






Why Teflon is so slippery while other polymers are not

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Polytetrafluoroethylene [PTFE (Teflon)] is a uniquely slippery polymer, with a coefficient of friction that is an order of magnitude lower than that of other polymers. Though known as nonsticky, PTFE leaves a layer of material behind on the substrate while sliding. Here, we use contact-sensitive fluorescent probes to image the sliding contact *in situ*: We show that slip happens at an internal PTFE-PTFE interface that has an unusually low shear strength of 0.8 MPa. This weak internal interface directly leads to low friction and enables transfer of the PTFE film to the substrate even in the absence of strong adhesion.

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I. INTRODUCTION

PTFE (polytetrafluoroethylene, better known as Teflon) is known for its low friction, with a friction coefficient similar to that of a skate on ice [1], which is much lower than other polymers [2]. A key difference with other polymers is that PTFE is nonsticky [3]: Its surface energy is the lowest [4] of commonly used engineering materials. It is tempting to explain its slipperiness from the lack of adhesion—friction in polymers is often governed by adhesion [5–8], and might thus vanish for a nonsticky polymer. Although this sounds reasonable, research has shown that PTFE friction is accompanied by the transfer of a PTFE film adhering to the substrate [9–13], which suggests that low PTFE friction finds its origins in weak interactions within PTFE rather than between PTFE and the substrate.

However, the fact that PTFE transfers does not offer a direct explanation of its slipperiness: Numerous other polymers transfer, yet their friction is much higher than that of PTFE [2,14–16]. An important observation is that PTFE forms a nanometer-thin, coherent transfer film [9,12] while other polymers feature a “lumpy” transfer of bigger fragments [14–16]. These findings raise two interrelated questions: Why is PTFE so exceptionally slippery, and how can it robustly transfer a nanometric film to the substrate while being the most nonsticky polymer? Answering these questions calls for quantitative measurements of the stresses working at the PTFE-PTFE and PTFE-substrate interfaces, which has so far been lacking due to very limited experimental access to the buried interfaces.

In this paper, we use state-of-the-art contact visualization experiments to show quantitatively that an unusually low PTFE-PTFE shear strength in the sliding contact is the key factor for low friction and transfer. This very weak shear cohesion allows for low friction despite a large contact area and robust transfer despite modest adhesion. These results

provide a quantitative understanding of low friction transfer film formation, which may lead to transformative applications in tribology such as the rational design of low friction materials.

Contact visualization experiments reported in this paper make use of surface-immobilized fluorescent probes [dicyanomethylenedihydrofuran (DCDHF)], which emit strongly when in a confined environment [17]. This visualization method allows us to resolve the real contact area between contacting solids with submicrometer in-plane resolution [17], and has been used in our laboratory to gain fundamental insight into contact mechanics [18,19]. In addition, the employed contact probes are so sensitive that we can resolve transfer films of a few molecules thick. We combine contact imaging with careful friction and nanometric-distance controlled adhesion force measurements to quantitatively resolve the stress balance in the contact zone with high resolution.

II. EXPERIMENT

A. Contact visualization

To visualize the PTFE interface during contact and sliding, we make use of a setup that combines careful force measurements with microscopy. A PTFE sphere ($D = 1.59$ mm, Goodfellow) is attached to a rheometer (Anton Paar DSR502) that is mounted on top of an inverted confocal microscope (Zeiss LSM Axiovert 200M). The sphere is brought into contact with the contact-sensitive surface, a glass coverslip functionalized with a monolayer of DCDHF rigidochromic dye, prepared according to a previously described protocol [17]. The contact is immersed in a small quantity of refractive-index-matched liquid [dimethyl sulfoxide (DMSO) or formamide] to suppress optical reflections at the interface. Contact area measurements with a “dry” contact visualization method for similar polymer contact have yielded very comparable results [20], precluding an influence of the liquid on contact area. Fluorescence images of the polymer-substrate

