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# Water adsorption on lubricated a-$CH_x$ in humid environments

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Humidity influences the tribological performance of the head-disk interface in magnetic data storage devices. In this work a quartz crystal microbalance was used to measure the uptake of water on amorphous hydrogenated carbon (a-$CH_x$) films at room temperature and pressures of water corresponding to relative humidities of ~25%. These experiments have used a-$CH_x$ films of varying thickness with and without lubricant. The lubricants used included Fomblin Z-03, Z-disoc, and Z-tetraol deposited on the surfaces of a-$CH_x$ films of various thickness. The amount of water adsorbed on the unlubricated a-$CH_x$ films is roughly independent of a-$CH_x$ film thickness. The presence of the lubricant reduces the amount of adsorbed water; however, the amount of water adsorbed in the presence of a lubricant does not depend significantly on the type of lubricant. These observations imply that water is adsorbed on the surfaces of the lubricant or the a-$CH_x$ film rather than being absorbed in their bulk.

**KEY WORDS:** head-disk interface; humidity; perfluoropolyalkylethers; water adsorption; amorphous carbon

## 1. Introduction

The operation of hard disk data storage devices relies on the performance of the interface between the read–write head and the data storage media. The head-disk interface is formed by a read–write head which flies on an air bearing over the surface of the magnetic media. The gap between the head and the magnetic media is defined as the fly-height and it is constantly decreasing due to the continuously increasing demand for higher areal density of stored data. The total budget for the gap between the head and the media is very limited and the current target for drives with storage densities of 1 Tb/in$^2$ is roughly 35 Å [1]. If contaminants adsorb on the surfaces of the head or the media, they will increase the head-media spacing and degrade the performance of the drive. The magnetic media is coated with a thin layer of amorphous hydrogenated carbon (a-$CH_x$) or amorphous nitrogenated carbon (a-$CN_x$) and a layer of lubricant [2,3]. In addition, the read–write head is coated with a layer of carbon. Both the read–write head and the media surface are susceptible to adsorption of contaminants. One of the most common contaminants is water, which is readily adsorbed on the carbon and lubricant covered surfaces of both the read–write head and the magnetic media. In this work we have focused on the adsorption of water on magnetic media and quantitatively determined the amount of water adsorbed on various lubricants and carbon films of various thicknesses at relative humidities of ~25%.

Water adsorption as a result of ambient humidity is known to influence the performance of the head-disk interface. Furthermore, as the head fly-heights continue to decrease, environmental conditions such as temperature and humidity that influence the lubricant-overcoat interactions become increasingly important to the tribological properties of the head-disk interface. Many studies have been conducted to investigate the effects of humidity on the tribological performance of the head-disk interface [4–13]. Those studies that have attempted to measured the amount of water adsorbed on a disk surface have used interferometry [11–13]. On lubricated surfaces water-film thicknesses in the range 2–20 Å have been reported depending upon the nature of the surface and the relative humidity. Using an estimate of 3 Å for the thickness of a monolayer of adsorbed water this corresponds to a range of <1 to 6 monolayers of adsorbed water. Smallen *et al.* suggest that the principal parameters that influence water adsorption are the relative humidity and the hydrogen concentration of the a-$CH_x$ films [11]. Dai *et al.* investigated the effects of humidity on the spatial distribution of perfluoropolyalkylether (PFPE) lubricants on hard carbon overcoats [4]. They used non-contact atomic force microscopy capable of generating nanometer-resolution images of soft materials and liquid surfaces and observed an increase of lubricant mobility in the presence of water. In another study using drag and contact start and stop (CSS) tests, Zhao and Bhushan concluded that the durability of lubricated disks was lower at high humidity for chemically bonded lubricant films [5]. The consensus of these studies is that

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there is a general enhancement of PFPE mobility on a-$CH_x$ films in humid environments. Some mobility of PFPE lubricants is desired for replenishment of areas depleted of lubricant by head-disk contacts; however, excess mobility will lead to lubricant spin-off, decreasing the durability of the hard disk. Clearly, understanding the factors that influence the adsorption of water on lubricated a-$CH_x$ films is important to the design and improvement of the head-disk interface.

