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Pattern Formation through Selective Chemical Transformation of Imine Group of Self-Assembled Monolayer by Low-Energy Electron Beam

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Introduction

In recent years much attention has been given to micro- and nanofabrication technology,[1] owing to the active application in various fields such as microelectronics,[2] biotechnology,[3] microanalysis,[4] sensors,[5] and so forth. The patterning required in the nanofabrication is usually carried out with the photolithographic method employing deep UV radiation.[6] However, the conventional photolithography is now facing a resolution limitation due to the wavelength of the light source. Therefore, irradiation with a shorter wavelength, utilizing extreme UV,[7] X-ray,[8] ion beam,[9] or electron beam,[10] has been progressively introduced to generate structures with smaller feature size. In particular, focused electron beam lithography[11] and electron projection lithography[12] have recently been widely used as versatile lithographic tools, because they are techniques for creating extremely fine patterns. Moreover, the latter method boasts parallel processing.

To fabricate a surface patterned at the molecular length scale, it is necessary to transform functional groups on the surface in a controlled manner with nanometer resolution. The feature size from electron beam lithography would be further downsized if thinner resist materials could be employed and the proximity effect could be avoided.[13] It is natural to regard a self-assembled monolayer (SAM) as an advanced material suitable for the ultrahigh-resolution electron beam patterning, because the SAM has a low defect density and its terminal functionality can be controlled at the molecular level.[14] Furthermore, use of a low-energy electron beam turns out to be effective with SAMs not only because low-energy electrons transfer their energy selectively to the top surface of the materials[15] but also because the proximity effect is minimized. On top of these merits, the high throughput efficiency of the process is a critical advantage over the focused e-beam lithography.[11] Also, recently characterized selective reactions with low-energy electron irradiation widen the window of choice.[16]

Thus, the chemoselective process efficiently promoted by the low-energy electron irradiation is crucial for the successful nanopatterning. Previously, other groups and we reported that the nitro group of aromatic monolayers was reduced to an amine group by irradiation with low-energy electrons.[11,16,17]

In this Note, we present an alternative path to create patterns by 500 eV electron projection lithography with novel self-assembling materials. We generated the patterns by transforming an imine group of an aromatic monolayer with the electron beam. In contrast to the previous methods, the reactive amine group is generated at the *unirradiated* region.[16] We compared the current methodology with the irradiation of a 4-nitrobenzamide monolayer in which a reactive amine group is generated at the irradiated region.

Experimental Section

General. The silane coupling agent (3-aminopropyl)diethoxymethylsilane was purchased from Gelest Inc. 4-Nitrobenzoic acid and benzaldehyde were purchased from Aldrich Chemical Co. Succinimidyl-6-(biotinamido)hexanoate (LC-NHS-biotin) was purchased from Molecular Probes. Streptavidin−Cy3 conjugate and bovine serum albumin (or BSA) were purchased from Aldrich Chemical Co. Aziridine was synthesized as described in the literature.[18,19] UV-grade fused silica plates were purchased from CVI Laser Co. The polished prime Si(100) wafers (dopant, phosphorus; resistivity, 1.5−2.1 Ω·cm) were purchased from MEMC Electronic Materials Inc. Deionized water (18 MΩ·cm) was obtained by passing distilled water through a Barnstead E-pure 3-Module system. Thickness was measured with a variable angle ellipsometer (model M-44) from J. A. Woolam Co. Surface FT-infrared spectra were recorded using a Bruker IFS 66v FT-IR spectrometer equipped with an MCT detector and an A513 variable angle reflection accessory. The sample was prepared on a gold substrate to obtain the best IR spectra. Self-assembly of 11-amino-1-undecanethiol was utilized to generate the terminal amine group on the gold substrate. Copper TEM grid (type G2150C, 1000 mesh) was purchased from Agar Scientific

