Mechanical Property Investigation of Soft Materials by Cantilever-Based Optical Interfacial Force Microscopy

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Summary: Cantilever-based optical interfacial force microscopy (COIFM) was applied to the investigation of the mechanical properties of soft materials to avoid the double-spring effect and snap-to-contact problem associated with atomic force microscopy (AFM). When a force was measured as a function of distance between an oxidized silicon probe and the surface of a soft hydrocarbon film, it increases nonlinearly in the lower force region below ~10 nN, following the Herzian model with the elastic modulus of ~50 MPa. Above ~10 nN, it increases linearly with a small oscillatory sawtooth pattern with amplitude 1–2 nN. The pattern suggests the possible existence of the layered structure within the film. When its internal part of the film was exposed to the probe, the force depends on the distance linearly with an adhesive force of ~20 nN. This linear dependence suggests that the adhesive internal material behaved like a linear spring with a spring constant of ~1 N/m. Constant-force images taken in the repulsive and attractive contact regimes revealed additional features that were not observed in the images taken in the noncontact regime. At some locations, however, contrast inversions were observed between the two contact regimes while the average roughness remained constant. The result suggests that some embedded materials had spring constants different from those of the surrounding material. This study demonstrated that the COIFM is capable of imaging mechanical properties of local structures such as small impurities and domains at the nanometer scale, which is a formidable challenge with conventional AFM methods. SCANNING 35: 59–67, 2013. © 2012 Wiley Periodicals, Inc.

Key words: COIFM, mechanical properties, AFM, interfacial force spectroscopy, force–feedback, snap-to-contact, AFM double-spring effect, force–distance curve

Introduction

Image acquisition of topographic structures and material properties in the same area is important to scientific understanding of various soft materials ranging from thin organic films to biomolecules (Radmacher et al., '92) and for future applications, such as the development of micromechanical machines (Mate, 2008). Atomic force microscopy (AFM) has been widely used in mapping topographic structures and mechanical properties, such as viscoelastic and adhesion properties (Maivald et al., '91; Mizes et al., '91; Radmacher et al., '92, '93; Akari et al., '94; Baselt and Baldeschwieler, '94; Bhushan and Koinkar, '94; Burnham, '94; Heuberger et al., '94; Overney et al., '94; Burnham et al., '96; Cappella et al., '97; Fretigny et al., '97; Hosaka et al., '97; Miyatani et al., '97; Troyon et al., '97; Oulevey et al., '98; Sugisaki et al., '99). Force–modulation techniques were introduced two decades ago to image topographic, elastic, and viscous images at the same time (Maivald et al., '91; Radmacher et al., '92, '93; Akari et al., '94; Baselt and Baldeschwieler, '94; Hosaka et al., '97; Miyatani et al., '97; Troyon et al., '97). This simultaneous imaging was realized by separating the signals in the frequency domains. This method has been applied to various materials including a living cell (live platelet) (Radmacher et al., '92), carbon fiber and epoxy composite (Miyatani et al., '97), self-assembling monolayers (SAMs) of organic thiols (terminated polystyrene) on gold (Akari et al., '94), nickel-based superalloy (MC2) (Maivald et al., '91), and cold plastic (Hosaka...
The stiffness of sample (face structure acts as another (see Fig. 1(A) and its cantilever acts as one spring and the adsorbed surface structure acts as another (see Fig. 1(A) and its related inset). The stiffness of sample ($k_i$) is related to the measured slope ($k_m$) by the following relationship (Burnham, '93, '94):

$$k_i = k_m/[1 - (k_m/k_{cb})], \quad (1)$$

where $k_{cb}$ is the cantilever spring constant. For quantitative measurement of the constant $k_i$, the cantilever spring constant must be deconvoluted from the measured data. However, the accurate calibration and determination of the constant $k_{cb}$ are not generally straightforward (Palacio and Bhushan, 2010). This equation suggests that, when $k_{cb}$ is infinite, the measured slope equals the sample stiffness. Also, this de-measurement approach requires extensive data acquisition time from $\sim 30$ min to several hours (Mizes et al., '91; Baselt and Baldeschwieler, '94; Heuberger et al., '94), which sometimes causes unwanted problems such as severe drift, in particular, for soft materials including biological samples (Sugisaki et al., '99).