There are a number of factors that one might want to know about the adsorption of water onto the carbon films and the lubricant films used on the surfaces of magnetic storage media. The adsorption isotherm, $\theta(P, T)$, gives the coverage of water as a function of the partial pressure, $P$, of water (humidity) at a given temperature, $T$. The adsorption isotherm is an equilibrium thermodynamic property of the system and is determined by the heat of adsorption, $\Delta H_{\mathrm{ads}}$. In addition to equilibrium properties the dynamic properties of humidity adsorption may be important under some circumstances. These are determined by the adsorption and desorption rate constants, which are in turn determined by the barriers and pre-exponents to adsorption and desorption. The factors that might influence these parameters are the nature of the a-$CH_x$ and a-$CN_x$ films, the film thickness, and the lubricant type and thickness. This paper addresses the influence of these parameters on the adsorption of water on the lubricated and unlubricated a-$CH_x$ overcoats used on data storage media.

In a previous paper we have described the results of measurements similar to those used in this work [14]. The amount of water adsorbed on an a-$CH_x$ film was measured using a quartz crystal microbalance (QCM) during exposure to various pressures of water vapor. The conditions corresponded to relative humidities of 0–50%. The results of those measurements showed that the rate of water adsorption and desorption at room temperature is relatively fast and that equilibrium is reached on timescales much shorter than the timescale of normal fluctuations in ambient humidity. This suggests that under the normal operating conditions of a hard disk drive the water adsorbed on the surface of the disk is in equilibrium with the ambient humidity. In addition, a comparison of the adsorption of $H_2O$ and $D_2O$ revealed that the interaction of the adsorbed water with the disk surface involves hydrogen bonding.

The work described in this paper has made use of a QCM to study the adsorption of water on the surfaces of a-$CH_x$ films with and without the presence of lubricant. This work has explored the effects of a-$CH_x$ film thickness in order to determine whether the majority of water adsorption occurs on the surface of the a-$CH_x$ overcoat or in pores within the bulk of the film. In addition, water adsorption has been studied on a-$CH_x$ overcoats lubricated with various PFPEs in order to explore the influence of different lubricant endgroups on the adsorption of water. These measurements reveal that the majority of water is adsorbed on the surface of either the lubricated or unlubricated a-$CH_x$ film. Therefore neither the thickness of the a-$CH_x$ film nor the type of lubricant have a significant influence on the amount of water adsorbed.

## 2. Experimental

All experiments were performed in a vacuum chamber evacuated by a turbopump and capable of operating in the pressure range $10^{-8}$–$10^{+3}$ Torr. This chamber housed the QCM and a valve for introducing water vapor at controlled rates. A capacitance manometer pressure gauge for measuring the absolute pressure in the range 0.1–1000 Torr was used to monitor the partial pressure of water in the chamber during experiments. The QCM housing was capable of holding two quartz crystals for simultaneously monitoring water adsorption on two surfaces.

The quartz crystals were prepared by coating with sputtered a-$CH_x$ films having thicknesses in the range 10–100 Å. The a-$CH_x$ films had a hydrogen content of 20% (atomic percentage). Some of the quartz crystals were coated with a-$CH_x$ alone to measure water adsorption on the carbon surfaces. Other quartz crystals were modified by dip-coating to apply a thin film of PFPE lubricant that was 20 Å in thickness. The thickness was controlled by using conditions for dip-coating that are known to deposit films of 20 Å onto hard disks. Once their surfaces were prepared the quartz crystals were mounted in the QCM housing and inserted into the vacuum chamber.

The exposure of the lubricated and unlubricated a-$CH_x$ films to water vapor was achieved by introducing the vapor into the vacuum chamber through a needle valve at a controlled rate. During exposure the gate valve to the turbopump was closed. The pressure and the QCM frequency were monitored simultaneously until the pressure reached the desired value of 5 Torr. At that point the needle valve was closed and the pressure allowed to remain constant for a few minutes before the water vapor was pumped away by opening the gate valve to the turbopump. The QCM frequency and the pressure were monitored throughout the exposures and for several minutes following the removal of water vapor from the chamber.

