

Synthesis of amorphous silicon/magnesia based direct opals with tunable optical properties

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ARTICLE INFO

Article history:

Received 23 June 2010

Received in revised form 8 October 2010

Accepted 3 November 2010

Available online 4 December 2010

Keywords:

Opals

Photonic crystals

Optical spectroscopies

ABSTRACT

The effective refractive index of silica based artificial opals can be strongly modulated through magnesiothermic and wet etching processes. The magnesiothermic reduction of silica spheres assembled in a fcc lattice produces amorphous silicon/magnesia matrix, which can be easily converted in oxidized porous silicon, preserving the ordered structure. These results are verified by electron microscopies and IR/Raman spectroscopies. The optical properties are analyzed in terms of the experimental reflectance spectra. By comparing the measured data to rigorous calculations, the good quality of the opaline replicas is demonstrated.

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1. Introduction

Since the pioneer works of Yablonovitch [1] and John [2], growing attention has been focused on the studies of photonic crystals (PhCs), which are structures where the dielectric function is spatially modulated with the period on the order of the light wavelength yielding the appearance of energy ranges in which the electromagnetic wave propagation is forbidden, well known as photonic bandgaps (PBGs) [3]. Within three-dimensional photonic crystals, synthetic opals represent a valuable structure obtainable from self-assembling methods concerning with nanosphere colloidal suspensions such as dip-coating, sedimentation or centrifugation [4–6] aimed to obtain 3D packing with the face-centered cubic (fcc) structure and the (1 1 1) plane parallel to the planar substrate.

From a fundamental point of view, several appealing properties of the opaline structures were analyzed such as controlled light emission [7–9], optical guiding [10], enhancement of optical second-harmonic generation [11] and electrically controlled optical birefringence [12]. On the applications side, the PBG features of the opal photonic crystals were exploited in optical sensing [13,14], multicolour pattern generation [15] and dye sensitized Solar Cells [16].

In the framework of the PhCs fabrication, 3D structures and in particular artificial opals involved more materials issues than the 'microelectronics' approach, typical of 2D PhCs. Actually, many efforts were devoted to the optimization of materials synthesis with different refractive indices to be involved in opal assemblies. Among the promising materials, silicon and related alloys have been extensively applied [17–19].

In high refractive index contrast inverted opals (i.e. crystalline silicon based), even a complete PBG, with a forbidden energy range independent of the direction and polarization states can be obtained [17]. In particular, amorphous silicon (a-Si) based inverted opals have been synthesized in the past through CVD infiltration of colloidal direct structures [20,21], exploiting the higher refractive index of a-Si with respect to polycrystalline Si. Besides such nanostructures, crystalline Si based direct opals were recently obtained by magnesiothermic reduction of silica opals [22], taking advantages of recipes that demonstrated the possibility to obtain silicon nanostructures from silica templates preserving the ordered mesoporous architecture [23,24].

In the present work, direct opals are obtained by reduction of silica opals into amorphous silicon/magnesia composites. Their optical responses are characterized by Bragg reflections spectrally tunable through a magnesiothermic process and HCl wet chemical etching. The experimental data are supported by a numerical modelling based on a scattering-matrix method [25,26]. Raman and FTIR spectroscopies verified that the wet etched opaline replicas consist of hydrogenated/oxidized nanostructured a-Si based spheres.

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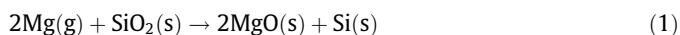
2. Materials and methods

