Published in final edited form as:

Ultramicroscopy. 1996 December ; 66(3-4): 237–249.

A constant compliance force modulation technique for scanning force microscopy (SFM) imaging of polymer surface elasticity

E.W. Stroup^a, A/ Pungor^b, and V. Hlady^b

^aDepartment of Materials Science and Engineering, University of Utah, Salt Lake City, Utah 84112, USA

^bDepartment of Bioengineering, University of Utah, Salt Lake City, Utah 84112, USA

Abstract

A new method of force modulation scanning force microscopy (SFM) imaging based on a constant compliance feedback loop is presented. The feedback adjusts the loading force applied by the SFM tip to the surface in order to maintain a constant compliance beneath the tip. The new method, constant compliance force modulation (CCFM), has the advantage of being able to quantify the loading force exerted by the tip onto the sample surface and thus to estimate the elastic modulus of the material probed by the SFM tip. Once the elastic modulus of one region is known, the elastic moduli of other surface regions can be estimated from the spatial map of loading forces using the Hertz model of deformation. Force vs. displacement measurements made on one surface locality could also be used to estimate the local modulus. Several model surfaces, including a rubber-toughened epoxy polymer blend which showed clearly resolved compliant rubber phases within the harder epoxy matrix, were analyzed with the CCFM technique to illustrate the method's application.

Keywords

Constant compliance SFM; Surface elasticity; Isocompliance force modulation

1. Introduction

Scanning force microscopy (SFM) has become a useful technique to image the topography of a sample surface in a variety of media without the need for extensive sample preparation [1]. Recently the scanning force microscope has been used to image the topography of phase separated polymer films [2–6]. These studies have shown that SFM is able to resolve topographic features to 10 nm width in these systems. Many of these studies were performed on relatively flat Langmuir–Blodgett films or self-assembled monolayers. Distinguishing the microphase separated structure of polymer films with more apparent topography has been more difficult [7–10]. Intrinsic problems of contact SFM lie in the deformation of the sample under the load exerted by the SFM tip and in the frictional property of the tip-sample contact. As a result of deformation and friction, the topography observed by SFM is, to a large degree, affected by those two effects leading to false information about the specimen surface. One expects that, by the virtue of reciprocity, the topography will influence the SFM measurements of the same mechanical properties of the sample under investigation.

The SFM technique has been used to measure mechanical properties of surfaces: investigations of the local friction [5, 11–18], compliance at a point of contact [19–23], and also mapping the local compliance [18, 24–30] have been accomplished on a variety of samples. Most of these studies, however, were performed on samples possessing little or no topography; the studies on topographically more featured samples have produced spatial maps of compliance that were still affected by topography [24, 31, 32]. These maps, while apparently displaying the regions of the surface differing in compliance, have not been able to quantify the material properties of these regions.

Mapping the local compliance of a surface has been performed by force modulation scanning method [18, 24–32] and also using the SFM in tapping mode [33]. In the force modulation method (Fig. 1) a small sinusoidal modulation is superimposed upon the existing z -position of the piezoelectric element controlling the tip-sample separation distance. With the tip in contact with the sample surface, this z -modulation imposes a small variation of tip loading force exerted onto the sample. In the isoforce version of this mode (Fig. 1a), the feedback regulation loop maintains a constant average angle of cantilever deflection, i.e. constant average load, during the scanning process by adjusting the position of the sample relative to the cantilever [24]. The SFM tip indents the sample in a sinusoidally varying fashion. The depth of indentation depends on the average loading force and the compliance of the sampled area and, for a given loading force, it will be smaller for stiff than it is for compliant areas. Measurement of the changes in the indentation depth is made by analysis of the change in the modulation amplitude experienced by the cantilever. The change in modulation amplitude can be detected with many different instrumental arrangements, but is commonly accomplished with an optical lever [34]. In this manner, the change in modulation amplitude is manifested as an instantaneous change in the magnitude of the angle of deflection experienced by the modulated cantilever [35]. The variation of the indentation depth (i.e. the change of the angle during each cycle) is used to create the map of the sample local compliance.

In this paper we describe a variant of the force modulation method that can also be used to map the local compliance of polymeric surfaces and to estimate the local elastic modulus from the applied loading force. The technique is based on a constant compliance feedback rather than on a constant loading force feedback. The constant compliance feedback, similar to the constant force feedback method, utilizes a modulation of the z -position of the piezoelectric element controlling the tip-sample separation distance. However, the constant compliance feedback method maintains constant the magnitude of cantilever angle change during each modulation cycle, rather than maintaining an average cantilever angle of deflection (Fig. 1b). We call this variant of the force modulation method constant compliance force modulation (CCFM), or isocompliance force modulation.