The mass of water adsorbed on the surface of the quartz crystal was calculated using the following expression:

$$\Delta f = -\mathrm{C}\Delta m.$$

The quantities $\Delta f$ and $\Delta m$ are the change in frequency and the adsorbed mass of water respectively. The quantity C is a constant which depends on the specific

density, the shear wave velocity and frequency of the quartz crystal [15]. The value of constant C in our experiments is $0.0565\,Hz \cdot cm^2/ng$.

Since only one side of the quartz crystal was coated with a-$CH_x$ it was necessary to perform some baseline measurements of water adsorption on the gold-coated quartz crystals. The contribution to the total amount of water adsorbed on the side coated with gold was subtracted in order to determine the amount of water adsorbed on the area coated with the a-$CH_x$ film.

The lubricants used were Fomblin Z-03, Z-disoc, and Z-tetraol with molecular weights of 2500, 1500, and 2500 amu. The lubricants were all obtained from Ausimont Inc. The water was kept in a small glass vial connected to the vacuum chamber through stainless steel tubing and a needle valve. Prior to use the water was degassed by pumping on the vial with the turbopump through the needle valve.

## 3. Results

Initial work focused on the adsorption of water onto the surfaces of a-$CH_x$ films without lubricant. The a-$CH_x$ films are quite complex materials from the perspective of both composition and structure. The densities of these films are on the order of 1.6–1.8 $gm/cm^3$, which is roughly 70% that of graphite and 50% lower than that of diamond. One of the reasons for the difference in densities is, of course, the fact that the a-$CH_x$ contains a significant amount of hydrogen. The other reason is that there may be some degree of porosity to the film structure. One of the issues that we have tried to address with these studies is whether water adsorbs primarily on the surface of the a-$CH_x$ or in pores. This has been accomplished by measuring the uptake or adsorption of water on films with different thicknesses.

The first issue to be addressed in this study is the nature of the dynamic or equilibrium properties of the water adsorption process. Figure 1 shows the uptake of water by a quartz crystal coated on one side with an 80 Å thick a-$CH_x$ film during exposure to water vapor at a temperature of 22 °C. The plot shows both the mass of adsorbed water and the water vapor pressure as a function of time during the exposure. Initially the pressure is zero and there is no water adsorbed on the surface. After three minutes the water vapor is introduced into the chamber at a rate of 2 Torr/min until the pressure reaches 5 Torr. During this time period the amount of adsorbed water increases at a roughly constant rate until it reaches 38 ng at a pressure of 5 Torr. While the pressure is kept constant the coverage of water on the surface increases slightly and then plateaus. The water coverage increases by only about 10% at this point, which suggests that during the exposure the adsorbed water is nearly equilibrated with

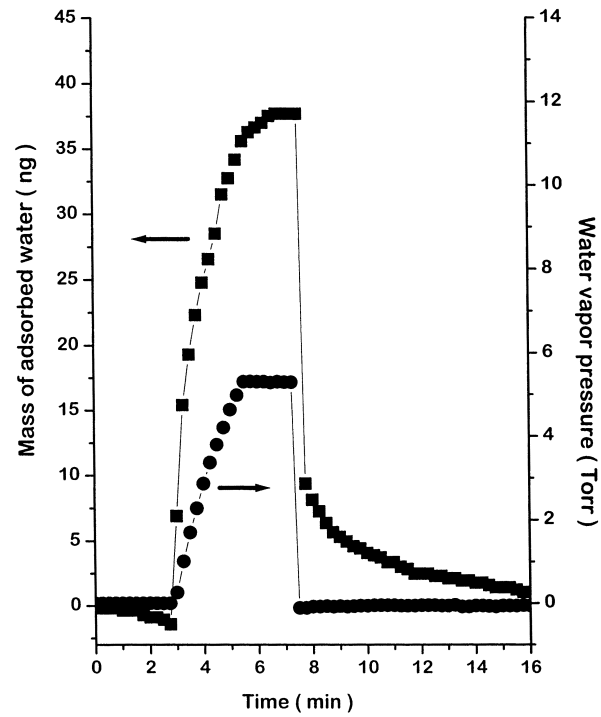


Figure 1. Water adsorption during exposure to water vapor of a quartz crystal coated on one side with 80 Å of a-$CH_x$. The circles show the pressure as a function of time during the exposure. The squares show the amount of adsorbed water as a function of time. The water adsorption temperature was 22 °C.