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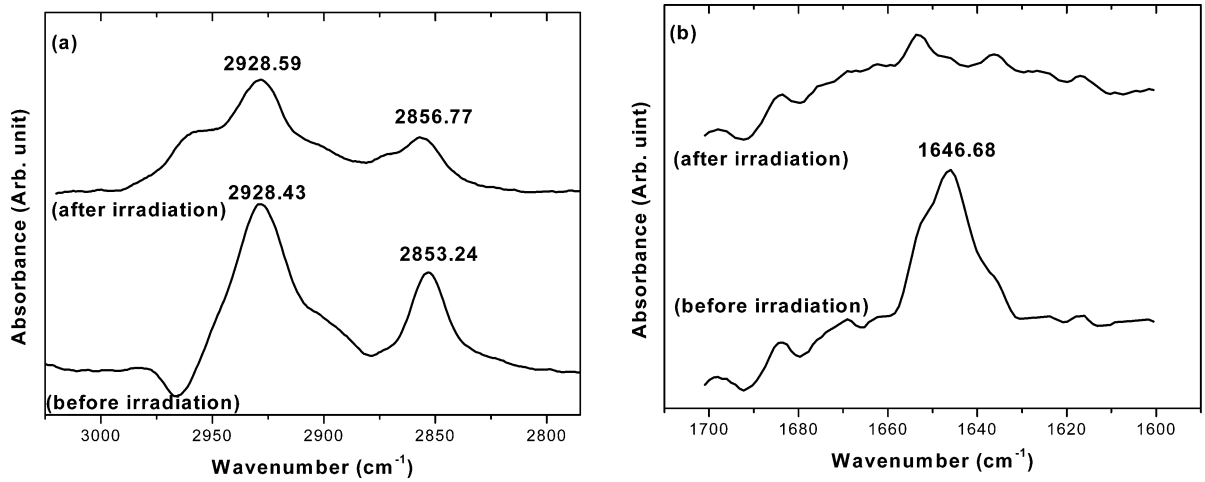
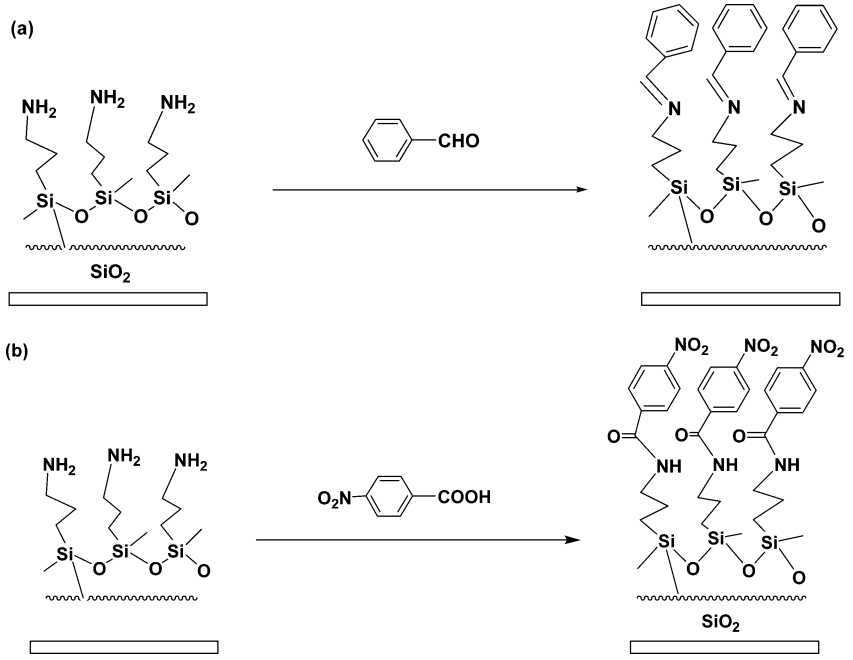


Figure 1. FT-IR spectra of benzaldimine monolayer on a gold substrate. Each spectrum is obtained before and after the irradiation by a low-energy electron beam (500 eV, 0.32 μA/cm^2). (a) Stretching vibration of the CH_2 group. (b) Stretching vibration of the C═N group.

Scheme 1. Formation of (a) Benzaldimine Monolayer and (b) 4-Nitrobenzamide Monolayer



(England). Fluorescence images were examined with a Zeiss Axioplan 2 microscope with a superpressure mercury lamp (Carl Zeiss) and filter sets for Cy3 fluorescent dye (Omega Optical). Images were collected by a high-resolution Axiocam color camera (Diagnostic Instruments, Inc.). AFM images were obtained by using a Nanoscope IIIA AFM (Digital Instruments) equipped with a "J "scanner. Data were acquired in the tapping mode and analyzed by using Digital Instruments software. Electron exposure was performed by using a LEG63 electron gun system (VG Microtech.) in an ultrahigh vacuum (UHV) chamber of a Pohang synchrotron beamline. The monolayer was irradiated with an electron beam of 500 eV with a current density of 0.32 μA/cm^2 (0.08 μA beam current, 5 mm × 5 mm beam size). The total dose of the electron irradiation was estimated by multiplication of the current density and the exposure time (8 min).

Preparation of Benzaldimine Monolayer. An aminosilylated substrate was immersed in anhydrous ethanol solution (25 mL) dissolving benzaldehyde (10 mg) under a nitrogen atmosphere at 50 °C for 12 h. The reaction flask was wrapped with aluminum foil to avoid the room light. The substrate was then sonicated for 1 min in methanol, dichloromethane, and acetone, sequentially. Finally, the substrate was dried under vacuum.[20]

Preparation of 4-Nitrobenzaldimine Monolayer. An aminosilylated substrate was immersed in *N*,*N*-dimethylformamide (or DMF) solution dissolving 4-nitrobenzoic acid (0.020 M) and 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (or EDC, 0.020 M) as a coupling reagent for 12 h.[21] The substrate was then sonicated for 3 min in methanol, dichloromethane, and acetone, sequentially. Finally, the substrate was dried under vacuum.