The starting point for interpretation of the loading forces is the deformation of two smooth isotropic elastic bodies in contact, in the absence of any adhesive force, given by the Hertz theory [36]. The depth of indentation (δ) of a flat material by a spherical indenter is described by

$$\delta^3 = (9F^2/16R)[(1 - \nu_0^2)/E_0 + (1 - \nu_1^2)/E_1]^2, \quad (1)$$

where F is the applied loading force, R is the radius of curvature of the indenter, ν is the Poisson's ratio, and E is the elastic modulus of the indenter (subscript 0) and indented material (subscript 1). The compliance of a material, denned as $dF/d\delta$, is related to the applied loading force and the Young's modulus of the material:

$$dF/d\delta = \{6R[(E_0E_1)/((1-\nu_0^2)E_1 + (1-\nu_1^2)E_0)]^2\}^{1/3} F^{1/3}. \quad (2)$$

The magnitude of the cantilever angle change depends on the local compliance sampled by the SFM tip. In order to achieve an equivalent local compliance, $dF/d\delta$, a greater loading force has to be applied to an area with a smaller modulus, than on an area with larger modulus. Spatial maps of loading forces exerted on the sample surface by the SFM tip, can be recorded by the action of the constant compliance feedback loop. The loading force maps could be further calibrated to provide quantitative information of the elastic properties of the sample surface regions.

Our long term aim is to apply the constant compliance feedback method to map the local compliance of phase separated materials. In this study we demonstrate that the constant compliance method results in spatial maps which, when calibrated, display the loading forces applied to the area beneath the tip. The loading force information leads to a method for determining spatial distribution of the sample local modulus.

2. Materials and methods

Two samples with different mechanical properties were used to test the CCFM-SFM method. The first sample, containing known topographic features and compliance regions, was prepared by applying a photoresist coating pattern to a silicon wafer. A 2 : 1 v/v solution of negative photoresist (IC28T-3, cyclized polyisoprene with a bis-azide photoinitiator, Olin Corporation, Stamford, CT) in xylene was spun cast onto a clean silicon wafer at 6000 rpm for 30 s. The film was masked and exposed to UV for 2 s and then washed to remove any unpolymerized material.

The second sample, a rubber toughened epoxy, was used to test the dynamic range of the elasticity mapping. The sample was a blend of an epoxy resin (Araldite, GY2600, Ciba-Geigy Co, Brewster, NY) with a rubber modifier. The rubber modifier was a copolymer of styrene and butyl acrylate with 50% styrene and 50% butyl acrylate. The polymer blend sample was mounted and then cut wafer thin [37].

SFM experiments were performed with a modified commercial force microscope (TMX 2000, Explorer SPM, TopoMetrix, Santa Clara, CA) in water. Microfabricated silicon cantilevers with integrated tips and nominal cantilever spring constant of 35 N/m were used [38]. The reported radius of curvature for the tips was 20 nm. No efforts were made to experimentally confirm the values of these parameters [39].

The cantilever was modulated at 7.7 kHz in the z -direction by adding a sinusoidal signal from a frequency generator (DSP lock-in amplifier, model SR830, Stanford Research Systems, Sunnyvale, CA) to the z -drive signal sent to the piezoelectric element holding the cantilever. The deflection of the cantilever was monitored by a laser beam reflected from the cantilever end onto a photo-detector. The detector signal was made up of two components. One was related to the average cantilever deflection (DC-component), and the other to the magnitude of the cantilever angle change during each modulation cycle (AC-component). The modulation signal, AC-component of the signal, was separated from the average cantilever deflection, DC-component, by a high-pass filter, and then followed by removal of high frequency noise by a low-pass filter (model 3550 band-pass filter, Krohn-Hite, Avon, MA). The absolute value of the effective cantilever angle change was obtained using custom-built analog circuitry. This absolute value was then amplified and filtered by a low-pass filter (model 113 pre-amplifier, EGG PARC, Princeton, NJ) in order to obtain the

feedback signal used by the electronic control unit of the TMX 2000 SFM data acquisition system to adjust the z -position of the piezo.

The feedback loop maintained constant the magnitude of cantilever angle change during each modulation cycle by adjusting the relative tip-sample position, which in turn resulted in a change of the average cantilever deflection and in a change of the loading force applied to the surface. The change in the average cantilever deflection was measured by a photodetector and sent as data input to the TMX 2000 SFM data acquisition system. From the average cantilever deflection signal a map related to the force applied to the surface was displayed during each x - y scan.

