# Roughness of molecularly thin perfluoropolyether polymer films

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X-ray reflectivity has been used to measure the roughness of perfluoropolyether (PFPE) polymer films on silicon substrates and carbon overcoats. For PFPE on smooth silicon, we find that the rms roughness of the PFPE–air interface increases slowly from about 2 to 4 Å as PFPE thickness increases from 5 to 33 Å. This increase is consistent with capillary waves roughening the polymer film, but inconsistent with current theories for the dewetting of polymer films. For PFPE on the rougher surface of amorphous hydrogenated carbon, we find that the PFPE polymer smoothes the surface with the rms roughness decreasing from 9 to 4 Å. We also discuss the implications of these results on the limits of disk drive technology. © *2000 American Institute of Physics.* [S0003-6951(00)05046-4]

Thin polymer films are widely used as protective coatings, dielectric layers, and lubrication films in high technology applications. As the trend for miniaturizing devices continues, so will the demand for increasingly thinner, more uniform polymer films. As the thickness of these films diminishes toward the dimensions of individual molecules and manufacturing tolerances on uniformity approach the atomic scale, a serious question arises as to what ''uniformity'' means at these submolecular length scales. One important aspect of film uniformity is roughness, or the variation in film height over short lateral length scales. In this letter, we use x-ray reflectivity to study the roughness of the polymer–air interface as the average polymer thickness increases from partial coverage, to complete coverage and, finally, to a thickness where dewetting occurs.

Perfluoropolyethers (PFPEs) were chosen for this study because molecularly thin films of these polymers, 5–20 Å in thickness, are commonly used to lubricate disk surfaces inside of disk drives. In previous articles,[1,2] we demonstrated the use of x-ray reflectivity to measure accurately the average thickness of PFPE films. The particular PFPEs used here are linear chain polymers consisting of a Fomblin-Z backbone

$$R\text{–}(OCF_2CF_2)_n\text{–}(OCF_2)_m\text{–}O\text{–}R,$$

with either alcohol end groups ($R=CF_2CH_2OH$ for Fomblin Zdol) or neutral end groups ($R=OCF_3$ for Fomblin Z). The molecular weights are 4700 g/mol for Fomblin Zdol and 4600 g/mol for Fomblin Z with a nearly monodispersed molecular weight distribution ($M_w/M_n<1.1$). Both polymers are liquids at 22 °C and have approximately the same dimensions: 160 Å end-to-end length, 6 Å chain diameter, and a 31 Å diameter of gyration.

As Fomblin Zdol films are known to dewet when the average film thickness is greater than a critical thickness $h_0$,[3] an important goal of this study is to determine the connection between surface roughness and the dewetting process. Theories of the roughness of liquid–vapor interfaces give the total rms roughness $\sigma$ as

$$\sigma^2=\sigma_0^2+(kT/2\pi\gamma)\ln(\lambda_l/\lambda_s), \tag{1}$$

where the first term $\sigma_0$ is the molecular roughness and the second term represents the roughness from thermally excited capillary waves on the liquid surface.[4–6] For the capillary wave term, $\gamma$ is the surface tension of the liquid–vapor interface, $k$ Boltzman's constant, and $T$ temperature. $\lambda_s$ and $\lambda_l$ are, respectively, the shortest and longest wavelength of capillary waves that are sustained by the film surface. $\lambda_l$ is limited by the attractive interaction of the film with the underlying substrate, expressed by the disjoining pressure $\Pi$, and is given by

$$\lambda_l=2\pi[\gamma/(-d\Pi/dh)]^{1/2}, \tag{2}$$

where $h$ is the film thickness. A previous study[7] has shown that, for Fomblin-Z films on silicon, $\Pi=A/6\pi h^3$ (where $A$ is the Hamaker constant), which indicates mainly van der Waals interactions between the film and substrate. This leads to

$$\lambda_l=2\pi h^2[2\pi\gamma/A]^{1/2}, \tag{3}$$

with $A=10^{-19}$ J for Fomblin-Z on silicon.[7] When $\lambda_l$ becomes large for thick films, $\lambda_l$ in Eq. (1) becomes limited by the lateral coherence length of the x rays, which is 2 $\mu$m for our instrument.[2]

For Fomblin Zdol on silicon, the alcohol end groups introduce a repulsive interaction between the liquid and substrate. This results in $d\Pi/dh=0$ at a critical film thickness $h_0$, which ranges from 0.75 to 1.0 times the diameter of gyration, and $d\Pi/dh>0$ when $h>h_0$; this leads to dewetting of Zdol on silicon for $h>h_0$.[3] Equations (1) and (2) would then predict for Zdol films that $\sigma\to\infty$ as $h\to h_0$. Instead, our x-ray reflectivity results show that no divergence of surface roughness occurs as $h\to h_0$ and that the roughness of Zdol films is the same as for Z films when the film thickness is near $h_0$.

