Experimental

The average size of the silver nanoparticles, prepared by the method of Korgel and co-workers [10], is approximately 5 nm. A solution containing 0.3 g of toluene and 0.5 mg of PS, with approximate molecular weight of 900,000, was then added to 0.5 mg of these silver nanocrystals in a vial. The corresponding volume ratio Ag/PS was estimated to be 0.1. The solution was sonicated for 20 min to evenly disperse the particles. Approximately 0.5 mL of the resulting solution was then cast on water, contained in a 3 inch petri dish. Evaporation of solvent was slowed by completely covering the dish. Under this condition, toluene molecules escaped from the tiny gap between the dish and its cover. After 1 h, the toluene evaporation was complete and a shining, wrinkle-free, purple colored nanocomposite film formed on the water surface. When the film preparation was accelerated by uncovering the dish, the toluene evaporation was non-uniform and wrinkles developed.

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Epitaxial Growth of High Dielectric Contrast Three-Dimensional Photonic Crystals**

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The facile creation of highly ordered and oriented three-dimensional (3D) photonic bandgap (PBG) materials in the visible and near infrared has remained an elusive but important goal for photonic technologies. Technological applications for photonic bandgap structures include low-loss waveguides, low-threshold lasers, optical-switching elements, and radically improved photochemical reactors.[1–6] Colloidal self-assembly has been suggested as an efficient and low-cost route to PBG structures,[7,8] however, hard-sphere colloidal assemblies typically contain a high density of stacking faults, are of random orientation with respect to the substrate, and are polycrystalline. Long-range 3D structure, defined orientation with respect to a substrate, and high refractive index contrast have yet to be unified in one system, which will be required for applications. Processes such as lithography, laser-induced chemical vapor deposition, and two-photon photopolymerization have also been suggested as routes to PBG structures,[9–12] but their stepwise nature and layer-to-layer registration issues restricts them to photonic crystals of limited dimension.

Colloidal-crystal templating provides a very promising approach for the production of high-resolution, micrometer-scale, three-dimensionally periodic photonic crystals,[13] but, conventionally applied to the fabrication of PBG structures, it has serious limitations. A range of approaches have been suggested to maximize the index contrast including solgel,[14–16] chemical vapor deposition,[17–19] imbibing of nanoparticles,[20–22] reduction of GeO2 to Ge,[23] electroless,[24] and electrochemical deposition.[25] The colloidal templates used in these attempts are commonly polycrystalline, and randomly oriented with respect to the substrate. Here we demonstrate, through the melt-imbibing of selenium under elevated temperature to an epitaxially grown face-centered cubic (fcc) colloidal crystal template, the largest, high refractive index contrast 3D photonic crystal of predefined orientation to date. Although theoretically straightforward, a route to construct and rigorously analyze the photonic properties of such structures has not been developed because the orientation and defect density of the colloidal templates were unknown. The photonic properties of our system will be reported in a subsequent publication.[26]

Prior to this work, large solvent-free fcc colloidal crystals of known crystallographic orientation had never been formed. Sedimentation of colloids typically leads to close-packed assemblies consisting of hexagonal planes randomly stacked in the vertical (gravity) direction, and of random orientation with respect to the substrate. It was previously demonstrated that well-oriented fcc crystals could be formed by sedimentation onto a patterned substrate in a glycerol/water system.[27] But, because glycerol is non-volatile, and the formed colloidal crystal is much too fragile to withstand liquid-phase solvent removal, the solvent cannot be removed without destruction of the crystalline order, and thus filling with a high refractive index material is impossible. Furthermore, filling the 3D interstitial space of a colloidal crystal with a high-index material has been problematic. Most techniques are limited because they either only deposit material in the top few layers of a colloidal crystal, or do not fully fill the colloidal crystal with a high enough refractive index material. Recent reports on Se,[28] Si,[19] and Ge[23] filling are intriguing: however, the structural perfection of the templates are unknown, and the templates are not ordered with respect to the substrate.


