Interaction of alcohols with a-CH$_x$ films*

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Temperature programed desorption has been used to study the desorption kinetics and desorption energies of a set of alcohols and fluorinated alcohols adsorbed on an a-CH$_x$ film. The alcohols serve as models for the hydroxyl end groups of Fomblin Zdol, the lubricant most commonly used with the amorphous carbon overcoats sputtered onto the surfaces of magnetic data storage disks. Temperature programed desorption has been used to measure the desorption energies of the alcohols over a range of coverages and to compare the desorption energies of fluorinated and hydrocarbon alcohols. The desorption energies are all coverage dependent and decrease with increasing alcohol coverage. This is believed to be due to heterogeneity of the a-CH$_x$ films surface. In all cases the low coverage desorption energies of the fluorinated alcohols were found to be higher than those of their hydrocarbon counterparts. The implications of this observation are that the interaction of the alcohols is through hydrogen bonding of the hydroxyl groups to the a-CH$_x$ films. This conclusion is consistent with that reached in a similar study of the adsorption of alcohols to the surfaces of a-CN$_x$ films. © *2000 American Vacuum Society.* [S0734-2101(00)05005-3]

I. INTRODUCTION

The magnetic layer in which data are stored on a hard disk is a thin alloy film sputtered onto the surface of the hard disk. In order to protect the magnetic film from damage and from corrosion it is coated with a thin layer ($\sim$100 Å) of sputtered amorphous carbon. Lubrication of the interface between the carbon overcoat and the read-write head which flies over the disk surface is provided by an ultrathin film (10–20 Å) of perfluoropolyalkylether. The properties of the lubricant film are influenced by its interaction with the carbon overcoat and the purpose of this study is to gain a fundamental insight into the nature of these interactions at the molecular level.

The carbon overcoats used to protect the surfaces of data storage media are of several different types. The most commonly used types are amorphous carbon films containing either hydrogen (a-CH$_x$) or nitrogen (a-CN$_x$). Other types that have been considered for possible use include diamond-like carbon and carbon deposited from ion beams. The focus of this work has been on the surfaces of a-CH$_x$ films, the most commonly used form. The a-CH$_x$ films used in this work have been supplied by a commercial vendor of magnetic media and are identical to those used in practice.

Fomblin Zdol is the most commonly used lubricant in the magnetic data storage industry and has been the focus of our attention. The Fomblins, in general, are linear polymers composed of fluoroether backbones with various types of functional end groups. Zdol, in particular, is terminated at either end by hydroxyl groups ($-$CH$_2$OH). The nature of these end groups and their interactions with the carbon films influence the properties of the lubricant film. Recent studies have compared the diffusion of Fomblins on various surfaces including amorphous carbon films.[1–3] The diffusion of Fomblin with trifluoromethyl ($-$CF$_3$) end groups was much faster than diffusion of Zdol with its hydroxyl end groups. Furthermore, the Zdol diffused to form a layered structure on the surface which was not observed in the case of the Fomblin with $-$CF$_3$ end groups. Clearly the differences in the behavior of the two lubricants must be related to the interactions of the hydroxyl and $-$CF$_3$ end groups with the amorphous carbon films. The nature of this interaction is the focus of this investigation.

Several previous studies have investigated the nature of the interactions of Fomblins with the surfaces of amorphous carbon films. These have used small compounds to model the nature of the interactions of different functional groups in the Fomblins with the surface. For example a set of small fluoroethers were used to study the interactions of the ether linkages with carbon films.[4,5] Comparison was made between the desorption energies of various fluoroethers and those of their hydrocarbon counterparts when adsorbed on a variety of amorphous hydrogenated carbon (a-CH$_x$) and amorphous nitrogenated carbon (a-CN$_x$) films. These comparisons invariably showed than the desorption energies of the fluorocarbon ethers were lower than those of their hydrocarbon counterparts. The implication of this observation was that the ethers interact with the carbon films by electron donation from the lone pair electrons on the oxygen atoms. Another study, similar to the one presented in this article, compared the desorption energies of hydrocarbon and fluorocarbon alcohols on a-CN$_x$ films.[6] That comparison showed that the desorption energies of the fluorocarbon alcohols were invariably higher than those of their hydrocarbon analogs. The implication of this observation is that the alcohols interact by hydrogen bonding with the a-CN$_x$ films. The purpose of the study presented here is to extend the work originally performed on a-CN$_x$ films to obtain an understanding of the interaction of alcohols with a-CH$_x$ films.

II. EXPERIMENT

All experiments were done in an ultrahigh vacuum (UHV) chamber with a base pressure of 3×10^{-11} Torr. The vacuum was achieved using a CTI 8 cryopump and a titanium sublimation pump. The chamber was equipped with leak valves and a Dycor mass spectrometer. Adsorption of alcohols onto the surface of the a-CH$_x$ sample was achieved by using the leak valves to introduce their vapor into the vacuum and hold the pressure constant for a given period of time. Desorption of the alcohols during heating of the sample was detected by tuning the mass spectrometer to the m/q ratio of one of the ionization fragments of the alcohol and monitoring that signal as a function of time.