Prior to depositing the PFPE polymers, the bare silicon wafers are cleaned by rinsing with isopropyl alcohol and

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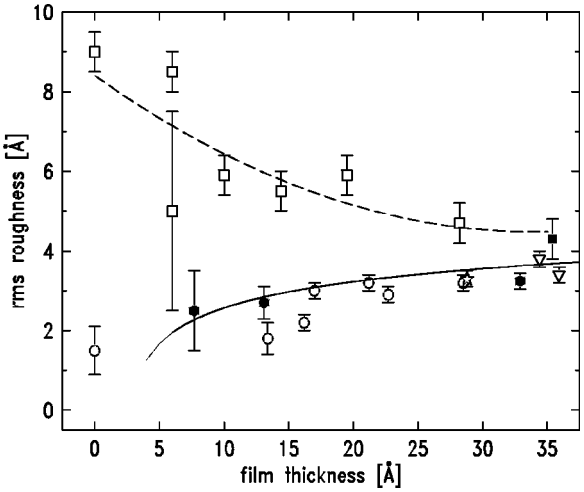


FIG. 1. Dependence of rms roughness of the polymer–air interface on polymer thickness. The open symbols are for Fomblin Zdol 4700, while the closed symbols are for Fomblin Z 4600. The squares are for polymer/carbon/Si, and the circles, triangles, and star for polymer/Si. The star is for a film covalently bonded to the Si surface and the triangles are for dewetted films; the solid line is that predicted by Eqs. (1)–(3), while the dashed line is a guide for the polymer on carbon.

perfluorohexane followed by exposure to ultraviolet-created ozone to remove surface contamination. The amorphous hydrogenated carbon films ($\approx$35% hydrogen) were sputter deposited onto silicon substrates with a 120 Å thickness and cleaned prior to polymer deposition by rinsing with perfluorohexane. PFPE films are deposited onto the substrates by dip coating[2] from a dilute solution of the polymer in the volatile perfluorohexane solvent.

X-ray reflectivity is well suited for accurately determining the geometric dimensions of very thin films. Here the reflected x-ray intensity is measured as a function of incidence angle $\theta$ (see Refs. 1, and 8–11 for details). The data are analyzed using a multilayer model[8–10] that incorporates several parameters—thickness and density of the polymer film and roughness of the polymer–air and the substrate–polymer interfaces—that are varied to produce the best fit to the data.[2] From this modeling of our data, the functional form that best fits the density profile of the polymer–air interface is an error function, implying a Gaussian distribution of surface heights.

In Fig. 1 we plot the rms roughness as a function of PFPE thickness on both the silicon and amorphous carbon substrates. The following trends are apparent:

(1) The initially smooth sample–air interface of the Si becomes progressively rougher with the addition of the PFPE polymer.
(2) The rougher sample–air interface of the carbon becomes progressively smoother with the addition of the PFPE polymer and eventually converges on the same rms value of approximately 4 Å as the PFPE–air interface on silicon.
(3) Both Fomblin Zdol and Fomblin Z have the same polymer–air interfacial roughness.

The solid line in Fig. 1 shows the rms roughness predicted from Eqs. (1) and (3) using $T=300\,\mathrm{K}$, $\gamma=24\,\mathrm{mN/m}$, $\sigma_0=1$ Å, $\lambda_s=10$ Å, and $A=1\times10^{-19}$ J. Our data are in agreement with this prediction and hence are consistent with a model where the roughness of the polymer–air interface on silicon wafers can be accounted for primarily by thermally excited capillary waves in the liquid polymer film, but only if we use a long wavelength cutoff determined by the attractive van der Waals interactions [Eq. (3)]. We also note that values for the molecular roughness $\sigma_0=1$ Å and the short wavelength cutoff $\lambda_s$, which provide good agreement with the data, are much smaller than the polymers' diameter of gyration, but similar to the polymers' chain diameter, indicating that the diameter of the polymer backbone is the relevant size parameter for surface roughness of a polymer film at molecular lateral length scales.