2.1. Synthesis and thermal processing: reduced Si/MgO and porous Si opals

Silica nanospheres were synthesized following the Stober–Fink–Bohn method [27], starting from tetraethyl orthosilicate (TEOS>98%, Aldrich), doubly distilled water (Labochem), ammonia (33%, Riedel), and absolute ethanol (99.9%, Labochem) as precursor alkoxide, hydrolyzing agent, catalyst and solvent, respectively. Two mother solutions were prepared: one containing ammonia–water with a fixed mole ratio, the other containing TEOS–ethanol with variable amount of the former and a fixed amount of the latter ($\text{NH}_3/\text{H}_2\text{O}/\text{C}_2\text{H}_5\text{OH}$ mole amounts 0.46/2.89/2.15). The same volumes of the two solutions were mixed in a thermostatically controlled water bath ($30 \pm 1^\circ\text{C}$), so that the TEOS amount determined the sphere diameters [5]. In particular, we selected the synthesis parameters aimed to obtain nanospheres with diameters of 340 and 375 nm (corresponding to 0.02 and 0.03 TEOS moles respectively). After 180 min, the resulting spheres were physically separated from the liquid phase and then redispersed into distilled water (0.5–1 vol.%). Subsequently, opals were produced through dip-coating technique dipping a nearly vertical substrate (glass slide) into the suspension of nanospheres. The water evaporation at a temperature around 60°C leads to the deposition of self-standing membranes with a thickness up to $100\ \mu\text{m}$, easily detached from the glass substrates. These membranes are characterized by spheres stacked along the (1 1 1) crystallographic direction of a fcc lattice. Two-dimensional fast Fourier transform performed on the SEM micrographs concerning with the opal surfaces yield hexagonal symmetry in the k -space over several tens of microns showing polydomains with the same preferential orientation. In detail, the hexagons built by the silica spheres in the direct lattice are oriented with the apex along the sample front growth. Besides such a surface order, recent polarized micro-transmittance measurements performed on 1 1 1-stacked silica opals with single oriented microdomains, identified twin structures with the two possible vertical stacking sequences (i.e. ABC, ABC, ... or ACB, ACB, ... stacking sequence in the close-packed fcc lattice [28]). On the other hand, these defects cannot influence the optical transmittance/reflectance measurements if the probing spot dimension is much larger than the order of the single oriented domain size, as in the case of the present work.

The silica opals experienced thermal treatments aimed at strengthening the structure by obtaining necks between neighbouring spheres; the sintering temperature were fixed at 630°C for 3 h with an initial heating rate of $1^\circ\text{C}/\text{min}$.

The calcinated opal membranes were placed into a tube furnace close to a vessel containing Mg pellets. The furnace were heated to 630°C for 5 h with a heating rate of $10^\circ\text{C}/\text{min}$; a-Si/MgO composite opal replicas were obtained following the below reported reaction of silica with gaseous Mg:



Selected samples were immersed in a 0.1 M HCl solution for a time ranging within 5–20 min in order to selectively dissolve the magnesia matrix, obtaining porous a-Si opals.

2.2. Characterization of the opaline structures

The morphological characterizations of the opal membranes were performed by Field Emission Scanning Electron Microscopy (FESEM, Zeiss Supra 40) equipped with an Energy Dispersive X-ray spectrometry (EDX, OXFORD INCA ENERGY 450). Transmission Electron Microscopy (TEM) was performed with a FEI Technai G²

F20 X-Twin equipped with EDX and Electron Energy Loss Spectroscopy (EELS).

FTIR measurements were performed using a Bruker Tensor with a cryogenic MCT detector in grazing angle configuration (30°). Micro-Raman spectra were obtained by a Renishaw inVia spectrometer coupled with a CCD detector and a laser excitation at $514.5\ \text{nm}$ in backscattering configuration. Finally, spectral specular reflectance spectroscopy were carried out by a Varian Cary 5000 diffraction spectrometer operating close to normal incidence conditions.

3. Results and discussion

Scanning electron microscopy images (top views) of opals with sphere diameter of 340 nm taken at different synthesis steps are shown in Fig. 1. The EDX microanalysis performed on the opal before the magnesium treatment shows the obvious presence of silicon and oxygen due to the silica matrix (Fig. 1a). The magnesiothermic reduction process yields a fcc replica characterized by magnesia and silicon (Fig. 1b). Following the products of reaction (1) A mixture of one mole of Si with 2 mol of MgO corresponds to 20 at.% silicon, 40 at.% magnesium, 40 at.% oxygen (corresponding to 35 vol.% silicon and 65 vol.% magnesia). Fig. 1c shows the sphere layer after the MgO dissolution by HCl etching. The corresponding microanalysis evidences the Mg disappearance due to the successful selective removal of MgO, while a significative presence of residual oxygen can be observed. A silicon based porous structure results after the HCl treatment as shown by high resolution FESEM analyses, in agreement with the optical response of the Si based opals later discussed.

