

Superb Mechanical Stability of n-Octadecyltriethoxysilane Monolayer Due to Direct Chemical Bonds between Silane Headgroups and Mica Surface: Part II

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Abstract

It is still controversial where the improved stability of n-octadecyltriethoxysilane self-assembled monolayer (OTE SAM) on plasma-pretreated mica surface exactly originates from. To date, it has been well known that the extensive cross-polymerization between silane headgroups is a crucial factor for the outstanding mechanical strength of the monolayer. However, this study directly observed that the stability comes not only from the cross-links but also, far more importantly, from the direct chemical bonds between silane headgroups and mica surface. To observe this phenomenon, n-octadecyltrichlorosilane monolayers were self-assembled on both untreated and plasma treated mica surfaces, and their adhesion properties at various stress conditions and force profiles in pure water were investigated and compared through the use of the surface forces apparatus technique. It revealed that, in pure water, there is a substantial difference of stability between untreated and plasma treated cases and the plasma treated surface is mechanically much more stable. In particular, the protrusion behavior of the monolayer during contact repetition experiment was always observed in the untreated case, but never in the plasma treated case. It directly demonstrates that the extensive chemical bonds indeed exist between silane head-groups and plasma treated mica surface and dramatically improve the mechanical stability of the OTE monolayer-coated mica substrate.

Key words : Self-assembled monolayer, N-octadecyltriethoxysilane, Plasma treatment, Mica

1. Introduction

Over the past decade, there has been active interest in depositing alkylsilane SAMs on mica^[1-8] because it can be prepared as molecularly smooth and broadly step free sheets. Therefore, such perfectly crystalline surface would be an ideal base substrate for very fine coating and patterning of alkylsilane monolayer on surfaces where the ultra-miniaturized integration is indispensable. However, since the mica surface does not contain any inherent functional groups such as hydroxyl groups, the preparation of a covalently linked silane headgroups on mica is not straightforward. Kim et al.^[9-12] recently reported that an n-octadecyltriethoxysilane self-assembled monolayer (OTE SAM) could be firmly anchored to plasma-treated mica surface most likely through covalent bonding. So the authors proposed that the OTE-

SAM or other hydrocarbon silane monolayers on plasma treated mica could be a potential base substrate for the construction of nano-structured electronic devices such as NEMS (nanoelectromechanical system).

Some previous works^[9-10] on OTE SAM also showed that at high enough relative humidities water vapor condenses on the OTE monolayer regardless of surface pre-treatment even though the amount of water adsorbed by the OTE monolayer on untreated mica surface is always greater than on plasma-treated mica. Tian et al.^[7] reported that as the humidity increases, despite the hydrophobicity of OTE, water molecules condense on the monolayer. Xiao et al.^[6] studied OTE SAMs on untreated mica and used AFM to show that monolayers with the highest contact angles were actually covered with polymerized OTE aggregates and the highest quality monolayers had contact angles of only ~ 40°. Static water contact angles measured by Kim et al.^[10] were 61° and 72° for the untreated and plasma treated cases respectively. On the contrary, the compressibility measurements of the OTE films also conducted by Kim et al. indicated that the monolayer film is in a crystalline-

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(Received : May 24, 2010, Revised : June 21, 2010, Accepted : June 24, 2010)

