Formation of free-standing micropyramidal colloidal crystals grown on silicon substrate

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The self-organization of microspheres is one of the simplest methods for fabricating three-dimensional (3D) photonic crystals (PhCs), but the 3D structure of such organized microspheres, colloidal crystals, is difficult to control. In this letter, we report a method for forming face-centered-cubic colloidal crystals into a pyramidal shape on an anisotropically etched silicon (100) and (110) substrate. The colloidal crystals were lifted from the substrate for observation after thermal bonding. Free-standing colloidal crystals with a well-defined ''micropyramid'' shape were obtained. This type of PhC formation is suitable for batch production as well as for handling a single pyramid. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1583138]

Since their proposal in late 1980s,[1,2] photonic crystals (PhCs) have been attracting interest from both basic and application points of view.[3,4] One of the characteristic properties of PhCs is the presence of a photonic band gap (PBG); at the PBG wavelength, propagation of photons is inhibited inside the PhC structure. Using this property, control over the radiative property of matter (for example, the lifetime of spontaneous emission) could be enabled.[5,6] The applications of PhCs include microwaveguides and low-threshold lasers.

The fabrication of three-dimensional (3D) PhCs is one of the most important and difficult tasks in this field. Many methods of fabricating PhCs have been proposed and performed. Among them, the self-organization of uniform diameter microspheres is one of the simpler and less expensive methods for the fabrication of 3D PhCs.[7] PhCs made by this method are called ''colloidal crystals'' or ''artificial opals.''

By gravitational sedimentation of microspheres with uniform diameters on a flat substrate, the bottom layer of a colloidal crystal tends to form a hexagonal lattice. Since there are two possible sedimentation geometries on a hexagonal lattice, the 3D crystal structure may become face centered cubic (fcc) or hexagonal close packed, or a mixture of both. One method for the intentional control of the 3D colloidal crystal structure involves the use of a microfabricated template.[8,9] The template let the bottom layer of microspheres into a tetragonal lattice. On a tetragonal lattice, the sedimentation geometry of microspheres is uniquely defined, so that a 3D crystal structure is defined as fcc. This technique, called ''colloidal epitaxy,'' is a straightforward method for fcc crystallization. However, the fabrication of templates is an expensive process requiring large-scale equipment. In addition, since the period of the microtemplate should be equal to the diameter of the microspheres, a template should be fabricated for each microsphere.

An alternative, simple, and diameter-independent method for defining a crystal structure uniquely involves the use of V-shaped grooves or pits having a specific angle, as shown in Fig. 1. With an adequate angle of ''V,'' microspheres adopt a regular organization due to the confinement by sidewalls. Anisotropically wet etched grooves and pits on silicon (100) substrates have been used for this purpose,[10–13] because this technique makes pits/grooves at exactly the required angles, while it is a simple and inexpensive technique. Sedimentation on such pits/grooves results in a fcc colloidal crystal as shown in Fig. 1(a), and the top surface is tetragonal, that is, (100) surface of fcc.

In the present letter, we report the growth of colloidal crystals by this technique. In addition, we describe the lift off of the grown colloidal crystals, and the observation of crystal surfaces. Thermal bonding of the microspheres was carried