Fig. 2 shows Scanning Transmission Electron Microscopy (STEM) analyses of typical spheres after the magnesiothermic reduction process. In particular, TEM–EDX–EELS probes evidence for the latter composites a uniform distribution of silicon, magnesium and oxygen interpretable as a continuous matrix of magnesia nanoparticles surrounded by amorphous silicon, which confirm the elemental composition of the pure silica and a-Si/MgO (20 at.% silicon, 40 at.% magnesium, 40 at.% oxygen as arguable by reaction (1))

As a further proof of the internal structure quality of the opals subjected to magnesiothermic reduction, Fig. 3 shows the FESEM cross-sectional view of a a-Si/MgO cleaved specimen, where the fcc ordered stacks well reproduce the starting silica based 3D photonic crystal. EDX measurements performed on cleaved opaline structures show that the magnesiothermic process allows to obtain homogeneous a-Si/MgO composites with the above discussed atomic composition up to $30\ \mu\text{m}$ from the free surface.

It is worth to underline that, despite the magnesization should induce a sphere size increase due to the Mg incorporation as MgO (around 5% by considering the molar volumes of silica, silicon and magnesia), just an increase of 2% of the sphere diameter size was verified comparing FESEM viewgraphs of opals before and after the thermal treatments, performing a statistics on hundreds of spheres. Such a moderate increase could be ascribed to a lower density of silica obtained by our sol–gel method with respect to ideal SiO_2 .

The material microstructure of the opals subjected to the thermal reduction and wet etching process was characterized by FTIR and Raman spectroscopies. Fig. 4 shows the FTIR spectra acquired with the infrared beam grazing (30°) to the (1 1 1) opals surface, for a sample subjected to the magnesiothermic reduction and to HCl etching with different dipping time. The infrared reflectance spectrum of the a-Si/MgO opal shows a typical resonance at $730\ \text{cm}^{-1}$ which is due to the Longitudinal Optical-like phonons (LO) of the MgO crystallites [29]. In the same spectra there are two absorption bands at $1450\ \text{cm}^{-1}$ and $1620\ \text{cm}^{-1}$, the former

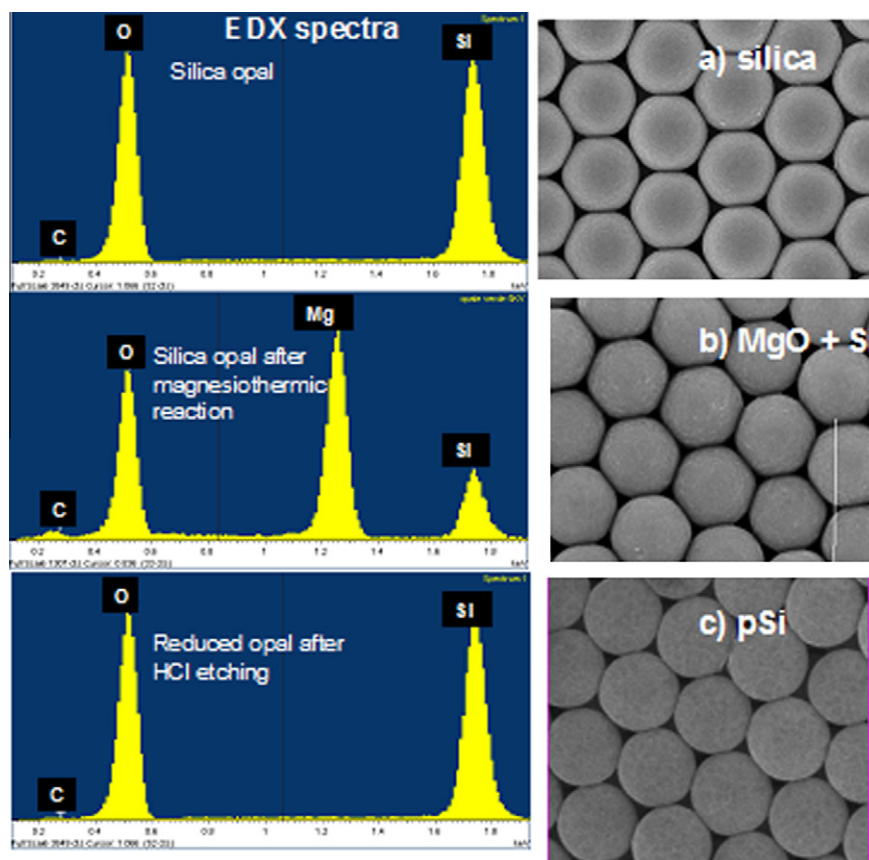


Fig. 1. EDX elemental analyses and FESEM viewgraphs of starting silica opals (a), a-Si/MgO structures synthesized by magnesiothermic reduction (b) and porous silicon replica obtained after HCl etching (c).

