



# Large-area inverse opal structures in a bulk chalcogenide glass by spin-coating and thin-film transfer



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## ABSTRACT

Large (cm × cm), uniform-thickness areas of an inverse-opal photonic crystal and an inverse-opal monolayer were fabricated in a high-refractive-index  $As_{30}S_{70}$  chalcogenide glass. We have developed an effective low-cost, solution-based process for fabrication of photonic structures in chalcogenide glass from silica-colloidal-crystal thin-film templates (multi- and monolayer). The chalcogenide-glass solution is spin-coated over the silica-opal film template and the infilled composite structure (chalcogenide/opal) is then lifted-off and transferred onto the chalcogenide-glass disc at 225 °C, followed by removal of the template in hydrofluoric acid. The extra step introduced in this work (lift-off and transfer) allows a reproducible and large-area structure to be fabricated on a bulk chalcogenide glass. Complete infilling of the silica template is possible due to the nano-colloidal nature (particle size 2–8 nm) of the chalcogenide-glass solution and effective solvent release from the spin-coated chalcogenide film during post-annealing. The resulting chalcogenide-glass inverse-opal multilayer exhibits a Bragg peak at 670 nm with a reflectance 70%, while the inverse-opal monolayer shows anti-reflectance behaviour <2% in the near-infrared region (1215–1660 nm).

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## 1. Introduction

Photonic crystals (PCs) are 1-D, 2-D and 3-D structures with a complex dielectric function that is periodically modulated on length-scales comparable to relevant wavelengths of light. PCs are necessarily composed of at least two different materials, for example silica/air. The defined modulation of the complex dielectric coefficient leads to the appearance of distinct photonic bandgaps (PBGs) in the frequency spectrum, defining where propagation of incident photons is allowed or forbidden. The PBG structures show intriguing optical properties such as strong localization of photons, in the ideal case loss-less wave guiding, and suppression or enhancement of light emission [1,2].

A wide variety of preparation techniques for 3-D PCs have been reported, falling into two categories: (1) *top-down*, such as lithog-

raphy followed by selective etching [3], multi-photon polymerization [4], and holography [5], or (2) *bottom-up*, such as colloidal-crystal (CC) growth using Colvin [6], Langmuir-Blodgett (LB) [7], and under-oil crystallization (UOC) methods [8–10]. The bottom-up methods differ in the degree of control of thickness uniformity, crystal order and growth rate. Highly ordered CC photonic films of silica [11] or polymers (e.g. polystyrene etc. [12]) are currently of growing interest because of their exploitable optical properties and of the possibilities for low-cost fabrication by spontaneous crystallization from suspension media. The self-assembly of micro- and nanoparticles into face-centred-cubic (fcc) crystals enables fabrication of large-area 3-D opal structures. The PBG of a monodisperse CC behaves as a Bragg reflector in the visible or infrared (IR) spectral regions, when the bead diameter ( $D$ ) is in the range 150–700 nm. Active topics in CC film research are: (a) fabrication of tunable structural PBG structures for all-optical sensing and imaging [13,14], (b) electronic papers [15], (c) complex PBG architectures [16], and (d) light-emitting planar defects for low-threshold flexible laser devices [17]. In CC opals a wide photonic bandgap, enhancing Bragg reflection, can be achieved either by infilling the low-refractive-index ( $n$ ) silica or polymer opals with higher-refractive-index materials like silicon [18], or by fabrication of inverse-opal (IO) PBG structures having an effective refractive index ( $n_{\text{eff}}$ )

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higher than that of the original CC film [19–21]. Next-generation PBG devices may require wide-bandgap photonic-crystal films as successfully demonstrated, for example, with SiC, TiO<sub>2</sub> etc. [12,22–24] and also much larger dimensions.

Our previous work [25] showed that spin-coating (SC) of a chalcogenide glass (ChG) solution is low-cost technique for infilling silica-opal films, and fabrication of IO structures was demonstrated. Nevertheless, the IO structures are found only when localized on defects such as sample edges. Here, we report on a significant advance, to cm × cm fabrication of IO nanostructures on the ChG using high-quality silica-opal film templates. Firstly, silica templates consisting of different number of monolayers are grown, then the chalcogenide-glass solution is spin-coated into the opal voids, followed by lifting-off the nanostructure composite onto the chalcogenide glass disc at higher temperature and finally removal of the original opal template by selective dissolution in hydrofluoric acid (HF). The resulting chalcogenide IO nanostructures exhibit either a wide stop-band (obtained from a silica multilayer template) or suppressed reflectance (obtained from a silica monolayer template). The interest in ChGs is mainly because of their high refractive index, infra-red transparency and optical non-linearity.

The extra lift-off and transfer steps developed in the present work allow different thin film/bulk chalcogenides to be combined, give access to improved surface quality, uniformity and reproducibility of the inverse structures, and permit easy control of the exact number of monolayers in the IO. In addition, the area of the inverse opal structure is limited only by the size of the CC template. All of these still represent significant challenges in chalcogenide glass technology and processing; in contrast, for other materials such as silicon such features can be readily controlled.

## 2. Experimental methods

### 2.1. Fabrication of the silica CC multilayer and monolayer templates

A CC multilayer template was prepared by the UOC method [26,27] from a suspension of mono-disperse silica beads ( $D \approx 280$  nm) (SEAHOSTER KE-W30, Nippon Shokubai Co. Ltd., Osaka, Japan) diluted in water to 1.1 wt.% and poured onto a silica-glass substrate. Subsequently, the CC suspension was covered with silicone oil (SH-200, kinematic viscosity of  $1 \times 10^{-5}$  m<sup>2</sup> s<sup>-1</sup> at room temperature, Toray Dow Corning, Inc., Tokyo, Japan). Once the crystallization finished, the silicone oil remaining within the voids of the silica CC film was removed by co-evaporation with iso-propanol at room temperature.