In addition to constant compliance scanning, two types of cantilever deflection versus tip-sample displacement measurements were performed for different areas of the sample while the modulation was imposed onto the cantilever. The two measurements were performed simultaneously. One was a measurement of cantilever deflection (i.e. applied loading force) as a function of the tip-sample displacement, or F versus D measurement. The other was a measurement of the magnitude of the cantilever angle change as a function of the tip-sample displacement, or A versus D measurement. The F versus D measurements were calibrated for force using the nominal stiffness of the cantilever. Calibration was achieved by fitting an F versus D measurement on silicon (with no cantilever modulation) to the expected response from a material with a modulus of 112 GPa (Young's modulus of silicon = 112 GPa [40]) indented by the tip made of the same material. The other F versus D measurements were then calibrated to the applied force, F (in N), using the signal of the SFM photodiode, S (in nA), due to the cantilever deflection occurring during the measurement using the relation: $F = \Omega S$, where Ω is the conversion factor between force and photodiode response (in nN/nA) obtained from the silicon F versus D measurement performed with the identical SFM settings.

All images were generated by raster scanning the sample in the x - y direction, at a typical scan rate of one line per second, while the feedback loop maintained a constant magnitude of cantilever angle change during each modulation cycle. Two types of images were recorded simultaneously: a map of the piezo z -displacement acting to maintain feedback and a map of the applied local loading force from the cantilever deflection. The CCFM loading force images were calibrated to show applied force in Newtons using the appropriate conversion factor, Ω , and the signal of the SFM photodiode, S , related to the cantilever deflection.

3. Results

A 35 N/m cantilever modulated at 7.7 kHz with an amplitude of 10 nm was used in the F versus D measurements performed on a silicon wafer and a photoresist material in water. The experimental results are shown in Fig. 2. As the tip came into the contact (designated as 0 nm displacement) with the silicon wafer surface (Young's modulus of silicon = 112 GPa [40]) the cantilever deflection increased with increasing displacement (Fig. 2a). Predicted F versus D response from a material with a Young's modulus of 112 GPa indented with a 112 GPa tip is shown in the same figure. The experimental F versus D points follow the predicted F versus D response very well: the variation in force at any given displacement is related to the applied 10 nm cantilever modulation amplitude.

When the SFM tip made the contact with the more compliant photoresist surface, (Young's modulus of uncrosslinked cyclized polyisoprene ≈ 0.03 GPa [41]), the applied loading force increased less steeply due to the increased indentation of the material by the tip (Fig. 2b). For a given displacement the cantilever deflected less than in the case of stiffer silicon. Fig.

2b also shows that the predicted F versus D response for a material with an elastic modulus of 5 GPa indented by a 112 GPa tip correlates very well with the experimental points. The variation in force at any given displacement due to the applied 10 nm cantilever force modulation amplitude gradually increased with displacement indicating that the photoresist becomes progressively stiffer upon further indentation.

Fig. 3 shows the result of the A versus D measurements performed simultaneously with the F versus D measurements (Fig. 2) on the same two materials in water. The magnitude of the cantilever angle change during modulation cycles displayed its lowest value before any contact was made between the tip and the sample. This is due to the nature of the optical lever detection method which detects only very small angular changes during the 10 nm z -modulation of the cantilever in the absence of contact. The 7.7 kHz modulation frequency used here is outside of the cantilever resonance and its harmonics. The largest angle change occurs when the tip, modulated in the z -direction, comes in contact with a stiff silicon surface: its modulation in z -direction becomes fully converted into a cantilever angle change by a pinned tip. The indentation of the silicon surface is very small: after the initial contact the A versus D slope increases rapidly over a displacement distance of 15 nm. On the contrary, the contact of the tip with the more compliant photoresist material causes a slower increase in the magnitude of the cantilever angle change with the displacement due to ever increasing indentation. Displacement beyond the initial 20 nm resulted in a progressively smaller increase in the magnitude of the cantilever angle change for both materials.

Further elucidation of the constant compliance approach to SFM imaging of a sample with distinct topographic differences and different compliance regions is shown in Fig. 4. The difference in the topography of the two areas will be shown on the F versus D response curves as a difference in the points of initial contact (Fig. 4b). After contact is established, because of the relatively small indentation, the F versus D response for the stiff material displays a cantilever deflection magnitude proportional to the change in the relative tip-sample displacement. When the tip makes contact with the more compliant material, a larger indentation will progressively occur, resulting in an F versus D curve that displays a gradually increasing slope with increasing tip-sample displacement. The difference between the two F versus D responses for the two regions relates both to the topographical height and the local compliance of each region.

