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Development of Nanoscale Patterning Method of Self-Assembled Monolayer using Photothermal Desorption in Near-field

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1. Introduction

Self-assembled monolayer (SAM), which is organic thin film formed by the intermolecular force and the interaction force between the constituent molecules and the substrate, gains much attention because of its ability to change and construct surface characteristics and nanostructures easily. In older to use SAM effectively, the patterning of SAM in nanoscale is very important. For example, a size and position controlled SAM can be applied to active sites for surface-enhanced Raman scattering (SERS), whose configuration is well controlled in nanoscale. However conventional patterning method, such as the electron beam lithography (EBL)[1], the micro contact printing (μCP) using the mold[2], and the direct laser patterning (DLP)[3] have some disadvantages respectively. EBL induces the defects of SAM resulting from cleavages of C-H bonds. In the μCP, a deformation of the mold causes a deterioration of the quality of SAM. In the opticall patterning method such as DLP, the pattern size is limited due to the diffraction limit of light.

From above aspects, we have proposed a novel patterning method of SAM using near-field photothermal desorption (NPTD), which can make noncontact, nondestructive and noncontaminated patterning of SAM in nanoscale. Because of its spatial resolution beyond the diffraction limit and clean process, nano-patterned SAM by NPTD can be applied to the various fields of engineering and science such as micro-TAS active sites and biosensors.

This paper reports the patterning principle and the validity of the proposed method both experimentally and theoretically.

2. Patterning Principle

Figure 1 shows a schematic image of the principle of NPTD, which is based on the thermal desorption of the binding layer (typically thiolate in our experiment).The desorption of thiolate is induced at high temperature (400 ~ 500 K[4][5]), and this process requires no photomask and no contact with sample. Therefore, a direct clean patterning can be carried out using NPTD. In our method, the irradiation of the near-field light, which is localized beyond the diffraction limit of light and generated in the proximity region at the tip of the near-field fiber probe, can induce the local heating in near-field.

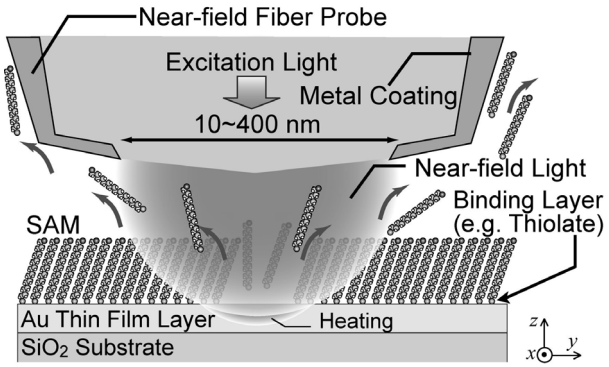

Fig.1 Principle of NPTD.

3. Preliminary Experiment

In order to verify the validity of the patterning of SAM using thermal desorption, the preliminary patterning of octadecanethiol (ODT) SAM by irradiating the laser beam was carried out. First, we have patterned ODT SAM by irradiating the laser beam whose spot size was the order of micro meter, followed by modifying 11-amino-1-undecanethiol (AUT) on the irradiated area. Since the contrast in the SEM image is attributed to the difference of the emission capability of the secondary electrons of the surface molecules, the nanoscale patterning of SAM can be evaluated. Figure 2 shows the image of the irradiated area.

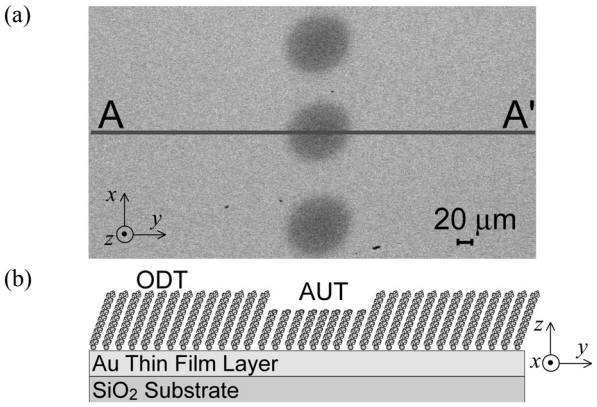

Fig. 2 Image of irradiated area.
(a) SEM image.
(b) Schematic image of the cross-section of A-A' in the (a).

The gray region in Fig. 2 (a) indicated ODT and the darker circular regions indicated AUT. This result suggested that the ODT was thermally desorbed, and the AUT was successfully modified onto the irradiated area as shown in Fig. 2 (b).

