Fabrication of Nano-structure by Diels–Alder Reaction

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A dip-pen nanolithography was applied to Diels–Alder reaction and fabricated nano-lines made of organic molecules.

Atomic force microscopy (AFM) ‘‘dip-pen’’ nanolithography has exhibited promising methods for fabrication of nanostructures on a surface.[1] The method uses an AFM tip as a deliverer of the molecules to put them on the surface under precise control.[2] The fixation of these molecules on the surface, that relates directly to the long-term stability of the constructed nanostructure, mainly depends on affinity between them; most of them use a coordination of thiols to Au surface.[3] A method that is based on electrochemical reaction has also been reported with consideration for the stable fixation.[4] To obtain the more stable structure, the construction would be better performed with concomitant formation of covalent bonds. A method to stick a flat unimolecular film of organic compounds on the surface of an inorganic material with covalent bonds is already known.[5] If dip-pen lithography was related with a C–C bond forming organic reaction with such organic material film, it would be promising for fabrication of an immobilized nano-structure.

The condition at the edge of the tip as a nib is not so mild as constant force is added on a nano-spot during the scanning. The spot at the tip on the film during scanning looks like a nano-scale reaction vessel filled with a neat substrate (a film) and a neat reactant (a compound on the tip) under high pressure;[6] it seems to be suitable for Diels-Alder reaction.[7] We would like to describe herein an organic C–C bond forming reaction with a dip-pen nanolithography technique (Figure 1).

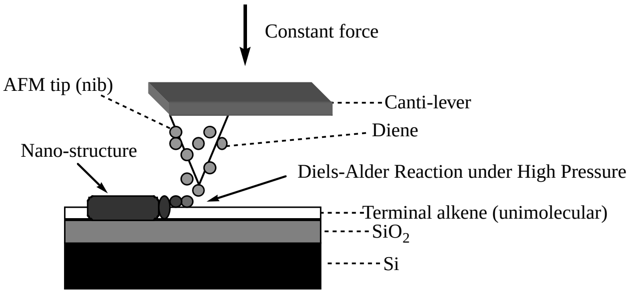

Figure 1. Schematic sketch of the Diels–Alder reaction with a dip-pen.

As the unit reaction, a reaction between 1-undecene and a furan derivative was chosen (Figure 2). The alkenes were lined up regularly on an SiO_2 face like an LB-film at the time of unimolecular film preparation.[8] A thermally oxidized silicone wafer with a flat surface, which is commercially available, was used for the reaction. It was covered with a thin layer of SiO_2, the thickness which was evaluated at 8.2 nm by XR measurement.[9] The roughness of the surface was evaluated at 0.96 nm (Rms, $1.0 \times 1.0\,\mu m^2$) by AFM measurement. A unimolecular film was attached by treatment of the silicone surface with triethoxy(10-undecenyl)silane following the reported procedure.[5] The thickness of the film on the wafer was evaluated at 1.1 nm by XR measurement that was consonant with a unimolecular film. The roughness of the surface was evaluated at 0.10 nm (Rms, $1.0 \times 1.0\,\mu m^2$).

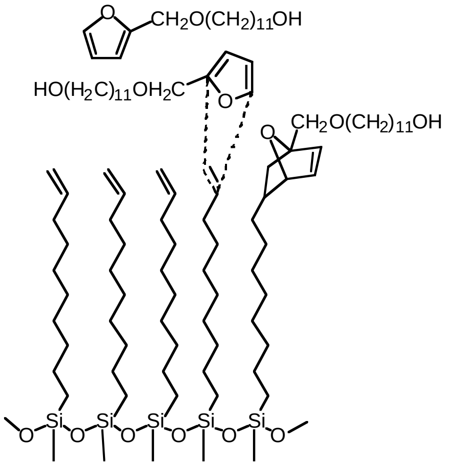

Figure 2. Diels–Alder reaction on the alkene surface.

The surface of the unimolecular film that was covered with a terminal alkene group was scratched with a tip covered with a diene. The AFM tip was dipped into a neat liquid of 2-(13-hydroxy-2-oxatridecanyl)furan[10] and brought close to the flat unimolecular film of alkene on the silicone wafer following a conventional AFM contact mode measurement. Three areas (100 nm × 100 nm) were scanned on 500 nm × 500 nm stage. The first area was scanned with 8 nN (site A in Figure 3, scanning speed 0.1 μm/s); the second one was scanned with 32 nN (site B in Figure 3, scanning speed 0.1 μm/s); the third one was scanned with 64 nN (site C in Figure 3, scanning speed 0.1 μm/s). After the scanning on the three different areas, the immobilized sites were observed by AFM contact mode by scanning the whole area (8 nN, 1 μm/s) on each area as shown in Figure 3. As shown in Figure 3, the height of the site A was 9.4 nm; that of the site B was 1.5 nm; that of site C was 10.4 nm. At the first approach of the tip, an excess drip from the dipped tip was transferred to the surface. After removal of such drip, the second approach gave a structure with a reasonable height (site B). The high pressure at the nib of the tip may also raise oligomerization of the furan and form a site with the rather bigger structure (site C). This result implies 32 nN is adequate for the performance of the nanolithography. The same procedure was repeated on an alkane film that was prepared from a silicone wafer (thermally oxidized) and trimethoxyundecanylsilane. On this surface, no C–C bond formation could happen. The

