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Wide Area Patterning of Organic Silane Molecules by Fountain-Pen Nanolithography

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We demonstrate patterning of micrometer-size dot array consisting of silane coupling molecules by using fountain-pen nanolithography (FPN). 3-Aminopropyltriethoxy silane (APS)-ink dot array pattern was drawn. A function by the end group in the molecule was confirmed by FITC fluorescence dyeing. Wide area patterning of 2-(4-Pyridylethil)triethoxy silane (PySi)-ink was done in the same manner. The dot array consisted of 50 × 50 dots and deployed at 1500 μm × 1500 μm area on the substrate. Although some defects were existed, most dots diameter was less than 10 μm. Our results indicate possibility that the FPN technique is able to fabricate micro-devices composed functional pattern surface by silane coupling molecules, such as bio-tip, sensor and more.

Keywords: dot array patterning; functional pattern; pen-type lithography; silane coupling molecules

1. INTRODUCTION

Recently, organic device fabrication by ink-jet process has been extensively studied [1–3]. Since ink-jet process is able to fabricate pattern without "stamp", it produces pattern for different purposes in each case at low cost. Furthermore, the direct drawing process effects reduction of ink usage and of process steps. It is expected that the direct drawing process will decrease environmental burdens. However, minimum printable line width by common ink-jet system is 10 μm. Although super ink-jet system, which is a special technique, is able to draw smaller lines than 10 μm, it is need additional modifying processes [4].

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Dip-pen nanolithography (DPN) is attracted as a technique to draw dots and lines with several tens of nanometer in diameter and in width [5–7]. Although DPN, using AFM probe as a penpoint, has an advantage for sub-micrometer-size drawing, it is not suitable for micrometer-size patterning at wide area.

On the other hand, fountain-pen nanolithography (FPN) has a potential to be effective patterning technique. The technique uses the modified AFM cantilever with an ink reservoir and a microchannel as a pen tip. In the FPN, the liquid-ink is filled in the reservoir on the AFM cantilever, and then flows onto the surface when in contact [8–13]. The technique is able to draw micrometer-size dots and lines at wide-area. There are several reports of patterning demonstration using water based ink such as fluorescence dye, quantum dot-ink [11,12].

It is expected that FPN, which is able to draw micrometer-size pattern, will become powerful tool to fabricate various micro devises as not only electronic device but also bio-tip, sensor, μ-TAS, and more. To realize these applications, patterned materials should have functions and provide reaction spaces. For example, silane coupling molecules are one of the suitable materials, since the molecules create various functional surfaces by selecting end group of the molecules. However, almost silane coupling molecules polymerize in moisture. Thus it is difficult to use these molecules as an ink of FPN.

In this work, we demonstrate wide area patterning of micrometer-size dot array consisting of silane coupling molecules by using FPN to show a potentiality of the technique for those fabrications process. At first, 3-Aminopropyltriethoxy silane (APS) dot array pattern was drawn. A function of the pattern was confirmed by FITC fluorescence dyeing. Wide area patterning of 2-(4-Pyridylethil)triethoxy silane (PySi) dot array pattern was drawn in the same manner. The dot array were consist of 50×50 dots and deployed at $1500\,\mu m \times 1500\,\mu m$ area on the substrate. Almost dots were smaller than $10\,\mu m$ in diameter.

2. EXPERIMENT

The substrates used for drawing were silicon and thermal oxide silicon wafer. Before drawing, these substrates were cleaned thoroughly by organic solvent and neutral detergent, and then these were exposed to UV/O_3 for the 30 minutes. The surfaces were completely hydrophilic with contact angle with water $<7^o$.

Used APS and PySi were purchased from Sigma-Aldrich Japan K.K. and Gelst Inc., respectively. The inks were APS 17 mM solution and PySi 25 mM solution in methanol and ethylene glycol mixture (1:2).

