Nanobump arrays fabricated by laser irradiation of polystyrene particle layers on silicon

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Two-dimensional (2D) nanobump arrays were fabricated by laser irradiation of a regular lattice of absorptive polystyrene (PS) microspheres on an undoped (100) Si wafer. The experiments were performed with single-pulse 248 nm KrF laser radiation. The structure of the arrays fabricated by this method was characterized by field emission scanning electron microscope and atomic force microscope. The near-field effects under the absorptive particle are studied. The ablation and thermal processes induced by the optical near-field around the particles are investigated. The formation mechanism of nanobumps is discussed.
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Fabrication technology on the nanometer scale is becoming important from the viewpoint of industrial applications, such as a high-resolution lithography for the manufacture of high integrated circuits, quantum devices or extremely high-density recording media. Several technologies, such as a nanoimprinting,[1] electron beam lithography,[2] and field ion beam patterning[3] have been investigated for nanofabrication. Recently, optical near-field lithography has been developed as a new technology to overcome the diffraction limit.[4] Many research groups have demonstrated patterning of surfaces at resolution below the diffraction limit using optical near-field effects. Their work has been realized by the use of light-coupling masks,[5] an evanescent near-field optical lithography method,[6] or an embedded-amplitude mask.[7] Nanofabrication was also attained by illuminating a local probe of a scanning tunneling microscope (STM)[8,9] or an atomic force microscope (AFM)[10] or a near-field scanning optical microscope (NSOM)[11] with a laser. We have also proposed a nanofabrication method induced by the optical near-field around transparent nanoparticles without using a scanning probe.[12,13] The latter technique permits one to employ all types of light-induced processes for direct single-step surface patterning by ablation, etching, deposition, and chemical or structural transformation.

In this letter we report on the fabrication of silicon nanobumps on an undoped (100) Si wafer. The method employs a regular two-dimensional (2D) lattice of microspheres. Such lattices were formed by well-known self-assembly processes from colloidal suspensions. In contrast to earlier investigations,[12–15] we used absorptive spherical particles for processes. The ablation and thermal processes induced by the optical near-field around the particles are investigated. The created nanofeature under the particles and its morphology under the ablated particles are examined and studied.

A polystyrene (PS) latex (Duke Science) with particles of diameter $d = 1.0$ μm was used. Monodisperse PS microspheres were applied to a freshly purchased and undoped silicon (100) substrate after the suspension had been diluted with deionized water. The substrate was kept still until all of the water had been evaporated. As a result, a PS bead monolayer array with a large area was obtained on the Si surface. The PS bead array was exposed to a single shot of a KrF excimer laser with a wavelength $\lambda = 248$ nm and pulse width $\tau = 23$ ns. A 25 mm $\times$ 5 mm rectangular laser spot with uniform light intensity was used. The laser fluence is in the range from 30 to 300 mJ/cm^2. The laser beam was incident normally on the sample with the particle array.

Figure 1(a) shows a field emission scanning electron microscope (FESEM) image of a small part of the Si substrate that has been patterned by a single KrF-laser shot. The laser fluence incident onto the sample was 150 mJ/cm^2. The arrangement of features generated on the Si surface reveals the hexagonal lattice structure of the PS microspheres. The distance between the features is equal to the diameter of spheres. During the experiment, it is found that when the fluence was above 45 mJ/cm^2, most of PS particles within the laser spot were removed from the Si surface. The white spheres are PS particles left on the surface shown in Fig. 1(a). Closer inspection of the irradiated spots with FESEM displays that the diameter of the created feature is about 260 nm shown in Fig. 1(b). Because the used Si substrate is undoped, the morphology, and the profile of the created features cannot be seen clearly in FESEM analysis. Figure 2 presents an atomic force microscope (AFM) image and height profile of the created features. AFM results clearly show that the created features are a nanocone array. The arrangement of nanobump exhibits the hexagonal lattice structure of the PS spheres. The curve in Fig. 2(b) shows an AFM profile of three bumps. Their full width at half maximum (FWHM) height is about 260 nm, and their depth is about 42 nm. The morphology and the profile of the created features are completely different from those reported in Refs. 12–14.

