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Fabrication of Nano Dot and Line Arrays Using NSOM Lithography

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Using a cantilever type nanoprobe having a 100 nm aperture at the apex of the pyramidal tip of a near-field scanning optical microscope (NSOM), nanopatterning of polymer films are conducted. Two different types of polymer, namely a positive photoresist (DPR-i5500) and an azopolymer (Poly disperse orange-3), spincoated on a silicon wafer are used as the substrate. A He-Cd laser with a wavelength of 442 nm is employed as the illumination source. The optical near-field produced at the tip of the nanoprobe induces a photochemical reaction on the irradiated region, leading to the fabrication of nanostructures below the diffraction limit of the laser light. By controlling the process parameters properly, nanopatterns as small as 100nm are produced on both the photoresist and azopolymer samples. The shape and size variations of the nanopatterns are examined with respect to the key process parameters such as laser beam power, irradiation time or scanning speed of the probe, operation modes of the NSOM (DC and AC modes), etc. The characteristic features during the fabrication of ordered structures such as dot or line arrays using NSOM lithography are investigated. Not only the direct writing of nano array structures on the polymer films but also the fabrication of NSOM-written patterns on the silicon substrate were investigated by introducing a passivation layer over the silicon surface. Possible application of thereby developed NSOM lithography technology to the fabrication of data storage is discussed.

OCIS codes : 140.3390, 160.5470, 180.5810, 210.4770, 260.5130

I. INTRODUCTION

Fabrication of nanostructures using a scanning probe microscope (SPM) has several advantages compared to existing methods such as photolithography, electron beam lithography, or x-ray beam lithography. In the SPM technique, patterning is done through a direct writing process. Therefore, there is no need for mask preparation that requires high cost and time as in photolithography. Due to the direct-writing characteristic of the SPM process, the fabrication can be completed in a single step. Also, the fabrication can be performed in air, that is, vacuum is not necessary, rendering the process simple and easy to control. More importantly, SPM technique allows the fabrication of nanostructures in a size below the diffraction limit of the light source that poses the ultimate resolution limit in a conventional optical lithography. Because of these advantages of scanning probe techniques for nanofabrication, scanning probe lithography has been investigated by many researchers for process and application developments. Among the different types of scanning probe technique, NSOM lithography is one of the favored techniques. In NSOM lithography, the optical near-field produced at the tip of a nanoprobe, within an order of tens of nanometer range, interacts with the sample to produce nanometer size patterns. Because the interaction between the optical near-field and the sample surface is basically a photochemical or photothermal process, conventional materials used in far-field optical lithogra-

phy, for example photoresists or photopolymers, can be used as well as a new material, which is another benefit of the NSOM lithography over other SPM techniques.

In NSOM lithography, nanoprobes with and without an aperture can be used. For the case of apertureless probe, the enhancement of optical field between the probe tip and the sample surface irradiated by a laser light induces topographical or photochemical changes on the surface [1,2]. However, a probe with an aperture in a typical size of 100 nanometer is more often employed in the NSOM lithography. With the use of a probe having an aperture, the irradiation dose on the sample surface can be directly controlled and more freedom is allowed in material selection. Examples of nanofabrication using NSOM lithography with an apertured-probe include photonic crystal on photoresist [3], nanodot arrays on azo-hybrid sol-gel films[4], nanodot arrays on conjugated polymer films [5], metal oxide structures on composite metal thin films [6], molecular nanostructures on self assembling monolayers [7], optical recording marks on photochromic materials for data storage [8], etc.

Although studies of NSOM lithography for nanofabrication have been increasing recently, the central aspects of this technique such as resolution limit or shape and size variations of the patterned structure with respect to process conditions are not fully understood. In this study, we report the experimental results for nanopatterning of photoresist and azopolymer using NSOM with a cantilever type nanoprobe. The effects of process parameters such as laser power incident on the nanoprobe aperture, scanning speed of the probe tip with respect to the sample surface, contact and noncontact mode operations of the NSOM on the pattern width and depth are examined. Nano dot and line arrays are fabricated using NSOM lithography to demonstrate the feasibility of this method for the application to data storage or nanograting fabrication. Also, the fabrication of a nanostructure in silicon substrate using a NSOMpatterned passivation layer, silicon nitride, as an etch mask is demonstrated for the potential application to nanodevice fabrication.

