ISSN 9125 0912. Вісник Дніпропетровського університету. Серія «Фізика. Радіоелектроніка». №2. Вип. 20. Т.21, 2013
Visnyk Dnipropetrovskogo universytetu. Fizyka. Radioelectronika. No 2. Issue 20. V. 21, 2013

UDC 535.36

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FABRICATION AND OPTICAL CHARACTERIZATION OF THIN SYNTHETIC OPAL FILMS FOR DESIGNING COATINGS OF SOLAR CELLS

A method for the fabrication of synthetic opal films with a thickness of 20 - 30 layers is given. Two methods for the characterization of synthetic opal thin films are described. The first method consists in studying the Bragg reflections spectra by using a special fiber-optic microprobe. In the measured spectra, together with the Bragg reflection peak, the presence of maxima due to thin film interference was observed. The film thickness of the samples is calculated by the position of the interference maxima. The second method is based on study of the laser diffraction on the structure of the synthetic opal film. The observed diffraction pattern consists of the six intense reflections, symmetrically located relative to the incident beam. The conditions for the observation of diffraction are described. The relation between structural parameters and the wavelength of radiation is installed. The peculiarity of the diffraction method is the ability to detect the defects related with the multidomain structure. The spectroscopic and diffraction techniques together provide a complete set of methods for the characterization of thin film opals.

Keywords: thin films of synthetic opals, Bragg diffraction spectra, laser diffraction, solar cells.

Приводится способ изготовления пленок синтетического опала с толщиной в 20 - 30 слоев. Описываются два метода характеризации тонких пленок синтетического опала. Первый метод заключается в исследовании спектров брэгговского отражения с использованием специального оптического волоконного микрозонда. В измеренных спектрах, наряду с пиком брэгговского отражения, наблюдаются максимумы, обусловленные интерференцией в тонкой пленке. По положению интерференционных максимумов вычисляются толщины пленок исследуемых образцов. Второй метод базируется на исследовании дифракции лазерного излучения на структуре пленки синтетического опала. Наблюдаемая картина дифракции состоит из шести интенсивных рефлексов, симметрично расположенных относительно падающего пучка. Описываются условия наблюдения дифракции. Устанавливается связь между структурными параметрами и длиной волны излучения. Особенность дифракционного метода заключается в возможности обнаружения дефектов, связанных с полидоменностью структуры. Спектроскопический и дифракционный методы вместе обеспечивают полноценный комплекс методов для характеризации тонких пленочных опалов.

Ключевые слова: тонкие пленки синтетических опалов, спектры брэгговской дифракции, дифракция лазерного излучения, солнечные элементы.

Наводиться спосіб виготовлення плівок синтетичного опала з товщиною в 20 - 30 шарів. Надається опис двох методів характеризації тонких плівок синтетичного опала. Перший метод полягає в дослідженні спектрів бреггівського відбиття з використанням спеціального оптичного волоконного мікрозонда. У виміряних спектрах, поряд з піком бреггівського відображення, спостерігаються максимуми, обумовлені інтерференцією у тонкій плівці. За положенням інтерференційних максимумів обчислюються товщини плівок досліджуваних зразків. Другий метод базується на дослідженні дифракції лазерного випромінювання на структурі плівки синтетичного опала. Спостережувана картина дифракції складається з шести інтенсивних рефлексів, симетрично розташованих відносно падаючого пучка. Надається опис умов спостереження дифракції. Встановлюється зв'язок між структурними параметрами і довжиною хвилі випромінювання. Особливість дифракційного методу полягає в можливості виявлення дефектів, пов'язаних з полідоменістю структури. Спектроскопічний і дифракційний методи разом забезпечують повноцінний комплекс методів для характеризації тонких плівкових опалів.

Ключові слова: тонкі плівки синтетичних опалів, спектри бреггівської дифракції, дифракція лазерного випромінювання, сонячні елементи.

Introduction

A great interest in applying synthetic opals in designing solar cells is caused by the following reason. These materials have the ability to convert the solar radiation spectrum either by selection of a certain part of the spectrum or by conversion of radiation energy (in the composite with luminescent materials, nonlinear optical materials, etc.). Currently, most of the experimental works in the field of photonic crystal research are performed on bulk synthetic opals. However, the presence of significant structural disorder in the bulk samples obtained by sedimentation lays obstacles to the complete exploitation of the features of their optical properties caused by photonic band structure. It is known [1] that film opals have an improved structure. Moreover, the creation of large surfaces with film opals is easier to implement.

In view of the above mentioned it becomes necessary to fabricate synthetic opals with the small number of layers as well as to carry out their optical characterization.

Samples

The opal structure has a face-centered cubic (fcc) lattice formed by hexagonal closely packed layers of monodisperse SiO_2 globules. Synthesis of silicon dioxide globules was carried out by modified Stöber method [2]. Opal films were grown by vertical pulling of quartz or glass substrate from suspension of nanodisperse silica globules with middle size of about $D = 280$ nm. Speed of pulling was about of 100 nm/s.