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The high refractive index contrast photonic crystal presented here was created through the melt-imbibing of a large, single crystal, silica fcc colloidal crystal with the chalcogenide glass selenium, followed by dissolution of the silica template. Selenium was selected because it has a high refractive index of 2.5, and thus will provide a nearly complete 3D photonic gap (Fig. 1), a very low optical-loss coefficient between 1 and 10 μm,[29] low melting point (217 °C), and relatively low surface tension (~100 dynes/cm). Importantly, it vitrifies easily, forming an optically isotropic glass.[29]

The single crystal, fcc colloidal template was prepared by sedimentation of colloidal spheres onto a lithographically patterned silicon substrate, followed by removal of the solvent (Fig. 2). This process can be described as epitaxial growth of colloidal crystals; the crystallographic orientation of the colloidal crystal is directly determined by the spatial orientation of the pattern on the substrate. An entirely new solvent system based on hydrazine hydrate, and careful control of the experimental protocol had to be developed. Hydrazine hydrate to minimize electrostatic interactions between the particles, leading to hard-sphere behavior, minimizing shrinkage and thus cracking upon drying. In addition, poly(vinyl alcohol) was added to serve as a binder in the latter stages of drying. Our attempts using simpler solvent systems generally resulted in highly defective structures. After a low temperature sintering step, the colloidal crystal was imaged with conventional optical microscopy and confocal microscopy confirming it is an ~20 μm thick single fcc crystal over the entire 5 mm by 5 mm substrate area (Fig. 3). Following this analysis, the colloidal crystal was imbibed under high pressure with molten selenium (Fig. 4). These lateral and thickness dimensions did not appear to be an upper limit for either the epitaxial colloidal crystallization or the subsequent melt imbibing.

The imbibed sample was converted to the high refractive index contrast selenium/air structure by carefully removing the silicon substrate, and dissolving the silica template with HF. Because selenium does not wet silica, small pores remained between the contact points of the silica spheres. Thus, the entire silica template could be dissolved by the HF. Larger pores could be engineered by partial sintering of the colloidal crystal, which may be attractive for PBG formation.[7] The 3D interconnectivity between air spheres is also of critical importance if these porous structures are to be applied to catalytic or biological applications. Because the colloidal template is of known orientation with respect to the substrate, it was straightforward to cut and polish the photonic colloidal crystal, exposing (001) and (110) facets (Fig. 4). Comparison of these micrographs with optical microscopy images of the colloidal single crystal before imbibing confirms that the melt-imbibing process does not disrupt the crystal structure. The lateral dimensions of the templated region were 5 mm by 5 mm, identical to the patterned area of the substrate, and the entire templated region was a single crystal. As can be observed in the micrograph of Figure 4c, the templated region is ~20 μm thick, which, as expected, is identical to the thickness of the silica template.

The facile creation of dry, large, oriented single crystal colloidal assemblies directly on a silicon substrate makes possible critical advances in optical engineering. Such colloidal crystals are directly amenable to any number of high index filling schemes. The route we chose, melt imbibing of a chalcogenide glass has great potential. The luminescence and lasing characteristics of rare earth doped chalcogenide glasses embedded in a PBG structure are likely to be impressive. Furthermore, higher refractive index chalcogenide glasses such as As<sub>2</sub>S<sub>3</sub>, which has a refractive index of 2.75, or other complex chalcogenide glasses with refractive indices approaching 3, should yield highly functional complete photonic bandgap materials.[30] Because the colloidal crystal template has a defined orientation with respect to a silicon substrate, it will be straightforward to integrate the resulting PBG materials with predefined on-chip optoelectronics.
Experimental

The colloidal crystal templates used in this study were created by settling 1.58 \( \mu \)m \( \text{SiO}_2 \) colloidal spheres (Duke Scientific) from solution onto a substrate patterned at a pitch of 1.60 \( \mu \)m. Surrounding the large colloidal crystal are colloids settled on non-patterned regions and regions patterned with pitches of 1.64 \( \mu \)m (lower left of (a)) and 1.68 \( \mu \)m. High magnification view of (a) demonstrating the sharp boundary between the colloidal crystal growth on patterned substrates and random colloidal assembly formation on unpatterned substrates. Also, contrast growth on (d) with growth on (c). The pitch of (c) is only 80 nm greater than that of (d), yet the colloidal crystal now contains a large number of defects that are clearly evident in the optical micrograph.

