Force titration of amino group-terminated self-assembled monolayers using chemical force microscopy

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Abstract.

Chemical force microscopy (CFM) was used to measure the adhesion force between an Au-coated Si_3N_4 tip functionalized with OH groups and a silicon substrate functionalized with NH_2 groups. The curve of the adhesion force as a function of the solution pH value (force titration curve) was obtained. The $pK_{1/2}$ of surface NH_2 groups estimated from the force titration curve is 7.4, about 3 pK units lower than the pK value of NH_2 functionality in aqueous solution, and in nice agreement with the value of $pK_{1/2} = 7.6$ determined by conventional contact angle titration. The surface $pK_{1/2}$ value that we obtained from the force titration or contact angle titration is the apparent surface pK value, which is expressed as the corresponding bulk solution pH value at which the functional groups at the interface are half-ionized.

Chemical force microscopy (CFM) [1], which uses a chemically modified tip as the force probe, is a new variant of atomic force microscopy (AFM) [2]. By CFM, one can investigate the intermolecular interactions on a nanometer scale and map a chemically inhomogeneous surface. It has demonstrated great capabilities in chemical specification and identification. Force titration, a new titration concept recently proposed by the present authors [3, 4] and independently by Lieber and co-workers [5], is a novel use of CFM for characterizing the dissociation properties of surface functional groups such as COOH and NH_2 etc. We have studied COOH-terminated self-assembled monolayers (SAMs) on gold by using this force titration technique, and obtained the surface $pK_{1/2}$ value of COOH groups [3, 4]. Herein, comparative studies using both force and contact angle titrations are conducted on the basic group terminated SAMs on silicon. Special attention has been paid to pretreating the silicon substrate and fabricating high-quality SAMs on the silicon surface.

1 Experimental

11-Mercaptoundecanol was synthesized and purified in our laboratory. (3-Aminopropyl) triethoxysilane (hereafter, APTES) and other reagents were of analytical grade and were used as received. Ultrapure water with a resistivity of above 16.8 MΩ • cm was used throughout the experiments. The ionic strength of the phosphate buffer solution was maintained at 0.01 M.

The silicon wafers used were n-type Si single crystals of (111) orientation, with a resistivity in the range 0.01–0.015 Ω • cm. After ultrasonicated in trichloroethene, acetone, and water, the silicon wafer was treated by the following procedure: (1) oxidation in $H_2SO_4 : H_2O_2$ (V : V = 4 : 1) at 80 °C for 10 min; (2) etching in buffered HF solution (V(49%HF) : V(40%NH_4F) = 1 : 7) for 60 s; (3) oxidation in $NH_3 : H_2O_2 : H_2O$ (V : V : V = 1 : 1 : 5) at 80 °C for 10 min; (4) oxidation in $HCl : H_2O_2 : H_2O$ (V : V : V = 1 : 1 : 6) at 80 °C for 10 min. Finally, the wafer was thoroughly rinsed with water and dried in a stream of high-purity Ar. Vapor-phase deposition [6] was performed by suspending the SiO_2/Si substrate above a refluxing ~ 8%(V/V) APTES/xylene solution in a glass sample chamber fitted with a condenser for 4 h. The SAMs-modified silicon substrate was then rinsed with ethanol, dried in a stream of high-purity Ar, and finally cured at 120 °C for 30 min.

A commercial Si_3N_4 tip (Digital Instruments (DI), Santa Barbara, CA) was sputter-coated sequentially with a 10 nm Ti adhesion layer and a 100 nm Au layer. The spring constant of this modified tip-cantilever was calibrated using the method described in [7]. The Au-coated tip was then immersed into 1 mM HS $(CH_2)_{11}OH$ ethanol solution for 24 h. Before use, the OH SAMs-modified tip was rinsed in ethanol and then in ultrapure water, and then dried with high-purity Ar gas sequentially. Adhesion measurements were conducted with a Nanoscope E System equipped with a fluid cell (DI). Contact angle measurements were carried out with a JJC-2 goniometer (No. 5 Optical Instrument Factory of Changchun, China).