The disk samples coated with films of 20% a-CH$_x$ were obtained from Seagate Technology Inc. The notation of 20% in this case indicates that the samples were sputtered in an atmosphere of 20% H$_2$ in a background of Ar. Previous work using carbon films from a variety of different vendors has shown that the trends observed in experiments such as the ones presented here are independent of the source of the films or the details of the film deposition conditions.[4,5] Small samples (1 cm diameter) were punched from these disks and were mounted in the chamber on an UHV manipulator. This manipulator allowed movement of the sample and also allowed heating and cooling. The sample was mounted by spot welding it between two Ta wires that were attached to a liquid nitrogen reservoir on the manipulator. Heating was performed by passing current through the sample and then measuring the temperature using a thermocouple spot welded to its back. The samples were used as provided, however, before each experiment they were heated to a temperature of 380 K to remove any adsorbed water. Such samples are mixtures of sp^2 and sp^3 hybridized carbon and having been exposed to air there are certainly partially oxidized groups exposed at the surface. Although the details of the surface characteristics are not known it is important to point out that the experiments performed on these materials were extremely reproducible. The thermal desorption spectra showed no evidence of any changes to the sample surface throughout the course of the many experiments performed. Care was taken to keep the sample temperature below 450 K since it is known from previous work that heating to temperatures in excess of 550 K is sufficient to cause dehydrogenation and other irreversible changes to the surface.[4]

Ethanol (CH$_3$CH$_2$OH, 99.5%), 2-propanol [CH$_3$CH(OH)CH$_3$, 99.5%] and perfluoro-tertiary-butanol [(CF$_3$)$_3$COH, 98%] were purchased from Aldrich Chemicals. 1,1,1-trifluoro-2-propanol [CF$_3$CH(OH)CH$_3$, 97%] and 1,1,1,3,3,3-hexafluoro-2-propanol [CF$_3$CH(OH)CF$_3$, 97%] were purchased from PCR Chemicals. 2,2,2-trifluoroethanol (CF$_3$CH$_2$OH, 99.5%) and tertiary-butanol [(CH$_3$)$_3$COH, 98%] were purchased from Lancaster Chemicals. All chemicals were purified by several freeze-pump-thaw cycles and the purity was checked using mass spectrometry.

Temperature programed desorption (TPD) spectra were obtained by first cooling the a-CH$_x$ hard disk sample to a temperature of ~90 K. The alcohols were then adsorbed onto the surface by introducing the vapor into the vacuum chamber while the sample was at low temperature. All exposures were measured in units of langmuirs (1 L=10^{-6} Torr s) without correction for ion gauge sensitivity. Analog mass spectra of the molecules were used to identify the highest intensity fragment in the mass spectrum and that m/q ratio was monitored during heating. To obtain reproducible desorption signals the sample was always moved to a fixed position in front of the mass spectrometer before heating. The sample was heated at a constant rate of 2 K s^{-1} and the mass spectrometer was used to measure the alcohol desorption rate as a function of temperature.

III. RESULTS

A. TPD experiments and analysis

The experiments performed in this work have generated TPD curves for various alcohols and fluorinated alcohols adsorbed on a-CH$_x$ films over a wide range of coverages. The objective has been to use these TPD curves to determine the desorption energies of the alcohols and to compare the desorption energies of hydrocarbon alcohols with those of their fluorocarbon analogs.

Attempting to determine the coverages of the alcohols from the desorption spectra has been complicated by the fact that the a-CH$_x$ surfaces are heterogeneous. This heterogeneity has been observed and discussed in earlier work.[4,5,8] The fact that the a-CH$_x$ films expose carbon atoms with different hybridization (sp^2 and sp^3) and carbon atoms that are partially oxidized means that the exposed adsorption sites have a range of different affinities for a given adsorbate. A brief look at Figs. 1 and 2 reveals the impact of this heterogeneity on the desorption of CH$_3$CH$_2$OH and CF$_3$CH$_2$OH from an a-CH$_x$ film. As the coverage increases the desorption peak temperature decreases monotonically. In other words, at low coverages the adsorbed molecules bind to the sites for which they have the highest affinity while at slightly higher coverages additional adsorbates must adsorb on sites with lower and lower binding affinities. Although it is possible that the systematic decrease in desorption temperature with coverage is due to repulsive adsorbate–adsorbate interactions rather than surface heterogeneity, this has been ruled out by studies on homogeneous single crystalline surfaces.[7,8] On Cu(111) and highly oriented pyrolytic graphite surfaces desorption of CH$_3$CH$_2$OH and CF$_3$CH$_2$OH at coverages of ≤1 monolayer occurs over very narrow temperature ranges and, if anything, the adsorbate–adsorbate interactions are attractive rather than repulsive.

One of the consequences of the heterogeneity of the a-CH$_x$ surfaces is that there is no clear resolution of the monolayer and multilayer desorption features. Instead, as the coverage increases the peak desorption temperature decreases smoothly and monotonically to the point at which multilayer desorption begins. Multilayer desorption is characterized by zero-order kinetics. This manifests itself as an overlapping of the leading edges of the desorption curves and an increase in the desorption peak temperature with adsorbate coverage in excess of one monolayer. At the highest
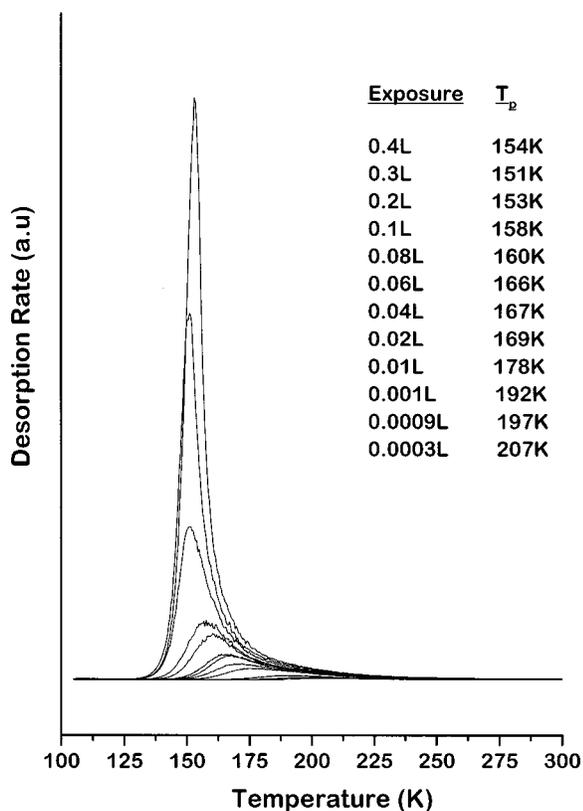
Exposure	T_p
0.4L	154K
0.3L	151K
0.2L	153K
0.1L	158K
0.08L	160K
0.06L	166K
0.04L	167K
0.02L	169K
0.01L	178K
0.001L	192K
0.0009L	197K
0.0003L	207K

