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

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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 head-groups is a crucial factor for the outstanding mechanical strength of the monolayer. However, this study clearly showed 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 examine this phenomenon, n-octadecyltrichlorosilane monolayers were self-assembled on both untreated and plasma treated mica surfaces, and their adhesion properties at various physical conditions (relative humidity, high stress, and contact repetition) were investigated and compared through the use of the surface forces apparatus technique. It revealed that, in highly humid conditions (> 90%RH), there is a substantial difference of stability between untreated and plasma treated cases and the plasma treated surface is mechanically much more stable. It obviously proves 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

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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 pretreatment 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-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.

However, little quantitative research has been done on interfacial properties of OTE-SAMs on mica especially in many different physical conditions, e.g., humidity and high stress while the temperature and water effect on the formation of alkylsilane monolayers have been actively studied.[4,5,13] Considering that very stable nano-structured 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 humidity, contact repetition and high stress 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 head-groups and plasma treated mica surface.

2. Materials and Methods

OTE was purchased from Gelest, Inc. (Tullytown, PA) and doubly distilled under vacuum. The OTE was filtered through a 0.2 μm PTFE filter prior to use. Deionized water was filtered through Easypure UV/UF (Barnstead) producing an ion- and organic-free water of 18.3 MΩ·cm resistivity. Tetrahydrofuran (THF), ethanol and cyclohexane were of spectral quality. They were used as received. Glassware for the preparation of pre-hydrolysis solution and self-assembly was cleaned with chromic acid solution and then with 10% nitric acid solution. The mica used in this study was a ruby mus-covite mica purchased from S & J trading, New York.

In some experiments, the mica samples were pre-treated with radio frequency (RF)-generated Ar/H_2O plasma (Harrick plasma cleaner, PDC-3XG) in order to introduce hydroxyl functional groups on the surface prior to OTE self-assembly. The initial vacuum pressure in the plasma chamber was 13.3 Pa. The vacuum pres-sure rose to 66.7 Pa as a result of water vapor and argon gas (1.5 mL/min) introduction. The mica surfaces were positioned so that they faced directly into the argon/water vapor stream and were exposed to the plasma for 2 minutes at 30 watts RF power.

Prior to self assembly on untreated and plasma treated mica the OTE was prehydrolyzed by dissolving 0.1 g of prefiltered OTE in 10 mL of THF containing 0.1 g of 1 N HCl. The solution was then stirred at room tem-perature for 3 hours. Then 2.63 mL of the prehydrolysis solution was diluted with 80 mL of cyclohexane result-ing in a bit cloudy solution that was left to stand for 25 minutes. The solution did become clearer however just prior to self-assembly, the hydrolyzed OTE solution was filtered through a 0.2 μm PTFE membrane filter. Filter-ing made the solution very clear and there were no vis-ible polymerized OTE aggregates at the air/solution interface. The OTE solution was slowly added to a clean jar containing a pair of either untreated or plasma treated mica sheets that had been previously back sil-vered and glued to cylindrically polished silica lenses. After 30 minutes, each mica surface was slowly and carefully removed from the solution and then baked in a vacuum oven for 2 hours at 110°C. Each sample was then rinsed with 3-5 mL of pure ethanol, blown dry with nitrogen and immediately mounted inside the SFA chamber. A vial of P_2O_5 was attached to a port on the chamber exterior and the chamber was purged with nitrogen for at least 4 hours in order to scavenge any remaining water. The temperature near the OTE surfaces inside the SFA chamber was maintained at 25.0±0.1°C or 38.0±0.2°C throughout the experiment. When necessary, the relative humidity was controlled by introducing an aqueous LiCl solution of known volume and concen-tration onto the bottom of the chamber. We allowed 12 hours for the system to come to equilibrium after the LiCl solution was injected into the chamber.

The experiments were carried out using a home-made Mark IV type SFA[14,15] with two OTE coated, musco-vite mica (plasma-treated or untreated) surfaces mounted as facing, crossed cylinders. The lower surface was mounted on either a flexible double cantilever spring [k~146 Nm^{-1}] or a stiff support [k~6.2 × 10^3 Nm^{-1}] and the upper surface was mounted on a cylindrical pie-zoelectric crystal, the expansion of which controls the surface separation with an accuracy of 0.1 nm. Details of the SFA experiments were introduced in our earlier publications.[9-11]

