

Large-area parallel near-field optical nanopatterning of functional materials using microsphere mask

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Abstract

Large-area parallel near-field optical nanopatterning on functional material surfaces was investigated with KrF excimer laser irradiation. A monolayer of silicon dioxide microspheres was self-assembled on the sample surfaces as the processing mask. Nanoholes and nanospots were obtained on silicon surfaces and thin silver films, respectively. The nanopatterning results were affected by the refractive indices of the surrounding media. Near-field optical enhancement beneath the microspheres is the physical origin of nanostructure formation. Theoretical calculation was performed to study the intensity of optical field distributions under the microspheres according to the light scattering model of a sphere on the substrate.

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1. Introduction

Nano-engineering of functional materials, such as the silicon and thin silver films, has received much research interest in recent decades. The feature size in the current trend of nano-engineering has been reduced down to 100-nm and beyond [1]. To obtain such a small feature size, a number of nanopatterning techniques were developed. The approach of near-field optical nanopatterning, for example, near-field scanning optical lithography, is attracting worldwide interest for its ability to overcome the optical diffraction limit, which has been a research challenge on conventional optical lithography [2]. However, this technique has a low throughput that is far below industrial needs. Therefore, low-cost and high-speed alternative nanofabrication techniques are needed. Recently, laser-assisted near-field optical nanopatterning using microsphere masks was

proposed as a promising parallel nanofabrication technique because it can offer the means to fabricate nanostructures over a large sample area [3]. When a transparent microsphere is irradiated by the laser light, it generates a strong enhancement of the light under the microsphere in near field. Uniform nanobumps on Si(100) wafers have been obtained using a single layer of microspheres as the mask [4–8]. However, the roles of the substrate and surrounding media around the microspheres on the results of nanopatterning are still not well understood. In this work we studied the formation of nanostructures on Si(111) surfaces. In addition, the working media was changed to vary the optical refractive indices during laser patterning of silver films. The change in refractive index is expected to affect the intensity of near-field optical enhancement, which leads to different patterning results.

2. Experimental

The experimental setup is illustrated schematically in Fig. 1. A KrF excimer laser of 30-ns pulse width and 248-nm wavelength was used as the light source. The laser beam was incident normally to the sample surface with a selected beam area using a 10 mm × 5 mm rectangular aperture to ensure the uniformity

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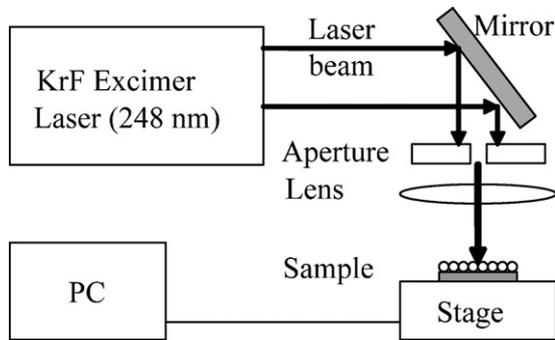


Fig. 1. Schematic diagram of the experimental setup.

of the light intensity. The laser fluence was adjusted to be in the range from 100 to 240 mJ/cm². The samples were put on a PC-controlled stage and irradiated with a single laser pulse at each processed area.

The mask was a layer of SiO₂ microspheres with a diameter of 1.0 μm from a commercially available colloidal suspension (Duke Science). The samples used in the experiment were Si(1 1 1) wafers and thin silver films with a thickness of 35 nm on the silicon substrates. Before applying the microsphere mask, the silicon samples were cleaned in ethanol and acetone followed by rinsing in deionized water, while the silver films were used as-prepared. The samples were baked in a vacuum oven at 80 °C for 1 h to reduce the humidity. After that, diluted microsphere colloids were deposited on the samples to form a hexagonally closed-packed monolayer by naturally vaporizing the solvent. Air and water were employed as processing media. The laser treatment was monitored with a high-magnification optical microscope (Olympus MX50). After the laser irradiation, the samples were further examined with a scanning electron microscope (Hitachi S-4100).

