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Measurement of disjoining pressure of Z-type perfluoropolyether lubricants on Si and SiN_x surfaces

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Abstract

An AFM based measurement of the disjoining pressure (Π) is described. For the measurement of nano-thin fluids on hard substrates it was shown that specific experimental requirements are placed on the cantilever stiffness and probe radius. The disjoining pressure of Fomblin Z03 was then measured on a Si surface and found to be consistent with literature values. The disjoining pressures (Π) of 25 Å Zdol on SiN_x films deposited under a flowing-gas of N_2 was measured and a sharp decrease in Π was observed with increasing N_2 concentration (in the gas) that was assigned to the decrease in the polarizability and/or the density of polarizable species in the surface.

Keywords: Z-type perfluoropolyether; Disjoining pressure; Si surface; SiN_x surface

1. Introduction

In the magnetic recording disk industry a layer of liquid lubricant is used to reduce friction and wear of the head-disk interface [1]. Polymers of perfluoropolyethers (PFPE) are most commonly used for this purpose, where their chemical inertness makes them particularly effective. Thin films of these PFPE polymers are routinely applied to the disk surface by a dip-pull process. The most typical polymers used to lubricate the disk surface have a Fomblin Z backbone, which are terminated with various end groups and are coated onto a protective overcoat of sputtered nano-thin carbon film (<50 Å) [2]. Due to the increasing need for greater areal density the magnetic spacing between the read/write transducer and the magnetic disk must be reduced. This can be partly achieved by reducing the thickness of this protective layer. Past studies have shown that sputter-deposited SiN_x films provide excellent coverage and have enhanced tribological attributes, including low pinhole densities and excellent durability. In particular, recent studies suggest that a stable 10–15 Å thick SiN_x film is obtainable using rf sputtering from a Si target, thus dramatically minimizing the overcoat thickness contribution to the magnetic spacing [3–5].

The concept of a disjoining pressure, Π, was first introduced by Derjaguin in 1936 [6,7]. It is defined as the negative derivative of the interaction free energy per unit area (E), and plays the role of an excess film pressure [8,9]

$$\Pi_{\mathrm{SLV}}(h) = -\frac{\partial E_{\mathrm{SLV}}}{\partial D} \quad (1)$$

This expression is derived by considering the energy contribution of each of the substrate (S), lubricant (L) and vapor (V) phases of the hard disk surface (where D is the dimension of the gap between these substrates). When formulated in terms of the chemical potential it is easily shown that $\Pi > 0$ in order that the lubricant spreads and $\partial\Pi/\partial D < 0$ that it is stable. Thus, Π is of central importance to the effective operation of the hard disk surface.

Lubricant layers of 1–2 nm thickness exhibit disjoining pressures of $\sim$1–2 MPa [10], which is beyond the detectable range of traditional methods of interface science [11]. However, the measurement of the disjoining pressure of thin lubricant films on magnetic disk surfaces has been an active area of research. Tyndall et al. have used the contact

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angle change of sessile drops of hydrocarbons and water on a series of Fomblin thin liquid films to derive functional relationships between disjoining pressure and lubricant thickness for both Z-type and Zdol lubricants [12–15]. In a more direct manner, Mate et al. [16] have investigated the possibility of using the AFM to probe this fundamental property of the lubricant film.

In this submission, the measurement of the capillary force between the liquid lubricant film and the AFM cantilever as a function of separation is used to obtain the disjoining pressure of lubricated Si and SiN_x surfaces. A fuller description of our experimental approach is given elsewhere [17]. Instead, we will highlight the important theoretical results and justify the experimental needs of this technique.

From the geometry of a meniscus in contact with a spherical probe it is easily shown that at the instant of pull off of the probe the adhesive force is given by, $4\pi\gamma R$, where γ is the surface tension of the fluid and R the sphere radius. Thus, the pull off force (in this geometry) is *not dependent on the meniscus radius*. If this experiment is performed under equilibrium conditions in which a capillary is maintained throughout the pull off, then the capillary force versus separation (D) is

$$F(D) \cong -4\pi\gamma R\left(1 - \frac{D-h}{r_{\mathrm{eff}}}\right) \tag{2}$$

for a surface film that forms a meniscus of radius r_{eff} [16] and lubricant thickness h. Thus, by measuring the entire equilibrium pull off curve and fitting it to the above expression, the meniscus radius is found, which then gives