FIG. 1. TPD spectra of ethanol (CH_3CH_2OH) on an a-CH_x film obtained at increasing coverages. As the coverage is increased both the peak desorption temperature and the peak desorption rate increase smoothly and monotonically. The monolayer is deemed to be saturated by an exposure of ~0.3 L at which point the initial desorption rate is zero order in coverage and the leading edges of the desorption curves are aligned. Adsorption was performed at 93 K. The heating rate was 2 K/s.

Exposure	T_p
0.4L	157K
0.3L	155K
0.2L	158K
0.1L	171K
0.07L	178K
0.04L	186K
0.02L	192K
0.01L	196K
0.001L	208K
0.0004L	220K
0.0002L	227K
0.0001L	229K

FIG. 2. TPD spectra of 2,2,2-trifluoroethanol (CF_3CH_2OH) on an a-CH_x film as function of increasing coverage. The peak desorption temperatures are all higher than those of ethanol at similar coverages. Adsorption was performed at 93 K. The heating rate was 2 K/s.

CH_3CH_2OH and CF_3CH_2OH coverages in Figs. 1 and 2 this is clearly occurring. Since there is no clear resolution of the monolayer and multilayer desorption features, we have chosen to define the monolayer as the coverage at which the onset of multilayer desorption occurs, as indicated by zero-order desorption kinetics and an overlapping of the leading edges of the desorption curves.

The determination of alcohol desorption energies has been done using the simplest approach, which is to use the desorption peak temperature (T_p) and the Redhead equation for analysis.[9] This analysis assumes that the preexponent for the desorption process is $10^{13}\,s^{-1}$ for all the alcohols. Since the intent is to compare the trends in the desorption energies, i.e., the effect of fluorination, we expect that this assumption will not influence these trends. Because the a-CH_x carbon films are heterogeneous it is not meaningful to quote a single value for the desorption energy of a molecule. In reality there is a distribution of desorption energies depending upon the type of adsorption site at which the molecule is adsorbed. In the past we have limited our discussions to the desorption energy that is measured in the limit of low coverage.[4–6] More recently, and in this article, we have attempted to quantify the distribution of desorption energies. Again, looking at the TPD curves in Figs. 1 and 2 it is clear that the
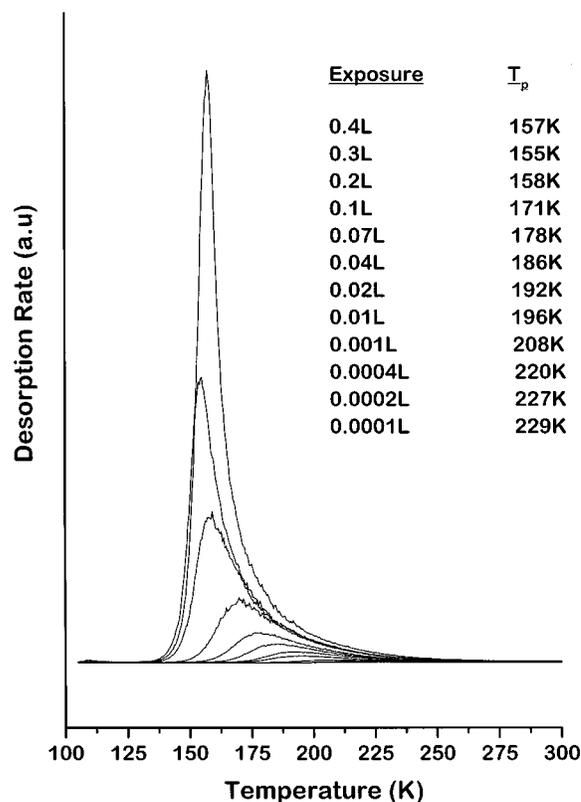
desorption peak temperature decreases smoothly while the peak desorption rate (peak height) increases smoothly and monotonically with increasing coverage. In essence, the peak desorption temperature at a given coverage can be used as a rough measure of the desorption temperature of the coverage increment between that desorption curve and the desorption curve with a slightly lower coverage. We have used the peak desorption temperatures for each coverage of adsorbate to estimate the desorption energy for that increment in coverage. This analysis yields the differential desorption energy versus coverage, $E_{des}(\theta)$, and examples of two such curves are shown in Fig. 3. It should be pointed out that this method gives virtually the same results as one in which we used the difference spectra between two desorption curves to determine the peak desorption temperature of the increment in coverage between the two. In this manner we have used the desorption spectra obtained over a range of coverages to generate estimates of the binding energy distributions or desorption energy versus coverage curves for all the alcohols and fluorinated alcohols on the a-CH_x surface.

