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Chemical-assisted laser parallel nanostructuring of silicon in optical near fields

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Abstract
The authors present a simple and efficient technique for producing hexagonal arrays of nanostructures on silicon surfaces in chemical solutions. It utilizes the effect of optical near-field enhancement by self-assembled particle-lens arrays and a thermally induced chemical reaction with an alkaline solution. About 10^8 features can be produced simultaneously by one single laser pulse. Furthermore, the shape of the structures was found to be controllable, from concave holes to convex bumps, by means of a post-etching process, in the same chemical solution.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Surface nanopatterning with lateral dimensions down to nanometer scale has become increasingly important as the size of silicon (Si) devices shrinks. It is well known that restructuring of Si from a bulk material into nano-scale structures could lead to massive changes in its band structure and optical properties [1]. Besides the conventional processing techniques such as e-beam, x-ray and UV photo-lithography for nano-scale processing of Si, several near-field laser processing techniques have been demonstrated in recent years, which include the near-field scanning optical microscope (NSOM) technique [2], laser-assisted atomic force microscopy/scanning tunneling microscopy (AFM/STM)-tip patterning technique [3], contacting particle-lens array patterning (CPLA) technique, and plasmonic lithography technique [4]. Among them, the CPLA is likely to be the most promising technique for industrial applications as it is a low-cost and parallel processing technique [5, 6]. It utilizes a regular two-dimensional array of small particles as a lens array, which converts a laser beam into a multiplicity of enhanced optical spots in parallel at focus. To the best of our knowledge, the CPLA technique is limited to being employed in a gas or air environment up to date. It is not clear how a liquid medium will affect the CPLA process. Due to the contacting nature of particles and substrates in the CPLA technique, introducing of the liquid media unavoidably leads to the simultaneous immersion of the focusing lens and workpiece inside the liquid environment. This is different from the general cases of laser processing of materials in liquid media as they were carried out in a far-field (lens–workpiece distance $d \gg \lambda$) configuration and only the workpiece is immersed in liquid [7]. In this paper, we demonstrated that the CPLA technique can also be employed in a liquid environment and more importantly it can be combined with a chemical etching (KOH solution in this paper) process for Si nanostructuring over a large-area surface. In our specific experiments below, we found that the profiles of the obtained surface structures could be controllable, from concave holes to convex bumps, by post-etching of the obtained Si samples in the same chemical solution KOH.

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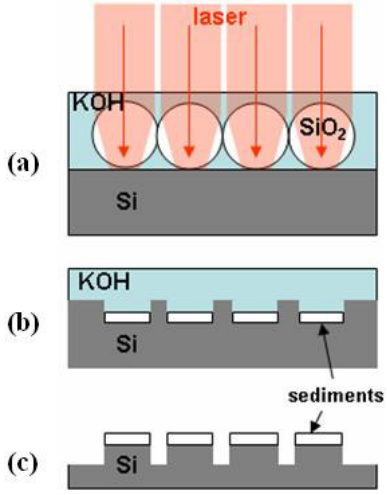

Figure 1. Schematic diagram of (a) the experimental configuration for proposed chemical-assisted laser surface patterning of Si with CPLA in 30 wt% KOH solution, and (b) 'u' shaped (concave holes) structures formed by laser-induced chemical reaction with reaction products left at bottom, and (c) 'n' shaped (convex bumps) structures generated by further etching in warm ($T = 40\,^{\circ}\mathrm{C}$) KOH solution.