In this experiment, as a means to make the constant $k_{cb}$ infinite, we used cantilever-based optical interference force microscopy (COIFM) to achieve two goals: (i) to obtain the stiffness of the sample, and (ii) to obtain mechanical property images. The COIFM was recently developed as an experimental technique to measure interfacial interactions at nanometer scales using force–feedback (Bonander and Kim, 2008; Kim et al., 2011a, 2011c) to remove the rapid snap-contact problem associated with AFM measurements (Lodge, '83; Meyer et al., '88; Burnham and Colton, '89; Aime et al., '94). The cantilever does not experience any deflection by applying counteractive forces to negate any tip-sample interaction forces acting upon the tip through the force–feedback mechanism, resulting in the zero compliance of the cantilever or infinite cantilever spring constant. Due to this zero compliance of the cantilever, the only observed spring results from the adsorbed material (see Fig. 1(B) and its related inset). More recently the COIFM’s force-feedback scheme was utilized for the development of a high-speed atomic force microscope for imaging large biological samples (Kim and Boehm, 2012).

**Experimental**

A soft film was grown on an oxidized silicon two-dimensional grating sample with $10 \, \mu m$ periodicity, which had been exposed to the ambient environment for 60 days at a relative humidity of $\sim 10$–$20\%$. Most studies of micromachines exposed to prolonged periods in the ambient environment are concerned with the effects of water more so than the effects of ambient formed hydrocarbon thin films (de Boer and Michalske, '97; de Boer et al., '98; Maboudian, '98; de Boer et al., '99; Tanner et al., '99; Cabuz et al., 2000; Ashurst et al., 2003; Zhao et al., 2003). AFM...
images, taken with an AutoProbe LS AFM system (formerly Park Scientific Instruments) using a Veeco NP-20 probe (Veeco, 2006), were used to study the structure of the layer. All data were collected at a relative humidity of 11% at a room temperature of 22°C. For the collection of force–distance and deflection–distance curves, the force–feedback voltage \( V_{ZnO} \) and the deflection voltages \( V_{A-B} \) were recorded, respectively, as a function of distance between the probe and the adsorbed material layer using the COIFM during both approach and retraction of the sample (Bonander and Kim, 2008; Kim et al., 2011a, 2011c). The conversion factors of 5 nN/V and 49 nm/V were used to convert voltages of \( V_{ZnO} \) and \( V_{A-B} \) into normal-force scale and deflection–length scale, respectively (Kim et al., 2011a). To incorporate imaging capability into the COIFM system, an additional z-feedback loop was added to the existing force–feedback loop of the COIFM (as shown in Fig. 2). The force–feedback loop for force images includes a force–feedback controller 1 (a modified Burleigh STM controller, Burleigh Instruments Inc., Fishers, NY), a commercially available dimension microactuated silicon probe (DMASP) fast cantilever with a ZnO stack (Veeco, 2006). The z-feedback loop involves the piezo tube and a z-feedback controller 2 (RHK SPM100 controller, RHK Technology Inc., Troy, MI). The output voltage for COIFM’s force–feedback was used as the input of the z-feedback controller 2. The RHK controller output was sent to the piezo tube via a high-voltage amplifier to control the movement of the sample in the z-direction. The maximum and minimum changes in movement that the system can control are 2.5 µm and ~1 pm, respectively, which depend on the actuation range of the piezo tube, and the voltage range and precision of the RHK controller. When the controller output was recorded for the entire scan area on the sample surface, the image represented a constant-force image. The set-force dependent constant force images were obtained by changing set-force in Figure 2. To interpret the observed constant-force images, the system captured two additional images: force and deflection images. An appropriate position of the z-feedback polarity switch of the RHK controller was selected, depending on the sign of slope desired at a chosen set-force in the force–distance curve. The root mean square (RMS) error was calculated for images using the image-processing program, RHK XPMPro. Since the force did not remain constant in areas containing abruptly changing large structures (such as the grating steps), flat areas were only included for the calculations of the average roughness.

Results and Discussion

A three-dimensional topographic view of the adsorbed material layer (lighter shaded) formed on top of the grating step (darker shaded) is presented in Figure 3(A). Granular structures with diameters of 300–500 nm were observed, which appeared to form from a mixture of atmospheric compounds, such as water and hydrocarbons. A hydrocarbon film would be predominately derived from atmospheric methane hydrocarbons composites and nonmethane hydrocarbons, primarily the result of fossil fuel combustion, and collectively being composed of propene, ethene, propane, etc. (Rudolph et al., 2002; Dewulf and Van Langenhove, 2003). The average thickness of the film was estimated to be ~50 nm (as marked with the double-headed arrow in Figure 3(A)).