3. Results and Discussion

3.1. Relative Humidity Effect on Adhesion

Pull-off forces between two contacting OTE surfaces on untreated mica were consecutively measured only at a contact area as a function of relative humidity (Figure 1a). Diamonds denote the averages of three different experiments. Interestingly, normalized adhesive force does not monotonically increase while the adhesive force of ionic surfactant monolayers such as CTAB increases as the RH increases.[16] The plot clearly shows a sudden increase after 80%RH, then a peak at 90%RH and a fast decrease after 90%RH. In addition, from high relative humidity (90 to 99%RH), the shape of the fringes starts to change. At low relative humidity (< 90%) the edges of the flatten part of the fringes are very sharp. At 90%RH we start to see rounded corners (Derjaguin-Muller-Toporov (DMT) type contact) indicating capillary condensed water is present at the edge of the contact zone (not measurable). More interestingly, at 95%RH, the size of the contact area becomes smaller as more contacts are made and the capillary condensed annulus becomes visible as a break in the fringes typically after two or three pull-off force measurements at the same RH. When the relative humidity is raised to 97%RH, the size of capillary condensed annulus becomes larger, the break in the fringes is clearer, and the size of the contact zone is reduced compared to 95%RH. Finally, at 99%RH, the contact area is very small (typically 2-4 μm diameter) and the jump distance during approach is larger than at lower RH. These observations clearly suggest that water droplets condense at certain spots on the OTE monolayers and grow as the RH increases. Therefore, once the water droplets reach a certain size and are large enough to hinder a secure adhesion between the OTE monolayers, capillary condensation predominates over direct monolayer-monolayer adhesion. Therefore, 90%RH is a crossover point, where capillary condensation starts to prevail while a combination of direct surface-surface adhesive force as well as Laplace pressure due to a capillary condensation prevails at 80-90%RH. Effect of capillary condensation on OTE surface deformation and adhesion was vigorously studied and previously reported elsewhere.[10] However, it is important to note that the adhesive force profiles presented in this study are somewhat different from the profiles reported in the previous publication,[10] which represent the pull off force data measured only at fresh contact areas. It means that, in this study, the previous contact(s) may affect the next pull off force data. Therefore, the contact history must be considered whenever the data is analyzed.

Pull off forces between contacting OTE monolayers on plasma treated mica surface were also measured consecutively at a contact area as a function of relative humidity (RH). Figure 1b shows the normalized adhesive forces corresponding to the pull off forces measured at various relative humidities (0-99%RH). Circles represent the averages of three different experiments and the bars indicate the standard deviations of adhesive force values obtained in the experiments. As
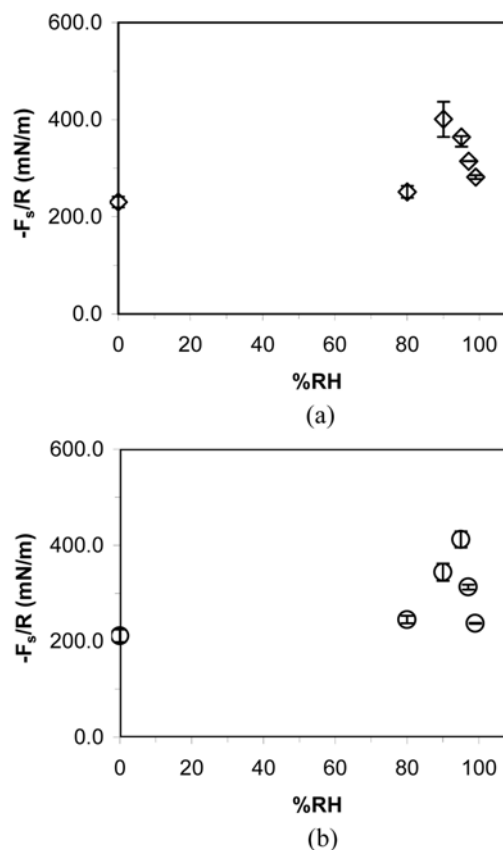

Fig. 1. Adhesive forces of OTE-SAMs on untreated (a) and plasma treated (b) mica corresponding to the pull off force measured at various relative humidities at 25°C. All of the pull off force measurements was carried out only at one contact area and limited to two or three times at each RH in order to minimize contact history.

noted, the adhesive force profile in the plasma treated case (Figure 1b) is very similar to the untreated case except the peak in the surface energy appears at 95 %RH. Similar to the untreated case, at high relative humidities (95-99%RH), a slight deformation of the flat contact was observed in the FECO fringes. While flat contact regions at 80-95%RH are still sharp, rounded contact fringes start to appear from 95%RH. After the RH is raised to 97%, the size of the contact areas becomes smaller as more contact is made. At 99%RH, the phenomenon is very similar to the untreated case as well. These results obviously indicate that 95%RH is a crossover point, where capillary condensation starts to prevail while a combination of adhesive force as well as Laplace pressure due to a capillary condensation prevails at 80-95%RH.