During the x - y scanning the constant compliance feedback method searches along the F versus D response curve for a pre-set value of the slope, $dF/d\delta$ ($\approx dF/dD$), which is proportional to the magnitude of the cantilever angle change. Indicated in Fig. 4b are the two identical slopes, each defined by their respective displacement (z_s and z_c), applied force (f_s and f_c) and the difference in topographic heights. When the modulated SFM tip is scanned from the stiff to the compliant region (i.e. from left to right in Fig. 4a) the constant compliance feedback loop will adjust the displacement on the compliant region until the pre-set magnitude of the cantilever angle change is reached. The displacement adjustment will be less than the topographical height difference; in fact, it will be smaller by a factor accounting for the difference between the indentations on the compliant and the stiff region. The average deflection of the cantilever on each region measured relative to the cantilever resting position will be a direct measure of the loading force applied by the SFM tip.

Fig. 4c shows the respective A versus D responses for the same material regions: a steeper slope for the stiff region than for the more compliant one. One recognizes that the contrast in the tip-sample displacement image can be positive ($z_s > z_c$) at low pre-set magnitude of the cantilever angle change, or negative ($z_c > z_s$) for higher pre-set magnitude of the cantilever angle change. Two important conclusions can be drawn from the above analysis:

1. the differences in local applied force can be used to create the spatial map of sample local compliance without any influence of topography, and
2. the sample topography can be faithfully imaged only at the limit of zero-loading forces.

Fig. 5 shows two $50 \times 50 \mu\text{m}$ images of a photoresist step on a silicon wafer obtained using the CCFM method. The images, recorded using a 35 N/m cantilever in water with a modulation frequency of 7.7 kHz and an amplitude of 10 nm, were not manipulated further in any way. Fig. 5a shows the change in the tip-sample displacement needed to maintain a constant feedback (i.e. constant magnitude of the cantilever angle change). For this practical geometry the contrast in the tip-sample displacement map is similar to the actual topography of the sample. A cross-section profile shows that at the photoresist step, the z -displacement of the piezo element with the cantilever was approximately 600 nm. It can also be seen from the cross-section that there was considerable tilt to the sample.

A map of the local force applied to the sample surface is shown in Fig. 5b. For each horizontal line scan the brighter area (i.e. where a greater local force has been applied) corresponds to the polymeric photoresist while the darker area is the silicon wafer. A cross-section of the applied-force map clearly shows the differences between the photoresist and the silicon wafer areas: the increase in applied force indicates that a greater local force was applied to the photoresist area to reach the pre-set compliance. A ridge running along the edge of the photoresist step is also apparent. This area next to the edge appears as being softer than the top of the photoresist step. It is possible that this area could be a wetting foot that has not crosslinked to the same extent as the middle portion of the photoresist due to diffraction effects occurring at the mask edge. The increased compliance near the edge may also be due to the absence of neighboring photoresist in which to distribute the load. Comparing the cross-sections for the tip-displacement image and the applied force image, it is seen that the tilt in the sample does not affect the measurement of the applied force. However, a drift of the applied force in the slow scan direction is observed presumably due to the drift in one of the experimental settings during the measurement.

Fig. 6 shows the two CCFM $25 \times 25 \mu\text{m}$ maps of a rubber-toughened epoxy surface consisting of an epoxy resin with a rubber copolymer modifier of styrene-butyl acrylate. The sample was imaged in water with a cantilever of 35 N/m nominal spring constant at a modulation frequency of 7.7 kHz and an amplitude of 10 nm. Fig. 6a shows the tip-sample displacement necessary to maintain a constant compliance while scanning the material. Bright and dark features approximately 2–5 μm in size occurring as both elevated “islands” and depressions appear to correspond to the regions of the rubber copolymer within the epoxy matrix. The applied loading force CCFM map is shown in Fig. 6b. Features of approximately 2–3 μm across surrounded by a darker background are areas where a greater force was applied in order to maintain a constant compliance. Many of the areas where a greater force was applied correspond to the “islands” in Fig. 6a, while others coincide with the depressions seen in Fig. 6a. This detected morphology is consistent with previous studies by Spinks [37], which have shown that the blends have a two phase microstructure consisting of 2.5–4 μm particles within an epoxy matrix. Thus, the initial hypothesis was that the areas of higher applied force are regions of the softer rubber copolymer embedded within the more rigid epoxy matrix.

In order to verify this hypothesis the F versus D response curves were obtained from the area scanned in Fig. 6 immediately following CCFM imaging. Fig. 7a shows the F versus D response from the epoxy matrix, while Fig. 7b shows the F versus D response obtained from one of the rubber copolymer areas. Predicted force curves for materials with Young's moduli of 2 GPa (Fig. 7a) and 0.5 GPa (Fig. 7b) indented by a 112 GPa tip are plotted along

with the experimental data. The predicted curves correspond reasonably well to the curves obtained from the epoxy and rubber copolymer. The experimental results for both areas show an increase in the force with displacement, however, the increase is much less on the rubber copolymer due to larger indentation. The variation in force due to the cantilever modulation is apparent; the force variation for a given displacement is less for the rubber copolymer than for the epoxy as expected.