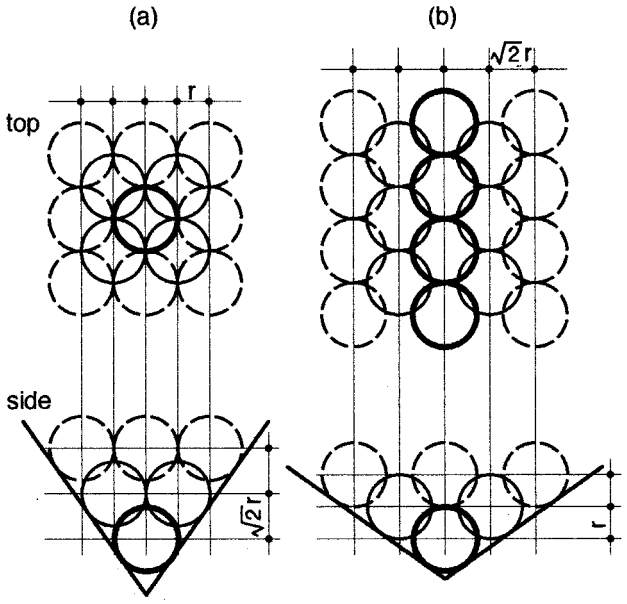

FIG. 1. Scheme of ordering of microspheres. (a) A-type sedimentation (tetragonal top surface) in a V-shaped pit and (b) B-type sedimentation (1:$\sqrt{2}$ rectangular top surface) in a V-shaped groove.

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out for the lift off. In addition to the pits anisotropically etched on a Si (100) substrate, we also report the use of grooves anisotropically etched on a Si (110) substrate. The scheme is shown in Fig. 1(b). In this case, the top surface of the colloidal crystal is a rectangular lattice with a ratio of $1{:}\sqrt{2}$, which is a (110) plane of a fcc crystal. To distinguish the two types of sedimentation, hereafter, the first type [on a Si (100) substrate, the top layer is the (100) plane of fcc crystal] is referred to as the A type, and the second one [on a Si (110) substrate, the top layer is the (110) plane of fcc crystal] is referred to as the B type.

For our experiments, Si substrates with a (100) or (110) surface (Sumitomo Mitsubishi Silicon Co.) were used, and they were cut into about 10×10 mm^2 pieces. The anisotropic etching of silicon substrates was performed in 33% KOH solution.

Polystyrene microspheres of a diameter of 1.038 μm (Sekisui Chem. Co.) were used for most of the experiments; in addition, microspheres of several other diameters were also used to prove the diameter-independent character of the present method. A microsphere suspension with a volume fraction of about 0.1%–1% were dropped onto the pits/grooves. After slow evaporation of water in wet conditions,[14] organized structures of microspheres were obtained.

Since the surface of the silicon crystal is naturally covered with a hydrophilic oxide layer, the adhesion of microspheres to the sidewalls occurred when the suspension was dropped into the pits/grooves. Such adhesion disturbed the regular organization of the microspheres. Hence, for surface modification, silicon substrates were immersed in a 2% dichlorodimethylsilane ethanol solution before use, so that hydrophobic surfacea was obtained. In this way, the adhesion was greatly suppressed and the microspheres were packed regularly from the bottom to the top.

Figure 2 shows scanning electron microscope (SEM) images of microspheres organized in the V pits/grooves on Si substrates. Figures 2(a)–2(c) show the growth of colloidal crystal in the V pit on a Si (100) substrate. Only one microsphere is found on the first bottom layer; on the second and third layers 2×2 and 3×3 microspheres are arranged into a tetragonal lattice, respectively. Figure 2(d) shows the top layer of large-scale crystal, where more than 15×15 microspheres form a tetragonal lattice. These images prove that the A-type sedimentation has occurred in the V pit as expected. In the manner of these 1.038 μm microspheres, microspheres of 320 nm [Fig. 2(e)] and 220 nm (not shown) diameters were also regularly ordered in the V pits. This result confirms the diameter-independent character of the present method.

B-type sedimentation in the V grooves on a Si (110) substrate was also observed. Figure 2(f) shows a B-type arrangement of microspheres. As seen, the microspheres are arranged into a $1{:}\sqrt{2}$ rectangular form. In this case, however, the fabrication of a large-scale colloidal crystal was not as easily performed as that of the A type.

