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Inverse opal photonic crystal of chalcogenide glass by solution processing

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ABSTRACT

Chalcogenide opal and inverse opal photonic crystals were successfully fabricated by low-cost and low-temperature solution-based process, which is well developed in polymer films processing. Highly ordered silica colloidal crystal films were successfully infilled with nano-colloidal solution of the high refractive index $As_{30}S_{70}$ chalcogenide glass by using spin-coating method. The silica/As–S opal film was etched in HF acid to dissolve the silica opal template and fabricate the inverse opal As–S photonic crystal. Both, the infilled silica/As–S opal film ($\Delta n \sim 0.84$ near $\lambda = 770$ nm) and the inverse opal As–S photonic structure ($\Delta n \sim 1.26$ near $\lambda = 660$ nm) had significantly enhanced reflectivity values and wider photonic bandgaps in comparison with the silica opal film template ($\Delta n \sim 0.434$ near $\lambda = 600$ nm). The key aspects of opal film preparation by spin-coating of nano-colloidal chalcogenide glass solution are discussed. The solution fabricated "inorganic polymer" opal and the inverse opal structures exceed photonic properties of silica or any organic polymer opal film. The fabricated photonic structures are proposed for designing novel flexible colloidal crystal laser devices, photonic waveguides and chemical sensors.

1. Introduction

Photonic crystals (PC's) are structures having spatial architectures (1D, 2D and/or 3D) with a periodically changing complex dielectric function at scales comparable to wavelengths of light in demanded frequency range. Consequently, the periodical distribution of complex dielectric function leads to appearance of distinct regions in the dispersion spectrum, where photons are either allowed or forbidden to propagate, i.e., formation of photonic bandgap (PBG). The PBG structures posses some intriguing optical phenomena such as strong localization of photons, theoretically lossless sharp bending of light direction, suppression or enhancement of light emission [1]. So far, there have been reports on large variety of preparation techniques for 3D PC structures, either the top-down methods such as lithography and selective etching [2], multi-photon polymerization [3], and holography [4] or the bottom-up methods such as colloidal growth [5–8].

Recently, highly ordered colloidal crystal (CC) photonic films of silica or polymers have been of growing interest because of their applicable optical properties and low-cost fabrication possibilities by spontaneous self-assembly from suspension media. The self-assembly of microparticles into the face-centered cubic (fcc) lattice enables fabrication of large area 3D opal structures. The PBG of uniform colloidal crystal behaves optically as the Bragg reflector in visible or near IR spectral regions, if the particles diameter ranges within few hundreds of nanometers. The recent topics in CC films research are fabrication of tunable structural PBG structures for all-optical sensing [9], electronic papers [10], complex PBG architectures [11,12], or light-emitting planar defects for low-threshold flexible laser devices [13]. Such novel PBG devices require wide bandgaps and large area photonic crystals films. In the CC opals the wide bandgap (enhancing the Bragg reflection) can be achieved either by functionalization of lower refractive index silica or polymer opals with higher refractive index materials [14] and/or by fabrication of inverse opal (IO) PBG structures [15–17].

In this paper, we report on a new method of chalcogenide glass (CHG) photonic crystal films fabrication by solution-based process. We employed the spin-coating method, which is extensively used in preparation of organic polymer films, light sensitive dyes, conducting ITO films or high resolution photoresist films. We demonstrate the spin-coating as suitable low-cost technique for in-filling films or materials having sub-micrometer porosity with nano-colloidal solutions of functional materials. The spin-coating is simple way for improving properties of photonic structures by using high refractive index inorganic polymers, i.e., chalcogenide glasses. The inverse opal chalcogenide photonic crystals, e.g., waveguides, could be achieved in silica/chalcogenide opal films by conventional lithographic techniques.

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2. Materials and experimental techniques

2.1. Fabrication of silica CC film template

We obtained large area CC films by the self-assembly of monodisperse silica beads (SEAHOSTER KE-W30, Nippon Shokubai Co., Ltd., Osaka, Japan) on a silica glass substrate by using the colloidal crystallization under silicon oil method [18]. An aqueous suspension of silica beads with diameter of 280 nm diluted in water by the ratio of 1:20 (1.1 wt.%) was loaded onto substrate surface. Subsequently, the silicone oil (SH-200 with viscosity of 10cSt, Toray Dow Corning, Inc., Tokyo, Japan) was deposited onto liquid surface of the silica suspension, which had been settled on substrate. The silicone oil prolonged crystallization time of the silica CC structure. Once the crystallization had been finished, the remaining silicone oil within void spaces of the silica CC film was removed by co-evaporation with propanol.

