

Surface-Potential Reversibility of an Amino-Terminated Self-Assembled Monolayer Based on Nanoprobe Chemistry

Nagahiro Saito,^{*,†} Sun-Hyung Lee,[‡] Ishizaki Takahiro,[§] Junko Hieda,[‡] Hiroyuki Sugimura,^{||} and Osamu Takai[§]

Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Department of Materials, Physics and Energy Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan, EcoTopia Science Institute, Nagoya University, Furo-cho, Chikusa, Nagoya 464-8603, Japan, and Department of Material Science and Engineering, Graduate School of Engineering, Kyoto University, Yoshida Honmachi, Sakyo-ku, Kyoto, 606-8501, Japan

Received: November 4, 2004; In Final Form: April 13, 2005

Nanoprobe chemistry offers a promising approach for the construction of nanostructures consisting of organic molecules by employing the tip of a scanning probe microscope. In a previous report, we demonstrated that a nitroso-terminated surface on an organosilane self-assembled monolayer could be converted into an amino-terminated surface by applying such a nanoprobe electrochemical technique. This paper reports on surface-potential reversibility originating from a reversible chemical reaction between amino and nitroso groups. In addition, we demonstrate surface-potential memory based on this chemical reversibility. Amino-terminated SAMs were prepared from *p*-aminophenyl-trimethoxysilane through chemical vapor deposition. Surface potentials were acquired by Kelvin force microscopy. When scanning probe lithography was conducted with a gold tip at positive-bias voltages, the surface potential of the scanned area shifted dramatically in the negative direction. Scanning with negative-bias voltages led to positive shift in the surface potential of the scanned area. The surface potential could be recovered even after multiple scanings with positive and negative applied bias voltages. On the basis of this discovery, we also succeeded in demonstrating surface-potential memory via our nanoprobe electrochemical technique.

Introduction

By control of chemical conversion in the nanoscale region, we are able to fabricate various nanofunctional materials. Scanning probe lithography (SPL)^{1–7} is considered to be a promising technique for such chemical conversion. When applied to organic thin films, SPL is usually conducted in order to destroy organic elements below the scanned area. By use of an ultra sharp tip, SPL allows us to fabricate high-resolution patterns. For example, atomic force microscopy (AFM) lithography has been applied to silicon oxides to achieve a lithographic line width resolution of 15 nm.⁸ SPL is based on either electron-beam emission, mechanical scratching, or electrochemical (EC) reactions. EC-SPL is the *softest* of these processes and has the potential to control chemical conversion. In the case of electrochemical conversion using a nanoprobe, the electrochemical reactions which proceed at the probe–sample junction are governed by the applied bias voltage and its polarity. When the substrate is polarized positively, anodic reactions, that is, oxidation reactions, proceed on its surface. On the contrary, when the substrate is polarized negatively, cathodic reactions, that is, reductive reactions, proceed. Many researchers have studied nanolithography based on these electrochemical principles, but there have yet been no reports on the chemical

properties of the scanned areas since it is difficult to analyze such submicro areas. Kelvin force microscopy (KFM), however, can be employed to detect surface-potential changes resulting from chemical conversion.¹⁰

In this study, an amino-terminated self-assembled monolayer (SAM) was chemically converted into an oxidized SAM by SPL at positive-bias voltages. Moreover, this oxidized SAM was then reconverted into an amino-terminated SAM by SPL at negative bias voltages. We examine the chemical changes undergone in the scanned area from the viewpoint of surface-potential reversibility.

Experimental Procedures

Figure 1 schematically illustrates our experiment. An amino-terminated SAM was prepared by chemical vapor deposition (CVD) from *p*-aminophenyl-trimethoxysilane (AphS: H₂N[CH₂]₆NH[CH₂]₃Si[OCH₃]₃) on *n*-type silicon (111) wafers with electrical resistivity of 4–6 Ω cm. First, the silicon substrate was cleaned in acetone, ethanol, and deionized water, in that order. After cleaning, the silicon substrate was irradiated by 172-nm vacuum ultraviolet light in air for 20 min. This removed organic contaminants and introduced silanol groups onto the substrate surface. Next, each cleaned silicon substrate was placed together with a glass vessel filled with AphS liquid in a Teflon container. The Teflon container was sealed and placed in an oven with the temperature kept at 100 °C. The reaction time was 1 h. The heated AphS liquid vaporized and hydrolyzed. The hydrolyzed AphS reacted with the silanol groups on the silicon substrate resulting in the fabrication of an amino-terminated SAM. The

* To whom correspondence should be addressed. E-mail: nagahiro@plasma.numse.nagoya-u.ac.jp.

