# Marangoni effect in nanosphere-enhanced laser nanopatterning of silicon

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We report a Marangoni effect in nanosphere-enhanced laser direct nanopatterning of silicon surface. A monolayer of nanosphere array was formed on the silicon substrate by self-assembly. A 248-nm excimer laser was used to irradiate the sample surface. Due to optical field enhancement between the nanosphere and the substrate, the silicon surface was locally melted. The molten material was redistributed due to surface tension forces, resulting in the formation of a nanodent array. The morphology of the nanodents changed from bowl-type to ''Sombrero'' with increase of laser intensity as a result of a Marangoni effect that arises due to the competition between a thermocapillary force and a chemicapillary force acting on the molten material. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1581387]

Traditional materials processing in the nanometer range using laser technology is very difficult with conventional optics due to the diffraction limit of the beam wavelength. Recently, a near-field technology has been developed to circumvent the diffraction limit,[1,2] permitting the spot size to be reduced down to 20 nm. In most near-field techniques, this resolution is achieved by placing a small aperture between the sample and the light source. If the aperture-to-sample separation is maintained to much less than a wavelength, the resolution will be determined by the aperture size rather than by the diffraction limit. This near-field technique using a single hollow near-field tip to deliver the laser beam has been proposed for surface modification and lithography on a nanoscale due to optical field enhancement in the near-field.[3] However, this approach is difficult to implement in an industrial setting due to sophisticated hardware to control the near-field distance (approximately 5 nm above the surface), possible blockage of the hollow tip due to material deposition from the machined surface, and limited throughput. Another approach involves illuminating the tip of a scanning tunneling microscope or an atomic force microscope with a pulsed laser.[4] Nanostructures with lateral dimensions below 30 nm and therefore well below half of the laser wavelength have been produced underneath the tip, but with very low serial throughput.

An approach that may lead to massively parallel nanostructuring was demonstrated by using an array of micro- or nanospheres as a mask to pattern a solid substrate.[5–7] If the diameter of the sphere is greater than the wavelength of the incident laser beam, the transparent sphere may act as a lens to focus the laser beam onto the substrate for surface modification. If the diameter of the sphere is equal to or smaller than the laser wavelength, near-field enhancement may play an important role in nanostructuring the substrate surface. In this letter, we report a Marangoni effect in nanosphere-enhanced laser direct nanopatterning of a solid silicon surface.

Silicon wafers of *n*-type, (100) crystal orientation were used as the substrate. This type of silicon wafer has a native oxide layer of 2 to 3 nm thick. Silica nanospheres with a diameter of 640 nm were used in this work. The nanospheres were monodispersed in an aqueous solution. We applied this solution to the silicon surface. After evaporation of the solvent, a monolayer of hexagonally close-packed nanospheres was formed on the silicon due to capillary forces (Fig. 1), measured by scanning electron microscopy (SEM). The sample was then irradiated with a KrF excimer laser ($\lambda = 248$ nm, full width at half-maximum = 10 ns). A lens of 50.8-mm focal length was used to focus the laser beam onto the sample mounted on a three-dimensional precision stage. Different laser intensities were used to study the laser energy dependence of the nanostructures. The laser energy was measured by a joulemeter located between the sample and the lens. All experiments were performed under ambient conditions.

The laser-patterned silicon surface was characterized by SEM, as shown in Fig. 2, and verified by atomic force microscopy (AFM). The spheres disappeared in the laser-irradiated area with nanostructures formed with the same hexagonal pattern on the silicon surface. Large-scale images indicated that nanodent structures were produced underneath the spheres. It is interesting to see that bowl-type dent struc-

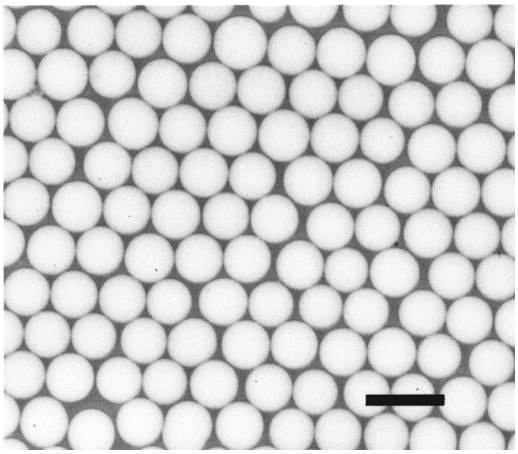

FIG. 1. SEM image of a hexagonally close-packed monolayer of silica nanospheres of 640 nm in diameter on a (100) silicon substrate. The scale bar indicates 1 $\mu$m.

