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Significantly improved stability of *n*-octadecyltrichlorosilane self-assembled monolayer by plasma pretreatment on mica

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Abstract

It has been well known that plasma pretreatment can stabilize the hydrocarbon silane monolayer self-assembled on a mica surface. However, the extent of this improvement is not well known. To explore this issue, *n*-octadecyltrichlorosilane (OTS) monolayers were self-assembled on both untreated and plasma-treated mica surfaces, and their interfacial properties were investigated and compared at various physical conditions (temperature, relative humidity, contact time, high stress, and contact repetition) through the use of surface force measurements. This study revealed that in highly humid conditions (>90% relative humidity) there is a substantial difference of stability between untreated and plasma-treated surfaces, the OTS monolayer on plasma-treated mica surface being much more stable. In particular, protrusion behavior in the monolayer was always observed in untreated samples, but never in plasma-treated samples during contact repetition experiments. This directly demonstrates that the significantly improved stability directly comes from extensive chemical bonds between OTS molecules and the plasma-treated mica surface.

Keywords: Octadecyltrichlorosilane; Self-assembled monolayer; Plasma; Mica

1. Introduction

The alkylsilane self-assembled monolayer (SAM) has been used to alter the properties of surfaces in both industrial and research applications because it is unusually stable. It has been widely accepted that the unusual stability stems from the ability of the alkylsilanes to cross-polymerize and attach covalently to hydroxyl groups on SiO_2-based oxide surfaces such as oxidized silicon wafers. For this reason, the alkylsilane SAM has been widely applied to areas such as coatings, lubrication, templating, optoelectronics, and microelectromechanical systems/nanoelectromechanical systems (MEMS/NEMS) [1]. Particularly, MEMS/NEMS have been one of most successful examples of the applications. MEMS is a suitable device for the system integration of sensors, actuators, and signal processing. The miniaturized integration offered by MEMS devices is attractive in applications where a smaller size and weight are desirable. However, as devices become smaller, the surface area-to-volume ratio becomes larger and surface forces become more important. For instance, many studies [2–4] have shown that nano-sized patterns in NEMS devices easily collapse and/or stick together, thereby producing a serious performance problem. The relevant industries and research areas commonly point out that strong surface forces, an overly floppy character, and rough profiles of patterned walls or lines together contribute to the pattern collapse. Therefore, preparing an alkylsilane layer very robustly cross-linked to molecularly smooth base substrates for NEMS devices is possibly an ideal solution for circumventing the problem, as it can simultaneously alleviate or remove all of the negative effects mentioned above. In fact, MEMS/NEMS devices currently demand ultra-smooth substrate materials that can allow more precise and delicate patterning with the monolayer.

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Over the past decade, there has been active interest in depositing alkylsilane SAMs on mica [5–12], as mica can be prepared as molecularly smooth and broadly step-free sheets. Such perfectly crystalline surfaces would be an ideal base substrate for the fine coating and patterning of alkylsilane monolayers on MEMS/NEMS devices. Alkylsilane molecules such as *n*-octadecyltrichlorosilane (OTS) and *n*-octadecyltriethoxysilane (OTE) can easily self-assemble on bare mica surface. Driving force for the alkylsilane self-assembly originates mainly from extensive electrostatic interaction between alkylsilane headgroups and bare mica surface. In fact, many studies for the formation of OTS [8,9,17] and OTE [6,13,16] SAMs show well-assembled and cross-polymerized monolayers on bare mica surfaces. However, as a mica surface does not contain any inherent functional groups such as hydroxyl groups, the preparation of covalently linked silane headgroups on mica is not straightforward. Curry's group at the University of Arizona recently reported that an *n*-octadecylsiloxane self-assembled monolayer is firmly anchored to plasma-treated mica surfaces most likely through covalent bonding [13–16]. Therefore, they proposed that octadecylsiloxane or other functionalized organosilane monolayers on plasma-treated mica could be a potential base substrate for the construction of MEMS/NEMS devices.

Considering that robust MEMS/NEMS 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. However, little quantitative research has been done on the interfacial properties of octadecylsiloxane monolayers on mica, especially in many different physical conditions, e.g., temperature and humidity. In contrast, the temperature and water effect on the formation of alkylsilane monolayers have been actively studied [8,9,17]. Particularly, under physically harsh and wet conditions, how and to what extent the stability of an alkylsilane SAM is affected by plasma pretreatment on mica is not yet clearly understood. Therefore, a surface-force apparatus (SFA) technique was employed to estimate and compare the effects of temperature, humidity, contact time, contact repetition and high stress on the molecular structure and stability of OTS monolayers self assembled on untreated and plasma-treated mica.

2. Materials and methods

n-Octadecyltrichlorosilane (OTS) was purchased from Gelest, Inc. (Tullytown, PA) and used as received. The OTS was filtered through a 0.2 μm polytetrafluoroethylene 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. Toluene and ethanol were of spectral quality. They were used as received. Glassware for the preparation of a dipping solution and for use in the self-assembly processes was cleaned with a chromic acid solution and then with a 10% nitric acid solution. The mica used in this study was ruby muscovite mica purchased from S & J Trading, New York.

In some experiments, the mica samples were pretreated 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 OTS self-assembly. The initial vacuum pressure in the plasma chamber was 13.3 Pa. The vacuum pressure 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. Then, they were exposed to the plasma for 2 min at 30 W RF power.

Prior to the self-assembly on untreated and plasma-treated mica, the OTS (0.1 g of prefiltered OTS) was dissolved into 12 mL of toluene. The OTS solution was slowly added to a clean jar containing a pair of either untreated or plasma-treated mica sheets that had been previously back silvered and glued to cylindrically polished silica lenses. After 30 min, each mica surface was slowly and carefully removed from the solution and then baked in a vacuum oven for 2 h at 110 °C. Each sample was then rinsed with 3–5 mL of pure ethanol, blown dry with nitrogen and immediately mounted inside an 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 h in order to scavenge any remaining water. The temperature near the OTS 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 (RH) was controlled by introducing an aqueous LiCl solution of a known volume and concentration onto the bottom of the chamber. 12 h were allowed 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 [18,19] with two OTS-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 [$k \sim 148$ N m^{-1}] or a stiff support [$k \sim 6.23 \times 10^3$ N m^{-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 direct current 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 that had been cleaved into molecularly flat sheets (1–5 μm thick) and then back silvered (~ 55 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 [18]. Before the plasma treatment or OTS coating, the contact fringe positions of the untreated mica surfaces were recorded for reference. Typical contact radii of two OTS surfaces were 25–33 μm, and the maximum resolution of the contact area measurement was ~ 1 μm. In addition, the radius of curvature of the undeformed surfaces was 1.5–2 cm.

The adhesion or pull-off force was determined by bringing two OTS-coated mica surfaces into contact under a zero external load and then separating them by moving the remote end of the spring on which one of the surfaces was mounted.