Patterning was carried out by Nano eNabler™ system with Surface Patterning Tool (SPT) (BioForce Nanoscience Inc., USA.) [8,12,13]. The Nano eNabler is equipped with a high-resolution XYZ motion control platform and surface contact force detection system. The SPT corresponds to the fountain-pen part in the system. It consists of a cantilever with a microchannel and an ink reservoir on a supporting substrate. The microchannel width of used SPTs was 10 μm and 30 μm. Also the SPTs were treated by UV/O_3 for 30 minutes before loading the ink. After patterning, the specimens were dried and annealed (100°C, 10 min). Laser confocal microscopy and AFM were used to confirm the pattern formation (SFT-3500, Shimadzu Co., Japan).

3. RESULTS AND DISCUSSION

Figure 1 (a) and (b) show laser confocal microscopy (LCM) image and fluorescence microscopy image of APS dot array on the surface of the silicon wafer, respectively. The dot array pattern was observed by LCM image (Fig. 1 (a)). Fluorescein-4-isothiocyanate (FITC), which was fluorescent-dye and was able to react with amino group, solution was dropped onto the surface, and then the specimen rinsed well by water. Then fluorescence image of the surface was observed by fluorescence microscopy (Fig. 1 (b)). The fluorescence pattern indicating amino group distribution corresponded to LCM image.

The patterning image of LCM and AFM were also obtained after rinsed by water and methanol. It indicates that these silane coupling

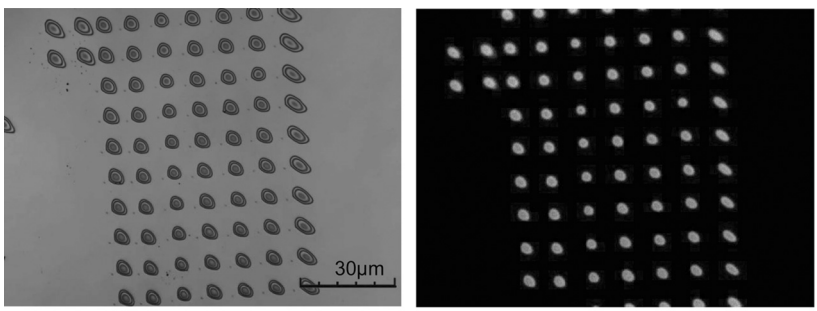

FIGURE 1 LCM and fluorescence microscopy image of APS dot array Substrate was the Si wafer. In the patterning, the SPT with 30 μm microchannel was used. (a) Laser Confocal Microscopy image, (b) Fluorescence Microscopy image, "B-2A" Fluorescence Filter Blocks ($\lambda_{ex} = 450 \sim 490$ nm, $\lambda_{dm} = 505$ nm, $\lambda_{em} = 520$ nm, Nikon Co.) was used to detect.

molecules are chemisorbed on the substrates. Fluorescence image (Fig. 1 (b)) indicates that FITC react with amino group, resulting in amino group existing on the surface of the dots. APS has amino group at the end of the molecule. It is suggested that the pattern is certainly composed of APS molecules. Furthermore, it is shown that the FPN fabricates functional pattern consisting of silane coupling molecules.

Figure 2 shows LCM image of PySi dot array on the surface of the silicon oxide wafer. The pattern consisted of 50×50 dots and was widespread $1500\,\mu m \times 1500\,\mu m$ area, although there were some defects. Drawing start point was left lower and end point was top right at the pattern. The distribution of the defects was found comparatively on the right area.

Figure 3 shows AFM image of one of dots in the PySi dot array. The diameter and height of the dot were 6.68 μm and 52.70 nm, respectively. These dots diameter and height were approximately from 5 to 12 μm and from 50 to 120 nm, respectively. The dots had domal structure.