B. TPD of CH_3CH_2OH and CF_3CH_2OH on a-CH_x

Alcohols have been studied as models for the hydroxyl end groups of Fomblin Zdol. By comparing the desorption energies of hydrocarbon and fluorocarbon alcohols from a-CH_x it will be possible to gain some insight into the nature
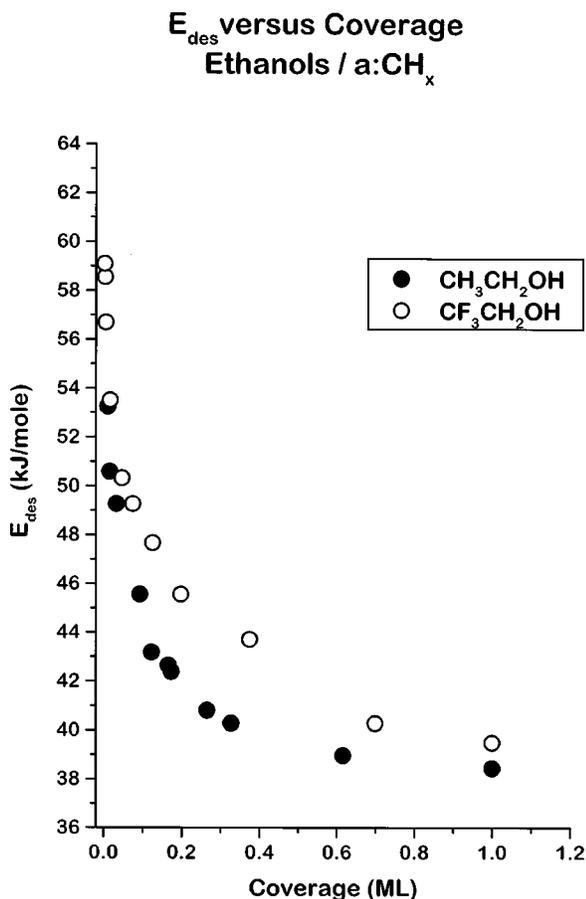
E_{des} versus Coverage
Ethanols / a:CH$_x$

FIG. 3. Desorption energies as a function of coverage for 2,2,2-trifluoroethanol (CF$_3$CH$_2$OH) and ethanol (CH$_3$CH$_2$OH) on an a-CH$_x$ film. The desorption energies decrease smoothly with coverage. At all coverages the desorption energy of CF$_3$CH$_2$OH is higher than that of CH$_3$CH$_2$OH.

of the interaction of the hydroxyl group with the a-CH$_x$ surface. The desorption spectra of CH$_3$CH$_2$OH adsorbed on a-CH$_x$ are shown in Fig. 1 for a range of initial coverages. Desorption spectra were obtained by using the mass spectrometer to monitor the signals from ion fragments with $m/q = 31$ (CH$_2$OH$^+$), $m/q = 45$ (CH$_3$CH$_2$O$^+$), and $m/q = 2$ (H$_2^+$). All three gave exactly the same desorption curves indicating that the desorption was molecular and that there was no decomposition or reaction of the CH$_3$CH$_2$OH on the surface. At low coverages the peak desorption temperature was 207 K. Multilayer desorption occurred at 154 K which is consistent with results obtained on metal surfaces: 155 K on Cu(100)[10] and 155 K on Ag(110).[11] The CH$_3$CH$_2$OH desorbs molecularly from the a-CH$_x$ surface with a peak desorption temperature that decreases smoothly and monotonically with increasing coverage.

The desorption of CF$_3$CH$_2$OH from the a-CH$_x$ surface has been studied in order to determine the influence of the $-$CF$_3$ group (versus $-$CH$_3$) on the desorption kinetics and desorption energy. Understanding its influence on the desorption energy will provide insight into the nature of the alcohol bonding or interaction with the a-CH$_x$ surface. The TPD spectra of CF$_3$CH$_2$OH from the a-CH$_x$ surface for a

range of initial coverages are shown in Fig. 2. In this case the ion fragments monitored by the mass spectrometer during desorption had $m/q = 31$ (CH$_2$OH$^+$) and $m/q = 69$ (CF$_3^+$). As in the case of CH$_3$CH$_2$OH the different ion fragments gave identical spectra indicating that the CF$_3$CH$_2$OH desorbs molecularly without reacting on the a-CH$_x$ surface. At the lowest coverage the peak desorption temperature for CF$_3$CH$_2$OH desorption is 229 K which is $\sim$20 K higher than for CH$_3$CH$_2$OH desorption from the a-CH$_x$ surface. This increase in the desorption temperature is consistent with the results previously obtained for CF$_3$CH$_2$OH and CH$_3$CH$_2$OH desorption from an a-CN$_x$ surface.[6] Comparison of the TPD spectra from the a-CH$_x$ and a-CN$_x$ films reveals that the peak desorption temperatures are higher on the a-CN$_x$ films for all coverages of either CF$_3$CH$_2$OH or CH$_3$CH$_2$OH. The important point is that fluorination of ethanol increases the desorption temperatures and the desorption energies on both a-CH$_x$ and a-CN$_x$ surfaces.

The results of the TPD experiments have been quantified by taking the peak desorption temperatures from the spectra at all coverages and determining the corresponding desorption energies using the Redhead analysis. This provides rough estimates of the differential desorption energy as a function of coverage, $E_{des}(\theta)$. Assuming that the coverage dependence of the desorption energy is due to surface heterogeneity, these differential desorption energy curves are equivalent to distribution functions of binding site affinities. These distribution functions are plotted in Fig. 3 for CF$_3$CH$_2$OH and CH$_3$CH$_2$OH on the a-CH$_x$ surface. They reveal that the differential desorption energy decreases smoothly and monotonically as the coverage of either molecule is increased. Most importantly Fig. 3 reveals that the desorption energy of CF$_3$CH$_2$OH is higher than that of CH$_3$CH$_2$OH at all coverages in the range from zero to one monolayer.

C. TPD of 2-propanols on a-CH$_x$

As in the case of ethanol we have measured the TPD spectra of 2-propanol and its fluorinated analogs adsorbed on a-CH$_x$. We have used the same molecules in this work as were used in a similar study of alcohol adsorption on the surfaces of a-CN$_x$ films:[6] CH$_3$CH(OH)CH$_3$, CF$_3$CH(OH)CH$_3$, and CF$_3$CH(OH)CF$_3$. By determining the effects of fluorination on the desorption energies of the 2-propanols we will generalize the observation made with the ethanols that fluorination increases the desorption energy.

