

Nanolithography of a full-coverage octadecylphosphonic acid monolayer spin coated on a Si substrate

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The authors describe a lithographic method based on a scanning probe technique to selectively remove octadecylphosphonic acid (OPA) molecules from their self-assembled monolayers (SAMs) spin coated on a Si substrate. This lithographic technique involves the use of a positively biased probe tip to scan an OPA SAM having a thickness of ~ 2 nm and provides an opportunity for developing a scanning probe based lithography that accommodates the need for ever-decreasing size of semiconductor devices. © 2007 American Institute of Physics. [DOI: 10.1063/1.2741119]

Atomic force microscopes (AFMs) have been used to write protruding nanoscale features onto a positively biased substrate with a conductive probe tip.^{1–5} An electrochemical process mediated by a water meniscus between the tip and the sample surface results in anodic oxidation of the sample surface.^{1–5} This anodic oxidation method has been used for patterning protruding features on substrates for device fabrication.^{1,2,4} Sugimura *et al.* applied this method to pattern silane self-assembled monolayers (SAMs),⁶ e.g., trimethylsilyl and octadecyltrimethoxysilane SAMs on a Si substrate.^{7–9} They found that the scanned areas became protruded, which was explained^{7–9} as the result of degradation of the monolayer that triggered anodization^{1–5} of the Si substrate. Maoz *et al.* also applied this method to silane SAMs on a Si substrate to oxidize the terminating hydrophobic group (vinyl or methyl) so that the scanned areas could be converted to carboxylic acid functional groups, on which they deposited another anchoring silane monolayer.^{10,11} It is clear that the system of silane SAM on a Si substrate is an excellent system for AFM-based patterning of SAMs.¹² However, there has been no report on removal of molecules from a SAM on a Si substrate using a biased probe tip in air *without* oxidizing the substrate.^{12,13}

Recently, we have developed a method that allows the formation of a full-coverage octadecylphosphonic acid (OPA) SAM on a Si wafer substrate, in which the OPA molecules appear to be bonded relatively weakly on the native oxide covering the Si substrate.¹⁴ The OPA molecular chains, however, are closely packed and have a similar orderliness comparable to the well-established octadecyltrichlorosilane (OTS) SAMs on a Si substrate. We report in this letter that the OPA SAM can be selectively removed from the Si substrate by scanning a positively biased tip across the surface of the monolayer because of the nature of the weakly bonded OPA molecular head group on the Si substrate. Our method provides a complementary approach to that of the dip-pen method¹⁵ that directly writes organic molecules including

OPA (Refs. 16 and 17) onto a substrate from an “inked” AFM tip.

An Omicron AFM and a PSIA XE-100 AFM were used to explore the lithographic application of OPA SAMs spin coated on an *n*-type Si (100) substrate cleaned by UV/ozone treatment. The details for preparing OPA SAMs on a Si substrate and clarification of their orderliness and strength have been reported elsewhere.¹⁴ AFM images were obtained in contact mode and imaging forces were nominally several nanonewtons. Cantilevers with a spring constant of 0.1–0.3 N/m and with a conductive probe tip coated by Co–Pt or Ti–Pt were used for the Omicron and the PSIA AFM systems, respectively. Experiments on lithographic applications were carried out in air at room temperature, in which a biased conductive tip was scanned a couple of micrometers on the surface of an OPA SAM on a Si substrate in the *y* direction. Then the bias voltage was set to zero and the same tip was used to collect an image to reveal the patterning.

In Fig. 1(a), a schematic illustration is shown for the lithography configuration of the biased probe tip and the OPA/SiO₂/Si sample systems, in which the polarity of bias voltage is referred to the tip. Shown in Fig. 1(b) is a contact mode AFM image obtained using a tip without metal coating under a small applied force of ~ 2 nN for a partial coverage OPA SAM freshly prepared on a Si substrate, which is used to estimate the thickness of the monolayer (a full-coverage OPA SAM surface would be featureless). Under these careful conditions, the thickness of the monolayer was estimated to be 1.8–2.0 nm, suggesting that the OPA molecules are tilted to the normal of the substrate. A typical profile is also shown in Fig. 1(b).