Fig. 8 shows two CCFM $10 \times 10 \mu\text{m}$ maps of the same epoxy–styrene–butyl acrylate blend. Using epoxy as a standard (Young's modulus, $E = 2 \text{ GPa}$, determined from the F versus D measurement), one can from the applied loading force map estimate the modulus of the styrene–butyl acrylate region to be approximately four times smaller, i.e. around 0.5 GPa , similar to what was predicted from Fig. 7b. These values for modulus are lower than the values reported by Spinks for microindentation measurements: the rubber copolymer's modulus was approximately 5 GPa and was approximately 10 GPa for the epoxy resin matrix [37]. The moduli estimated from the CCFM imaging were almost one order of magnitude greater than what is generally reported for the Young's modulus of butyl acrylate, but similar to that expected for the epoxy matrix [41].

4. Discussion

The aim of this study was to map the local compliance of materials surfaces and to quantify their elastic properties. To accomplish this goal a new SFM feedback system that maintains a constant compliance beneath the scanning tip through a constant magnitude of cantilever angle change was designed. The constant compliance force modulation (CCFM) method has been able to detect local differences in compliance and thus to produce spatial maps based on the differences in local surface elasticity. In addition to the spatial mapping, the CCFM loading force images could be interpreted in a quantitative manner. The quantitative estimate of local surface elasticity required: (1) an appropriate in situ elasticity “standard”, or a local F versus D measurement from which the elasticity of a local surface region could be computed and (2) a suitable deformation model.

The model used in this study is based on the Hertz theory of the deformation of two smooth isotropic elastic bodies in contact [36]. The problem of the measurement of the local surface elasticity of a composite sample can be analyzed by comparing two different materials indented by the same indenter until the same compliance, $dF/d\delta$, is reached. From Eq. (2), one finds that the ratio of the Young's moduli terms (r.h.s.) is equal to the inverse square root ratio of the respective loading forces:

$$\frac{(1/F_s)^{1/2}}{(1/F_c)^{1/2}} = \frac{[(E_0 E_s)/((1 - \nu_0^2)E_s + (1 - \nu_s^2)E_0)]}{[(E_0 E_c)/((1 - \nu_0^2)E_c + (1 - \nu_c^2)E_0)]} \quad (3)$$

where the subscripts s and c denote stiff and compliant materials, respectively. When indented by the same indenter applying equal loading force, F , the two material's Young's moduli ratio is equal to the ratio of their respective compliances raised to the power of $3/2$:

$$\frac{(dF_s/d\delta)^{3/2}}{(dF_c/d\delta)^{3/2}} = \frac{[(E_0 E_s)/((1 - \nu_0^2)E_s + (1 - \nu_s^2)E_0)]}{[(E_0 E_c)/((1 - \nu_0^2)E_c + (1 - \nu_c^2)E_0)]} \quad (4)$$

Comparison of Eqs. (4) and (3) reveals both the similarities and the differences between the constant force and constant compliance approach in spatial mapping of sample elasticity: any change in the ratio of elastic moduli (r.h.s. in Eqs. (3) and (4)) will correspond to

changes in either the material compliance or the applied force depending on the approach utilized, i.e. isoforce or isocompliance. The sensitivity of the constant force modulation technique is related to the ratio of the compliances raised to the power of 3/2. The constant compliance modulation method measures the change in loading force for a pre-set compliance; its sensitivity is related to the inverse square root ratio of the respective loading forces.

The ability of the CCFM method to establish feedback on a material was dependent on the cantilever properties as well as the mechanical properties of the material. The feedback action results in the adjustment of the tip sample distance until a constant compliance, $dF/d\delta$, i.e. a constant gradient of the applied loading force, is achieved. For the more compliant surface regions, the tip sample distance is decreased allowing larger indentation depth by the tip. Although the tip itself has a finite compliance, it is the cantilever stiffness that determines the upper practical limit of the CCFM method. Once the force gradient becomes much greater than the stiffness of the cantilever, the tip is not able to effectively indent the sample anymore. Accordingly, cantilevers with a greater stiffness will allow larger force gradients to be mapped, however, using too stiff a cantilever can introduce some irreversible damage to the scanned region. Hence, the stiffness of the cantilever has to be “tuned” to match the stiffness of the specimen. For a 35 N/m cantilever, the sample modulus range lies approximately between 0.1 and 10 GPa. In this range, the 35 N/m cantilever can resolve moduli that differ by at least 10%. Surface areas with moduli approaching 100 GPa can still be used to maintain feedback as shown by the silicon-photoresist sample (Fig. 5). On the lower end of the pre-set compliance range, the limit is determined by the magnitude of the modulation amplitude and maintenance of the contact between the tip and the sample: intermittent tip sample contacts lead to a false estimate of surface modulus. Another problem is the presence of the adhesive contact at negative loading forces. The appearance of adhesive contact may also occur due to the capillary forces when scanning in ambient moist air. In order to minimize the effect of adhesive forces, all samples in this study were scanned under water.

