Opal chips: vectorial growth of colloidal crystal patterns inside silicon wafers†

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A simple, quick, reproducible and inexpensive method is described that combines self-assembly, micro-fluidics and soft lithography, to achieve a novel example of vectorial control of thickness, area, orientation and registry of patterned single crystal silica colloidal crystals in silicon wafers, coined opal chips, for potential applications in photonic chip and lab-on-chip technologies.

Close-packed arrays of mono-disperse silica and latex micro-spheres have numerous uses, such as chromatography and photonics.[1,2] Colloidal crystals are usually prepared from mono-disperse micro-spheres through the use of dip-coating,[3] sedimentation[4] or specially designed micro-cells.[5] These micro-sphere lattices may be prepared in the form of crystals and films. In particular, sphere sizes > 800 nm in silica have proven to be notoriously difficult to make mono-disperse and coerce into well ordered lattices. Colloidal crystals and films display varying degrees of disorder that arise from sphere size polydispersity, site randomness, intrinsic point, line and planar defects, and polycrystalline domains. The defect tolerance of colloidal crystals on properties like completeness of photonic band gaps in photonic crystals and the separation efficiency of chromatographic stationary phases is a subject of intense current interest.

The patterning of mono-disperse micro-spheres on top of various substrates has been explored *via* micro-molding,[6] electrostatic assembly[7] and micro-robotic techniques.[8] These methods of organizing micro-spheres usually require long preparation times and special instrumentation and are unable to simultaneously control order, defects, thickness, area, orientation and registry of patterned colloidal crystals. Moreover, colloidal crystals obtained in these ways have a face centered cubic lattice oriented in the (111) direction. Colloidal crystals displaying a specific (100) orientation have been grown by sedimentation of micro-spheres onto a lithographically patterned substrate, a technique known as colloidal epitaxy.[9] Access to such sophisticated substrates requires use of expensive chrome masks and photolithography, both of which are unfamiliar and unavailable to most research chemists. Further, epitaxial growth of colloidal crystal film is slow and structural order is limited to layers close to the lithographically patterned substrate.

Herein we report a straightforward, fast, reproducible and cost effective way, that combines self-assembly and soft lithography for the fabrication of micron scale patterned single crystal colloidal crystals in silicon wafers and which circumvents many of the aforementioned problems. The attractiveness of this method to opal chips is that it has the capability of controlling defects in colloidal crystals as well as the number, area, orientation and registry of close-packed layer planes of micro-spheres in the colloidal crystals embedded within a single crystal silicon (100) wafer.

Soft lithography encompasses a suite of techniques that have proven to be remarkably useful for the fabrication of micron to sub-micron patterns on a range of planar and curved sub-strates.[10] The procedures are facile and can be readily handled in an ordinary laboratory environment. In the context of the work described in this study, a line patterned polydimethylsiloxane (PDMS) master is obtained by casting a pre-polymer gel (Sylgard 184, Corning) from the corresponding lithographically defined photo-resist pattern. When access to lithographic instrumentation is not available, PDMS masters may be easily made by non-lithographic methods, such as the use of transmission electron microscopy (TEM) grids or optical gratings as templates for making micro-molds (see below). A procedure for fabricating V-shaped groove patterns inside a Si(100) wafer begins with a PDMS master that is inked with 2 mM hexadecanethiol in ethanol and then printed onto a Au (50 nm) coated Si(100) wafer (5 nm Ti is used as an adhesion layer). The bare gold surface is then etched away by a $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}/S_2O_3^{2-}/KOH$ solution, and the underlying Si(100) substrate is then anisotropically etched by 3 M KOH in Pr^iOH/H_2O at 70 °C to give V-shaped grooves with 70.6° apex angles beneath the surface of the wafer, as seen in the scanning electron microscopy (SEM) image in Fig. 1(a).[11] The etching rate along the Si(100) direction is *ca.* 1 µm min⁻¹.[12]

