

Selective removal of octadecylphosphonic acid (OPA) molecules from their self-assembled monolayers (SAMs) formed on a Si substrate

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Abstract. We show that physisorbed octadecylphosphonic acid (OPA) self-assembled monolayer (SAM) molecules on a Si substrate can be removed by a biased conductive probe tip. Our experimental results suggest that the OPA headgroups are negatively charged and adsorbed on the Si substrate through weak electric charge interaction, allowing one to selectively remove these molecules from their SAMs with an electric field.

1. Introduction

A method for delivering physisorbed octadecylphosphonic acid (OPA) self-assembled monolayers (SAMs) onto a Si wafer substrate using a hydrophobic solvent with a dielectric constant close to 4 has been previously developed [1]. The driving force behind the successful formation of the physisorbed OPA SAMs on a Si substrate using the hydrophobic solvent scheme lies in the fact that the hydrophobic solvent, e.g., trichloroethylene (TCE) or chloroform, allows hydrophilic OPA headgroups to concentrate and self-assemble on the surface of the hydrophobic medium, thus greatly reducing the activation energy for SAM formation and resulting in a fast growth rate. The orderliness of the methylene chains as well as the terminating methyl groups was confirmed using appropriate analytical techniques [1]. It is worth noting that OPA monolayers would not form at all on a Si substrate when a hydrophilic solvent were used; instead, “liquid-like” stacks or aggregates would [1,2]. In comparison, stable OPA SAMs readily grow on mica and oxidized aluminum. These experimental facts indicate that the OPA headgroup has a much weaker interaction with a Si substrate than with a mica substrate or an oxidized aluminum film.

Using organic SAMs as a mask for patterning has received increasing attention as the thickness of these films is only about a couple of nanometers, which should allow patterning at a finer scale than does a thicker film. To fabricate nanoscale devices, one can use a scanning probe microscope to directly write nanoscale features onto a positively-biased substrate by scanning a conductive tip across the substrate surface [3-6]. This is attributed to anodic oxidation of the substrate surface through a water bridge formed between the tip and the sample surface, which behaves as an electrochemical cell. Sugimura *et al* has applied this method to trimethylsilyl [7,8] or octadecyltrimethoxysilane [9] SAMs. They found that the scanned areas were degraded and the underlying Si surface was anodized.

We have shown that by taking the advantage of the physisorption nature of OPA SAMs formed on a Si substrate, we can selectively remove OPA molecules from their SAMs by pulling the molecules

from the substrate with a positively-biased conductive tip [10]. Only the positively-biased-tip scheme allows a well-defined removal of the molecules that lie within the tip-scanned area, without anodic oxidation of the exposed Si substrate. The mechanism responsible for the observed removal of the OPA molecules from a Si substrate is clearly an electrostatic effect, which suggests that the hydrophilic OPA headgroup is negatively charged. In this article, we propose a simple model for the estimation of the energy required to remove the OPA molecules by considering the tip/OPA/SiO₂/Si as capacitors in series.

2. Experimental

Solutions of 2 mM OPA [CH₃(CH₂)₁₇P(O)(OH)₂; Alfa Aesar, Ward Hill, MA] in TCE were used for preparing OPA SAMs on UV/Ozone cleaned n-type Si(100) substrate with a resistivity of 35-130 ohm-cm. The thickness of the native silicon dioxide was ~2 nm for Si exposed to UV/ozone for ~45 min. The solution was heated to ~40 °C before use to ensure that OPA molecules were completely dissolved in the hydrophobic solvent. In order to spin-coat OPA SAMs on a substrate, the solution was applied to the Si substrate rotated at a speed of 5,000 rpm. Details about the orderliness and strength of the OPA SAMs on a Si and other substrates have been reported elsewhere [1].