Hydrolysis of the Irradiated Benzaldimine Substrate. The irradiated substrate was dipped into 0.20% aqueous acetic acid and heated at 30 °C for 1 h for the hydrolysis. After the reaction, the substrate was sonicated for 1 min in water and methanol, sequentially. Finally, the sample was dried under vacuum.

Reaction of Aziridine on the Patterned Surface. The patterned monolayer was immersed in dichloromethane solution (15 mL) dissolving aziridine (0.15 mL) and a catalytic amount

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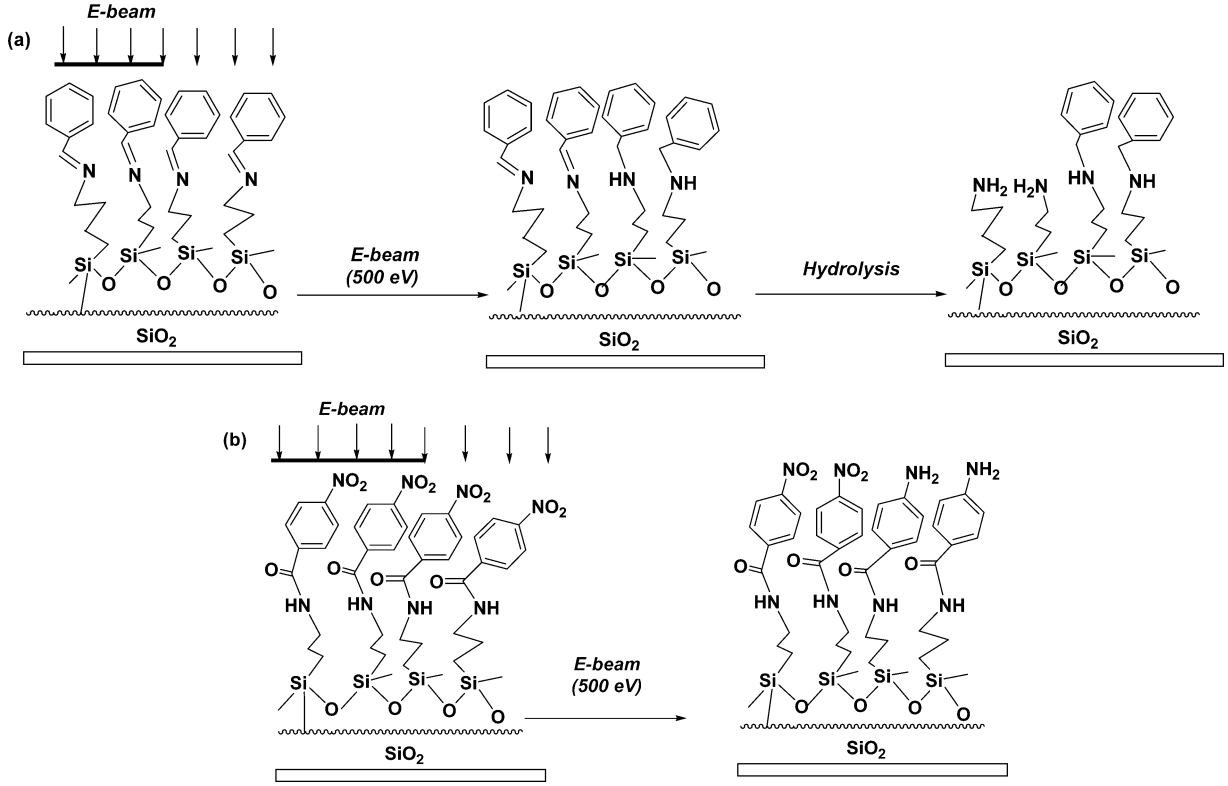
Scheme 2. Transformation of (a) Benzaldimine Monolayer and (b) 4-Nitrobenzamide with a Low-Energy Electron Beam (500 eV, 0.32 μA/cm^2)



of acetic acid. *(Caution: Aziridine is toxic, carcinogenic, and teratogenic. Use only in a well-ventilated hood).* The heavy wall glass tube having a large Teflon screw cap was used as reaction container and heated at 80 °C for 20 h. The resulting substrate was then sonicated for 5 min in methanol, and the sonication was repeated with new methanol. Finally, the substrate was dried under vacuum.[22]

