

## Water adsorption on lubricated fullerene-like $CN_x$ films

E. Broitman<sup>a,\*</sup>, V.V. Pushkarev<sup>a</sup>, A.J. Gellman<sup>a</sup>, J. Neidhardt<sup>b,c</sup>, A. Furlan<sup>b</sup>, L. Hultman<sup>b</sup>

<sup>a</sup> Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA

<sup>b</sup> IFM, Linköping University, SE 581-83 Linköping, Sweden

<sup>c</sup> Christian Doppler Laboratory for Advanced Hard Coatings, University of Leoben, 8700 Leoben, Austria

Available online 25 September 2006

### Abstract

Humidity influences the tribological performance of the head–disk interface in magnetic data storage devices. In this work we compare the uptake of water of amorphous hydrogenated carbon (a- $CH_x$ ) and carbon nitride (a- $CN_x$ ) films, widely used as protective overcoats in computer disk drive systems, with two types of amorphous non-hydrogenated carbon (a-C and a- $C_{sp^2}$ ) films, and fullerene-like carbon nitride (FL- $CN_x$ ) films. Carbon films were deposited on quartz crystal substrates by reactive dc magnetron sputtering in Ar/ $N_2$  discharges. After deposition, some of the films were coated with a 2-nm-thick layer of Z-tetraol, a lubricant used in hard disk devices. A quartz crystal microbalance placed in a vacuum chamber was used to measure the adsorption of water at room temperature and at pressures of water corresponding to relative humidities in the range RH=0 to 90%. Water adsorption and desorption is fast, indicating that equilibrium with ambient humidity is reached on time scales of minutes, much faster than the time scales for fluctuations in ambient humidity. The amount of water adsorbed on the non-lubricated amorphous carbon films is significantly higher than that on the fullerene-like films. The presence of the lubricant influences water adsorption but its impact differs on different carbon films.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Carbon nitride; Water; Adsorption; Sputtering; Fullerene-like

### 1. Introduction

Magnetic data storage disk drives must operate flawlessly for several years in environments where there can be extremes in humidity [1]. It is well known that the lifetime of disk drives is strongly dependent on the tribological behavior of the head–disk interface, which is dominated by the interactions between a thin layer of lubricant and a carbon-based overcoat [2]. A number of papers have reported that humidity can affect lubricant mobility, and ultimately disk lifetime [2–4]. Also, it is known that humidity plays an important role in media corrosion [1].

Sputtered carbon films containing hydrogen and/or nitrogen are the overcoat material of choice on hard disk magnetic media. In all cases, the deposited coatings are amorphous, containing hydrogen to saturate the dangling carbon bonds and to prevent oxidation, and containing nitrogen to improve the overcoat durability [5]. Recently, a new type of nanostructured carbon nitride film has been described. Resembling parts of a fullerene

structure, it consists of  $sp^2$ -coordinated graphitic basal planes that are buckled due to the incorporation of pentagons and cross-linked at  $sp^3$ -hybridized C sites, both of which are caused by structural incorporation of nitrogen [6]. This nanostructured coating, called fullerene-like carbon nitride (FL- $CN_x$ ), has many tribological advantages over amorphous a- $CN_x$  in properties such as hardness, friction coefficient, wear resistance, and elastic recovery [7–10]. In this work we have studied the amount of water adsorbed on lubricated and non-lubricated amorphous and fullerene-like carbon nitride overcoats.

### 2. Experimental

Carbon films were deposited on quartz substrates by magnetron sputtering. A pure hot-pressed graphite target (75 mm diameter) with a density of approximately  $1.83 \text{ g cm}^{-3}$  was reactively sputtered in an  $N_2$ /Ar (99.9999% purity) discharge at a variety of  $N_2$  partial pressures by means of a DC unbalanced magnetron operated at a constant total pressure of 0.4 Pa and at a constant discharge current of 400 mA. The plasma was confined in front of the substrate by a mirrored magnetic field generated from a second magnetron.  $CN_x$  coatings were deposited onto

\* Corresponding author.

E-mail address: [broitman@andrew.cmu.edu](mailto:broitman@andrew.cmu.edu) (E. Broitman).