For the observation of the pyramidal shape of colloidal crystals, the microspheres should be lifted off from the V pits/grooves. However, the bonding between microspheres is too weak to maintain its crystalline structure through the lift-off process. To avoid this problem, the organized polystyrene microspheres were thermally bonded, that is, heated

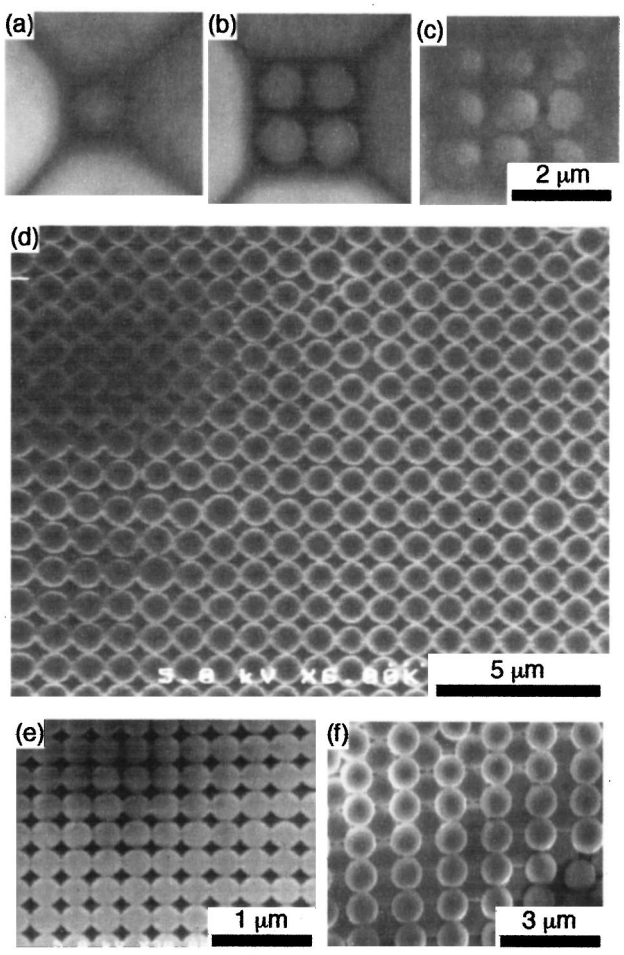

FIG. 2. SEM images of top layers of organized microspheres. (a)–(e) microspheres organized in V pits etched on Si (100) substrates. (a)–(d) microspheres with a diameter of 1.038 μm; (a) 1×1, (b) 2×2, (c) 3×3, and (d) more than 15×15 microspheres with a diameter of 1.038 μm organized into a tetragonal lattice. (e) Microspheres with a diameter of 320 nm. (f) 1.038 μm microspheres organized in a V groove etched on Si (110) substrates.

and kept at a certain temperature for 3 min and cooled naturally. To determine an optimum temperature for obtaining sufficient bonding strength without disordering the colloidal crystal structure, transmission spectra were measured after thermal treatment and mechanical perturbation. The mechanical perturbation was performed by dropping a small amount of methanol onto the colloidal crystal. Colloidal crystals of 220 nm microspheres grown in transparent glass cells were used for this experiment, which has been previously proven to show a deep PBG at 500 nm.[14] As seen in Fig. 3, the colloidal crystal bonded at 90 °C shows the most significant PBG effect at 500 nm after perturbation. Hence, thermal bonding was carried out at 90 °C, and the colloidal crystals were then lifted off using adhesive tape.

Free-standing colloidal crystals lifted off from V pits/grooves were observed by SEM. Figure 4(a) shows a colloidal crystal of 1.038 μm microspheres grown in a V pit of about a 15 μm side length. A well-ordered ''micropyramid'' structure is clearly seen. The structure has a sharp apex, sharp edge lines, and flat surfaces similar to the ''cleaved'' surfaces of atomic crystals. The surfaces of the ''pyramid'' is formed of hexagonal lattice of microspheres. The top view [Fig. 4(b)] also indicates a well-ordered organization of mi-