Fig. 2. Schematic illustrating epitaxial growth of colloidal crystals and the melt imbibing of selenium into colloidal crystals.

Fig. 3. Optical microscopy of epitaxially grown colloidal crystals. a) Low magnification view of the entire 5 mm by 5 mm colloidal crystal formed on the region of the substrate patterned at a pitch of 1.60 \( \mu \)m. Surrounding the large colloidal crystal are colloids settled on b) non-patterned regions and regions patterned with pitches of 1.64 \( \mu \)m (lower left of (a)) and c) 1.68 \( \mu \)m. d) High magnification view of (a) demonstrating the sharp boundary between the colloidal crystal growth on patterned substrates and random colloidal assembly formation on unpatterned substrates. Also, contrast growth on (d) with growth on (c). The pitch of (c) is only 80 nm greater than that of (d), yet the colloidal crystal now contains a large number of defects that are clearly evident in the optical micrograph.

Fig. 4. Scanning electron microscopy (SEM) images of the selenium photonic crystal, cut and polished to expose specific crystallographic faces. a) The polished (001) facet, which is perpendicular to the settling direction. The contact points between the spheres on adjacent layers are clearly visible as pores, while within the (001) plane the voids do not appear to be interconnected. This pore morphology is the result of a 1.25 \% mismatch between the sphere diameter and the template size. b) The (110) face, proof that the selenium photonic crystal is indeed fcc. Again, the voids are generally not interconnected within the (001) plane, but are interconnected between (001) planes. c) Low magnification SEM micrograph of the (110) face, presenting a cross section of the entire thickness of the selenium photonic crystal. The sample was mounted in epoxy prior to polishing, which is observed below the photonic crystal, while above the photonic crystal, solid selenium is present. Importantly, the structure is highly ordered throughout the entire crystal, including the top layer. Because of a ~1.5° misorientation of the polished sample with respect to the (110) face the size of the pores appears to change from left to right across the sample.
Mer thin films are useful as lithographic templates.\[1–4\] By periodically ordered microdomain patterns in block copolymers, one can fabricate well-oriented microstructures that can develop.\[10–13\] The microstructure of the film may be transferred to a substrate through further etching or decoration with small particles.\[5,6\]

Several approaches have been developed to manipulate the morphological and microdomain orientation in block copolymers.\[10–15\] If an applied bias field (mechanical, electric, and magnetic, etc.) is present during the self-assembly process, well-oriented microstructures can develop.\[10–13\] The microstructure can also be controlled by surface topography as well as chemistry of a substrate.\[14,15\]

Alteration of Classical Microdomain Patterns of Block Copolymers by Degenerate Epitaxy**

By Cheolmin Park, Claudio De Rosa, Lewis J. Fetters, Bernard Lotz, and Edwin L. Thomas*

Pattern formation for nanostructure fabrication requires the achievement of periodic long-range order. For instance periodically ordered microdomain patterns in block copolymer thin films are useful as lithographic templates.\[1–4\] By removing one polymer chemically or by etching, the patterns may be transferred to a substrate through further etching or by deposition (chemical vapor deposition, thermal evaporation, etc.).\[1–4\] Another possibility is to use metal-containing block copolymer microstructures as nanoreactors for periodic decoration with small particles.\[5,6\]

Block copolymers consist of chemically distinct macromolecules covalently linked to form a single chain. Owing to their mutual repulsion, dissimilar blocks tend to segregate into different domains, the spatial extent of the domains being limited by the constraint imposed by the chemical connectivity of the blocks and the molecular weight. Area minimization at the interface of two blocks takes place due to the interfacial energy difference of two blocks. As a result self-organization of periodic microstructures occurs on the nanoscopic length scale. Advanced lithographic techniques can currently achieve feature sizes below 30 nm.\[7\] Various techniques for nanometer-scale surface patterning, based on the self-assembly in synthetic materials such as block copolymers, are being developed.\[8,9\]

Several approaches have been developed to manipulate the morphology and microdomain orientation in block copolymers.\[10–15\] If an applied bias field (mechanical, electric, and magnetic, etc.) is present during the self-assembly process, well-oriented microstructures can develop.\[10–13\] The microstructure can also be controlled by surface topography as well as chemistry of a substrate.\[14,15\]

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