like phase.^[12] Based on these mixed results, the authors concluded somewhat heterogeneous phase state of OTE-SAM, i.e., the monolayer is composed of highly packed crystalline OTE domains and interspersed tiny gaseous regions. On the other side, this conclusion also gives rise to an inevitable question as to whether the surface coverage of monolayer is always a satisfactory measure of film quality. Undoubtedly, better covered the monolayer is better quality the film has. However, it does not necessarily mean the fully covered monolayer is always stable and useful. Rather, less than perfectly covered but very stable monolayer would be much more advantageous than fully covered but rather unstable (only physisorbed) monolayer for many real industrial applications. For example, for tenaciously immobilizing biological molecules on NEMS devices, if its base layer is very robust and stable particularly under water environment would be much more critical factor than if the monolayer coverage is good enough or not. If the base layer is not robust and stable enough, the fixed molecules would not stay there long. If so, at this stage, it is imperative to understand where the mechanical stability of OTE-SAM on plasma treated mica exactly originates from. Therefore, in order to elucidate this issue, it is necessary to carefully investigate and compare interfacial properties such as adhesion and force profiles of untreated and plasma treated OTE SAMs since it may provide in-depth information as to the mechanical stability of OTE SAMs on mica.

However, little quantitative research has been done on interfacial properties of OTE-SAMs on mica especially in various physical conditions while the water effect on the formation of alkylsilane monolayers have been actively studied.^[4,5,13] Considering that very stable nanostructured electronic devices must operate well in vastly different environments understanding how the alkylsilane monolayer behaves in various environments is crucial in order to construct a patterned monolayer that is satisfactorily stable in a physically harsh and wet environment. Therefore, in this study, we employed a surface forces apparatus (SFA) technique to estimate the effect of stress and water on the molecular structure and mechanical stability of OTE monolayers on untreated and plasma-treated mica. It directly demonstrated that the plasma pretreatment on mica surface dramatically improves the mechanical stability of OTE SAM and the superb stability exclusively originates from extensive

chemical bonds between OTE headgroups and plasma treated mica surface.

2. Materials and Methods

Details of OTE-SAM preparation and plasma treatment were described in the experimental section of the part I article.

The force measurements were carried out using a home-made Mark IV type SFA^[14,15] with two OTE coated, muscovite mica (plasma-treated or untreated) surfaces mounted as facing, crossed cylinders. The lower surface was mounted on either a flexible double cantilever spring [$k \sim 146 \text{ Nm}^{-1}$] or a stiff support [$k \sim 6.2 \times 10^3 \text{ Nm}^{-1}$] and the upper surface was mounted on a cylindrical piezoelectric crystal, the expansion of which controls the surface separation with an accuracy of 0.1 nm. Coarse surface separation was controlled directly with a dc motor on the translation stage attached to the lower surface, and fine control was achieved with the piezoelectric device attached to the upper surface. The mica which had been cleaved into molecularly flat sheets (1-5 μm thick) and then back silvered ($\sim 55 \text{ nm}$) was glued to cylindrically polished silica disks using an epoxy resin (Epon 1004, Shell Chemical Co.). The interferometer formed by the back-silvered surfaces transmits only certain discrete wavelengths that are passed through a diffraction grating and observed directly with an eyepiece as fringes of equal chromatic order (FECO) at the exit slit of the spectrometer. The fringes allow measurements of the surface separation and refractive index of the medium between the surfaces.^[14] Before the plasma treatment or OTE coating, the contact fringe positions of the untreated mica surfaces were recorded for reference. Typical contact radii of two OTE surfaces were 25-33 μm and the maximum resolution of the contact area measurement was $\sim 1 \mu\text{m}$. Also, the radius of curvature of undeformed surfaces was 1.5-2 cm. For force measurement, ultrapure water was heated under vacuum in order to remove dissolved air bubbles. The apparatus has an approximately 0.4 L volume capacity and was filled with the preheated water via a filling flask through the large inlet in the front plate. When the liquid level was within 1 cm of the lower disc, the apparatus was tilted $\sim 90^\circ$ and the filling continued. Tilting the apparatus minimized bubble and contaminant attachment on the hydrocarbon sur-

face. As soon as the filling was finished, the apparatus was focused using white light and the temperature was stabilized before starting the force measurements. Details of force measurement are extensively described elsewhere.