Table 1  
Deposition parameters for the analyzed films along with their composition, densities and respective growth rates

Name	N <sub>2</sub> fraction in plasma	T <sub>substrate</sub> (°C)	U <sub>Bias</sub> (V)	C <sub>nitrogen</sub> <sup>a</sup> (at.%)	Density <sup>a</sup> (g cm <sup>-3</sup> )	Growth rate <sup>a</sup> (× 10 <sup>-1</sup> nm s <sup>-1</sup> )
a-C	0	150	25	–	2.1	0.42
a-C <sub>sp<sup>2</sup></sub>	0	450	25	–	0.6	1.52
FL-CN <sub>x</sub>	0.16	450	25	17	2.2	0.35
a-CN <sub>x</sub>	1	150	25	25 ± 5%	2.3 ± 0.6%	0.95
a-CH <sub>y</sub>	Commercial overcoat provided by Seagate Inc. containing ~ 20% of H					

<sup>a</sup> From Ref. [8].

both sides of quartz crystals mounted in a biased substrate holder that was rotated and resistively heated from the reverse side. It was mounted at the focal point between the two magnetrons at a distance of 120 mm. More details on the deposition setup as well as a detailed process characterization can be found elsewhere [8].

The apparatus designed and constructed for measurement of humidity adsorption on lubricated overcoats has been described previously [11,12]. It consists of a vacuum chamber that can be evacuated by a turbopump or a sorption pump and it operates in the pressure range of 10<sup>-6</sup>–10<sup>-5</sup> Pa. The turbopump is used initially to achieve a base pressure of 10<sup>-6</sup> Pa, while the sorption pump is utilized during the experiments to avoid vibrations of the quartz crystal microbalance (QCM). The chamber houses a valve for introducing water vapor at controlled rates. A capacitance manometer was used to measure the partial pressure of water in the range 10<sup>1</sup>–10<sup>5</sup> Pa. The QCM housing is capable of holding 3 quartz crystals for simultaneously monitoring water adsorption on three surfaces. The temperature of the QCM is measured by a K-type thermocouple spot-welded to the quartz crystal housing. The QCM is controlled at 50 °C using flowing water.

Some of the quartz crystals were coated with CN<sub>x</sub> alone to allow measurement of water adsorption on the carbon surfaces. Other coated quartz crystals were modified by dip-coating to apply a 2-nm-thick layer of Z-tetraol, a lubricant used in hard disk devices [13]. Once their surfaces were prepared, the quartz crystals were mounted in the QCM housing and inserted into the vacuum chamber.

The exposure of the lubed and unlubed CN<sub>x</sub> 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 valve to the sorption pump was closed. The pressure and the QCM frequency were monitored simultaneously until the pressure reached the desired value. At that point, the needle valve was closed and the pressure allowed to remain constant until the drift in QCM frequency was lower than 0.1 Hz over a period of 5 min. At that point, the water vapor was pumped away by opening the valve to the sorption pump, and the QCM frequency was monitored until the drift was again lower than 0.1 Hz in a period of 5 min.

The mass of water adsorbed on the surface of the quartz crystal was calculated using the Sauerbrey equation [11,12],

$$\Delta f = -C\Delta m$$

where  $\Delta f$  and  $\Delta m$  are the change in frequency and the adsorbed mass of water, respectively. The quantity  $C$  is a constant that depends on the specific density, the shear wave velocity and frequency of the crystal quartz. The value of constant  $C$  in our experiments is 0.0565 Hz cm<sup>-2</sup> ng<sup>-1</sup> [12]. Because both sides of the quartz crystal were coated with the CN<sub>x</sub> films and lubricants, the contribution of both surfaces were used for the calculation of the adsorbed mass.

### 3. Results and discussion

#### 3.1. Film composition and structure

CN<sub>x</sub> coatings were grown at different bias voltages, N<sub>2</sub> pressures and substrate temperatures ( $T_s$ ) in order to synthesize fullerene-like (FL-CN<sub>x</sub>) and amorphous (a-CN<sub>x</sub>) carbon nitride coatings as well as nitrogen-free graphite (a-C<sub>sp<sup>2</sup></sub>) and DLC (a-C)-type coatings (see Table 1).