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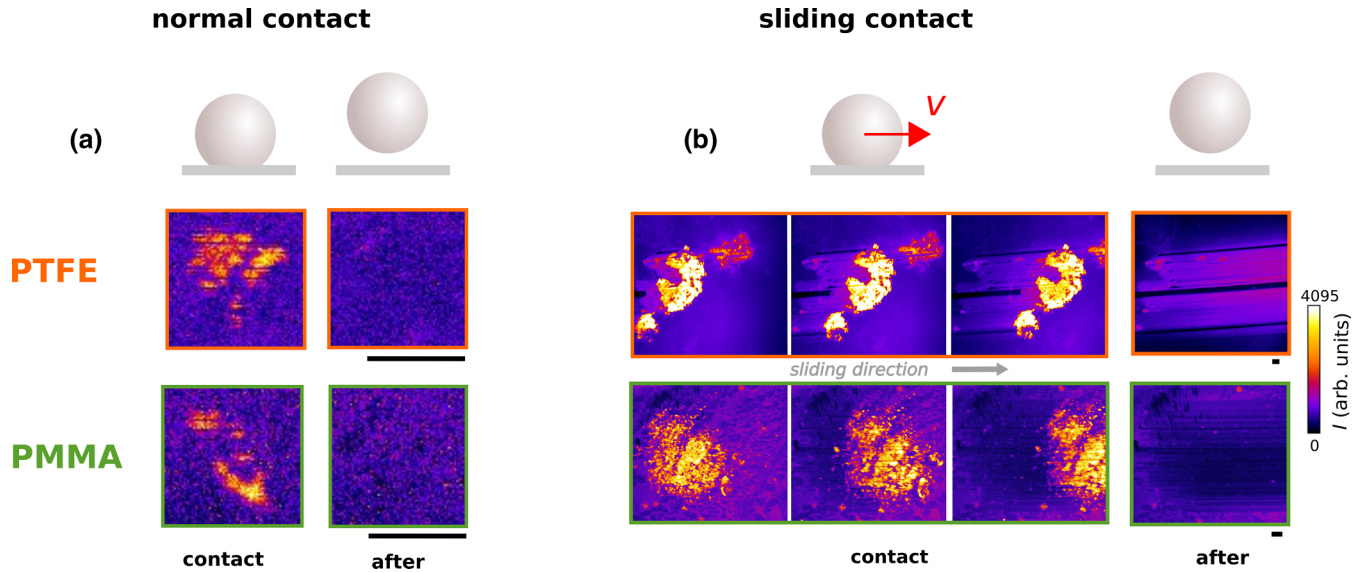


FIG. 1. Fluorescent probes emit strongly when confined, which reveals the area of contact between a polymer sphere and a DCDHF-coated glass coverslip [(a) and (b) “contact”]. After the contact is broken, fluorescence emission uncovers the presence of a residual transfer film [(b) “after”], which only forms in a sliding PTFE contact, not in a purely normal contact, nor when PMMA is the contacting polymer. Normal force is ≈ 1 mN for contact images shown in (a), and 85 mN in (b). The scale bar indicates $10 \mu\text{m}$. In (b), the intensities of the “after” images are adjusted to correct for background fluorescence and inhomogeneous lighting. The contact plane is immersed in a refractive-index-matched liquid (formamide or DMSO) during measurements.

interface are point-scanned using 488-nm excitation light, and a suitable emission bandpass filter is used to prevent reflected light from reaching the detector. The contact area is quantified by applying an Otsu threshold to the fluorescence images and multiplying the number of high-intensity pixels with the pixel area [18].

B. Friction and adhesion

In sliding experiments, the rheometer rotates the polymer sphere at constant velocity, inducing slip at the polymer-substrate interface while carefully recording normal and friction forces. Sliding experiments are performed both immersed in refractive-index-matched liquid (for imaging purposes) as well as dry, without a noticeable change in friction coefficient (see Appendix A, Fig. 5).

To measure adhesion, we carefully separate a polymer sphere from a DCDHF-coated glass coverslip while monitoring normal force as a function of distance separating the sphere and substrate. The substrate is clamped to a nanometer-precision piezostage (Physik Instrumente, PI-611.Z0), while the polymer sphere is attached to a stiff force sensor (Instron 2530 series 5N static load sensor) to ensure precise force measurements.