2 Results and discussion

(3-Aminopropyl) triethoxysilane forms a monolayer on the silicon surface via Si–O linkage [6]. The key point for producing a high-quality monomeric monolayer on silicon is to avoid the self-polymerization that often occurs with the silanization treatment. We employed a vapor-phase deposition method in this work: the APTES/xylene solution was refluxed in a glass chamber fitted with a condenser, and the silicon substrate was suspended in the vapor phase above the solution. By finely controlling the heating temperature and the sample location, a monomeric monolayer of APTES was deposited on the silicon surface. An AFM image of the APTES-modified SiO_2/ Si(111) surface is shown in Fig. 1. The surface is uniform in most areas and the rms value for the 1 μm x 1 μm scanned area is only 0.247 nm. We did not find any polymeric features in the scanned areas [8], which demonstrates the formation of a monomeric self-assembled monolayer of APTES on silicon.

The adhesive interaction between the OH-terminated tip and the NH_2-terminated silicon sample was measured in a fluid cell filled with phosphate buffer solution. The force curve, which represents the variation of the tip-cantilever deflection, which is equivalent to a force and can be inter-convertable using the tip-cantilever spring constant, was first measured as the sample approached, contacted, and separated from the tip. The point at which the sample separates from the tip is called the pull-off point. The pull-off force at the pull-off point corresponds to the adhesion force between the tip and the sample. To ensure that comparable data were obtained from different pH solutions, one tip was used throughout one set of force titration experiments. Typical force curves obtained using different pH solutions are shown in Fig. 2. By plotting the adhesion force versus the pH value, we obtained the force titration curve of NH_2-terminated SAMs on silicon as shown in Fig. 3a, in which each data point was a statistical average of more than 400 individual adhesive force measurements, using a Gaussian fit [1b]. Obviously, the adhesion force nearly dropped to zero at $pH < 6$, indicating a repulsive tip-sample interaction after the sample surface was positively charged; or, in other words, the surface amino groups were protonated. In fact, such repulsive interactions have been clearly observed in the force curves when the sample was gradually approaching the probe tip at $pH < 7.1$: this may originate from the long-range electrostatic interaction between the electrically charged surface and the tip (overlapping of two double layers) [5]. A sharp increase in the adhesion force occurred from pH 6, and for a fully deprotonated state of surface NH_2 groups it reaches a maximum, as seen in the alkaline region of the force titration curve. The adhesive force here may arise from the Van der Waals interaction between neutral NH_2 and OH groups. At $pH > 8.0$, a similarly attractive interaction was observed in the force curves when the sample–tip distance was gradually decreased. From Fig. 3a, we estimated the $pK_{1/2}$ value to be 7.4, about 3 pK units lower than the bulk solution value ($pK = 10.6$) [9], which is characteristic of surface amino groups.

For comparison, we also titrated the NH_2-terminated silicon surface by a contact angle measurement, which is widely used as a simple approach to determining the surface functional group pK value [10]. The results of the contact angle measurement are given in Fig. 3b, in which four independent measurements were conducted for each pH value to obtain the average contact angle. From the contact angle titration curve, we know that the protonation of NH_2 groups brought about an increase in the surface wettability, as expected. The $pK_{1/2}$ value thus estimated was 7.6, which is nicely consistent with the force titration result. It should be pointed out that the change in the contact angle throughout the pH range examined was only 12° for the surface amino groups, which apparently leads to a large error in determining the $pK_{1/2}$ value, as seen from Fig. 3b. In contrast, the remarkable change in the adhesion force in Fig. 3a allows a precise evaluation of the surface $pK_{1/2}$ value.

We noted that the quality of the amino monolayer on the silicon strongly affects both the force and the contact angle titration results. Actually, it is not an easy task to prepare a perfect and reproducible self-assembled monolayer on a silicon surface by silanization. With our modified silanization procedure and experimental know-how, a relatively reproducible APTES monolayer has been produced on the silicon substrate. Occasionally, we have also obtained a very small $pK_{1/2}$ value for surface amino groups, as Lieber and co-workers have reported (see [5]). As they explained, the extremely small $pK_{1/2}$ value arises from the disordered SAM structure which exposes methylene groups at the surface, and thus does not truly reflect the intrinsic dissociation property of surface amino groups [5].