Pure carbon coatings are known to form an amorphous and low density structure at higher temperatures and low ion bombardment, due to the incorporation of exclusively sp<sup>2</sup>-hybridized carbon into aromatic structures [8,14]. This is the case for the sample grown in a pure Ar discharge at  $T_s$ =450 °C and

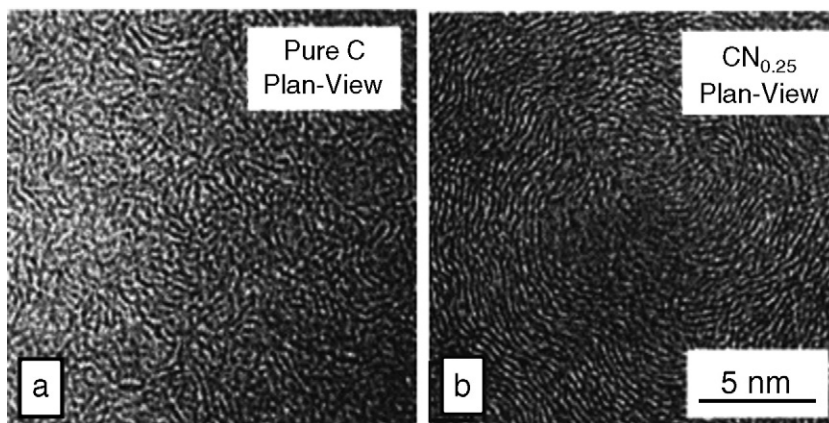


Fig. 1. Plan-view TEM micrographs of: (a) amorphous carbon film grown in pure Ar; (b) fullerene-like CN<sub>x</sub> film deposited with 16% N<sub>2</sub>, indicating concentric arrangements.

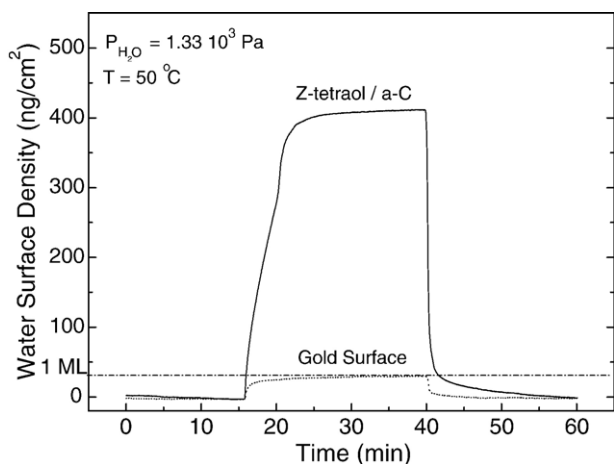


Fig. 2. The mass of water adsorbed on the surface of quartz crystals covered with gold and with a lubricated a-C film during exposure H<sub>2</sub>O vapor. The dotted line indicates the value of 1 ML of H<sub>2</sub>O on the surface.

$V_{\text{Bias}} = -25$  V (sample a-C<sub>sp<sup>2</sup></sub>, Table 1). If the growth temperature is lowered, as for the sample grown at 150 °C and  $-25$  V (sample a-C), sp<sup>3</sup>-hybridized carbon generated by ion bombardment is incorporated and the aromatic sp<sup>2</sup>-hybridized structures network is disrupted; hence, denser amorphous coatings can be formed, as shown in the plan-view transmission electron microscopy of Fig. 1a [8,14].

When the films are grown at  $T_s = 450$  °C with 16% nitrogen present in the sputtering gas (sample FL-CN<sub>x</sub>), plan-view transmission electron microscopy (Fig. 1b) indicates a fullerene-like structure in the form of curved basal planes resembling the arrangement of a leek or onion, but with buckling and interlinking of planes [14]. A lower substrate temperature of 150 °C significantly affects the coating structure and properties. The desorption of volatile nitrogen-containing species from the growth surface during deposition (chemical sputtering) is suppressed, the FL sheets are no longer observable and the material is considered amorphous [8]. This is the case for the coating grown in a pure N<sub>2</sub> discharge at  $T_s = 150$  °C (sample a-CN<sub>x</sub>).