3. Results and discussion

Fig. 2(a)–(c) shows the surfaces of Si(1 1 1) wafers patterned with the SiO₂ microsphere mask in air at the incident laser fluences of 100, 160 and 240 mJ/cm² respectively. It can be observed that the silicon wafers have been patterned with nanoholes. These nanoholes have a mean diameter of 300 nm when prepared at a laser fluence of 100 mJ/cm² and increase up to 500 nm at a laser fluence of 160 mJ/cm². When the laser fluence was further increased up to 240 mJ/cm², cracks appeared due to the surface strains induced by the melting process. The exact physical origin of the formation of the nanoholes still needs to be elucidated. From the point of view of laser annealing, the melting-resolidification process is essential for the formation of nanoholes on Si(1 1 1) surface [4,6,8,9]. After being enhanced by the microspheres, the intensity of the laser light on the silicon surface has a Gaussian-like distribution as shown in Fig. 2(d). Theoretical calculation indicates that the enhancement of electrical field intensity, the component carrying the energy, can be as high as 76 times of the incident one. The absorption of the intense laser light causes the silicon melting to generate a high temperature field that radially decreases from the center of the molten zone to the edge. As a consequence, the temperature gradient induces strong thermocapillary force in the molten area, which leads to an outward flow that moves the liquid silicon away from the molten center. After a rapid self-cooling and solidifying process, nanoholes are created. When