2. Experiments and simulations

Figure 1(a) illustrates the schematic diagram of the experimental configuration. In our experiments, an n-type single crystal Si(100) wafer (refractive index $n_{\mathrm{Si}} = 1.57 + 3.565\mathrm{i}$) with a resistance 3–5 $\Omega\ \mathrm{cm}^{-1}$ was used as the sample. A close-packed hexagonal array of SiO_2 spheres (Duke Scientific, diameter $2a = 500$ nm, refractive index $n_{\mathrm{SiO_2}} = 1.51$) was formed on the Si surface in monolayer form by a self-assembly process, as shown in figure 2. It is estimated that an amount of 10^8 spheres were uniformly distributed in an area of 0.5 cm^2. The prepared samples (Si substrate with particles on the top) were left in air to dry completely, which ensures the establishment of the strong adhesion between particles and Si surface. This adhesion force is strong enough to hold the particles on Si surface even when the sample was subjected to a water flow. The liquid medium used in our experiments is 30 wt% KOH alkaline solution. The dried sample was fixed onto the bottom of a small container and KOH solution was then added into the container to completely immerse the sample and particles. The whole solution temperature was controlled by a hot-plate. The samples were irradiated with a KrF Excimer laser system (GSI-Lumonic IPEX848, wavelength $\lambda = 248$ nm, pulse duration $\tau = 15$ ns and repetition rate from 1 to 10 Hz, non-polarized light). Before characterization or post-etching processes, the irradiated samples were cleaned with de-ionized (DI) water and remained particles on the top of Si sample were carefully wiped away by a cotton pad. The final samples were characterized by scanning electron microscopy (Philips XL30 ESEM-FEG) and atomic force microscopy (Vecco AFM CP2).

In order to understand the focusing properties of particle-on-surface inside liquid, we have applied a widely used finite difference in time domain (FDTD) program to simulate the optical near-field distributions around the particles [8].

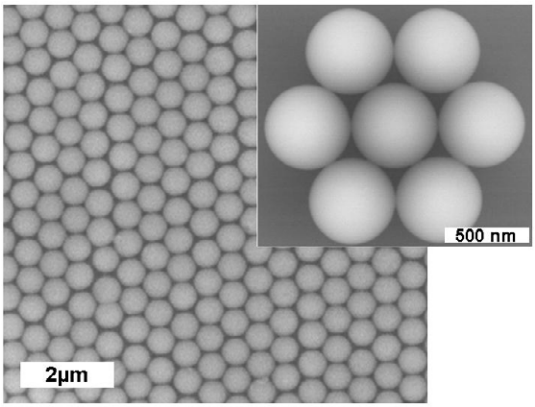

Figure 2. SEM images of a hexagonal monolayer of SiO_2 spheres ($2a = 500$ nm) formed by self-assembling process.

3. Results and discussions

Figure 3 shows the normalized electric field amplitude ($|E|$) plot around the hexagonal array of spheres on Si surface immersed in the KOH solution. As it can be seen, the particles act as focusing lenses and the electric field is enhanced within the regions near the particle–substrate contacting points. Due to high absorption coefficient ($\alpha = 4\pi\kappa/\lambda = 1.81 \times 10^6\ \mathrm{cm}^{-1}$) of Si at 248 nm wavelength, the regions with enhanced field distributions will be heated locally and the following chemical reactions between Si and KOH etchants could be greatly enhanced [9–12]:

$$\mathrm{Si} + 2\mathrm{OH}^- + 2\mathrm{H_2O} \rightarrow \mathrm{SiO_2(OH)_2^{2-}} + 2\mathrm{H_2}. \qquad (1)$$

Figure 4 shows the SEM and AFM images of a typical hexagonal array of u-shaped (cross-sectional view) hole structures produced on the Si surface in 30 wt% KOH solution at room temperature by a single laser pulse irradiation at a laser fluence of 0.98 $\mathrm{J\ cm}^{-2}$. There are around 10^8 holes in our processed sample. The holes are not perfectly round in shape and some of the hole edges are broken and linked together with neighboring holes. We think the main reason could be the fluctuation of the optical near fields due to the additional scattering by H_2 bubbles (as in equation (1)) as well as the possible perturbation of the stationary liquid solution during process. The average hole diameter and depth are 300 nm and 50 nm, respectively. The hole diameter is slightly larger than the theoretical spot size (~200 nm) of areas with field enhancement (see figure 3(b)) due to heat diffusion. The etching depth, on the other hand, is related to the thickness of the depletion layer that is also controlled by the heat diffusion process [13]. The penetration depth of the heat into the silicon under laser irradiation is determined either by the optical absorption length or the heat diffusion length. For a 248 nm wavelength laser irradiation of Si, the heat diffusion process slightly dominates over the optical absorption process for Si [14].