## 3.2. Water adsorption

### 3.2.1. Nature of the adsorption process

Initial work compared water adsorption on quartz crystals with and without lubricated overcoats. A blank gold-coated quartz crystal and one modified with Z-tetraol/a-C were introduced into the chamber at the same time and subjected to the same humidity and temperature conditions. Fig. 2 shows both the adsorption and desorption of H<sub>2</sub>O from the surfaces during exposure to H<sub>2</sub>O vapor at 50 °C followed by evacuation. The chamber was first under vacuum, with a base pressure of  $1.0 \times 10^{-4}$  Pa. After 15 min, H<sub>2</sub>O vapor was admitted into the chamber through the needle valve; the pressure rose to a final vapor pressure of  $1.33 \times 10^3$  Pa and then the valve was closed. At room temperature, a H<sub>2</sub>O vapor pressure of  $1.33 \times 10^3$  Pa is estimated to correspond to 50% relative humidity (RH), while at 50 °C it corresponds to 10% RH. The frequency changes of the crystals were monitored until a steady constant value was

reached and then the H<sub>2</sub>O vapor was rapidly pumped out from the chamber by the sorption pump.

An important feature of Fig. 2 is the difference between the amounts of H<sub>2</sub>O adsorbed on the lubricated carbon surface and the gold surface. As expected, the adsorption on the lubricated overcoat is higher than on the gold surface as the latter is probably quite inert. Typically, at a pressure of  $1.33 \times 10^3$  Pa the amount of H<sub>2</sub>O adsorbed on the gold surface is  $29 \pm 5$  ng cm<sup>-2</sup> while the amount of H<sub>2</sub>O on Z-tetraol (lubricated overcoat on sample a-C) is  $405 \pm 5$  ng cm<sup>-2</sup>.

Another important feature to be noted about Fig. 2 is the rate of adsorption and desorption of H<sub>2</sub>O from the surface of the lubricated overcoat. During introduction of the H<sub>2</sub>O vapor into the chamber, the adsorbed mass of H<sub>2</sub>O roughly increases linearly in time. As the pressure reaches  $1.33 \times 10^3$  Pa, the coverage of H<sub>2</sub>O reaches a plateau. During evacuation the amount of adsorbed H<sub>2</sub>O drops to approximately to zero in a few seconds. The implication of this observation is that there exists a dynamic equilibrium between the adsorbed water on the surface and the water vapor phase presented in the chamber. It is clear that on the time scales in which the humidity within a normal hard disk drive changes, the coverage of the adsorbed H<sub>2</sub>O on the media surface is in equilibrium with the humidity in the drive [11].

It is important to determine the coverage of H<sub>2</sub>O on the lubricated carbon overcoats in the presence of humidity. The volume of a water molecule is roughly 30 Å<sup>3</sup> and thus the area per molecule is approximately  $10^{-15}$  cm<sup>2</sup> and the mass corresponding to one monolayer coverage is roughly 30 ng cm<sup>-2</sup>, as indicated by the dotted line in Fig. 2. We have made several assumptions in arriving at this estimate. One is that the packing of water in the adsorbed layer on the lubricated overcoats is similar to the packing density of water in the condensed state. Secondly, the surface area of the lubricated overcoat is roughly its apparent surface area, neglecting possible surface roughness and porosity. In Fig. 2, this result indicates that a clean gold surface adsorbs roughly 1 monolayer (ML) of water at a H<sub>2</sub>O vapor pressure of  $1.33 \times 10^3$  Pa and a temperature of 50 °C.

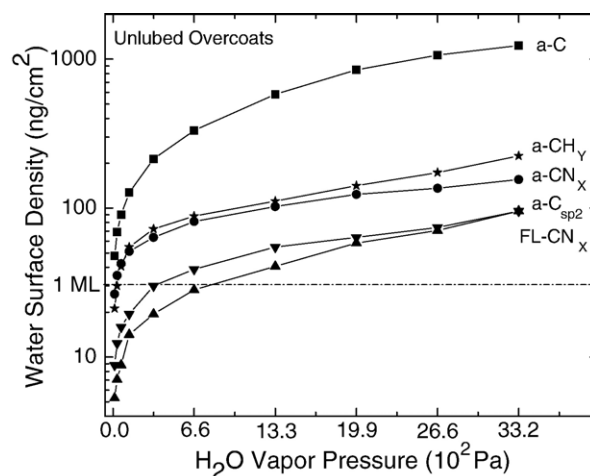


Fig. 3. The mass of water adsorbed on the surface of quartz crystal with unlubricated carbon overcoats at 50 °C versus pressure. The dotted line indicates the value of 1 ML of H<sub>2</sub>O on the surface.