III. RESULTS AND DISCUSSION

To see how the transfer of PTFE is related to frictional slip, we perform normal pull-off and sliding experiments while simultaneously imaging the contact. In one case the sphere is slid over the substrate ($v_{\text{sliding}} = 250 \text{ nm s}^{-1}$), and in the other case the contact is static. Reference experiments are carried out with PMMA [poly(methyl methacrylate)] instead of PTFE, as it is a polymer not known to transfer during

sliding. During contact, the fluorescence intensity is high at the real contact area between the polymer and substrate (Fig. 1). After normal pull-off, for both PTFE and PMMA, the fluorescence intensity drops to background noise levels: There is no transfer from either of the polymers to the substrate [Fig. 1(a)]. In contrast, after sliding, a fluorescent signal persists for PTFE [Fig. 1(b)], indicating transfer of a film of PTFE to the substrate, which keeps the fluorophores at the surface confined. For PMMA sliding on the same substrate, no residual fluorescence is observed after sliding, in line with it being a nontransferring polymer. X-ray photoelectron spectroscopy (XPS) and ellipsometry analysis on the substrate after PTFE sliding confirm that the residual fluorescence originates from a transferred PTFE film, which has an average thickness of 3 nm (see Appendixes B and C, Figs. 6 and 7). These results provide an *in situ* observation of PTFE transfer. Due to the nanoscale sensitivity of the fluorescent contact probes, we show unambiguously that transfer happens exclusively during sliding motion. This anisotropy of transfer suggests that PTFE features especially weak local cohesion in the shear direction, a few molecular diameters from the substrate.

We can directly experimentally quantify the frictional shear strength ($\tau_{\text{frict}} = F_f/A$) by combining contact visualization experiments with friction force measurements ($v_{\text{sliding}} = 3 \mu\text{m s}^{-1}$). PTFE exhibits an unusually low frictional shear strength of 0.8 MPa [Fig. 2(a)], which is an order of magnitude lower than that of PMMA (11 MPa). Even though the contact area for a given normal force is relatively large [Fig. 2(b)], the ultralow shear strength leads to low PTFE friction [Fig. 2(c)], since $F_{\text{frict}} = \tau_{\text{frict}}A$. For sliding PTFE, slip happens within PTFE [Fig. 1(b)], which means that this measured frictional shear strength corresponds to the shear strength of the PTFE-PTFE sliding interface, whereas

