Available online at www.sciencedirect.com

ScienceDirect

Photonics and Nanostructures – Fundamentals and Applications 19 (2016) 55–63

PHOTONICS AND NANOSTRUCTURES Fundamentals and Applications

www.elsevier.com/locate/photonics

Indium oxide inverse opal films synthesized by structure replication method☆

Sabrina Amrehn[a], Daniel Berghoff[b], Andreas Nikitin[b], Matthias Reichelt[b], Xia Wu[a], Torsten Meier[b], Thorsten Wagner[a,*]

[a] *Faculty of Science, Department of Chemistry, University of Paderborn, Warburger Str. 100, 33098 Paderborn, Germany*
[b] *Faculty of Science, Department of Physics, University of Paderborn, Warburger Str. 100, 33098 Paderborn, Germany*

Received 25 October 2015; received in revised form 19 February 2016; accepted 25 February 2016
Available online 3 March 2016

Abstract

We present the synthesis of indium oxide (In_2O_3) inverse opal films with photonic stop bands in the visible range by a structure replication method. Artificial opal films made of poly(methyl methacrylate) (PMMA) spheres are utilized as template. The opal films are deposited via sedimentation facilitated by ultrasonication, and then impregnated by indium nitrate solution, which is thermally converted to In_2O_3 after drying. The quality of the resulting inverse opal film depends on many parameters; in this study the water content of the indium nitrate/PMMA composite after drying is investigated. Comparison of the reflectance spectra recorded by vis-spectroscopy with simulated data shows a good agreement between the peak position and calculated stop band positions for the inverse opals. This synthesis is less complex and highly efficient compared to most other techniques and is suitable for use in many applications.

Keywords: Photonic crystal; Indium oxide; Inverse opal; Band gap calculations; Structure replication

1. Introduction

In recent years photonic crystals have attracted increasing interest for use in many applications. Besides new devices in communication electronics [1], e.g. for optical switches [2] or high quality optical fibers [3,4], 2D- and 3D- photonic crystals are also utilized in solar cells for increasing efficiency[5], for sensor applications [6,7], colloidal lithography [8] and next generation optical components e.g. for spectrometers [9].

For many applications inverse opal structures are of special interest since they allow the design of materials with full photonic band gaps [10].

Besides applications in optics, metal oxide inverse opals are also used in the field of semiconducting gas sensors as sensitive layers. Due to their relatively large specific surface area combined with good pore accessibility, the sensitivity of the sensors can be increased compared to conventional nano-granular layers [11].

☆ This work was partially funded by the German Federal Ministry of Education and Research (project funding reference number 13N12969).

* Corresponding author. Tel.:+49 5251602486;
fax: +49 5251603423.
E-mail address: thorsten.wagner@upb.de (T. Wagner).

http://dx.doi.org/10.1016/j.photonics.2016.02.005
1569-4410/

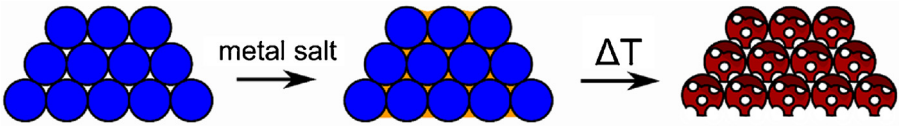

Fig. 1. Scheme of the synthesis process: (i) PMMA opal deposition; (ii) impregnation of the PMMA opal with indium nitrate solution; (iii) thermal conversion of the indium nitrate to indium oxide and PMMA structure matrix removal.

In this study, indium oxide (In_2O_3) was chosen since it is a promising material for gas sensing applications [12]. Also indium oxide is a transparent semiconductor in the visible region, which is a necessary prerequisite for building photonic crystals. To the authors' knowledge this is the first report on the synthesis of In_2O_3 inverse opal structures.

In the field of ordered mesoporous materials indium nitrate in combination with the incipient wetness impregnation technique has been found to yield high quality replica structures [13]. It was shown in former works that optical activation of In_2O_3 allows fabrication of low power ozone sensors [14]. However, the layer structure is important for light penetration [15]. Therefore the photonic In_2O_3 presented here will be used in future work to further improve gas-sensing properties.

For many of the previously mentioned applications efficient synthesis methods are required. The casting strategy presented here offers the possibility to synthesize inverse opals with relatively low effort using a wide range of materials, e.g. metal oxides, metals, silica, polymers as reviewed by Stein [16]. A schematic drawing of the full synthesis procedure is shown in Fig. 1.

The method allows the full amount of the synthesized PMMA to be used without leaving any residual metal salt after the impregnation of the PMMA opal. However, compared to lithographical methods typically the number of defects is higher. To reduce the number of defects after the casting process, we studied the influence of the residual solvent and crystallization water in the composite material on the quality of the structure. The residual liquid in the opal pores was influenced by the drying time at room temperature and at 60 °C after impregnating the PMMA opal with the metal salt. It is known that the quality of the inverse opal is influenced by different parameters such as precursor species, infiltration method, conversion temperature, solvent, and drying procedure used during the casting procedure [17,18].

The measured band gaps of the indium oxide photonic crystals were compared with the calculated band gaps in a plane-wave basis set. The influence of the lattice constant and the wall thickness of an inverse opal were investigated.

2. Experimental

2.1. PMMA spheres

Monodisperse poly(methyl methacrylate) (PMMA) colloidal spheres were synthesized by surfactant-free emulsion polymerization [19]. 400 mL water was added to a two-necked flask sealed with a septum, heated to reflux and flushed with nitrogen. The nitrogen flow was stopped and the monomer (methyl methacrylate, 21.3 mL, 0.5 mol/L, Merck, 99%) and the cross linking agent (ethylene glycol dimethacrylate, 0.57 mL, Merck, 97.5%) (both destabilized by filtrating with Al_2O_3) were added. The mixture was stirred for another 20 min. Then the initiator ($K_2S_2O_8$, Bayer, 27 mg dissolved in 1 mL water) was added. After stirring for 2 h at 100 °C the septum was removed and the mixture was cooled to room temperature. The dispersion was filtered through a paper filter to remove large aggregates.

2.2. Opal films

The PMMA spheres were deposited in the opal structure on glass microscope slides. The cleaned slides (rinsed with ethanol and acetone) were put in the custom built sample holder and placed in the ultrasonic bath (ca. 45 kHz, VWR Ultrasonic Cleaner, USC300TH). Then 20 μL of the PMMA dispersion was placed in the center of the slide and dried under ultrasonication.

2.3. Inverse In_2O_3 opal film

The pores in the prepared PMMA opal films were filled with indium nitrate solution (Sigma Aldrich, 99.99% indium nitrate: 0.375 g in 1 mL ethanol) by placing a drop of this solution (7 μL) on the opal film. Then the composite was dried at room temperature and subsequently at 60 °C, details about the drying times are given in Table 1.

After drying the composites, the indium nitrate was converted to indium oxide in a tube furnace at 300 °C for 2 h with a heating rate of 0.5 °C/min.