The adhesion or pull-off force was determined by bringing two OTE coated mica surfaces into contact under zero external load and then separating them by moving the remote end of the spring on which one of the surfaces was mounted. When the resulting force on this surface equals the pull-off force the surfaces jump apart and from the jump distance (measured from the fringes) and the spring constant the pull-off force (F_s) is calculated. Surface energy was also calculated from two independent force measurements in dry condition – JKR fitting of a^3 - F plot and pull off force measurement based on JKR theory where contact radius (a) and pull off force (F_s) are related to the surface energy (γ) by

$$a^3 = \frac{R}{K_B} [F + 6\pi\gamma R + (12\pi\gamma R F + (6\pi\gamma R)^2)^{1/2}] \quad (1)$$

and

$$F_s = 3\pi R \gamma \quad (2)$$

respectively. R , K_B and F are the radius of curvature of the surfaces, the bulk elastic modulus of monolayer system and the normal load applied to OTE films in that order.

3. Results and Discussion

3.1. Hydrophobicity of OTE-SAM

The force curves between plain OTE SAM surfaces were measured in pure water at 25°C. Figure 1 shows three different force curves for untreated (\square) and plasma treated (\circ, \bullet) cases. Open and closed circles denote the force curves at two different contact areas, respectively. From these curves, it is important to note that there is a clear difference between the long range interactions for untreated and plasma treated cases, respectively. The force measured between untreated OTE surfaces is weakly repulsive over a long-range distance as shown in Figure 1. It means the surface is weakly charged and a double layer force exists between the monolayers. It is quantitatively more evident. In fact, the force curve for untreated case deviates far from that predicted by classical DLVO theory. However, after

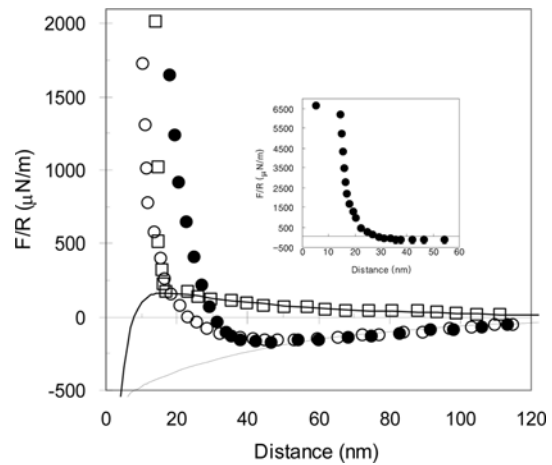


Fig. 1. Normalized force as a function of distance between OTE-SAM surfaces in pure water at 25°C. Square and circle denote for untreated and plasma treated cases, respectively. Both plots deviate far from classical DLVO theory. The solid lines are DLVO fits after the subtraction of exponential force law, $F/R = C \exp(-D/\lambda)$. The DLVO fits for both cases assumed a constant potential boundary condition and 0.8×10^{-20} J of Hamaker constant. For untreated case, the assumed surface potential and Debye length were 37 mV and 41.7 nm, respectively. Additional hydrophobic attraction was $F/R = 2.8 \text{ mN/m} \exp(-D/3 \text{ nm})$. For plasma treated case, additional hydrophobic attraction was $F/R = 0.6 \text{ mN/m} \exp(-D/45 \text{ nm})$.

the subtraction of an exponential hydrophobic force law, $F/R = C \exp(-D/\lambda)$, the plot was well predicted. The corresponding solid line in Figure 1 is the force calculated from DLVO theory with the additional exponential attraction. The DLVO fit assumed a constant potential boundary condition of 37 mV and Debye length of 42 nm. Hamaker constant used was 0.8×10^{-20} J, which is the value for typical hydrocarbon surfaces. The values of pre-exponential factor, C , and exponential decay length, λ , required to fit the data were 2.8 mN/m and 3 nm, respectively. Excellent fitting with the additional exponential hydrophobic attraction strongly indicates that the monolayer surface is fairly hydrophobic but charged due to defect sites on it. On the other hand, the plasma treated case shows a weak but noticeable long range attraction starting from ~ 150 nm. In this case as well, the curve did not fit well to classical DLVO theory. So the exponential hydrophobic attraction was added to the theory and it was fitted as a corresponding solid line in Figure 1, too. The same Hamaker constant