Immobilization of Biotin on the Patterned Surface and Binding of Streptavidin. The patterned monolayer was treated for 12 h with a solution of succinimidyl-6-(biotinamido)hexanoate (LC-NHS-biotin) (6.0 mM) dissolved in sodium bicarbonate buffer (55 mM, pH 8.5). (The solution was prepared by dissolving 2.0 mg of succinimidyl-6-(biotinamido)hexanoate (LC-NHS-biotin) in DMF (0.10 mL) and then diluting 10-fold with the buffer.) After the reaction, the substrate was placed in a washing solvent (~100 mL) for 1 h with stirring. DMF, THF, 2-propanol, MBST buffer (consisting of 50 mM MES, 100 mM NaCl, and 0.10% Tween-20; pH 6), and deionized water were employed sequentially as the washing solvents and dried under vacuum. The substrate was then exposed to bovine serum albumin by placing the plate in an MBST solution dissolving 3.0% BSA for 1 h. After the blocking, the substrate was washed with MBST. Subsequently, the blocked substrate was dipped into a stock solution of Cy3 tagged streptavidin (3−9 tags per streptavidin) in MBST buffer dissolving 1.0% BSA for 30 min. After the binding, the substrate was washed with MBST buffer and dried under vacuum.[23]

Results and Discussion

The benzaldimine monolayer and 4-nitrobenzamide monolayer used in this study were prepared by treatment of the aminosilylated silicon wafer with benzaldehyde and 4-nitrobenzoic acid, respectively, under nitrogen atmosphere (Scheme 1).[20,21] The thickness increase upon the formation of the aromatic layers was 5−6 Å.

Pattern Formation using a Benzaldimine Monolayer. The benzaldimine monolayer was exposed to an

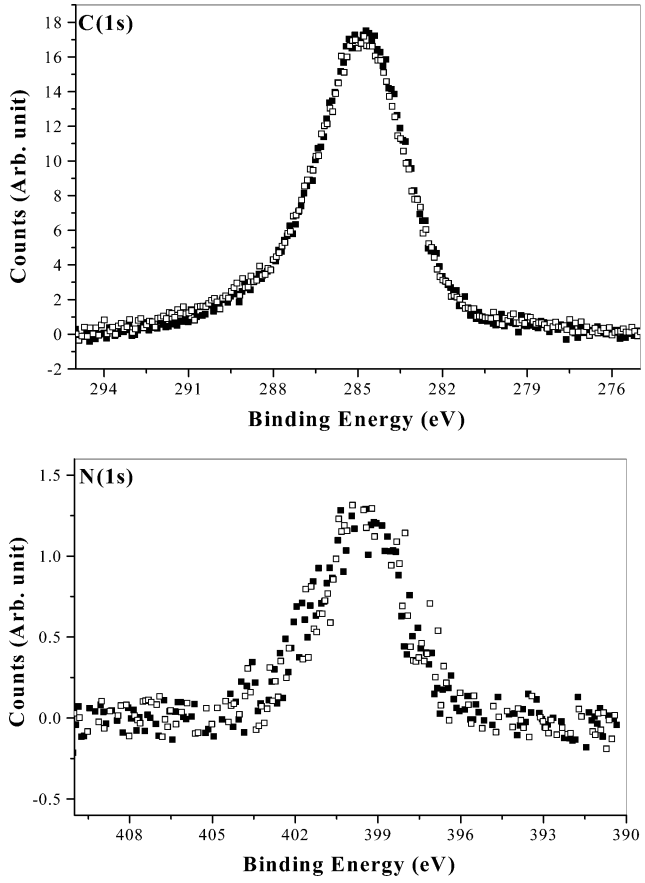


Figure 2. XPS spectra of benzaldimine monolayers on a silicon wafer. Each spectrum is obtained before (■) and after (□) the irradiation by a low-energy electron beam (500 eV, 0.32 μA/cm^2).

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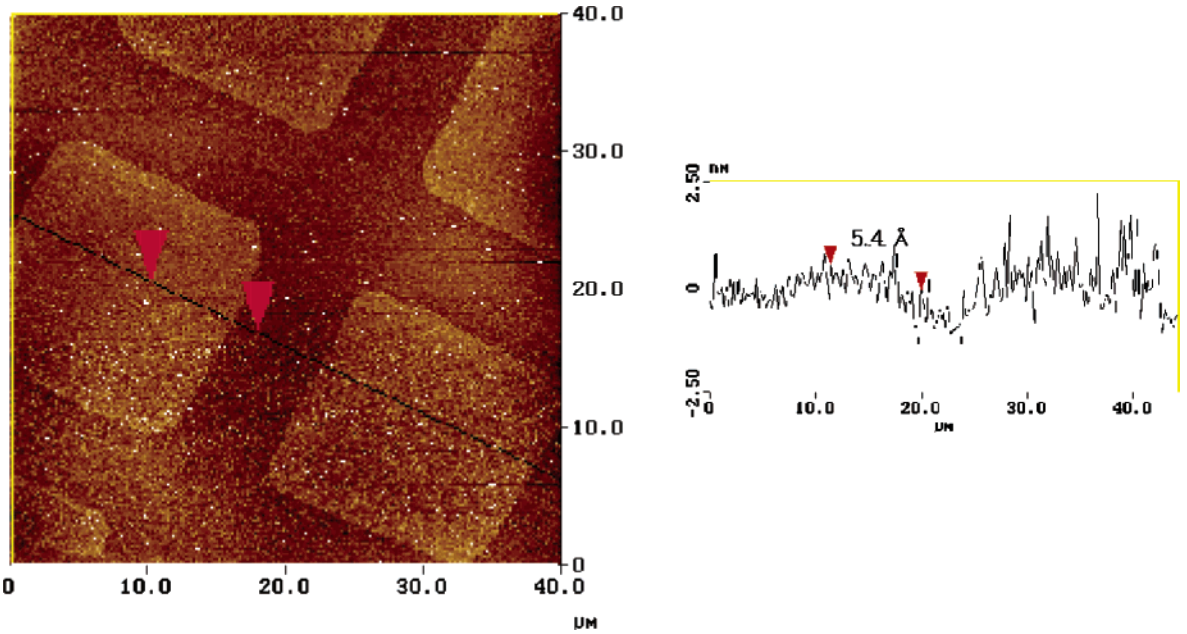


