. P. *Surf. Sci. Rep.* **1991**, *12* (5), 185.

(31) Cornaglia, L.; Gellman, A. J. *J. Vac. Sci. Technol., A* **1997**, *15* (5), 2755.

(32) Tagawa, N.; Mori, A. *IEEE Trans. Magn.* **2005**, *41* (2), 825.

(33) Paserba, K.; Shukla, N.; Gellman, A. J.; Gui, J.; Marchon, B. *Langmuir* **1999**, *15* (5), 1709.

(34) Jhon, M. S.; Izumisawa, S.; Guo, Q.; Hsia, Y. T. *Simulation of Perfluoropolyether Lubricant Films*; American Society of Mechanical Engineers: Cancun, Mexico, 2002; p 77.

(26) Shukla, N.; Gellman, A. J. *J. Vac. Sci. Technol., A* **2000**, *18* (5), 2319.

(27) Paserba, K. R.; Gellman, A. J. *Phys. Rev. Lett.* **2001**, *86* (19), 4338.

(28) Paserba, K. R.; Gellman, A. J. *J. Chem. Phys.* **2001**, *115* (14), 6737.

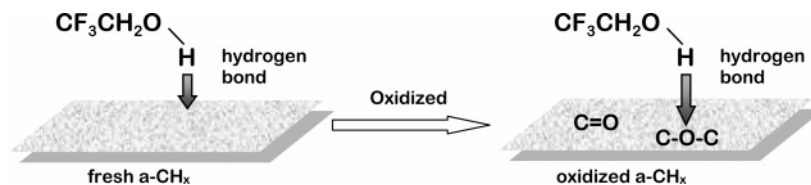


Figure 5. Proposed models for the interaction of $\text{CF}_3\text{CH}_2\text{OH}$ with fresh and oxidized $a\text{-CH}_x$ films. The hydroxyl end group binds to the $a\text{-CH}_x$ surface through a hydrogen bond. Exposure to air or O_2 forms oxidized carbon species such as $\text{C}=\text{O}$, $\text{C}-\text{OH}$, and $\text{C}-\text{O}-\text{C}$ on the $a\text{-CH}_x$ film surface. These create sites at which $\text{CF}_3\text{CH}_2\text{OH}$ can bind with higher affinity than on the fresh $a\text{-CH}_x$ film.

One of the features of the dependence of ΔE_{des} on adsorbate coverage that is common to past studies is that the value of ΔE_{des} decreases monotonically with increasing adsorbate coverage. The decrease in ΔE_{des} as a function of coverage is understood to arise from the heterogeneity of the surface. Initially, adsorbed molecules occupy sites with the highest ΔE_{des} and then, as the coverage is increased, they sequentially occupy sites with monotonically decreasing values of ΔE_{des} until the molecules begin to adsorb in multilayers. In principle, the decrease in the value of ΔE_{des} with increasing coverage could be attributed to repulsive interactions between adsorbed molecules. Studies of $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$ desorption from the surface of graphite have, however, shown that this is not the case.¹⁵ The basal plane of graphite exposes a homogeneous surface for adsorption, and the desorption kinetics from that surface reveal clearly resolvable monolayer and multilayer desorption features. Furthermore, the desorption feature at submonolayer coverages reveals a peak desorption temperature that increases slightly with coverage, indicating that the natural interactions between adsorbed $(\text{CF}_3\text{CF}_2)_2\text{O}$ molecules or between adsorbed $\text{CF}_3\text{CH}_2\text{OH}$ molecules are weakly attractive. Thus, the decreases in the value of ΔE_{des} with increasing coverage revealed in Figure 4 can be attributed to surface heterogeneity. If anything, those data underestimate the degree of heterogeneity because the measured values of ΔE_{des} include the contributions from the inherently attractive intermolecular interactions.

