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# Water adsorption and desorption on ultra-low friction sulfur-doped hydrogenated carbon films

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## Abstract

Water adsorption on hydrogenated carbon film surfaces can drastically affect friction behaviour. In this work, we investigate water adsorption and desorption properties of sulfur-doped hydrogenated films, which we have observed to retain ultra-low friction properties of hydrogenated carbon films in humid air. Water adsorption studies using a quartz crystal microbalance show that there is an almost threefold reduction in equilibrium water coverage at room temperature on hydrogenated carbon films doped with 5 at.% sulfur. Thermal desorption studies indicate that sulfur doping weakens the binding of water molecules on hydrogenated carbon film surfaces.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Properties of diamond-like carbon (hydrogenated carbon) films vary drastically with preparation methods and composition. This subject has been extensively reviewed (see [1] and references therein). When surfaces are coated with highly hydrogenated carbon films, one obtains friction coefficients of less than 0.01 in dry nitrogen. This low-friction behaviour is attributed to low adhesive force acting at the coating–coating interface, which is influenced by many factors such as the hydrogen content and testing environment [2–6]. For example, the coefficient of friction increases from 0.001 in dry nitrogen to >0.05 in nitrogen with relative humidity of 25% or higher. The strong dependence on humidity has been attributed to viscous and capillary forces induced by adsorbed water [7]. Therefore, there is interest in suppressing the humidity sensitivity of friction for these films by reducing water adsorption on the film surface.

Our recent studies showed that by doping hydrogenated carbon films with a few atomic percent of sulfur, we completely suppress the moisture sensitivity of friction in air with

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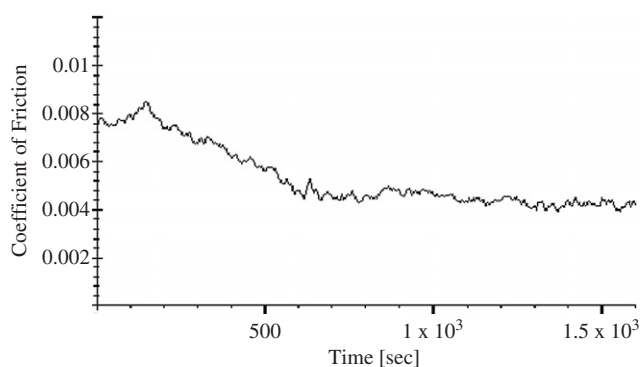
relative humidity as high as 70%. The purpose of this paper is to present results of temperature-programmed desorption and quartz crystal microbalance (QCM) measurements on the activated desorption and equilibrium adsorption of water vapour on undoped and sulfur-doped hydrogenated carbon films in an attempt to understand the role of sulfur in suppressing moisture sensitivity of friction. QCM measurements can detect subnanograms  $\text{cm}^{-2}$  of adsorbed materials on surfaces, enabling detection of partial monolayer coverage [8]. Water adsorption on carbon-based overcoats has been studied in relation to hard disk data storage devices. Smallen *et al* measured water coverage on hydrogenated carbon overcoats with an ellipsometer. They observed the increase of water coverage with humidity and hydrogen concentration in the film. They measured  $\sim 1.5$  monolayers of water on films synthesized with the highest hydrogen concentration in sputtering gas [9]. Shukla *et al* observed water adsorption as a function of humidity on hydrogenated carbon-coated quartz crystals. Saturation coverage of about 1.5 ML of water ( $\sim 0.45$  nm thick) was measured on the hydrogenated carbon surface at 60% relative humidity. They observed that thickness and therefore pore volume did not increase water adsorption on hydrogenated carbon films [10].

## 2. Experimental details

Hydrogenated carbon films were deposited in a single-cathode unbalanced magnetron sputter-deposition system with a base pressure of better than  $5 \times 10^{-6}$  Pa ( $5 \times 10^{-8}$  Torr). A 5 cm diameter pure graphite target was used. The target power was set at 100 W pulsed at 150 kHz (80% duty cycle), with the positive voltage set at 10% of the negative voltage. The sputter-gas was an argon–hydrogen–hydrogen sulfide mixture. The argon–hydrogen ratio remained constant at 15% hydrogen, balance argon at a sputtering pressure of 6 mTorr (0.8 Pa). For results reported in this paper, the hydrogen sulfide partial pressure was set at 0.02 mTorr, resulting in 5 *a/o* sulfur concentration in these carbon films. Low-resistivity silicon(100) wafers and 6.35 mm diameter stainless steel ball bearings were used as substrates for friction testing. Prior to carbon film deposition, the ball bearings were coated with 75 nm of silicon by sputtering to improve film adhesion. All substrates were ultrasonically cleaned in acetone and methanol before being introduced into the deposition chamber and sputter-cleaned in argon before deposition. The substrate was pulse-biased at  $-25$  V 20 kHz to improve the efficiency of ion bombardment during film growth. The film thickness was set at  $1.0 \mu\text{m}$  for all friction samples and temperature-programmed desorption samples.