$$\Pi = -\frac{\gamma}{r_{\mathrm{eff}}} \tag{3}$$

Fig. 1 presents a schematic of the experiment in outline form, which we will use to highlight the experimental requirements of this AFM based technique. At a critical separation between the AFM tip and the substrate the film on the substrate will engulf the tip and exhibit strong capillary forces so that a 'jump-into-contact' of the surfaces occurs at point a on the idealized curve shown in Fig. 1. The AFM stage displacement is then reversed; initially, the tip stays stationary and the elastic stresses in the tip are relieved. The adhesive force is progressively transferred to the cantilever deflection, which increases rapidly. When the adhesive forces are balanced by the cantilever (point b on the curve), any further downward motion of the stage results in the recession of the meniscus down the tip and a rapid decrease in the adhesive force. The tip 'jumps' away from the substrate with a slope K_c at point b on the curve, which is the spring constant of the cantilever (see Fig. 1). If the cantilever has low stiffness then the resulting 'jump-out' will by-pass a large amount of the force curve (or possibly the entire curve). However, with a high stiffness spring constant the tip will jump out to a point where the meniscus is maintained and the capillary force curve can be measured until a second 'jump-out' ruptures the meniscus at point d on the curve.

Thus, the above approach requires that the capillary force curve be adequately probed by the AFM and places a limitation on the experimental conditions such that the AFM cantilever stiffness (K_c, see Fig. 1) and probe tip radius (R) must satisfy the following condition:

$$\frac{2\pi\gamma R}{r_{\mathrm{eff}}} < K_c \tag{4}$$

Meeting this condition insures that the probe 'jumps-out' to intercept the capillary curve. In order to measure large disjoining pressures (small r_{eff}) a tip of smaller radius and larger spring constant is needed. In this study, we have used, where necessary, a sphere with relatively large radius (R) glued to the AFM cantilever or a 'sharp' AFM probe tip to meet these conditions.

Mitsuya and Ohshima [18] have investigated the withdrawal velocity dependence of the capillary force of a Zdol film (5 nm) on a magnetic disk surface with an AFM probe. They reported an increase of force on the cantilever with increasing withdrawal velocity and assigned this result to the presence of viscous forces. Fig. 2 presents similar data taken on a Zdol coated (4.9 nm thick) silicon wafer in which

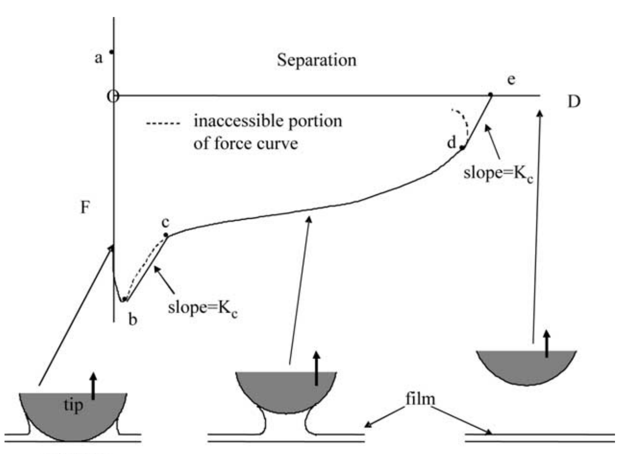

Fig. 1. Schematic of the AFM based measurement of Π. Idealized depiction of the force versus separation curve.

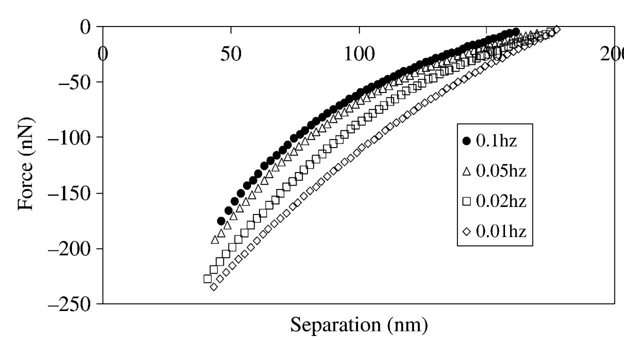

Fig. 2. Effect of scan rate on the capillary force curve (4.9 nm Z03 film on Si surface) probed with a spherical tip.

the rate of the approach and retract is incrementally increased (increasing velocity) and the full force versus separation curves are plotted. Immediately noticeable is the effect of increasing the rate is to decrease the capillary force. Thus, in our experimental configuration the change in force with scan rate (withdrawal velocity) is not due to viscosity effects, i.e. Reynolds drainage. If present, these effects would give rise to a more negative force at faster withdrawal rates. Instead, the change of the capillary force, with velocity, indicates that a meniscus with a larger effective capillary radius is formed at slower scan rates. For this reason all AFM derived data in this study have been taken under manual control (except where noted), which allows the quasi-static removal of the probe tip and the formation of an equilibrium meniscus. These effects and a more detailed description of the experimental parameters are given in Ref. [17].