To study the adsorbed material layer, deflection–distance and force–distance curves were collected simultaneously. The deflection signal (Fig. 3(B)) remained constant during both approach and retraction, confirming that the tip had zero compliance or infinite spring constant. All measurements of force–distance curves were collected at a tip-speed of ~40 nm/s. Even though the tip interaction with a soft film coating could be dependent on the tip approaching rate, this is beyond the scope of this study. The force–distance curve (as seen in Fig. 3(C)) displayed minute attractive force, implying that the outer surface of the adsorbed material has hydrophobicity. Because the majority of air molecules are nonpolar, the nonpolar hydrophobic surface preferred to orient outward to be exposed to those ambient nonpolar molecules. If the sample’s surface was hydrophilic, then thin water films formed on the surface would result in a slowly ramping attractive force before experiencing the sudden large jump in attractive force in the
Fig 3.  (A) A 2.3 μm × 2.3 μm three-dimensional AFM image of the 10 μm periodicity grating structure after being exposed to the ambient environment for ∼60 days, taken at an imaging rate of 256 s per frame. Average thickness of adsorbed material layers is ∼50 nm, demonstrated by the lighter layer above the dark section as indicated by the double headed arrow between two white lines indicating silicon surface height and adsorbed material height. (B) Graph of deflection signal (V_{A–B}) compared to the relative tip-position from the silicon substrate or tip-position from the top of the adsorbed material film. (C) Force–distance curves between the tip and the grating structure, with a force-activated voltage-feedback system during approach and retraction measured at 11% relative humidity. The zero point position for the lower x-axis (used in the text) of both the force–distance and deflection graph was defined as where the probe came into contact with the adsorbed layer. The zero point position for the upper x-axis was defined to be at the surface of the silicon substrate in which the adsorbed material covers. The dashed fitted line represents a fitting of the approach curve with the Hertzian model for the range indicated by the double arrow between the two small vertical lines. Inset is a zoomed in sectioning of the force–distance curve.

force–distance curves (Mate, 2008). However, if the tip was hydrophobic and approached a hydrophilic sample, then the force–distance curves would display a slowly increasing repulsive force before the tip comes into contact with the sample (Knapp and Stemmer, '99). These characteristics were not observed in the force–distance data shown in Figure 3(C), thus confirming that the surface is hydrophobic in nature.

The force–distance approach curve (Fig. 3(C)) displayed a nonlinear behavior before the steep linear increase. The nonlinear behavior can be described with the Hertzian model, which describes the relationship between the applied load and the contact area between a spherical tip and an elastic sample surface when they are being pressed against each other. Fitting the nonlinear section of the approach curve (from ∼0.2 nm to −6.8 nm) with the Hertzian model equation (Persson, 2000; Mate, 2008; Kaupp and Naimi-Jamal, 2010):

\[
F = \frac{4}{3} E \sqrt{R \delta}^{3/2},
\]

where the force (F) is related to the elastic modulus (E), the radius of contact (R) of 10 nm (Veeco, 2006), and the indentation depth (δ), allows for the determination of an E value of 54 ± 2 MPa with a correlation coefficient of 0.98073. When indentation depth is comparable to the tip radius, the force curve follows the Hertzian model; however, when the indentation depth is larger than the size of contact, the force increases linearly (as seen in Fig. 3(C) after a 10 nm indentation depth). The force changes linearly with distance once the tip comes into full contact with the surface. The sample compliance is found to be ∼1 N/m. The sawtooth-like oscillation pattern in the linear section suggests possible layered structures. Whenever the tip-repulsive force exceeds the covalent bond strength, the tip punctures each internal film layer (Persson, 2000). The rupturing force of the layers (as seen by the inset in Fig. 3(C)) is between ∼1 nN and 2 nN, which is consistent with earlier observations of silicon–carbon covalent-bond rupturing forces (Grandbois et al., '99). This oscillatory pattern indicates the existence of layered structures built during the process of film formation.

