

Chemical Force Microscopy: Probing and Imaging Interactions Between Functional Groups

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Adhesion and friction forces between surfaces with pre-determined terminal groups were measured by chemically modified scanning probe microscopy tips. Surfaces composed of various terminal groups (CH_3 , NH_2 , and SO_3H) were obtained by direct chemisorption of silane based compounds on silicon/silicon nitrides. Work of adhesion and friction coefficients were obtained for different types of modified tips and surfaces in aqueous solutions with variations in pH. Absolute values of work of adhesion between various surfaces, W_{ad} , are in the range of 0.5 to 8 mJ/m². Friction properties vary with pH in a register with adhesive forces showing a broad maximum at intermediate pH values. This behavior can be understood by considering changes in surface charge state which is determined by the zwitterionic nature of silicon nitride surfaces with multiple isoelectric points.

Recently, "chemical force microscopy" (CFM) has been introduced as a new scanning probe microscopy (SPM) mode (1-8). This technique allows discrimination of local surface forces related to intermolecular interactions of different chemical groups with nanometer resolution. CFM involves a chemical modification of the SPM tip by fabricating a robust molecular layer firmly tethered to the tip's surface. The most widely implemented approach in this field uses self-assembly monolayers (SAMs) from thiol molecules on gold (9, 10). Presently, several examples of modified tips with surface CH_3 , COOH , CH_2OH , CO_2CH_3 , CH_2Br , and NH_2 groups have been demonstrated. "Nanotitration" data were obtained by CFM for different functional surfaces (5, 10). The acid-base behavior of the modified SPM tips is controlled by the nature of the surface terminal groups and can show dramatic changes in the vicinity of isoelectric points. The exhibited

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friction behavior closely follows variations in adhesive properties. It has been demonstrated that this characteristic can be exploited to identify different microphases on multicomponent surfaces with nanoscale resolution (6-10).

Presently, we discuss the fabrication of SPM nanoprobe applied directly via silane-based modification of the silicon nitride and silicon materials. We will present our results on adhesive interactions and friction forces between chemically modified surfaces (SAMs with different terminal groups) in various aqueous environments.

Experimental

Chemisorption of silane-based molecules with various functional terminal groups is used to modify surface properties of silicon and silicon nitride SPM tips as described previously (12). All titration curves (adhesive forces versus pH) are obtained by variation of pH from 2 to 10. The results are averaged over a total set of 50 - 100 curves. Pull-off forces are determined from the cantilever deflection in a retraction mode. To study frictional properties of the film surfaces, a cross-section of surface topography and variation of torsional deflection (a friction loop) are detected simultaneously according to the well established protocol (13, 14). Calibration plots (15) are used to determine normal spring constants, $k_n = 0.235$ N/m, and torsional (lateral) constant, $k_t = 115$ N/m for short, narrow leg V-shaped DI cantilevers used in this study.

Results and discussion

Adhesive forces in aqueous solution. An example of SPM force-distance curves that demonstrates significant variation of adhesive forces (designated as ΔF) for different tip-surface pairs is presented in Figure 1a for modified silicon nitride and silicon surfaces. Strong adhesion is observed for both unmodified tip-surface pairs and NH_2 terminated SAMs. Both SO_3H and CH_3 terminated pairs of tip - substrate possess much smaller adhesive forces. Adhesive forces, ΔF , are in the range of 0.1 to 8 nN for different pairs of modified tips and substrate surfaces. For further comparison, work of adhesion for separating the surfaces and the SPM tip, W_{ad} , is evaluated using the JKR relationship: $W_{ad} = \Delta F/1.5\pi R_c$ (16). Absolute values of W_{ad} are in the range of 0.5 mJ/m^2 to 8 mJ/m^2 at pH = 6 (Figure 2).

Liquid-solid surface energies, γ_{ls} , can be estimated from work of adhesion for symmetrical surfaces according to the known relationship: $W_{ad} = 2\gamma_{ls}$ (17). Absolute values of surface energies for different surfaces in water are substantially (several times) lower than the solid-vapor surface energies, γ_{sv} , for similar surfaces. The γ_{sv} values are in the range of 20 mJ/m^2 (CH_3 SAMs) to 50 mJ/m^2 (NH_2 SAMs) (17). Using the Hamaker constants, A , for different surfaces separated by various media calculated in Ref. 18 and the relationship $\gamma \sim 0.45 \cdot 10^{21} \times A$ (17), the reduction of surface energies at solid-liquid interface by 2 - 8 times can be justified.