In general, organic solvents are used to prepare thin film of silane coupling molecules [14]. Almost silane coupling molecules are polymerized by water. Many organic solvent is highly-volatile. In the case of using volatile solvent, ink would be dried at the small ink-reservoir. Thus, the ink preparation is needed to prevent evaporation on the SPT during patterning. Methanol and ethylene glycol mixture solvent inhibited evaporation at the reservoir, and became possible to flow on the microchannel of the SPT pen-tip. The ink-solvent allowed not only patterning but also wide area patterning of silane coupling

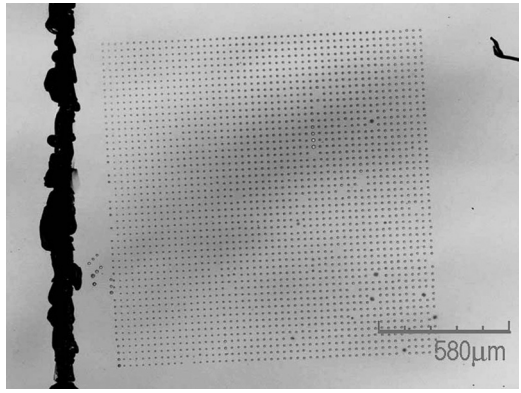

FIGURE 2 LCM image of the PySi dot array Substrate was the thermal oxide silicon wafer. In the patterning, the SPT with 10 μm microchannel was used.

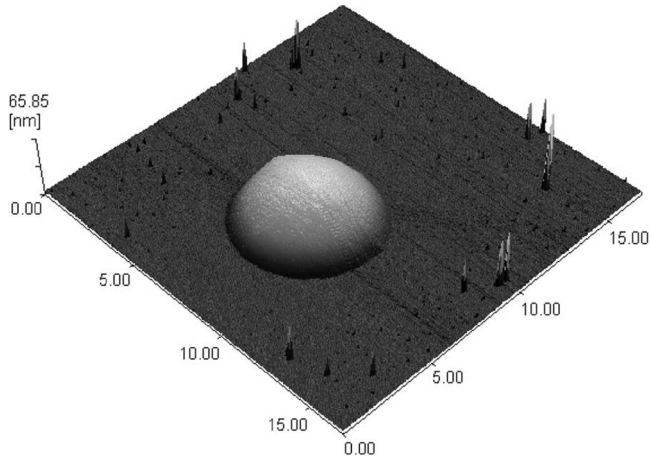

FIGURE 3 AFM image of one of the PySi dot array Observed area was 16.87 μm × 16.87 μm.

molecules for the FPN, as shown PySi patterning (Fig. 2) (50 × 50 dot array, 1500 μm × 1500 μm area).

These dots size were around 10 μm, but a lot of dots were smaller than 10 μm. It indicates that the FPN able to draw narrower line as compared with general ink-jet print method. However, there were some defects (as shown in Fig. 2) and variation in size. We considered that it was caused by variation in ink-dropamount and local contamination on the surface. The ink-drop quantity would be changed by local contamination on the surface, change in the penpoint condition as adhesion of dirt, denaturalization of the microchannel by the ink-molecules absorbtion, and deviation of the distance between penpoint and surface, with drawing and time. Meanwhile, these dots have around 100 nm height and domal structure. It indicates that molecules polymerized with aggregation not forming monolayer.

4. SUMMARY

We demonstrated wide area patterning of silane coupling molecules, APS and PySi, by using the FPN. The ink-solvent, which is methanol and ethylene glycol mixture, allowed patterning of silane coupling molecules by the FPN. In the APS dot array, a functional dot array surface was confirmed by FITC dyeing. In the PySi dot array, it was consist of 50 × 50 dots and deployed at 1500 μm × 1500 μm area on the substrate. Almost dots were smaller than 10 μm in diameter.

However, there were some defects and variation in size. Size control and decreasing miss shots of patterns would become possible by clarifying factors in determining size and figure of dots.

Our results suggest that the FPN technique has the ability of micro-size patterning for various silane coupling molecules. Furthermore, it is expected that the direct drawing process such as the FPN have the potential to become a fabrication technique for functional micro-patterning. It indicates that the FPN is able to produce various sensing pattern surface by changing functional group in silane coupling molecules, and further become one of the techniques for device fabrication such as bio-tip, sensor, organic device and more.

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