Friction properties were measured using a CETR Micro-Tribometer (UMT) in a standard ball-on-flat configuration at room temperature at a track radius of 1 mm to minimize levelling problems. Both the ball and flat were coated. Friction and water absorption measurements took place in a glove box. The humidity was controlled by the amount of humid air introduced via an ultrasonic humidifier into the glove box containing dry air. For water adsorption measurements, Maxtek Inc. 5 MHz AT-cut quartz crystal sensor crystals with Cr/Au electrodes were coated under the same conditions to a thickness of about 15–20 nm at a substrate bias of  $-50$  V 20 kHz. The QCM apparatus was allowed to equilibrate at each humidity level between 0 and 70% relative humidity at room temperature before the mass change was recorded.

Temperature-programmed desorption experiments were carried out in a stainless steel ultra-high vacuum chamber with a base pressure of  $1.5\text{--}3 \times 10^{-10}$  Torr equipped with sputter-ion gun, gas handling, and residual gas analyser (SRS RGA 100). A sputter-cleaned sulfur-doped hydrogenated carbon film was cooled down to 140 K by a copper contact with a liquid nitrogen reservoir.  $\text{H}_2\text{O}$  was then introduced into the chamber through a needle doser placed  $\sim 1$  cm from the sample. Gas exposures were expressed in Langmuir units where 1 Langmuir (L) =  $1 \times 10^{-6}$  Torr s. To achieve a certain gas exposure, the  $\text{H}_2\text{O}$  pressure in the vacuum



**Figure 1.** Friction coefficient versus time for sulfur-doped hydrogenated carbon films, obtained at 65% relative humidity air and 55 g load.

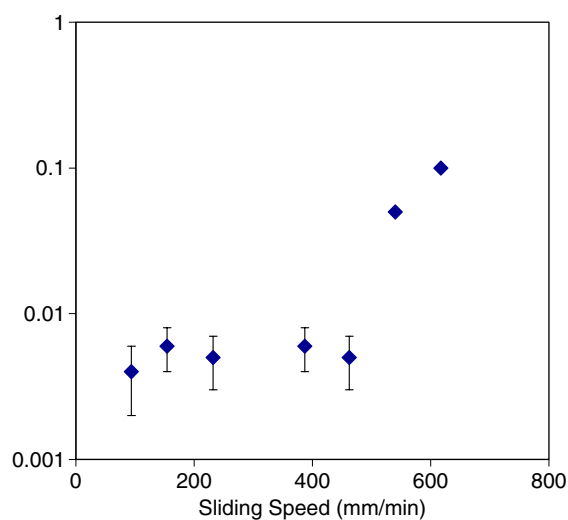
chamber was kept at  $1 \times 10^{-7}$  Torr for a specific time. The sample was then heated to room temperature at about  $2 \text{ K s}^{-1}$ . The water desorption signal ( $m/e = 18$ ) from the sample surface was monitored with the residual gas analyser.

### 3. Results and discussion

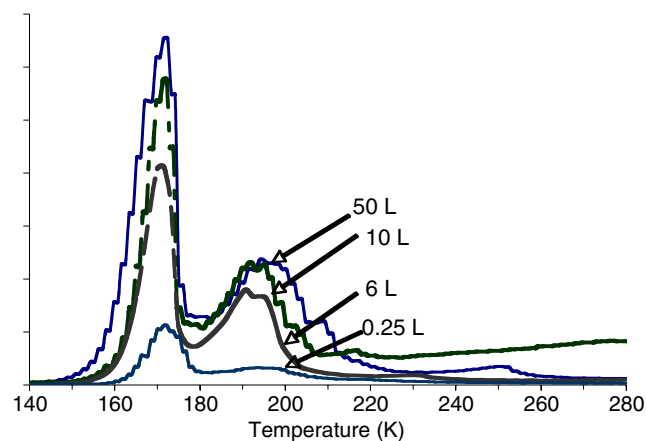
Figure 1 shows friction data for hydrogenated carbon films doped with 5 at% sulfur, tested at 1 mm radius, linear speed of  $0.386 \text{ m min}^{-1}$ , and 65% relative humidity. The steady-state coefficient of friction is 0.005 after a run-in period. The run-in period is probably due to the removal of a thick layer of adsorbed impurities accumulated during air exposure. In dry air, the steady-state coefficient of friction under otherwise identical testing conditions is  $0.004 \pm 0.001$ , for both the undoped and sulfur-doped films. On the other hand, the steady-state coefficient of friction for undoped films increases to  $>0.03$  at 65% relative humidity, i.e. almost tenfold increase.

