CHARACTERIZATION OF SYNTHETIC OPALS FILLED WITH COPPER

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Photonic crystals based on synthetic opals filled with copper were produced by using the electrochemical deposition technique. Copper nanocrystal formation together with some quantity of their oxides inside opal pores was proved by the X-ray diffraction pattern. An angular behavior of reflectance maximum for opals with different copper content was satisfactorily described in the framework of the Bragg light diffraction model. Effective dielectric constant of the opal-copper structures was determined.

Keywords: photonic crystals, electrochemical deposition, synthetic opal, synthesis, effective dielectric constant, Bragg diffraction.

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1. Introduction

Over the past decade, investigations of the metal-dielectric structures have revealed new effects caused by the interaction of light with surface plasmons [1]. This has given rise to a new area of research aimed at creating a new type of nano-optoelectronics and nano-photonics devices. Among the most popular objects are metal-dielectric photonic crystals, which are promising for creating structures with negative refraction and implementing new ways of light control [2].

One of the various templates to produce metal-dielectric photonic crystals are synthetic opals. Such structures composed of sequential layers of close-packed monodisperse spherical silica particles provide the permittivity modulation with a period close to light wavelengths. As a consequence, in the visible region synthetic opals have a photonic stop band in the [111] direction (point L in the Brillouin zone for a face-centred cubic lattice). In this regard, opals containing metals with surface plasmon frequencies in the visible region (Ag, Au, Cu) are of particular interest [3, 4].

The aim of this work is to obtain metal-dielectric photonic crystals based on synthetic opals filled with copper and to investigate their structural and optical properties.

2. Sample fabrication and experimental technique

Silica SiO_2 particles were synthesized by the modified Stöber method as a result of the hydrolysis of tetraethyl orthosilicate $Si(OC_2H_5)_4$(TEOS) in an ethanol–water solution in the presence of ammonia hydroxide as catalystat high water concentrations. Bulk original opals were obtained by sedimentation of silica particles under gravity for several months. After drying in air, the obtained precipitates were annealed at 125°C for 1 hour and then at 750°C for 2 hours.

The samples were plane-parallel plates with a thickness of about 2 mm and an area of large sides of about 1 cm^2. The plane (111) of the face-centered cubic lattice of the opals was oriented parallel to these sides. An average size of silica particles was controlled by determination of the center position λ_c and halfwidth $\Delta\lambda_g$ of the non-transmission (reflection) band in the corresponding spectra measured at 0° ($\theta = 17°$), respectively.

Copper ions were introduced into the pores of original synthetic opals by electrochemical deposition from the $CuSO_4$–water solution. The electrolyte was prepared from 200 ml of distilled water and 64.5 g of copper sulfate. To increase the efficiency of introduction, a thin film sublayer of copper was previously applied to one of the large sides of the opal samples by thermal vacuum evaporation. After that, the sample was attached to the prepared cathode and placed 2 cm from the anode in the electrolyte. The electrolysis was

carried out at a current of 100 mA from the DC source for 120 s and 180 s.Estimated mass of copper introduced into original opal was varied from 2 mg to 3 mg.

To characterize the internal volume of the obtained structures by using the X-ray diffraction (XRD) and optical spectroscopy techniques, a half-millimeter layer of the sample surface was sanded off before measurements.

Reflection spectra of samples were measured at different angles θ relative to the normal to the growth surface. All the spectra were obtained by using a modified spectrometer based on a double monochromator DFS-12 within the 400 – 650 nm range. Reflectance coefficients were derived from the corresponding spectra by dividing them by the emission spectrum of incandescent lamp used for sample illumination. The light beam diameter on the sample surface was no more than 1 mm. An error in angle setting did not exceed 1.5°, and accuracy in defining spectral position was ±0.15 nm. XRD patterns were obtained in Debye-Scherrer geometry with a DRON-3 diffractometer (Cu K_α radiation, $\lambda = 1.5418$ Å).

3. Results and discussion

XRD pattern of the opal infiltrated with copper consists of well-distinguished lines placed against a background of broad diffusive halo with maximum at about 22°, indicating amorphous state of silica particles (Fig. 1). Comparing the interplanar distances derived from the XRD pattern for lines marked by numbers in Fig. 1 with the reference data testifies to the formation of copper together with its oxide Cu_2O inside opal pores (Table 1). The width of the observed lines indicates the crystalline state of the obtained compounds.