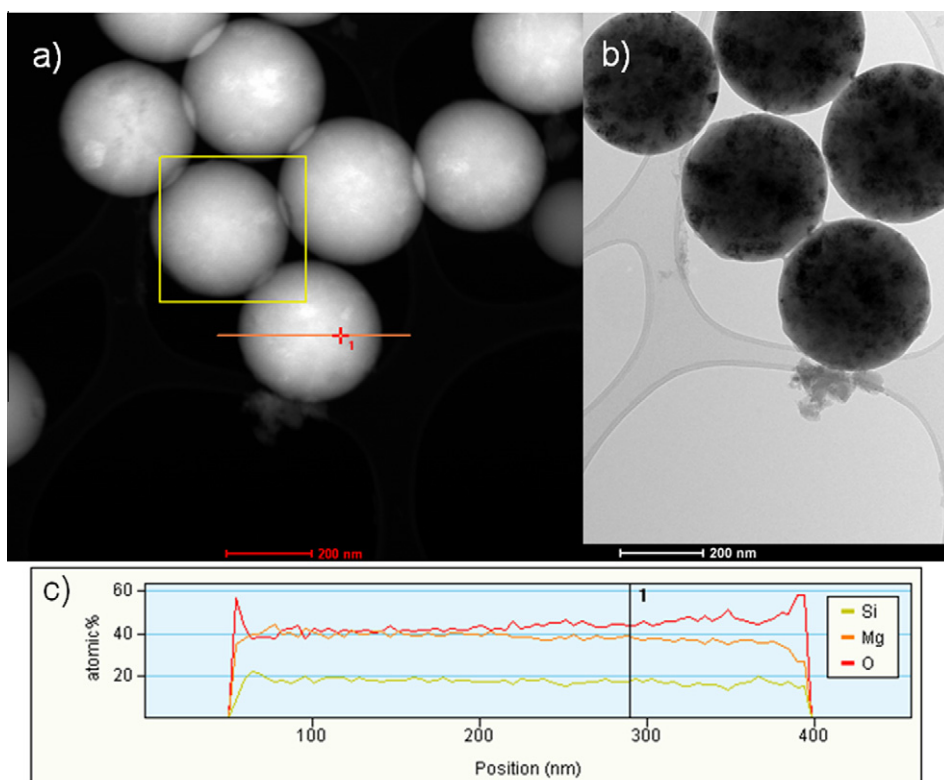


Fig. 2. Bright-field (a) and dark-field (b) STEM images of representative a-Si/MgO particles obtained after magnesiothermic reduction of silica spheres. The line shown in (a) represents the EDS and EELS line scan across a single sphere from which is extracted the elemental composition profile shown in (c). The dark-field image evidences the presence of the MgO and a-Si phases.

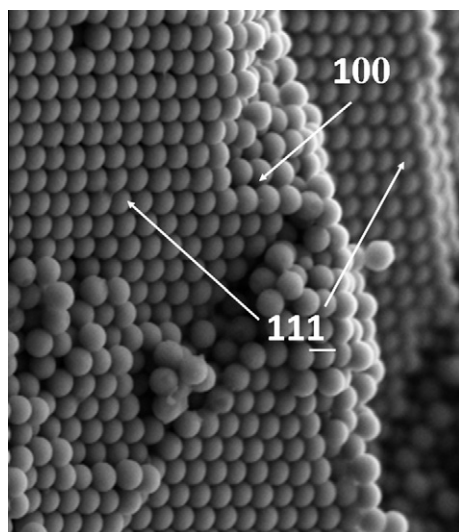


Fig. 3. Representative FESEM cross section of an a-Si/MgO cleaved opal. Typical crystallographic axes are evidenced.

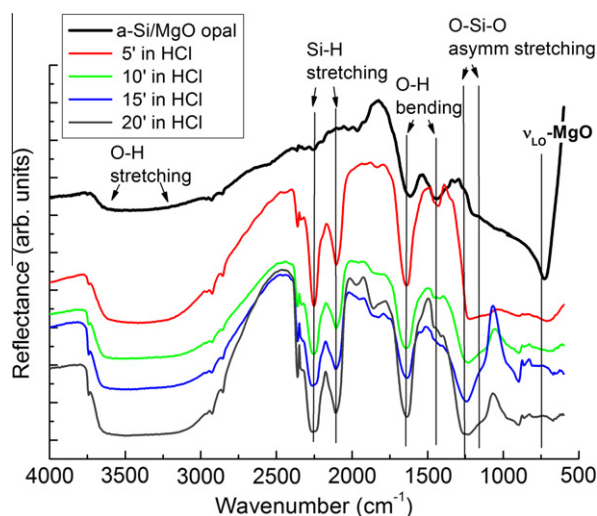


Fig. 4. Grazing angle FTIR spectra of an opal subjected to the thermal reduction and wet etching process for several HCl dipping times.

attributed to the OH bending mode of a hydroxyl group bonded to a Mg atom and the latter to the bending of physisorbed H₂O [30]. The corresponding OH stretching modes appear as a broad band at 3000–3700 cm⁻¹.