To investigate the mechanical properties of the internal material, the tip was used to agitate the adsorbed material. The tip was forced to penetrate the adsorbed material by applying a set-force value of 2 nN high enough to overcome the tensile strength of the adsorbed film. Then the tip was invasively scanned repetitively at the high-speed of 2.5 μm/s with the use of the feedback mechanism. Deflection and normal force signals were measured simultaneously during tip approach and retraction to understand the internal mechanical properties of the adsorbed layer. The deflection–distance curve (Fig. 4(A)) confirmed that the deflection remained constant due to the force–feedback for all distances except for those distances where a small peak and a small valley appear, as marked with vertical arrows. The peak and valley at ∼9 and ∼27 nm during approach and
retraction, respectively, were due to the limited response time of the current force-feedback system to the sudden force changes. The result suggests that the COIFM has exceptional ability in isolating the force generated by the mechanical properties of the adsorbed material from the mechanical response of cantilever spring associated with AFM measurements. The force–distance curve (Fig. 4(B)) showed that initially the tip did not experience any force until the tip and adsorbed layer joined together as shown in Figure 4(C). On approach the tip experienced a sudden attractive force of $-7 \text{nN}$ due to the tip contact with the material surface (seen to be $\sim 9.5 \text{ nm}$ from the force–distance curve). The tip force then increased linearly as the tip-substrate distance decreased, causing the tip to push against the adsorbed material.

When the tip retracted, the linear force followed the original approaching curves, indicating that the observed force is similar to a reversible process. However, below the tip distance of zero, the adhesive force linearly continued until it reached 27 nm, when the attractive force rapidly increased toward zero and then slowed down near zero. The relatively large pull-off force (21 nN), in comparison to the attractive force (7 nN) on approach in the force–distance curve, indicates the existence of adhesive bonding between the tip and the adsorbed material. This strong adhesion indicates that the adhesive internal parts of the adsorbed film were exposed to the ambient environment during the invasive scanning process. After the breakage of the adhesive bonding, van der Waals and electrostatic interactions are the only contribution to the observed attraction at the distance larger than 27 nm, as the distance increases. Based on this observation, the force–distance curves were divided into four regions: repulsive-contact (below 0 nm); attractive-contact (between 0 and 27 nm); attractive-noncontact (above 27 nm); and zero-force (above 30 nm) regimes (see Fig. 4(B)). The adsorbed material between the tip and sample is modeled to form a meniscus-like column (see Fig. 4(C)). This force–distance curve suggested that the adsorbed material behaves like a linear spring that follows Hooke’s law, as shown in the inset of Figure 4(C). The spring-constant ($k_s$) was
Fig 5. Constant-force image collected with a scan size of 5 μm × 5 μm on the grating structure at an imaging rate of 12.8 s per frame at (A) 1.25 nN set-force under normal polarity, (B) 1.25 nN set-force under reversed polarity, and (C) −1.25 nN set-force under reverse polarity. The white dashed squared area is zoomed in and displayed as (D) for the normal polarity 1.25 nN set-force image, (E) for the reversed polarity 1.25 nN set-force image, and (F) for the normal polarity −1.25 nN set-force image. The dashed boundary and the dotted boundary encircle areas considered as representative areas having high spring constant, while the solid boundary encircles an area representative of having a low spring constant.

measured to be 0.94 N/m from a linear curve fit on the portion from −50 to 10 nm. The stiffness of sample $k_i$ is related to the elastic modulus $E$ and the radius of contact $R$ as follows:

$$k_i = fRE,$$  \hspace{1cm} (3)

where $f$ is a geometric factor between 1.9 and 2.4 (Pethica and Oliver, ’87). Using the $k_i$ of 0.94 N/m, $E$ is estimated to be between 40 and 50 MPa, which is consistent with the value of 54 MPa, obtained with the Hertzian model above.

Spring models, in which the adsorbed materials on both the tip and sample surfaces are represented in each force regime, are displayed along the force–distance curve seen in Figure 4(B). On approach, once the tip came into close proximity of the adsorbed material layer, the attractive forces pulled the adsorbed material and the material coating the tip together to form a singular extended spring. When the tip reached the initial surface location of the undisturbed adsorbed material, the spring was in its relaxed state. As the distance further decreased the tip then slowly compressed the material. As the tip retracted, it slowly decompressed the material until it passed the initial undisturbed starting position. The adhesive property of the material caused it to continue to cling to the tip as the tip continued to retract. Thus, the spring was stretched until the column was no longer able to maintain its adhesive bonding, separating and snapping back to its initial resting state.

