A HYBRID MOLECULAR/CONTINUUM ANALYSIS OF IFM EXPERIMENTS ON A SELF-ASSEMBLED MONOLAYER

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Summary An interfacial force microscope (IFM) has been used to probe self-assembled monolayers of octadeciletrichlorosilane (OTS) on silicon. Its unique self-balancing force sensor allows the full attractive and repulsive portions of the force-displacement response of the tip/surface interactions to be obtained. The measured force profile is used to validate a molecularly based continuum model of the adhesive contact between the tip and the surface of the OTS monolayer.

EXTENDED SUMMARY

Polymeric self-assembled monolayers on silicon are used in MEMS devices as stiction reducers[1]. They can also be used to control adhesion[2 3 4]. As a result, such monolayers are becoming critical elements in such applications and it is important to understand their mechanical behaviour. Such understanding may come from complementary approaches such as molecular dynamics simulations and experiments with scanning probe microscopes.

The self-assembled monolayer considered in this work is octadecyltrichlorosilane (OTS) on silicon. It is quite commonly used in MEMS applications as it forms covalent bonds with the silicon substrate and has a methyl terminal group which has very weak interactions with other surfaces. The monolayer was probed with an IFM (Fig. 1), which provides complete force profiles in the attractive and compressive regimes due to a unique self-balancing force sensor[5]. This is in contrast to atomic force microscopes (AFM), which encounter an unstable response when the force gradient of the surface interaction exceeds the spring stiffness of their cantilever force sensor. The measured force profiles were compared with continuum level analyses that accounted for surface interactions via traction-separation laws and considered the OTS to be isotropic and (a) linearly elastic and (b) nonlinearly elastic. The latter was motivated by molecular dynamics simulations of simple stress states.

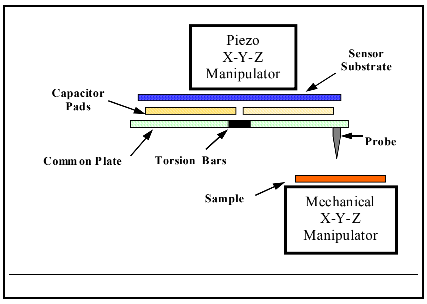

Fig. 1. Schematic of an IFM

The substrate used for the OTS deposition was a polished boron P-type single crystal silicon wafer (100). Its native oxide layer is usually contaminated[6] so it was removed with a dilute hydrofluoric acid solution. A new oxide layer was produced by placing the chips in a piranha solution (96% H_2SO_4 : 30% H_2O_2, 2:1 vol.),which oxidizes and hydrolyzes the silicon surface. An anhydrous, millimolar solution of OTS in dicyclohexyl was prepared in a dry box, the silicon chips were placed in it for 24 hours and then removed and treated with a series of solvents and sonicated to remove any physisorbed layers. Ellipsometry measurements indicated that the oxide and monolayer were 2 and 2.5 nm thick, respectively. Several other contact angle, spectrographic and AFM diagnostics confirmed that a monolayer had indeed been formed.

An electrochemically etched tungsten tip was attached to the sensor of the IFM as an indenter. The geometry of the tungsten tip was measured with a scanning electron microscope (SEM). Tips that had a parabolic shape and radii ranging from 100 nm to 500 nm were recorded and kept for future use. The force profiles (Fig. 2) from bare and coated silicon shows that the IFM is capable of detecting the OTS monolayer.

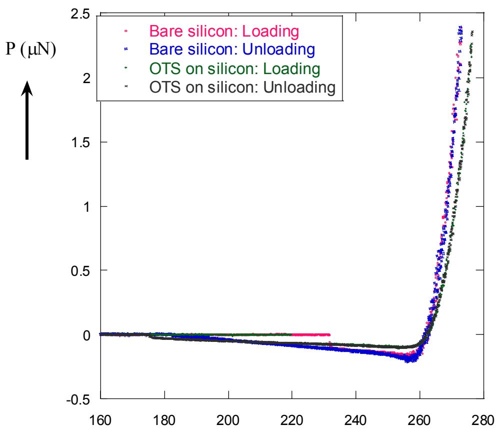

Fig. 2. Comparison of force profiles for bare and coated silicon

The analysis of the IFM experiments was conducted at the continuum level with the finite element package ABAQUS. An axisymmetric analysis was used due to the spherical contact. The tungsten indenter, oxide layer and silicon were all considered to be linearly elastic and isotropic. The OTS was first considered to be the same, but a second series of analyses took it to be a hypoelastic material on the basis of the molecular dynamics analysis described below. Geometrically nonlinear analysis was used in all simulations due to large deformations in the contact region. Quadrilateral linear axisymmetric elements with reduced integration were used for both the indenter and specimen. Infinite elements were used for the farfield region (>20 times the maximum contact radius) of the half space so that no boundary conditions needed to be enforced on the unbounded domain.