Figure 3. AFM topographic image of the patterned benzaldimine monolayer on a silicon wafer. At the dark region of the above image there are amine groups recovered from the hydrolysis (scan size: 40 μm × 40 μm).

electron beam of 500 eV, and the induced chemical transformation was examined with FT-IR spectrometry and X-ray photoelectron spectrometry (XPS). Figure 1 shows FT-IR spectra of the benzaldimine monolayer before and after the irradiation. FT-IR spectra show that the CH_2 stretching peaks of the alkyl chain at 2928.43 and 2853.24 cm^{-1} decrease, and their positions slightly shift to higher frequencies, in addition to their peak broadening (Figure 1a). Loss of hydrogen by the cleavage of the C−H bond and disordering of the monolayer during the irradiation could explain the change. Most significantly, the C═N stretching peak of the imine group at 1646.68 cm^{-1} entirely disappears after the electron beam irradiation (Figure 1b). The spectral analysis indicates that the imine functionality is transformed into a new chemical species, presumably with the concomitant C−H bond cleavage of neighboring alkyl groups. XPS was utilized for analyzing the change of carbon and nitrogen atoms involved in the transformation. Figure 2 shows the XPS peaks of C(1s) and N(1s) for the benzaldimine monolayer. The filled squares (■) were obtained before the electron beam exposure, and the open squares (□) were recorded after the electron beam irradiation for 8.0 min (0.32 μA/cm^2). In Figure 2, no change is noticeable in terms of shape and intensity. This observation supports the idea that the carbon and nitrogen atoms of the molecular layer are not eliminated during the electron beam irradiation. Moreover, the constant shape and intensity strongly support the idea that the aromaticity of the phenyl group is maintained during the irradiation. However, the spectroscopic method is not diagnostic to detect the particular change of the nitrogen atom indicated from FT-IR spectrometry. Inherent overlap of N(1s) peaks for the imine and the expected amine group is problematic for the analysis. Also, XPS is not sensitive to the expected hydrogen abstraction and cross-linking between the alkyl groups.

These FT-IR and XPS analyses indicate that the C═N group is transformed into a new functionality, most likely into the amine group, that is, a nonhydrolyzable one, whereas the other regions of the benzaldimine monolayer without the electron beam irradiation are intact and the hydrolysis restores the surfaces of amine functionality

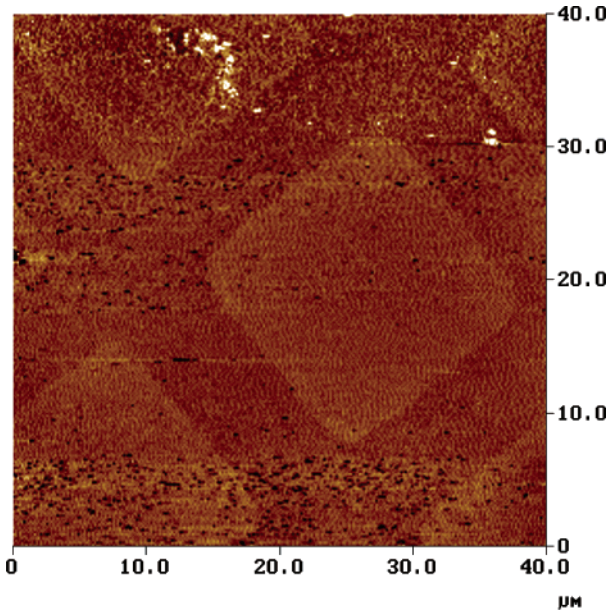


Figure 4. AFM phase image of the patterned 4-nitrobenzamide monolayer on a silicon wafer. At the bright region of the image there are amine groups generated from the reduction of a nitro group (scan size: 40 μm × 40 μm).

