Thin Film Micromachining Using Femtosecond Laser Photo Patterning of Organic Self-assembled Monolayers

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Self-Assembled Monolayers (SAMs) formed by alkanethiol adsorption to thin metal film are widely being investigated for applications as coating layer for anti-stiction or friction reduction and in fabrication of micro structure of molecules and bio molecules. Recently, there have been many researches on micro patterning using the advantages of very thin thickness and etching resistance of Self-Assembled Monolayers in selective etching of thin metal film. In this report, we present the several machining method to form the nanoscale structure by Mask-Less laser patterning using alknanethiolate Self-Assembled Monolayers such as thin metal film etching and heterogeneous SAM structure formation.

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1. Introduction

Self-assembled monolayers (SAMs) formed by alkanethiol adsorption to thin metal film are widely being investigated for applications are coating layer for anti-stiction or friction reduction and in fabrication of micro structure of molecules and bio molecules. Recently, there have been many researches on micro patterning using the advantages of very thin thickness and etching resistance of self-assembled monolayers in selective etching of thin metal film after AFM tip scratching or laser beam irradiation. Specially the methods using near-field optics have actively been performed using the superior characteristics of SAMs as a stable photoresist.[1,2] We present the micro-machining of thin metal film by maskless laser patterning of alkanethiolate self-assembled monolayers. SAMs formed by the adsorption of alkanethiols onto gold substrate are used as very thin photoresists. It is well known that deep UV light of wavelength is necessary for oxidation of SAMs to occur. Instead of DUV light source, we showed that it is possible to make nano structures in SAMs and thin metal film, which are smaller than the diffraction limit of half wavelength using the 800nm wavelength femtosecond laser coupled NSOM system.

In this study we focused on using the visible range femtosecond laser as an optical source with several advantages such as easy optical alignment, cheap optical components, reduction of line width by self-focusing effect and fast processing time.

2. Self-Assembled Monolayers

2.1 Overview

The most common methods for forming supported organic films are the Langmuir-Blodgett and self-assembly techniques, with their primary difference being that they produce physisorbed and chemisorbed monolayers, respectively. The Langmuir-Blodgett technique is based on the physical transfer of a molecular film at the air/water interface onto a flat substrate of interest. This assembly was a result of unfavorable interactions between water and the hydrophobic tails of the molecules and geometrical packing considerations that limited the formation of three-dimensional self-assembled structures from these cylindrical molecules.[3]

As the self-assembly process shown in Figure 1, liganting chemical interactions between the head group of a molecule and a metal surface could drive the formation of an oriented monolayer film by absorbing alkylamines onto gold from water. The specificity of the gold-sulfur interaction has provided an efficient procedure for the formation of chemisorbed molecular films. The coated surface characteristics including optical properties can be modified by proper selection of thiol molecules.[4]

2.2 Procedure of SAMs formation

2.2.1 Gold Substrate Preparation

As substrates to be used for coatings, metal films of gold were deposited to a thickness of 100 nm on Si(1 0 0) by using RF-sputtering technique. A thin layer of chromium (20nm) was deposited on the silicon surface prior to the gold film deposited process in order to improve the adhesion.

2.2.2 Cleaning

The metal coated specimens were first cleaned in the Piranha solution, which was made with H_2SO_4 and H_2O_2 in 3:1 ratio and then immersed in a 0.01-0.1M ethanolic solution of alkanethiols for 0.5-24h at room temperature.

