NEAR-FIELD ENHANCED MASSIVELY PARALLEL NANOSCALE MODIFICATION OF SOLIDS

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ABSTRACT

Direct massively parallel nano patterning of solid surfaces (silicon and borosilicate glass) is accomplished by utilizing the optical field enhancement between the silica nanospheres and substrate, when irradiated with an Nd:YAG laser. Nano-patterns such as hole array or an island array of 300 nm were created on both silicon and glass by using nanospheres of 640 nm diameter. However, for silicon, in addition to the dent array formed at low laser energy, a sombrero-type nano-bump array was produced at higher laser energy due to Marangoni effect. It is found that non-linear absorption of the enhanced field is the primary reason for the creation of nano-features on glass. Also for patterning glass, the contribution of scattering towards field enhancement is minimized by irradiating the spheres from the back side.

INTRODUCTION

Fabrication technology on the nanometer scale has attracted much attention in the last decade due to the industrial demand for smaller and smaller structures for the manufacture of quantum devices and extremely high-density recording media. As a result, a lot of structuring techniques such as lithography [Dial et al, 1998] and field ion beam patterning [Terris et al, 2000] have been investigated for nanofabrication. However, most of these techniques are limited either by their inability for large-area fabrication or by the diffraction limit and in most cases the high manufacturing costs. To overcome the diffraction barrier and spatially-control matter on a nanometer scale, a variety of nanofabrication techniques employing optical near field has been proposed.

The physics of evanescent electromagnetic waves, which is the central concept used in near-field optics dates back to Newton when he first recognized the phenomenon of total internal reflection. But the importance of such waves was ignored for a long time in optical and surface physics until the existence of an exponentially decaying field near the exit of an aperture was proved [Leviatan, 1986]. The branch of near-field optics has come a long way since then, due to its enormous potential for applications in super-fine optical microscopy, high-resolution photofabrication, single-molecule detection and local spectral analysis.

The application of near-field for fabrication, where structuring is done with the utilization of laser radiation by overcoming the diffraction limit with the use of nanospheres is the latest in the development of near-field technology. The accidental discovery of particle induced damage during dry laser cleaning of irregularly shaped Al_2O_3 particles on glass [Halfpenny et al, 1999] has led to this exciting yet simple technique. Nanosphere based fabrication induced by the optical near-field was also employed for patterning a urethane-urea copolymer containing a push-pull type azobenzene. In this kind of polymers, the surface deformation is attributed to the gradient force of the optical near-field [Ikawa et al, 2001].

In this article, we report a massively parallel nanopatterning method for creating nanofeatures on silicon and glass by depositing a monolayer of silica nanospheres. When the laser beam is incident on the top surface of spheres, there is a field enhancement at the interface between the sphere and the substrate. This optical field enhancement by nanospheres can be explained by Rayleigh and Mie scattering theories [Moreno et al, 1998]. Rayleigh scattering takes place when the diameter of the sphere is less than the wavelength of the light. In this case, the sphere is treated as a dipole radiator and the electric field enhancement is at its sides along the direction of polarization of the incident light and there is hardly any focusing. In contrast, when the diameter of the sphere is equal to or greater than the laser wavelength, light is scattered elastically and the field is enhanced several times at the exit side of the spheres. Mie theory calculations show that this enhancement is due to both near-field and scattering effects [Munzer et al, 2001]. Such optical enhancement can lead to local melting or even vaporization of the substrate materials for nanoscale surface patterning. It has been reported that the intensity distribution changes dramatically with the size of the sphere and also the distance between the sphere and the substrate [Watanabe et al, 2001].

For the patterning of silicon we use the field enhancement by an excimer laser beam (248nm, 10ns) incident on the top side of silica spheres. The second objective is to separate these two optical effects and use only the near-field effect for surface modification. This is achieved by delivering the laser beam from the backside of the sample which minimizes the effect of scattering on surface modification. To satisfy this criterion, the sample has to be transmissive to the laser wavelength used. So we used glass as the substrate for fabrication and an infrared Nd:YAG laser (1064nm, 7ns) for illumination from the back side. The features created by illuminating from both the front and back sides are studied in detail using a scanning electron microscope. Also Marangoni effect and nonlinear absorption phenomenon observed in silicon and glass respectively are investigated and the results are explained.