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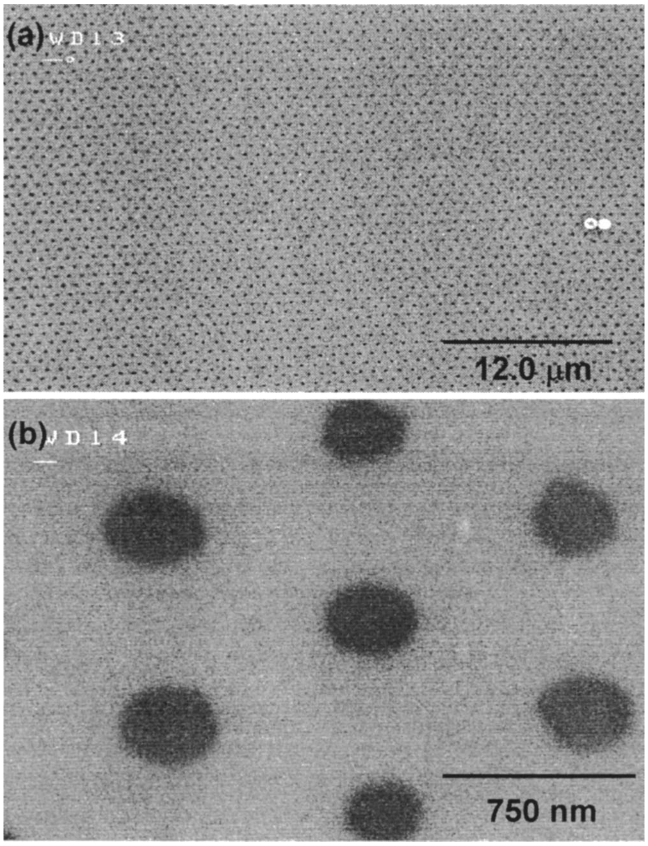

FIG. 1. (a) and (b) FESEM images of nanobump array formed on silicon by single-shot KrF laser radiation using a regular lattice of PS microspheres (d=1.0 μm).

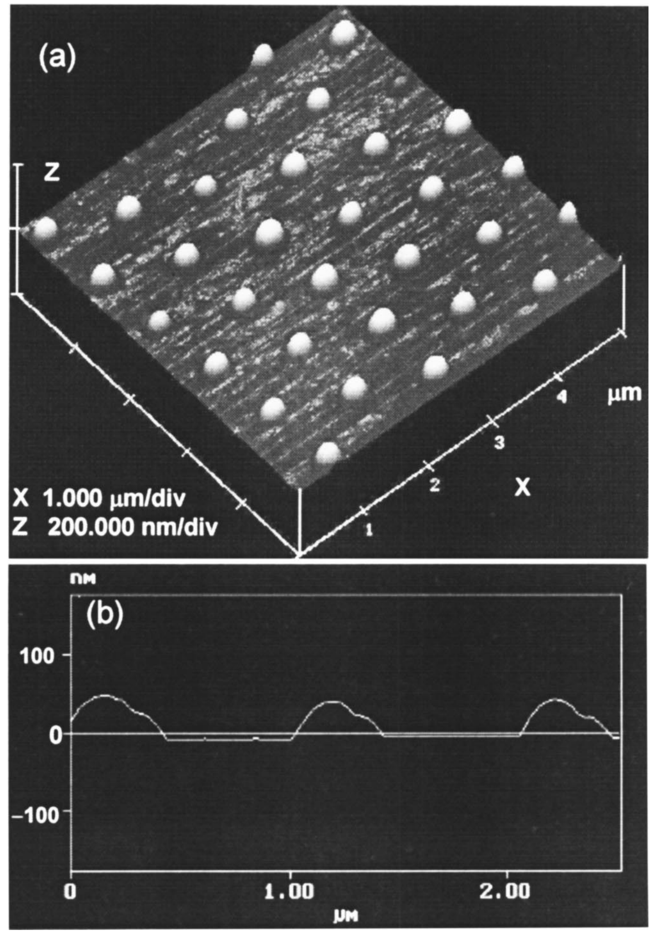

FIG. 2. (a) and (b) AFM image and depth profile of nanobump array formed on silicon by single-shot KrF laser radiation using a regular lattice of PS microspheres (d=1.0 μm).

Although Bäuerle *et al.* once reported submicrometer Si cones produced by microspheres in Ref. 15, they used SiO_2 microspheres of diameter $d=6$ μm with the Si substrate placed in the focal plane of microspheres deposited on a quarts support. The SiO_2 spheres have negligible absorption at 248 nm, and for spheres of this size, geometric optics plays an important role in laser-induced surface patterning but for smaller spheres, evanescent waves and near-field effects become important. Numerical calculations according to Mie theory and in the presence of the substrate in our previous papers[12,13] have demonstrated that energy localization under a transparent particle on the substrate surface can be below the diffraction limit.