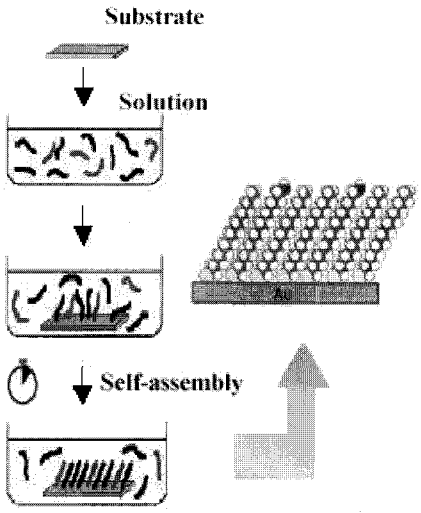

Fig. 1 Schematic diagram of self-assembled monolayers

2.2.3 Thiol Solution Preparation

Alkanethiols used in this work were single chain *n*-alkanethiol ($CH_3(CH_2)_nSH$) with various chain lengths, n: 1-dodecanethiol (DDT, n = 12), and 1-octadecanethiol (ODT, n = 18). It is known that alkyl chains which have more than 12 carbons generate stable monolayer on the surface.[5]

A study of the effect of immersion time on thiol structure showed that no significant changes were observed in the chemical composition of the monolayers. It was also reported that the electrochemical properties of thiol layers that formed within a few seconds in a solution with concentrations above 0.02M were equivalent to those formed in 24 h.

2.2.4 Self-assembly

The prepared specimen is immersed in thiol solution for 1 day. When we use ODT the solution is heated to 35°C by a hot plate to maintain the temperature of solution up to the melting point of ODT. After that, specimen is rinsed by ethanol and DI water sequentially. Finally, the surface is dried using nitrogen gas. Process conditions are shown in Table 1.

Table 1 Process conditions of SAMs

Material	Concentration (mM)	Temperature (℃)	Time (Days)
DDT	2	20	1
ODT	2	34	1

2.2.5 Inspection

Contact angle of water droplets on SAM coated surface were measured because alkanethiol SAMs show low surface energy and hydrophobic property. A few micro-liters of deionized water were dropped on the SAM surface for the contact angle measurements. The measurement was carried out at room temperature and relative humidity level 20%. Spectroscopic ellipsometer was used for the measurements of the thickness of SAMs (angle of incidence 70°). The measurement resulted in 2nm thickness of SAM on the gold substrate.

3. Experimental Setup and Process

3.1 Near-field Laser Patterning System

The layout of the femtosecond laser coupled NSOM system is shown in Figure 2. A straight, hollow metalized micropipette is used as the near-field aperture for both imaging and patterning. Micropipettes, rather than optical fibers, are employed since only micropipettes have the ability to collimate sufficient power into the substrate without themselves being damaged. A standard shear-force AFM feedback is employed to track the tip over the surface. A Ti:sapphire femtosecond laser is fed into the micropipette for NSOM lithography. Amplifier generated 800nm NIR output with a few microjoule pulse energy at 100 kHz repetition rate. The scanning is performed by a hollow compound flexure stage with 2 μm absolute accuracy over 20 cm travel and 20 nm repeatability over a 50 μm scan field.

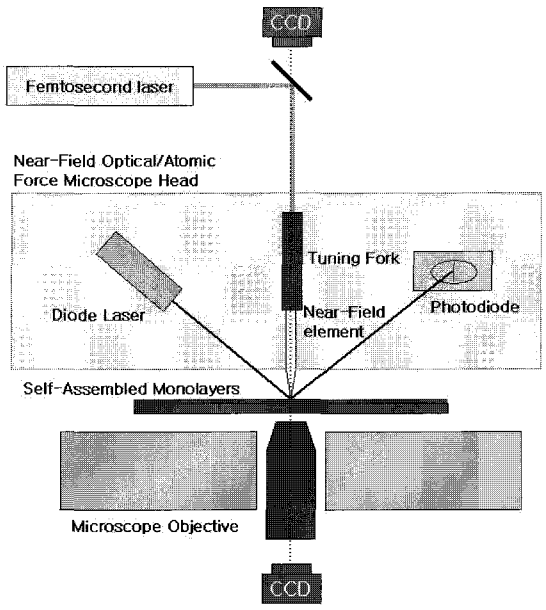

Fig. 2 Schematic diagram of lithography system

3.2 Patterning Process

3.2.1 Patterning of Thin Metal Film

As shown in Figure 3 SAM that is used as a protective layer against the chemical etchant is selectively removed by photo-oxidation. Chemical etching is then performed to remove the workpiece material at locations where the SAMs has been removed. Since the main mechanism of material removal of the workpiece is chemical reaction, the problem of surface contamination such as redeposition of debris of laser machining can be overcome. By adjusting the chemical etching time and condition, three-dimensional structures with relatively high-aspect ratio on various metal surfaces as well as on silicon-based materials can be fabricated.