(Scheme 2a). The secondary amine shown in Scheme 2a represents a hypothetical functional group that is most likely to be formed as a result of the imine transformation in this system. Using the selective chemical transformation of the imine group by the electron beam irradiation, we were able to generate a pattern. To generate the pattern on the surface, the benzaldimine monolayer on a silicon wafer was exposed to a low-energy electron beam (500 eV, 0.32 μA/cm^2). The beam was passed through a TEM grid that is placed at 2 μm away from the surface by using a spacer. A copper TEM grid (1000 mesh) was used as the mask. After the irradiation, sample was hydrolyzed in deionized water containing a catalytic amount of acetic acid. As mentioned above, the hydrolysis restores the reactive amine functionality of the unirradiated region, which is one of the key chemical features of the system.

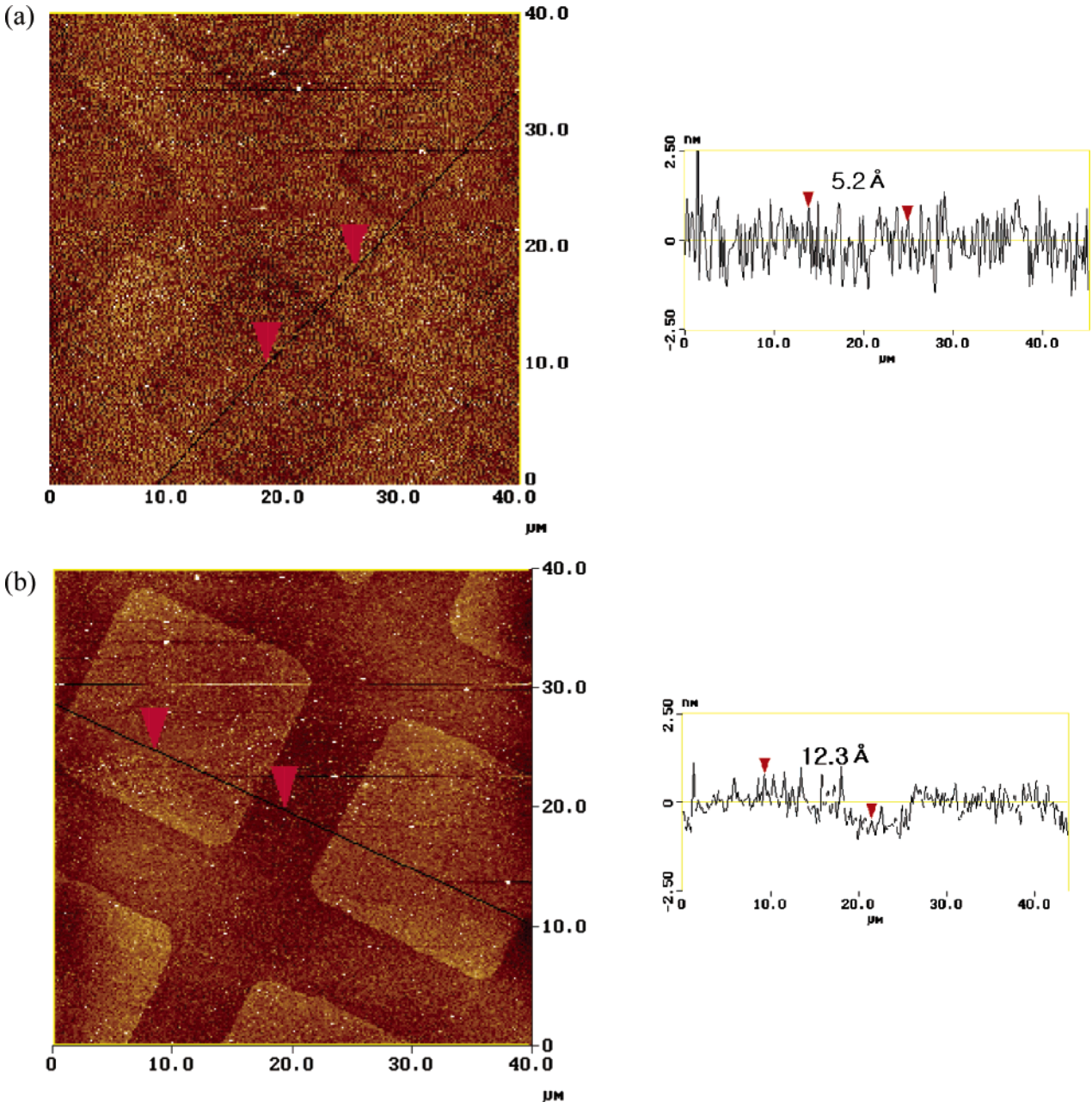
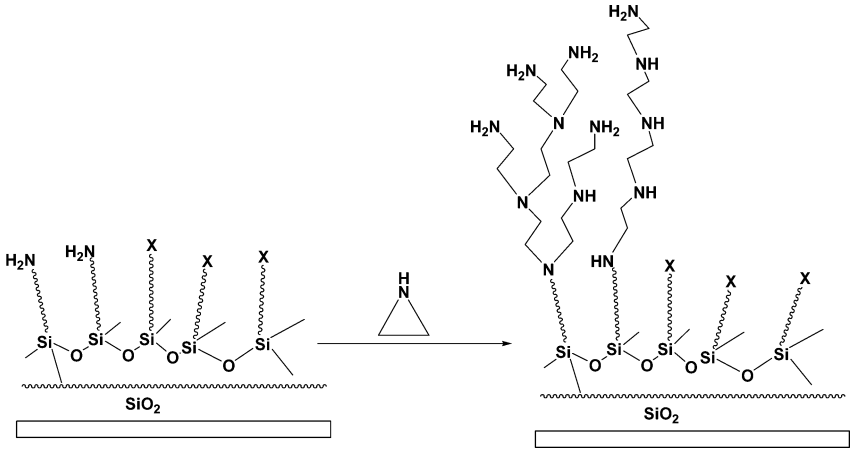
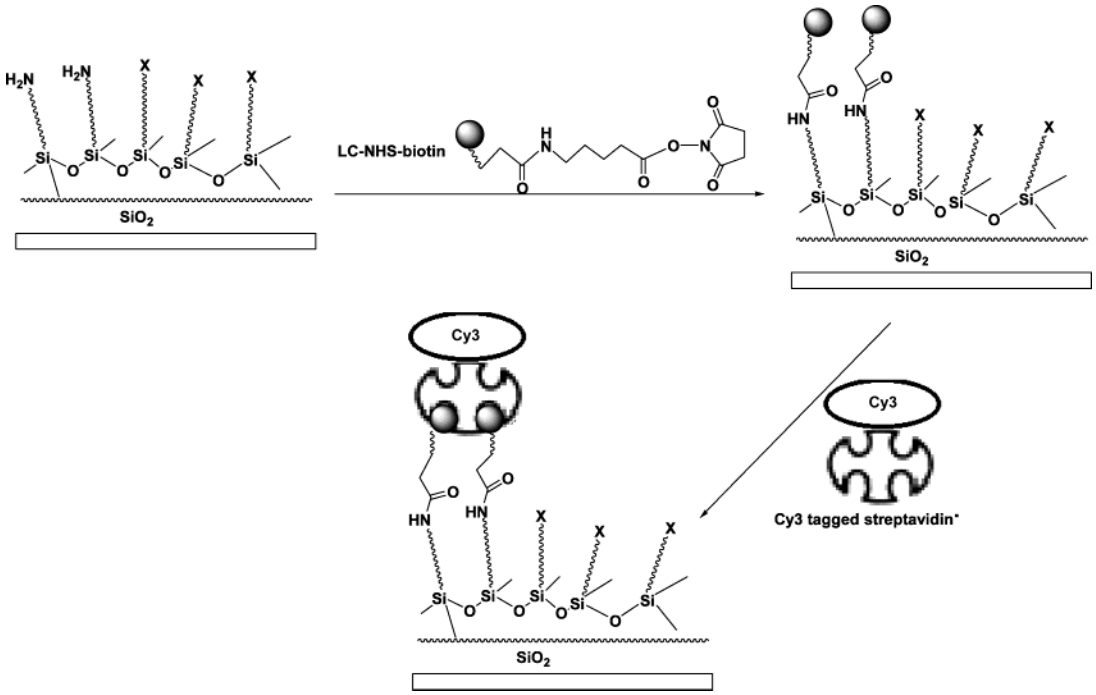


