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Citation: Applied Physics Letters **82**, 1126 (2003); doi: 10.1063/1.1542945

View online: http://dx.doi.org/10.1063/1.1542945

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APPLIED PHYSICS LETTERS VOLUME 82, NUMBER 7 17 FEBRUARY 2003

Electrostatic response of hydrophobic surface measured by atomic force microscopy

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(Received 1 October 2001; accepted 9 December 2002)

The arrangement of water molecules at aqueous interfaces is an important question in material and biological sciences. We have measured the force acting on neutral tips as a function of the distance to hydrophobic silicon surfaces and cetyltrimethylammonium bromide monolayers covering mica surfaces in aqueous solutions. The unusually large magnitude of this force is attributed to an electrostatic response of the aqueous fluid structure (hydration layer) which is generated by the reorientation of water molecular dipoles. The exchange of a volume of this region with a dielectric permittivity (ε_{int}) by the tip with a dielectric permittivity (ε_{tip}) is responsible for the tip attraction when it is immersed in the polarization (hydration) layer. Variable permittivity profiles starting at $\varepsilon \approx 11$ at the interface and increasing to $\varepsilon = 80$ about 10 nm from hydrophobic silicon surfaces and about 50 nm from cetyltrimethylammonium bromide monolayer covering mica surfaces were measured. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1542945]

The nanometer-scale structure of interfacial water is a fundamental subject of material and biological sciences that has until now eluded a direct study because of the lack of suitable microscopic techniques with the required level of resolution. Knowledge about interfacial water structure near hydrophobic surfaces is crucial for the understanding of many important surface problems involving water.[1–3]

Measurements of the forces between macroscopic bodies with hydrophobic (high contact angle) surfaces show remarkable long-range attractions.[4–6] Experiments performed[7,8] exhibit forces measurable at 70–90 nm, which exceed the usual van der Waals force by some two orders of magnitude.

Previous studies using atomic force microscopy (AFM) were performed using large radii of curvature tips and flat surfaces; here we used macroscopic-size flat hydrophobized surfaces and nanosized ~ 5 nm radius of curvature hydrophobic tips and we have assumed that the tip polarization charge is much smaller than the one associated with $\sim 1 \times 1\ \text{cm}^2$ flat substrate surfaces. The force acting on the tip when immersed in the interfacial polarization layer of hydrophobic silicon and cetyltrimethylammonium bromide (CTAB) monolayers covering mica surfaces immersed in water was probed. This force is modeled by the gradient of the electrostatic energy variation involved in the exchange of a volume of the interfacial region with a dielectric permittivity (ε_{int}) by the tip with a dielectric permittivity (ε_{tip}).

We have obtained best results in measurements with very soft cantilevers with silicon nitride tips, typically ~ 0.03 N/m (Microlever™, type B, ThermoMicroscopes). The commercial silicon nitride tip surface has been found to be close to electrically neutral over a wide pH range (from at least pH 6–8.5), thus indicating equal densities of silanol and silylamine surface groups.[9] The surface of a silicon nitride tip in aqueous solution is composed of amphoteric silanol and basic silylamine [secondary (silazane, $-\text{Si}_2\text{NH}_2$) and possibly primary (silylamine, $-\text{SiNH}_3$) amines although the latter is rapidly hydrolyzed] surface groups[9,10] at $p\text{H} \sim 6$; with no added electrolyte the silicon nitride surface is either zwitterionic (zero net charge) or slightly negatively charged.[9] To verify the surface charging behavior of the tips, force versus separation curves in mica/H_2O in solutions with pH between ~ 5.2 and 6.8 were measured, and the isocharging point (icp) for silicon nitride was determined to be $p\text{H}_{\text{icp}} \approx 6.3$.

We prepared hydrophobic surfaces by immersion of Si ⟨100⟩ polished substrates in 48% HF solution for 5 min followed by extensive rinsing with Milli-Q water. Fig. 1 shows the 15 min after immersion force versus distance curve.

The second hydrophobic surface probed was prepared by depositing a monolayer of CTAB on the surface of freshly cleaved mica surfaces by means of a standard immersion of the substrate in a 10^{-5} M CTAB solution.[11] The hydrophobicity of the surface came from a layer of closely packed hydrocarbon chains and is determined by measuring the water drop contact angle ($\sim 90°$). This surface was previously investigated and the results are described in our previous work.[11] The corresponding force versus distance curve is shown in Fig. 2.