In this case, under action of surface tension forces of particle suspension, globules were stacked in a uniform layer. Such method, as experience shows, is the most effective and occupies much less time than the method of film growing in a region of moving meniscus by liquid evaporation from suspension [1]. The obtained samples were dried up during a day at room temperature with the subsequent annealing at $T = 480\ ^0C$.

Experiment and results

Characterization of samples means the determination of their structural parameters (diameter of globules and interplanar distance). For this purpose, the Bragg diffraction spectra in the reflected beams have been measured. According to the Bragg law, a spectral position λ_{max} of the reflection peak is connected with the interplanar distance d as follows

$$\lambda_{max}(\theta) = 2d\sqrt{\varepsilon_{eff} - sin^2\theta}$$

where θ is an incident angle of light beam on the system of the {111} planes, $\varepsilon_{eff} = 0.74 \cdot \varepsilon_{SiO_2} + 0.26 \cdot \varepsilon_{pore}$ is an effective dielectric constant; ε_{SiO_2} is a dielectric constant of SiO_2 globules, ε_{pore} is a dielectric constant of the substance into pores (for the composition of substances the dielectric constant also will be effective). The connection between the globule diameter D and the interplanar distance d along the [111] direction is given by the ratio $D = d \cdot f$ where $f = \sqrt{3/2}$ for fcc lattice.

To measure the Bragg diffraction spectra a special optical probe shown in Fig. 1, *a* was used. In the probe scheme the light was gathered to the optical concentrator *2* through the fiber bundle *1*, and then light was incident on the sample *3* at angle θ. The reflected from the sample surface light was gathered to the fiber *4* at the same angle. The spectra were registered with using a modified spectrometer based on a double monochromator DFS-12.

One of these spectra is shown in Fig. 1, *b*. The spectrum has a characteristic peak at 630 nm, its position is determined by the above described Bragg law. Thus, the structural parameters of the opal sample can be determined from the spectral position of the peak. Along with the Bragg diffraction spectra the interference maxima marked in Fig. 1, *b* as *m* (maximum position coincides with the Bragg diffraction peak), and *m*+1, were able to register. The presence of these maxima is caused by the phenomenon of interference in thin films. The thickness of the film *t* is determined by the position of these maxima λ_m and λ_{m+1} in such a way

$$t = 1\big/2n_{eff}\left(1/\lambda_{m+1} - 1/\lambda_m\right)$$

where n_{eff} is an effective refraction index. For investigated samples the film thickness is in the range from 2 μm till 4 μm.

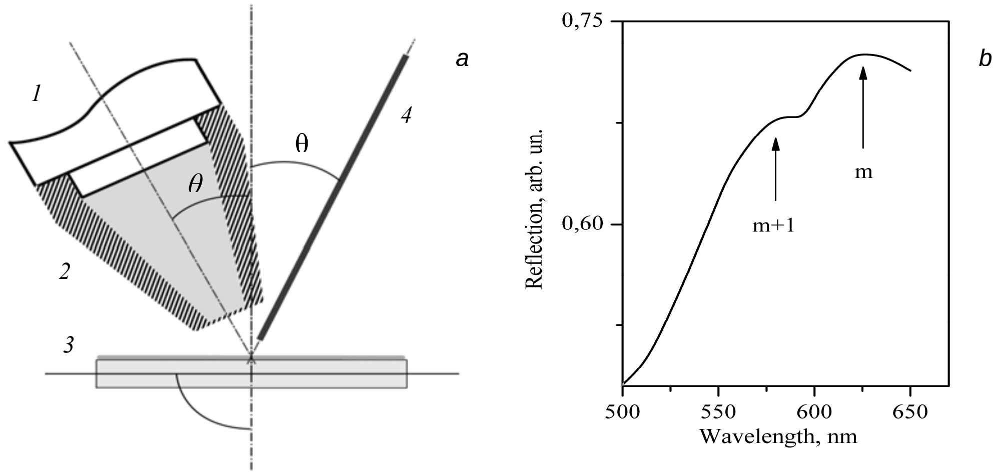

Fig. 1. Measurements of Bragg diffraction spectra. *a* **– optical probe scheme;** *b* **– Bragg diffraction spectrum measured with the optical probe.**

Investigation of the light diffraction in synthetic opals is also an important method for the characterization of opal films [3, 4]. To describe the laser radiation diffraction on the synthetic opal structure, the widely known approach developed by Laue [5] and used for describing the X-ray diffraction in ordinary crystals is applicable.

The observed diffraction pattern was characterized by symmetry C_6 and consisted of six intense reflections, symmetrically located relative to the incident beam (see Fig. 2, *a*). An optical scheme used to observe the diffraction is shown in Fig. 2, *b*. For this scheme, one DPSS and two semiconductor lasers with wavelengths of λ_{green}=532 nm, λ_{blue}=407 nm, and λ_{red}=635 nm, respectively, were used. The beam was oriented along the [111] direction, normal to the film surface.