3.2.2 Heterogeneous Structure Formation

To generate surface patterning with different properties we performed heterogeneous SAM patterning as shown in Figure 4. The alkylsulfonates that result from the photo-oxidation of alkanethiolate adsorbates are susceptible to displacement by a wide variety of solution-phase reagents. After laser scanning, samples were immersed in 10 mmol dm^{-3} solutions of contrasting thiols for 10 min to displace oxidized material and create a pattern.

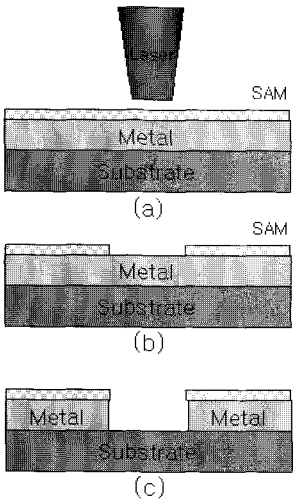

Fig. 3 Process flow of micromachining thin metal film

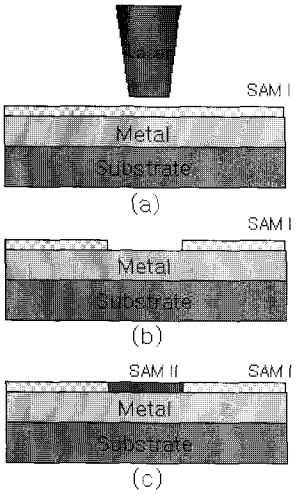

Fig. 4 Process flow of heterogeneous structure formation

4. Experimental Results and Considerations

4.1 Measurement of SAMs Thickness and Properties

We investigated the organic thin film thickness and optical properties of DDT and ODT using a wide spectral range ellipsometer as shown in Table 2 and Figure 5. The DDT and ODT have abrupt refractive index change at high photon energy and show the peak of absorption coefficients at deep UV range. It means that the refractive index change and photochemical effect of DDT and ODT can be induced only by multi-photon effect when near IR laser beam is irradiated to the specimen.

Table 2 Optical structure of SAMs

Material	Measured Film Thickness (Å)	Theoretical Film Thickness (Å)
DDT	13.0 ± 0.8	17
ODT	30.3 ± 0.9	23

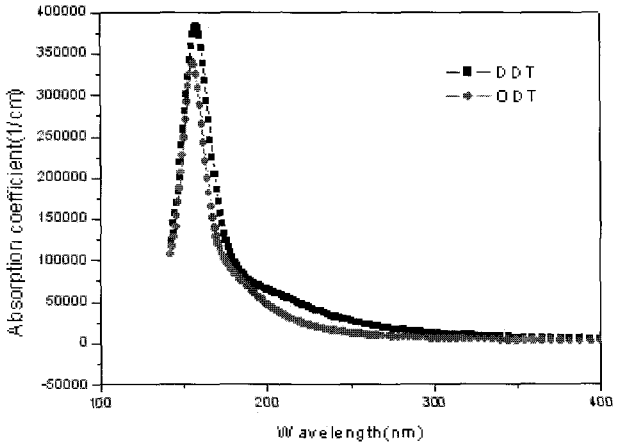

Fig. 5 Absorption curve for SAMs

4.2 Patterning of Thin Metal Film

4.2.1 Patterning Using Focusing Lens

The combination of aqueous, alkaline cyanide ion (1M KOH, 0.1M KCN) and dioxygen rapidly etches Au(0).

$$4Au + 8CN^- + O_2 + 2H_2O \rightarrow 4[Au(CN)_2]^- + 4OH^-$$

The etch solution consisted of 1M KOH and 0.1M KCN in distilled water. The solution container was open to the ambient air and stirred vigorously.[6] SAMs of long-chin alkanethiolates on the surface of the gold block the etching. After removal of the sample from the etch solution, it was rinsed with distilled water and ethanol and dried in a stream of nitrogen. Thus, by using this etching method, it was possible to verify where or not the thiol film was oxidized from the surface during the ultrafast laser writing. By combining these techniques for forming patterns with selective etching using the CN^-/O_2 solution, high-resolution patterns of gold on silicon could be fabricated with dimensions as small as sub-micron scale.