The general features of the TPD curves for all three 2-propanols on the a-CH$_x$ film are similar to those observed for the ethanols. 2-propanol and its fluorinated analogs all desorb molecularly from the a-CH$_x$ surface without any evidence of dissociation or reaction on the surface. The TPD curves for CH$_3$CH(OH)CH$_3$ (Fig. 4) show that the desorption peaks shift to lower temperature and increase in magnitude smoothly and monotonically with increasing coverage. These TPD curves reveal the same heterogeneity of the a-CH$_x$ surface as was revealed by the ethanol TPD spectra.
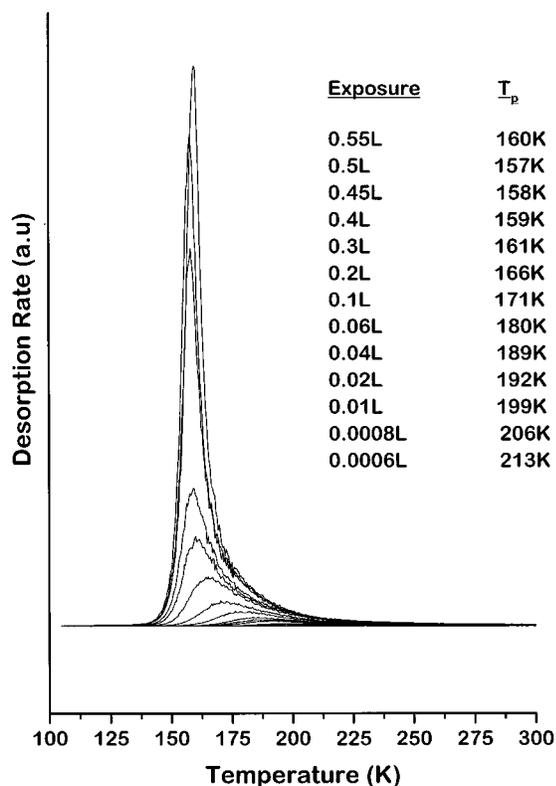
Exposure	T_p
0.55L	160K
0.5L	157K
0.45L	158K
0.4L	159K
0.3L	161K
0.2L	166K
0.1L	171K
0.06L	180K
0.04L	189K
0.02L	192K
0.01L	199K
0.0008L	206K
0.0006L	213K

FIG. 4. TPD spectra of 2-propanol [CH$_3$CH(OH)CH$_3$] on an *a*-CH$_x$ film as function of increasing coverage. The peak desorption temperature decreases smoothly with increasing coverage. Adsorption was performed at 93 K. The heating rate was 2 K/s.
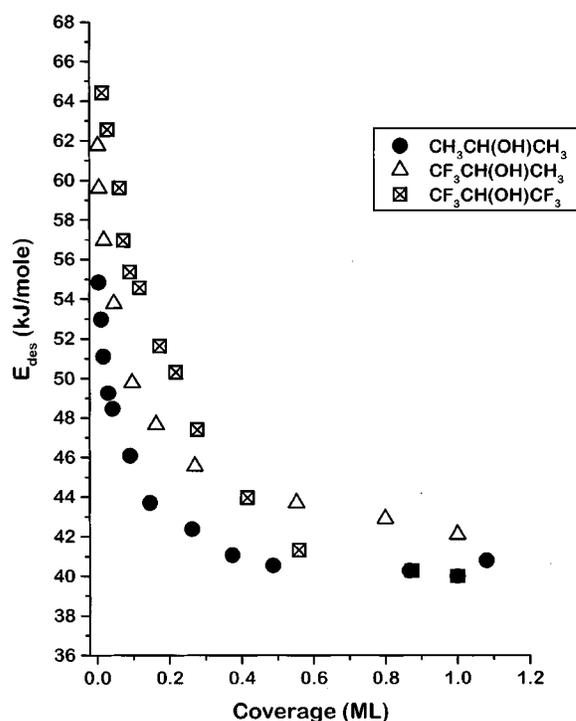

FIG. 5. Desorption energies as a function of coverage for 2-propanol [CH$_3$CH(OH)CH$_3$], 1,1,1-trifluoro-2-propanol [CF$_3$CH(OH)CH$_3$], and 1,1,1,3,3,3-hexafluoro-2-proponal [CF$_3$CH(OH)CF$_3$] on *a*-CH$_x$. The desorption energies decrease smoothly with increasing coverage. In the coverage range up to 0.4 monolayers the desorption energy increases with the degree of fluorination of the 2-propanol.

The desorption curves for the three different 2-propanols have been obtained as a function of coverage and have been analyzed to estimate the differential desorption energy as a function of coverage. These desorption energy curves are shown in Fig. 5. For all three molecules the desorption energy is highest in the limit of low coverage and decreases smoothly as the coverage approaches the multilayer regime. More importantly, in the coverage range up to 0.4 monolayers it is clear that the desorption energy increases with the degree of fluorination. At higher coverages the curves cross and the dependence on the degree of fluorination becomes more complicated. The observation that fluorination of the 2-propanols increased the desorption energy in the limit of low coverage was also made on the *a*-CN$_x$ surfaces.[6]

D. TPD of tertiary butanols on *a*-CH$_x$

The final set of experiments of this study measured the TPD spectra of tertiary butanol [(CH$_3$)$_3$COH] and its perfluorinated analog [(CF$_3$)$_3$COH]. Both of these molecules desorb molecularly from the surface and the TPD spectra of both reveal the same general features as the TPD spectra of the ethanols and 2-propanols. As examples the desorption spectra of (CH$_3$)$_3$COH from the *a*-CH$_x$ surface are shown in Fig. 6. These spectra and those of (CF$_3$)$_3$COH have been analyzed to estimate the differential desorption energy as a function of coverage. These desorption energy versus coverage curves are illustrated in Fig. 7 and reveal the heteroge-

neity of the *a*-CH$_x$ surface. The primary point of interest in this work is that in the coverage regime up to 0.4 monolayers the desorption energy of the (CF$_3$)$_3$COH is higher than that of (CH$_3$)$_3$COH. This was also observed in the limit of low coverage on the *a*-CN$_x$ films. The net result of our TPD studies of the ethanols, 2-propanols, and tertiary butanols is that, at least in the low coverage regime, the desorption energies of the alcohols increase with increasing degree of fluorination.