As discussed earlier, the plots for the untreated (a) and plasma treated (b) cases commonly show a sudden decrease of surface energy at high humidity. It is attributed to a weaker adhesion between the OTE surfaces due to coalescence of water droplets on the surface. In addition, in the untreated case the peak is at 90%RH whereas in the plasma treated case the peak is at 95 %RH. This indicates that water droplets are condensed at lower RH on the untreated surface and that for a given RH the droplets are larger on the untreated surface compared to the plasma treated surface. It also agrees well with our previous experiments,[9,10,12] which showed that the OTE monolayer on untreated mica more readily absorbs water at high humidities and it has a slightly lower surface coverage when compared to the plasma treated case.

3.2. Effect of contact repetition at various relative humidities

We also measured adhesive forces at various relative humidities as a function of contact order. The adhesive force was measured repeatedly at same contact area as RH increases. Each series of adhesive force values was then normalized by the adhesive force of the respective first contact. The variation in the adhesive forces for untreated and plasma treated cases as the number of contacts increases is shown in Figures 2 and 3 respectively. Figure 2 shows that the adhesive force starts to drop with the number of contacts at 95 %RH. As noted, after four consecutive pull off force measurements at 95%RH, the surface energy starts to

decrease. The fringe observation also supports this trend. At 95%RH, the contact zone of fringes becomes quickly smaller as more contacts are made, indicating a fast coalescence of water droplets at the edge of the contact zone. After the seventh pull off force measurement, a sudden appearance of a discontinuity nearby the middle of the fringes was observed and then during the
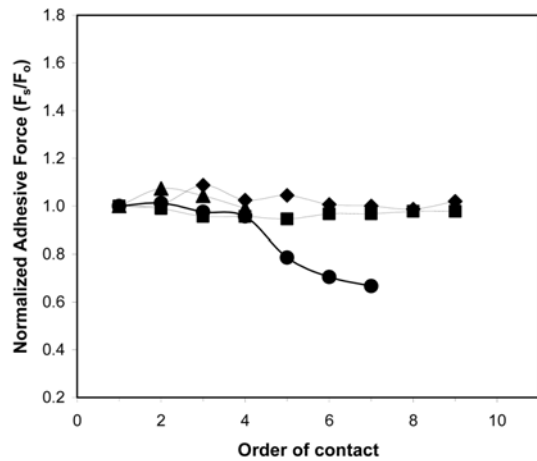

Fig. 2. Variation of normalized adhesive force of an untreated OTE-SAM for a series of relative humidities as a function of contact order at 25°C. All of the surface energies were consecutively measured only at a contact area. ■: 0%RH, ▲: 80%RH, ◆: 90%RH, ●: 95%RH.
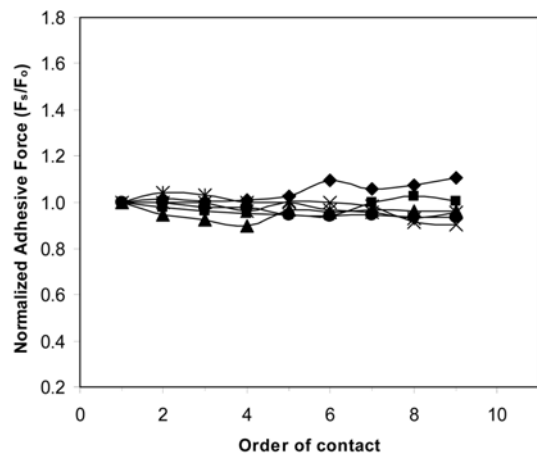

Fig. 3. Variation of normalized adhesive force of a plasma treated OTE-SAM for a series of relative humidities as a function of contact order at 25°C. All of the surface energies were consecutively measured only at a contact area. ■: 0%RH, ▲: 80%RH, ◆: 90%RH, ●: 95%RH, *: 9 %RH, ×: 99%RH.