After the HCl etching, the IR spectra markedly change. First of all, the resonances at 1450 cm⁻¹ and at 730 cm⁻¹ respectively assigned to the Mg-OH bending and to the MgO skeletal mode progressively disappears, as expected from the magnesia dissolution. Other interesting characteristics are related to the oxidation and hydrogenation of the silicon matrix induced by the wet etching process. In detail, a band at 1240 cm⁻¹ appears, convolved with a shoulder at 1120 cm⁻¹ related to Longitudinal Optical and Transversal Optical (TO) Si-O-Si asymmetric stretches respectively. Such vibrational modes are a clear silica fingerprint, where the shrinking of the almost unresolved TO-LO splitting ($\nu_{\text{TO3}} = 1076 \text{ cm}^{-1}$ and $\nu_{\text{LO3}} = 1240 \text{ cm}^{-1}$ in ideal SiO₂) can be ascribed to the porous morphology [31]. The small peak at 3747 cm⁻¹ is assigned to the stretching vibration of an isolated silanol, which together with the Si-O-Si stretching modes can be

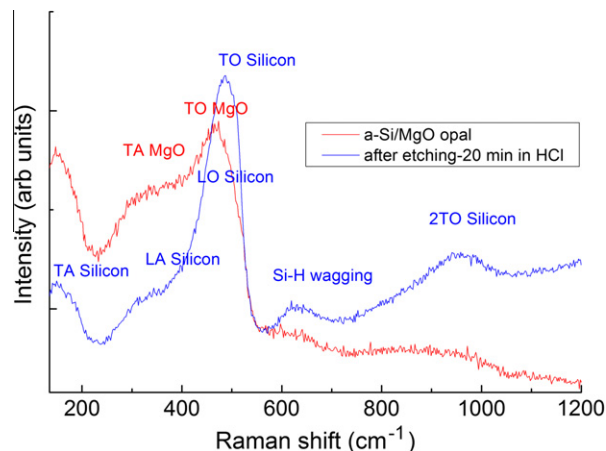


Fig. 5. Raman spectra of an a-Si/MgO opal before and after the HCl etching. Phonon-like bands of amorphous silicon/magnesia and molecular vibrations are indicated as reference.

taken as a proof of a partial surface oxidation of the Si structure. Besides these resonances, intense bands appear at 2100 cm⁻¹ due to Si-H stretching and at 2250 cm⁻¹ due to O₂Si-H₂ stretching [32,33], evidencing also a hydrogenation process involving the amorphous porous silicon surface.

a-Si/MgO opals have also been analyzed with Raman spectroscopy before and after HCl etching. Since magnesium oxide has a rocksalt structure with inversion symmetry, first order Raman scattering is forbidden for ideal crystals, while the second order is well defined in the energy range of 600–1200 cm⁻¹ with strong features due to high Phonon Density of States (PDOS) near critical points in the Brillouin zone [34]. On the other hand, for MgO based nanocrystalline or clustered structures, Raman spectra should reproduce all the PDOS features due to the k-vector selection rule relaxation [35], as demonstrated for amorphous silicon networks [36]. Fig. 5 shows the spectra of a-Si/MgO composites which are characterized by broad bands ascribable to the convolution of the vibrational density of states of the MgO and Si matrices. The Raman spectrum of the same sample after HCl etching (0.1 M concentration) performed for 15 min shows the typical features of a-Si with two preminent structures related to Transversal Acoustic phonons (TA) at 50–200 cm⁻¹ and Transversal Optical phonons (TO) at 440–520 cm⁻¹ with the shoulder on the low-wave number tail of the TO band at 250–440 cm⁻¹ ascribed to Longitudinal Acoustic (LA) and LO collective vibrations. In agreement with the FTIR measurements, the Raman bump at 640 cm⁻¹ ascribable to Si-H wagging vibrations, evidences the hydrogenation of the porous a-Si matrix. The etched sample shows Raman spectra with a growing baseline at high wave numbers (not shown here) due to the luminescence activity of the silica phase evidenced by FTIR spectroscopy. Despite the presence of silica, it does not yield any measurable SiO₂ Raman signal due to silica transparency to the involved excitation wavelength (514.5 nm) and to the lower silica scattering cross section compared with those of a-Si.