A flat PDMS block is next put into conformal contact with the patterned wafer and a drop of a 0.1 wt% aqueous dispersion of monodisperse silica micro-spheres (diameter = 840 ± 20 nm, modified Stöber synthesis) was added at the interface between
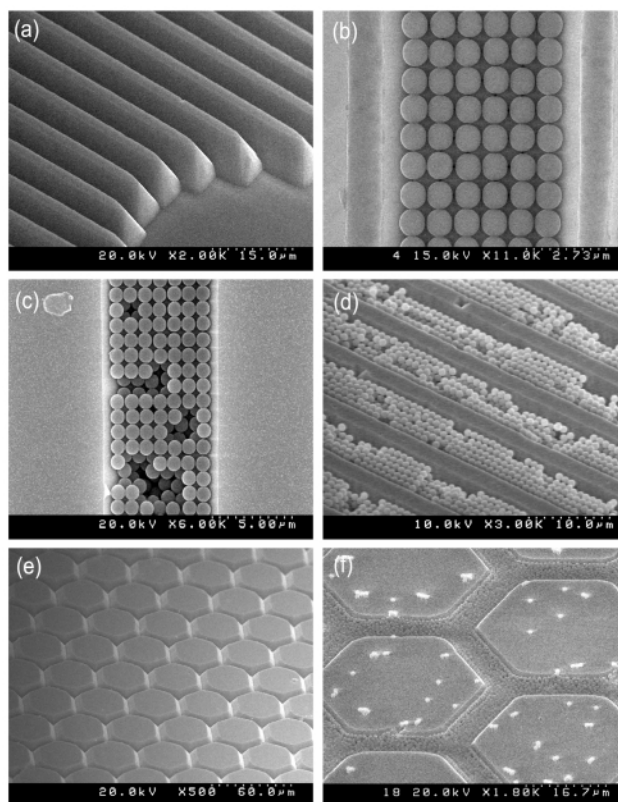

Fig. 1 SEM study illustrating vectorial control of thickness, area, orientation and registry of silica colloidal crystals grown inside silicon wafers – see text.

the patterned silicon wafer and the PDMS block. Micro-spheres are driven into the V-shaped grooves by capillary forces and close-pack inside the grooves upon evaporation of the water-dispersing agent. Owing to the 70.6° angular geometry of the V-shaped grooves, micro-spheres nucleate and grow in a vectorial fashion exclusively within the grooves to form a pattern of fcc colloidal crystal parallel lines. It is noteworthy that {100} layer planes are well ordered and organized parallel to the [100] face of the single crystal Si(100) wafer. This can be seen in the SEM images shown in Fig. 1(b)–(d). Over spatial areas sufficiently large for construction of photonic crystal and chromatographic micro-devices, colloidal crystals are seen to be single crystals and can be made essentially free of defects [Figs. 1(b), 2(a)]. When vacancy defects are present in the silica colloidal crystals they can easily be identified and their effect on optical and separation properties evaluated, [Fig. 2(b), (c)].

Interestingly, the first micro-spheres to nucleate in the V-shaped grooves are single-file contiguous arrangements and these linear constructions are found to be located in the apex of the V-shaped groove, [Fig. 3(a)]. These 1-D chains of micro-spheres dominate in the early stages of infiltration and when dilute aqueous dispersions of micro-spheres are used. At later stages the micro-spheres self-assemble adjacent to the 1-D chains and continue to grow up the walls of the V-shaped grooves to eventually fill them with well ordered patterns of colloidal crystals, Fig. 3(b). The edges of the grooves seem to be filled first with well defined lines of micro-spheres. Further, the observed registry of {100} layer planes of micro-spheres between adjacent grooves provides additional evidence for vectorial control of colloidal crystal nucleation and growth. These steps may provide an insight into the control mechanism
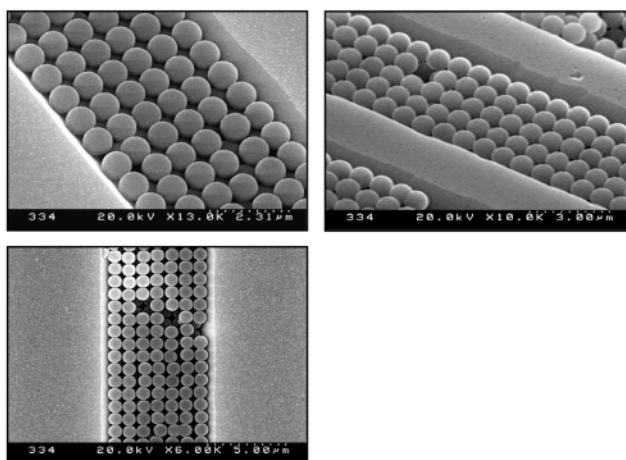
Fig. 2 SEM images depicting (a, top left) *six-layer* (100) single crystal silica colloidal crystal in a V-shaped channel of Si(100) wafer and devoid of vacancy defects. (b, top right) *Five-layer* (100) single crystal silica colloidal crystal in a V-shaped channel of Si(100) wafer depicting a single vacancy defect in top layer of micro-spheres. (c, bottom) *Seven-layer* (100) single crystal silica colloidal crystal in a V-shaped channel of Si(100) wafer depicting three vacancy-type defects in the top layer of micro-spheres.
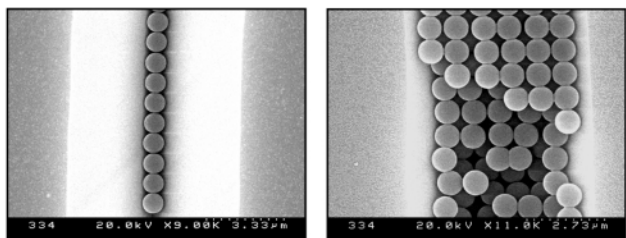
Fig. 3 SEM images depicting (a, left) the formation of a 1-D chain of silica micro-spheres grown in the apex region of a V-shaped groove that had been anisotropically etched within the surface of a single crystal (100) silicon wafer. (b, right) Vectorial growth of *six-layer* (100) oriented silica colloidal crystal within the V-shaped channel exposing the top three micro-sphere layer-planes.

that enables command of thickness, area, orientation and registry of the patterned colloidal crystal in the silicon wafer.