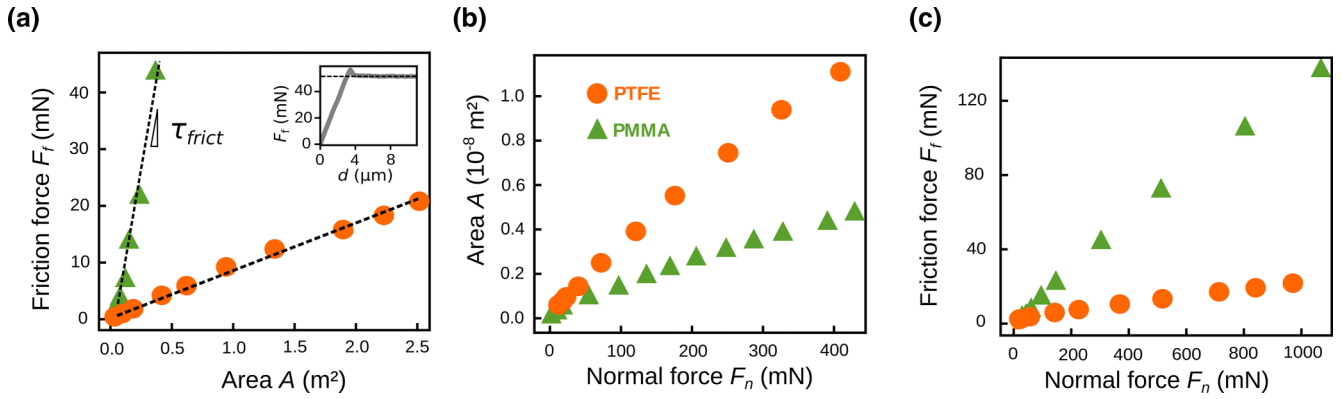


FIG. 2. Friction force, normal force, and contact area are measured for PTFE and PMMA spheres contacting DCDHF-coated glass coverslips. (a) The kinetic friction force is proportional to the contact area, frictional shear strength $\tau_{\text{frict}} = F_f/A = 0.8$ MPa for PTFE and 11 MPa for PMMA. Inset: Kinetic friction force is the measured steady state force after the static friction peak. (b) The contact area evolves sublinearly respective to the normal force, indicative of elastoplastic strain hardening contact mechanics [18,21]. (c) The kinetic friction force is approximately proportional to normal force, $\mu_{\text{PTFE}} = F_f/F_n \approx 0.02$, whereas $\mu_{\text{PMMA}} \approx 0.12$.

for PMMA the frictional shear strength originates from PMMA-substrate interactions. Thus, low PTFE friction is a direct consequence of the weak *intra*-PTFE interactions that govern the remarkably low PTFE-PTFE shear strength. This low PTFE-PTFE shear strength is apparently lower than the PTFE-substrate interaction, so that a transferred film remains at the surface.

For a transfer film to form during sliding, adhesion must exceed cohesion. We do not have access to the adhesive shear stress acting between PTFE and substrate during the sliding experiment, since the friction force we measure is the force needed to induce slip at the weaker internal PTFE interface, rather than at the adhesive PTFE-substrate interface. To approach the adhesive stress in a different way, we perform pull-off experiments using the same geometry as the sliding experiment, which allows us to find the interfacial energy acting between PTFE and substrate.

The measured PTFE-substrate force-displacement curve shows a clear adhesive minimum during pull-off (Fig. 3). We use Johnson-Kendall-Roberts (JKR) theory as an approximation to relate pull-off force to interfacial energy [$W =$

$-\frac{2}{3} F_{\text{pull-off}}/(\pi R)$], as is commonly done in the literature [22]. Our experiment yields an interfacial energy $W = 21$ mJ/m² acting between PTFE and DCDHF-coated glass, which is well in agreement with what we expect for PTFE-glass contact based on van der Waals interactions (± 25 mJ/m²).

Comparing the adhesion of PTFE and PMMA, it seems odd that we do not measure any adhesion in the case of PMMA, since PMMA has a higher surface energy than PTFE [23]. However, PTFE and PMMA surfaces are rough ($h_{\text{rms}} \sim 1$ μm across the contact area): At a rough interface the energy stored in the elastic deformation of the surface roughness (partly) cancels the effect of adhesion [24]. For stiffer interfaces, more elastic energy is stored in the deformation of the rough interface, which reduces the measured adhesion. Since PMMA is a few times stiffer than PTFE [25], this effect reduces the measured adhesion more strongly for PMMA, while for PTFE the measured interfacial energy remains close to the theoretical van der Waals value for a smooth contact.

To compare PTFE adhesive and cohesive strengths in the contact zone, we need to convert the found interfacial energy to an adhesive strength. The shear strength of an adhesive frictional interface τ_{adh} may be approximated as the interfacial energy W divided by a molecular length scale δ [4]: $\tau_{\text{adh}} \approx W/\delta$ [26]. Assuming δ is nanometric [27], we find $\tau_{\text{adh}} \approx 21$ MPa. This is more than an order of magnitude larger than the measured PTFE-PTFE shear strength, which readily explains why PTFE transfers during shear (Fig. 4): Cohesion is much weaker than adhesion in the contact zone. In fact, we may even strongly suppress adhesion in a refractive-index-matched liquid (Fig. 3), without any change in transfer and friction behavior (see Appendix A, Fig. 5), which emphasizes even more that PTFE tribology is governed by its low internal shear strength: Adhesion is largely irrelevant to its friction and transfer behavior.