the water vapor. After the amount of adsorbed water ceased increasing and had reached equilibrium with the water vapor the gate valve to the turbopump was opened to remove the water vapor from the chamber. The amount of adsorbed water drops extremely rapidly. The fact that water desorption is rapid is consistent with the suggestion that the adsorbed water is nearly equilibrated with the ambient vapor during the exposure. This measurement was repeated 3–5 times on the carbon-coated quartz crystals in order to determine the amounts of water adsorbed on their surfaces.

A separate set of measurements using quartz crystals without a-$CH_x$ has shown that $\sim 7.5\,ng/cm^2$ of water adsorbs on the surface of the gold-coated quartz crystal during exposure to 5 Torr of water vapor at room temperature. Since the a-$CH_x$ was only sputtered onto one side of the quartz crystal, the amount of water adsorbed onto the back side (gold only) was subtracted from the total amount adsorbed in order to determine the amount adsorbed on the a-$CH_x$ film itself. For the 80 Å thick a-$CH_x$ film the amount of water adsorbed was $46 \pm 1\,ng/cm^2$. Using the bulk density of water we estimate that the amount of water adsorbed on the a-$CH_x$ surface corresponds to a thickness of $\sim 4.5$ Å or a coverage of $\sim 1.5$ monolayers. This, of course, assumes that the water is adsorbed on the exposed surface of the a-$CH_x$ rather than within any pores in the bulk of the film.

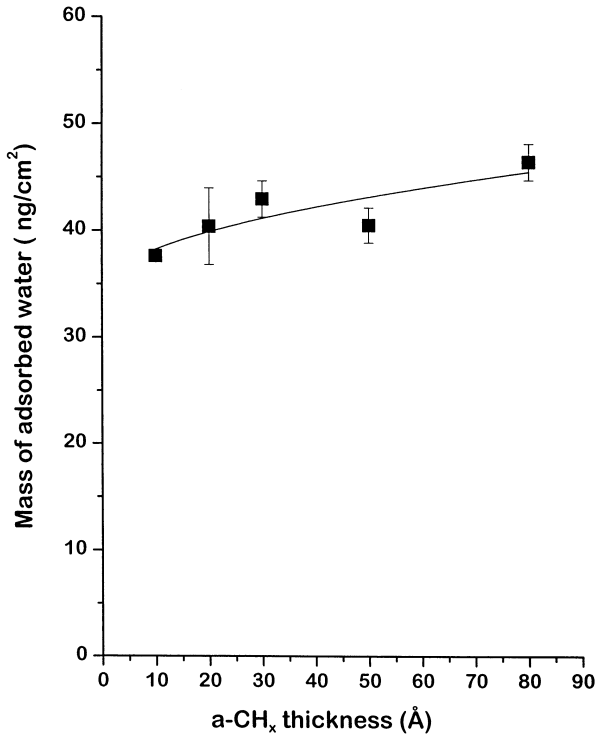


Figure 2. Water coverage at 5 Torr versus the a-$CH_x$ film thickness. The squares show the amount of water adsorbed as a function of a-$CH_x$ film thickness. The amount of water adsorption is almost independent of the a-$CH_x$ film thickness. The solid line is a fit to the functional form $a + bt^{\gamma}$ and gives an exponent of $\gamma = 0.51 \pm 1.4$. The temperature for water adsorption was 22 °C.