For Zdol films on Si, the alcohol end groups are strongly attracted via hydrogen bonding to underlying surface of the silicon oxide layer,[3] but still behave as liquid films in that the polymers can move across the silicon surface. The alcohol end groups can be covalently bonded to the surface by heating to react the alcohol end group with hydroxyl surface groups. The star in Fig. 1 shows the rms roughness for a Zdol film on silicon covalently bonded by heating for 1 h at 120 °C. This bonded film has the same roughness as the unbonded film with the same thickness, indicating that the polymer backbone at the polymer–air interface can still support thermally excited capillary waves even though the ends of the polymer chains are bonded to the silicon surface.

For the Zdol films on Si, dewetting is observed by optical microscopy when the x-ray reflectivity thickness exceeds 30 Å. The physical origin of Zdol dewetting can be understood as follows: For films less than a monolayer, the Zdol alcohol end groups sit at the $SiO_x$–PFPE interface orienting the molecules' backbones toward the polymer–air interface. This structure lowers the film's surface energy, which goes below bulk surface tension when the film thickness exceeds $h_0$. When the average film thickness is increased above $h_0$, the excess coalesces into dewetting droplets rather than spreading uniformly over the monolayer. The data points for Zdol with $h>30$ Å (triangles) in Fig. 1 correspond to the thickness and roughness of the PFPE film between the dewetting droplets. The x-ray reflectivity thickness for these dewetted samples is less than the average thickness deposited as determined by ellipsometry (40 and 53 Å), indicating that the film thickness between the dewetting droplets remains close to the critical thickness for dewetting.

Theories of dewetting indicate that liquid films are thermodynamically unstable when $d\Pi/dh>0$ with the dewetting process occurring via spinodal decomposition initiated by fluctuations in the film thickness generated by thermally excited capillary waves.[12–14] Equations (1) and (2) illustrate this proposed dewetting mechanism: As $h\rightarrow h_0$, $d\Pi/dh\rightarrow0$, and $\sigma\rightarrow\infty$. The results in Fig. 1 apparently contradict this theory as the rms surface roughness remains constant rather than diverging, as the Zdol film thickness increases to the dewetting thickness $h_0$. This indicates the dewetting process is initiated by a different mechanism than capillary wave fluctuations. Our hypothesis for resolving this paradox is that the minimum in disjoining pressure, where $d\Pi/dh=0$, actually occurs at a thickness somewhat larger than the thickness $h_0$, where the onset of dewetting is observed, due to the finite size of the polymer molecule. Effectively, if

fluctuations in the polymer film surface result in part of a polymer molecule being above a thickness where $d\Pi/dh = 0$, then the dewetting process will tend to pull the whole molecule above this film thickness. Once the molecule is pulled out of the polymer film, it can quickly run around on the polymer surface until it coalesces with similar molecules pulled out of the polymer film to form dewetting droplets. Since the x-ray reflectivity experiment is started several hours after the dewetting process has occurred, it only measures the roughness of polymer film between the dewetting droplets and is insensitive to the roughness produced by the dewetting droplets.

Next we discuss the results for PFPE/carbon overcoats. The initial carbon surface roughness is about 9 Å, similar to that found by others.[15,16] When the PFPE polymer film is deposited on the carbon film, the top surface of the polymer now becomes smoother, and the rms surface roughness drops to about 4 Å at the thickest films we have measured. We attribute this surface smoothing to the surface tension of the liquid polymer pulling the polymer–air surface flat over the rougher carbon surface. The degree to which surface tension can smooth the polymer surface is again limited by thermally excited capillary waves. For Zdol films on carbon surfaces, dewetting droplets are not observed, but steps in spreading films have been observed.[17]