In summary, we have used a uniquely sensitive fluorescence-based contact visualization method to quantitatively disentangle contact mechanics, surface interactions, and internal interactions during low friction PTFE sliding. PTFE features a weak internal interface a few

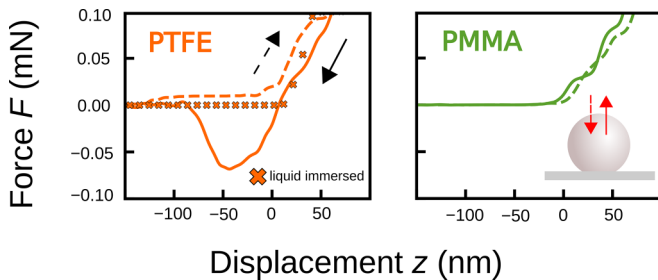


FIG. 3. Force-displacement curves for PTFE and PMMA spheres ($D = 1.59$ mm) approaching (dashed line) and retracting from (solid line) the substrate (a DCDHF-coated glass coverslip). Crosses show PTFE retracting from the coverslip immersed in refractive-index-matched liquid (formamide). Negative displacement indicates separation between surfaces. The approach and retraction velocity is 10 nm s⁻¹.

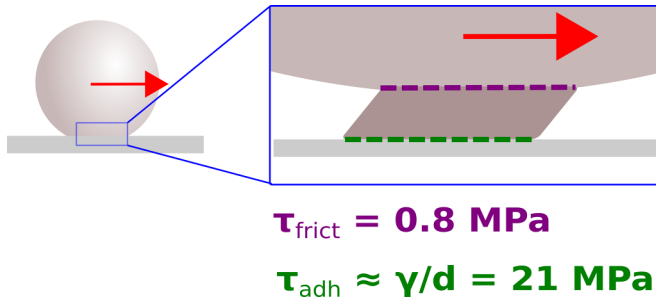


FIG. 4. Schematic image of relevant interfaces in the transfer process. Slip happens at the weaker, PTFE-PTFE interface (purple). The adhesive shear strength at the PTFE-substrate interface (green) is more than an order of magnitude larger than the frictional shear strength, thus more than enough to keep the film stuck during sliding.

nanometers from the contact, the shear strength of which is so low that PTFE generates much lower friction than other polymers despite a relatively large contact area. Nanoscopic transfer film formation is a direct consequence of the ultralow internal shear strength, as even weak PTFE-substrate van der Waals adhesion exceeds shear cohesion by an order of magnitude. Although the absolute value of the adhesive strength between PTFE and substrate will change with surface roughness and substrate surface chemistry, we expect the order-of-magnitude difference with the cohesive strength to be robust enough to ensure transfer for a large variety of PTFE contact situations, consistent with the ubiquitous use of PTFE as a low friction solid lubricant against a variety of counter surfaces.

Our quantitative understanding of PTFE tribology raises the question from which physical principles the very low PTFE shear strength originates. It is important to note that the local shear strength that we have measured during sliding is more than an order of magnitude lower than PTFE bulk strengths measured in experiments where deformations extend over macroscopic length scales [28–30]. This difference

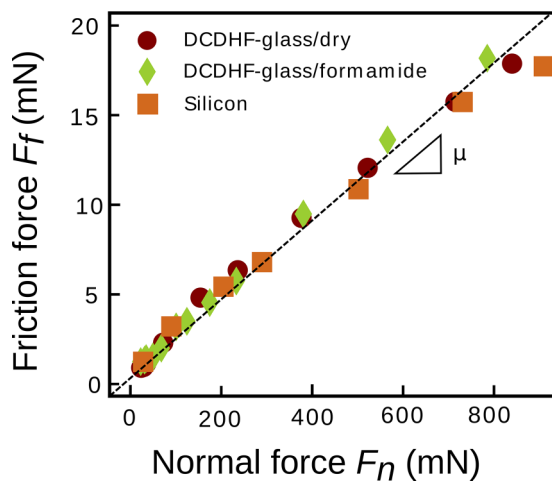


FIG. 5. PTFE spheres sliding on a dry or a liquid-immersed DCDHF-coated glass coverslip, or on a plasma-cleaned silicon wafer all show the same low friction, $\mu_{\text{PTFE}} \approx 0.02$. The dashed line is a guide to the eye.

