STUDY ON NANOSCALE PATTERNING METHOD OF SELF-ASSEMBLED MONOLAYER USING NEAR-FIELD PHOTOTHERMAL DESORPTION

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ABSTRACT

We have proposed a novel patterning method of self-assembled monolayer (SAM) using near-field photothermal desorption (NPTD), which can make noncontact, nondestructive and noncontaminated patterning of SAM in nanoscale. In order to verify the validity of the patterning of SAM using photothermal desorption, the patterning of SAM by irradiating the laser beam was carried out. Furthermore, the analytical simulation of the temperature distribution using the finite element method was demonstrated in near-field. The results indicated that the applicability of the proposed patterning principle was confirmed.

KEYWORDS: Nanoscale Patterning, Near-field Light, Photothermal Desorption, Self-assembled Monolayer

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 construct nanostructures and to change surface characteristics easily[1]. In order to use SAM effectively, the patterning of SAM in nanoscale is very important. For example, nano-patterned SAM can be applied to the surface-enhanced Raman scattering (SERS) active sites[2], the uniformly-sized nanocatalyst[3], and sensors for biomolecules[4]. From a point of view of a nano-engineering, the nanoscale patterning of SAM is necessary for the application of SAM, and various patterning methods have been invented. Electron beam lithography can decompose SAM in nanoscale[5], however, the irradiation of electron beam induces a cleavage of a carbon chain and a formation of a new undesirable bond resulting in an organic residue at the patterning area. Micro contact printing has advantages of high throughput and large area patterning[6], however, the deformation of the mold induces the defect of the film quality and the restriction of the capability of patterning.

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

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 : R-S −). The desorption of thiolate is induced at high temperature (400 ~ 500 K[7][8]), and this process is noncontact with the sample and can remove the thiolate completely from the substrate without any organic residue, therefore a direct clean patterning can be carried out. Moreover, because the local heating is induced by the irradiation of the near-field light that is localized in the proximity region of the sample beyond the diffraction limit of light, our method can pattern SAM in nanoscale. In order to generate the near-field light, the near-field fiber probe coated with metal is utilized.

Figure 1:  Principle of NPTD

EXPERIMENTAL DISCUSSION

In order to verify the validity of the proposed method of the patterning of SAM using photothermal desorption, the preliminary patterning of octadecanethiol (ODT) SAM by irradiating the laser beam was carried out. First, a 10×10 mm² triple-layered substrate, Au (100 nm thickness)/Ti/Silica, was immersed in a piranha solution (3:1 concentrated...
H₂SO₄/H₂O₂) for about 20 min to remove organic contaminants from the surface[1][9]. By dipping the substrate into a 1.0 mM ethanolic solution of ODT at ambient temperature for 24 h, ODT-SAM was formed uniformly on the sample surface. Next, the sample was periodically irradiated with the laser beam (wavelength : 405 nm, intensity : 45 mW, gaussian radius : 8 µm, irradiated time : 1 s). Finally, the sample was immersed in a 1.0 mM ethanolic solution of 11-amino-1-undecanethiol (AUT) at ambient temperature inducing the modification of AUT onto 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. The gray region in Figure 2 (a) indicated ODT, which had high ability to emit the secondary electrons, and the darker circular regions indicated AUT, which had low ability to emit the secondary electrons. The darker circular regions in a straight line suggested that the ODT was thermally desorbed by the irradiation of the laser beam, and the AUT was successfully modified onto the irradiated area as shown in Figure 2 (b). Additionally, the diameter of the desorption area in the Figure 2 (a) was estimated about 30 µm, and it was good agreement with the analytical result considering the heat transfer[10]. Consequently, the validity of the principle of NPTD was confirmed.

Figure 2: Image of the irradiated area
(a) SEM image
(b) Schematic image of the cross-section of A-A’ in the Figure 2 (a)

ANALYTICAL DISCUSSION

Analytical simulations of the temperature distribution using the finite element method were 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. The thin metal coating was sputtered at the tip of the probe, and Ag was employed on the coating metal in terms of the low optical absorptance to the excitation laser beam. The aperture of 300 nm in diameter was created at the tip of the probe. In this analysis, not only the absorption of the near-field light at the sample surface but also that of the excitation laser beam at the probe head coated with Ag was considered. The wavelength of the excitation laser beam was 445 nm and the energy density of the near-field light was about 16 MW/cm².

Figure 4 shows the analysis result of the temperature distribution after heating. The large temperature distribution was only generated at the sample surface around the irradiated area, because the Ag coating that had low optical absorptance led to the local heating at the sample surface in nanoscale without any other heat source. On the other hand, in the case of Au as the coating metal, the temperature of the probe head was extremely high when the temperature of the sample surface reached the desorption level. Figure 5 shows the analysis result of the relationship between the energy density of the near-field light and the temperature ratio of the sample surface (Tₛ) and the probe head (Tₚ) in the case of

Figure 3: Image of 3D analytical model
Figure 4: Analysis result of the temperature distribution
Ag or Au as the coating metal of the probe head. In the case of the Ag coating, the change of the temperature ratio was inversely proportional to that of the energy density of the near-field light. On the other hand, the temperature of the probe head was extremely high compared with that of the sample surface in the case of the Au coating. In this case, the sample surface was simultaneously heated by the Au coated probe head while the near-field light was heating the sample, therefore, the temperature distribution became larger. Figure 6 shows the relationship between the energy density of the near-field light and the width of the desorption area. The desorption width in the case of the Ag coating was significantly smaller than that in the case of the Au coating, and thereby, it is indicated that the Ag coated probe is suitable for the nanoscale patterning. Consequently, the desorption width can be controlled by changing the energy density of the near-field light generated by using the near-field fiber probe coated with Ag.

CONCLUSION

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 by irradiating the laser beam and the modification of AUT were successfully observed in the SEM image. It was analytically suggested that the sample surface was locally heated in nanoscale by utilizing the near-field light generated by the use of the near-field fiber probe coated with Ag. As a result, the validity of the nanoscale patterning of SAM using NPTD was confirmed.

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REFERENCE