EXPERIMENTAL SETUP

The samples used for patterning were silicon and glass wafers of 500 μm thickness. A colloidal suspension of monodispersed silica spheres of 640 nm diameter diluted with deionized water was applied on the samples and let to dry. These spheres arranged themselves to form a hexagonally closed-packed monolayer by means of a self-organizing process [Mosbacher et al, 1999]. This was confirmed by observing the sample under a scanning electron microscope (SEM), shown in Figure 1.

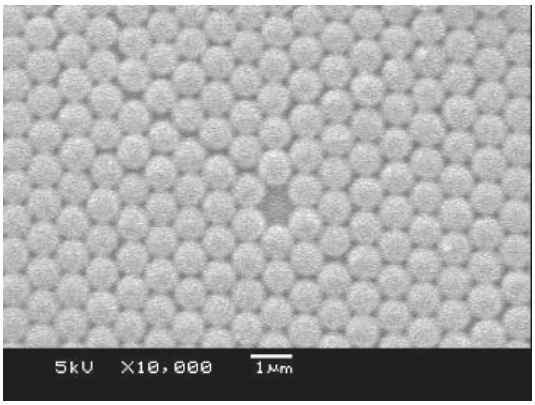

FIGURE 1. SEM MICROGRAPH OF THE HEXAGONALLY CLOSE-PACKED MONOLAYER OF SILICA NANOSPHERES.

The schematic of our experimental setup is shown in Figure 2a. The output of the laser beam passes through a beam splitter which is used to split the incident laser beam into two - one part to be used for nanopatterning and the other for measuring the energy of pulses used for fabrication. The sample is mounted on a 3-D stage and the laser beam is focused on to the

sample by using a plano-convex lens. The monolayer was then irradiated by a single laser pulse and the resulting features formed on the sample were studied using a scanning electron microscope.

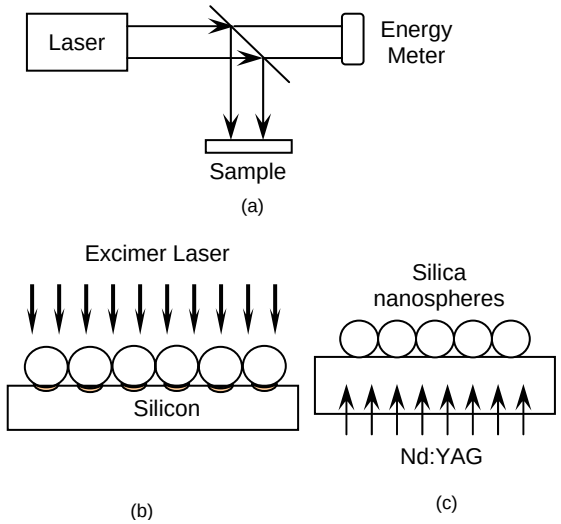

FIGURE 2. (A) SCHEMATIC OF THE EXPERIMENTAL SETUP, (B) IRRADIATION OF SILICA SPHERES ON SILICON FROM THE TOP SIDE, (C) IRRADIATION OF SILICA SPHERES ON GLASS FROM THE BOTTOM SIDE.

RESULTS AND DISCUSSION

An excimer laser of 248 nm wavelength and 10 ns pulsewidth was used for the nanopatterning of *n*-type (100) silicon samples. This type of silicon has a native oxide layer of 2 - 3 nm thickness. When irradiated with a single pulse, the spheres were ejected out and features on the nanometer scale were created on the substrate. Since the diameter of spheres is larger than the wavelength of irradiating laser they are called Mie spheres. According to Mie theory the spheres act as spherical lenses and the incident intensity is enhanced as a result of focusing and the maximum field intensity is right at the interface between the spheres and the substrate. It has been shown that the enhanced optical near-field could be several orders of magnitude higher than the original incident intensity and can eventually lead to local melting and evaporation of silicon [Munzer et al, 2001].

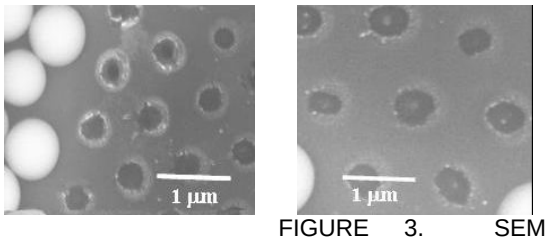

FIGURE 3. SEM MICROGRAPH OF HEXAGONALLY ARRANGED NANODENTS ON SILICON PRODUCED AT DIFFERENT LASER FLUENCES: (A) 4.0 mJ/Cm^2, (B) 8.0 mJ/Cm^2.