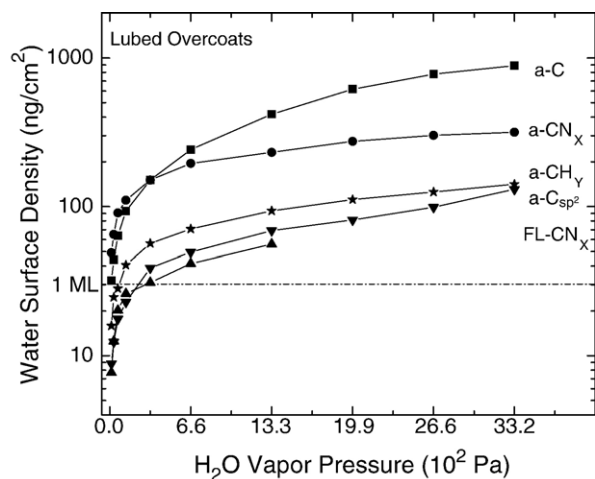


Fig. 4. The mass of water adsorbed on the surface of quartz crystal with lubricated carbon overcoats versus pressure. The Z-tetraol lubricant film was dip-coated to produce a thickness of 2 nm. The dotted line indicates the value of 1 ML of H<sub>2</sub>O on the surface.

### 3.2.2. Adsorption of H<sub>2</sub>O on unlubed CN<sub>x</sub> overcoats

Fig. 3 shows the adsorption of water versus the water vapor pressure for films deposited under different conditions (see Table 1). For comparison, the adsorption of water on a commercial overcoat (a-CH<sub>y</sub>) is also indicated. All films show a characteristic dependence of water coverage on the H<sub>2</sub>O vapor pressure. There are, however, differences in the amounts of the adsorbed water. We can classify the films into three different groups. A first group of films, FL-CN<sub>x</sub> and a-C<sub>sp<sup>2</sup></sub>, show the lower adsorption. Taking into consideration that one monolayer coverage is roughly 30 ng cm<sup>-2</sup> (cf. Section 3.2.1) and that at 50 °C  $1.33 \times 10^3$  Pa of H<sub>2</sub>O vapor is equivalent to 10% RH, these films adsorb less than 2 ML of water on their surface at that pressure. The second group of films, a-CN<sub>x</sub> and the commercial a-CH<sub>y</sub>, has adsorbed roughly 2–3 times more water than the first group. Finally, the film a-C adsorbs more than 14 times the amount adsorbed by FL-CN<sub>x</sub>.

There are very few comparative studies on the adsorption of water on carbon films with different microstructure and/or composition. Smallen et al. [15] have measured water adsorption of CH<sub>y</sub> films deposited by sputtering in different Ar–C<sub>2</sub>H<sub>2</sub> gas mixtures (0 to 30% of C<sub>2</sub>H<sub>2</sub>). Their ellipsometric measurements of the thickness of adsorbed water have shown that the adsorption increased with the relative humidity (RH) and concentration of hydrogen in the film. Lee et al. [16] studied indirectly the adsorption of water on a-CN<sub>x</sub> films. They measured the electrical properties of the coatings as a function of ambient humidity, and proposed the carbon nitride film as a novel humidity sensor. Broitman et al. [17] also compared the electrical properties of a-C, a-CN<sub>x</sub> and FL-CN<sub>x</sub> films. It was found that, after exposure to atmosphere, FL-CN<sub>x</sub> films were unaffected by humidity, while the a-C films were very sensitive to H<sub>2</sub>O vapor exposure.

It has been shown that the adsorption of water on carbon films is proportional to the hydrogen content of the overcoats [15]. This result has been correlated to the incorporation of

hydrogen into the carbon structure, which makes the film more polar. As all our films (except a-C) have an amount of hydrogen below 0.1% [17], they should adsorb less water than a-CH<sub>y</sub>, however, Fig. 3 indicates that this is not the case. The differences in adsorption on our films must be understood based on the differences in the microstructural and morphological properties of the films.

