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Thermal stability of self-assembled octadecyltrichlorosilane monolayers on planar and curved silica surfaces

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Abstract

Understanding the structural and functional integrity of self-assembled monolayers (SAMs) of alkytrichlorosilane on Si/SiO$_2$ interface with change in temperature is critical for realizing their utility as antistiction coatings during the fabrication and functioning of microelectromechanical systems. Here we describe the thermal stability of two dimensional (2D) octadecyltrichlorosilane (OTS) monolayers on both n-type Si substrate (planar surface) and silica spheres (curved surface) using results of various surface sensitive spectroscopic techniques like the grazing angle Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. Densely packed OTS monolayer on n-type Si surface is found to be thermally stable up to 525 K, while a significant enhancement in the thermal stability is interestingly observed for the case of OTS SAM (up to 625 K) on freshly prepared spherical silica surfaces. Despite this difference in the thermal stability, the results of temperature dependent infrared spectra demonstrate monolayer decomposition in both cases through the involvement of both Si–C and C–C bonds leaving Si–O–Si bond intact.

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1. Introduction

Self-assembled monolayers (SAMs) have attracted a great deal of attention in recent years due to their interesting properties as candidates for isolating interfaces and improving interfacial adhesion in newly evolving integrated circuit architectures, an interest arising because of its crucial importance in modern nanotechnology [1–4]. For example, SAMs of alkyltrichlorosilane on Si/SiO$_2$ interface have been extensively studied due to their fundamental importance in surface modification and also for their diverse potential applications, as emerging flexible memory storage modules, nano electromechanical devices, interconnects in molecular electronics [5,6], interfacial adhesive promoters and molecular lubricants [7,8]. The close packing of the molecules with a saturated methylene chain via coordinated interchain van der Waals interactions is expected to create a vacuum-like potential barrier at the interface that inhibits phenomena such as ionization and diffusion, making these extremely useful for interfacial isolation. In addition, the low sticking property of SAMs onto themselves is conducive for forming conformal layers whose thickness is essentially the length of the comprising molecules facilitating a remarkable control by manipulating the chemistry of the terminal functional group. As a result, many structure–function correlation studies have been reported so far using various characterization techniques.

Alkyl trichloro or trimethoxy silane SAMs are particularly useful for micro-electromechanical systems (MEMS) to tackle the well-known stiction problem [9–12] since their mere presence provides a suitable low energy surface coating. These types of organic monomolecular films acting as a passivation layer can, not only alleviate capillary forces and direct chemical bonding on Si–O surface, but also reduce electrostatic forces if the terminal group is tailored to possess controlled hydrophobicity. The formation of close packed,

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covalently bounded monolayer with tunable chain length and hydrophobic terminal group on silicon oxide surface would eliminate the release stiction and reduce the in-use stiction. However, during the fabrication of MEMS, a small variation in the processing temperature may cause the device failure because most of MEMS packaging processes contain steps at elevated temperatures [13]. Therefore, the assessment and understanding of the growth and thermal stability of these monolayers are important prerequisites for their proper utilization with respect to both micro fabrication and device performance. The onset of performance degradation can be unpredictable and hence it is important to monitor the thermal behavior, as some of the organic films are unstable at high temperature. For example, Calistri-Yeh et al. have reported permanent structural changes of octadecyltrichlorosilane (OTS) monolayers in air [14] above 400 K while the stability is extended up to 675 K in nitrogen [9] atmosphere as a function of the annealing temperature. Similarly, Kluth et al. have recently reported the stability of hydrocarbon chains up to 750 K in vacuum, whereas the perfluorodecytrichlorosilane film is stable up to 675 K in air and 775 K in nitrogen [9]. However, all these studies are for 2D SAMs on planar surfaces and it is important to compare the behavior of SAMs of same molecule on both planar and curved surfaces in order to understand the effect of curvature on thermal stability. In this work, we report such a comparison of the thermal stability of OTS monolayer on planar and curved surfaces i.e., on n-type Si substrate and spherical silica surfaces, respectively. We demonstrate the superior thermal stability of OTS monolayer on curved silica surface by using a variety of techniques like temperature dependent Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), thermogravimetric/differential thermogravimetric analysis (TG/DTG) and contact angle measurements.

