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Selective deposition of gold particles on DPN patterns on silicon dioxide surface

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1. Introduction

Methods for fabricating nanostructures are essential for developing and capitalizing upon the field of nano-science [1-3]. Dip-pen nanolithography (DPN) utilizes the tip of atomic force microscope as a “nano-pen” to transport an “ink” containing organic molecules onto a substrate surface via a water meniscus. DPN allows one to fabricate one molecule thick nanostructures with feature size from micron to sub-100 nm dimensions on solid substrates. DPN has also emerged as a useful tool that allows one to make multi-component nanostructures on a surface with near-perfect registration capabilities [4].

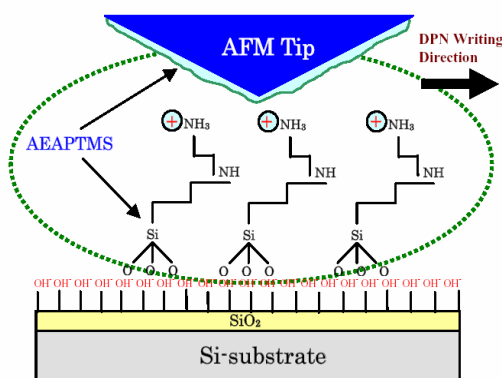


Fig. 1 Schematic of the dip-pen nanolithography on the hydrophilic surface of SiO₂ sample.

In this study, we report a technique, which utilizes DPN to write organic structures directly onto silicon oxide surfaces, as shown in Fig. 1. In the DPN experiment, we utilized the N-(2-aminoethyl)-3-amino-propyl-trimethoxy-silane (AEAPTMS) as the “ink” through the silanation modification to deposit nano-patterns on hydroxyl-terminal surface. Nano-patterns with feature size less than 100 nm line widths onto oxidized silicon surface can be easily generated. Furthermore, citrate-coated gold nanoparticles were used to deposit selectively onto the AEAPTMS-patterned area via static charge force. It is believed that the proposed nanofabrication technique can be further applied in both nano-electronics and nano biochemical sensor applications.

2. Experimental details

Silicon sample was cleaned by using standard RCA cleaning process to remove surface organic contamination.

The hydroxyl-terminal surface of oxidized silicon substrate was prepared by immersing the sample into a piranha solution (1:3 (v/v) mixture of H₂O₂ and H₂SO₄) for 10 min at 120°C, rinsed copiously with de-ionized water, and dried with N₂ gas. AEAPTMS-coated tips was prepared by immersing a commercial PtIr tip (tip diameter =10 nm) into a 2.2mM AEAPTMS solution for 30 sec. For gold particles, solution of 100ml of 2.2mM sodium citrate (C₆H₈O₇Na₃·2H₂O) as a reductant was heated to boil. And then a 40ml of 0.815mM hydrogen-tetrachlorauric acid (HAuCl₄·3H₂O) was added with rapidly mixing and heated to boil. Gold nano-particles with diameter of 15 nm were obtained.

After DPN writing procedure, the amino-functional silane nano-patterns formed on the hydroxyl-terminal surface, which provides a surface bearing free amine (-NH₂), was dried with nitrogen and baked at 120 °C for 30 min in a hot plate. Then, the silanation modification sample was immersed in citrate-coated gold nano-particles solution for 1 hr. Then, the sample was rinsed with DI water and dried with N₂ gas. This procedure led to the selective deposition of gold nano-particles on the AEAPTMS-patterned region via interaction of static charge attraction force between AEAPTMS-patterned region and gold nano-particles. Gold nano-particles on hydroxyl-terminal surface were imaged by AC mode atomic force microscopy.

3. Results and Discussions

In DPN for AEAPTMS nano-patterning, water meniscus controls the effective tip-substrate contact regions; molecules can be deposited on hydroxyl-terminal surfaces with precise control over pattern shape and feature size. Fig. 2 shows that line width increase with longer tip-substrate contact times, and the feature sizes of the patterns depend upon writing speed and relative humidity. It was found that line widths depend on two coefficients, contact width and diffusion coefficient. Contact width is obtained from the finite size of the tip peak results in a minimum contact width and depends upon relative humidity. Diffusion coefficient is assumed proportional to the dwell time and inversely proportional to DPN tip drawing speed. Experiments showed that we could perform nano-scale patterning directly on SiO₂ surface via proper control of parameters in DPN process.

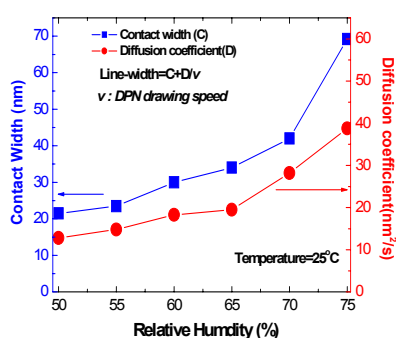


Fig. 2 Characteristic relation curve between drawing speed versus relative humidity of the dip-pen lithography for AEAPTMS.