4. Simulation of the Local Heating

Analytical simulation of the temperature distribution and the heatflux magnitude using the finite-element method was demonstrated. Figure 3 shows a 3D analytical model of a near-field fiber probe head with an aperture at the tip of the probe head. In this analysis, the absorption of the excited light at the probe head was considered.

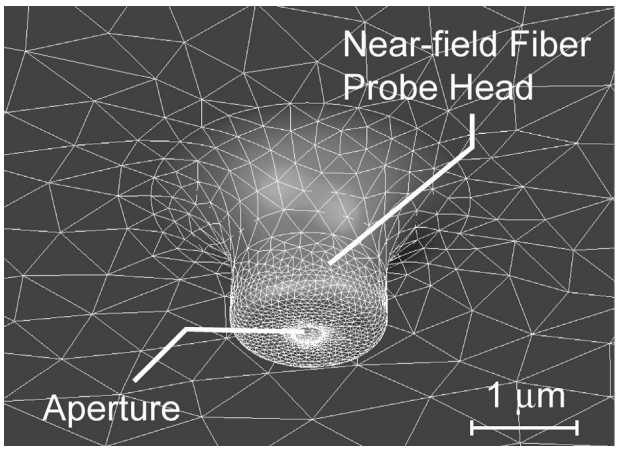

Fig. 3 Image of 3D analytical model.

Figure 4 shows the analysis result of the distribution of the heatflux magnitude after heating. The sample surface was locally heated and the high heatflux was generated in nanoscale at the heating area resulting from the irradiation of the near-field light. On the other hand, the heatflux from the probe head due to the absorption of the excited light was negligibly small.

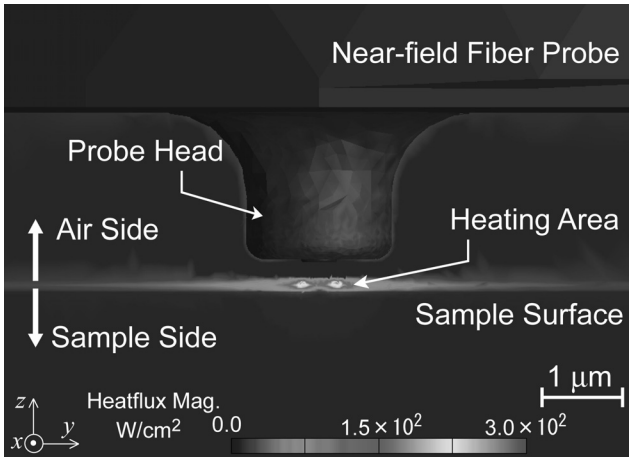

Fig. 4 Analysis result of the distribution of the heatflux magnitude.

Figure 5 shows the temperature distribution around the heating area. In Figure 5, the desorption width is around 90 nm when the threshold of the desorption temperature is estimated to be 400 K. Consequently, the size of the desorption area could be controlled in nanoscale by controlling the intensity of the near-field light, and thereby, nano-patterned SAM can be formed.

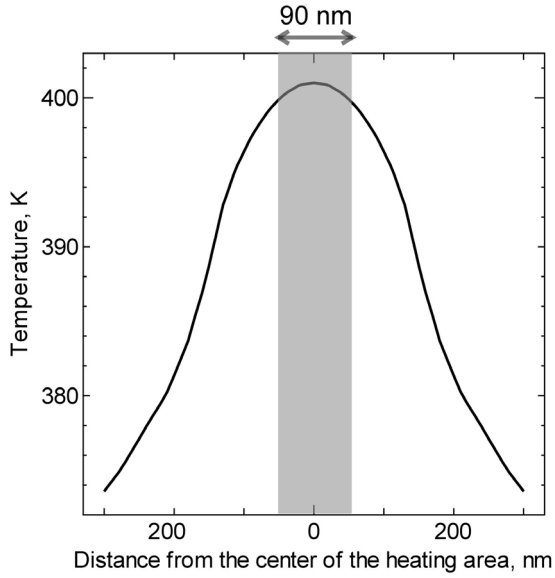

Fig. 5 The temperature distribution around the heating area.

5. Conclusions

The novel patterning method of SAM using NPTD enabling noncontact, nondestructive and noncontaminated patterning of SAM have been studied. In the preliminary experiment, the desorption of ODT was successfully observed in the SEM image. It was analytically suggested that the sample was locally heated in nanoscale by using the near-field fiber probe. As a result, the validity of the nanoscale patterning of SAM using NPTD was confirmed.

Acknowledgements

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