The disjoining pressure data obtained with this experimental arrangement is presented in Section 3.1. This technique is then extended to the Zdol/SiN_x system in Section 3.2, where it exhibits a strong dependence on the substrate composition. Finally, this dependence is discussed in terms of the polarizability of the substrate in Section 4.

2. Experimental details

The cleaned silicon wafers used in this study have been coated with PFPE fluids by the dip coating procedure. In the case of the Z03 coated wafer an ellipsometer was used to measure the film thickness, whereas a FT-IR spectrometer was used for Zdol films on the SiN_x surfaces. All PFPE fluids used for these experiments were purchased the from Montedison Co. Z-type PFPE (number average molecular weight, 4000 g/mol) was applied to the Si surface. This PFPE is terminated with a CF_3 function and is expected to minimize dipolar and chemical forces with the surface. It was used without further refinement. The hydroxyl terminated Zdol-type PFPE (number average molecular weight 4000 and $M_w/M_n = 1.15$) was applied to the SiN_x surfaces.

The SiN_x films used in this study were rf-magnetron sputtered from doped Si targets. A turbo (400 l/s) and titanium sublimation pumped deposition system was used for this purpose which had an operating base pressure of 5×10^{-9} Torr. A series of depositions were performed with an argon and nitrogen gas mixture at a pressure of 1.3 mTorr. The N_2 concentration in this gas was varied between 5 and 30%. All depositions resulted in a deposited film thickness of 100 Å. These films are labeled according to their N_2 concentration in the flowing gas (5, 10, 20 and 30%). Approximately 25 Å of Zdol was deposited onto these surfaces using the dip-pull method.

All AFM experiments were performed at 20% relative humidity using a commercial instrument (Nanoscope IIIa, Digital Instruments, Inc., Santa Barbara, CA). Two types of cantilevers were used in this study, a rectangular cantilever with a nominal spring constant of 0.1–15 N/m and a silica sphere (R ~0.5–10 μm) glued to its end (Novascan Technologies, Inc., Ames, IA) were used to probe the Z fluids. A conical silicon probe was used on the Zdol films. It had a nominal spring constant of 0.1–10 N/m and a sharp conical tip, R ~15–100 nm (Veeco Metrology LLC, Santa Barbara, CA). Except where noted, all AFM measurements were performed while the instrument was under manual control.

A Woollam VASE ellipsometer was used to measure the refractive indices of the deposited SiN_x films in the wavelength range from 270 to 1300 nm.

3. Results and analysis

3.1. Fomblin Z03 on silicon surfaces

Fig. 3 presents retraction force curves of increasingly thick Z03 lubricants (33, 42 and 50 Å) on a Si surface. This data was acquired under manual control of the retraction process, thus limiting non-equilibrium effects. A large decrease in the slope of the force versus separation curve is observed as the film is made thicker, indicating that the meniscus radius increases with increasing thickness. Importantly, the curvature of the individual curves, are ‘upwards’, and are indicative of the formation of an equilibrium capillary (Eq. (2)). A fit of the 3.3 nm thick Z03 curve to Eq. (2) is presented in Fig. 4 and shows the sensitivity of the fit to the meniscus radius. The disjoining pressures derived from the retraction curves fit in this manner are shown in Fig. 5. Π is observed to decrease monotonically with Z03 film thickness and spans the range from approximately 0.02 MPa at about 50 Å to about 0.7 MPa at about 10 Å. These values are in reasonable agreement with prior studies [19]. Furthermore, Π is positive at every lubricant thickness and its change with thickness is negative, indicating that this fluid wets this surface and is stable (see Section 1).

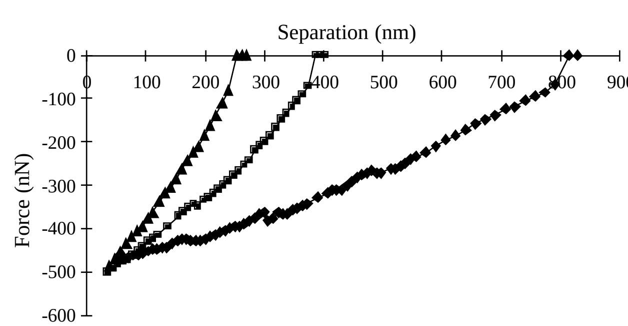

Fig. 3. The retraction force versus separation curves for increasing thickness of Z03 (33 Å, triangle; 42 Å, square; and 50 Å, diamond, thick films) on Si surfaces.