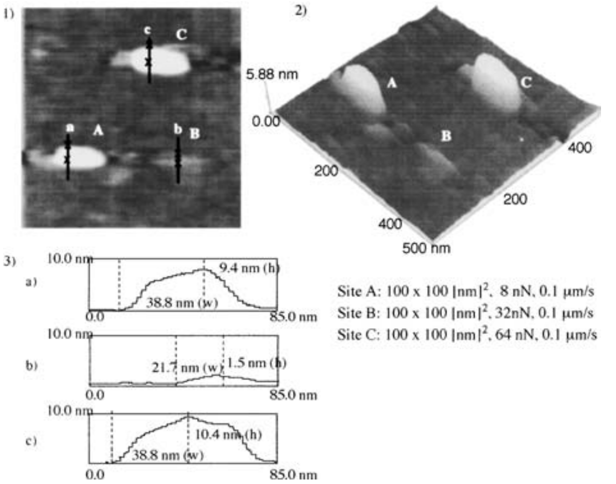

Figure 3. The Diels–Alder reaction on three sites ($100 \times 100\,[\mathrm{nm}]^2$). Reactions on three sites with a different force (8 nN, 32 nN, 64 nN). 1) $500 \times 500\,[\mathrm{nm}]^2$ topological image after the site forming Diels–Alder reaction (left); 2) its 3D image (right). 3) Profiles line a, b, c (85 nm length).

diene was adhered on the film at the beginning, but the sites were distorted and scattered during the repeated AFM contact mode measurement (8 nN, 1 μm/s). This observation implies that the former nanolithography on alkene surface with diene did give an immobilized line via chemical reaction, Diels–Alder reaction, while only adherence force (the latter case, alkane–diene) cannot do it.

The method was applied for nano-line writing. As shown in Figure 4, three lines were constructed. The dipped tip was scanned with 32 nN (scanning speed 0.2 μm/s) for the line shape area (1000 nm × 12 nm). This scanning was repeated three times with 200 nm interval. The first line (line A) has an exceptionally higher wall. This was also considered to result from the transfer of an excess amount of drip on the tip.[11] After the transfer of the drip, the two line shaped nanostructures were constructed like a parallel wall with a unimolecular height (2.5 nm).

The method is based on the Diels–Alder reaction. It provides a simple method to construct a nano-line and a nano-site which contain hetero-atoms regularly on the flat hydrophobic alkene face.

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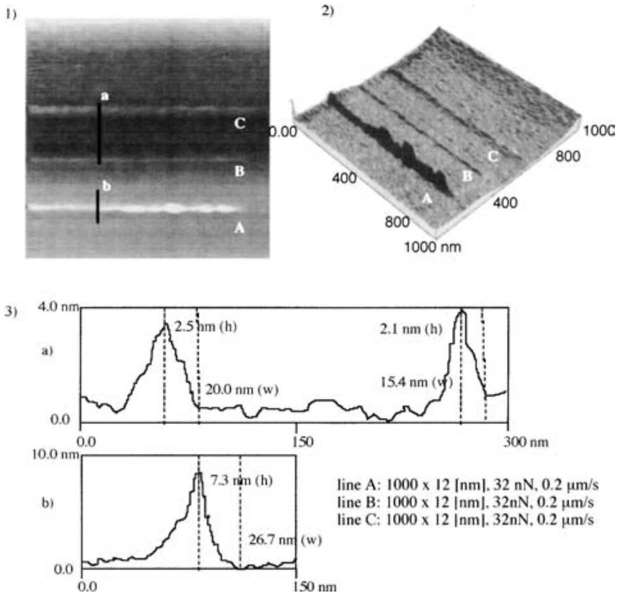

Figure 4. Diels–Alder reaction on $1000 \times 12\,[\mathrm{nm}]^2$ line shape areas. 1) $1000 \times 1000\,[\mathrm{nm}]^2$ topological image after the three line forming Diels–Alder reaction (left) 2) its 3D image (right). 3) Profiles line a (300 nm), b (150 nm).

References and Notes

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6 The contact mode AFM was performed using a 100 μm-long microfabricated V-shape Si_3N_4 cantilever with a spring constant of 0.09 N/m. The curvature radius of the AFM Si_3N_4 tip was about 20 nm. When 32 nN was charged at the tip during scanning, a simple calculation tells that a pressure over 26 MPa rubs the substrate of the tip to the surface of the film. AFM apparatus, Shimadzu SPM-9500J2 was used.
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10 The alkoxyalkyl group on furan was introduced in order to get favourable adhesion of the furan derivative to the tip.
11 Furan itself also undergoes Diels–Alder reaction intermolecularly under high-pressure condition. Excess furan adds a structure to the desired line via intermolecular Diels–Alder reactions.