In order to see whether the produced hexagonal array of u-shaped hole structures on Si surface is stable or not in different environments, we carried out the post-etching experiments. We

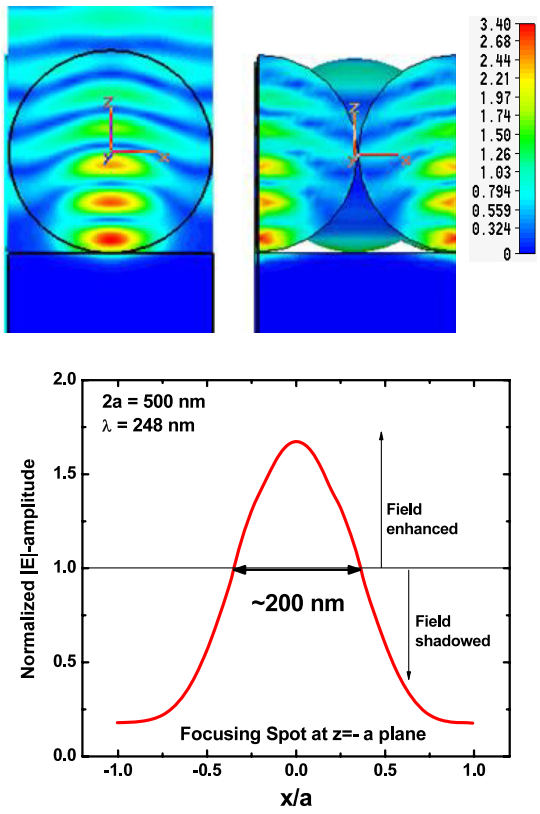

Figure 3. (a) Normalized $|E|$-field amplitude plot around a hexagonal array of particles sitting on Si surface inside a KOH solution under KrF laser irradiation (248 nm, 15 ns). The incident radiation has amplitude $|E_0| = 1$. The particles are transparent to laser source and act as focusing lens. (b) Shows the focus spot within the top plane of Si surface and just beneath the particles.

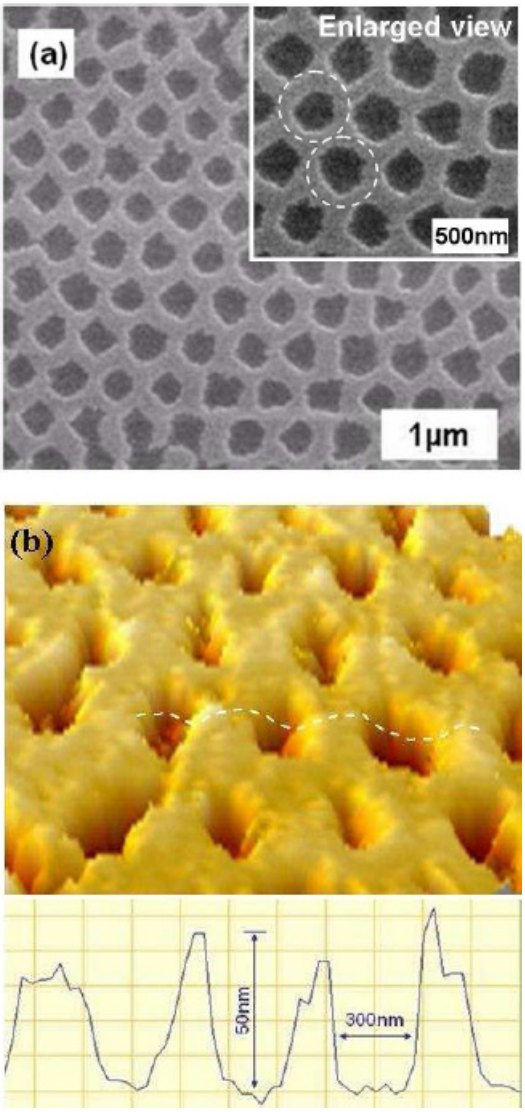

Figure 4. (a) SEM image of a hexagonal array of 'u' (cross-sectional view) shaped structures produced in 30 wt% KOH at room temperature by KrF laser irradiation at a laser fluence of 0.98 J cm^{-2}. (b) AFM profile showing average width and depth are 300 nm and 50 nm respectively.