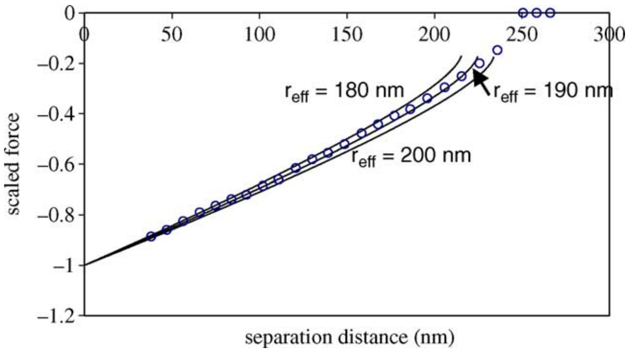

Fig. 4. Fit of the theoretical curve (Eq. (2)) after scaling to the experimental force versus distance curve. For a 3.3 nm Z03 film on Si surface using sphere (R=2.33 μm) mounted on the AFM probe.

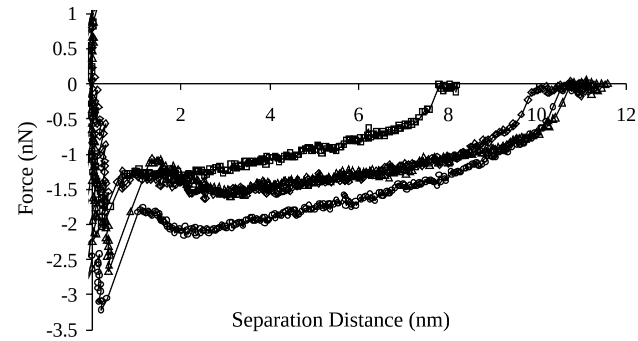

Fig. 6. The retraction force versus separation curves for Zdol on 5%, square; 10%, diamond; 20%, triangle and 30%, circle N_2 concentration in the flowing gas mixture (25 Å Zdol, SiN_x ∼100 Å thick).

3.2. Zdol on SiN_x surfaces

The Zdol coated SiN_x films deposited with 5, 10, 20 and 30% N_2 in the flowing gas were investigated at a fixed Zdol thickness (25 Å), thus both the substrate and film have been changed from Section 3.1. Fig. 6 presents the retraction (force versus separation) curves of Zdol on these four SiN_x films. Immediately noticeable in this figure is the small magnitude of the adhesive force of these curves when compared to the previous results (see Fig. 3), this is due to the necessary change to a smaller tip radius in order to stay 'on' the capillary curve (see Eq. (4)). A strong positive deflection in all the retraction curves takes place at approximately 1.5 nm separation. This reproducible effect will be the subject of a later study. These curves were fit to Eq. (3) in the region of the retraction curve beyond 1.5 nm separation and subject to the condition that they all pass through the same point when extrapolated to zero separation. The disjoining pressures measured in this way are given in Fig. 7. The disjoining pressures of Zdol on SiN_x are seen to be a strong function of the nitrogen content of the flowing gas used to deposit these films (especially between 5 and 10%). Its value ranges from approximately 1.3 to 3.3 MPa at the greatest nitrogen concentration and is intermediate between Zdol (∼2000 g/mol) on a hydrogenated sputter deposited carbon overcoat [10] and Zdol (∼4700 g/mol) on a clean Si surface [20], thus indicating the importance of the substrate.

4. Discussion

An AFM based method was used to measure the disjoining pressure of both Z03 PFPE on Si surfaces and Zdol PFPE on sputtered SiN_x surfaces. This method extends the approach of Mate et al. [16] by probing the necessary experimental conditions to reproducibly measure the disjoining pressure (see conditions on cantilever stiffness and tip radius, Section 1) [17]. The disjoining pressures measured when Z03 is coated on silicon decreases rapidly with increasing film thickness (Fig. 5). This result is consistent with a dominating van der Waals interaction [21].