A PSIA atomic force microscope (AFM), the XE-100 model, was used to explore the lithographic applications of OPA SAMs formed on a Si substrate. Cantilevers having a spring constant of 0.3 N/m were used. AFM images were obtained by scanning the tip across the sample surface at a nominal applied force of 2 nN. The Ti-Pt coated probe tip had a radius of ~50 nm. The lithography was done by scanning a biased conductive tip across the surface of an OPA SAM on a Si substrate.

3. OPA SAMs formation on a Si substrate

Shown in Figure 1a is a schematic illustration for the hydrophobic hydrocarbon chain and the hydrophilic headgroup of an OPA molecule. In the present work, the OPA molecules are dissolved in a hydrophobic solvent (TCE) and the solution is added drop by drop onto a Si substrate in a spin-casting process. As shown in Figure 1b, the molecules are distributed in a hydrophobic solvent droplet, where the hydrophilic molecular headgroups are concentrated at the hydrophobic medium surface with their hydrocarbon tails residing in the hydrophobic solvent because the headgroups tend to escape from the hydrophobic environment and the tails want to stay in the solvent. Once a hydrophilic Si substrate is in

contact with the hydrophobic solvent medium, the interaction between the hydrophilic OPA headgroups and the hydrophilic substrate is facilitated. The pre-deposition organization of the OPA molecules on the solvent droplet surface greatly reduces the activation energy of SAM formation, thus allowing OPA SAMs to form on a Si substrate [1]. In conventional methods, OPA molecules are first randomly adsorbed on the substrate when it is immersed into a hydrophilic OPA solution. Then the self-assembly process begins, during which there may be a de-sorption process for the OPA molecules adsorbed on the substrate surface. After a certain time of immersion, the substrate is taken out of the solution. This is usually followed by a rinse using an appropriate solvent to remove possible excess molecules on the SAMs surface. This SAM formation requires a strong interaction between the molecular headgroup and the substrate [1]. As such, for OPA on Si, because of the very weak headgroup-substrate interaction, no SAMs can be formed if a hydrophilic solvent is used [1,2].

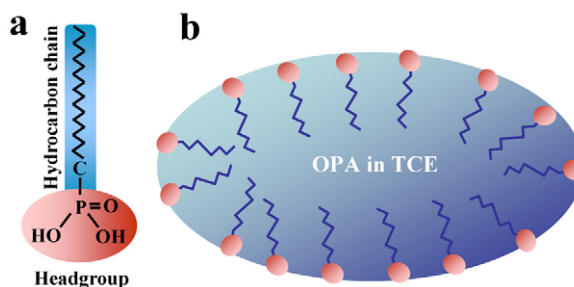


Figure 1. Schematic illustration for an OPA molecule (a) and the distribution of OPA molecules in an appropriate hydrophobic solvent such as TCE (b), where the hydrophilic molecular headgroups tend to align on the medium surface.

Shown in Figure 2a and 2b are AFM images for OPA SAMs spin-coated on a Si substrate having a partial and a full coverage, respectively. The profile in Figure 2c taken from the partial coverage SAM sample shows that the SAM thickness is ~ 1.8 nm. On the other hand, the profile in Figure 2d shows that the full-coverage SAM surface has a root mean square roughness of ~ 0.05 nm. While the OPA SAMs on a Si substrate have a closely-packed structure as evidenced from the infrared absorption analysis, the molecular headgroups are weakly bonded on a Si substrate as they are prone to alcohol and even water attack [1]. This new type of SAMs formed on the native oxide surface of a Si wafer may have applications where easy removal of the SAMs is required, such as scanning probe based lithography [10].