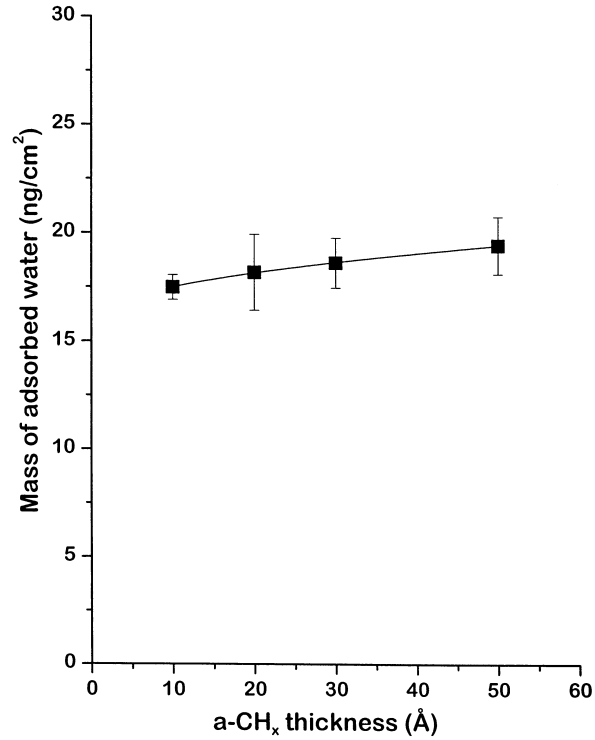


Figure 3. Water coverage at 5 Torr versus the a-$CH_x$ film thicknesses for films lubricated with 20 Å of Z-tetraol. The squares show the amount of water adsorbed as a function of a-$CH_x$ film thickness. The a-$CH_x$ film thickness does not influence water adsorption significantly. The solid line is a fit to the functional form $a + bt^{\gamma}$ and gives an exponent of $\gamma = 0.48 \pm 0.12$. The temperature for water adsorption was 22 °C.

The adsorption of water has been studied on a-$CH_x$ films with thicknesses in the range 10–80 Å. The purpose of this study was to try to determine the extent to which water is adsorbed in pores rather than on the exposed surface of the film. If water adsorbs on the surfaces of the a-$CH_x$ films then the film thickness should not significantly influence water adsorption. On the other hand if a significant amount is adsorbed in pores, water adsorption should increase linearly with film thickness. Figure 2 shows the amount of water adsorbed at a pressure of 5 Torr at temperatures in the range 23–26 °C. These were measured for a-$CH_x$ films of thickness 10, 20, 30, 50, and 80 Å. Clearly, the amount of water adsorbed on the a-$CH_x$ films is almost independent of the film thickness. There is a slight increase in the amount of adsorbed water as the film thickness increases; however, the increase is far from being proportional to film thickness. These results imply that water adsorption occurs predominantly on the surface of the a-$CH_x$ films rather than in pores. The increase in water adsorption that is observed might be due to some porosity of the film or possibly to increases in surface roughness as the a-$CH_x$ film thickness increases.

The next goal of the study was to investigate whether the presence of a lubricant on the surface of the a-$CH_x$ film influences the adsorption of water. Water is either dissolved in the bulk of the lubricant or adsorbed at the surface. Figure 3 shows the water coverage at 5 Torr water vapor pressure (25% relative humidity) on a-$CH_x$ films of varying thickness lubricated with 20 Å of Z-tetraol. The first thing to notice is that the amount of water adsorbed on these surfaces is roughly half that adsorbed on the unlubricated a-$CH_x$ films. The presence of the PFPE lubricant appears to be inhibiting water adsorption on the media surfaces. This is consistent with the fact that the surfaces of the media are hydrophobic once coated with the PFPE lubricants. Smallen *et al.* measured water adsorption on disks at 90% relative humidity using interferometry and observed very little influence of the presence of lubricants such as Zdol, Z25, and AM2001 [11]. Our measurements also show that the amount of adsorbed water increases slightly with increasing a-$CH_x$ film thickness; however, the increase is far from being proportional to the film thickness.