After laser scanning, samples were immersed in a solution of alkaline cyanide etchant, the sulfonates were be displaced and the underlying gold was dissolved. Unoxidized thiols protect the substrate from erosion. Thus photopatterned SAMs may be used as masks for the selective etching of gold. The feasibility of using femtosecond laser with such wet etching processes was explored. To investigate the possibility of scale-down of patterning, the process was performed using high NA objective lens (100X) and thiols which have different chain length such as DDT and ODT. The process condition is shown in Table 3.

AFM topographical image of the results are shown in Figure 6 and 7. The photooxidation of the alkanethiol monolayers proceeds essentially by a two-step mechanism. First, laser exposure causes C-S bond scission and subsequent desorption of the hydrocarbon chain.[8] Second, the exposed sulfur is oxidized to sulfite and sulfate species. Femtosecond laser has enough power to cause the first step to occur due to the multi-photon effect. As chain length is longer, van der Waals force between each molecule is increased. It means that photo-oxidation of SAMs with longer hydrocarbon chains need higher photon energy.

Table 3 Laser patterning conditions

Material	Power (mW)	Feed Rate (mm/s)	Line Width (μ m)
DDT	5.5	70	1.6
ODT	5.5	70	0.8

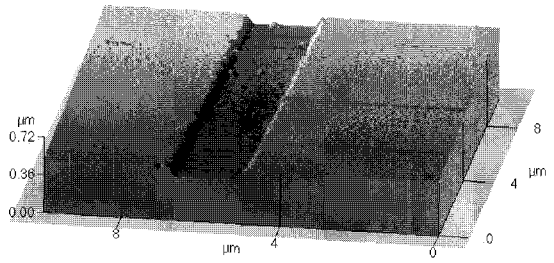

Fig. 6 AFM 3D image of the line pattern of DDT

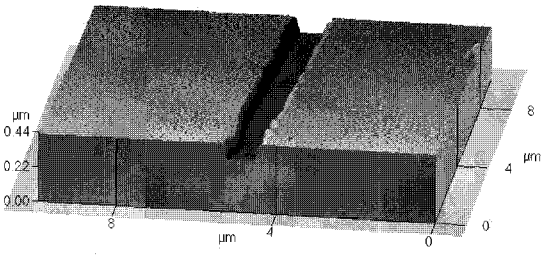

Fig. 7 AFM 3D image of the line pattern of ODT

4.2.2 Patterning Using Micro Pipette

From these results, we applied NSOM lithography coupled with femtosecond laser to fabrication of 3D nanostructures. Figures 8, 9 and 10 show a sample that has been patterned in this way. Using this method we have achieved line widths as small as 400nm with quartz micro pipettes which have 400nm aperture size. This result illustrates that ultrafast laser lithography offers potential for the fabrication of three-dimensional nanostructures, as well as chemical patterns, suggesting that it may be a versatile tool for the construction of a wide range of micro/nanoscale structures.