The results of the current study show that ΔE_{des} of $\text{CF}_3\text{CH}_2\text{OH}$ is sensitive to the oxidation of the $a\text{-CH}_x$ film. Oxidation of the surface increases ΔE_{des} , and it appears that ΔE_{des} increases with increasing oxidation. The results of previous studies have suggested that $\text{CF}_3\text{CH}_2\text{OH}$ interacts with the surface through hydrogen bonding of its hydroxyl group. That suggestion was based on the observation that the desorption energies of the fluorinated alcohols are higher than those of their hydrocarbon analogues.^{11,26} It does, of course, raise the question of the nature of the sites to which the hydroxyl groups are hydrogen bonded. Exposure of $a\text{-CH}_x$ films to air or O_2 generates oxidized carbon species such as $\text{C}-\text{O}-\text{C}$, $\text{C}-\text{OH}$, and $\text{C}=\text{O}$ on the surfaces of $a\text{-CH}_x$.¹⁷⁻¹⁹ It is likely that these are proton accepting sites to which $\text{CF}_3\text{CH}_2\text{OH}$ can bind with greater affinity than on the fresh $a\text{-CH}_x$ film, as illustrated schematically in Figure 5. The net effect of surface oxidation is to increase the strength of bonding with the hydroxyl end-groups of PFPE lubricants such as Fomblin Zdol.

Our results show that the ΔE_{des} of $(\text{CF}_3\text{CF}_2)_2\text{O}$ is insensitive to oxidation of the $a\text{-CH}_x$ film. This may be rationalized by our understanding of the bonding of $(\text{CF}_3\text{CF}_2)_2\text{O}$ to $a\text{-CH}_x$ surfaces. The results of previous studies suggest that ethers bind to $a\text{-C}$ surfaces of various types through a dative bond formed by

donation of the lone pair electrons on the oxygen atom.^{8-11,15,26,33} This suggestion is based on the observation that fluorocarbon ethers all have lower values of ΔE_{des} than their hydrocarbon counterparts. This observation has been made on a variety of different types of $a\text{-C}$ surfaces. Given this interaction mechanism and the observation that ΔE_{des} is unaffected by oxidation of the $a\text{-CH}_x$ film, it seems quite likely that the ethers are not interacting with the oxidized sites on the surface at all.

Our measurements clearly reveal, for the first time, the effects of surface oxidation on the adsorption of fluorocarbons and on the interaction of $a\text{-CH}_x$ films with PFPE lubricants used in magnetic data storage applications. Although these effects have been assumed to exist, they have not been observed directly or quantified. The results of this work have several implications for the development of vapor-phase disk lubrication technologies. First, the fact that oxidation of the $a\text{-CH}_x$ surface influences its interactions with the PFPE lubricant means that to reproduce the lubricant-overcoat interactions of current disks, it will be necessary to controllably oxidize the disk surface prior to application of the lubricant. The second implication is that because surface oxidation affects the hydroxyl end-groups and the ether backbones of PFPE lubricants differently, the oxidation process offers a means of controlling or tailoring the surface properties to optimize the properties of the lubricant-overcoat interface. Vapor lubrication aside, this work provides valuable insight into the bonding of hydrocarbons to carbon films.

5. Conclusion

Vapor-phase lubrication has been emulated by preparing fresh and oxidized $a\text{-CH}_x$ films and then adsorbing $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$ as models of the different functional groups in PFPE lubricants such as Fomblin Zdol. The values of the ΔE_{des} of $(\text{CF}_3\text{CF}_2)_2\text{O}$ and $\text{CF}_3\text{CH}_2\text{OH}$ on these surfaces have revealed that they are heterogeneous and expose a variety of different sites with different affinities for adsorption. More importantly, oxidation of the surface increases the ΔE_{des} of $\text{CF}_3\text{CH}_2\text{OH}$ but has no observable impact on the ΔE_{des} of $(\text{CF}_3\text{CF}_2)_2\text{O}$. The interaction with $\text{CF}_3\text{CH}_2\text{OH}$ is increased by increasing the degree of oxidation of the $a\text{-CH}_x$ film. These results imply that oxidation of the fresh $a\text{-CH}_x$ film may be critical to the successful implementation of vapor-phase lubrication technologies for the preparation of hard disks. It also implies that oxidation of the surface may be a variable that can be used to control the properties of the lubricant on the disk surface.

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