The data in figures 2 and 3 reveal a slight increase in the amount of adsorbed water as a function of a-$CH_x$ film thickness. One of the possible sources of such an increase is an increase in the a-$CH_x$ surface roughness with film thickness. Since the a-$CH_x$ film is deposited by a low energy process the roughness of the films is expected to increase with the functional form $t^{\gamma}$ where '$t$' is the thickness and the exponent has a value on the order of 0.5 [16]. The data in figures 2 and 3 have been fit

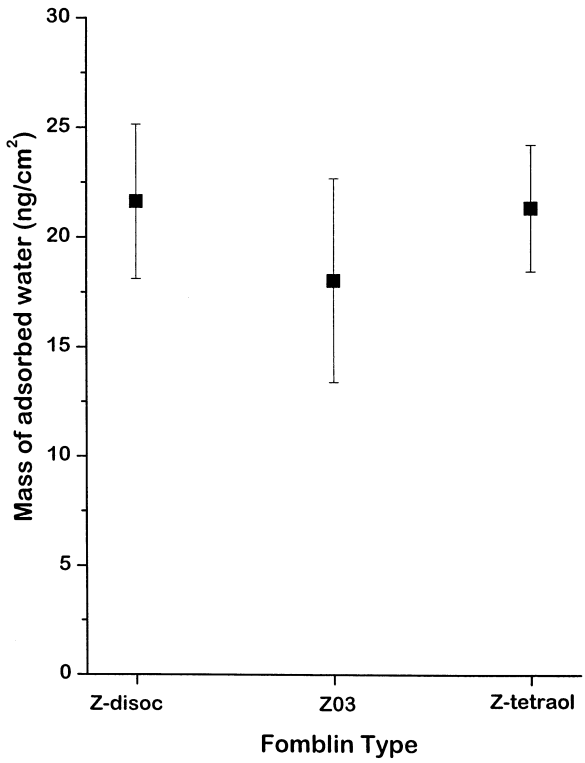


Figure 4. Water coverage at 5 Torr and for 100 Å thick a-$CH_x$ films lubricated with 20 Å of Fomblin Z-03, Z-disoc, and Z-tetraol. The squares show the amount of water adsorbed as a function of a-$CH_x$ film thickness. Adsorption was measured at temperatures in the range 14–16 °C.

to functions of the form $a + bt^{\gamma}$. The resulting fits are shown as the solid lines in the figures and both have exponents of $\gamma \sim 0.5$. These fits suggest that the source of the increase in the amount of adsorbed water on the a-$CH_x$ surfaces is due to an increase in surface roughness with increasing thickness.

In principle, the type of lubricant can influence water adsorption on a disk surface. Although the PFPE lubricants used for data storage all have the same fluoroether backbone they differ in the types of endgroups and this can, in principle, influence water adsorption. This has been explored by measuring water adsorption on a-$CH_x$ films lubricated with three different types of lubricants. Figure 4 shows the water coverage during water exposure at 5 Torr to 100 Å thick a-$CH_x$ films coated with different types of lubricants at 20 Å thickness. These adsorption isotherms were measured at temperatures in the range 14–16 °C and thus the amounts adsorbed are slightly higher than those in figures 2 and 3, which were measured at slightly higher temperatures. The data in figure 4 do not reveal any significant differences in the amounts of water adsorbed on surfaces lubricated with the different PFPEs. This is consistent with the observations made by Smallen *et al.* but differs from those of Bhushan *et al.*, who saw a roughly 50% difference in the amounts of water adsorbed on disk surfaces lubricated with Zdol and Demnum SA [11,13]. Our data indicate that the type of lubricant does not significantly affect water adsorption on the surfaces of magnetic media. In retrospect perhaps this should not be too surprising since the total contribution of endgroups to the composition of the lubricant is only of order 1% while the majority of the lubricant molecular structure is the fluoroether backbone.

## 4. Conclusions

QCM measurements have probed the effects of various characteristics of magnetic media surfaces on the adsorption of water. In principle, the a-$CH_x$ thickness can influence the adsorption of water, if the water adsorbs into pores in the a-$CH_x$ films. Apparently this does not occur since the thickness of the a-$CH_x$ films does not influence the amount of adsorbed water. The presence of lubricant and the characteristics of different lubricants can, in principle, affect the adsorption of water if the endgroups are involved. This work clearly demonstrates that the adsorption of water is decreased by the presence of the lubricant but not by the differences in the endgroups of the different PFPE lubricants. The latter may not be too surprising since the endgroups represent less than 1% of the PFPE lubricant mass. It is probably important to point out the fact that although the endgroups do not have a significant influence on the amount of adsorbed water the adsorbed water may still have grossly different influences on the properties of the lubricants with different endgroups.

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