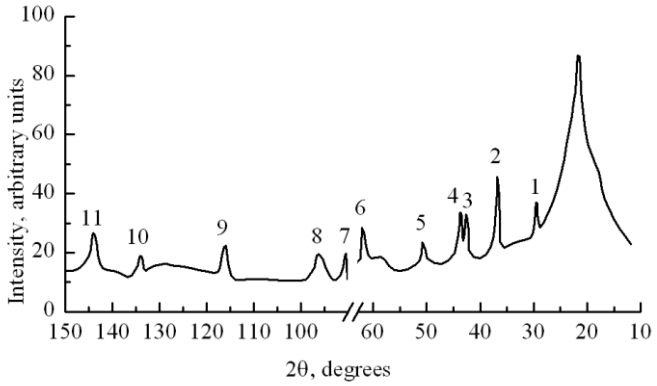

Fig. 1. The XRD pattern of opal infiltrated with cooper. The numbers mark the lines attributed to copper and its oxide (presented in Table 1).

Table 1

Identification of the X-ray diffraction pattern of opal infiltrated with copper

No.	2θ, degrees	d_{exp}, 10^{-10}m	d_{ref}, 10^{-10}m (XRD intensity, arb. un.) [5]			
			Cu	Cu_2O	CuO	$CuSO_4 \cdot 5H_2O$
1	29.4	3.04		3.00(3)		3.03(20)
2	36.5	2.46		2.45(100)		2.42(33)
3	42.5	2.12		2.12(31)		2.14(7)
4	43.5	2.06	2.08(100)			2.08(3)
5	50.6	1.81	1.798(86)			
6	61.8	1.50		1.51(44)	1.50(15)	
7	90.3	1.09	1.083(86)		1.086(3)	
8	95.8	1.04	1.038(56)			
9	116.4	0.91	0.900(26)			
10	139.7	0.82	0.826(56)			
11	144.0	0.81	0.806(42)			

All measured reflection spectra have one distinct reflection band whose maximum position and halfwidth are correspondent to the center λ_c and halfwidth $\Delta\lambda_g$ of photonic stop-band, respectively. As represented in Fig. 2, the embedding of copper into opal pores leads to a longer wavelength shift of the reflection bandwith the respect to the original opal reflection spectrum. With increasing the copper content, the value of the shift increases. For samples obtained at two electrolysis durations, 120 s and 180 s, the shifts are 27 and 72 nm, respectively.

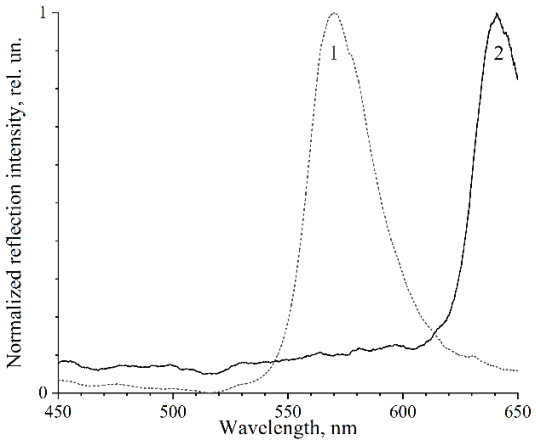

Fig. 2. Reflection spectra of original opal (1) and opal with higher copper content (2) at angle of incidence 17°.

Besides, the narrowing of the reflection bandwidth by 35 % (11 nm) with respect to the reflection bandwidth in the original opal spectrum is observed for the sample with higher copper content (Fig. 2).