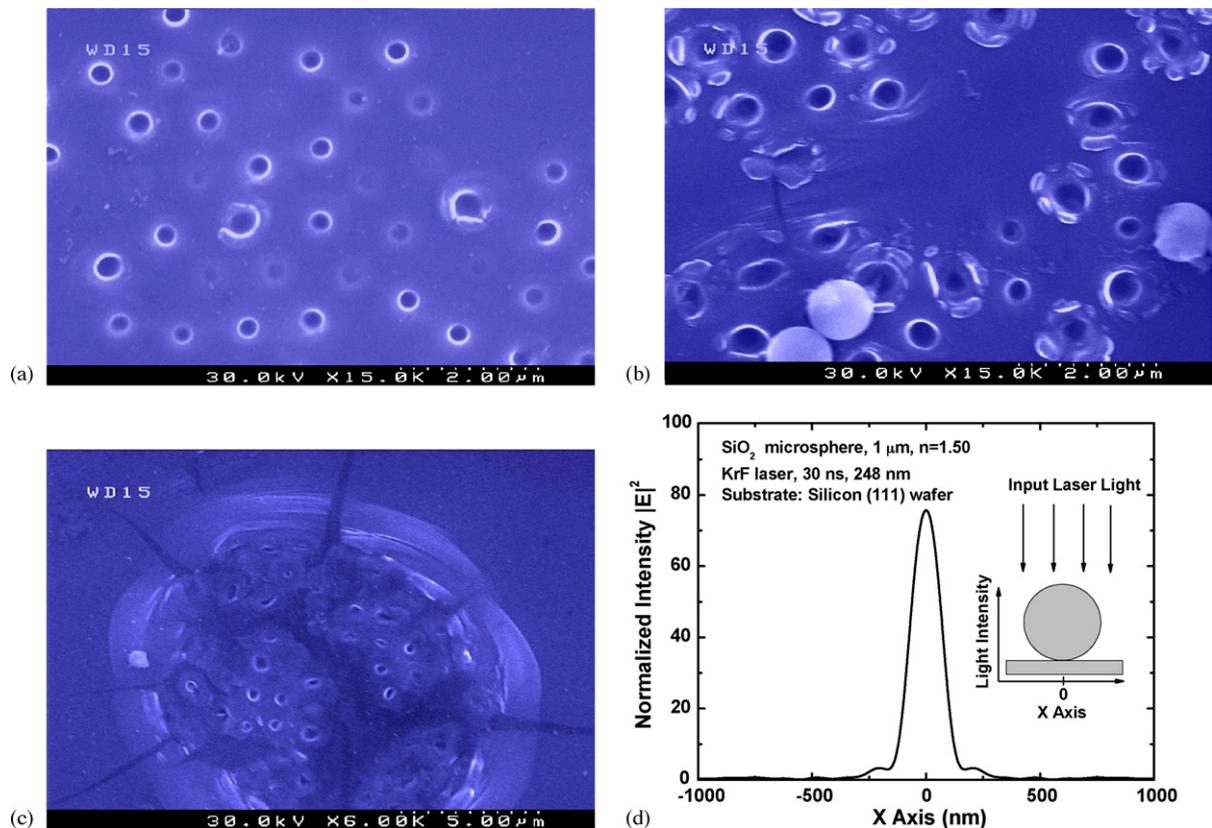


Fig. 2. SEM images of Si(1 1 1) wafer patterned with SiO₂ microsphere mask at laser fluences of (a) 100 mJ/cm², (b) 160 mJ/cm² and (c) 240 mJ/cm². (d) The calculated intensity of the laser light on the silicon surface. The intensity E^2 is normalized to input intensity E_0^2 .

the laser energy is high enough, vaporization and ablation can occur to enhance the removal of silicon. As demonstrated in Fig. 2(b) and (c), higher laser fluence can make bigger nanoholes due to the removal of more silicon. As the threshold laser fluence for ablating silicon is around 1500 mJ/cm^2 , it reveals that when the microspheres are irradiated at an incident laser fluence of 240 mJ/cm^2 , the light intensity beneath the microspheres is enhanced greatly over the threshold to cause the removal of silicon, which results in nanohole patterns on the sample surface. We also noted that similar works have been done on Si(1 0 0) wafers to create unique hillock-like nanostructures [4–8]. The difference on the formation of nanoholes and nanohillocks can be attributed to the different crystalline properties between silicon (1 0 0) and silicon (1 1 1) wafers. These different surface orientations can result in different distributions of the thermoelastic fields, which further cause different nanostructures under sufficiently high intensity of laser illumination [10].

To study the effect of the surrounding media on the results of nanopatterning by microspheres, we performed laser irradiation of the silver films both in air and with a layer of water deposited on the surface. The original silver films were smooth without any defect. When the sample is irradiated through a microsphere mask in air ($n = 1.0$), uniform nanopatterns are created as presented in Fig. 3(a). Most of the microspheres are removed with a single laser pulse. Due to the strong enhancement of the optical field, there are silver nanoparticles formed at the optically enhanced area with an average size of $130 \pm 40 \text{ nm}$. The patterned nanopoints have an average diameter of $520 \pm 50 \text{ nm}$. When the refractive index of the medium is increased by the

addition of water ($n = 1.333$), the patterns become dim, and the size of silver nanoparticles is reduced to $100 \pm 20 \text{ nm}$ as displayed in Fig. 3(b). The patterned nanopoints have an average diameter of $460 \pm 50 \text{ nm}$. It demonstrates that the optical enhancement in water is greatly reduced. This study is in good agreement with a previous report on steam laser cleaning, which found that a properly selected high optical refractive index medium can lower the damage of the substrate surface by decreasing the near-field focusing [11].

The SiO_2 microspheres focus the incident laser radiation onto the substrate, while the incident optical field is coupled with multiple scattered and reflected optical fields. This coupling process is further increased with the presence of a substrate. The distributions of near-field optical intensity can be estimated within the framework of classical Mie theory and the improved exact model for light scattering with a sphere on the substrate [12]. Fig. 4(a) and (b) show the normalized intensity distribution of light just beneath the microsphere on a 35-nm silver film. As

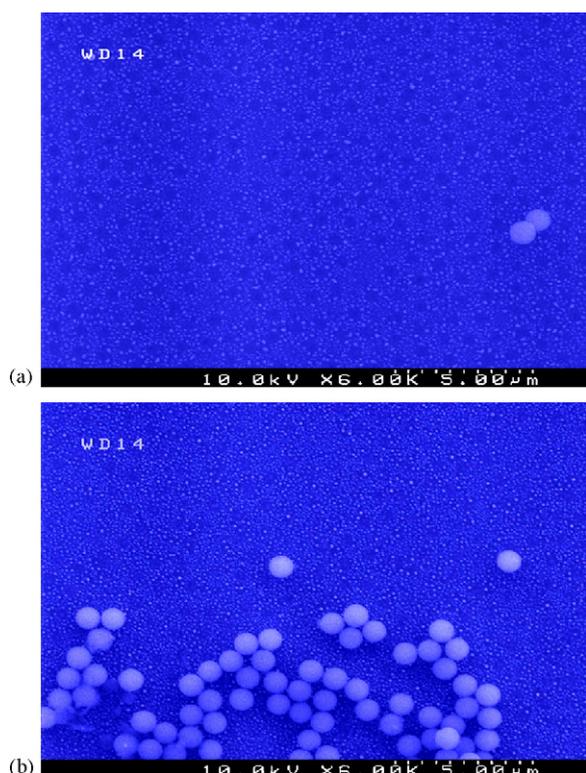


Fig. 3. SEM images of (a) 35-nm silver films patterned with SiO_2 microsphere mask in air, and (b) in water. The laser fluence was 240 mJ/cm^2 .