In summary, we have titrated the NH_2-terminated self-assembled monolayer on a silicon surface by the force titration technique and obtained the $pK_{1/2}$ value of the surface amino group to be $pK_{1/2} = 7.4$, which is consistent with the contact angle titration result of $pK_{1/2} = 7.6$. The force titration curve is also a sensitive measure of the assembling quality of molecules on the substrate surface.

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List of Figures

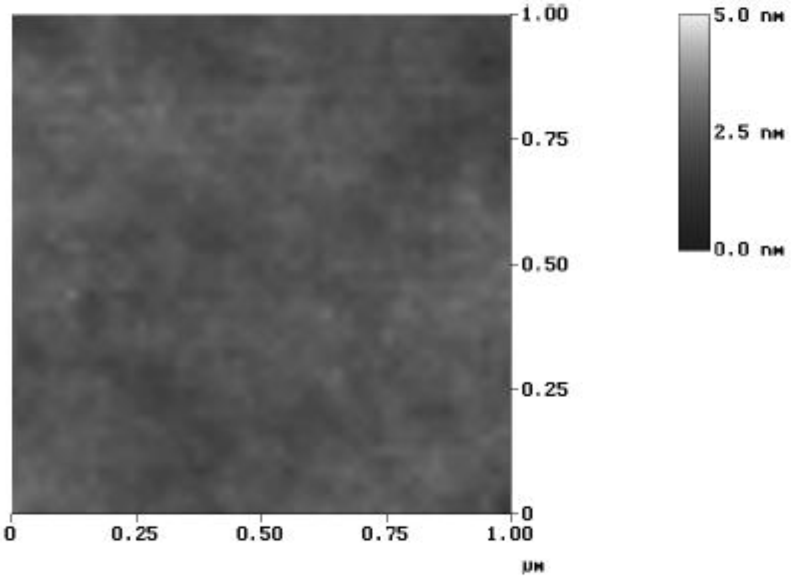


Fig.1.