The synthesis processes has been finally monitored by specular reflectance spectroscopy operating in quasi-backscattering configuration (12.5° with respect to the (1 1 1) axis of the fcc structures). Fig. 6 shows the reflectance spectra of opals with different sphere size (340 and 375 nm) concerning with the silica based structures, the a-Si/MgO composites and HCl etched specimens. The main features characterizing the reflectance spectra are the (1 1 1) Bragg peaks corresponding to the first gap at L point in the first Brillouin zone associated with the fcc structure [20]. The wavelength of the characteristic (1 1 1) Bragg peak is strictly dependent upon the

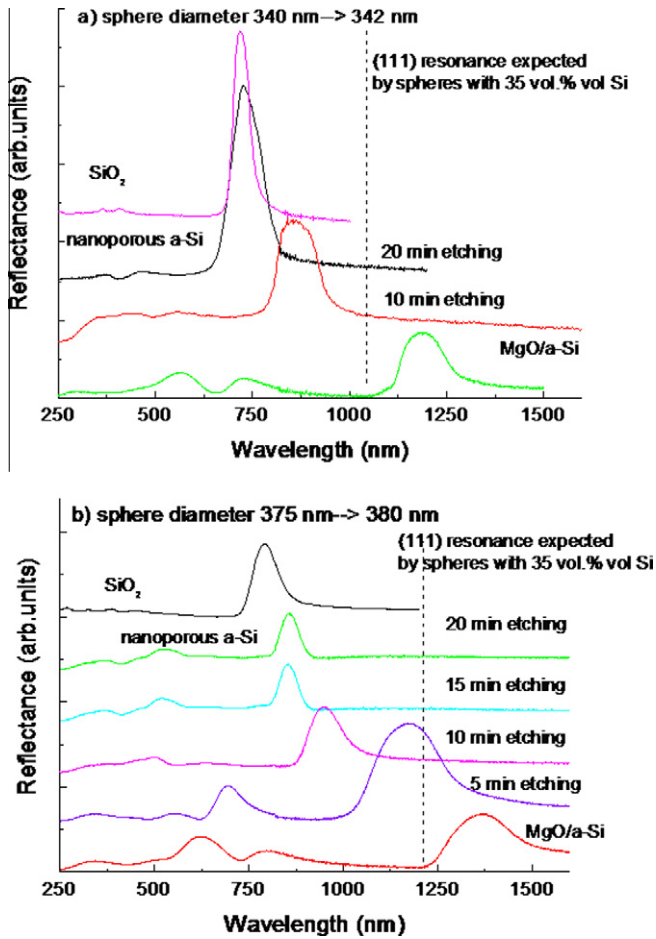


Fig. 6. Reflectance spectra (quasi-backscattering configuration) of silica opals subjected to magnesiothermic reduction and to HCl etching for different dipping times. The experimental data concern with two structures with spheres diameter of 340 (a) and 375 nm (b). The expected energies of the (111) resonances for pure porous silicon spheres with 65% porosity are shown for comparison. The spectra are vertically shifted for sake of clarity.

refractive index of the periodic structure following the relationship [5]

$$\lambda_{111} = 2d\sqrt{\frac{2}{3}}n_{\text{eff}}\cos\theta_{\text{int}} \quad (2)$$

where θ_{int} is the internal angle imposed by the Snell law, d is the sphere diameter, n_{eff} is an effective refractive index. n_{eff} can be estimated within the effective medium approximation as $n_{\text{eff}}^2 = n_{\text{MAT}}^2 f_{\text{SPHERE}} + n_{\text{AIR}}^2 f_{\text{AIR}}$ where n_{MAT} is the refractive index of the material constituting the sphere and f_{SPHERE} and f_{AIR} are the sphere and interstice volume fraction respectively ($f_{\text{SPHERE}} = 0.74$ for the ideal fcc structure).

After the magnesiothermic reduction, the (111) Bragg peaks show a marked red shift due to the higher refractive index of the opaline structure. Actually, an increase of n_{MAT} from 1.4 (typical of silica) to 2.5 (considering a mixture of 35 vol.% silicon and 65 vol.% magnesia) can be expected.