Polarization (hydration) of the silicon hydrophobized surface immersed in water is predominantly driven by the direct water binding.[12] In the absence of ions, the local electric field in an interfacial region is a manifestation of the distribution of the surface polar residues. For the simplest electrostatic description of silicon hydration, it is consequently enough to consider the coupling between the interfacial charges and the corresponding polarization charges on the solvent molecules described here by the dielectric permittivity (ε_{int}). The phenomenological description of the in-

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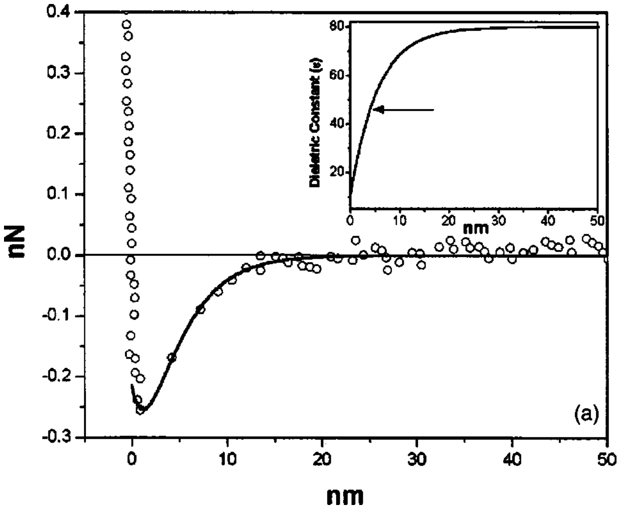

FIG. 1. Force vs separation curve measured after 15 min immersion of hydrophobic silicon surfaces in Milli-Q water. The full line indicates the curve calculated using Eq. (1). Inset: The full line corresponds to the dielectric permittivity spatial variation that results in the best fitting to the experimental points.

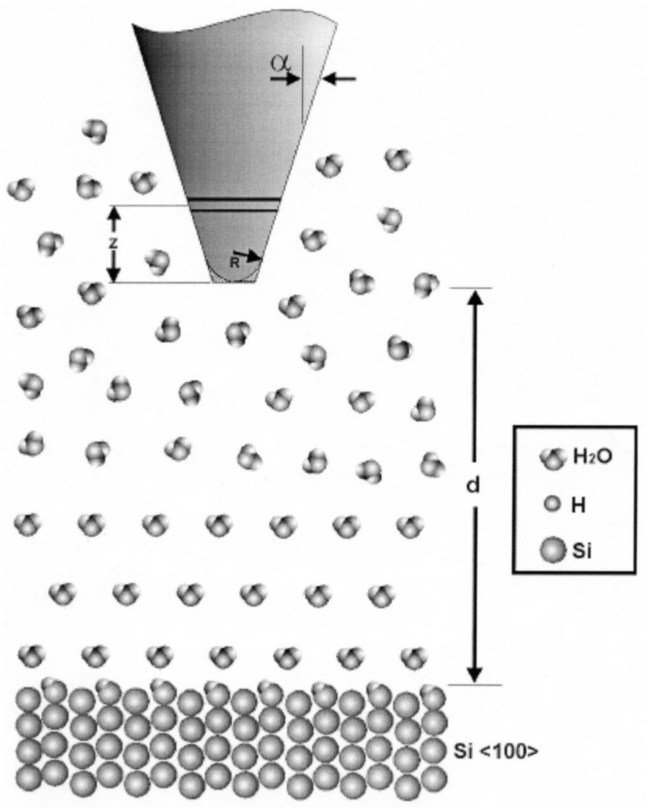

FIG. 3. Conical shaped tip with a cone angle α, a flat end with an area of πR^2 immersed in the polarization layer region, z is the integration variable of the elemental volume with a width Δz, and d is the distance between the surface and the end of the tip. The hydrophobic silicon surface is described using an idealized model of ordering of water. The first few layers of water molecules are highly ordered, while, at some distance from surface liquid has normal undisturbed bulk structure. Observe the difference in the lattice constant of the bulk structure and the one of the ordered layer.

terfacial region is as follows: the polarization charge at the interface results in an electric field E with an exponential decay length λ, i.e., $E(z)=E_0 e^{-(z/\lambda)}$ and the orientation of the water molecules are described by a spatially variable dielectric permittivity given by expression $\varepsilon_{\mathrm{int}}(z)=\varepsilon_{\mathrm{bulk}}-[\varepsilon_{\mathrm{bulk}}-\varepsilon(z=0)]\exp(-z/\lambda)$.

To estimate the size of the force acting on the tip, we assumed that the energy change involved in the immersion of the sharpened conical shaped tip inside the polarization layer is given by the product of the immersed tip volume times the dielectric permittivity variation and times the square of the electric field vector. The tip was defined to have a sharpened conical shape with one flat end with an area of πR^2 (see Fig. 3). The elemental volume (dv) of the sharpened conical tip immersed in the interaction region is given by $dv=\pi[R+(\tan\alpha)z]^2 dz$, where z is the integration variable of the conical volume and d is the distance between the surface and the end of the tip. The change in the electric energy involved in the exchange of the dielectric permittivity of the polarization layer by that of the tip is calculated by integrating the energy expression over the tip immersed volume in the polarization layer region. The force is obtained by the gradient of the energy expression, i.e., $F_z=-(\partial/\partial z)\Delta W$, where

$$\Delta W=\frac{1}{2}\int_0^{10\lambda-d}(\varepsilon_{\mathrm{tip}}-\varepsilon_{\mathrm{int}})E^2\varepsilon_0\pi[R+(\tan\alpha)z]^2 dz. \tag{1}$$