II. EXPERIMENT

Schematic diagram of the experimental system used for this study is shown in Fig. 1. A continuous wave helium-cadmium (He-Cd) laser (wavelength 441.6 nm, maximum output power 130 mW, TEM_{00} mode) was used as the light source. A variable neutral density filter was installed at the laser output side to control the laser beam power. To measure the power incident on the nanoprobe, the laser beam was split into two beams of which one is coupled into the optical fiber and another is directed to the photodetector for measurement. The ratio of light energy transmitted through

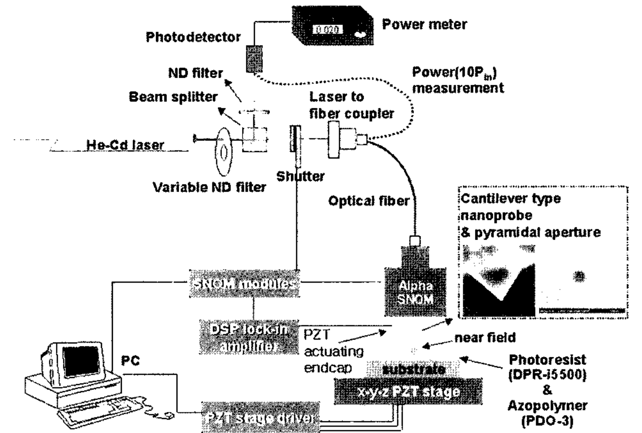


FIG. 1. Experimental setup for NSOM lithography.

the optical fiber to that measured by the photodetector was precalibrated. Also, the laser beam power at the end of the optical fiber, that is, before being connected to the NSOM (alpha SNOM, WITec Co.), was compared to the laser light power emerging from the objective lens after passing through all the optical surfaces in the beam path inside the NSOM. The ratio of the laser beam power emerging from the objective lens to that from the optical fiber was 0.1. The laser beam power described in the following sections is that of the beam emerging from the objective lens, which is irradiating on the entrance side of the nanoprobe. An electromagnetic shutter was employed to turn on and off the laser light during fabrication. A cantilever type nanoprobe with an approximately 100nm aperture at the apex of the pyramidal tip is used for patterning. Both contact and noncontact mode operations are utilized for the experiments.

A multirange positive photoresist (DPR-i5500, Dongjin Semichem) was used as the patterning material. For sample preparation, the photoresist was spincoated on a silicon wafer (100) as follows. First, hexamethyldisilane (HMDS) was spincoated on wafer to improve the adhesion of photoresist to the wafer surface and baked at 110℃ for 10 min in a convection oven. Then the photoresist was spincoated (5sec at 2000 rpm and 35 sec for 4000 rpm) and baked for 20min at 110℃. The thickness of the thereby prepared photoresist film was approximately 1 μm as measured with a surface profiler (alpha step 500, KLA Tencor Co.). For fabrication of fine structures through the entire thickness of photoresist, the photoresist was mixed with a solvent (tetra hydro furan) to produce a coating thickness below 100 nm.

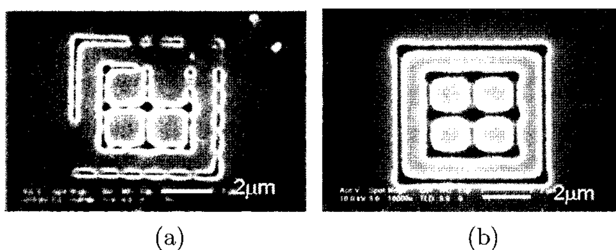
An azopolymer (Poly disperse orange-3) was also used as the patterning material. Azopolymer has a special property such that when irradiated by a laser light, material in the irradiated region moves to the surrounding nonirradiated region, making a hole. With this

phenomenon, nanopatterning without post processing is possible. The azopolymer powder was dissolved into cyclopentane with 10 wt.% and then filtered using 0.2 μm mesh filter. Filtered azopolymer solution was spincoated on Si wafer at 2,000 rpm 5 sec and 4,000 rpm 35 sec. Then it was baked in convection oven at 80℃ at ambient pressure for 1 hour to remove the solvent.