as above was assumed and the pre-exponential factor and decay length for the data were 0.6 mN/m and 45 nm, respectively. In an overall review on hydrophobic forces between hydrocarbon surfaces, Christenson and Claesson^[16] note that the decay lengths, λ in cases showing long-range hydrophobic attraction, vary between 5 and 50 nm. Thus, the decay length, 45 nm in plasma treated case, unlike 3 nm in untreated case, quantitatively warrants that the hydrophobicity of plasma treated OTE SAM surfaces is a long range. These suggest that the surface is nearly fully covered and its charge is almost neutral.

Campos et al.^[8,17] recently reported force curves between OTE monolayers deposited by LB technique on plasma treated mica surface in pure water. Very interestingly, our force curves at small separations (<20 nm) are very similar to the ones reported by Campos et al.^[8,17] The authors concluded that the repulsive barrier originates from nano-sized air bubbles formed on the monolayer surfaces. Air bubbles^[8,16-25] have been previously reported with many silylated hydrophobic surfaces similar to the ones studied here. In particular, from SFA force measurements of air bubble-formed OTE SAM surfaces, Campos et al.^[8,17] showed that the repulsive barrier generally occurs at the range of 10 to 20 nm and the force curves always features an inward jump into the soft contact after steep repulsion. Carambassis et al.^[22] also identified a highly repulsive region at small separations (<20 nm) from force measurements between silylated glass surfaces by using an atomic force microscope. The authors defined that the region is an enhanced hydrodynamic repulsion that arises from the increased drainage due to the displacement of water by the spreading bubbles. In the case of plasma treated OTE SAMs in this study, a steep repulsive barrier as well as a soft jump-in after the repulsion were identified and very similar to the results from references 8 and 17, i.e., two plasma treated OTE monolayer surfaces in water medium jumped in at 14 nm and 6.18 mN/m (inset of Figure 1). These strongly support that the strong and steep repulsive barriers measured from the OTE SAM surfaces on plasma treated mica substrates are caused by nano-sized air bubbles. In addition, in the plasma treated case, we visually observed a noticeably strong inward jump into a flat contact upon slow approaching of two OTE SAM surfaces immediately after filling the SFA chamber with deaerated pure water.

Unfortunately, force could not be measured due to heavy temperature drift. However, after an hour of a minimum temperature settling time, the jump-in was never observed again, indicating something was formed on the monolayer surfaces in an hour. This also strongly supports the existence of air bubbles on plasma treated OTE SAM surfaces.

In contrast, the force curve measured between untreated OTE SAM surfaces immersed in pure water never showed a jump into a soft contact after very steep repulsion even though the force was measured up to ~ 20 mN/m. In addition, upon slow approaching immediately after filling the SFA chamber with pure water, the inward jump was never observed as well. Rather, the curve showed a weak but clearly visible inward jump from 23 nm to 17 nm just before the onset of the steep repulsion. Considering that the measured force at large separations is a balanced one of long-ranged electrostatic and hydrophobic forces between the monolayer surfaces composed of highly compact and hydrophobic OTE domains and charge-exposed defect sites, it is apparent why the expected long-range attraction is absent in the untreated case. Namely, the electrostatic repulsion masks the hydrophobic attraction. Nevertheless, the small inward jump at 23 nm obviously supports the existence of hydrophobicity on untreated OTE SAM surfaces. However, no observation of a jump into a contact at zero separation after nearly vertical repulsive barrier suggests that the repulsion is considerably different from plasma treated case. Kim et al.^[9] previously reported that the total thickness of water films adsorbed under two opposing OTE monolayers was ~ 14 nm at 95% relative humidity, and, based on the result, the authors concluded that the monolayer was not anchored to bare mica surface at all. Interestingly, this thickness is not so far from the starting distance of the repulsion at 17 nm. This may suggest that the monolayer is lifted off the bare mica surface due to no direct chemical bonds between them, and the steep repulsive region mainly originates from a strong drainage resistance of thick water films trapped under the monolayers.