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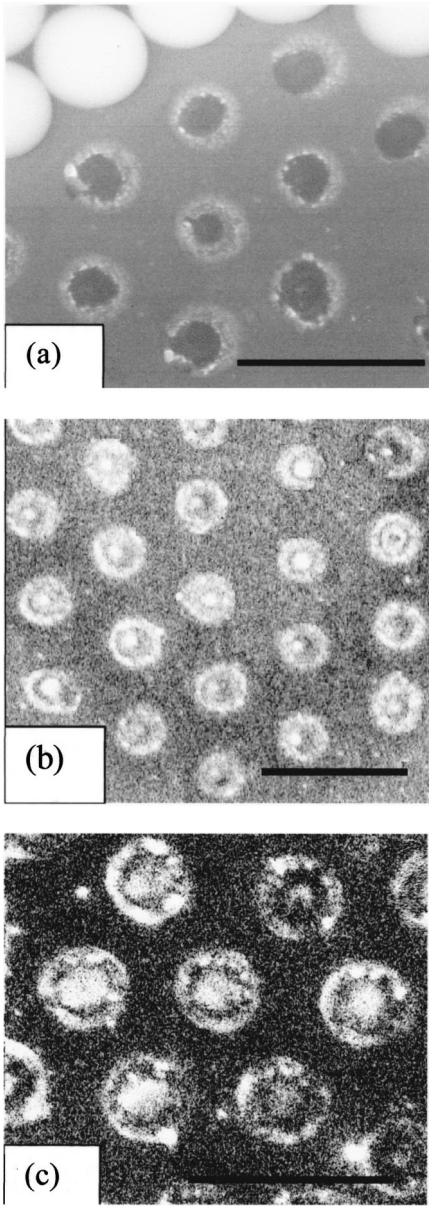


FIG. 2. SEM images of hexagonally arranged nanostructures on a silicon substrate with a naturally oxidized layer. Nanodents were produced upon irradiation of 248-nm KrF excimer laser at different laser fluences: (a) 4.1 mJ/cm$^2$, (b) 8.0 mJ/cm$^2$, and (c) 10.1 mJ/cm$^2$. The scale bar indicates 1 $\mu$m.

tures with a raised outer rim were formed at 4.1 mJ/cm$^2$ [Fig. 2(a)]. ''Sombrero-type'' bumps with a central peak start to form at around 8 mJ/cm$^2$ [Fig. 2(b)]. The central peak increases its height slightly with the laser intensity [Fig. 2(c)].

To provide a better understanding of the phenomenon in Fig. 2, we calculated the optical field around the nanosphere according to the Mie scattering theory.[8] Figure 3 shows the laser intensity as a function of the angle in the sphere. Since the laser intensity of the tail part is low and will unlikely lead to material removal, we may treat this type of intensity distribution as Gaussian; that is, $I(r,t)=I(t)\exp(-r^2/r_0^2)$, where $r_0$ is the radius of the Gaussian beam and $I(t)$ is the laser pulse shape. Moreover, it is seen that the high intensity part is located within 20° of the sphere. This corresponds to a spot size of 35% of the sphere diameter. This value agrees well with the measured dent size of approximately 300 nm, depending on incident laser energy (Fig. 2).

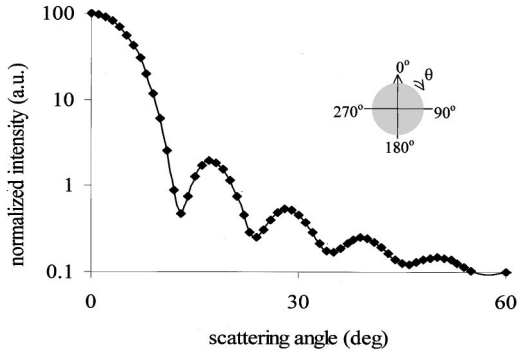


FIG. 3. Calculated laser intensity distribution as a function of angle around the nanosphere.

We propose a Marangoni-driven flow mechanism for the formation of the nanostructures on the silicon surface. The Marangoni flow is the motion of a liquid due to surface tension gradients. This Marangoni effect was demonstrated in a microscale in our previous work on texturing of NiP material using a laser beam with a Gaussian type intensity distribution.[9,10] There are two distinct components, thermocapillary and chemicapillary, which result from the thermal potential of a temperature gradient and the chemical potential of a compositional gradient, respectively. The thermocapillary force moves the material towards cooler regions having higher surface tension. The chemicapillary force also moves material toward regions of higher surface energy with a lower surfactant concentration. The surface compositional gradient can arise from the depletion of a surfactant.

As shown in Fig. 3, the enhanced optical field has a Gaussian-like intensity distribution through the nanosphere. 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.[11] The result in Fig. 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.

In summary, we have demonstrated that nanosphere-

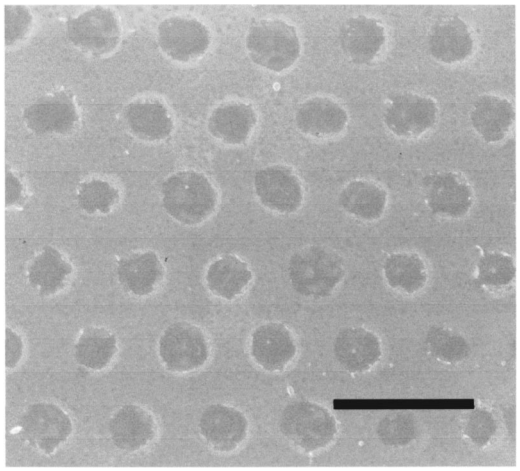

FIG. 4. A SEM image of hexagonally arranged nanostructures on a hydrogen-terminated silicon substrate. The laser fluence is 10.0 mJ/cm$^2$. The scale bar indicates 1 $\mu$m.

enhanced optical field can be utilized to pattern a solid surface in a nanoscale. By forming a monolayer of nanosphere array on the substrate, this direct nanopatterning process can be highly parallel. The enhanced laser intensity has a Gaussian-like profile, leading to a Marangoni effect in the molten zone: the thermocapillary effect moves the materials outward from the hottest center to the edge while the chemicapillary effect acts to move the molten materials inward towards the center if the laser intensity is high enough to trigger surfactant depletion. 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.

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