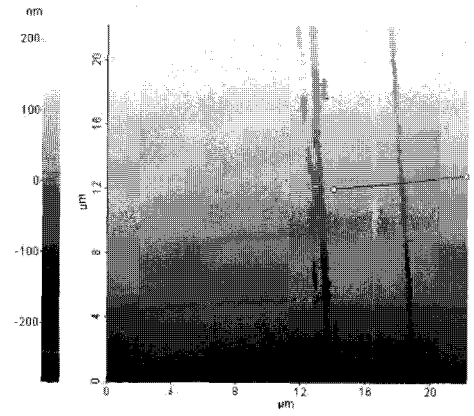

Fig. 8 AFM image of the line pattern of DDT

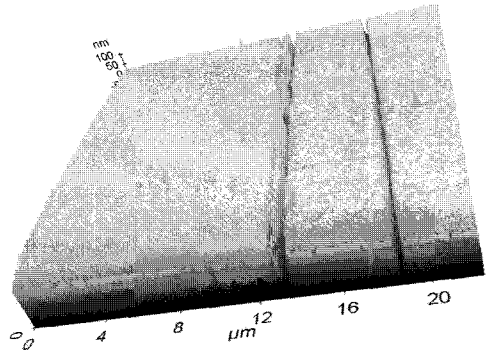

Fig. 9 AFM 3D image of the line pattern of DDT

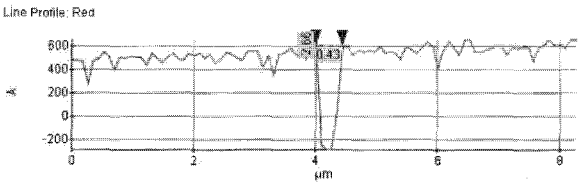

Fig. 10 Line width measurement of the line pattern of DDT in AFM

4.3 Heterogeneous Structure Formation

The alkylsulfonates that result from the photo-oxidation of alkanethiolate adsorbates are susceptible to displacement by a wide variety of solution-phase reagents. After laser scanning, samples were immersed in 10 mmol dm^{-3} solutions of contrasting thiols for 10 min to displace the oxidized material and create a pattern. Figure 11 shows an AFM data for the sample patterned by femtosecond laser before and after immersing in thiol solutions. These lines have been traced across a methyl terminated monolayer, and the sample immersed in carboxylic acid terminated monolayer. The lateral force microscopy image reveals distinct contrast change. The cantilever used here was fabricated from silicon nitride, the outer surface of which is polar. The tip thus interacts more strongly with polar regions of the surface. Consequently a higher friction force is measured for polar regions, leading to dark contrast on the photo-oxidized lines. After immersing the sample in a solution of a contrasting thiol, lateral force microscopy image showed pattered materials with the opposite contrast. It is thought the photo-oxidized lines are replaced by carboxylic acid terminated adsorbates. It also implies that the fabrication of heterogeneous SAM layer is possible using the NIR femtosecond laser.

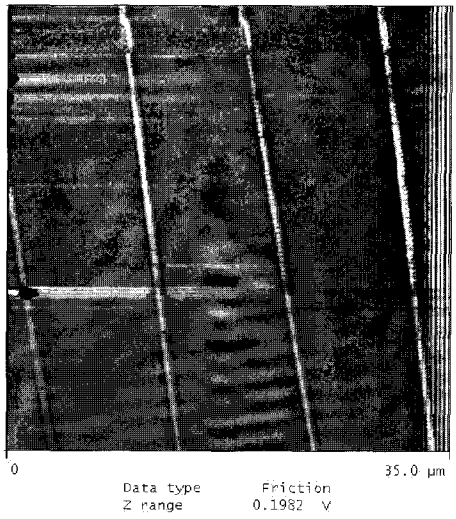

Fig. 11 LFM image of the line pattern

5. Conclusions

Using 800nm wavelength femtosecond laser coupled to high NA objective lens, we have demonstrated that it is possible to fabricate structure in SAMs that are smaller than the theoretical beam spot size. Ultrafast laser facilitates not only the patterning of surface chemical structure, but also the creation of three-dimensional sub-micron structures by combination with suitable etching methods without using deep UV laser source[9] like previously studied.[1,7] Photochemical methods provide powerful and flexible means to immobilization of biological molecules at surfaces, and the data presented here demonstrate that these methods may now be utilized in the creation of biological nanostructures through femtosecond laser coupled SNOM

patterning. It is expected to be used for versatile applications in biological or chemical nanotechnology and molecular electronics.

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