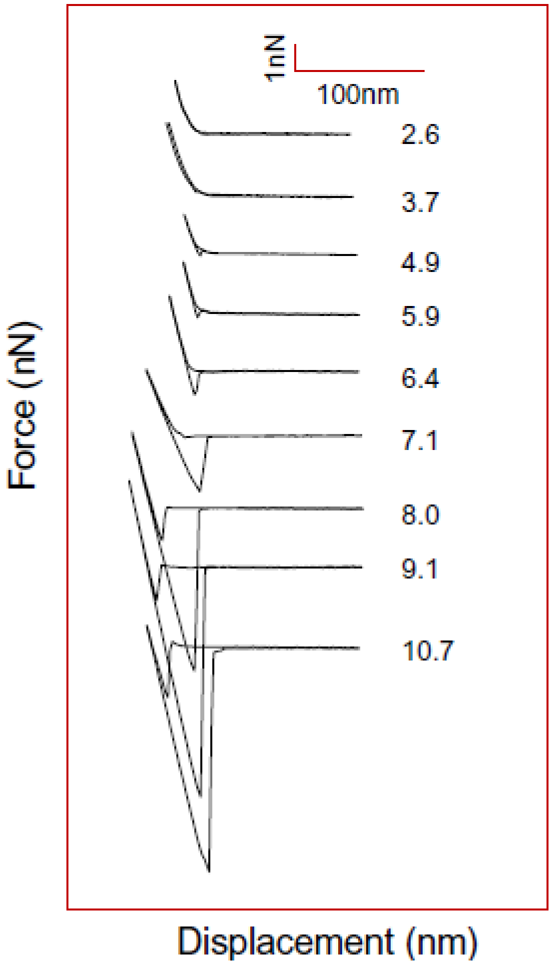
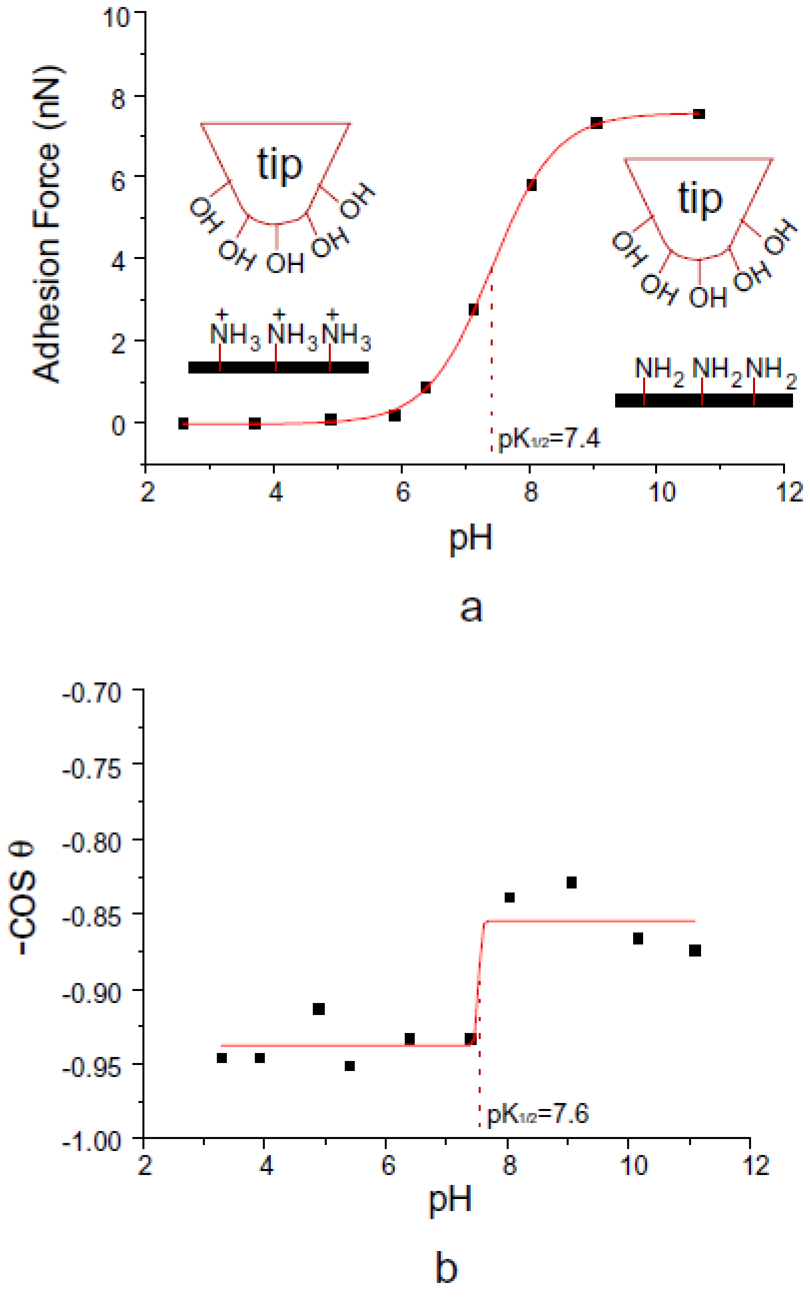


Fig.2.


Adhesion Force (nN)
10
8
6
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2
0
2
4
6
8
10
12
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OH
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OH
$\overset{+}{N}H_3$ $\overset{+}{N}H_3$ $\overset{+}{N}H_3$
tip
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OH
OH
NH_2 NH_2 NH_2
$pK_{1/2}$=7.4
a
-COS θ
-0.70
-0.75
-0.80
-0.85
-0.90
-0.95
-1.00
2
4
6
8
10
12
pH
$pK_{1/2}$=7.6
b

Fig.3.