Figure 5. AFM topographic images of the patterned surface after the aziridine treatment. The reaction of aziridine with the amine group increases the thickness of the organic layer. The bright region of the images represents the thicker part. (a) Benzaldimine monolayer (scan size: 40 μm × 40 μm). (b) 4-Nitrobenzamide monolayer (scan size: 40 μm × 40 μm).

Scheme 3. Reaction of Aziridine on the Patterned Surfaces (X Symbolizes Either Phenyl Group or Nitro Group)



Scheme 4. Selective Binding of Streptavidin through the Immobilized Biotin on the Patterned Surface



The height variation after the hydrolysis between the two different regions should be associated with the height of the phenyl ring. An AFM topographic image shows that the height difference between the exposed (bright) and the unexposed (dark) regions is 5−6 Å, which is well coincident with the height of the phenyl ring (Figure 3).

Pattern Formation Using a 4-Nitrobenzamide Monolayer. For comparison, similar patterning was performed on the 4-nitrobenzamide monolayer. Previously, we reported selective reduction of a nitroaromatic group promoted by electron beam irradiation.[17] Under the circumstance, the nitro group is converted into the amine group, while the underlying organic layer is dehydrogenated and cross-linked (Scheme 2b). With a proper mask, a pattern formation on the 4-nitrobenzamide monolayer is easily imagined. In the exposed region, the nitro group is converted into the amine group; meanwhile, the nitro group is intact in the unexposed region. Therefore, a pattern with the alternating functionality is generated. Figure 4 shows a phase image measured by AFM. The phase difference between the exposed (bright) and the unexposed (dark) regions is evident in Figure 4. At the dark (unexposed) region the grid protected the nitro group, and the electron beam irradiation generated the amine group at the bright (exposed) region.

