Single-step fabrication of silicon-cone arrays

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A regular lattice of SiO_2 microspheres on a quartz support is used as a microlens system for laser-induced single-step fabrication of arrays of silicon cones on a (100) Si surface. The experiments were performed with single-pulse 248 nm KrF laser radiation. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1538347]

Regular two-dimensional (2D) lattices of microspheres formed by well-known self-assembly processes were recently employed for micro- and nanopatterning of substrate surfaces.[1–8] Here, such lattices have been used as lithographic masks for consecutive standard processing,[6–8] for direct laser-induced patterning of the support,[4,5] or as an array of microlenses that focus the light onto a nearby placed substrate.[1–3] This 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.[9]

In this letter we report on the fabrication of silicon cones on a (100) Si wafer. The experimental setup employed is similar to that described in Refs. 1 and 2. We use 248 nm KrF laser radiation and a fused quartz support covered with a hexagonally close-packed monolayer of a-SiO_2 microspheres of diameter $d=2r_{sp}=6\pm0.6\ \mu$m. The 2D lattice of microspheres was produced from a commercially available colloidal suspension (Bangs Laboratories Inc.) by employing a technique similar to that described in Ref. 10. The substrate was placed in the focal plane of the microspheres, i.e., at a distance $f\approx nr_{sp}/2(n-1)$ from the center of spheres. Here, r_{sp} is the radius and n the refractive index of spheres which is $n\approx1.4$.

Figure 1 shows an atomic force microscope (AFM) image of a small part of the Si substrate that has been patterned by a *single* KrF-laser shot of pulse length $\tau_\ell\approx28$ ns. The laser fluence incident onto the support was $\phi\approx250\ \mathrm{mJ/cm}^2$. The arrangement of cones generated on the Si surface reveals the hexagonal lattice structure of the microspheres. The distance between the cones is equal to the diameter of spheres. The full curve in Fig. 2 shows an AFM profile of a single cone. Its diameter at full width at half maximum (FWHM) is about 495 nm and its height about 350 nm. Both quantities are measured with respect to the surface of the silicon wafer. The cones are surrounded by a ring-shaped trench whose volume is, within $\pm5\%$, equal to the volume of the cone.

The formation mechanism of the cones observed in our experiments is completely different from that described in Refs. 11–13.

In the present experiments, cone formation can be explained by the anomalous behavior of the density of solid and liquid silicon. With the experimental conditions employed, the silicon surface becomes molten within the foci generated by the microspheres. Due to spherical aberration, the maximum intensity within these foci is $I_d\propto(r_{sp}/\lambda)I_0$ where I_0 is the incident intensity. After laser-induced melting, the silicon resolidifies. Resolidification starts at the edge of the molten zone and proceeds towards its center. In contrast to the usual behavior of materials with melting, the density of liquid Si, $\rho_\ell(\ell\text{-Si})=2.52\ \mathrm{g/cm}^3$, is *bigger* than the density of solid Si, $\rho_s(c\text{-Si})=2.32\ \mathrm{g/cm}^3$. 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. As a result, a solid cone surrounded by a ring-shaped trench is formed.

For a semiquantitative description of the solidification process we ignore any surface tension effects and start with a certain volume of liquefied silicon, V_ℓ. Because $\rho_\ell>\rho_s$, the level of the liquid, h_ℓ, is *below* the original silicon surface, h_s. Both h_ℓ and h_s refer to the maximum depth of the molten zone. From mass conservation we find

$$\rho_\ell dV_\ell+\rho_s dV_s=0, \tag{1}$$

where dV_ℓ and dV_s denote volume changes of the liquid and the solid, respectively. If F is the molten area at a certain time t and dh the change in height due to solidification, the total change in volume can be described by $dV=Fdh=dV_\ell+dV_s$. Then, we find from Eq. (1):

$$\Delta\rho dV_\ell+\rho_s F dh=0, \tag{2}$$

where $\Delta\rho=\rho_\ell-\rho_s$. We describe the liquefied volume at the time t by its radius r and its depth h', so that V_ℓ

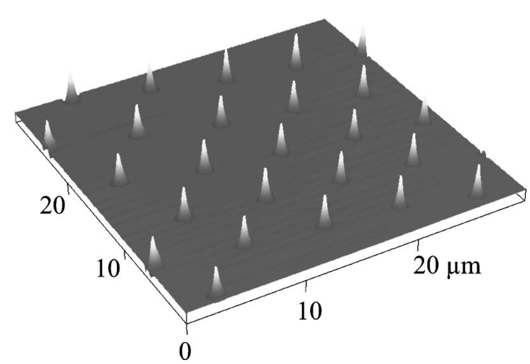

FIG. 1. Silicon cones fabricated on a (100) Si surface by single-shot KrF-laser radiation ($\phi=250\ \mathrm{mJ/cm}^2$, $\tau_\ell=28$ ns) using a regular lattice of SiO_2 microspheres ($d=6\ \mu$m) for focussing. The height of cones with respect to the original surface is 350 ± 30 nm.