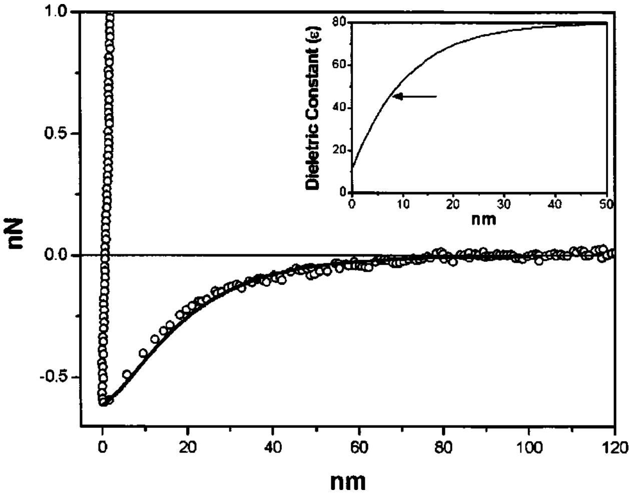

FIG. 2. Force vs separation curve for CTAB monolayer covering mica surfaces. The full line indicates the curve calculated using Eq. (1). Inset: The full line corresponds to the dielectric permittivity spatial variation that results in the best fitting to the experimental points.

We fitted experimental curves by adjusting the parameters $E(z=0)$, $\varepsilon(z=0)$ and λ in Eq. (1). The results are shown in Table I.

The hydrophobic silicon surface can be described at the molecular level as follows: The silicon (100) surface is covered by hydrogen atoms. Due to the difference in the electroaffinity of the H atoms (0.754 eV) and the Si atoms (1.385 eV) an interfacial charge delocalization is created. Simultaneously water molecules are ordered by the hydrophobic surface due to the geometric constraints of the surface[13] resulting in a region with a larger aligned molecular distribution than in the bulk and described in this work by a spatially variable dielectric permittivity with a measured value of ≈11 at the interface $(d=0)$ and increasing to ~80 in the bulk, as shown in the inset of Fig. 1. If, arbitrarily, we assume the polarization layer width [indicated by → in the inset of Figs. 1 and 2] to be the one corresponding to half the

TABLE I. Measured parameters of the polarization and the double layer.

Surface	Exponential decay length (nm) Average	Interfacial electric field E (V/cm) (polarization layer) ($\times 10^6$) Average	Polarization layer width (nm)	ε at the interface Average
Hydrophobized silicon	7	1.7	4	~11
CTAB monolayer covering mica	32	1.0	8	~11

amplitude variation of the dielectric-permittivity in the inset of Fig. 1 we obtain for the polarization layer width of hydrophobic silicon surfaces in Milli-Q water ~4 nm.

The good agreement obtained in the fitting of Eq. (1) to the experimental curves, shown in Fig. 2, is an indication that the attractive hydrophobic force behavior can be associated with the gradient of the electrostatic energy variation involved in the exchange of a volume of the interfacial region with a dielectric permittivity (ε_{int}) by the tip with a dielectric permittivity (ε_{tip}) (see inset of Figs. 1 and 2).

In the case of a hydrophobic mica substrate prepared by surface coverage with a monolayer of tightly packed alkyl chains (CTA^+ ions) water molecules appear to form a tight packed arrangement resulting in an aligned hydrogen bonding network presence at larger distances from the interface (~8 nm) than the one measured for hydrophobic silicon surfaces (~4 nm).

By comparing the ordered layer thickness of CTAB monolayers and silicon surfaces it is possible to define different degrees of hydrophobicity that previously could not be quantified by contact angle measurements since both surfaces show a contact angle close to 90°; in this work an electric field intensity at the water/solid interface and the dielectric permittivity profiles [see inset of Figs. 1 and 3] are determined.

In conclusion we report AFM measurements made on two hydrophobic interfaces. One was a water-mica interface, where mica was rendered hydrophobic by a monolayer coating of surfactant (CTAB) and the other was a water-silicon interface rendered hydrophobic by the immersion of silicon in HF solutions. In both cases, the hydrophobic interaction was characterized by the appearance of a attractive force as the tip approaches the interface and this force was modeled by the dielectric exchange force. The force versus distance curves measured for these two interfaces, fitted to the dielectric exchange force expression [Eq. (1)] determine the interfacial dielectric permittivity profiles. This profile is associated with the interfacial water structure. The water molecules against the solid wall of surfactant appeared to be more bond-ordered since the measured polarization layer width is ~8 nm for CTAB covering surface and ~4 nm for hydrophobic silicon surfaces.

The authors are grateful to J. R. Castro and L. O. Bonugli for technical assistance and acknowledge economical support from CNPq Grant Nos. 523.268/95-5 and FAPESP 98/14769-2.

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