Adhesive forces at different pHs. Examples of force-distance curves for the same interacting surfaces (symmetrical NH_2 - NH_2 terminated SAMs) at different pHs are shown in Figure 1b. Strong adhesion is observed at intermediate pH (see examples for pH = 5, 7). At very acidic and basic pH conditions, adhesion becomes very

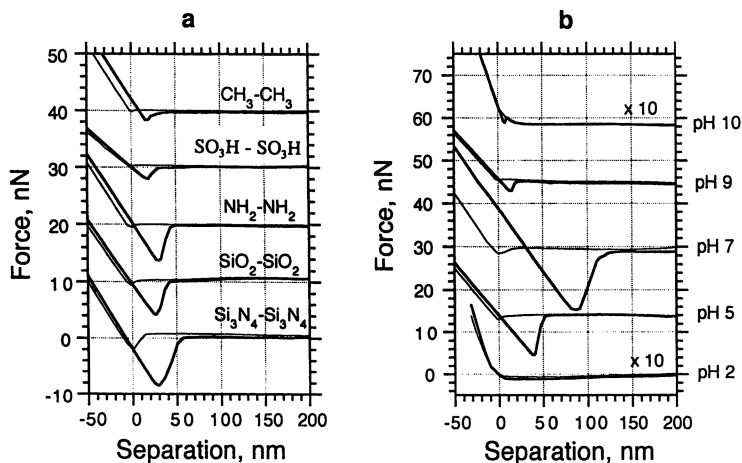


Figure 1. Force-distance curves for five different symmetrical tip-surface pairs in aqueous solution at neutral conditions, pH = 6 (a) and for NH_2 terminated surfaces at different pHs (b). The curves offset along the vertical axis to avoid overlapping. Thin solid lines represents the approaching mode and thick solid line is the retracing mode.

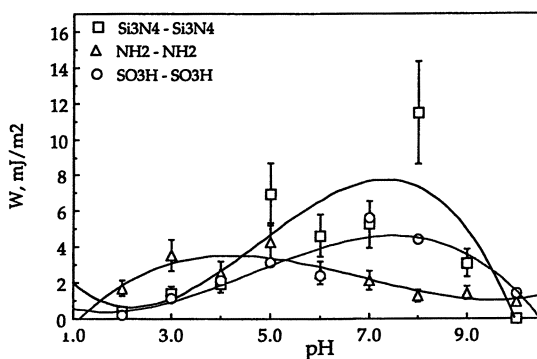


Figure 2. Variations of work of adhesion, W_{ad} , for $\text{Si}_3\text{N}_4\text{-Si}_3\text{N}_4$, $\text{NH}_2\text{-NH}_2$, and $\text{SO}_3\text{H-SO}_3\text{H}$ surfaces versus pH.

minute (see data for pH = 2 and 10 in Figure 1b, note that the force scale is magnified by 10 times).

Adhesion behavior of bare silicon nitride, NH, and SO₃H modified surfaces studied at different pH conditions is shown for symmetrical surface pairs (Figures 2). For silicon nitride tip - silicon nitride substrate, W_{ad} (pH) is a non-monotonic function with minima at 2 and 10 (the lowest level of adhesion forces detected here is close to 0.03 nN). A broad maximum of 7 - 8 mJ/m² is observed in the pH range from 7 to 8. Adhesion energy between SO₃H terminated surfaces reduces to 4 - 5 mJ/m². Amine terminated modification also results in lowering of adhesion energy. Maximum adhesion is shifted to the acid range (pH = 4) for amine terminated tip - substrate pair and a broad plateau of very low energy (~ 1 mJ/m²) is observed in the pH ranging from 7 to 10 (Figure 2).

The observed pH behavior of the silicon nitride - silicon nitride pair correlates with electrochemical surface properties of these materials.¹⁸⁻²⁰ Non-monotonic variation of adhesive forces can be qualitatively explained by interplay of electrostatic and van der Waals forces between the surfaces by considering the presence of multiple isoelectric points with different pKs on interacting surfaces (17, 21). Expected behavior for two interacting surfaces with two different expected pKs within the framework of a double-layer theory is presented in Figure 3a. The total balance of electrostatic forces acting between surfaces can be understood by taking into account complex chemical composition of silicon nitride surfaces.

Silicon nitride tip surfaces in water are, in fact, composed of relatively thin silicon oxide layers (SiO₂ bonds, pK = 2 - 3), silanol groups (SiOH, pK ~ 6), and silylamine groups (SiNH, SiNH₂, pK = 10 - 11) (18, 22). In addition, a partial dissolution of the substrate and tribochemical reactions can take place during shearing contact at high pH with the formation of silicic acid (Si(OH)₄, pK = 9.8) (23). Studies of various silicon nitrides showed a wide range of isoelectric points from 3 to 9 depending upon composition. Such zwitterionic behavior is caused by variation of acid-base equilibrium for such multicomponent surfaces.