We obtained topographic images using the non-contact electrostatic interactions in the attractive-noncontact regime for constant-force imaging. This topographic imaging method is effectively analogous to scanning polarization force microscopy (Hu et al., ’95). By changing the $z$-feedback polarity at the set-force of −1.25 nN value, the tip was positioned around 27 nm above the surface of the adsorbed material in the attractive-noncontact regime, as marked with the vertical dashed arrow in Figure 4(B). The resultant constant-force image (Fig. 5(A)) exhibits a relatively smooth surface with the average roughness of only $\sim 5.6 \pm 0.9$ nm for the entire image (disregarding the step height of the grating sample). When the structure was imaged at the set-force of +1.25 nN in the repulsive-contact regime (Fig. 5(B)), an average roughness was calculated to be $\sim 10.7 \pm 1.5$ nm, an increased value by a factor of 2. This roughness increase was also observed when imaging the same surface at the set-force of −1.25 nN in the attractive-contact regime (Fig. 5(C)) with a resulting roughness of $\sim 10.6 \pm 2.2$ nm. This result indicates that the average roughness was dependent only on the existence of contact, not on the polarity of loading force. However, when three images were compared, some locations showed contrast variations in comparison with surrounding structures. These features were
emphasized in Figures 5(D–F), which were obtained by zooming in on the square areas bounded by the white dotted lines in Figure 5(A–C), respectively. While the noncontact image appeared relatively smooth over the entire zoomed area as shown in Figure 5(D), the surface is rougher in the contact regimes in their respective areas (Figure 5(E, F)). For example, the enclosed area with the dashed boundary was more protruded in the contact regime than in the noncontact regime. In the same contact regimes, some areas show the contrast reversals, depending on the polarity of applied forces. For example, the area encircled with the dotted white boundary showed elevated height for the positive applied force and compressed depth for the negative applied force. An area bounded with the solid line showed a compression when the applied force is positive, whereas it showed a stretching when the applied force is negative.

This local contrast difference, dependent on the polarity of the applied set-force, suggests that some materials embedded in the adsorbed material have different mechanical properties, such as elastic modulus from surrounding materials. The mechanical difference led to the varying compression depth and stretching height, creating images dependent on the polarity of the set-force. This embedded material is modeled with a weak spring surrounded with two strong springs with different heights that represent the corrugated surrounding materials, as shown in Figures 6(A–C). During the noncontact imaging, the tip follows the trace of the topographic structure, as drawn with a dashed line in Figure 6(A). It is important to note that the topographical contributions by electrostatic and van der Waals forces only contribute to the observed roughness difference between noncontact and contact images, as seen in Figures 5(A–C). Additionally, it explains the contrast variation dependent on the polarity of the applied force for different contact modes imaging. This model suggests that the COIFM system is capable of differentiating a local area with a different set-force from that of surrounding material by comparing the repulsive- and attractive-contact images. The effect of varying thicknesses and porosity of the film on its observed structural and mechanical properties could be an interesting future topic.

**Conclusion**

A newly developed COIFM system was used to investigate mechanical and structural properties of a soft hydrocarbon thin film developed on a solid oxidized silicon surface in air. The COIFM’s force-distance measurement and analysis showed the film stiffness of ~1 N/m and elastic modulus of ~50 MPa. A small oscillatory sawtooth pattern with amplitude of 1–2 nN in the linear repulsive regime suggests the possible existence of the layered structure within the film. The system was also applied to the constant-force imaging of the film in both contact and noncontact regimes. Both constant-force images taken in the repulsive and attractive contact regimes revealed additional features that were not observed in the images taken in the noncontact regime. Interestingly, some contrast reversal features were observed between the two contact regimes, while the average roughness remained constant. The contrast change was explained by modeling the adsorbed materials and embedded impurities with simple springs with different spring constants. The result shows that the COIFM is capable of resolving buried nanoscale structures. This study suggests that the COIFM
technique can be applied to biological materials including DNA (Kim et al., 2011b) and many industrial processes where the mechanical and structural properties and their relationship are critical. In chemical–mechanical planarization (CMP) processes and microelectromechanical systems (MEMS), for example, the in-depth understanding of the indentation depth under constant and varying load forces and the understanding of structure of buried materials are important (Sniegowski, ’96; Xie and Bhushan, ’96; Liang et al., ’97; Yang et al., ’98; Gad-el-Hak, 2001; Kasai and Bhushan, 2008; Saka et al., 2008; Kim, 2010; Arnold et al., 2011). The combination of the COIFM with other optical methodology, such as with Raman spectroscopy or infrared spectroscopy, will provide more opportunity to understand the mechanical and structural properties of soft materials in relation to chemical composition.

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