After selective etching of MgO performed by HCl immersion, an opposite shift is observed. The (111) resonances shift towards lower wavelengths as the samples dipping time increases. This behaviour can be due to the MgO removal, followed by a partial etching of the silicon skeleton and a silicon surface oxidation evidenced by the FTIR analysis. In detail, the opals subjected to the longer HCl dipping time yield a noticeable red shifted reflectance

resonance. Such a shift can be ascribed to a silicon fraction much lower with respect to a Si filling fraction amount of 35%, corresponding to the ideal case where all the MgO present in the thermal reduced Si/MgO spheres is removed leaving intact the Si skeleton, as found by the Lopez group [22]. This ideal configuration (pure porous Si with 65% porosity) would yield reflectance resonances at much larger wavelengths with respect to our experimental

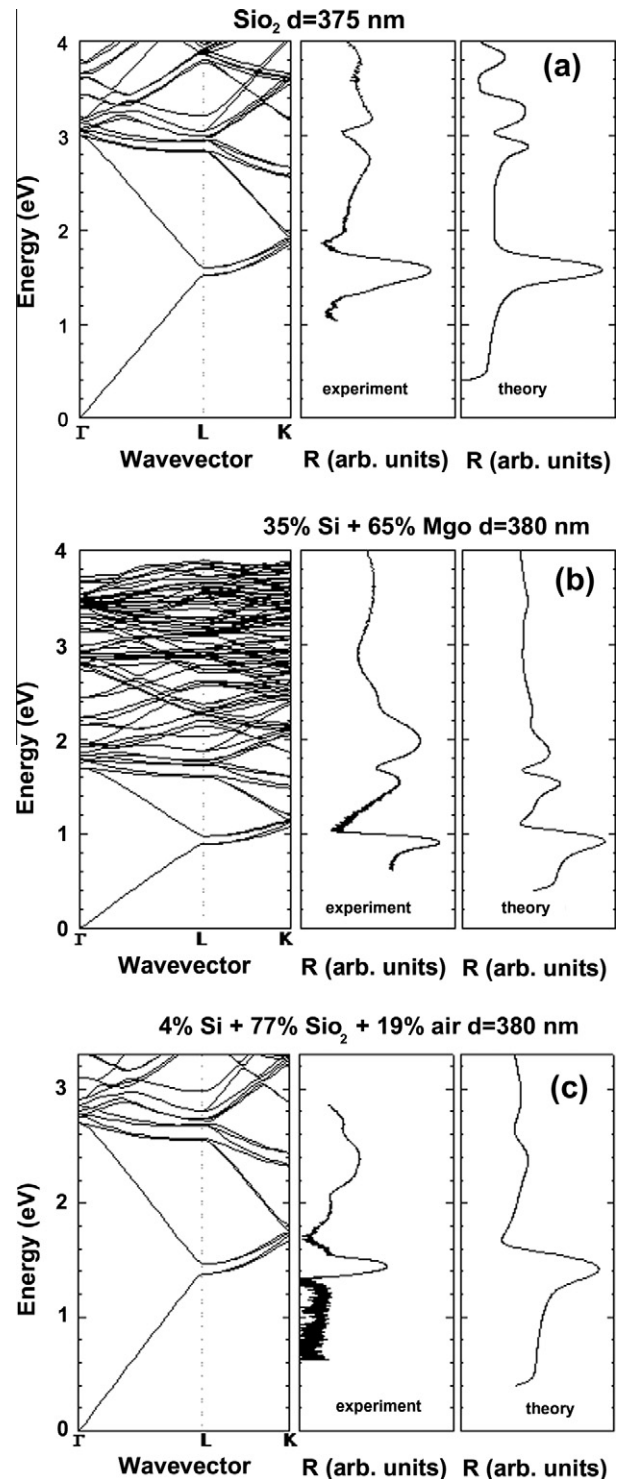


Fig. 7. Photonic band diagrams, measured and calculated reflectance spectra for bare silica (a), a-Si/MgO (b) and oxidized porous silicon (c) opaline structures. The reflectance spectra are shown in log scale in order to evidence also the high energy bands.

data (see the energies of the (1 1 1) resonances expected for pure 35% porous silicon shown in the reflectance spectra of Fig. 5).