Patterning of the photoresist and azopolymer was carried out by moving the sample on the piezo stage of the NSOM while laser light is irradiated through the nanoprobe aperture and at various conditions to examine the influence of process variables on the variation of the width and depth of the nanopatterns. In the case of photoresist, to find the nanopatterns easily, 70 μm size micropatterns were produced around them using a far-field light from the objective lens. Then the patterned sample of photoresist was developed in a developer solution for 1 min and rinsed with deionized water. For the azopolymer sample, far-field patterning is not required because an addressed wafer substrate was utilized. The width and depth of the nanopatterns were measured with a scanning electron microscope or an atomic force microscope (AFM, XE-100, PSIA Co.). In the following, the pattern width is represented by the value of full width at half maximum (FWHM) and the depth is measured from the sample surface.

III. RESULTS AND DISCUSSION

As explained in Section II, two operation modes are available for the NSOM, that is contact (DC) and noncontact (AC) modes. To examine the effects of operation modes on the patterning results, a test pattern using a photoresist sample was fabricated using both modes and the results are shown in Fig. 2. For the noncontact mode, a characteristic discontinuity along the probe path was observed in most cases. This discontinuity is considered most certainly due to the variation of the gap between the sample surface and the tip of vibrating probe. In the noncontact mode operation, the probe vibrates at its resonance frequency and the gap control is made through monitoring the resonance amplitude. Considering the fact that near-field reduces exponentially from the output aperture, it looks like that energy input to the photoresist varies drastically with the variation of sample-tip distance. On the other hand, the result for contact mode showed a very uniform pattern with no discontinuity. Based on this results, we conclude that in the case of photoresist patterning contact mode operation is more advantageous than the noncontact mode. Accordingly, we conducted all the experiments below using the contact mode.



(a) (b)

FIG. 2. Patterning results for (a) noncontact (AC) and (b) contact (DC) operation modes of the NSOM. Experimental conditions are (a) P_{in}=10 μW, V=4 μm/s and (b) P_{in}=15 μW, V=6 μm/s.

Fundamentally, the NSOM lithography is done through photochemical reaction induced by near-field light in the photoresist and azopolymer. Thus the key parameter that affects the pattern width and depth should be the total amount of energy irradiated on the sample surface [9]. As the energy input into the material increases, the volume of photochemically reacted region also increases from the irradiation spot, resulting in a wider and deeper pattern. Generally, in our experiment, the width and depth decreases for decreasing laser beam power or increasing scan speed which means less energy input into the material.

By controlling the laser beam power or scan speed, a desired nanopattern would be produced on the substrate. First, we fabricated line arrays as a preresearch for nanograting fabrication. Line array fabricated at different scan speed of V=10 and 20 μm/s are shown in Fig. 3 (a). In the cross-sectional AFM image (Fig. 3 (b)), it is shown that a line array with 500 nm period, 100 nm width, 11 nm depth can be fabricated. The empty area between the patterns for V=10 μm/s and V=20 μm/s is the region where the line scanning is done with the shutter closed. From this nonpatterned part, we can confirm that the patterned lines are produced by photochemical reaction of the photoresist, not by the friction of sample surface with the tip of nanoprobe. Surface roughness (r_{rms}) is measured to be about 5 nm, which could deteriorate the patterning resolution as the pattern width and depth become very small. Improving contrast even when the pattern is very fine, on the order of a few nanometers, would be further studied.

With the success of line array fabrication, we tried the fabrication of nanograting on a silicon substrate by incorporating masking and etching processes for the possible application to functional nanodevice or nanomask fabrication using NSOM lithography. As etching process, wet etching on (110) silicon is adopted because vertical etching is theoretically possible in (110) silicon, which could lead to the fabrication of high aspect ratio nanostructures. For the etch mask, silicon nitride of 50 nm thickness is deposited on the (110) silicon with LP-CVD (low pressure chemical vapor deposition) process. Photoresist is spincoated over the silicon nitride film to a thickness of 120 nm and subsequently patterned