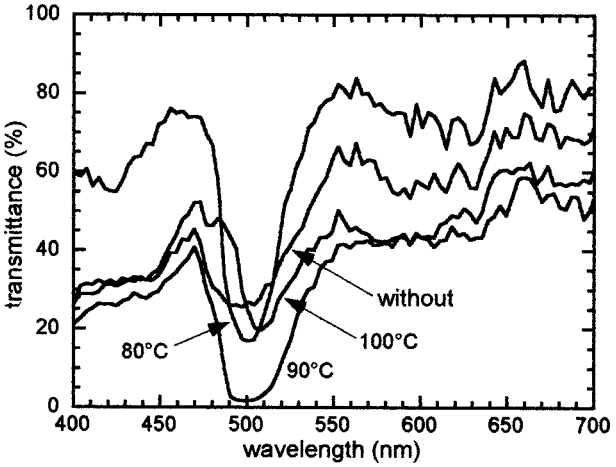

FIG. 3. Transmission spectra of colloidal crystals of 220 nm polystyrene microspheres after thermal bonding and intentional perturbation (dropping small amount of methanol). The temperatures indicated in the figure (80 °C, 90 °C, and 100 °C) show the temperature of thermal bonding. The trace indicated as "without" shows the spectrum of colloidal crystal without thermal bonding (only perturbation was performed).

crospheres. A colloidal crystal lifted off from a V-shaped groove etched on a Si (110) substrate is shown in Figs. 4(c) and 4(d) (close-up view). Again, an ordered structure was observed. While the structure does not have a pyramid apex, a well-defined edge line, which corresponds to the bottom line of the groove, is evident.

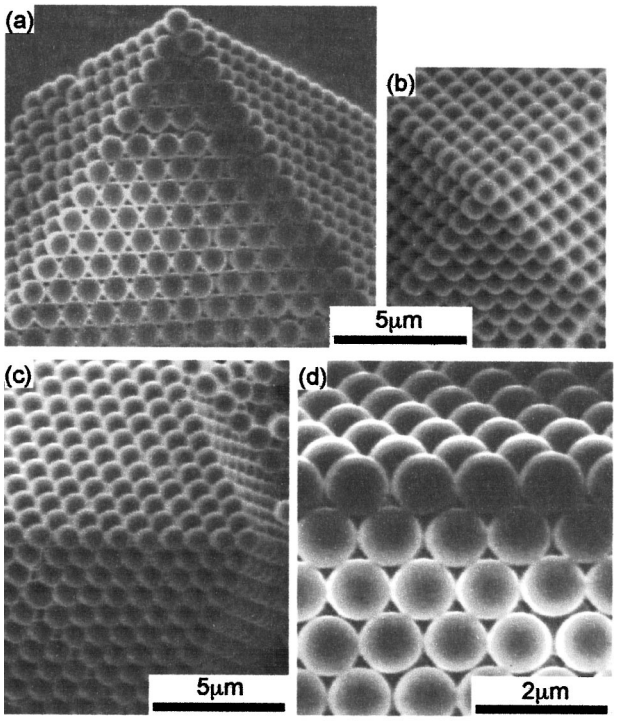

FIG. 4. SEM images of thermally bonded polystyrene microspheres. (a) and (b): Microspheres were organized in V-shaped pits etched on Si (100) substrates; (c) and (d): in V-shaped grooves etched on Si (110) substrates.

While the fabrication of V pits/grooves was carried out through a simple conventional method of wet etching, the present method has several advantages for the fcc crystallization of microspheres. The pits/grooves are independent of the diameter of microspheres; this is a significant difference compared to the microfabricated template. In addition, since these colloidal crystals are fabricated on silicon substrates, they are applicable for silicon-based optoelectronic devices.[15] The orientation of the colloidal crystal is predetermined by the crystallinity of the substrates.

Unique characteristics and applications might be found on these free-standing colloidal crystals due to the well-defined micropyramidal shape. For example, the optical resonance inside a colloidal pyramid is expected to show complex behavior due to the microcavity effect of each microsphere and the pyramidal shape effect of the whole colloidal crystal.

In conclusion, fcc colloidal crystals were grown by the sedimentation of microspheres in anisotropically etched pits and grooves on silicon substrates. The colloidal crystals were observed by SEM after thermal bonding and after they were lifted off from the pits/grooves. Sharp apex and edge lines with cleaved crystalline surfaces were clearly observed. In particular, colloidal crystals grown in V pits of a Si (100) substrate looked like a micropyramid, and may find attractive applications due to this well-defined shape.

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