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Fabrication and characterisation of SbI_3-opal structures

Mirosława Kępińska [a,*], Anna Starczewska [a], Iwona Bednarczyk [b], Janusz Szala [b], Piotr Szperlich [a], Krystian Mistewicz [a]

[a] Institute of Physics – Center for Science and Education, Silesian University of Technology, Krzywoustego 2, 44-100 Gliwice, Poland
[b] Department of Materials Science, Silesian University of Technology, Krasińskiego 8, 40-019 Katowice, Poland

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ABSTRACT

This work is focused on forming opal-antimony triiodide (SbI_3) structures with direct SiO_2 opal. SbI_3 is a semiconductor having relatively high refractive index so potentially is very useful in fabrication of photonic crystal. Additionally, crystalline SbI_3 exhibits the second-harmonic generation so obtained structures provide a wide range of opportunities for optoelectronic devices. Presented structures are fabricated by infiltration opal with SbI_3 dissolved in ethanol and drying in room temperature. The morphology of the samples was characterized by scanning electron microscopy (SEM). The chemical composition of the samples was analyzed using energy dispersion spectroscopy (EDS). Optical properties were investigated by reflectance spectroscopy for wavelengths from 380 nm to 1050 nm.

1. Introduction

Photonic crystals are structures with a periodically modulated dielectric constant [1] resulting in the formation of a photonic band gap (PBG). These structures can be used in fabrication of different photonic devices [2]. A good example of a three-dimensional photonic crystal is synthetic opal composed of monodisperse nanoscale SiO_2 spheres. When the size of SiO_2 spheres (period of the structure) is varied, the PBG position for opals can be tuned in a wide spectral range from ultraviolet to near infrared [3]. The fulfilment of free space between spheres in opals with various substances allows changing the effective refractive index and the optical contrast parameter, thereby changing the PBG position and its width [4]. Furthermore embedding the substance in the opal structure can improve the existing properties and even reveal the new ones e.g. photoluminescence [5–7] or the second-harmonic generation [8]. One of the most promising materials not yet used in the production of photonic crystals is antimony triiodide (SbI_3). It is a semiconductor having relatively high refractive index [9], which exhibits the second-harmonic generation. Photosensitive films of SbI_3 have found applications among others in high-resolution image microrecording and in information storage [10]. 3D nanocomposites fabricated on the based on opal matrices can also be used as active elements of the amplifying or generating systems, as control systems in fiber optics laser, in semiconducting nanoelectronic apparatus, and in other devices [11]. The fabrication of SbI_3-opal structure should be useful in optimization of optoelectronic devices based on SbI_3. It may also open up new application possibilities.

In this work we have demonstrated a very simple and low cost method of fabrications of SbI_3-opal structure by infiltration of SiO_2 opal template with SbI_3 dissolved in ethanol. The morphology, chemical composition and optical properties of obtained SbI_3-opal structures have been investigated.

2. Experiment

Monodisperse silica spheres with diameter of several hundred nanometers range have been prepared using procedure described in [6] based on the Stober method [13]. Their size (D_{SEM}) has been determined from electron micrographs as it was described in [14]. For opal fabrication we have used the gravity sedimentation method [15]. The obtained plates of opals had thickness of ~0.3 mm. Two kinds of opals composed of spheres of different diameters (see Table 1) have been chosen. A difference in sizes of the spheres building opals is related to the color variation.

Antimony triiodide solution has been prepared with ethanol as a solvent. Mixture of 0.268 g of SbI_3 single crystalline platelets and 0.5 ml of ethanol has been ultrasonically mixed for about 30 min. Opals have been infiltrated with the SbI_3 solution and dried in room temperature for 24 h. This procedure has been repeated five times. Formed SbI_3-opal structures have a shiny surface without the need of cutting and/or polishing of the sample after infiltration.

* Corresponding author. Tel.: +48 32 603 41 88.
E-mail address: Miroslawa.Kepinska@polsl.pl (M. Kępińska).

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The morphology of formed structures has been characterized by SEM using Hitachi S-4200 microscope in the case of bare opals and STEM HITACHI HD-2300A microscope in the case of SbI_3-opal structures.

The chemical composition of the prepared structure has been analyzed using EDS in scanning electron microscope (Hitachi S-4200 with Thermo Scientific EDS).

Optical properties have been investigated by reflectance spectroscopy. Spectra of optical reflectance were registered in room temperature using PC2000 (Ocean Optics Inc.) spectrophotometer with master card with 600 lines grating blazed at 500 nm. Investigations have been performed for wavelengths (λ) from 380 to 1050 nm. Spectrophotometer was equipped with appropriate reflection probe R7 × 400-2-LOH and the deuterium-halogen light source DH2000-FHS from Ocean Optics Inc. The illuminated opals have been mounted horizontally, perpendicular to the light beam. For angular investigations samples have been mounted on the table of GUR-5 (LOMO) goniometer. Using Glan–Thomson polarizer (LOT-Oriel) the incoming radiation beam was linear polarized with the electric vector parallel (p) or perpendicular (s) to the plane of incidence. The multiple averaged spectral characteristics of optical reflectance (R) containing 2048 data points for various wavelengths (λ) have been registered using the OOI-Base program from Ocean Optics Inc.