The CC monolayer template was deposited by the LB method using a LB bath (NIMA, trough model 1222D2) with an alternate dipper mechanism [7] and a sub-phase of doubly distilled deionised water. The mono-disperse silica beads ( $D \approx 230$  nm) were prepared by the Stöber method [8] without any further functionalization. One unit of 4 wt.% SiO<sub>2</sub> solution in ethanol was diluted with five units of chloroform. A sufficient quantity of this mixture was spread on the air/water interface in the trough and compressed to 3 mN m<sup>-1</sup>. At such surface pressure, a well ordered 2-D hexagonal lattice is formed. The compressed monolayer was transferred onto the glass substrate. The deposition was carried out on the upstroke with the rate of withdrawal kept constant at 5 mm min<sup>-1</sup>.

### 2.2. Spin-coating of the chalcogenide nano-colloidal solution and fabrication of the inverse-opal structures

Chalcogenide glass of composition As<sub>30</sub>S<sub>70</sub> (at.%) was prepared by direct synthesis from 5 N purity elements, which were weighed in a pre-cleaned fused-silica ampoule in the required molar ratio.

The evacuated ( $\sim 10^{-4}$  Pa) and sealed ampoule was placed in a rocking furnace and heated at 650 °C for 24 h (heating rate 2 °C min<sup>-1</sup>). The As<sub>30</sub>S<sub>70</sub> liquid was air-cooled to obtain the bulk glass. The nano-colloidal glass solution was prepared by dissolving 1 g of the ChG in 5 ml of propylamine (99.95 wt.%, Sigma–Aldrich, St. Louis, MO, USA). The as-prepared solution was filtered through a polytetrafluoroethylene filter (pore size 200 nm) to remove any undissolved particles of the glass and dust.

The silica opals were filled by spinning the nano-colloidal solution of the As<sub>30</sub>S<sub>70</sub> glass on to the surface of the template at 4000 rpm for 1 min under inert argon atmosphere. The silica/chalcogenide opal composite was annealed at 120 °C for 20 hours at a reduced pressure of 10 Pa.

To obtain IO As<sub>30</sub>S<sub>70</sub> nanostructures over a large area, it is necessary to transfer the silica/chalcogenide opal film onto a suitable substrate. A bulk disc of glassy As<sub>30</sub>S<sub>70</sub> glass disc was used as the substrate because of the compatibility of its optical, mechanical and thermal properties with the spin-coated film. The As<sub>30</sub>S<sub>70</sub> bulk substrate was polished on one side to optical quality (roughness <3 nm) using sand paper and diamond paste in silicon oil. Lift-off and transfer of the silica/chalcogenide film onto the substrate were performed inside furnace at the softening temperature of the As<sub>30</sub>S<sub>70</sub> bulk glass,  $T_s = 225$  °C. The transfer consisted of heating up the composite/disc substrate to 225 °C in 40 min, holding at that temperature for 40 min, and cooling down to room temperature in 1.5 hour. At  $T_s$  the glass disc becomes soft and sticks to the silica/chalcogenide glass opal film via the As<sub>30</sub>S<sub>70</sub> thin film left on the infilled silica template after the spin-coating. The only pressure applied is the weight of the bulk glass substrate which is positioned on top of the silica/chalcogenide glass opal film. The infilled opal film, now completely adherent to the As–S glass disc substrate, detaches from the original silica-glass substrate during cooling. The newly formed opal film, on the chalcogenide-disc substrate, has smooth surface adopting the optical-quality surface of the silica-glass substrate. The IO nanostructures (multi or monolayer) were obtained by rinsing the infilled opal film/As<sub>30</sub>S<sub>70</sub> bulk-glass substrate in 3 wt.% HF acid for 2 min.

### 2.3. Characterization techniques

The normal incidence reflectance ( $R$ ) was measured by using a UV-vis-near-IR spectrometer (JASCO V-570) and the angular reflectance (transverse-electric and transverse-magnetic polarizations, TE and TM, respectively) and optical functions were measured by variable-angle-spectroscopic ellipsometry (VASE, J.A. Woollam). The ellipsometric data were fitted using the Tauc-Lorentz formula [28,29]. The microstructures of thin films were recorded using scanning electron microscopy (SEM) (JEOL FEG-SEM, JMS-7600F). Samples for SEM observation were gold-coated to prevent charging of samples under the electron beam.

## 3. Results and discussion

The composition of the films was confirmed to be As<sub>30</sub>S<sub>70</sub> ( $\pm 1$  at.%) by energy-dispersive analysis in SEM and the amorphicity of the annealed films was confirmed by X-ray diffraction.

Dissolution and clustering mechanisms in amine-based solutions are described elsewhere [30,31]. It should only be noted here that chalcogenide-glass solutions in aliphatic amines consist of glass nano-clusters with average radii 1–4.5 nm depending on glass concentration in amine solution [31]. Spin-coating gives a thin film in which the glass nano-clusters form aggregates [32] with average radius increased by factor of 20–25 [31]. Long-term annealing at an appropriate temperature is essential to get spin-coated chalcogenide films with a refractive index ( $n_{SC} = 2.209$ )

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