IV. DISCUSSION

A. Bonding of hydroxyl groups to *a*-CH$_x$

Our understanding of the nature of hydroxyl group bonding to *a*-CH$_x$ films comes from an understanding of the effects of fluorination on the alcohol desorption energies. The most important observation of this work has been that the desorption energies of the alcohols increase as a result of fluorination, at least in the coverage regime below 0.4 monolayers. This is also true on the *a*-CN$_x$ film studied previously.[6] The fact that fluorination increases the alcohol desorption energies suggests that the primary interaction mechanism of the alcohols with the *a*-CH$_x$ films is one of hydrogen bonding. In this type of interaction the hydroxyl

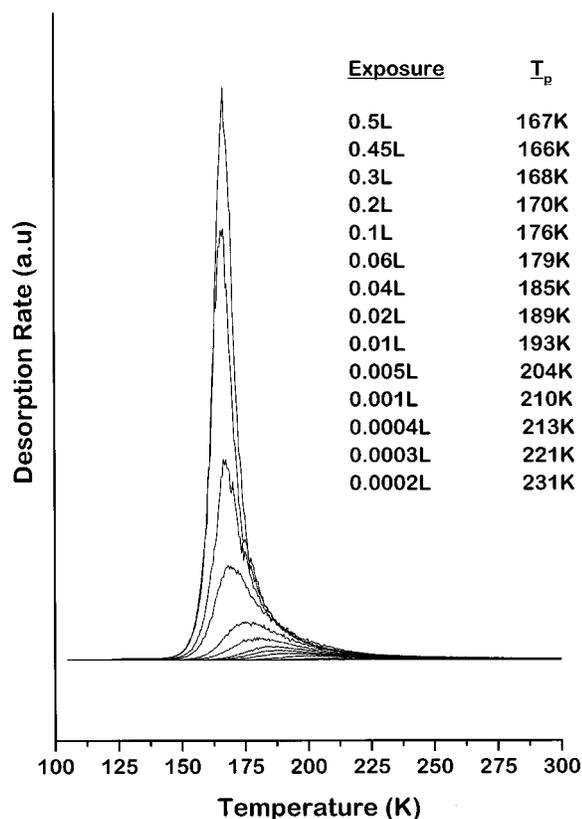| Exposure	T_p
0.5L	167K
0.45L	166K
0.3L	168K
0.2L	170K
0.1L	176K
0.06L	179K
0.04L	185K
0.02L	189K
0.01L	193K
0.005L	204K
0.001L	210K
0.0004L	213K
0.0003L	221K
0.0002L	231K

FIG. 6. TPD spectra of tertiary-butanol [(CH$_3$)$_3$COH] on an a-CH$_x$ film as function of increasing coverage. The peak desorption temperature decreases smoothly with increasing coverage. Adsorption was performed at 93 K. The heating rate was 2 K/s.

FIG. 7. Desorption energies as a function of coverage for tertiary butanol [(CH$_3$)$_3$COH] and perfluoro-tertiary-butanol [(CF$_3$)$_3$COH] on an a-CH$_x$ film. The desorption energy decreases smoothly with increasing coverage. In the coverage range above 0.4 monolayers the desorption energy of the (CF$_3$)$_3$COH is greater than that of (CH$_3$)$_3$COH.

group of the alcohols is acting as a proton donor to some nucleophilic group on the surface of the a-CH$_x$ film. An illustration of such an interaction is shown in Fig. 8. If the interaction is through hydrogen bonding, then on adsorption of the alcohol from the gas phase, the oxygen atom of the hydroxyl group becomes slightly anionic or electron rich

$$\text{ROH} + a:\text{CH}_x \rightarrow \text{RO}^{\delta-} \cdots \text{H}^{\delta+} \cdots a:\text{CH}_x .$$

The observed differences in the desorption energies of the alcohols are due to the differences in the properties of the $-$CH$_3$ and $-$CF$_3$ groups. Fluorination of the methyl group increases its inductive effect.[12,13] In essence, the methyl group becomes dipolar as a result of the high electronegativity of fluorine with respect to carbon. This dipole is oriented such that it energetically stabilizes the electron rich oxygen atom in the adsorbed alcohol. Energetic stabilization of the adsorbed species with respect to the gas phase species increases the desorption energies of the fluorinated alcohols over those of the hydrocarbon alcohols. This type of understanding of substituent effects on reaction energetics is commonly used in physical organic chemistry and provides strong evidence for the role of hydrogen bonding in the adsorption of alcohols on a-CH$_x$ films.