next approach a small inward jump and an immediate stop of the fringes were also observed clearly indicating the formation of a water bridge between OTE surfaces. Therefore, the experiment was stopped since we were not able to proceed to more pull off force measurement and then the chamber was quickly dried out by nitrogen and P_2O_5 while the surfaces were separated. After overnight, the surfaces were brought together again and we found very interesting phenomena, i.e. observation of a big pyramid-like protrusion of OTE-SAM. Campos-Teran et al.[8] recently reported a protrusion in OTE monolayer prepared by Langmuir-Blodgett technique. The authors speculated the protrusion originates from pre-polymerized OET aggregates in spreading solution for LB deposition. However, our result is not the case since our OTE-SAM was prepared by downward deposition method in self-assembly solution and its smoothness was directly observed by FECO fringes. Furthermore, we stress that the protrusion in this study occurred after many contact repetition, not from a natural condition.

As for the untreated case, the variation in the surface energies for plasma treated case is shown in Figure 3. All the pull-off forces were measured in the same contact area. Figure 3 shows there is little variation in surface energy with repeated contacts suggesting that the adhesion is not at all affected by the previous history of pull off force measurement. In fact, this result is also supported by a discontinuity of fringes not easily seen in the plasma treated case even at 99%RH. Thus, these results evidently suggest that the monolayer is firmly anchored to plasma treated mica surface and no molecular rearrangement takes place between, inside and under the monolayers even in the presence of water droplets during repeated pull off force measurements. Therefore, there is no doubt that the plasma treated OTE SAM is mechanically very robust and stable.

3.3. Effect of high stress on monolayer stability

We also investigated how high compression (up to 350 mN) between the OTE monolayer surfaces affects the stability of OTE SAM. At each different RH (0-99 %RH), a normal force was applied to the adhering OTE monolayers on plasma treated mica surface typically two or three times and then adhesive force was measured repeatedly at the same contact area. These normalized forces were compared to the ones measured
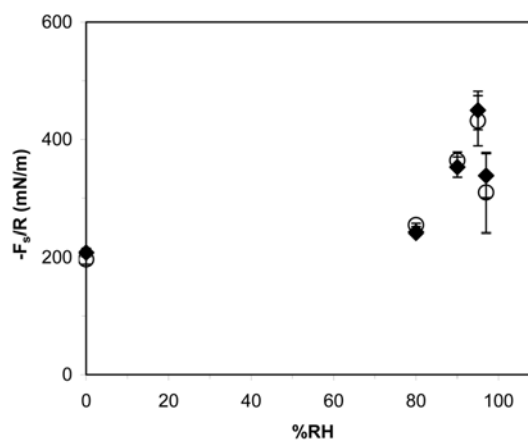

Fig. 4. Adhesive forces of plasma treated OTE-SAMs corresponding to the pull-off forces measured at various relative humidities at 25°C. Diamonds and circles denote the surface energies from compressed and uncompressed surfaces respectively. Maximum compression was approximately 350 mN. The surface energies from highly compressed surface were measured only at one contact area while the energies from uncompressed surfaces were measured at fresh contact areas whenever the RH is changed.

at previously uncompressed fresh contact areas. Figure 4 shows the comparison between adhesive forces measured from compressed and uncompressed surfaces. The result shows that, even after several high compression-decompression cycles, the adhesive forces are almost same as the ones at fresh contact areas, indicating OTE molecules inside the monolayer are not re-arranged or deformed at all. Therefore, no dependence of adhesion on repeated high stress directly demonstrates that OTE monolayer on plasma treated mica surface is mechanically robust and tenacious.

4. Summary and Conclusions

Adhesion properties of OTE monolayers self-assembled on untreated and plasma treated mica surface were investigated and compared at various physical conditions such as relative humidity, high stress, and contact repetition. In dry condition, no any noticeable difference of adhesive properties between untreated and plasma treated SAMs was observed. On the other hand, more interestingly, in highly humid conditions (> 90%RH), a series of physical tests showed a substantial difference of stability between untreated and plasma treated cases.

For example, the peak of adhesive force profile for plasma treated case is placed at higher RH (95%RH) than for untreated case (90%RH), which tells us that the plasma treated OTE monolayer absorbs less water than untreated case does. It means that the water vapor-condensed gaseous region (or defect) on plasma treated monolayer surface is generally smaller than on untreated surface. In addition, we found that high stress and contact repetition at variable RHs do not affect the adhesive force for plasma treated OTE SAM at all whereas, for untreated case, the adhesion highly depends on previous contact history. That is, the 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. Consequently speaking, the results summarized above, especially obtained in highly 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 stability 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

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