[†] Department of Molecular Design and Engineering, Nagoya University.

[‡] Department of Materials, Nagoya University.

[§] EcoTopia Science Institute, Nagoya University.

^{||} Kyoto University.

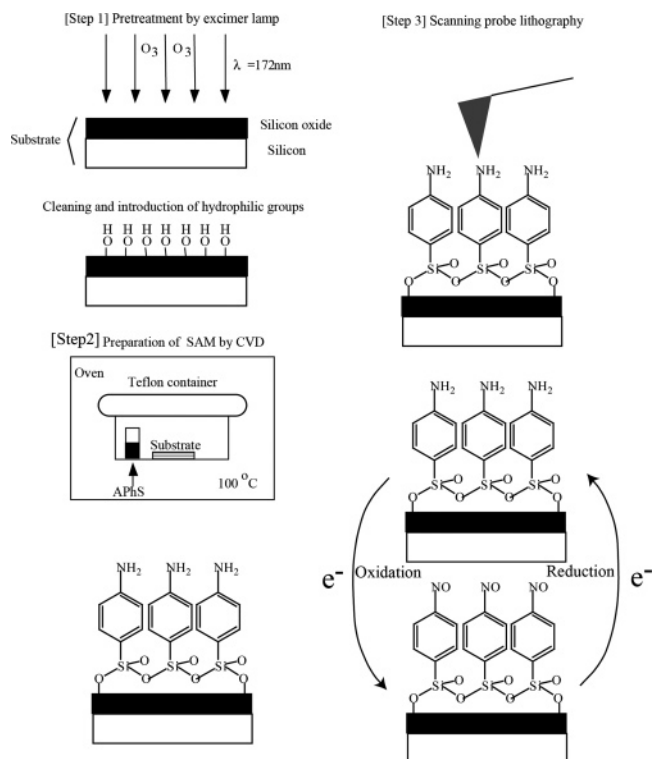


Figure 1. Fabrication and scanning probe lithography of amino-terminated SAMs.

SAMs thus obtained were characterized by X-ray photoelectron spectroscopy (SHIMADZU-KRATOS, AXIS), water contact angle measurement (KULUSS DSA10-MK2), and ellipsometry (PRASMOS-2300). XPS measurements were conducted with an Mg K α X-ray source operated at 10 mA and 12 kV, a pass energy of 10 eV, and an electron takeoff angle of 5°. All binding energies were referenced to bulk Si (2p) at 99.3 eV. Film thickness was measured by ellipsometry.

In our SPL system, electrons were transferred between a gold-coated nanoprobe and the silicon substrate through the APhS-SAM and an adsorbed water layer. The adsorbed water played the same role as water does in a typical, macroscopic electrochemical cell system. The electrochemical conversion was conducted with a gold-coated silicon nanoprobe with a force constant of 1.8 N/m and a resonance frequency of 23.2 kHz. The probe was scanned in air at a relative humidity of 35% to 40%. The sample surfaces were imaged in air by a Kelvin force microscope (Seiko Instruments Inc., SPA-300HV+SPI-3800N) using a gold-coated Si cantilever with a force constant of ca. 1.8 N/m and a resonance frequency of 23.2 kHz. The Q factor of the cantilever was approximately 180. Other conditions of KFM measurements were as follows. The cantilever was vibrated at a frequency of 23.3 kHz. An alternating current voltage of 2.2 V at a frequency of 21.2 kHz was applied between the probe and sample.

To confirm surface-potential reversibility, a nanoprobe scanning series was performed as follows. At first, a 80 μm \times 80 μm square region was oxidized, and a 60 μm \times 60 μm square region in the 80 μm \times 80 μm square region was reduced. Moreover, the 40 μm \times 40 μm square region in the 60 μm \times 60 μm square region was oxidized, and then the 20 μm \times 20 μm square region the 40 μm \times 40 μm square region was reduced. The scan rates were 0.5, 0.7, 1.0, and 2.0 Hz, respectively. By making use of surface-potential reversibility, we demonstrated surface-potential memory. First, a square region 6 μm \times 6 μm was oxidized at the bias voltage of 1 V.