As further justification for the claim that the hydroxyl groups of the alcohols are hydrogen bonded to the a-CH$_x$ film, we can compare our results to those from a similar
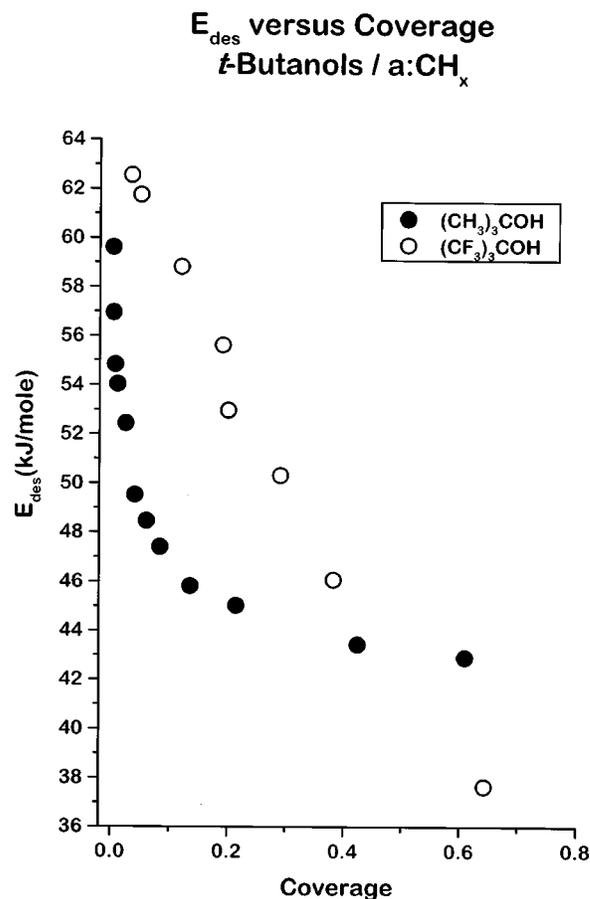
system in which alcohols are known to be hydrogen bonded to a nucleophile. The comparison is to the results of a computational study of the bonding of isopropanols and fluorinated isopropanols to water.[14] That study modeled the same three isopropanols as were used in this work: CH$_3$CH(OH)CH$_3$, CF$_3$CH(OH)CH$_3$, and CF$_3$CH(OH)CF$_3$. Table I compares the measured strength of the isopropanols' desorption energies on a-CH$_x$ (in the limit of low coverage) to the computed interaction energies of the three isopropanols with water. In both cases the effect of fluorination is to increase the interaction strength and by roughly the same magnitude. Since it is known in the computational study that the isopropanols are hydrogen bonding to the water, it is reasonable to suggest on this basis that they are hydrogen bonded to the a-CH$_x$ surface.

The suggestion that the alcohols are hydrogen bonding to the surface is valid in the coverage regime below 0.4 monolayers. It is in this coverage range that fluorination of ethanol, isopropanol, and tertiary butanol increases their desorption energies. At higher coverages the effects of fluorination are not consistent among the different alcohols and the situation becomes more complex. This is undoubtedly due in part to the surface heterogeneity of the carbon films. At low
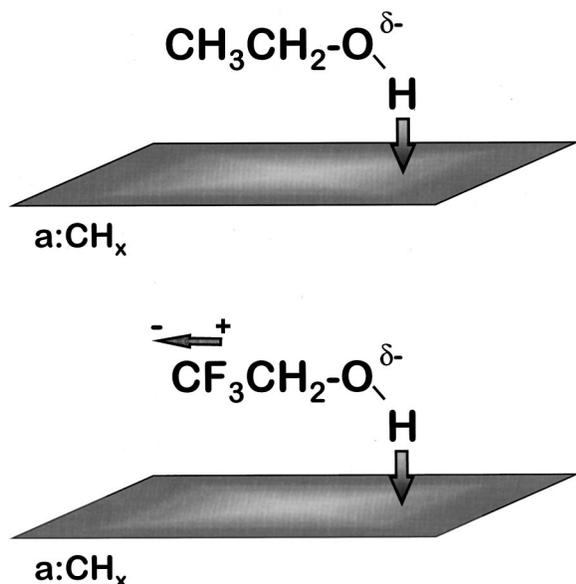
$$CH_3CH_2-O^{\delta-}$$
$$H$$

a:CH$_x$

$$CF_3CH_2-O^{\delta-}$$
$$H$$

a:CH$_x$

FIG. 8. Proposed model for interaction of alcohols and fluorinated alcohols with a-CH$_x$ films. If the interaction mechanism is one of hydrogen bonding to the surface through the hydroxyl proton then adsorption leaves the O atom electron rich with respect to the gas phase. Substitution of fluorine into the methyl group creates a dipole moment on the methyl group that energetically stabilizes the electron rich oxygen atom. The net effect of fluorination is that it increases the adsorption energy for a mechanism of hydrogen bonding to the surface.

coverages the alcohols can adsorb to the sites with highest binding affinity, presumably those that are nucleophilic. At higher coverages the types of sites to which the alcohols adsorb are different from those occupied at low coverage.

It is important to pointed out that the low coverage regime is likely to be the one that is most relevant to the understanding of Fomblin Zdol adsorption on a-CH$_x$ films. The Fomblin Zdol used to lubricate the surfaces of data storage media is a polydispersed perfluoroalkylether polymer with molecular weights ranging from 2000 to 8000 amu. These are polymer chains with something on the order of 50–150 –CF$_2$– groups and only two hydroxyl groups (at either end). The typical thickness of the lubricant film on the surface is 10–20 Å which represents 2–3 monolayers of the Fomblin Zdol molecules when oriented parallel to the surface. Even at these coverages of Fomblin Zdol the fractional coverage of the hydroxyl groups is well below 0.1 monolayers. Furthermore, previous work has shown that the strength of the interaction of the alcohols with the a-CH$_x$ and a-CN$_x$ surface

TABLE I. Comparison of the desorption energies (E_{des}) of the 2-propanols on the a-CH$_x$ surface at low coverage with computed hydrogen bond strengths (E_{HB}) of the 2-propanols bonded to water.