As known in this geometry not for every wavelength and the incident beam orientation the diffraction can be observed. Condition for the occurrence of diffraction is

$$\vec{k} - \vec{k}_0 = \vec{G}$$

where $\vec{k}_0$ and $\vec{k}$ are the wave vectors of incident and diffracted beams and $\vec{G}$ is the reciprocal lattice vector. This condition is equivalent to the set of equations:

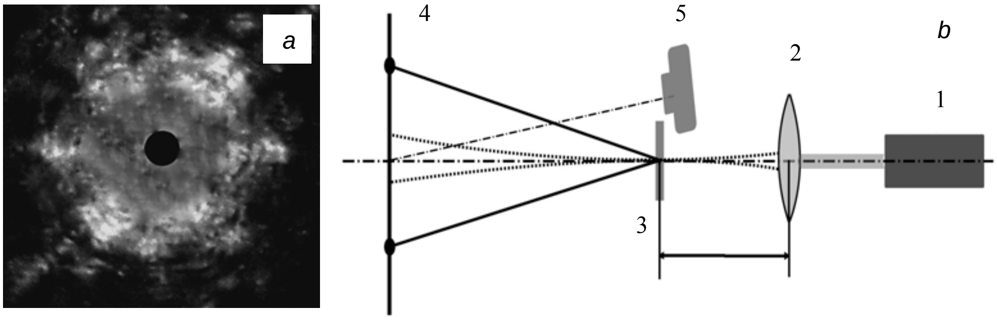

Fig. 2. Experiment on observation of diffraction. *a* **– diffraction pattern;** *b* **– optical scheme of the experiment of the laser beam diffraction in the opal film.**
1 - laser; 2 – lens; 3 – sample; 4 – screen; 5 – camera.

$$\begin{cases} d_1 n_{eff} = (\cos\alpha - \cos\alpha_0) = m_1\lambda; \\ d_2 n_{eff} = (\cos\beta - \cos\beta_0) = m_2\lambda; \\ d_3 n_{eff} = (\cos\gamma - \cos\gamma_0) = m_3\lambda; \end{cases}$$

where d_1, d_2, and d_3 are periods of nodal lines forming a certain system of coordinates, in general, oblique. The beam incident to the origin of the coordinate system will form angles α_0, β_0, γ_0 with its axes, while the diffracted beam forms angles α, β, γ. For each wavelength, and orientation of the incident beam in respect to the sample, an own coordinate system for the implementation of diffraction will be determined. It is possible to find the relation between D and λ. Using also the geometric condition $\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$ and assuming $m_1 = m_2 = m_3 = 1$, we can obtain

$$D = \frac{\lambda}{2} \cdot \frac{1}{n_{eff}^2} \cdot \frac{(f_1^2 + f_2^2 + f_3^2)}{(f_1 \cos\alpha_0 + f_2 \cos\beta_0 + f_3 \cos\gamma_0)}, \quad f_i = \frac{D}{d_i}.$$

The table below gives the values of the angles and f_i for which the diffraction is possible in this experiment. The calculated values of *D* are also given.

Table

Values of angles and f_i for which the diffraction is possible, D - the calculated size of the globules

λ, nm	α_0, ^{0}	β_0, ^{0}	γ_0 ^{0}	f_1	f_2	f_3	D, nm
407	90	90	30	$1/\sqrt{3}$	1	1	295
532	90	45	45	1	$1/\sqrt{2}$	$1/\sqrt{2}$	286
635	90	30	30	1	1	1	296

Characterization with using this method provides a great opportunity to analyze the quality of the sample. Defects and the overall disorder of the structure directly affect the diffraction pattern. The character of distribution and brightness of diffraction reflexes in the obtained diffraction patterns were various in some different sites of the sample. This fact testifies a polydomain structure of the film (Fig. 3).

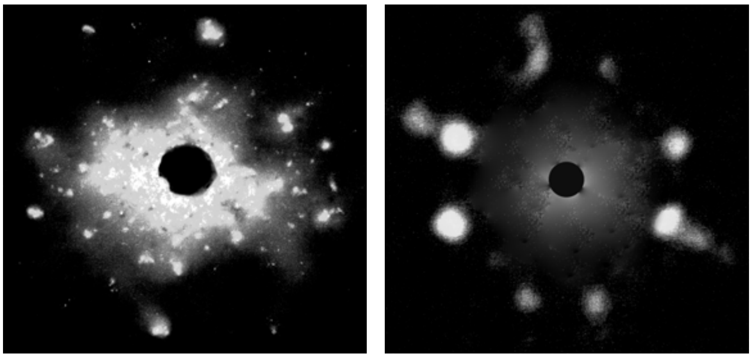

Fig. 3. The diffraction patterns obtained in sample sites, where the structure disruptions occur.

Conclusions

Two methods for the characterization of synthetic opals are described. The spectroscopic method has shown the presence of interference in a thin film along with Bragg diffraction. The conditions of the laser diffraction occurrence in performed experiments were identified. It is found that the diffraction method, as a method for characterization, gives also the information about the types of defects. Together, these methods provide an indispensable instrument for the characterization and analysis of thin coatings based on synthetic opals.

Acknowledgments

This work is supported by the Ukrainian–Russian Project No. F53.2/030 “Creation and investigation of active matrix nanocomposites on the base of photonic glasses and crystals for solar cells”.

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Received 13.07.2013.