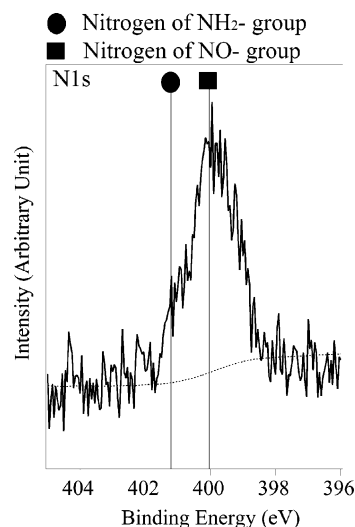


Figure 2. XPS N1s spectrum of the SAM surface prepared through thermal CVD.

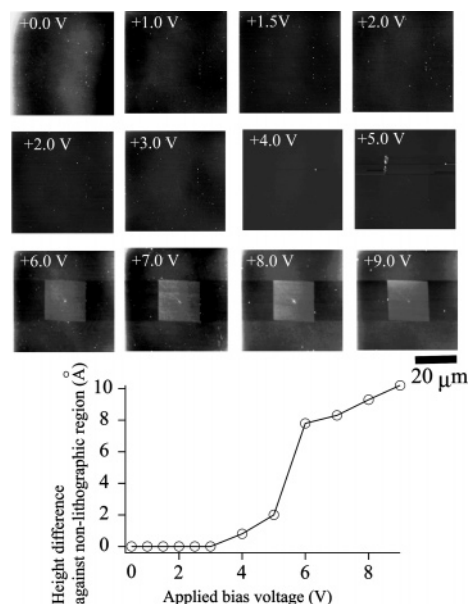


Figure 3. AFM topographic images and the height difference against the nonlithographic region after scanning at positive bias voltages.

Next, dotted areas in the oxidized region were selectively reduced at the bias voltage of -2 V. Finally, the 6 μm \times 6 μm square region was again oxidized.

Results and Discussion

1. SAM Preparation. The static water contact angle of the sample surface after preparation was about 60°. Its film thickness obtained by ellipsometry was ca. 0.58 nm. This thickness was considered reasonable since the chain length of the APhS molecule was estimated to be 0.6 nm by semiempirical molecular orbital calculation using the AM1 Hamiltonian. The XPS N1s spectrum of the sample seen in Figure 2 shows that the N1s binding energy was 399.9 eV. This binding energy agrees approximately with a previously reported value (400.0 eV).¹¹ However, another peak is also observed in this spectrum at around 401.0 eV. This spectrum line corresponds to that of nitroso groups (401.3 eV)¹² and indicates that the amino groups of the precursor might have partly oxidized and converted to nitroso. In short, the presence of nitroso groups is due to the atmospheric thermal CVD process. Thus, to be accurate, some

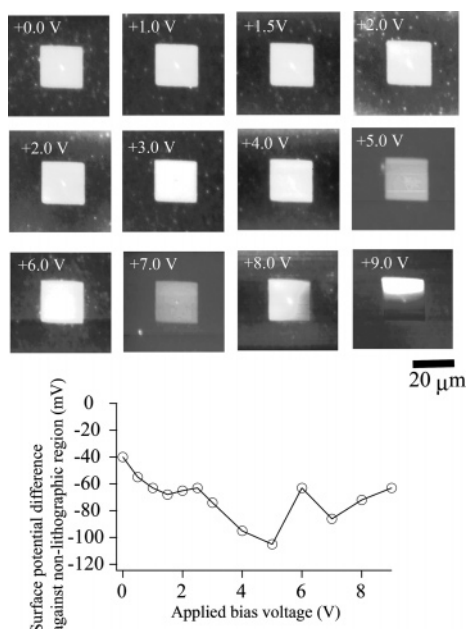


Figure 4. Surface-potential images obtained by KFM and the change in surface potential on the scanned region after scanning at positive bias voltages.

amino groups of the SAM in Figure 2 should be replaced with nitroso groups. Hereafter, for the sake of simplicity, the actual SAM is referred as the as-deposited APhS-SAM.