The angular dependence of the reflectance of the sample with higher copper content is shown in Fig. 3. For all obtained samples it can be described by the typical dependence for the first order diffraction in the periodic structures

$$\lambda_c(\theta) = 2d\sqrt{\varepsilon_{eff} - \sin^2\theta} \qquad (1)$$

where ε_{eff} is the value of effective permittivity of the sample. The latter is defined as the sum of partial permittivities of the sample components as follows

$$\varepsilon_{eff} = 0.74\cdot\varepsilon_{SiO2} + (0.26 - x)\cdot\varepsilon_{air} + x\cdot\varepsilon_{copper}. \qquad (2)$$

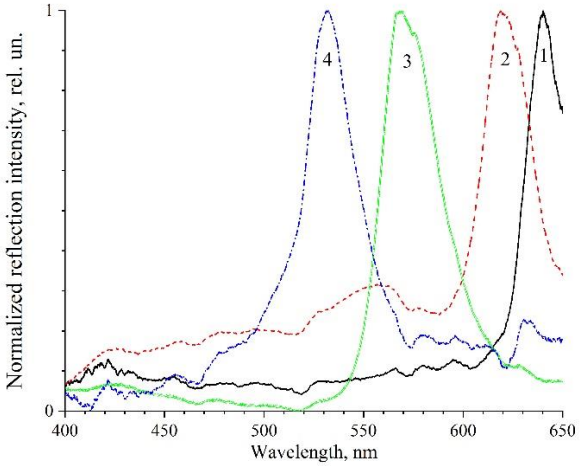

Fig. 3. Reflection spectra of the sample with higher copper content measured in specular geometry for angles of incidence 17° (1), 30° (2), 45° (3) and 60° (4).

We interpret the observed reflection band shifts, tracking the change in the photonic stop band position, and the change in the reflection bandwidth in terms of the modification of the effective permittivity of the samples as the pores are filled. The best match of the measured reflectance maximum position λ_c and that derived from (1) can be obtained for the following values of the effective permittivity: $\varepsilon_{eff1} = 2.01 \pm 0.03$ for opals with lower copper content, and

ε_{eff2} = 2.35 ± 0.02 for opals with higher copper content (Fig. 4). (The value of effective permittivity in original opal is 1.86.)

Exploring the obtained values and the known values for the copper permittivity in the corresponding spectral region we can estimate from (2)the copper concentration in the sample volume. It amounted to 3% for the sample with lower copper concentration and 6 % – for the sample with higher copper concentration.

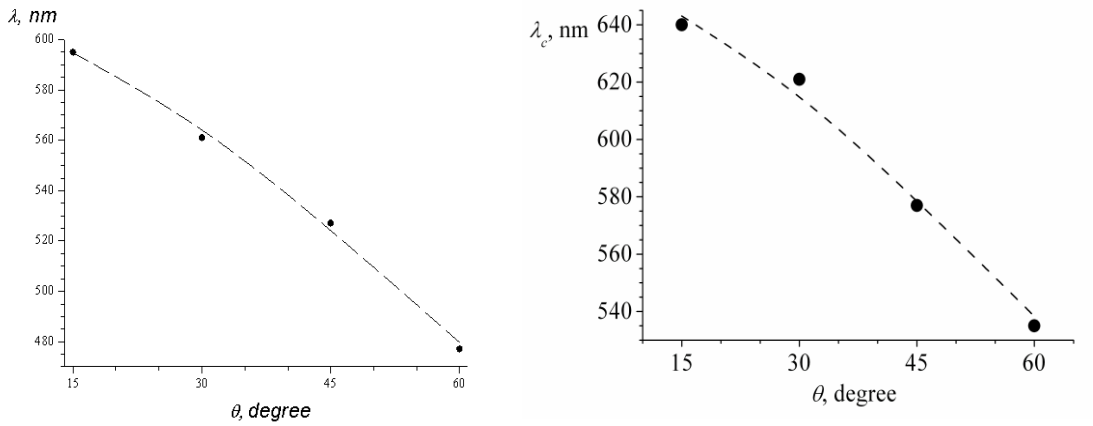

Fig. 4. Angular dependences of the reflection band maximum position for samples with lower (left) and higher (right) content of copper together with dashed curves calculated from (1) for ε_{eff1} = 2.01 ± 0.03 (left) and ε_{eff2} = 2.35 ± 0.02 (right).

4. Conclusions

The samples of photonic crystals based on synthetic opals infiltrated with copper were obtained by electrochemical deposition and characterized by X-ray diffraction and optical spectroscopy techniques. It was found that the possible copper-containing components embedded in the pores are copper and copper(I) oxide Cu_2O, both in a crystalline state. An increase in the concentration of copper in the samples leads to an increase of the effective permittivity of the sample. The average value of volumetric copper concentration in opal pores achieved in the experiments was 6 %.

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