suggests that the origins of low PTFE shear strength during sliding are to be sought at microscopic length scales, where molecular rather than continuum descriptions of materials are most adequate. Comparative studies have shown that polymer tribology is strongly dependent on polymer shape [2] and size [2,5,14]: Long, unbranched chains without bulky side groups (“smooth” chains) are a prerequisite for low friction transfer film formation. The only polymer which exhibits similar low friction transfer film tribology as PTFE is ultrahigh molecular weight polyethylene (UHMWPE), which fits this description, while shorter, more branched chains of the same molecular makeup (LDPE) feature much higher friction [2]. These findings suggest that the physical origins of the exceptionally low shear strength that PTFE exhibits during sliding may lie in the local molecular ordering [12] made possible by the particular polymer chain length and topology rather than its chemical composition.

A considerable number of works have attributed PTFE transfer to “strong adhesion” acting between PTFE and the substrate [2,9,10,13,31]. Since PTFE is normally nonsticky, the origin of this strong adhesion has been argued to lie in the tribochemical reactions of PTFE happening in the sheared contact zone [31–33]. Our work, however, shows that adhesion strength plays little to no role in PTFE transfer: The weak van der Waals adhesion of PTFE is more than enough for transfer film formation [32,34].

IV. CONCLUSIONS

We have shown that the low friction of PTFE is an internal material attribute rather than a surface phenomenon, which may be the main reason PTFE is widely used as a lubricant in many different applications and environments. We expect our understanding of transfer film formation to be generalizable beyond the case of PTFE: Other commonly used solid lubricants such as graphite also feature transfer during sliding [35]. Tuning internal interactions rather than surface interactions may provide another design paradigm to engineer different low friction materials.

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APPENDIX A: FRICTION OF PTFE UNDER DIFFERENT CONDITIONS

To improve the image quality in simultaneous sliding and imaging experiments, we immerse the contact between PTFE and DCDHF-coated glass in a refractive-index-matched fluid (formamide). To ensure the presence of liquid does not change the PTFE friction behavior, we measure the friction as a function of normal force in liquid-immersed as well as dry conditions. Furthermore, we measure the friction between PTFE and a dry silicon wafer, which is the substrate used in XPS and ellipsometry measurements. Figure 5 shows that the

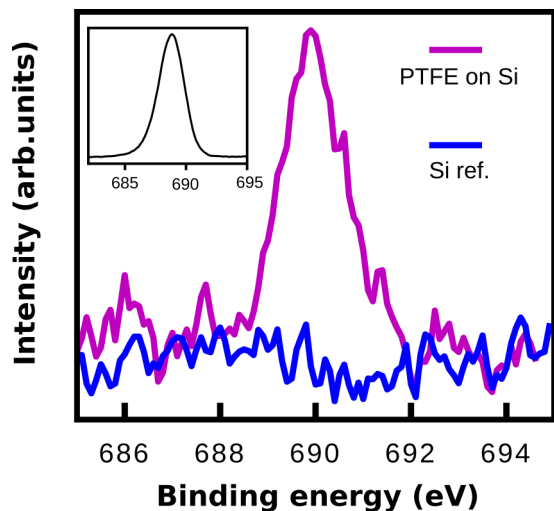


FIG. 6. XPS spectrum (Pass energy (PE) = 300 eV) of the F 1s region of the Si/PTFE substrate (magenta) and the Si control substrate (blue). The distinct peak at 690 eV for the Si/PTFE substrate is consistent with PTFE transfer. The inset shows the F 1s spectrum of the pristine PTFE sphere prior to sliding and serves as a reference. The PTFE reference spectrum has been shifted to correct for surface charging, while the spectra on Si have been aligned to the Si 2p position. The offset in the F 1s position shows that the transferred layer also shows surface charging, indicating an insulating character that is consistent with PTFE.

friction coefficient is the same whether measured on dry or wet functionalized glass or on a silicon wafer.

