Large Photonic Films by Crystallization on Fluid Substrates

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Periodic dielectric superstructures diffract electromagnetic radiation, if the lattice constant matches the wavelength of light. Such structures are called photonic crystals because of the analogy to the behavior of electrons in semiconductors.[1−4] The most popular structure presently under investigation is opal—a face-centered cubic package of several 100-nm-sized beads, which consist of silica (real opal) or polymer (polymer opals). If the refractive index contrast between beads and voids (air) is low, these materials possess an incomplete photonic band gap. In this case the propagation of light is prohibited in those directions, which satisfy the Bragg scattering conditions. If the refractive index contrast exceeds about 3, multiple scattering becomes very important. As a result, a full photonic band gap evolves. In this case the propagation of light of certain frequencies is prohibited in all directions. Photonic crystals with a full photonic band gap have been realized for the near-IR in a silicon replica of opals.[5,6] They have not yet been realized for the visible spectrum because transparent materials with a refractive index larger than 3 are extremely rare and an incomplete filling reduces the effective refractive index in replica further.[7]

Making large monocrystalline photonic structures with a low defect density is far from trivial and limits the use of photonic crystals.[8] Thin opaline films on glass substrates give large (cm) well-ordered structures[7,9−11] in which the 111 plane is parallel to the glass slide. The individual crystals are, however, separated by cracks, which appear due to shrinkage at a late stage of drying, as the volume density of the colloidal crystal approaches 74%.[10] Depending on the preparation (crystallization) conditions, these cracks separate crystallites of 40 μm (quickly dried) to 250 μm (very slow drying, 1 week[10]). From a general point of view, their appearance is hard to prevent, as they form as a result of the shrinkage of the colloidal crystal, which has already formed at a volume ratio much lower than 74%. And since a high refractive index contrast is desired, it is not acceptable to fill the voids. So a large lateral shrinkage with respect to the solid support has to happen. Liquid surfaces have been used to study two-dimensional crystallization.[12−14] As to be expected, this eliminated the problem of a lateral sticking. Here, we report the three-dimensional crystallization of PMMA colloids on molten metals (Ga or Hg) as liquid substrates, which result in crack-free, nearly monocrystalline (low defect density) photonic crystal films of millimeter size.

For this purpose we worked preferably with PMMA colloids prepared according to refs 7, 9, and 10 with diameters in the range of 180−600 nm. These colloids crystallize well on hydrophilic glass slides from an aqueous suspension[9,10] and form large (cm), homogeneously looking films. Inspection with a microscope shows, however, the internal cracks. The cracks are formed both in samples crystallized by spreading and drying according to the procedures of refs 9 and 10 or by crystallization in a moving meniscus[15,16] (Figure 1a). Despite the existence of cracks, these films show good optical properties in transmission (see Figure 1b). The reflection of light at the 111 plane causes a peak during a typical absorption measurement, which can be related to the size of the beads with a modified Bragg equation.[9,10] The extinction is 2.4, which means that more than 99% of the light is reflected.

In the following we present examples obtained with 260-nm PMMA spheres.[9] For crystallization on fluid substrates two or three drops of a 5 wt % colloidal suspension are carefully spread with a pipet onto the surface of the liquid substrate. After 24 h at room temperature crystallization and drying of the photonic film is finished (see Figure 2).

In this way crack-free crystals of a size of nearly a centimeter squared can be prepared both on gallium and on mercury. The absence of cracks was checked by optical microscopy (resolution at least 1 μm). Polymer colloids prepared from PEMA, poly *tert*-butyl methacrylate, or fluorinated methacrylates by surfactant-free emulsion polymerization[10] gave the same results (to be published later). Therefore, this method is of general applicability, at least for organic colloids with a density similar to that of water. Colloids from silica (density