The whole process outlined above is reproducible and can be finished in less than 2 h. The actual capillary infiltration and crystallization of micro-spheres in the patterned silicon wafer can be as short as seconds to minutes. As the depth of the V-shaped grooves in Si(100) is proportional to the etching time, it is easy to control groove depth to accommodate a pre-determined number of layers of silica micro-spheres. This has been achieved for one to ten layers of patterned colloidal crystals. The number of micro-spheres observed in the top (100) layer corresponds to the thickness of the colloidal crystal in the V-shaped grooves. The strategy described in this work alleviates the 'sagging' and 'pairing' problems in PDMS, which has been utilized for patterning latex micro-spheres through micro-molding in capillaries, MIMIC, on top of a silicon substrate.[6,10]

As mentioned above, PDMS masters can be made by non-lithographic approaches involving the use of TEM grids or optical gratings.[13] To exemplify this methodology, we used a hexagonal 600 mesh TEM grid to prepare the PDMS master. The bar width of the grid is *ca.* 7 µm and the pitch width is *ca.* 35 µm. A TEM grid was first laid down to a flat poly-(methylmethacrylate) (PMMA) substrate and a PDMS pre-polymer gel is then cast upon the grid. After curing at 60 °C, the PDMS master is used for the micro-contact printing followed by Au and Si(100) anisotropic etching as described above. The SEM image shown in Fig. 1(e) depicts a representative hexagonal symmetry V-shaped groove network and Fig. 1(f) displays a typical silica micro-sphere array following influx of micro-spheres into the grooves of the hexagonal pattern using the capillary infiltration method described above.

In summary, the process of growing single crystal colloidal crystal patterns of known thickness, area, orientation and registry within a substrate is experimentally straightforward, generally applicable, able to be easily integrated into chip fabrication facilities and amenable to mass production. The creation of colloidal crystal wafers, opal chips, is rapid, reproducible and cheap. They may, for example, be easily adapted for engineering lattice dimensions, refractive index contrast, structural defects, location and integration of photonic crystals coupled to optical fibers on photonic chips.[2] Additionally they may find utility for positioning and connecting lab-on-chip arrays of micro-fluidic and micro-reactor devices that perform chemical and catalytic transformations, as well as ion, molecule and macromolecule separations with simultaneous optical detection.[1] The opal chip described here is a significant advance on anything reported in the open or patent literature.

Notes and references

1 R. D. Oleschuk, L. L. Shultz-Lockyear, Y. Ning and D. J. Harrison, *Anal. Chem.*, 2000, **72**, 585.
2 E. Chomski and G. A. Ozin, *Adv. Mater.*, 2000, **12**, 1071.
3 P. Jiang, J. F. Bertone, K. S. Hwang and V. L. Colvin, *Chem. Mater.*, 1999, **11**, 2132.
4 M. Holgado, F. Garcia-Santamaria, A. Blanco, M. Ibisate, A. Cintas, H. Miguez, C. J. Serna, C. Molpeceres, J. Requena, A. Mifsud, F. Meseguer and C. Lopez, *Langmuir*, 1999, **15**, 4701.
5 S. H. Park, D. Qin and Y. Xia, *Adv. Mater.*, 1998, **10**, 1028.
6 E. Kim, Y. Xia and G. M. Whitesides, *Adv. Mater.*, 1996, **8**, 245.
7 J. Aizenberg, P. V. Braun and P. Wiltzius, *Phys. Rev. Lett.*, 2000, **84**, 2997.
8 H. T. Miyazaki, H. Miyazaki, K. Ohtaka and T. Sato, *J. Appl. Phys.*, 2000, **87**, 7152.
9 A. van Blaaderen, R. Ruel and P. Wiltzius, *Nature*, 1997, **385**, 321.
10 Y. Xia and G. M. Whitesides, *Angew. Chem., Int. Ed.*, 1998, **37**, 551.
11 Y. Xia, X.-M. Zhao, E. Kim and G. M. Whitesides, *Chem. Mater.*, 1995, **7**, 2332.
12 I. Zubel, *Sens. Actuators A: Phys.*, 1998, **70**, 260.
13 Y. Xia, J. Tien, D. Qin and G. M. Whitesides, *Langmuir*, 1996, **12**, 4033.