APPENDIX B: X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

To verify the transfer of PTFE through measurement of the surface elemental composition, a clean Si wafer was used as a substrate since it is chemically well defined and has the same friction as glass substrates used in fluorescence microscopy experiments (Fig. 5). Measurements of the surface composition of the Si control substrate and Si/PTFE transfer substrate were performed in an ultrahigh vacuum (UHV) XPS setup ($p < 10^{-9}$ mbar). The setup consists of a monochromated Al $K\alpha$ x-ray source (1486.6 eV) and electron energy analyzer (R4000 HiPP-3, Scienta Omicron) used with a slit entrance setting of 1 mm. Survey and detailed spectra are acquired at pass energies of 500 and 300 eV, respectively. Peak positions are referenced to Si 2p at 99.4 eV [36]. Detailed F 1s spectra are reported in Fig. 6. For the Si/PTFE substrate, the PTFE sliding mark was located by optimizing the detector signal

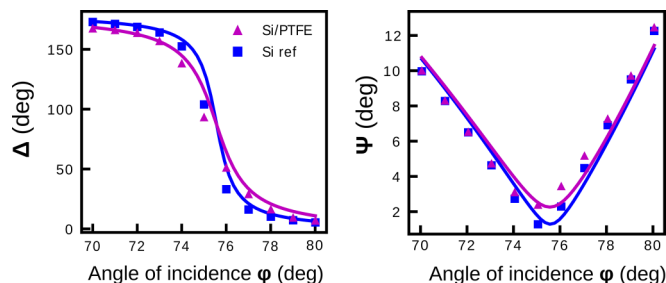


FIG. 7. Ellipsometric angles Δ and Ψ as a function of angle of incidence ϕ for a Si wafer with a native oxide layer (Si ref) and a Si wafer after PTFE has slid over it (Si/PTFE). A two-layer fit to the reference Si wafer data reveals a thickness of the silicon oxide layer of around 2 nm. A three-layer fit to the Si/PTFE data shows that on top of the silicon oxide layer, 3 nm of PTFE are present.

at the binding energy value expected for F 1s p -(CF₂=CF₂) species at 688–690 eV [36,37]. A raster scan of the x and y positions of the Si/PTFE sample with respect to the x-ray spot was performed. The intensity of the F 1s signal stemming from the Si/PTFE substrate depends on the location of the substrate with respect to the x-ray spot. The sample position showing the highest intensity of F 1s photoelectrons was selected for further measurements. A control measurement was performed on the Si substrates to rule out any inherent fluorine contamination. For the Si control substrate no F 1s peak could be identified above noise level.

APPENDIX C: ELLIPSOMETRY

To determine the thickness of the PTFE transfer film on the substrate, ellipsometry measurements were performed on a commercial ellipsometer (Optrel GBR), at 632.8 nm, for different angles of incidence ϕ (Fig. 7). Silicon wafers were used as substrates since they are flat and chemically well defined. Wafers were plasma cleaned to create a nanometric silicon oxide (SiO₂) layer, after which PTFE spheres were slid over it many times in the area where the laser beam would be focused, in order to obtain a relatively homogeneous PTFE film in the measurement region. From a reference plasma cleaned Si wafer, we determine the thickness of the native oxide layer, which we use as input in the fit to determine the thickness of the PTFE layer. The two-layer (Si-SiO₂) fit of ellipsometric angles gives $h_{\text{SiO}_2} = 2.1 \pm 0.4$ nm. The three-layer fit (Si-SiO₂-PTFE) for Si/PTFE surfaces gives a reliable estimation of PTFE transfer film thickness, $h_{\text{PTFE}} = 3 \pm 1$ nm. The larger error compared to the SiO₂ layer thickness may be due to the inhomogeneity of the formed PTFE film.

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