In order to gain an insight into the opal microstructures, the experimental reflectance spectra were compared to those calculated numerically by means of a Fourier modal method. In particular, we used a scattering-matrix method according to the formulation of Whittaker and Culshaw, which allows for the description of periodically patterned multilayers [25]. This method requires to subdivide the structure in layers that are homogeneous in the z direction (in our case along 1 1 1), so that each sphere is approximated with a stack of concentric cylinders arranged in a periodic lattice [37]. Recently, we proposed a formulation of the scattering matrix method [26] that allows to vertically subdivide the opal in an arbitrary large number of layers to efficiently describe the high energy features of the opal spectra. Scattering effects and disorders have been described using an artificial Gaussian smoothing (with $\sigma = 0.05$ eV) of the theoretical spectra. In the calculations, we have assumed the sample to be composed of 30 spheres layers with a stacking sequence ABC, ABC, ... on a glass substrate. We consider a sphere diameter of 375 nm in the case of the silica opal, and of 380 nm for the a-Si/MgO and porous silicon structures. The results for the three structures are shown in Fig. 7 along with the calculated photonic bands dispersion.

In particular, Fig. 7a shows the results for a bare silica opal considering $n_{\text{SiO}_2} = 1.4$. From left to right, the band diagram, the measured reflectance spectrum at quasi-normal incidence, and the calculated spectrum are reported. The width and position of the main stop-band region (first pseudo-gap at L point) agree with those of the experimental curve. In the theoretical and experimental spectrum there are high energy features, which can be considered as a fingerprint of the good periodicity and stacking order [38]. Fig. 7b shows the case of the a-Si/MgO opal with the spheres diameter stretched to 380 nm, considering the refractive-index dispersion of amorphous silicon ($n_{\text{a-Si}} = 3.5\text{--}4$ for the wavelength range of 700–1500 nm and $n_{\text{MgO}} = 1.74$). The best matching between the theoretical spectra with experimental ones yields a MgO volume fraction of 65%, in excellent agreement with calculation taking into account Eq. (2) and the TEM–EDX compositional analyses previously discussed.

Finally, Fig. 7c shows the case of the porous silicon structure obtained after 20 min of HCl etching. In such a case, we took into account an oxidation process actuated by the HCl aqueous solution which yields a highly oxidized porous silicon skeleton. Actually, the best agreement between experimental and calculated reflectance spectra for the etched opals is obtained for a structure with 4% Si, 77% SiO₂ and 19% air volume fractions. The agreement concerns both the first pseudo-gap and the higher order one, where we have considered the a-Si refractive-index dispersion in the energy range of 1–3 eV, which imposes a useful constrain aimed to match the optical response of the porous Si/SiO₂ structure starting from different compositions. This result is fully compatible with the molar volumes of Si and SiO₂, taking into account that most of the silicon present in the a-Si/MgO opal after the magnesiothermic reduction process could be converted in silica during the wet etching process. The oxidation process allows to reach a moderate air filling fraction with respect to the ideal case before discussed (nanostructured Si matrix with 65% air filling fraction), increasing the robustness of the opal replicas.

4. Conclusions

In conclusion, we reported the synthesis of amorphous silicon/magnesia based direct opals with optical responses dealing with photonic pseudo-gaps tunable in the visible-near infrared range. The effective refractive index of the starting monodisperse silica

spheres can be easily changed by magnesiothermic reduction and HCl based wet etching through which the porosity of the Si/SiO₂ nanostructure can be controlled. The good quality of the opaline replicas was verified by electron microscopy and reflectance spectroscopy, corroborated by calculations exploiting a scattering-matrix method.

The synthesis process here analyzed are suitable to produce a-Si/MgO opals; such a process could be exploited for the fabrication of other photonic crystals with different symmetry (i.e. Yablonovite or Woodpile structures synthesized from silica templates) where the high refractive index would allow to reach full photonic bandgap regimes. On the other side, the wet etching of the MgO matrix allows to obtain an oxidized porous silicon skeleton. These structures could be suitable for emitting dye impregnations, taking advantage of the porous structure. Thus, the opal optical tunability controlled by the HCl time dipping, could allow experiments of inhibited/enhanced spontaneous emission induced by the photonic dielectric structures.

Acknowledgements

The authors wish to thank Dr. Anna Carlsson (Nanoport Europe FEI Company) for the TEM, EDX and EELS analyses. This work has been partially supported by the National Project CIPE 2004 “Nanostructures for Applied Photonics”.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.optmat.2010.11.003.

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