We conducted experiments of patterning a full-coverage OPA SAM by applying bias voltages of 1, 2, 4, 6, and 7 V to the tip while scanning a line on an OPA/Si sample. As indicated by the inserted numbers in the AFM image [Fig. 2(a)], a bias voltage was applied to the tip under a relative humidity of $\sim 45\%$, while it scanned $2 \mu\text{m}$ in the *y* direction at a fixed *x* position for a couple of scans with a scan rate of 1 Hz. The AFM image shows that there is no apparent change in the OPA surface when the tip was biased at 1–4 V. However, scanning the tip biased at 6 and 7 V on the

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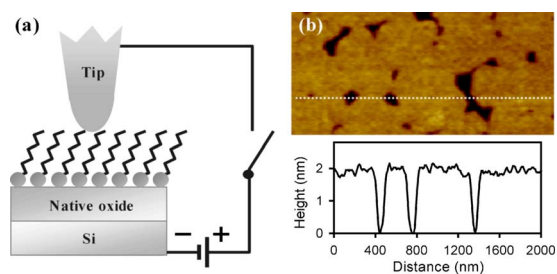


FIG. 1. (Color online) (a) Illustration of applying a positive bias voltage to the probe tip that contacts with the OPA SAM prepared on a Si substrate, in which the OPA headgroup and tail are represented by a circle and a zigzag line, respectively. (b) Topographic image for a partial coverage OPA SAM on a Si substrate for monolayer thickness estimation. Also shown in (b) is a profile isolated from the image (indicated by the inserted dotted line) showing the thickness of the monolayer.

OPA/Si produced a narrow cut having a width of 50 and 80 nm, respectively. The depth of the cuts was estimated to be 1.8–2.1 nm by averaging the depth along the cut. A profile isolated from the image as indicated by the inserted line is also shown in Fig. 2(a). From the depth of the cut patterned by the positively biased tip, it is inferred that scanning a positively biased tip across the OPA SAM results in a removal of the OPA molecules from their monolayer on the Si substrate. The width of the cut may be determined by the size of the tip and the water meniscus, as well as the strength of the electric field applied between the tip and the substrate. As the electric field becomes stronger, the broadening effect of the field at the tip apex is more effective in removing the OPA molecules in the proximity of the tip, thus increasing the width of the cut.

The existence of threshold voltage (6 V) for removing the OPA molecules suggests that the polar interaction between the OPA head group and the Si substrate has to be overcome for molecular removal. Thus, the threshold voltage should be an indicator for the energy needed to remove the OPA molecules from their SAMs, which might be collectively regarded as desorption energy for the removal process. Assuming the electric potential mainly drops at the OPA monolayer and the native oxide layer of the Si substrate,

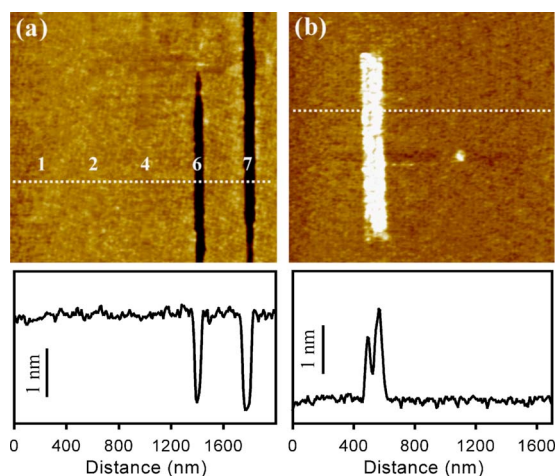


FIG. 2. (Color online) (a) AFM image and a profile showing the threshold voltage for removing OPA molecules from their SAM. The numbers 1, 2, 4, 6, and 7 indicate the bias voltages applied to the tip while it scanned the surface across the y direction at a fixed x position. (b) AFM image and a profile showing possible OPA deposition on a clean Si substrate from a tip used for removing OPA molecules. The experiments were conducted under a relative humidity of 45%.