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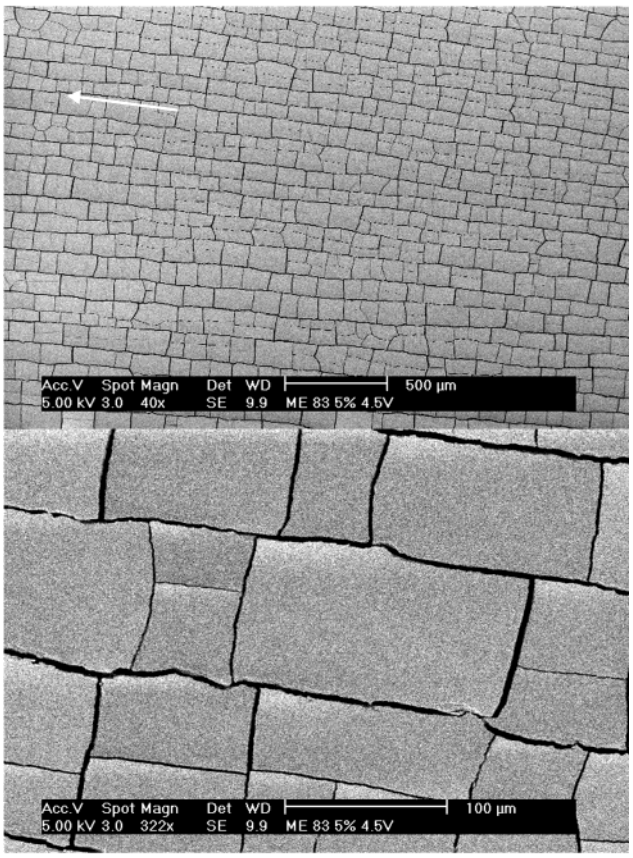

Figure 1. Crack structure and optical properties of polymer beads crystallized on solid supports. (a) SEM images of opaline (PMMA) films crystallized in the vertical position by pulling a glass slide out of a suspension of 4 wt % colloids. The bead size is 288 nm in diameter. The main crack direction is parallel to the pull direction (white arrow). As one can see, the size of the crystallites is up to 100 × 150 μm^2, whereas the cracks build angles of 90° and (b) transmission spectrum therefrom. The Bragg peak displays a very high intensity, which suggests both a high monodispersity of the beads and a very well crystallized structure.

larger than that of water, sedimentation preferred) were not tested. For further experiments we worked preferably with gallium, which is less toxic than mercury (Caution: Hg vapor is toxic. It has to be handled in a hood. Spilled droplets have to be adsorbed with iodine-loaded charcoal or with commercial adsorbants for Hg.) In addition, it is easier to clean the surface of gallium

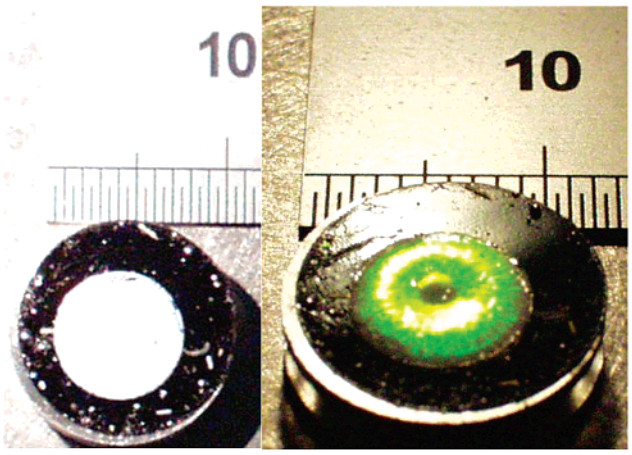

Figure 2. Photo of an opaline film (crystallized on gallium) on a SEM holder. Left, top view; right, front view. The bar shows 10 mm.

from impurities. Care has to be taken in all cases to prevent a mechanical breaking due to shaking of the liquid.

After crystallization the film has to be transferred to a solid substrate for further characterization and use. For that purpose two techniques are applied. For the investigation of the upper side of the film, one dives, for example, a microscope slide under the crystal and lifts it slowly. Because of the very high surface tension of the gallium, a strong bend builds up at the meniscus. That leads to a breaking of the crystal. As a result, we could not yet transfer the intact crystal to a glass or silicon substrate, but the preserved fragments are at a size of more than 2 mm^2 (Figure 3). These samples show no cracks and have a low defect density.

For the investigation of the underside of a crystal we used another separation method, with which one can separate the crystal in larger pieces or even in one piece from the liquid surface. For that purpose a tape is fixed on the plate of a Philips SEM sample holder (12.5-mm diameter). With this sample holder the crystal is approached vertically from the top, until the tape touches the crystal gently. Very cautiously, the crystal is lifted from the liquid. Gallium rests are slipped off using a pipet. With this method crystals of a size of 7 mm in diameter could be separated without breaking.

To inspect the crystal surface more closely, SEM images were taken on gold-sputtered photonic crystal films. The coating was done with the sputter coater S150B of the company Edwards using a pressure of ≈0.3 atm and an anode current of 40 mA. The coating time was 1 min. The coated films were studied with the SEM XL 30 TMP of Philips. The acceleration voltage had to be lower than 5 kV to prevent damage to the crystal.