Sliding speed has been observed to affect friction of undoped films. Heimberg *et al* observed that slow speeds produced larger friction coefficients. At faster speeds, the exposure time of the testing track to ambient air between passes is shorter, resulting in shorter exposure to ambient gas (water vapour) adsorption and hence lower friction coefficient [6]. Figure 2 shows friction behaviour tested at 100 g load and 65–70% RH at various testing speeds. The friction coefficient is independent of sliding speed between 0.1 and  $0.5 \text{ m min}^{-1}$ . The constant friction coefficient is evidence that ambient gas adsorption has minimal effects on the friction coefficient. Above  $0.5 \text{ m min}^{-1}$ , the friction coefficient increases with sliding speed. A back-of-envelope calculation shows that the temperature rise for the system involved should be only about 10 K, assuming that the surfaces are smooth. However, asperity flash heating may result in significantly higher local temperatures, resulting in sulfur loss and hence degradation of friction performance. The friction increase to levels comparable to those of undoped films in ambient air is consistent with this interpretation.

Figure 3 shows a series of temperature-programmed desorption spectra due to water desorbing from a sulfur-doped hydrogenated carbon film. Two peaks were observed, with one at 172 K and the other at 195 K. Based on numerous previous studies of water adsorbed on surfaces, the 172 K peak is attributed to water desorbing from ice multilayers, while the peak at 195 K is attributed to desorption of the first water layer adsorbed on the film surface. The fact that the multilayer peak exists even at the lowest exposure suggests that the surface is non-



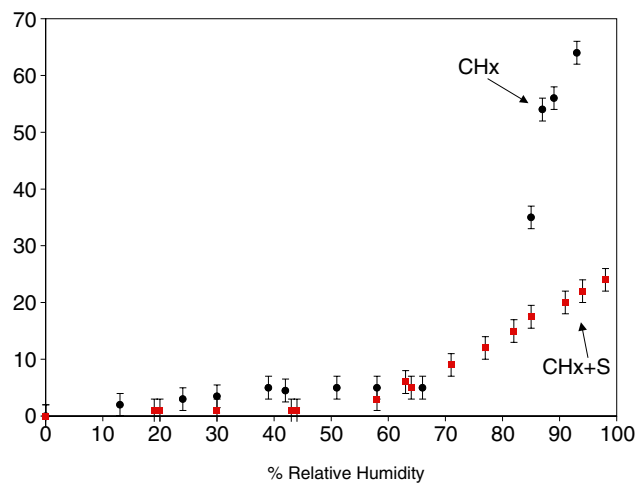
**Figure 2.** Coefficient of friction versus sliding speed, tested at 100 g load and 65–70% relative humidity.



**Figure 3.** Temperature-programmed desorption spectra for water desorption as a function of initial exposure at 140 K.

wetting, with the formation of microscopic water droplets. Assuming first-order desorption kinetics, one can show that the activation energy for thermal desorption is  $50.4 \text{ kJ mol}^{-1}$ . Preliminary experiments show that for the undoped films, the higher temperature desorption peak occurs at 206 K, corresponding to an activation energy for desorption of  $53.2 \text{ kJ mol}^{-1}$ . This indicates that the binding of water molecules is slightly weaker on the sulfur-doped surface. At room temperature, this  $2.8 \text{ kJ mol}^{-1}$  reduction in the desorption energy results in about threefold reduction in the average residence time for adsorbed water molecules at room temperature and hence lower equilibrium concentration of adsorbed water molecules on sulfur-doped film surfaces.

Figure 4 presents the amount of water adsorbed per  $\text{cm}^2$  of the film surface (undoped and sulfur doped) as a function of relative humidity at room temperature, as measured by



**Figure 4.** Weight gain due to water adsorption on undoped and sulfur-doped hydrogenated carbon films as a function of relative humidity, as measured by a quartz crystal microbalance.

the QCM. At 90% relative humidity, the undoped film adsorbed a maximum of  $56 \text{ ng cm}^{-2}$ , corresponding to 1.8 ML of water, while the sulfur-doped film adsorbed a maximum of  $21 \text{ ng cm}^{-2}$ , corresponding to 0.68 ML of water. The latter number represents about a factor of 2.7 reduction in water coverage, consistent with the reduction in residence time on the sulfur-doped surface.

Tagawa *et al* observed a direct link between water coverage on a hydrogenated carbon surface and friction coefficient. The friction coefficient increases markedly when the water coverage exceeds two monolayers [11]. Therefore, the observed reduction of water coverage to less than a monolayer for sulfur-doped carbon film surfaces may explain why sulfur-doped films retain the low-friction properties in ambient air.

#### 4. Conclusions

In this study, we show that sulfur-doped hydrogenated carbon films give low friction under ambient air conditions, independent of relative humidity up to 70%. Results of thermal desorption and quartz crystal microbalance measurements suggest that this low-friction performance may be related to reduced uptake of water (less than one monolayer) under normal ambient air conditions. This in turn results in reduction of meniscus and viscous forces attributed to water adsorption, and hence suppression of moisture effects.

#### Acknowledgments

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