To insure the stability of the imaging, the samples were scanned in the x -direction at a very slow speed (approximately one line per second). The slow scanning speed allowed for a more sensitive feedback response to changes in the force gradient, and also helped to compensate for the feedback “overshoot” at the end of each scan line. The overshoot effect commonly caused the feedback loop to become destabilized. However, imaging at very slow scan speeds made the system very sensitive to thermal drifts of the SFM instrumentation which resulted in a drift of the pre-set magnitude of the cantilever angle change. For example, the loading force image in Fig. 5b shows a strong drift effect in the slow scan (perpendicular) and no drift effects in the fast scan (horizontal) dimension. Because of the drift, quantitative modulus comparison between the surface regions shown in Fig. 5b could be made only for the regions scanned on the same fast scan line.

All CCFM images presented in this study were recorded while modulating the cantilever at a frequency of 7.7 kHz. This frequency was primarily chosen to be outside of the resonance of the instrument which showed a high resonance below 4 kHz, and above 10 kHz, but also because it was outside the resonance range of the cantilever (nominal resonant frequency of a free cantilever was 171–193 kHz). For a more dynamic description of surface elastic properties, it would be desirable to modulate the cantilever at a range of frequencies and to monitor both the modulation amplitude and phase changes. Such work is in progress in our laboratory.

5. Conclusions

A new feedback loop has been designed for spatial mapping of the local compliance of a surface. The feedback adjusts the loading force applied by the SFM tip to the surface in order to maintain a constant compliance beneath the tip. The new method, constant compliance force modulation (CCFM), has the advantage of being able to quantify the loading force exerted by the tip onto the sample surface and thus to estimate the modulus of the material probed by the SFM tip. If the elastic modulus of one surface region is known, the elastic moduli of other surface regions can be estimated from the spatial map of loading forces using the Hertz model of deformation. Force versus displacement measurement made on one surface locality could also be used to estimate the local elasticity modulus. Several model surfaces were analyzed with the CCFM technique to illustrate the method's application including a rubber-toughened epoxy polymer blend which showed clearly resolved compliant rubber phases within the harder epoxy matrix. The dynamic range of the method is expected to depend on the stiffness of the cantilever used.

Acknowledgments

Support for this work was provided by NIH (HL44538) grant. One of us (EWS) thanks Becton Dickinson Vascular Access, Sandy, Utah for a fellowship during the initial stage of the work. The authors gratefully acknowledge Dr. Manfred Radmacher for his assistance in the initial stage of this work and for many inspiring discussions, and Dr. Geoff Spinks for providing the rubber-toughened epoxy samples.