Figure 3 shows the lateral force microscope images (LFM) of DPN-generated AEAPTMS monolayer grid line patterns on SiO_2 surfaces. Grid line patterns on the SiO_2 surface were obtained by DPN with a writing speed from $0.1 \mu\text{m/s}$ to $0.6 \mu\text{m/s}$ with step of $0.1 \mu\text{m/s}$, respectively. And the line width corresponds to the writing speeds are 212nm, 140nm, 96nm, 78nm, 72nm, 60nm, respectively. Silanation modification nano-pattern with $4 \mu\text{m}$ long and 60 nm wide has been successfully deposited on the SiO_2 surfaces via DPN technique at 65% relative humidity environment. It is possible to obtain smaller patterns via the proper control of humidity and the amino silanation modification on hydroxyl-terminal surface.

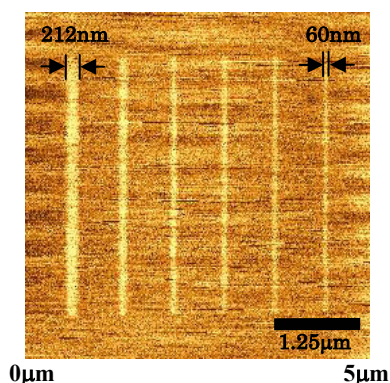


Fig. 3 LFM images of DPN-generated AEAPTMS monolayer patterns on silicon oxide surfaces. LFM images were recorded at a scan rate of 6 Hz.

Fig. 4(a) shows LFM images of DPN-generated AEAPTMS monolayer square patterns ($741\text{nm} \times 741\text{nm}$) on SiO_2 surface with a writing speed of 741nm/s (1Hz scan). It was found that the brighter contrast areas correspond to the deposited silanation modification of AEAPTMS patterns and darker areas are due to the hydrophilic ($-\text{OH}$ group rich) SiO_2 surface. After amino silane modification of the hydroxyl-terminal surface, the amino-terminal samples were then immersed in gold nano-particle solution for 1 hr. When sample immersed in the gold colloidal solution the NH_2 group become protonated forming NH_3^+ and bind to the negatively charged citrate-passivated gold nano-particles. It was found that the amino groups on the

AEAPTMS molecules were used to immobilize gold particles onto SiO_2 substrate due to the specific affinity of the amino group to the negative citrate ions on the surface of the gold nano-particles as shown in Fig. 4(b) by AC-mode AFM. It was also found that the selective deposition process of 15nm-scaled gold particles resulted in broadening of AEAPTMS patterns in gold nano-particle solution through lateral diffusion effect.

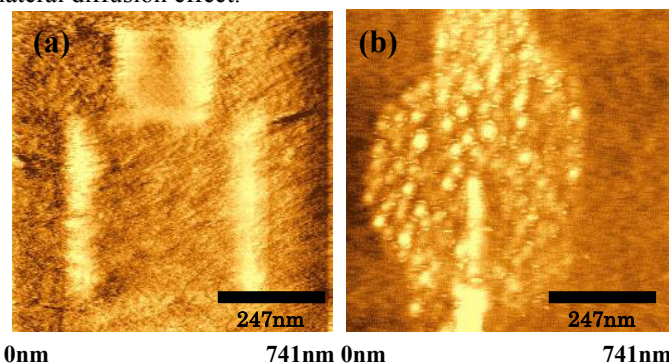


Fig. 4 (a) LFM images of DPN-generated AEAPTMS monolayer patterns on SiO_2 surfaces. (b) AC-mode AFM topography image of gold nano-particles selective deposition on the silanation modification square pattern by DPN drawing after immersion in the gold nano-particle solution for 1 hr.

4. Conclusions

DPN-assisted silane modification nano-pattern with $4 \mu\text{m}$ long, 60nm wide has been successfully produced and smaller patterns are expected to be possible. We also have successfully deposited the gold nano-particles in silanation modification nano-patterns on hydroxyl-terminal SiO_2 surface. Because of the gold nano-particles has been widely used for variety bio-medical applications, it is believed that the proposed nanofabrication technique can be further applied in both nano-electronics and nano-biochemical applications.

Acknowledgements

This work was supported by the Nation Science Council, Taiwan under the contract No. NSC-93-2120-M-009-010.

References

- [1] Albena Ivanisevic and Chad A. Mirkin, *J. Am. Chem. Soc.*, **123**, (2001)7887.
- [2] Hun Zhang, Ki-Bum Lee, Zhi Li and Chad A Mirkin, *Nanotechnology*, **14**, (2003)1113.
- [3] Ki-Bum Lee, Jung-Hyurk Lim, and Chad A.Mirkin, *J. Am. Chem. Soc.* **125**, (2003)5588.
- [4] P. John Thomas, G. U. Kulkarni and C. N. R. Rao, *J. Mater. Chem.* **14**, (2004)625.