To date, one or more air bubble bridges formed between hydrophobic surfaces have been one of most potent explanations for the long range attractive force. However, some studies including ours revealed that air bubbles formed on hydrocarbon surfaces cause strong drainage repulsion between them. In addition, the force

measured between plasma treated OTE SAM surfaces in this study shows both the short range repulsion and long range attraction together. Such seemingly conflicting results make it more complicated to conjecture the physical behavior of air bubbles on OTE SAM surfaces when they approach each other. Unfortunately, clarifying this issue in more detail is beyond the scope of this study. More scrutinization is under way.

3.2. Surface energy and adhesion hysteresis of OTE-SAM in dry condition

Surface energy was obtained from two independent but intimately related JKR methods (refer to Eqs. 1 and 2) described in experimental section. Figure 2 shows advancing and receding a^3 - F curves for untreated (a) and plasma treated (b) cases in dry nitrogen, together with fits to the JKR theory. The values for γ_A and γ_R obtained from the JKR fits are given in Table 1, where they are also compared with the values of γ_S determined from the pull-off forces. These values are in the very close range for the OTE hydrocarbon surface of previous studies^[2,26] From Table 1 and Figure 2, it is important to note there is a small but noticeable adhesion hysteresis for both the untreated and plasma treated cases. They are ~ 7 and ~ 3 mJ/m² for the untreated and plasma treated cases, respectively. These values are very similar to that reported by Lee et al.^[27] and Kiely et al.^[28] for OTS (octadecyltrichlorosilane) self-assembled monolayer on SiO₂ surface even though Peanasky et al.^[2] found no adhesion hysteresis in a similar study of OTE self assembled on bare mica. In particular, a recent study from Lee et al.^[27] showed that the hysteresis ($\Delta\gamma$) is ~ 5 mJ/m² even at a very slow unloading rate (20 nm/sec) which is almost same as our peeling rate. The authors claimed that the hysteresis is likely to originate from a mechanical cause, not from a molecular origin. It has been generally accepted the origin of the hysteresis are molecular and/or mechanical. However, unfortunately it is very difficult to distinguish the origin.^[29] Our previous study concluded that the OTE-SAM is composed of highly packed crystalline OTE domains and interspersed tiny gaseous regions.^[9] Based on the conclusion, it seems unlikely that the adhesion hysteresis comes from interdigitation due to molecular interdiffusion, i.e., a molecular origin. Rather, it is quite obvious that such small hysteresis originates from a mechanical cause such as bulk deformation of glue.