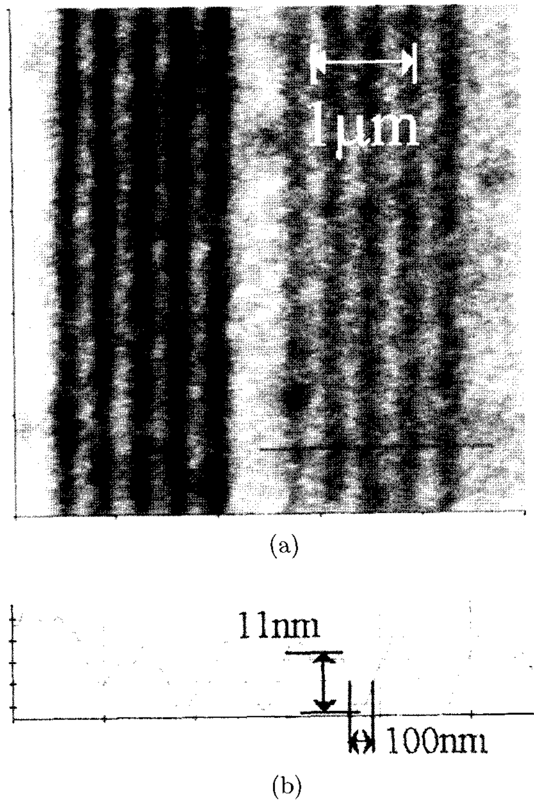
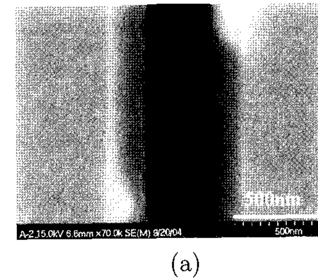
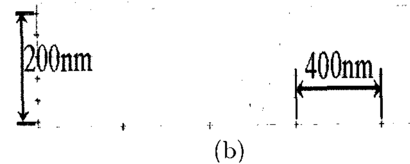


FIG. 3. Fabrication of line array on photoresist (a) AFM image of patterned line array. Line period p=500 nm, experimental conditions are P_{in}=2 μW, V=10 μm/s for left 5 lines and V=20 μm/s for right 5 lines. In the middle of these two patterns, a line was lithographed while the shutter was closed (V=10 μm/s). (b) Cross-sectional image of line array lithographed at V=20 μm/s (indicated in Fig. 3 (a) using a horizontal line). Line width (FWHM) and depth are approximately 100 and 11 nm, respectively.

for a line array using NSOM lithography. The patterned sample is then washed and dry etched for 40sec using RIE (reactive ion etching) under the condition of O_2 5 sccm, CF_4 50 sccm, 150 W, 55 mtorr so that the silicon nitride along the NSOM pattern can be completely removed while the silicon nitride in the non-patterned area survives the etching. After dry etching, silicon is exposed along the initial photoresist pattern so that a wet etching can be done. However, the original resolution on the photoresist was not conserved on the silicon because this was our first experiment on silicon and the process parameters for dry etching were not set properly. The dry etched sample is wet etched in 45% KOH etchant at 70℃ for 5min using the silicon nitride as etch mask while ultrasonic wave excites the etchant to remove generated bubbles easily. After the etching, measured silicon nitride's thickness was almost 50 nm, which means that silicon nitride works very well as an etch mask. The resultant etched pattern is shown in Fig. 4 (a). The width at the top of the etched groove is approximately 400 nm and the etched depth excluding the thickness of silicon nitride is approximately 160 nm (Fig. 4 (b)). It is expected that by reducing the thicknesses of the photoresist and silicon nitride the fabrication of a nanograting with finer resolution could be possible.

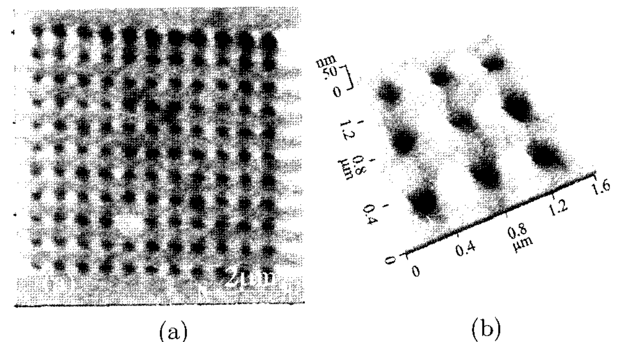
AFM measured image of nano dot array fabricated on photoresist is shown at Fig. 5. The periodic distance between each dot is 500 nm (Fig. 5 (a)). The average depth of dot is 36 nm and average diameter (FWHM) is 223 nm approximately (Fig. 5 (b)). The intentional absence of the mid-bottom position's dot in Fig. 5 (a)


(a)



(b)

FIG. 4. Example of NSOM-written pattern transferred on the silicon substrate using masking and etching processes. The etched depth excluding the silicon nitride layer (thickness≈50 nm) is approximately 160 nm and the width at the top surface is 400 nm.