The disjoining pressures of Zdol on SiN_x decreases rapidly with *increasing N_2 concentration in the flowing gas*. However, since both the Zdol and SiN_x film thickness have been kept constant this result cannot be derived from decreasing dispersion forces due to increasing distance, instead the nature of the SiN_x surface is likely changed by the probable incorporation of increasing amounts of

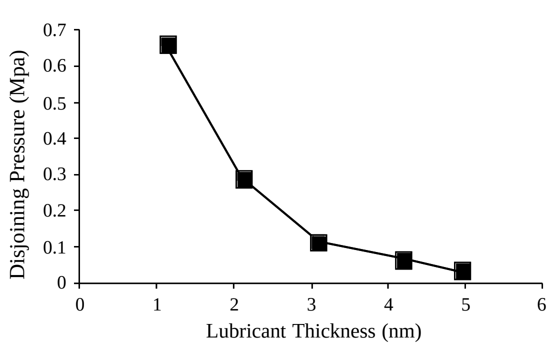

Fig. 5. The disjoining pressure (MPa) of increasingly thick Z03 Fomblin on a Si surface.

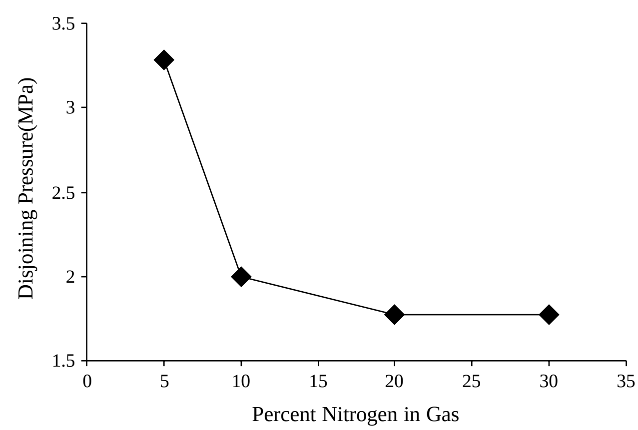

Fig. 7. The disjoining pressure (MPa) of Zdol (25 Å) on sputtered SiN_x surfaces (100 Å). Sputtered with increasing N_2 concentration in the flowing gas.

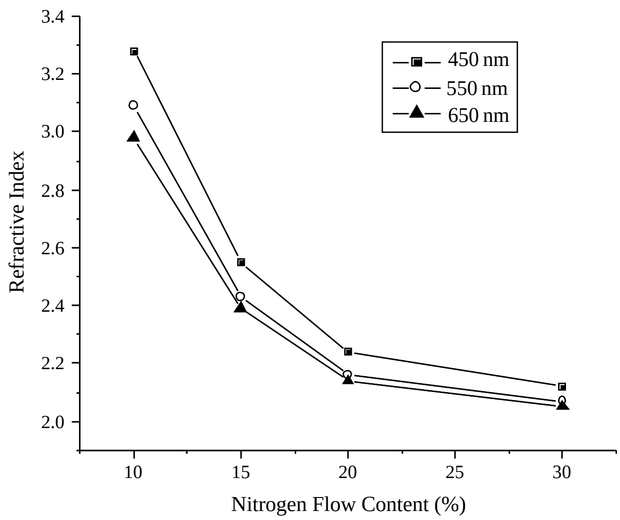

Fig. 8. Refractive index (n) of the SiN_x films sputtered with increasing N_2 concentration in flowing gas.

nitrogen (and/or other species). Fig. 8 presents refractive index data (n), at various wavelengths, of these SiN_x surfaces (10, 20 and 30% N_2). A sharp concentration dependent drop is observed. Thus, an explanation for the decrease in disjoining pressure, in the SiN_x films, may be articulated with the help of the Clausius–Mossotti equation, which relates the macroscopic dielectric constant to the microscopic polarizability [22]. From this relationship a decrease in n indicates that a similar decrease has taken place in the product αN (polarizability and number of species, respectively). This product likely decreases with increasing nitrogen content in the SiN_x film. This may be accomplished in two ways: (1) a lower density of the film with increasing nitrogen content leading to a decreased number of polarizable species, or (2) the increasing concentration of nitrogen, an atomic species with lower polarizability than Si, incrementally decreasing the overall polarizability. Since simple formulations of the Hamaker constant contain this product to various orders [21,23] a net decrease in the film polarizability, as discussed above, would decrease the dispersion force. Thus, the disjoining pressure of Zdol lubricant on sputtered SiN_x films may be varied over a wide range by small changes in the composition of the sputtering gas used to deposit these films.

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