An illustration of combined electrostatic and van der Waals interactions at different pHs is presented in Figure 4. Tip-surface interactions at various pHs can be rationalized as follows: at very low pH, the silicon nitride surfaces bear strong *positive charges* due to ionization of both silanol and silylamine groups that compensates for strong van der Waals forces within the contact area and results in repulsive behavior at small separation (Figure 3). Gradual decrease of surface group ionization at higher pH results in increase the role of van der Waals attraction due to diminishing electrostatic contribution. Within the pH range of 6 - 8, surfaces are essentially *neutral* which should result in maximum adhesion caused by non-compensated van der Waals forces. Further pH increase causes gradual decrease of adhesive forces because of additional repulsive contribution between *negatively charged* silicon nitride surfaces. At pH higher 8.5, increased repulsion between highly negatively charged surfaces results in decreasing net adhesion.

For silicon nitride surfaces, we observe a very broad maximum in pH ranging from 7 to 8 that indicates a minor shift of the acid-base balance towards larger contribution of the basic groups. This difference apparently is caused by excess amine groups in surface composition of the SPM tip. A minute percentage increase in basic amine groups on a surface can shift pK of silicon nitrides by several pH units. Using the results obtained through theoretical calculations in Ref. 18, an estimate of the silicon nitride surface composition of up to 35 - 40% of silylamine groups (SiNH and SiNH₂) and 60 - 65% of silanol groups (SiOH) can be made.

Coverage of silicon nitride surfaces with a thin molecular layer bearing acid terminal groups leads to a shift of W_{ad} (pH) maximum to higher pH (Figure 2). Replacement of Si-OH groups with SO₃H terminal groups (expected pK is in the range 1 to 2) does not significantly change the overall acid-base balance of

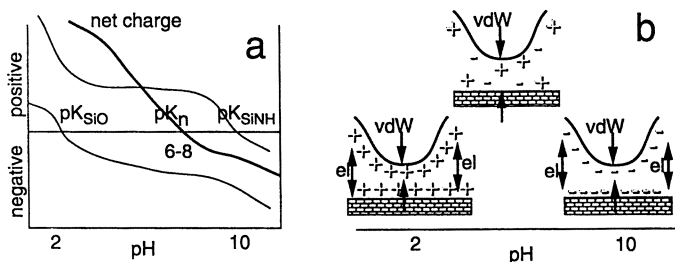


Figure 3. Surface potential variation for silicon nitride tip-surface pair studied in this work (a), and a scheme of tip-surface pairs with different surface charge distribution and force balance at different pH (b).

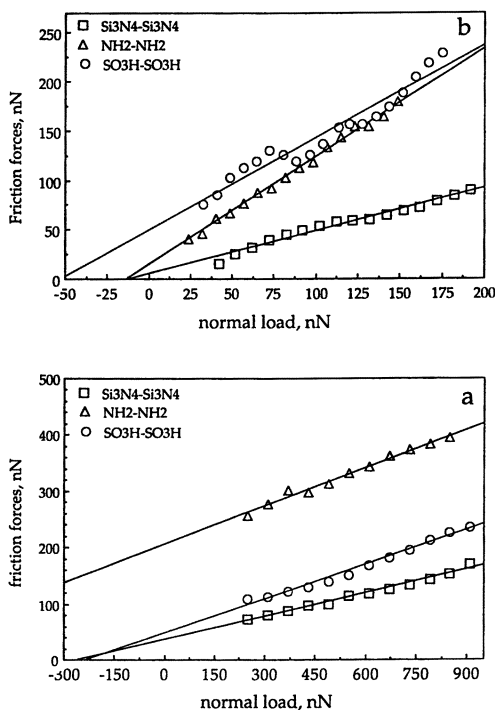


Figure 4. Loading curves (friction forces versus normal spring load) and their linear fits for different mating pairs in air (a) and in aqueous solution at normal conditions (b).

intermolecular interactions for multicomponent surfaces of silicon nitrides. Amine termination significantly modifies the force behavior of silicon nitride surfaces. The maximum adhesive interactions between NH_2 - NH_2 terminated SAMs is observed at $\text{pH} = 4$. This change cannot be explained by variation of ionized state of the modified surfaces alone. In fact, if we accept usual value $\text{pK} = 7 - 9$ for amine groups (24), we can expect the maximum force range to be shifted to higher pH . A reasonable explanation of the observed adhesive maximum at low pH can be a significant shift of pK for amine groups confined by SAM surface. Actual pK values for amine terminated SAMs can be 3 - 5 units pH lower, due to the difficulty of forming charged state at constrained SAM surfaces (24). Substantial decrease of adhesive forces between modified surfaces at high pH can be related to ongoing tribochemical reaction into the contact area that results in the formation of silicic acid $\text{Si}(\text{OH})_4$ surface groups.