The surface of sputtered carbon-based films are heterogeneous and composed of different hybridized carbon atoms (sp, sp<sup>2</sup> and sp<sup>3</sup>) and dangling bonds. As soon as the surface is exposed to air, its dangling bonds react with oxygen and form oxygen containing polar groups such as C–O–C, C–OH, C–H, and C=O [18,19]. Because of the hydrogen bonding tendency of water, the adsorption of water is sensitive to the polarity of the adsorbent surface [15] and is enhanced by the presence of oxidized carbon. We should expect that, because of the fullerene-like structure (cf. Section 3.1), FL-CN<sub>x</sub> films have the lowest number of dangling bonds and, as a consequence, low water adsorption.

Another factor that could play an important role on the water adsorption is the surface roughness, as pointed out by Smallen et al. [15]. In a previous work [17] we found that the a-C sample has an rms roughness of 15 nm, the a-CN<sub>x</sub> sample has an rms roughness 2.5 nm, and FL-CN<sub>x</sub> has the lowest roughness (rms=0.4 nm). The surface roughness correlates well with the water adsorption shown in Fig. 3. Increased surface roughness increases the surface area and creates valleys with micro-crevices. At high RH, capillary condensation can occur in the valleys giving thicker water films.

### 3.2.3. Adsorption of H<sub>2</sub>O on lubed CN<sub>x</sub> overcoats

Fig. 4 shows water adsorption isotherm for the overcoats lubricated with 2 nm of Z-tetraol. The dependence of the adsorption on the water pressure is similar for the lubricated and the unlubricated films. However, when we compare the amount of water adsorbed before and after lubrication, we observe a non-uniform behavior: as illustrated in Fig. 5 for a pressure of  $1.33 \times 10^3$  Pa, the lubricated a-C and a-CH<sub>y</sub> overcoats adsorbed less water than the unlubricated ones. We should note that these

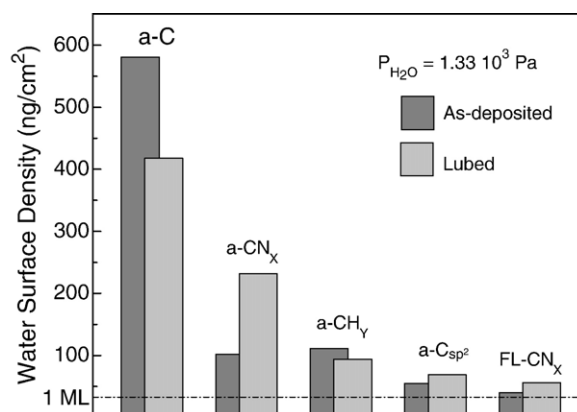


Fig. 5. The mass of water adsorbed on the surface of quartz crystal with unlubricated and lubricated carbon overcoats at  $1.33 \times 10^3$  Pa and 50 °C. The dotted line indicates the value of 1 ML of H<sub>2</sub>O on the surface.

two films are the only ones containing hydrogen: a-C film has a hydrogen content of about 25% [17], while the commercial a-CH<sub>y</sub> sample has about 20% hydrogen.

Shukla et al. [12] measured the adsorption of water on lubricated a-CH<sub>y</sub> films, and noticed that the amount of water adsorbed was roughly half that adsorbed on the unlubricated a-CH<sub>y</sub> films. The inhibition was correlated to the fact that the surfaces of the media are hydrophobic once coated with the lubricants. Smallen et al. [15] reported that water adsorption on unlubricated and lubricated carbon overcoats disks depends on the hydrogen content of the films. In our case, the only correlation we can use is the presence of hydrogen in the films: when a film contains hydrogen, the lubricated film adsorbed less water. The reason for this dependence is unknown. Further investigation of the subject is planned.

#### 4. Conclusions

QCM measurements have probed the effect of microstructure and composition of carbon overcoat surfaces on the adsorption of water. We have shown that the water adsorbed on the unlubricated or lubricated surfaces is in equilibrium with the ambient humidity, and any change in ambient humidity can cause significant changes in the coverage of adsorbed water on a time scale of seconds.