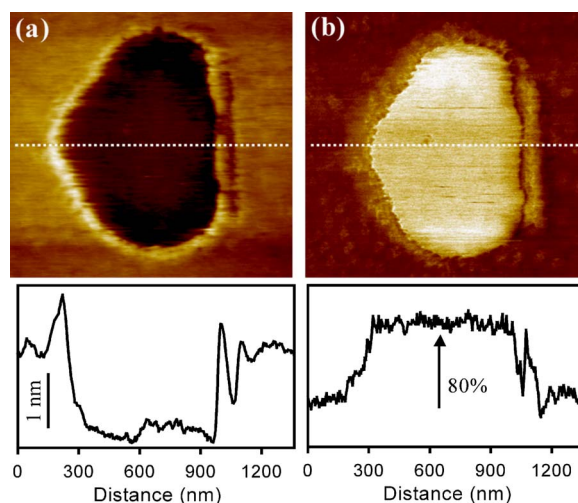


FIG. 3. (Color online) (a) Topographic and (b) lateral force images for making a crater on OPA SAM on a Si substrate by applying a negative bias voltage (-7 V) to the tip under a relative humidity of 50%. Also shown in (a) and (b) are profiles isolated from the topographic and lateral force images (indicated by the dotted lines), respectively. A relative increase of 80% in the lateral force on the crater is indicated by the arrow in the profile in (b).

which were both ~ 2 nm thick, the magnitude of the electric field at the threshold voltage could be on the order of 10^9 V/m. The threshold voltage under relative humidity of 45%–50% was around 6 V when fresh tips were used. However, for used tips, this value often increases, apparently resulting from degradation of the conductivity of the tip, most likely by OPA molecules transported in the patterning process. If this is true, one may be able to deposit the molecules from the tip onto a substrate using the dip-pen approach.¹⁷

To prove this, we scanned, under a relative humidity of $\sim 45\%$, a bare Si substrate cleaned by UV/ozone treatment in the y direction at a fixed x position with a tip used to remove OPA molecules from their SAMs. As shown in Fig. 2(b), this action resulted in a protruding feature on the clean Si substrate. This observation appears to be consistent with the dip-pen writing of OPA molecules on a Si substrate, that is, the OPA molecules on the tip are transported onto a substrate through the water meniscus between the tip and the substrate.¹⁷ Once this feature was formed on the bare Si substrate, scanning the tip on other locations no longer brought any changes on the substrate. The profile isolated from the image in Fig. 2(b) indicated by the inserted line shows the height of the feature being 1–2 nm. It is thus inferred that the protruding feature seen in Fig. 2(b) is due to the deposition of OPA molecules transported from the probe tip. Our experimental observations shown in Fig. 2 thus suggest that the removal of OPA molecules by a positively biased tip is likely dominated by an electrostatic process.

When a negative bias voltage was applied to the tip while scanning it under a relative humidity of 50%, a crater-like feature was created, suggesting a long-distance effect of modifying OPA molecules around the biased tip by the electric field. Shown in Figs. 3(a) and 3(b) are the topographic and lateral force images, respectively, for the surface where it was scanned $1 \mu\text{m}$ long in the y direction and 10 nm wide in the x direction (five scan lines with an interval of 2 nm/line) by a tip biased at -7 V. The crater is ~ 700 nm wide and its depth is estimated to be ~ 1.6 nm in average; a typical profile isolated from the image is also shown in Fig. 3(a). Dependent on the magnitudes and durations of the

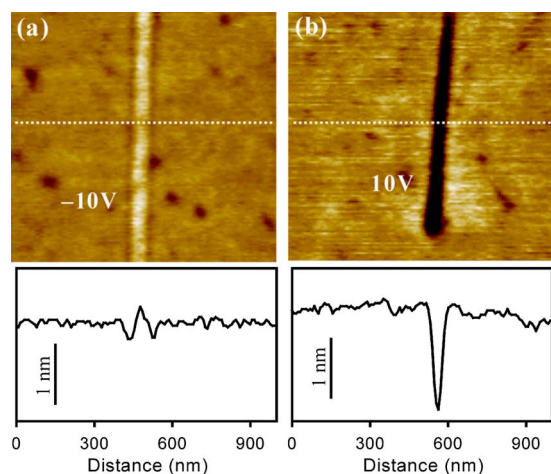


FIG. 4. (Color online) Applying a (a) negative and (b) positive bias voltages to the tip under a relative humidity of 30% result in the formation of a protrusion on the surface and a removal of OPA molecules from the Si substrate, respectively. Note that there are pits in the OPA SAMs. Also shown in (a) and (b) are profiles isolated from the image (indicated by the dotted line).