(a) (b)

FIG. 5. Fabrication of nano dot array on photoresist (a) AFM image of 11×11 dot array, period=500 nm, P_{in}=2 μW, irradiation time t=0.02 sec except for the 1st row (t=0.04 sec) (b) three dimensional AFM image of dot array, average dot diameter (FWHM) 223 nm, average dot depth≈36 nm.

demonstrates that arbitrary sequences can be fabricated.

Azopolymer material has unique characteristic of photodriven mass transport such that when it is irradiated by light, the azobenzene group polymer in the irradiated region moves to the outer region, resulting in an indented pattern [10]. Therefore, no development process is necessary for this material. We examined the patterning characteristic of azopolymer using NSOM lithography for the possible application to data storage devices. The results for line array fabrication are shown in Fig. 6 (a). Even at the scan speed of V=0.2 μm/s, a uniform line pattern is produced. The area between the line of V=0.05 μm/s (1st line from the left) and V=0.03 μm/s (3rd line from the right), the nanoprobe scanned on the surface at V= 0.04 μm/s while laser is turned off (shutter closed). We see that there is no trace of a line. From this result, we confirm that patterning on azopolymer material is also done by photochemical reaction of azopolymer, not by the friction of sample surface with the tip of the nanoprobe. Surface roughness of the patterned sample is measured to be less than 1nm so that high contrast patterning can be achieved even when the pattern size is very fine. Fabrication

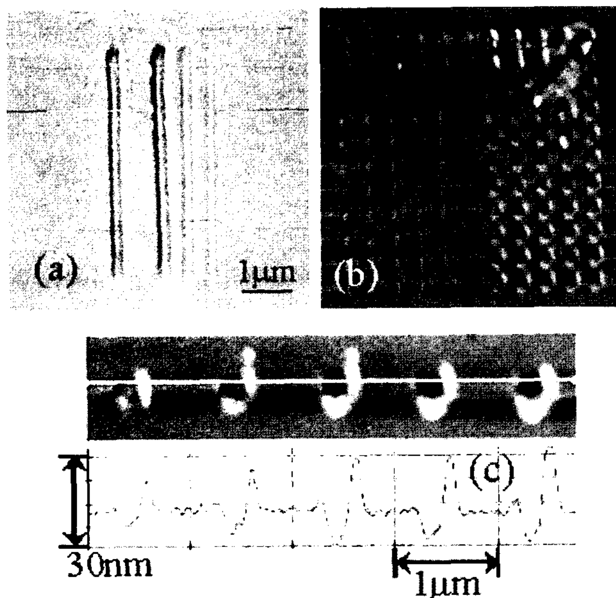


FIG. 6. Fabrication of nano line and dot arrays on azopolymer (a) AFM image of line array with one line missed intentionally(between the line of V=0.05 μm/s and line of V=0.03 μm/s) by closing the shutter during lithography, period=500 nm, P_{in}=10 μW, V=0.05 μm/s, 0.03 μm/s, 0.1 μm/s, 0.2 μm/s from left to right (b) AFM image of nano dot array, 5×5 μm^2, period=500 nm, P_{in}=10 μW, t=1 sec for left 6 columns and 3 sec for right 5 columns, dot width≈80~100 nm, depth≈4~6 nm for t=1 sec (c) cross-sectional view of AFM measured dots for various irradiation time, P_{in}=10 μW, t=1,2,3,4,5 sec from left to right.

results of nano dot array on azopolymer with spatial period of 500 nm are shown in Fig. 6 (b), which corresponds to the data density of 9 bit/μm^2. By further reducing the distance between each dot and minimizing the dot size, application of NSOM lithography to data writing on azopolymer would be possible. Note that as the irradiation time increases, dot size also increases because more azobenzene group polymer moves to the outer region of the irradiated spot (Fig. 6 (c)).

IV. CONCLUSION

With a He-Cd laser as the light source and a nanoprobe that has 100 nm aperture, NSOM fabrication of nano line and dot arrays with 500 nm period on photoresist and azopolymer is demonstrated. The minimum resolution was 80~100 nm for azopolymer. As the laser beam power decreases or scan speed increases, finer structures can be fabricated while the contrast weakens due to the surface roughness of the sample. The feasibility of NSOM lithography for the fabrication of nanograting on silicon is demonstrated by employing an etching mask. Using direct writing process of NSOM lithography, fabrication of functional nanostructures with a customized design would be possible.

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