In principle, the microstructure of the unlubed overcoat seems to influence the adsorption level: amorphous coatings absorb more water than the nanostructured fullerene-like carbon nitride films. Also, surface roughness plays a role in the adsorption of water at high levels of RH.

The presence of lubricant affects slightly the films: they show a similar dependence on the humidity as the unlubricated ones. However, the adsorption level seems to depend on the presence of hydrogen in the film.

The water adsorption of fullerene-like carbon nitride films is lower than that of the commercial a-CH<sub>y</sub> overcoats and is comparable to the inert gold films. Given their superior tribological properties, FL-CN<sub>x</sub> overcoats have a potential application in the hard disk industry.

#### Acknowledgments

EB, VVP, and AJG acknowledge the National Science Foundation, Grant No. CMS-0408574. JN, AF, and LH acknowledge the European Commission and The Swedish Foundation for Strategic Research (SSF) Strategic Research Center in Materials Science for Nanoscale Surface Engineering. In addition, all the authors would like to thank Seagate Inc. for supplying the a-CH<sub>y</sub> samples and coating other samples with Z-tetraol.

#### References

- [1] D.E. Fowler, R. Duque, T. Anokin, J. Zhou, *IEEE Trans. Magn.* 39 (2) (2003) 769.
- [2] Q. Dai, G.H. Vurens, M. Luna, M. Salmeron, *Langmuir* 13 (1997) 4401.
- [3] T.E. Karis, *J. Colloid Interface Sci.* 225 (2000) 196.
- [4] P.H. Kasai, V. Raman, *Tribol. Lett.* 16 (1–2) (2004) 29.
- [5] E.V. Anokin, M.M. Yang, J.L. Chao, J.R. Elings, D.W. Brown, *J. Vac. Sci. Technol., A, Vac. Surf. Films* 16 (3) (1998) 1741.
- [6] L. Hultman, J. Neidhardt, N. Hellgren, H. Sjoström, J.E. Sundgren, *MRS Bull.* 28 (3) (2003) 194.
- [7] E. Broitman, N. Hellgren, O. Wännstrand, M.P. Johansson, T. Berling, H. Sjoström, J.E. Sundgren, M. Larsson, L. Hultman, *Wear* 248 (1–2) (2001) 55.
- [8] J. Neidhardt, L. Hultman, E. Broitman, T.W. Scharf, I.L. Singer, *Diamond Relat. Mater.* 13 (10) (2004) 1882.
- [9] E. Broitman, W. Macdonald, N. Hellgren, G. Radnoczi, Z. Czigany, A. Wennerberg, M. Jacobsson, L. Hultman, *Diamond Relat. Mater.* 9 (12) (2000) 1984.
- [10] E. Broitman, W.T. Zheng, H. Sjoström, I. Ivanov, J.E. Greene, J.E. Sundgren, *Appl. Phys. Lett.* 72 (20) (1998) 2532.
- [11] N. Shukla, A.J. Gellman, X. Ma, J. Gui, *Tribol. Lett.* 12 (2) (2002) 105.
- [12] N. Shukla, E. Svedberg, R.J.M. van der Veerdonk, X. Ma, J. Gui, A.J. Gellman, *Tribol. Lett.* 15 (1) (2003) 9.
- [13] Samples were dip-coated with 2 nm of Z-tetraol at Seagate, Inc.
- [14] E. Broitman, N. Hellgren, K. Jarrendahl, M.P. Johansson, S. Olafsson, G. Radnoczi, J.E. Sundgren, L. Hultman, *J. Appl. Phys.* 89 (2) (2001) 1184.
- [15] M. Smallen, J.K. Lee, A. Chao, J. Enguero, *IEEE Trans. Magn.* (1994) 4137.
- [16] G.L. Lee, S.L. Lee, *Sens. Actuators, B, Chem.* 108 (2005) 450.
- [17] E. Broitman, N. Hellgren, J. Neidhardt, I. Brunell, L. Hultman, *J. Electron. Mater.* 31 (9) (2002) L11.
- [18] N. Shukla, A.J. Gellman, J. Gui, *Langmuir* 16 (16) (2000) 6562.
- [19] R.H. Wang, R.L. White, S.W. Meeks, B.G. Min, A. Kellock, A. Homola, D. Yoon, *IEEE Trans. Magn.* 32 (5) (1996) 3777.