applied bias voltage, as well as relative humidity, we observed craters showing different sizes both in width and depth. As seen in the profile, though very faint in the image, there is a slightly protruding line in the location where the surface was scanned by a tip biased at -7 V. We found that the height of the protruding line grew higher with increasing bias voltage. This is apparently a result of anodic oxidation of the underlying Si substrate.¹⁻⁵

These particular experiments with a negatively biased tip were carried out in an area just adjacent to a cut produced by a positively biased tip, which is seen beside the right-hand side of the crater. The cut shows a modifying effect on the shape of the crater produced that would be otherwise an oval. The lateral force image and a profile isolated from the image in Fig. 3(b) show a significant increase in the lateral force, suggesting that the crater is highly hydrophilic. We stress that we have confirmed that, under the same conditions that allow the formation of a crater on an OPA/Si surface, no craters have ever been observed on a bare Si or on OTS/Si surface; instead, there are only protruding features (i.e., oxidation) observed.

Humidity of the air has a strong effect on the results for the negative bias voltage experiment. We noticed that the width of the crater was strongly dependent on the relative humidity, indicating that water was highly involved in the crater formation process. The result shown in Fig. 3 was obtained under a relative humidity of 50%. At a lower relative humidity of 30%, as shown in Fig. 4(a), we have confirmed that no apparent crater in the OPA monolayer could be made under the negatively biased-tip scheme. Instead, a protrusion was observed in Fig. 4(a), which may be similar to the oxidation of the SAM/Si system observed and discussed on the system of silane SAMs on Si.⁷⁻¹¹ On the other hand, as shown in Fig. 4(b), at this level of humidity, the positively biased-tip scheme still allows one to remove OPA molecules, resulting in a cut of ~ 40 nm wide and ~ 1.8 nm deep.

We propose a tentative mechanism to explain our experimental observations by assuming that the OPA head group as an entity be negatively charged when weakly bonded to a Si substrate. Therefore, under the positively biased-tip scheme, the negatively charged OPA head groups would be removed

by the tip biased sufficiently to overcome the strength of the polar interaction between the molecular head group and the Si substrate; this results in a well-defined cut feature presenting the removal of OPA molecules [Figs. 2(a) and 4(b)]. The observed threshold voltage for removing OPA molecules may be an indicator for the polar interaction strength between the molecular head group and the Si substrate. On the other hand, under the negatively biased-tip scheme and low humidity, the negatively charged OPA head groups will be pushed onto the Si surface, leaving open an area that would undergo anodic oxidation [Fig. 4(a)]. The resultant oxide would disrupt the previously well-ordered array of OPA molecules. This appears to be similar to oxidation observed for silane SAMs on a Si substrate.⁷⁻⁹ The observed crater formation of OPA molecules under the negatively biased-tip scheme and high humidity (Fig. 3) might be mediated by solvation of the OPA head groups as well as water meniscus. In this case, the OPA head groups have a tendency to move laterally to release the stress produced by the electric field in molecules in the proximity of the tip, causing the adjacent molecules to collapse outward. This hypothesis explains why a cut [Fig. 3(a)] may have an effect of blocking the propagation of the stress that rips the OPA monolayer. Under the negatively biased-tip scheme, both the molecules and the Si substrate are subjected to anodic oxidation. Therefore, we infer that the formation of the observed crater [Fig. 3(a)] probably results from the collapsed and oxidized molecules.

In summary, we have developed a scanning probe based lithographic method to pattern a full-coverage OPA SAM that is weakly bonded on a Si substrate. This is accomplished by scanning a positively biased tip across the surface, with the result of selective removal of OPA molecules from their SAM. It is apparent that, with a weakly bonded OPA head group on a Si substrate, one may build a system for field-assisted patterning of OPA SAMs on a nanoscale.

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