Friction behavior of modified surfaces. Loading curves F_f (F_n) (friction versus normal load) for silicon nitride surfaces and two modified surfaces at neutral conditions in aqueous solution and in air are shown in Figure 4 along with linear regression analysis. General frictional behavior of the surfaces studied here is very similar to earlier reports for modified surfaces (5-10) revealing the generalized Amontons law:

$$F_f = f_0 + \mu F_n$$

where μ is a friction coefficient defined as $\mu = \partial F_f / \partial F_n$ and F_0 is "residual force" (i. e., normal force not accounted in a spring normal load) (25-27). "Residual" force, F_0 , is related to adhesion between mating surfaces and can be thought as amount of "negative" spring forces to be applied to overcome this attraction. The value of F_0 usually correlates but is not equal to adhesion forces obtained from approaching-retracing cycles. Values of residual forces, F_0 , determined from intersection of corresponding linear fits with the horizontal axes (Figure 4) are much higher in air (200 - 600 nN) than in aqueous solution (10 - 50 nN) which is related to the overwhelming contribution of capillary forces in humid air.

Friction coefficients for identical surfaces in aqueous solutions vary in a wide range from 0.3 for silicon nitrides in the basic range to 2.3 for SO_3H terminated SAMs in the acidic range (Figure 5). Friction coefficient is in the range 1.0 - 1.6 for amine surfaces if measured in the acidic range. These values are within the parameters reported for thiol SAMs with similar terminal groups (10). Absolute values of friction coefficients for SAMs are very high when compared to standard values reported for organic surfaces from macroscopic measurements (28). Friction coefficients for all surfaces studied in humid air (estimated humidity was about 30%) are significantly lower with typical values being 0.14 for silicon nitrides and 0.23 for NH_2 terminated surfaces (26). On the other hand, friction coefficient for any of NH_2 - NH_2 and SO_3H - SO_3H surfaces is substantially higher than for silicon nitride - SAMs pairs and other SAMs studied previously (27). This is due to strong intermolecular interactions (e. g., hydrogen bonding) between these chemical groups and high shear strength of short-chain monolayers.

pH variation of aqueous solution results in significant changes of both F_0 and μ for all mating surfaces. Friction coefficients possess maxima at intermediate values of pH for all mating surfaces studied (Figure 6). For bare silicon nitride surfaces, friction coefficient of 0.2 - 0.4 is the lowest at $\text{pH} = 2$ and 10 and a maximum of 0.5 is reached within 6 - 7 range (Figure 5).

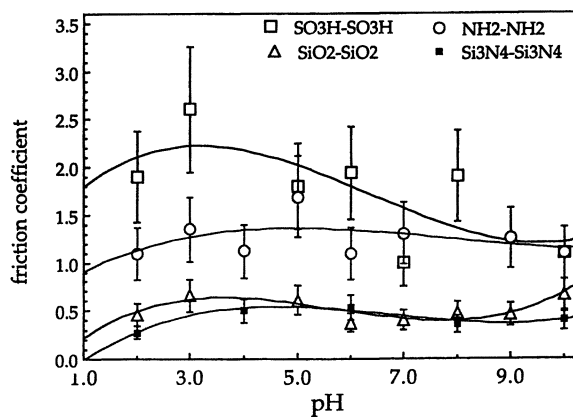


Figure 5. Variation of friction coefficient versus pH for silicon-silicon, Si₃N₄ - Si₃N₄, NH₂ - NH₂, and SO₃H - SO₃H tip-substrate pairs.

Conclusions

Functional alkylsilane SAMs were used to modify surfaces of silicon nitride and silicon SPM tips. Adhesive and friction forces between CH_3 , NH_2 , and SO_3H terminated surfaces were investigated at different environments by SPM technique.

We measured work of adhesion, effective residual forces, and friction coefficients for different chemically modified SPM tips and surfaces in air, neutral water, and aqueous solutions with pH ranging from 2 to 10. Absolute values of work of adhesion between these surfaces, W_{ad} , are in the range 0.5 to 8 mJ/m^2 at normal conditions. Maximum adhesive forces revealed at intermediate pHs are due to a predominant role of van der Waals interaction between essentially neutral surfaces with balanced charges of acidic and basic terminal groups on the zwitterionic silicon nitride surfaces. The silicon nitride surfaces possess complex composition with approximately 2 : 1 ratio of silanol (SiOH) and silylamine (SiNH and SiNH_2) groups.

Absolute values of the friction coefficient in aqueous solution vary in a wide range from 0.2 for silicon nitride-silicon nitride mating pair at low pH to 2.3 for SO_3H surfaces at intermediate pH. The friction properties vary in a register with adhesive behavior showing a broad maximum at intermediate pH values for silicon nitride - silicon nitride pair. This maximum is shifted from the intermediate position for NH_2 and SO_3H terminated SAMs

Acknowledgments

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