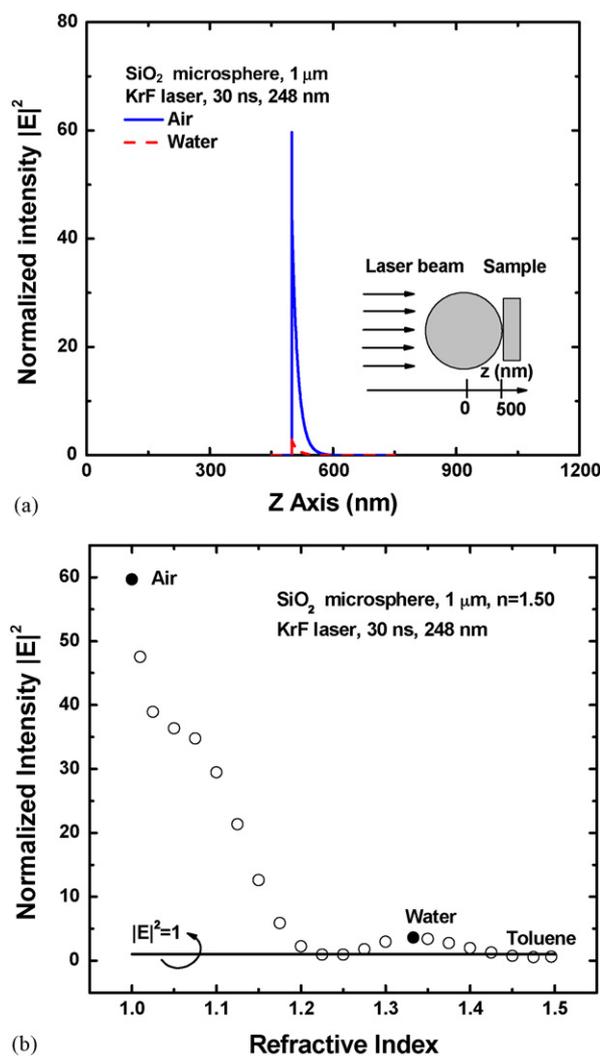


Fig. 4. Results of near-field optical calculations of laser irradiation of a SiO_2 microsphere on 35-nm silver film. (a) Normalized optical enhancement along the z axis; (b) normalized optical enhancement under SiO_2 microsphere in different media. The intensity E^2 is normalized to input intensity E_0^2 .

shown in Fig. 4(a), the experimental configuration is the same, but the intensity profiles change significantly with different optical refractive indices of the surrounding media. It indicates that a higher optical refractive index gives rise to a lower optical enhancement. By changing the optical refractive indices, the calculation results of optical enhancement show that there is a main peak at $n=1.0$ and a second minor peak at $n=1.333$ (refractive index of water). Though the origin of the minor peak needs to be studied, its relative low intensity due to the presence of water is in good agreement with the experimental results.

4. Conclusions

Uniform nanoholes have been patterned on Si(1 1 1) surfaces using laser irradiation of a layer of microsphere mask at laser fluence far below the ablation threshold of silicon. Thermocapillary force, which is created by melting silicon due to strong near-field optical enhancement, is believed to be responsible for the formation of the nanoholes. The near-field optical enhancement is affected by the optical refractive indices of the surrounding media. Bigger nanopatterns and silver nanoparticles were made on the thin silver films using the microsphere mask in the media, with a lower optical refractive index. Theoretical calculation indicates that there are two peaks of the enhancement

with a main peak at the optical refractive index of air and a second minor peak at the optical refractive index of water. This study can provide useful information for the near-field optical nano-engineering of functional materials.

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