References

1. Binnig G, Quate CF, Gerber C. Phys. Rev. Lett. 1986; 56:930. [PubMed: 10033323]
2. Tillman RW, Radmacher M, Gaub HE. J. Phys. Chem. 97:2928.
3. Chi LF, Fuchs H, Johnson RR, Ringsdorf H. J. Vacuum Sci. Technol. B. 1994; 12:1967.
4. Leporatti S, Cavaleri O, Rolandi R, Tundo P. Langmuir. 1994; 10:1334.
5. Ge S, Takahara A, Kajiyama T. Langmuir. 1995; 11:1341.
6. Saremi F, Maassen E, Tieke B, Jordan G, Ram-mensee W. Langmuir. 1995; 11:1068.
7. Collin B, Chatenay D, Coulon G, Asserre D, Gallot Y. Macromolec. 1992; 25:1621.
8. Schwark, DW.; Thomas, EL. Characterization of the Morphology of Polymer Surfaces, Interfaces and Thin Films by Microscopy Techniques. In: Tong, SPKHM.; Saraf, R.; Chou, NJ.; Fitzpatrick, LE., editors. Characterization of Polymers. Boston: Butterworth-Heinemann; 1994. p. 92
9. Nick L, Kindermann A, Fuhrmann J. Colloid Polymer Sci. 1994; 272:367.
10. Nick L, Lippitz A, Unger W, Kindermann A, Fuhrmann J. Langmuir. 1995; 11:1912.
11. Chi LF, Fuchs H, Johnston RR, Ringsdorf H. Thin Solid Films. 1994; 242:151.
12. Ruan J-A, Bhushan B. Tribology. 1994; 16:378.
13. Ascoli C, Dinelli F, Frediani C, Petracchi D, Salerno M, Labardi M, Allergini M, Fuso F. J. Vacuum Sci. Technol. B. 1994; 12:1642.
14. Bhushan B, Israelachvili JN, Landman U. Nature. 1995; 374:607.
15. Meyer E, Heinzelmann H, Grüttner P, Jung T, Hidber HR, Rudin H, Güntherodt HJ. Thin Solid Films. 1989; 181:527.
16. Meyer E, Overney R, Brodbeck D, Howald L, Lüthi R, Frommer J, Güntherodt H-J. Phys. Rev. Lett. 1992; 69:1777. [PubMed: 10046311]
17. Overney RM, Meyer E, Frommer J, Brodbeck D, Lüthi R, Howald L, Güntherodt H-J, Fujihira M, Takano H, Gotoh Y. Nature. 1992; 359:133.
18. Wilbur JL, Biebuyck HA, MacDonald JC, Whitesides GM. Langmuir. 1995; 11:825.
19. Burnham NA, Colton RJ. J. Vacuum Sci. Technol. A. 1989; 7:2906.
20. Burnham NA, Dominguez DD, Mowery RL, Colton RJ. Phys. Rev. Lett. 1990; 64:1931. [PubMed: 10041531]

21. Landman U, Luedtke WD, Burnham NA, Colton RJ. *Science*. 1990; 248:454. [PubMed: 17815594]
22. Thomas RC, Houston JE, Michalske TA, Crooks RM. *Science*. 1993; 259:1883. [PubMed: 17836246]
23. Radmacher M, Fritz M, Hansma PK. *Biophys. J.* 1995; 69:264. [PubMed: 7669903]
24. Maivald P, Butt HJ, Gould SAC, Prater CB, Drake B, Gurley JA, Elings VB, Hansma PK. *Nanotechnol.* 1991; 2:103.
25. Radmacher M, Tillmann RW, Fritz M, Gaub HE. *Science*. 1992; 257:1900. [PubMed: 1411505]
26. Radmacher M, Tillmann RW, Gaub HE. *Biophys. J.* 1993; 64:735. [PubMed: 19431876]
27. Florin E-L, Radmacher M, Fleck B, Gaub HE. *Rev. Sci. Instr.* 1994; 65:639.
28. Overney R, Bonner T, Meyer E, Ruetschi M, Lüthi R, Howald L, Frommer J, Güntherodt H-J, Fujihara M, Takano H. *J. Vacuum Sci. Technol. B.* 1994; 12:1973.
29. Overney RM, Meyer E, Frommer J, Güntherodt HJ, Fujihira M, Takano H, Gotoh Y. *Langmuir*. 1994; 10:1281.
30. Kajiyama T, Tanaka K, Ohki I, Ge SR, Yoon JS, Takahara A. *Macromolec.* 1994; 27:7932.
31. Stroup EW, Pungor A, Hlady V, Andrade JD. *ACS Polymer Preprints*. 1992; 33:749.
32. Stroup EW, Pungor A, Hlady V, Andrade JD. *ACS Polymer Preprints*. 1993; 34:86.
33. Höper R, Gesang T, Possart W, Hennemann O-D, Bosek S. *Ultramicroscopy*. 1995; 60:17.
34. Sarid, D. *Scanning Force Microscopy: With Applications to Electric, Magnetic, and Atomic Forces*. New York: Oxford University Press; 1991.
35. It is worthwhile to recall that the optical lever technique is by two orders of magnitude more sensitive to the changes in the cantilever angle than to the changes in the cantilever *z*-displacement. Hence, large depths of indentation (on compliant areas) will result in smaller changes of cantilever angle, while no indentation (on stiff areas) will produce the largest change in cantilever angle. We will refer to the extent of the change of the cantilever angle during each modulation cycle as the magnitude of the cantilever angle change.
36. Johnson, KJ. *Contact Mechanics*. New York: Cambridge University Press; 1985.
37. Spinks, GM.; Stachurski, ZH. *Proc. Interfaces II, Micro-indentation of Rubber-toughened Epoxy Resins*, Institute of Metals and Materials. Australia: Ballarat; 1993.
38. Topoprobes® were purchased from TopoMetrix, Santa Clara, CA. The nominal cantilever stiffness and resonant frequency was 35 N/m and 171–193 kHz, respectively.
39. Microfabricated cantilevers have been shown to have spring constants that can vary by a factor of 7 between different wafers and by a factor of 2 on the same wafer. (a) Hoh JH, Cleveland JP, Prater CB, Revel J-P, Hansma PK. *J. Amer. Chem. Soc.* 1992; 114:4917. (b) Cleveland JP, Manne S. *Rev. Sci. Instru.* 1993; 64:403. (c) Senden TJ, Ducker WA. *Langmuir*. 1994; 10:1003.
40. (a) Ross, RB. *Metallic Materials Specifications Handbook*. 4th Ed.. New York: Chapman and Hall; 1992. (b) Boyer, HE.; Gall, TL. *Metals Handbook Desk Edition*. Metals Park Oh: ASM; 1985.
41. Brandrup, J.; Immergut, EH. *Polymer Handbook*. New York: Wiley; 1989.