The compressive regime of the nanoindentation was modeled as frictionless contact using standard ABAQUS surface contact interactions. The default contact pressure-clearance relationship in ABAQUS is referred to as the "hard" contact model. It only transmits pressure once the surfaces come into contact. This interaction model is not sufficient for analyzing indentation experiments where the adhesive effect is large. As a result, user-defined elements were incorporated in the abovementioned mesh when adhesive interactions were required. A triangular traction-separation law with three parameters was used[7]: the maximum adhesive traction σ_0, the corresponding displacement δ_0 and the cut-off displacement δ_t. The surface energy was then $\omega = \frac{1}{2}\sigma_0\delta_t$. The adhesive portion of the response was best fitted with $\sigma_0 = 37.5$ MPa, $\delta_t = 7$ nm, $\delta_0 = 5$ nm and $\omega = 131.3$ mJ/m^2. This relatively long-range interaction is probably due to adventitious water on the surface as the experiments were not conducted in vacuum. The results from the linearly elastic analyses indicated that modulus of OTS monolayer was 15±5 GPa when Poisson's ratio was zero, and 5±2.5 GPa when Poisson's ratio was 0.44 (Fig. 3). These values reflect the higher degree of order that is present in self-assembled monolayers.

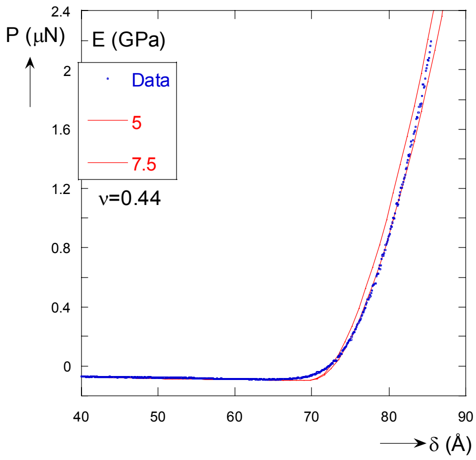

Fig. 3. Comparison of the measured force profile with linear solutions.

The linear elastic solutions were not satisfactory in the low and high force regimes. This suggested that a nonlinear model of the OTS might be preferable. Guidance was sought from molecular dynamics analyses which were used to simulate the self-assembly of an OTS monolayer on an SiO_2 substrate as well as the compression of the monolayer by a tungsten plate. The simulation was performed with the molecular dynamics simulation package DL_POLY 2.0. Room temperature was maintained during the calculation and both the SiO_2 substrate and tungsten plate were modeled as surfaces with one layer of atoms. The SiO_2 was modeled as trydimite[8]. Both SiO_2 and tungsten were treated as rigid because they were expected to be much stiffer than the OTS monolayer. United atoms were used to model the OTS molecular chain, where the CH_3, CH_2, and OH groups were represented as pseudo-atoms. Slab periodic boundary conditions, which are periodic in the plane, were used to represent the infinite extent in the two in-plane directions. The repeating cell had dimensions of 26×27 Å^2 containing 30 OTS molecules. All the OTS molecular chains were initially arranged perpendicular to the SiO_2 surface. A highly nonlinear response resulted, which was then modeled as a hypoelastic material in an ABAQUS analysis of the IFM experiment. The results are compared with the measured force profile (Fig. 4). Better agreement was achieved at low force levels, but a more comprehensive representation of the OTS is required in order to improve the solution at higher load levels. This is currently being pursued in molecular dynamics analyses of simple shear loadings which will then be incorporated in continuum representations such as the Ogden[9] model.

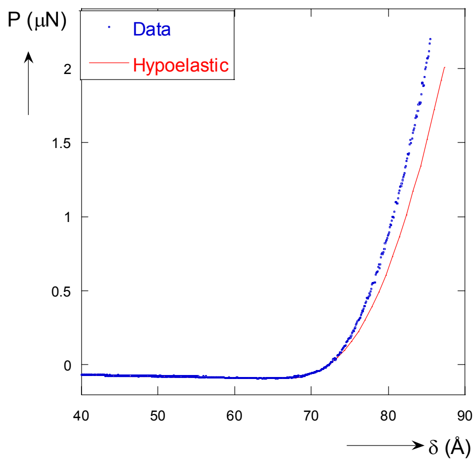

Fig. 4. Comparison of the measured force profile with a nonlinear elastic analysis

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