Finally, we comment on what the roughness determined here implies for magnetic recording technology. In disk drives, a recording head reads and writes information on a magnetic film on a rotating disk. The closer the recording head is to the magnetic film, the higher the signal. However, to prevent the head from wearing the magnetic film, the disk is overcoated with amorphous carbon and PFPE lubricant, and the head is flown on air bearing, typically less than 300 Å in thickness in today's drives. To minimize the separation between the head and magnetic medium, it is desirable to have the smoothest possible disk surface. Recent results from our lab[18] indicate that state of the art disks without lubricant can currently be made with a rms roughness of 8–11 Å (from x-ray reflectivity). The results in this letter indicate that adding a PFPE lubricant can reduce this to about 4 Å, when it becomes limited by thermally excited capillary waves within the lubricant film. Consequently, we conclude that the inherent roughness of the lubricant film will soon be the major contributor to the roughness of disk surfaces inside of disk drives, eventually limiting how closely a recording head can fly over a disk surface without contact.[19]

In summary, our results show that PFPE films roughen the film–air interface when deposited onto atomically smooth silicon surfaces. The film roughness is attributed primarily to thermally excited capillary waves. In contrast, the same polymer smoothes out the rougher surface of amorphous carbon films, due to the smoothing effect of surface tension. For dewetted PFPE films, the roughness of the polymer film does not diverge as the thickness approaches the dewetting thickness and remains unchanged between the dewetting droplets after dewetting has occurred. That the roughness does not diverge during dewetting, as predicted by theory, is attributed to the effect that the finite size of the polymer has on the dewetting process.

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[1] M. F. Toney, C. M. Mate, and D. Pocker, IEEE Trans. Magn. **34**, 1774 (1998).
[2] M. F. Toney, C. M. Mate, K. A. Leach, and D. Pocker, J. Colloid Interface Sci. **225**, 119 (2000).
[3] H. I. Kim, C. M. Mate, K. A. Hannibal, and S. S. Perry, Phys. Rev. Lett. **82**, 3496 (2000).
[4] I. M. Tidswell, T. A. Rabedeau, P. S. Pershan, and S. D. Kosowsky, Phys. Rev. Lett. **66**, 2108 (1991).
[5] B. M. Ocko, X. Z. Wu, E. B. Sirota, S. K. Sinha, and M. Deutsch, Phys. Rev. Lett. **72**, 242 (1994).
[6] A. K. Doerr, M. Tolan, W. Prange, J.-P. Schomka, T. Seydal, W. Press, D. Smilgies, and B. Struth, Phys. Rev. Lett. **83**, 3470 (1999).
[7] C. M. Mate and V. J. Novotny, J. Chem. Phys. **94**, 8420 (1991).
[8] T. P. Russell, Mater. Sci. Rep. **5**, 171 (1990).
[9] M. F. Toney and C. Thompson, J. Chem. Phys. **92**, 3781 (1990).
[10] M. Born and E. Wolf, *Principles of Optics* (Pergamon, Oxford, 1970).
[11] E. Findeisen, R. Feidenhans'l, M. E. Vigild, K. N. Clausen, J. B. Hansen, M. D. Bentzon, and J. P. Goff, J. Appl. Phys. **76**, 4636 (1994).
[12] A. Vrij, Discuss. Faraday Soc. **42**, 23 (1966).
[13] M. Sferrazza, M. Heppenstall-Butler, R. Cubitt, D. Bucknall, J. Webster, and R. A. L. Jones, Phys. Rev. Lett. **81**, 5173 (1998).
[14] F. B. Wyart and J. Daillant, Can. J. Phys. **68**, 1084 (1990).
[15] C. A. Lucas, T. D. Nguyen, and J. B. Kortright, Appl. Phys. Lett. **59**, 2100 (1991).
[16] Y. Huai, M. Chaker, J. N. Broughton, E. Gat, H. Pepin, T. Gu, X. Bian, and M. Sutton, Appl. Phys. Lett. **65**, 830 (1994).
[17] X. Ma, J. Gui, L. Smoliar, K. Grannen, B. Marchon, M. S. Jhon, and C. L. Bauer, J. Chem. Phys. **110**, 3129 (1999).
[18] C. M. Mate, B. K. Yen, D. C. Miller, M. F. Toney, M. Scarpulla, and J. E. Frommer, IEEE Trans. Magn. **36**, 110 (2000).
[19] C. M. Mate, M. F. Toney, and K. A. Leach, IEEE Trans. Magn. (submitted).