Figure 3 shows an SEM micrograph of the nanodents created on the silicon sample. The hexagonally arranged dents were approximately 300 nm in diameter and the distance between the centers of the features was about 640 nm which is the same as diameter of spheres used. This confirms the formation of features right underneath the location of spheres. To provide a better understanding of the enhancement phenomenon, we calculated the intensity enhancement due to scattering by the dielectric spheres according to Mie theory for a laser wavelength of 248 nm and 640 nm silica spheres with a refractive index of 1.39. The intensity enhancement calculations show that the high intensity part is located within 20^o of the vertical axis on the beam exit side of the sphere, which corresponds to a spot size of 35% of the sphere diameter. A similar figure obtained based on Mie theory for 1064 nm laser wavelength is shown in Figure 6.

Also it was found that at low intensities bowl-type dent structures with a raised outer rim were formed (Figure 3a) and “Sombrero-type” bumps with a central peak start to form at an energy density of around 8mJ/cm^2 (Figure 3b). With a further increase in intensity the central peak increases in height. Marangoni-driven flow is believed to be the mechanism responsible for the formation of nanostructures [Chen et al, 2000]. Also the enhanced optical field has a Gaussian-like intensity distribution. This creates a temperature field in the silicon substrate that decreases from the center to its edge of the molten zone induced by the enhanced optical field upon pulsed laser irradiation. The temperature-gradient-induced thermocapillary force results in an outward flow. Such thermocapillary effect is believed to be responsible for the formation of the outer rim and the bowl-type nanostructure. However, when the laser intensity is high enough to trigger surfactant vaporization such as SiO_2 in this work, a surface compositional gradient will be

established in the molten zone where the hottest central region of the melt has a lower SiO_2 concentration due to the highest local laser intensity. Therefore, the highest surface tension exists in the center of the molten zone, resulting in an inward flow of the molten material towards the center if the chemicapillary force dominates. However, the edge region remains the same trend for the ring formation because the laser energy is still not high enough to evaporate SiO_2 there and therefore the thermocapillary effect dominates. It is observed that the height of the center peak increases with pulse energy for the laser intensities used in this work.

To verify this hypothesis, we repeated the experiment using a hydrogen-terminated silicon substrate by dipping the silicon wafer into a HF solution before depositing the monolayer of nanospheres [Morita et al, 1995]. The result in Figure 4 indicates the chemicapillary effect is minimized due to the removal of SiO_2 at a similar laser intensity of 10 mJ/cm^2, and therefore, only bowl-type nanostructures were formed.

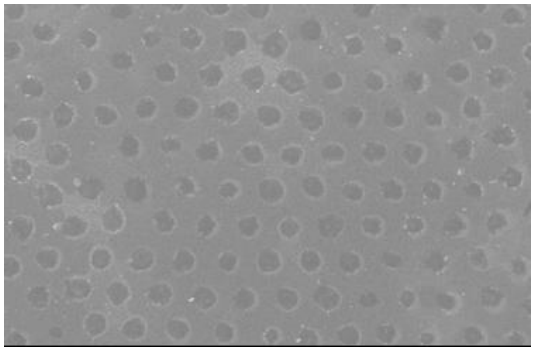

FIGURE 4. BOWL-LIKE NANO STRUCTURES CREATED ON HYDROGEN-TERMINATED SILICON SURFACE.

In order to better understand the nature of optical field enhancement it is desirable to separate the focusing and near-field optical effects and use only the near-field effect for surface modification. To illustrate this concept, we deposited silica nanospheres on borosilicate glass samples and irradiated it from the bottom side with a 1064 nm Nd:YAG laser. Since glass is transparent to this wavelength, the laser beam passes through the glass substrate and is incident on the bottom surface of the spheres. The schematic of irradiation from the back side of spheres is shown in Figure 2c.

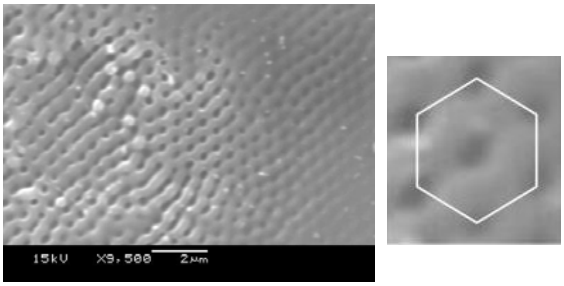

FIGURE 5. HEXAGONAL ARRANGEMENT OF NANOSTRUCTURES CREATED ON GLASS BY IRRADIATION WITH ND:YAG LASER.