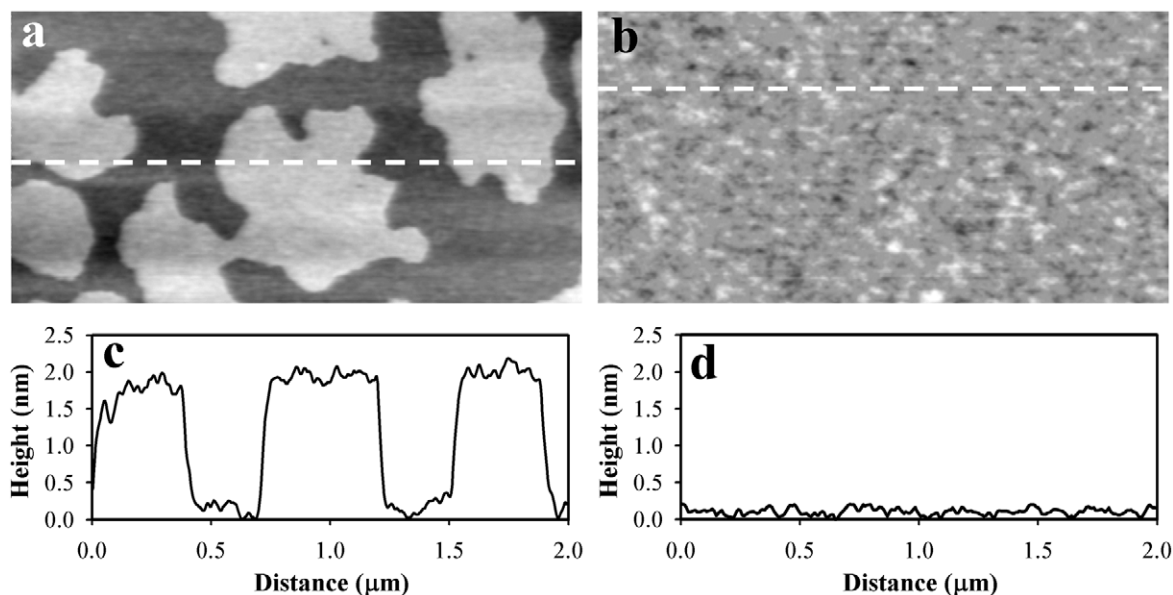


Figure 2. AFM images (scan area: $2 \mu\text{m} \times 1 \mu\text{m}$) for a partial (a) and a full-coverage (b) OPA SAMs on a Si substrate. The profiles isolated from the inserted broken lines in (a) and (b) for the partial and full-coverage OPA SAM are shown in (c) and (d), respectively.

4. Selective removal of molecules from their SAMs on a Si substrate

Shown in Figure 3a is an AFM image of a groove created on OPA/Si surface by applying a positive bias of 10 V to the conductive tip while scanning the tip across the surface under a relative humidity of $\sim 50\%$. Other values of bias also work as long as the electric energy provided by the bias is such that it is enough to remove the molecules. As shown in Figure 3b, the thickness of the groove is ~ 1.8 nm, close to the thickness of the OPA SAM.

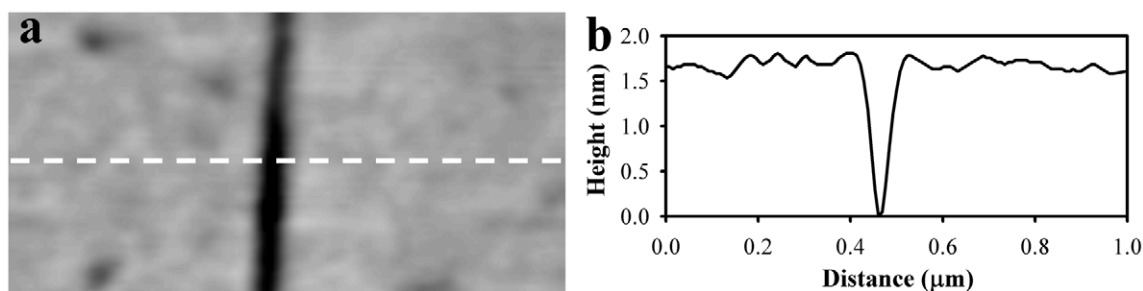


Figure 3. AFM image (scan area: $1 \mu\text{m} \times 0.5 \mu\text{m}$) of a groove created on OPA/Si (a) and its profile (b) isolated from the broken line shown in (a).