Reactivity of the Amine Group on the Patterned Surfaces. To examine whether the amine group on the patterned surfaces is still reactive, the patterned surfaces were treated with aziridine. Previously, we reported that the primary amine on the substrate was reactive enough to initiate the ring opening polymerization of aziridine and then the thickness of the film increased more than 10 Å due to the reaction (Scheme 3).[22] Parts a and b of Figure 5 are AFM topography images of the patterned and aziridine-treated benzaldimine monolayer and 4-nitrobenzamide monolayer, respectively. For the benzaldimine monolayer, the lower part of the surface became higher because of the selective polymerization from the amine group. Given the height difference of 5 Å before and after the polymerization and the inversion of the topological contrast, the total thickness increase is about 10 Å. On the other hand, there was no height difference

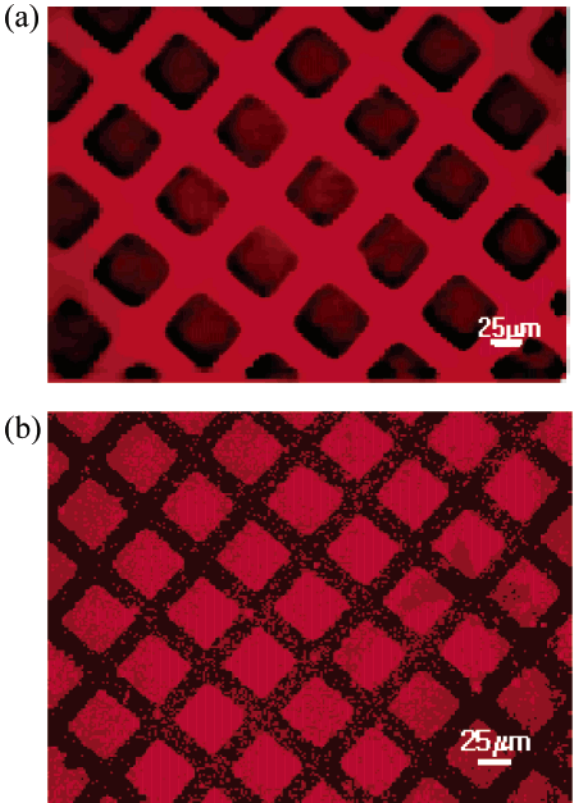


Figure 6. Fluorescence images of the patterned surfaces that bind selectively Cy3 tagged streptavidin. The bright red color of the images is from the tagged streptavidin bound to the immobilized biotin. (a) Benzaldimine monolayer. (b) 4-Nitrobenzamide monolayer.

before the polymerization for the 4-nitrobenzamide monolayer; an increase of 12 Å was observed after the polymerization. These observations clearly demonstrate that the amine group on the patterned surfaces retains its reactivity.

Immobilization of Biotin and Binding of Cy3-Tagged Streptavidin on the Patterned Surfaces. We

examined whether the patterned surface is suitable for the template for the selective immobilization of biomolecules. The patterned monolayer is treated with biotin and streptavidin having Cy3 fluorescence tags in a sequential manner (Scheme 4).[23] Parts a and b of Figure 6 show fluorescence images of the streptavidin bound on the patterned and biotin immobilized benzaldimine monolayer and 4-nitrobenzamide monolayer, respectively. For the benzaldimine monolayer, the unexposed region with the restored amine functionality through the hydrolysis appears bright (light red color), while the exposed region with the amine functionality generated through the nitro group reduction appears bright (light red color) for the 4-nitrobenzamide monolayer. As seen in Figure 6, the contrast is higher for the benzaldimine case, but the line width of the pattern is narrower for the 4-nitrobenzamide case. Also, it is worthwhile to note that the fluorescence intensity of the bright region is stronger for the former case. The high fluorescence intensity, that is, the high immobilization efficiency, reflects the fact that the amine density from the hydrolysis is larger than that generated from the nitro group reduction. These observations clearly confirm that the new approach for the patterning is as effective as the conventional method, that is, the nitro group reduction with an electron beam. Also, the inversed contrast in the fluorescence image clearly shows that the new methodology is *complementary* to the conventional approach. In other words, the selected biomolecules can be bound on the *unirradiated* region with the new methodology. The two approaches that are complementary to each other are expected to find many applications for high-density biochips, miniaturized biosensors (or chemical sensors), and labs-on-a-chip.

Conclusion

Chemical transformation of the imine group of the benzaldimine monolayer was observed when low-energy electron beam irradiation was used. The reactivity of the restored amine group at the unexposed region is confirmed. The characteristic reaction caused by the electron beam was applied successfully for the patterning of the surface. It is found that the new method is as effective as the e-beam induced nitro group reduction in terms of the resolution and the immobilization efficiency. Considering the parallel processing nature, the new approach in combination with the conventional one is expected to find many applications in fabrication of miniaturized devices and related areas.

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