Molecule	E_{des}/a-CH$_x$	$\Delta E_{des}/a$-CH$_x$	E_{HB}/H_2O	$\Delta E_{HB}/H_2O$
CH$_3$CH(OH)CH$_3$	52.7 kJ/mol[a]	6.7	25.3[b]	9.6
CF$_3$CH(OH)CH$_3$	59.4		34.9	
CF$_3$CH(OH)CF$_3$	64.1	4.7	36.9	2.0

[a]Experimentally determined desorption energies from this work.
[b]Computationally determined hydrogen bond strengths from Ref. 14.

is always greater than that of the ethers.[6,7] This implies that in spite of the presence of the ether linkages in the Fomblin Zdol chain, the hydroxyl end groups are able to compete for the adsorption sites for which they have the greatest affinity. These sites would be those occupied at low coverages in the experiments described in this work. The net conclusion is that the hydroxyl end groups of Fomblin Zdol, like the alcohols studied in this work, probably interact with the a-CH$_x$ surface by hydrogen bonding.

Finally, it is worth noting that the bonding mechanism proposed for the hydroxyl end groups of Fomblin Zdol is different from that proposed for the ether linkages of the Fomblin backbone. A set of studies similar to those described here have measured the desorption energies of several ethers and fluorinated ethers on a-CH$_x$ and a-CN$_x$ films.[4–7] In all cases fluorination of the ethers resulted in a weakening of the interaction with the film surface. This is opposite to the effect of fluorination that has been observed for the alcohols in this work. Using arguments similar to those presented earlier for the hydrogen bonding of alcohols to the a-CH$_x$ surface, it has been proposed that the ethers bond to the a-CH$_x$ and a-CN$_x$ films by electron donation from the oxygen lone pair electrons to the carbon films.

B. Alcohol adsorption sites on a-CH$_x$

If the alcohols interact with a-CH$_x$ film by hydrogen bonding, they must do so by interacting with adsorption sites that are nucleophilic proton acceptors. At first thought it might not seem that a material such as a-CH$_x$ should be nucleophilic, however, the surfaces of the a-CH$_x$ films and a-CN$_x$ films are heterogeneous and are known to contain many types of partially oxidized functional groups. It is known from many studies using Raman spectroscopy that the a-CH$_x$ films contain carbon atoms with sp^2 and sp^3 hybridization in varying amounts.[4,15] Furthermore, the presence of hydrogen in the films implies the presence of –CH$_n$– groups with degrees of hydrogenation probably ranging from $n=0$ to 3. Finally, in real use the carbon films are exposed to air between the film deposition step and the application of the lubricant and this certainly results in the partial oxidation of the surface. There have been some attempts to identify and to quantify the types and relative concentrations of the species that might exist at the surface of an a-CH$_x$ film.[16,17] These studies have identified the presence of groups such as –OH, CO$_2$H, >C=O, and C–O–C. In addition there is strong evidence for the presence of unpaired electrons or dangling bonds in the films.[16] There are two points to be taken from this. The first is that the heterogeneity in the film surface that we have characterized in terms of desorption energy distributions is not surprising. The second is that among the many possible species that have been proposed to exist at the surface of the a-CH$_x$ films there are several candidates that might serve as nucleophilic proton acceptors for hydrogen bonding of the alcohols or the hydroxyl end groups of Fomblin Zdol.

V. CONCLUSIONS

By using short chain alcohols as models for the hydroxyl end groups of Fomblin Zdol lubricants we have been able to propose a mechanism for the interaction of these hydroxyl groups with the a-CH$_x$ films used to protect the surfaces of magnetic data storage media. Alcohols and hydroxyl groups interact with these a-CH$_x$ surfaces by hydrogen bonding. The surfaces of the a-CH$_x$ films are heterogeneous and expose adsorption sites with a range of affinities for alcohol adsorption.

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[1] X. Ma, J. Gui, L. Smoliar, K. Grannen, B. Marchon, M. S. Jhon, and C. L. Bauer, J. Chem. Phys. **110**, 3129 (1999).

[2] X. Ma, J. Gui, L. Smoliar, K. Grannen, B. Marchon, M. S. Jhon, and C. L. Bauer, Tribol. Lett. **6**, 9 (1999).

[3] T. M. O'Connor, Y. R. Back, M. S. Jhon, B. G. Min, D. Y. Yoon, and T. E. Karis, J. Appl. Phys. **79**, 5788 (1996).

[4] L. Cornaglia and A. J. Gellman, J. Vac. Sci. Technol. A **15**, 2755 (1997).

[5] L. Cornaglia and A. J. Gellman, Adv. Info. Stor. Sys. **8**, 57 (1998).

[6] K. Paserba, N. Shukla, A. J. Gellman, J. Gui, and B. Marchon, Langmuir **15**, 1709 (1999).

[7] N. Shukla and A. J. Gellman (unpublished).

[8] C. F. McFadden and A. J. Gellman, Langmuir **11**, 273 (1995).

[9] P. A. Redhead, Vacuum **12**, 2 (1962).

[10] K. D. Rendulic and B. A. Sexton, J. Catal. **78**, 126 (1982).

[11] R. Zhang and A. J. Gellman, J. Phys. Chem. **95**, 743 (1991).

[12] R. W. Taft and R. D. Topsom, Prog. Phys. Org. Chem. **1** (1987).

[13] C. Hansch, A. Leo, and R. W. Taft, Chem. Rev. **91**, 165 (1991).

[14] K. Kinugawa and K. Nakanishi, J. Chem. Phys. **89**, 5834 (1988).

[15] J. Robertson, Surf. Coat. Technol. **50**, 185 (1992).

[16] M. Yanagisawa, STLE Spec. Publ. SP-36, Park Ridge, IL, 1994, Vol. 9, p. 25.

[17] R. H. Wang, R. L. White, S. W. Meeks, B. G. Min, A. Kelloeck, A. Homola, and D. Yoon, IEEE Trans. Magn. **32**, 3777 (1996).