Output:
modulated
cantilever
angle
change

Input:
modulation
of the tip
or sample
position

a

Output:
modulated
cantilever
angle change
superimposed on
change in the
average loading
force

Input:
modulation
of the tip
or sample
position

b

Fig. 1.

Schematic representations of isoforce and isocompliance force modulation methods. In each method a small sinusoidal variation in tip-sample distance causes a small variation of the tip-loading force to be applied to the area beneath the tip. (a) isoforce: The feedback system maintains a constant average angle of cantilever deflection by adjusting the tip-sample position. Compliance map of the surface is generated from the variation in the indentation depth (i.e. the changes in the magnitude of the cantilever angle change), (b) isocompliance: The feedback system maintains a constant magnitude of the cantilever angle change. A map of the surface compliance is generated from differences in the applied local force necessary to maintain feedback.

a

b

Fig. 2. Force versus tip-sample displacement curve, F versus D , obtained using a 35 N/m cantilever modulated at 7.7 kHz with a 10 nm amplitude in water on (a) a silicon wafer and (b) a photoresist surface. Curves for predicted response from materials with Young's moduli of (a) 112 GPa and (b) 5 GPa as predicted from the Hertz relationship (—) are plotted along with experimental data (.....).

Fig. 3. Magnitude of the cantilever angle change versus tip-sample displacement curve, A versus D , obtained using a 35 N/m cantilever modulated at 7.7 kHz with a 10 nm amplitude in water on a silicon wafer ((—)) and photoresist (---) surface.

Fig. 4. (a) Case of a hypothetical sample with topographic features and with regions of differing compliance, (b) Schematic F versus D curves for the two different regions. Isocompliance conditions are indicated with the tangents drawn at points (z_s, f_s) and (z_c, f_c) for the stiff and compliant regions, respectively, (c) Schematic A versus D curves for the two different regions. The stiff material has a slope steeper than the compliant material.

Fig. 5.

Unprocessed CCFM images of a photoresist step on a silicon wafer taken using a 35 N/m cantilever in water with a modulation frequency of 7.7 kHz and an applied amplitude of 10 nm. (a) Map of the tip-sample displacement: the profile below indicates the tip-sample displacement as the tip scans across the sample and encounters the photoresist step, (b) Map of the local loading force applied to the surface: the profile below shows greater loading force applied to the area of the sample corresponding to the photoresist step.

Fig. 6.

Unprocessed CCFM images of rubber toughened epoxy taken using a 35 N/m cantilever in water with a modulation frequency of 7.7 kHz and an applied amplitude of 10 nm. (a) Map of tip-sample displacement shows elevated “islands” and depressions against the epoxy matrix. Islands and depressions are apparently the rubber modifier within the epoxy matrix, (b) Map of local loading force applied to the surface. A greater loading force was applied to rubber regions compared to the epoxy matrix. Applied force map is calibrated to show force in newtons.

Fig. 7. Force vs. tip-sample displacement curve, F versus D , obtained using a 35 N/m cantilever modulated at 7.7 kHz with a 10 nm amplitude in water on (a) a epoxy matrix and (b) a rubber modifier area identified from Fig. 6. Curves for predicted response from materials with Young's moduli of (a) 2 GPa and (b) 0.5 GPa as predicted from the Hertz relationship (—) are plotted along with experimental data (.....).

Fig. 8.

Unprocessed CCFM images of rubber toughened epoxy taken using a 35 N/m cantilever in water with a modulation frequency of 7.7 kHz and an applied amplitude of 10 nm. Material scanned is from same sample as Fig. 6, but a different area, (a) Map of tip-sample displacement shows elevated “islands” and depressions against the epoxy matrix, (b) Map of local loading force applied to the surface. As greater loading force was applied to rubber regions compared with the epoxy matrix. Applied force map is calibrated to show-force in newtons.