EM inspection confirms that the fragments show no cracks (larger cracks had already been ruled out by optical microscopy). Figure 3 shows a crystallite of the size of nearly 2 mm^2 in different magnifications. This image shows the upper side of the crystal. The order of the beads is hexagonal. Mostly holes, caused by loose beads, and terraces can be recognized. In addition, there are a few dislocation lines. EM pictures taken at the

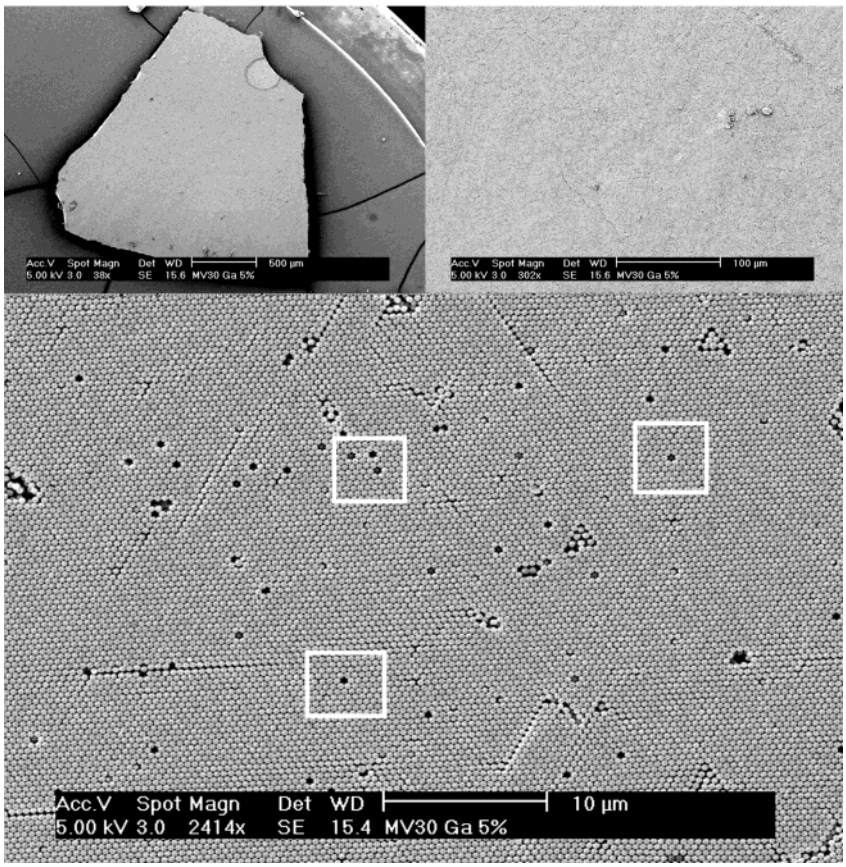

Figure 3. Colloidal crystal prepared from a 5 wt % suspension crystallized on a liquid substrate at three different magnifications. No cracks are recognizable. Just a few disclination lines and holes (marked with white squares) appear. The hexagonal structure extends to millimeters. In the background the tape on the sample holder can be seen.

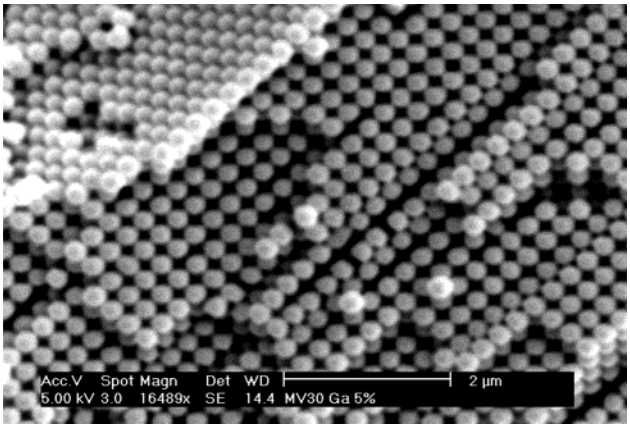

Figure 4. SEM image of the edge of the crystallite shown above. One can see on top (left side) the hexagonal ordered (111) layer and on the sides (right side) several periods of the square (100) layer.

fracture edge of the crystal (Figure 4) show the hexagonal arrangement of the beads at the surface (111 plane) and the square lattice of the 100 plane. This proves the fcc packing of the bulk structure.

As a result, large photonic single crystals are accessible, which are the precondition for the preparation of resonators or—more generally—for wave guiding in photonic structures. In this context it must be mentioned that PMMA, the chemical basis of these photonic crystals, is an E-beam resist. This allows the generation of defects in these photonic materials[9] with resolutions of one bead size.

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