2. Experimental details

2.1. Chemicals

n-Octadecyltrichlorosilane (OTS) (95%) and Tetraethyl orthosilicate (TEOS) were obtained from Aldrich, while toluene (99.5%), ethanol (99.5%) and ammonia were purchased from Qualigens. Commercially available n-type, one-side polished, silicon wafers of (100) orientation with 0.001–0.007 Ω-cm resistivity were used as substrates. These silicon wafers (1×1 cm^2) were rinsed by deionized water (18 MΩ cm), sonicated in ethanol and dried under a flow of nitrogen. These wafers were soaked in 10:1 deionized H_2O: HF solution for 30 s to remove the native SiO_2 layer. A piranha solution (7:3 concentration $H_2SO_4:H_2O_2$) was prepared and the wafers were soaked for 30 min at 363 K to grow a fresh oxide layer. These clean wafers were subsequently rinsed with deionized water, dried in a stream of nitrogen and used for further experiments. Silica spheres were prepared by using the well-known Stober's method as reported elsewhere [15]. These silica spheres were further redissolved in ethanol and refluxed for 2 h to get monodispersed silica particles.

2.2. Silanization

2.2.1. SAM formation on n-type Si substrate

Freshly cleaned Si wafers were immersed in 1 mM OTS solution for 10 min. Subsequently, they were removed from OTS solution, rinsed several times with toluene, dried under nitrogen atmosphere and used for further characterization [16].

2.2.2. SAM formation on silica particles

Prior to functionalisation, the silica particles were dried for 10 h at 423 K under nitrogen atmosphere and were used immediately. In a typical synthesis procedure, 10 mg silica particles (400–500 nm) were dispersed in dry toluene with intermediate stirring for 1 h. To the above mixture 10 ml, 1 mM OTS solution was added drop wise, and in order to ensure a complete monolayer formation of OTS on silica, the mixture was refluxed for 24 h under nitrogen atmosphere. This solution was then allowed to stand for few hours, filtered and washed several times with toluene and ethanol in order to remove unreacted OTS. This (OTS-silica) was subsequently dried in a vacuum oven at 343–353 K for 4 h and used for further characterization. A schematic comparison of the steps involved during the formation of SAMs on both planar and curved surfaces is represented in Scheme 1.

2.3. Characterization

Scanning electron microscopic (SEM) measurements were carried out on a Leico stereoscan model 440 instrument equipped with Phoenix energy dispersive analysis of X-ray (EDAX) attachment. The contact angle on Si (100) substrate was measured using water sessile drop on RAME-HERT NRL-model CA goniometer. FTIR spectra of the OTS monolayer on Si substrate as well as OTS-SiO_2 were recorded using a Perkin Elmer 1615 spectrometer in a diffuse reflectance mode (DRIFT) although OTS-silica sample was made in the form of pellet after mixing with spectroscopic grade KBr. The OTS monolayer on Si substrate was also characterized by grazing angle FTIR spectroscopy after recording the background spectra at a resolution of 4 cm^{-1} over 256 scans at room temperature using bare Si wafers. Thermogravimetric analysis was carried out on a Seiko thermal analyzer model No: TCA/DIA-32. Thermal stability of OTS monolayer on Si substrate was studied by water sessile drop contact angle measurements after annealing the Si substrate in air for 5 min at different temperatures. XPS measurements were carried out using a VG scientific ESCA-3 MK II spectrometer operated at a pressure below 1.33×10^{-7} Pa (electron take of angle 60°, and overall resolution ~1 eV) using Mg–Kα source ($h\nu = 1253.6$ eV). The alignment of the binding energy was carried out using the C 1s binding energy of 285 eV as a reference to compensate for surface-charging effects. The X-ray flux (power 70 W) was kept deliberately low in order to reduce the induced damage. The core spectra were background corrected using the Shirley algorithm. The deconvolution of overlapping peaks in the final, high resolution spectra was accomplished using standard