2. Scanning Nanoprobe Chemical Conversion. The nanoprobe was scanned across the sample surface over an area of $20\ \mu\text{m}$ at bias voltages of 0.5–9 V. Figure 3 shows both AFM topographic images and the height difference against the nonlithographic region after scanning. A slight protuberance can be detected in the topographic images of samples scanned at the bias voltages of 4 and 5 V. This protuberance became much higher at the bias voltages of 6–9 V. These protuberances are due to the production of SiO_2 , which resulted from the decomposition of the as-deposited APhS-SAM and the oxidation of silicon. This demonstrates that there is no possibility of chemical reversibility at these bias voltages since the SAM has been damaged. Specifically, there is no possibility of surface-potential reversibility. On the other hand, no change can be observed in the topographic images of samples scanned at the bias voltages of 0–4 V. At these voltages, it is possible that the framework of the SAM molecules remained intact. Figure 4 shows both surface-potential images obtained by KFM and the change in surface potential on the scanned region. The surface potential shifted negatively, which can be roughly explained by the apparent dipole moment of the SAM.¹⁰ The apparent dipole moment of the untreated APhS-SAM is in the direction from the sample surface to the substrate. On the other hand, the scanned area's apparent dipole moment is in the direction from the substrate to the sample surface, provided that some amino groups in the scanned area were converted to oxidized groups such as nitro or nitroso groups. This can explain the negative shift of the surface potential in the scanned area. The negative shift of the surface potential in the area scanned at the bias voltage of 0 V must be discussed. Under this condition, the surface potential in the scanned area can shift due to the contact potential between the gold-coated nanoprobe and the sample surface. Since the Fermi levels of silicon and gold are 4.85 and 4.20 eV, respectively,¹³ gold electrons transfer to the silicon. This electron transfer led to the oxidation of the amino groups.

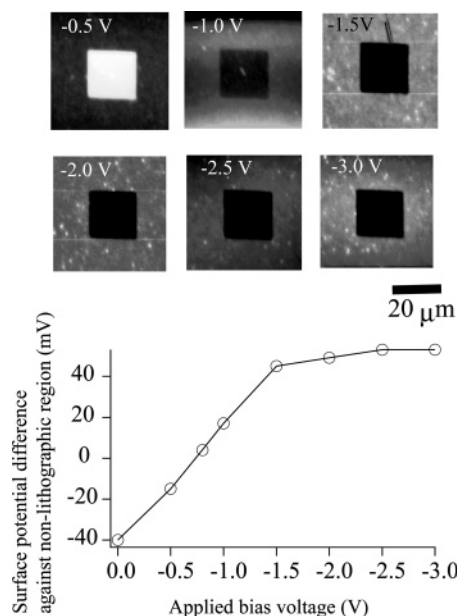


Figure 5. Surface-potential images obtained by KFM and the change in surface potential on the scanned region after scanning at negative-bias voltages.

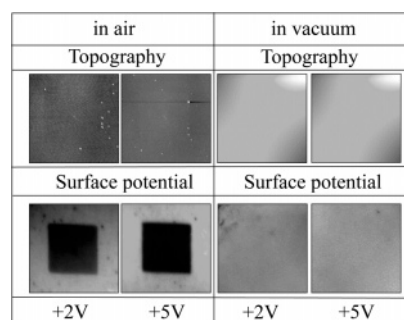


Figure 6. Topographic and surface-potential images scanned at +2 and +5 V in air and vacuum.

To reveal details of the surface-potential shift that occurred near the bias voltage of 0 V, the nanoprobe was scanned at bias voltages from 0 to $-5\ \text{V}$. No changes can be observed in obtained AFM topographic images and the height difference against the nonlithographic region after scanning. Figure 5 shows both surface-potential images obtained by KFM and the change in surface potential on the scanned region. On the contrary, the surface potential in the scanned area became more positive with increasingly negative-bias voltage (Figure 5). This was due to the reduction of nitroso groups. The surface potential did not change at bias voltages more negative than ca. $-2.0\ \text{V}$. The nitroso groups in the as-deposited APhS-SAM were completely converted into amino groups.

3. Effect of Adsorbed Water. To show the effect of adsorbed water, the nanoprobe was scanned at the pressure of $10^{-6}\ \text{Pa}$. Figure 6 shows topographic and surface-potential images scanned at +2 and +5 V in both air and vacuum. On the basis of these images, it is obvious that the chemical reaction did not proceed in a vacuum. Thus, adsorbed water is considered necessary for the chemical conversion to take place.