While the positively-biased-tip scheme gives well-defined removal of the molecules from an OPA SAM on silicon oxides, a negatively-biased-tip scheme causes very different results that are strongly dependent on the relative humidity [10]. It is concluded that the negatively-charged OPA molecular headgroup is pulled by the positively-biased probe tip. On the other hand, the negatively-biased probe tip repels the molecular headgroup, resulting in a massive removal of OPA assisted by a water film under a high relative humidity [10]. Under low humidity, however, the underlying Si seems to be oxidized when the tip is negatively biased [10], similar to that reported by Sugimura *et al* [7-9].

For the positively-biased-tip scheme, we propose a model in terms of energy change upon removal of the OPA molecules to explain the observed removal of the molecules from their SAMs on a Si substrate. To simplify the assessment of the energetic changes in the process of the electric-field assisted removal of OPA molecules, as shown in Figure 4a, we treat the system as two parallel-plate capacitors in series (insert in Figure 4a) to address the issue. In practice, the tip-SAM junction is only part of the more complicated system of the tip/SAM/oxide/Si/oxide/sample-stage configuration. Therefore, removal of OPA molecules would be affected largely by a number of parameters, such as the conductivity and the interface between the substrate and the sample holder.

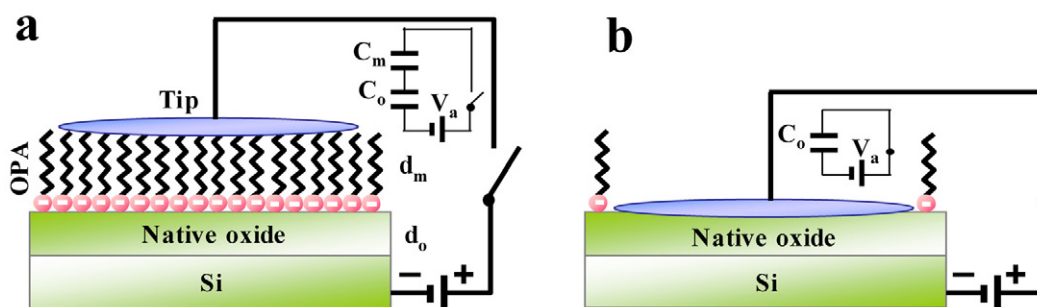


Figure 4. The capacitance model for the removal of OPA molecules from their SAMs formed on a Si substrate. (a) Before applying a positive bias to the conductive tip, the capacitance is composed of C_o for the native oxide layer of the Si substrate and C_m for the OPA SAMs, having a thickness of d_o and d_m , respectively. (b) After the action, OPA molecules under the contact area of the probe tip are removed. Due to the AFM feedback system, the probe tip will make a contact with the native oxide surface so that the capacitance will increase due to the removal of OPA molecules. Equivalent electric circuits are shown in the inserts in (a) and (b) with an applied voltage V_a .

For simplicity, we assume two capacitors in series in the system (insert in Figure 4a), one for the native silicon dioxide layer that has a thickness of d_o and a dielectric constant of k_o and the other for the OPA SAM whose thickness is d_m and dielectric constant k_m . Then the capacitance for the OPA monolayer and the oxide layer can be written as $C_m = k_m \epsilon_0 A / d_m$ and $C_o = k_o \epsilon_0 A / d_o$, respectively, where ϵ_0 is the permittivity of free space, A the contact area of the tip. The equivalent capacitance for the two capacitors in series is thus $C = k_m k_o \epsilon_0 A / (k_o d_m + k_m d_o)$. As shown in Figure 4b, removal of the OPA molecules results in a new equivalent capacitance of $C' = C_o$ (insert in Figure 4b). The increase in capacitance due to the removal of the OPA molecules is thus $\Delta C = C' - C = k_o^2 d_m \epsilon_0 A / (k_m d_o^2 + k_o d_m d_o)$. An increase in energy stored in the capacitor under the applied voltage V_a is thus $\Delta E = \frac{1}{2} \Delta C V_a^2 = \frac{1}{2} k_o^2 d_m \epsilon_0 A V_a^2 / (k_m d_o^2 + k_o d_m d_o)$. This energy increase would be favorable if it is larger than the desorption energy of OPA SAM, which is the energy needed to remove the OPA molecules from their SAMs from the native oxide surface. To relate ΔE to OPA molecular desorption energy, one needs to convert ΔE associated with an area A to the energy corresponding to a mole of molecules. The OPA molecules occupying an area A can be estimated from A/n_m , where n_m is the molecular area having a dimension of area/molecule, i.e. the area one molecule occupies. The energy increased on an area A that has A/n_m molecules is $\Delta E / (A/n_m)$. This energy per molecule can be normalized to energy per mole using the Avogadro constant N_A : $\Delta E_m = n_m N_A \Delta E / A$. The final result for the increase of stored