kept the temperature of the solution at 40 °C and re-immersed the above samples in the solution for around 2 minutes. Interestingly, we found that the shape of the nanostructures had changed from the original concave u-shape to a convex n-shape (also in the cross-sectional view) after this process, as shown in figure 5. We believe such structure reversion is due to the generation of a thin protection layer at those reaction sites (see marked dash circles in figure 4(a) or figure 5(a) inset), which is supported by our EDX (energy dispersive x-ray) analysis results: the composition of the residue at those reaction sites contains a very high percentage of oxygen (mainly SiO_2). Although the whole KOH solution will not be saturated by the limited reaction products (very locally with 300 nm width and 50 nm depth at each reaction site), the reaction region tends to have a much higher concentration of $SiO_2(OH)_2^{2-}$ than other places. Consequently, the over-saturation of the solution in these regions will result in the formation of residue (see figure 1(b)). The reaction may be described by [15, 16]:

$$SiO_2(OH)_2^{2-} \xrightarrow{\text{oversaturated}} SiO_2 + 2OH^-. \qquad (2)$$

This explains the formation of SiO_2-rich layer at all reaction sites. Because of the dramatic difference in the Si/SiO_2 etch rate (ER) ratio (much higher for Si), the residue can work as a protection mask for the post-etching process. From previous work [9, 10, 17], it was suggested that 30 wt% KOH solution at 40 °C will have a ER(Si/SiO_2) ratio of 1000:1. At this temperature, the enchant will consume significantly less oxide and the etching rate for Si(100) is approximately 100 nm min^{-1} [9]. The similar phenomenon was observed by Ip Yam *et al* [11] in Cesium hydroxide, by Finne and Klein [18] in ethylenediamine, by Bhatnagar *et al* [19] in pyrocatechol and by Wu *et al* [16] using hydrazine for etching of Si. Wu *et al* also identified that the residue was mainly composed of SiO_2 [16]. In the words of Seidel *et al* [9, 10], such residue formation is attributed to the quicker formation of orthosilicic acid compared to its dissociation.

As a final note, we would like to point out that the shapes of the nanostructures produced by the current technique could be extended to arbitrary shapes instead of only the holes or bumps described in this paper. This can be done by applying

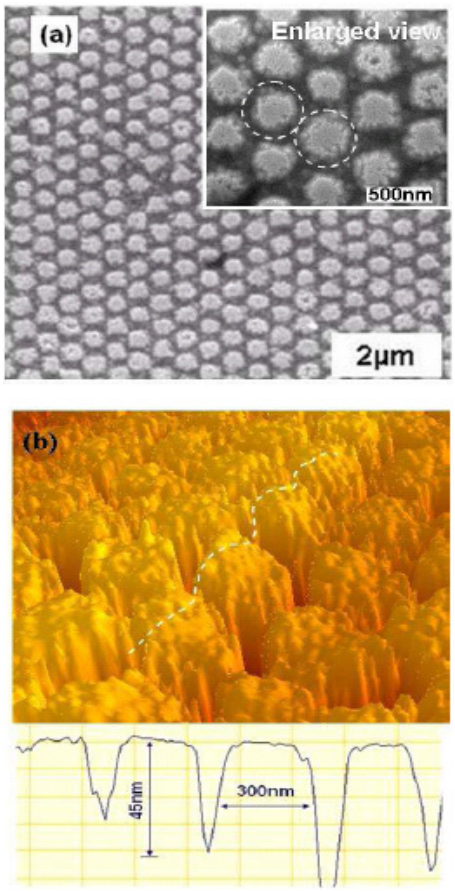

Figure 5. (a) SEM image of 'n' (cross-sectional view) shaped structures produced with the post-process in 40 °C 30 wt% KOH solution for 2 min and (b) AFM profile showing average width and depth are 300 nm and 45 nm respectively.

an angular-incident laser beam. The basic principle for laser parallel nanofabrication of arbitrary-shaped patterns has been demonstrated in a previous paper [20] in air environment. In the next step, we will combine the chemical-assisted laser parallel nanostructuring technique with angular-incident beam to achieve arbitrary-shaped chemical etching over a large-area surface.

4. Conclusion

In summary, we have demonstrated chemical-assisted laser nanofabrication of hexagonal arrays of nanostructures with different shapes on the Si surface over a large-area surface. It confirms that contacting particle-lens array patterning (CPLA) technique can be employed in liquid environment. About 10^8 features can be produced in an area of 0.5 cm^2 by just one single laser pulse. The shape of obtained structures can be further modified, from convex hole shapes to concave bumps by a post-etching process in the same chemical solution at a higher temperature.

Acknowledgments

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