After a single pulse of 3 J/cm^2, the spheres were ejected from the glass substrate and nanostructures were produced on the surface as shown in Figure 5. The SEM micrograph shows a periodic array of 350 nm dents on the surface and as before the features were arranged hexagonally. In order to confirm the elimination of the focusing effect, calculations based on Mie theory were again performed for a laser wavelength of 1064 nm. The results presented in Figure 6 show that the intensity enhancement is symmetrical about the vertical center-axis and there is no intensity enhancement due to scattering for angles between 90^o and 270^o. This means that at the interface between the sphere and the glass substrate, the scattering effects are negligible.

Since the linear absorption coefficient of glass is very low at the experimental wavelength, we believe pattern formation is due to nonlinear absorption of the enhanced optical field by the glass material. Although the physical mechanisms responsible for infrared photosensitivity are still under investigation, the process is believed to be initiated by a multiphoton absorption process and therefore exhibits a highly nonlinear dependence on the intensity of the illuminating beam [Varel et al, 1997]. These intensity-dependent changes in the material's optical properties affect the propagation of the incident light. The refractive part of the nonlinearity gives rise to self-lensing, which can lead to optical damage. The absorptive part of the nonlinearity can decrease the transmittance at high intensity and provide a path for optical damage in the material at lower irradiances than conventional dielectric breakdown [Soileau et al, 1989]. Also the presence of a surface breaks the inversion

symmetry of the medium normal to the boundary and makes nonlinear interaction possible.

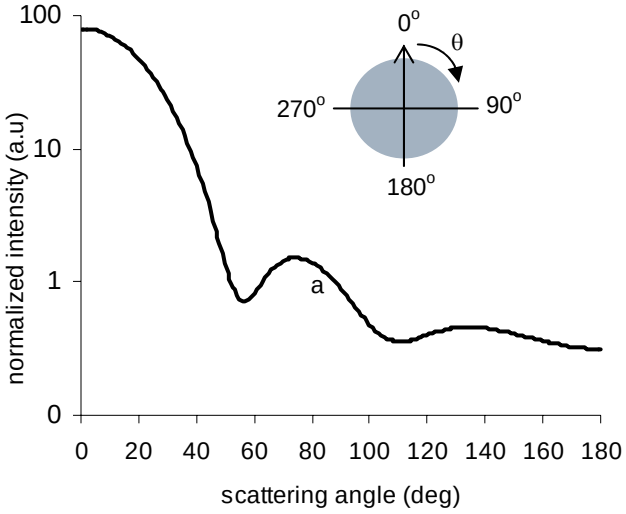

FIGURE 6. CALCULATED LASER INTENSITY DISTRIBUTION AROUND THE NANOSPHERE AS A FUNCTION OF SCATTERING ANGLE FOR AN INCIDENT LASER WAVELENGTH OF 1064 nm.

The optical field enhancement could also come from the rear surface interference effect. Due to the interference of the incoming and reflected waves, the electric field strength is higher at the rear side of a weakly absorbing slab with n>1, so that optical breakdown threshold is lower at the rear side. Rear surface ablation has been previously reported for fused silica and borosilicate glasses at 193 nm, which is very well absorbed by these glasses [Crisp et al, 1972]. Despite this enhancement on the rear side, no damage was observed at the rear side in the experiments performed with 1064 nm laser in the absence of spheres at similar laser fluences.

CONCLUSIONS

A massively parallel nanopatterning technique is implemented successfully for creating nanodents on silicon and glass wafers. In patterning silicon by illuminating the spheres from the top surface, competition between the thermocapillary force and chemicapillary force resulted in a bowl-type nanostructure at lower laser energy and a Sombrero-type structure at higher laser energy. The formation of only bowl type nanostructures with a hydrogen-terminated silicon substrate confirms the Marangoni-driven flow mechanism in silicon. In order to have a better understanding of the formation mechanism and to separate the scattering from near-field effect, the laser beam is delivered from the backside of the sample which minimizes the effect of scattering on surface modification. This work gives more insight in to characterizing the effect of near-field as well as studying the mechanism of surface deformation. Also, the patterning of glass using a nanosecond 1064 nm laser will open up new applications and new topics of research.

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