3. Results and discussion

Fig. 1a presents TEM image of SbI_3 crystals obtained from ethanol solution. When the crystallization takes place in the interior of the opal, the crystallite size is limited by the dimensions of the space between the balls [11], which favours the formation of nanocrystallites.

Typical SEM micrographs of bare opal as well as both SbI_3-opals structures are presented in Fig. 1b–e. They show view of top surface of SbI_3-opal structure consisting of spheres with diameter $D_{SEM}=244(7)$ nm (Fig. 1c), and $D_{SEM}=333(12)$ nm (Fig. 1d,e) obtained with different magnifications. Fig. 1f shows the cross-section of one of SbI_3-opal structures. They confirm the rather good quality of the obtained opals. One can see hexagonal network structure typical for the (111) layers in the terms of the fcc lattice. The pores of the opal-SbI_3 composite are filled uniformly (see Fig. 1c–f) with SbI_3. This fact was confirmed by EDS investigations.

Fig. 2a and b presents the EDS spectra of the surface and interior (after cutting the sample) of SbI_3-opal structure, respectively. The characteristic peaks for antimony, iodine, silicon and oxygen are observed. The source of silicon and oxygen peaks is silica spheres of opal template. The source of antimony and iodine peaks is material surrounding and filling empty spaces between spheres. The elemental atomic ratios of 0.247:0.753 for Sb and I averaged over the surface of SbI_3-opal structure and 0.278:0.722 for Sb and I averaged over the interior of structure have been obtained. These last values are only a little different from the appropriate for a stoichiometric SbI_3.

Prepared opals have been investigated by the optical method described in [12], which is based on measuring of Bragg's peak position for opals infiltrated with liquids of known refractive indices. This method allowed determining not only the diameter of the spheres building opals (D_{opt}) but also the filling factor (f). Results of obtained parameters are presented in Table 1 in

Table 1
Parameters of bare opals and of SbI_3-opal structures evaluated using reflectance spectroscopy and analysis of SEM micrographs (D_{SEM}).

Sample	D_{SEM} (nm)	for bare opal			for SbI_3-opal structure				
		λ_c (nm)	D_{opt} (nm)	f	$\lambda_{c(SbI_3)}$ (nm)	n_{eff}	$\overline{n}_{SbI_3}$	ff	$(1-f-ff)$
#1	244(7)	508(1)	234(1)	0.6792(3)	632(2) for $\theta=0^\circ$ $\lambda_{c(SbI_3)}(\theta)$	1.651(6) 1.668(3)	2.60(1)	0.165(2) 0.176(3)	0.149(3) 0.144(3)
#2	333(12)	689(1)	325(1)	0.6049(6)	878(2) for $\theta=0^\circ$ $\lambda_{c(SbI_3)}(\theta)$	1.652(6) 1.648(2)	2.43(1)	0.214(3) 0.212(2)	0.177(3) 0.182(4)

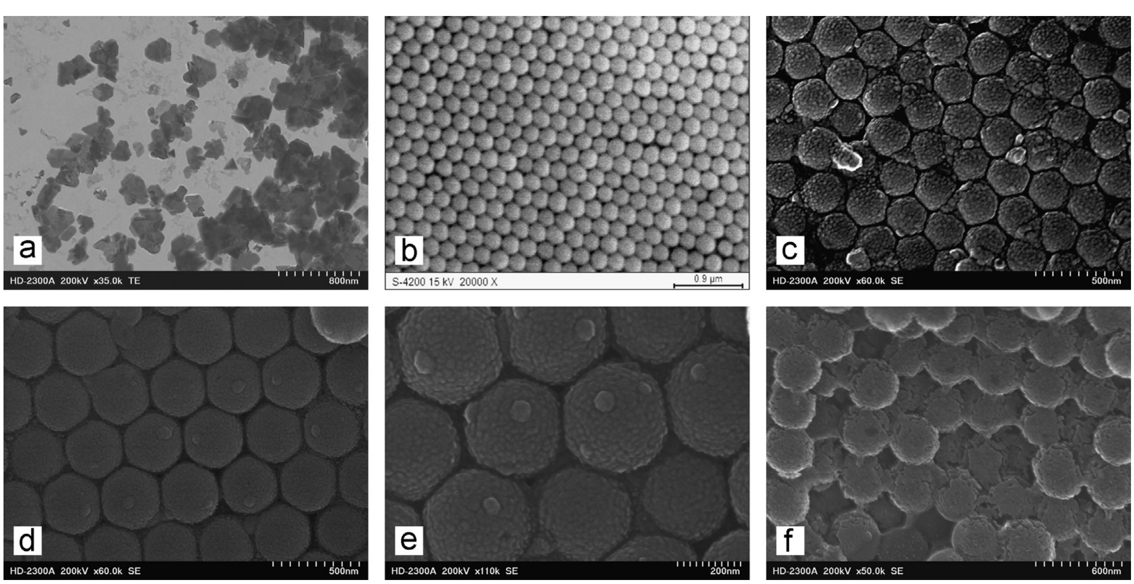

Fig. 1. Typical SEM micrographs of bare opal (a), SbI_3-opal structure consisted of spheres of diameter $D_{SEM}=244(7)$ nm (b,c), and $D_{SEM}=333(12)$ nm (d,e,f) obtained with different magnifications.