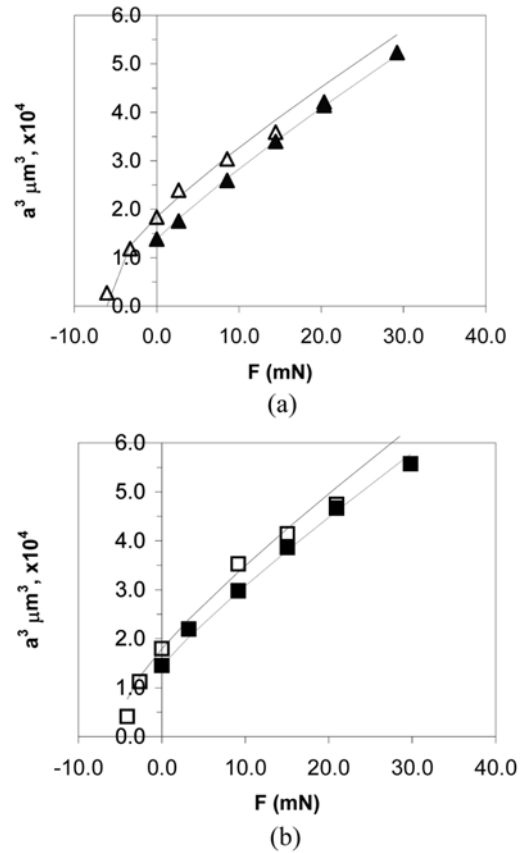


Fig. 2. Measured advancing and receding a^3 - F curves at 25°C in dry conditions for the OTE films on untreated (a) and plasma treated (b) mica surfaces at approximately 20 nm/sec loading and unloading rate. Filled and unfilled symbols denote advancing and receding plots respectively. The solid lines are based on fitting the advancing and receding plots to the JKR theory. γ_A and γ_R are 20.8 and 27.9 mJ/m² respectively for the untreated case (a) and 20.0 and 23.9 mJ/m² for the plasma treated case (b).

Table 1. Advancing, receding and pull-off surface energies were obtained from at least three different experiments. The units for the surface energy are mJ/m²

	Advancing, γ_A	Receding, γ_R	Pull-off, γ_S
Untreated	20.8±1.8	27.7±4.6	24.5±1.2
Plasma treated	21.5±3.1	24.4±2.1	22.4±1.4

Therefore, due to excellent compactness of OTE molecules in monolayer, it is quite reasonable to conclude there is no apparent difference in monolayer quality and stability between untreated and plasma treated OTE SAMs in dry condition. However, slightly

higher hysteresis for untreated case may reflect less stable and fewer covered monolayer for that case.

4. Summary and Conclusions

Adhesion properties of OTE monolayers self-assembled on untreated and plasma treated mica surface were investigated and compared at various stress conditions. In dry condition, no any noticeable difference of adhesion hysteresis between untreated and plasma treated SAMs was observed. On the other hand, more interestingly, in totally opposite conditions (under pure water), a series of surface force measurements showed a substantial difference of stability between untreated and plasma treated cases. Namely, a number of force curves were measured between OTE SAM surfaces on untreated or plasma treated mica completely immersed in pure water. The force curves showed that untreated OTE surface is charged but still hydrophobic as a whole as quantitatively identified by DLVO theory with the additional hydrophobic attraction while plasma treated OTE surface is considerably more hydrophobic as supported by the existence of long-range hydrophobic attraction and a jump into soft contact after steep repulsion due to nano-sized air bubbles. Such huge difference of hydrophobicity between untreated and plasma treated cases reflects plasma pretreatment on mica surface produces better surface coverage and homogeneity of monolayer. In addition, a protrusion behavior of untreated monolayer after many repeated contacts while no such behavior observed in plasma treated case directly demonstrates that the monolayer is extensively bonded to plasma treated surface while it is not anchored to bare mica surface at all but only cross-linked quite thoroughly inside OTE domains (refer to part I article). This conclusion is further supported by the existence of a jump into a soft contact after steep repulsion in the force profile for plasma treated case, but no inward jump for untreated case, which means no direct chemical bonds between the monolayer and bare mica surface. Consequently speaking, the results summarized above, especially obtained in completely wet environment, clearly suggest that the plasma treated OTE monolayer is mechanically much more stable than the untreated monolayer. Therefore, we dare conclude that plasma pretreatment on mica surface dramatically improves the monolayer stability and the improved sta-

bility stems exclusively from extensive covalent bonds of the OTE molecules to the plasma treated mica surface. As a result, it is thought that the OTE SAM on plasma treated mica surface could be potentially an ideal base substrate for nano-structured bio-electronic devices such as bio-NEMS, which must be very stable and operate well in physically harsh and highly wet environment.

Acknowledgement

This work was supported by the Year 2009 internal research fund of PaiChai University.

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