2.2. Spin-coating of CHG nano-colloidal solution and fabrication of IO structure

The chalcogenide glass of composition $As_{30}S_{70}$ (As–S) was prepared by direct synthesis from elements of 5 N purity weighted in 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 temperature of 650 °C for 24 h. The $As_{30}S_{70}$ melt was then air-cooled to obtain the chalcogenide bulk glass. The nano-colloidal glass solution was prepared by dissolving 1 g of the chalcogenide glass in 7 ml of propylamine (99.95 wt.%, Sigma–Aldrich, St. Louis, MO, USA). The dissolution and clustering mechanisms are described elsewhere [19,20]. The as-prepared solution was filtered through the PTFE filter (pore size 250 nm) to remove any undissolved particles of the CHG and dust. The silica/chalcogenide opal film was prepared by spinning the nano-colloidal solution of As–S glass onto the silica CC film surface at 4000 rpm for 1 min under inert atmosphere. The silica/chalcogenide opal film was consequently annealed at 125 °C for 20 h at reduced pressure of 10 Pa. Annealing led to releasing of propylamine out of the silica/chalcogenide opal film structure while nano-clusters of CHG got fully cross-linked forming their compact amorphous network [18]. The IO As–S photonic crystal was obtained by etching the silica opal film template in hydrofluoric acid (HF) solution (10 wt.%) for 2 min. We etched edge of silica/chalcogenide opal film. The entire process of CC, silica/chalcogenide opal and IO As–S photonic crystal preparation is schematically illustrated in Fig. 1.

2.3. Characterization of photonic opal films

The normal incidence reflectivity of the opal films was measured by using the optical-fiber spectrometer Ocean Optics, USB2000, Dunedin, FL, USA. The response of signal in the fiber (diameter of ~400 μm) was enhanced by using 21 W light source (halogen lamp). Images of the opal films were recorded by the JEOL FEG-SEM, JMS-7600F, Tokyo, Japan. The PBG structures of the opal films were calculated in the BandSOLVE software using the Plane Wave Expansion (PWE) algorithm, Rsoft Corp, Fort Lauderdale, FL, USA.

3. Results and discussion

Fig. 1 schematically illustrates the solution-based preparation process of the inverse opal As–S photonic structure via the silica CC opal film template and the spin-coating of nano-colloidal chalcogenide glass solution. For successful in-filling, mechanical stability of the CC opal film template is required to withstand a flow of glass solution during the spin-coating process. Therefore, we used the CC films obtained by the crystallization under silicone oil [18]. The films possess well-ordered close packed fcc lattice of silica beads with high structural cohesion. The films are uniform over a large area and they have good adhesion to the glass substrate.

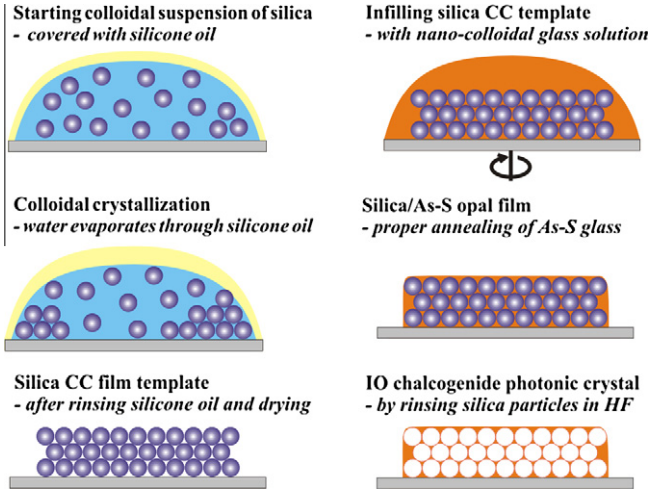

Fig. 1. Scheme of solution-based preparation of the inverse opal chalcogenide photonic structure via the silica CC opal film template and the spin-coating of nano-colloidal solution of the $As_{30}S_{70}$ chalcogenide glass.

Some chalcogenide glasses can be dissolved in highly volatile amines such as propyl- or butylamine forming nano-colloidal solutions [19,20]. Dissolution mechanism of the As–S glass in propylamine was reported by Chern and Lauks [19]. Authors proposed a formation of nano-colloidal clusters of glass with nano-meter size, which are solvated by molecules of solvent. The size of nano-clusters in solutions of the As–S glass was studied by using the Dynamic Light Scattering method [20] and found in the range of 2–8 nm over broad range of concentrations ~1–10^3 mg ml^{-1}. It is right the nano-colloidal character of chalcogenide glass solution that enables the in-filling of sub-micrometer sized void spaces in the silica CC film templates. Amorphous network of solid chalcogenide films [21] is formed during the spin-coating process by an aggregation of the glass nano-clusters accompanied by solvent release from film structure. Post-annealing of the chalcogenide glass film significantly enhances the process of solvent residua removal and cross-linking of neighboring glass cluster aggregates [20]. Cross-linking of glassy nano-cluster aggregates is also accompanied by a significant volume compression and densification in chalcogenide film. Decrease in thickness of the CHG film can reach up to 30–40% as the void spaces within glass cluster aggregates vanish. The CHG film compression during annealing thus strongly contributes to the in-filling of the void regions in opal films.

Indeed, there are only few chalcogenide glass/amine solvent systems providing the spin-coated chalcogenide films of favorable optical quality. It is because the demands on the amine solvents are contradictory, i.e., easy dissolution (clustering) of chalcogenide glass and deposition of uniform film contrary to complete removing of solvent residua from the film structure by annealing at low-temperatures. If the solvent is not completely removed by films annealing at temperatures below their glass transition temperature, then the captured solvent residua represents main problem for practical application of the spin-coated chalcogenide films as the optical materials [22].

In our case, the boiling point of propylamine is ~48 °C but the spin-coated $As_{30}S_{70}$ chalcogenide film needs to be annealed at $T \sim 125$ °C for 20 h at reduced pressure ~10 Pa to "completely"