In this work, PS microspheres have a significant absorption α^{PS} at the 248 nm laser wavelength ($\alpha^{PS}=6.3\times10^3$ cm^{-1}),[16] due to the $S_0\rightarrow S_1$ electronic transition in a PS phenyl group[17] compared to the negligible SiO_2 microsphere absorption at 248 nm. Because of the PS absorption at 248 nm one may expect direct laser heating to result in the melting of PS particles at temperatures of 110–125 °C.[18] The melting threshold for PS spheres is 50 mJ/cm^2 for $d=1$ μm, estimated from calculations of the maximum rise in temperature at the end of a 248 nm excimer laser pulse on the front and back sides of PS particles using a simple linear absorption model,[19] heat capacity $C_p^{PS}\approx1.6$ J/cm^3 K, thermal diffusivity $\chi^{PS}\sim10^{-3}$ cm^2/s (Ref. 18) and neglecting the role of the Si substrate. The large thermal coefficient of expansion for molten PS particles (typically 10^{-4} K^{-1} relative to 10^{-6} K^{-1} for Si)[18] may decrease thresholds for laser removing of particles because of an enhanced "hopping" effect. For such a low thermal conductivity material as PS, the onset of ablation near the threshold fluence occurs at the end of the pulse, since the material effectively stores the incident laser energy. As a result, PS particles can be removed almost completely from the Si surface with a fluence just above 45 mJ/cm^2. This value is competing with dry laser cleaning at fluences above the ablation threshold of the material in air of 100–120 mJ/cm^2.[19,20] It is even less than a half of the threshold laser fluence for cleaning of SiO_2 spheres of $d=1$ μm on Si substrate.[20] It is because of the low removing threshold fluence of PS particles that nanocone arrays with large area and uniform cone size can be fabricated by a single shot.

For an absorptive spherical PS particle $d=1$ μm, assuming that the incident plane wave at 248 nm is normalized to unity, and wave propagates along the z coordinate, the electric vector along the x coordinate, and magnetic vector along the y coordinate. The contacting point between the PS particle and the Si surface is set to be (0, 0). Figure 3 shows the calculated field intensity directly below the PS particle. It is shown that the PS particle is half transparent at 248 nm. When the laser normally irradiates the substrate with the particle, the laser fluence was greatly enhanced due to the optical near-field resonances under this half transparent PS particle. The optical field enhancement is about 36 at the contact point. The laser energy is mainly localized in the area with a FWHM enhancement $\cong$200 nm. The width of the created nanobump shown in Figs. 1 and 2 is very close to this confined dimension. Because of the near-field resonance, for the

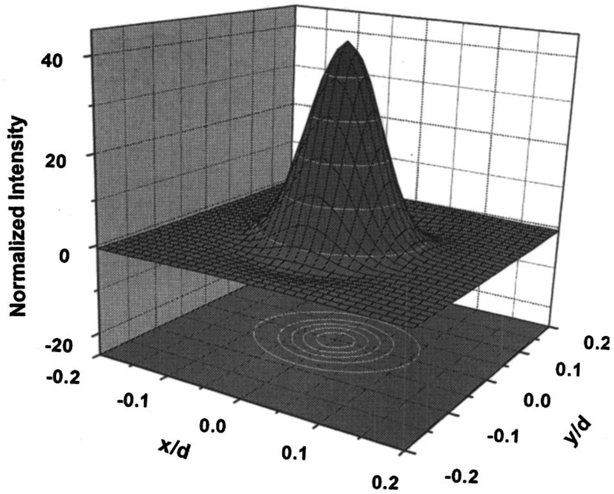

FIG. 3. Calculated field intensity under an absorptive PS microsphere (d=1.0 μm) on the Si surface at 248 nm.

incident fluence of 150 mJ/cm^2, the fluence at the contact point is well above the Si melting threshold at 248 nm of 500–750 J/cm^2.[21] Surface melting of the Si substrate takes place within the energy localized area.

Theoretically, there are two possible mechanisms for the nanobump formation.[22] The enhanced optical field shown in Fig. 3 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 upon pulsed laser irradiation. The temperature-gradient-induced thermocapillary force results in an outward flow. However, the highest surface tension exists in the center of the molten zone, inducing chemicapillary force. The chemicapillary force results in an inward flow of the molten material towards the center. The formation of bump in Fig. 2 indicates the chemicapillary effect may dominate. In addition, the anomalous behavior of the density of solid and liquid silicon may also contribute to the formation of the nanocone. With the experimental conditions employed, the silicon surface becomes molten within the confined area. After laser-induced melting, the silicon resolidifies. In contrast to the usual behavior of material melting, the density of liquid Si, $\rho^l(l\text{-Si}) = 2.52$ g/cm^3, is bigger than the density of solid Si, $\rho^s(c\text{-Si}) = 2.32$ g/cm^3. Thus, the volume of silicon increases during solidification. As a consequence, during cooling, the liquid silicon is squeezed radially to the center and forms a protrusion.

In summary we demonstrated that regular lattices of PS microspheres formed by self-assembly processes can be employed for single-shot fabrication of large regular arrays of nanobumps on Si surfaces. Nanobumps formation can be attributed to the optical near-field resonance of the PS particles, the anomalous behavior of the density of silicon near the melting point and the competition between the thermocapillary force and chemicapillary force. The distance between nanobumps can be varied via the diameter of microspheres. Potential applications of such Si-nanobump patterns include low dimensional electric systems, enhanced Raman scattering, displays, and sensors. Moreover, the method can be developed as a technology to create nanobumps on media disks for performance of the nanoscale flight height calibration.

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