energy in the capacitance when OPA molecules are removed is thus $\Delta E_m = \frac{1}{2} n_m N_A k_o^2 d_m \epsilon_0 V_a^2 / (k_m d_o^2 + k_o d_m d_o)$, from which the area A vanishes. In order to give a crude estimation of the desorption energy, we assume $n_o = 25 \text{ \AA}^2/\text{molecule}$ [11] or $2.5 \times 10^{-19} \text{ m}^2/\text{molecule}$, dielectric constant for organic compound [12,13] $k_m = 3$, dielectric constant for SiO_2 [14] $k_o = 4$, $d_m = d_o = 2.0 \times 10^{-9} \text{ m}$, the increase in the energy stored in the capacitor under an applied voltage of $V_a = 7 \text{ V}$ [10] due to the removal of the OPA SAM is thus equal to or less than 37 kJ/mol . Considering the applied voltage loss at the native oxide of the backside of the Si substrate as well as the fact that $V_a = 7 \text{ V}$ was not necessarily the minimum applied voltage to remove the molecules, the desorption energy of OPA on a Si substrate should be well below 37 kJ/mol , consistent with the physisorption nature of the OPA SAMs on a Si substrate. A more accurate way to measure the desorption energy is apparently to (1) use a Si substrate with an ohmic contact at the backside and (2) increase V_a gradually until molecular removal is detected, during which the charging current, if monitored, might give information leading to a better understanding of how the molecules are removed.

Because the adsorption energy should be an intrinsic property of the OPA/Si system, it would not be affected by the tip potential energy relative to the OPA headgroup. However, the tip potential relative to the OPA headgroup is a portion of the applied voltage [i.e., $V_a C_o / (C_o + C_m)$], which decreases with the increase of the oxide layer thickness, or equivalently, the decrease of the monolayer length. Therefore, the actual potential difference between the tip and the OPA headgroup is determined by the relationship between d_o and d_m . It is apparent that given the same oxide layer (i.e., d_o) and provided the same desorption energy for the molecular headgroup, an organophosphonic acid having a shorter hydrocarbon chain (i.e., a smaller d_m) would need a higher V_a for molecular removal, merely because the potential energy of the tip relative to the charged headgroup would be smaller for the same V_a . This is also reflected from the ΔE_m equation shown above, where a smaller d_m requires a larger V_a to reach the same ΔE_m . Note that the use of the tip potential energy to estimate the desorption energy assumes, by definition, that an OPA headgroup has a unit charge, which may not be the case for the OPA headgroup. Therefore, differences in estimated desorption energy between the above two calculations may be related to the effective charge of an OPA headgroup.

5. Summary

We have described a scanning probe based lithographic method to pattern an OPA SAM covering a Si substrate in ambient at room temperature through pulling the negatively-charged OPA molecular headgroup by a positively-biased probe tip. This electric-field assisted patterning technique using OPA SAMs on a Si substrate may have applications in lithography. A capacitance model for assessing the desorption energy of the OPA molecules from their SAMs is proposed and demonstrated to give adequate interpretation of our experimental results.

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