4. Surface-Potential Reversibility. To confirm surface-potential reversibility, a nanoprobe scanning series was performed, followed by acquisition of a surface-potential image, as seen in Figure 7. The respective regions correspond to (1) oxidized region, (2) reduced region, (3) reoxidized region, and (4) rereduced region. The surface potential reversed with the

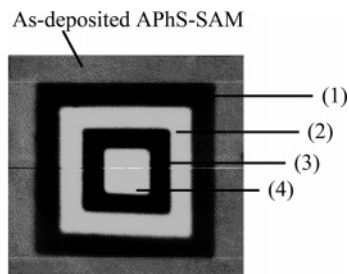


Figure 7. An evidence of surface-potential reversibility through a nanoprobe scanning series.

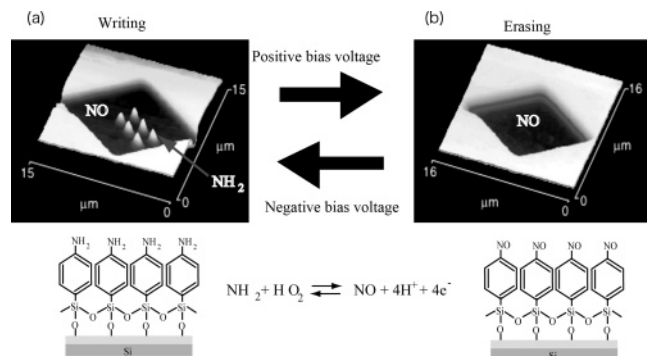


Figure 8. Surface-potential memory: (a) corresponds to memory “writing” while (b) corresponds to “erasing.”

applied bias voltage. Thus, we were able to control the surface-potential reversibility on the amino-terminated SAM by controlling the applied bias voltage.

Finally, by making use of this phenomenon, we demonstrated surface-potential memory. Figure 8 shows the surface potential changes corresponding to (a) “writing” and (b) “erasing.” In Figure 8a, six bright areas corresponding to the chemically

converted region can be observed. These six areas disappeared after “erasing,” as shown in Figure 8b. Although this “surface-potential memory” has not yet been highly integrated, it has the potential to perform as ultraintegrated memory.

We have successfully demonstrated the surface-potential reversibility of an organosilane based on electrochemistry using a nanoprobe. Chemical and surface-potential reversibility was confirmed at the bias voltages of -2 to 2 V. Our results here could be applied to fabricate new high-density reversible memory devices. This scanning probe electrochemistry making use of an SPM tip, an APhS-SAM surface, and adsorbed water allows the nanopatterning of organic molecules with 100-nm scale resolution. Furthermore, our SPL method is expected to enable nanopatterning for the fabrication of specifically designed, spatially arranged molecular assemblies.

References and Notes

- (1) Ross, C. B.; Sun, L.; Crooks, R. M. *Langmuir* **1993**, *9*, 632.
- (2) Snow, E. S.; Campbell, P. M. *Science* **1995**, *270*, 1639.
- (3) Müller, W. T.; Kelein, D. L.; Clarke, J.; McEuen, P. L.; Schultz, P. G. *Science* **1995**, *268*, 272.
- (4) Nyffenegger, R. M.; Penner, R. M. *Chem. Rev.* **1997**, *97*, 1995.
- (5) Piner, R. D.; Zhu, J.; Xu, F.; Hong, S.; Mirkin, C. A. *Science* **1999**, *283*, 661.
- (6) Blackledge, C.; Engebretson, D. A.; McDonald, J. D. *Langmuir* **2000**, *16*, 8317.
- (7) Liu, S.; Maoz, R.; Schmid, G.; Sagiv, J. *Nano Lett.* **2002**, *2*, 1055.
- (8) Saito, N.; Maeda, N.; Sugimura, H.; Takai, O. *Langmuir* **2004**, *20*, 5182.
- (9) Tello, M.; García, F.; García, R. *J. Appl. Phys.* **2002**, *92*, 4075.
- (10) Hayashi, K.; Saito, N.; Sugimura, H.; Takai, O. *Langmuir* **2002**, *18*, 7469.
- (11) Jones, T. S.; Ashton, M. R.; Richardson, N. V.; Mack, R. G.; Unertl, W. N. *J. Vac. Sci. Technol., A* **1990**, *8*, 2370.
- (12) Batich, C. D.; Donald, D. S. *J. Am. Chem. Soc.* **1984**, *106*, 2758.
- (13) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 80th ed.; CRC Press: Boca Raton, FL, 1999–2000.