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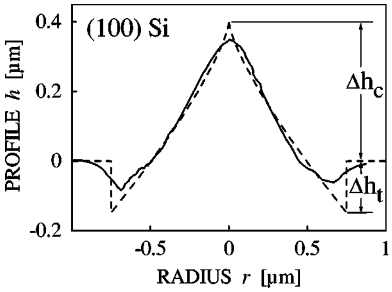

FIG. 2. Full curve shows an AFM profile of a silicon cone. The dashed curve was calculated from Eq. (5) using $h_\ell = 1.73\ \mu$m and $w_m = 0.75\ \mu$m as fit parameters.

$= V_\ell(r,h')$, and assume that the thickness of the resolidified material at the bottom is δ. The surface of the liquid can then be described by $h = h' + \delta$. The final surface profile is then described by $h = h(r)$. If the rates of solidification in axial and radial directions are related by $d\delta = -k dr$ we obtain from Eq. (2) with the Ansatz $k = \xi h'/r$:

$$\Delta\rho dV_\ell + \rho_s F\left(dh' - \xi h' \frac{dr}{r} \right) = 0. \tag{3}$$

We now describe the molten zone by a cylinder, i.e., by $V_\ell = \pi r^2 \ h'$, and set $\xi = 1$. With $\xi = 1$ the shape and the aspect ratio of the molten bath will vary weakly during solidification and r and h' will disappear simultaneously. With this Ansatz we find

$$\Delta\rho(2\pi r h' dr + \pi r^2 \ \ dh') + \rho_s \pi r^2 \left(dh' - h' \frac{dr}{r} \right) = 0,$$

which yields

$$\frac{dh'}{h'} = \beta \frac{dr}{r}, \tag{4}$$

with $\beta = 3\rho_s/\rho_\ell - 2 \approx 0.76$. With the boundary condition at the edge of the molten zone, i.e., with $r = w_m$, the height of the solidified surface is $h = h_\ell$, integration of Eq. (4) and substitution of h' by h yields

$$h = h_\ell \left(1 - \frac{1}{\beta} \right) \left(\frac{r}{w_m} \right)^\beta + \frac{1}{\beta} h_\ell . \tag{5}$$

The dashed curve in Fig. 2 shows a fit of this equation to the AFM profile. We used the depth and width of the molten zone as fitting parameters with values $h_\ell = \rho_s h_s/\rho_\ell = 1.73\ \mu$m and $w_m = 0.75\ \mu$m, respectively. The present model describes the main features of cones, including the curvature of the side walls. Clearly, the sharp drop in h at $r = w_m$ which is related to the assumptions and the boundary condition employed, is washed out due to heat diffusion and surface tension effects. The same effects cause the smoothening of the peak at $r = 0$. In Eq. (5) we find for the height of the cone with respect to the surface $\Delta h_c = h(r=0) - h_s = 2\Delta\rho h_s/(\rho_s - 2\Delta\rho)$ and for the depth of the trench $\Delta h_t = h_s - h_\ell = \Delta\rho h_s/\rho_\ell$. This yields a ratio of $\Delta h_c/\Delta h_t = 2\rho_\ell/(\rho_s - 2\Delta\rho) \approx 2.63$, which is in reasonable agreement with the measured profile.

The melt depth h_ℓ can be estimated *independently* from the heat balance.[9] If we compare the energy focused by a microsphere of radius r_{sp} into the molten zone, w_m, with the energy required for melting, we obtain $h_\ell \approx A\phi r_{\mathrm{sp}}^2/w_m^2 \rho_\ell (c_p \Delta T_m + \Delta H_m)$, where A is the absorptivity and c_p the specific heat of the material at an average temperature between $T = 300$ K and the melting temperature $T_m \cdot \Delta T_m$ is the laser-induced temperature rise, and ΔH_m the melting enthalpy. With the material parameters listed for c-Si in Ref. 9 we obtain $h_\ell = 1.88\ \mu$m. This value is in good agreement with the value of h_ℓ derived from the fit in Fig. 2.

In summary we demonstrated that regular lattices of microspheres formed by self-assembly processes can be employed for single-step fabrication of large regular arrays of cones on Si surfaces. Cone formation can be explained semiquantitatively by the anomalous behavior of the density of silicon near the melting point. The distance between cones can be varied either via the diameter of microspheres (presently available with sizes between 0.1 and 10 μm) or via higher order light interference patterns.[3] Potential applications of such Si-cone patterns include field-emitter arrays,[14] displays, or sensors.

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