REVIEWS OF TOPICAL PROBLEMS

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Optical properties of porous-system-based nanocomposites

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<u>Abstract.</u> We consider the optical properties of semiconductor – insulator and insulator – insulator nanocomposites, including porous materials such as silicon, gallium phosphide, aluminum oxide, and structures based on them. The main focus is on the effect of form birefringence, which is caused by the anisotropy of pores in the materials under study. The applicability of the effective-medium model for describing the optical properties of nanocomposites is discussed. The effects of light localization due to the scattering of light in such inhomogeneous media are analyzed.

1. Introduction

Investigating the properties of nanocomposite media is an important problem of modern solid-state physics. The properties of such media may considerably differ from the properties of both bulk materials and separate nanoparticles forming the composites. Thus, nanocomposite media are a basis for creating new materials with given structural, electronic, and optical properties, which are determined by the sizes, shapes, and ordering of the nanoparticles composing them, as well as by nanoparticle filling factors.

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Received 18 October 2006 Uspekhi Fizicheskikh Nauk **177** (6) 619–638 (2007) Translated by M V Chekhova; edited by A M Semikhatov Among the variety of nanostructured media, special attention should be given to porous semiconductors and insulators formed by removing part of the material from the bulk. Pores created this way and the remaining nanocrystals have sizes from nanometers to hundreds of nanometers. The physical properties of the resulting structures differ, often radically, from those of the original material. Three main reasons for these differences can be pointed out:

(1) quantum-size effects for nanoobjects whose sizes are comparable with the de Broglie wavelength of the electron;

(2) surface effects caused by the creation of new electron and phonon states of the surface whose area is considerably (often, by several orders of magnitude) increased due to the formation of pores;

(3) local fields in the nanocomposite medium that are determined by the shape, size, and ordering of the nanoobjects.

Due to the simplicity of production and the possibility of controlling their properties by changing the formation conditions, porous semiconductors are very convenient media for the study of physical phenomena in nanostructures and for creating novel photonic media. Among the important properties of porous semiconductors, we mention that their refractive index and dielectric permittivity are smaller than those of bulk materials. This can be useful for creating various optical coatings, as well as for forming media with low dielectric permittivity (low-k insulators), which is a crucial task from the standpoint of miniaturizing components in the computer industry [1]. Other properties important for practical applications are the extended surface of porous materials and the possibility of filling them with various gases or dielectric liquids, which allows using such media as sensors.

Special attention should be paid to nanocomposite media where the nanoobjects are more or less ordered and/or have anisotropic shapes. This anisotropy of shape is responsible for the creation of optical anisotropy and, in particular, form birefringence in such media [2].

Considerable achievements in the study of porous nanostructures have been made, for instance, for porous silicon (PS), which consists of silicon nanocrystals separated by pores [3-5]. Where the typical sizes of pores and nanocrystals are much less than the radiation wavelength, a nanostructured semiconductor can be considered a homogeneous optical medium with some effective refractive index, which differs from the refractive indices of the substances composing the nanostructure (the so-called effective-medium model) [6]. Choosing the parameters of processing allows controlling the structural properties of porous semiconductors (such as porosity and the size and shape of pores and nanocrystals) and, hence, their optical properties (such as the refractive index, birefringence, and dichroism) in a wide range. In addition, it is possible to control the thickness of formed porous layers in order to create the desired optical media and devices, including photonic crystals.

Another important area is the study of light propagation in an inhomogeneous medium, a good example of which are many nanocomposite materials such as porous gallium phosphide [7]. Such effects are extremely significant for both developing the principles of lasers based on inhomogeneous media (random lasers) [8] and increasing the efficiency of nonlinear optical processes (see, e.g., Refs [9-11]).

The present work reviews the results of studies on the optical properties of nanostructured semiconductors and insulators, in particular, on the effects of anisotropy and localization of light.

2. Effective-medium models

An important role in the optics of nanocomposite materials is played by the so-called effective-medium model. The basic idea is that the ensemble of nanoclusters can be considered a certain new medium with an effective dielectric permittivity. An evident advantage of this approach is that it allows analyzing the propagation of radiation in a nanocomposite medium without solving Maxwell's equations at each point of space.

The effective-medium model is typically applied to solving optical problems within the electrostatic approximation, in which both the sizes of nanoparticles and the distances between them are considered small compared to the optical wavelength in the medium [6]. Otherwise, the scattering of radiation by nanoparticles composing the medium and the interference of scattered waves must be taken into account.

If the optical parameters of all components and their concentrations and shapes are known, the effective-medium model, in principle, allows finding the effective parameters of the composite medium as a whole. For this, it is necessary to find the relation between the electric induction $\langle \mathbf{D} \rangle$ averaged over a volume V that is much larger than the typical size of the dielectric permittivity inhomogeneities,

$$\langle \mathbf{D} \rangle = \frac{1}{V} \int_{V} \mathbf{D}(\mathbf{r}) \, \mathrm{d}\mathbf{r} = \frac{1}{V} \int_{V} \varepsilon(\mathbf{r}) \, \mathbf{E}(\mathbf{r}) \, \mathrm{d}\mathbf{r} \,,$$
(1)

and the external electric field \mathbf{E}_0 . Here, $\mathbf{D}(\mathbf{r})$, $\mathbf{E}(\mathbf{r})$, and $\varepsilon(\mathbf{r})$ are local (corresponding to a point with the radius vector \mathbf{r}) values of the electric induction, electric field, and dielectric permit-

tivity. The resulting relation determines the effective dielectric permittivity ε_{eff} of the composite medium,

$$\mathbf{D}\rangle = \varepsilon_{\rm eff} \, \mathbf{E}_0 \,. \tag{2}$$

The local field $\mathbf{E}(\mathbf{r})$ depends on the shape of a particle. In the most general case, integration in (1) causes considerable difficulties. The exact value of the effective dielectric permittivity ε_{eff} can be found only in a few special cases, such as that of a laminar structure consisting of alternating parallel layers of insulators with permittivities ε_1 and ε_2 [2, 12]. Other cases should be considered within various approximations with local fields determined by solving electrostatic problems. The most popular effective-medium models are the Maxwell-Garnett model [13] and the Bruggeman model [14], which, although being among the oldest, are still widely used due to their physical clarity.

2.1 Models of an isotropic effective medium

Local field in a ball. The Maxwell-Garnett and Bruggeman isotropic effective-medium models are based on the standard electrostatic problem of finding the local field inside a ball. We consider a ball with a dielectric permittivity ε_1 surrounded by an insulating medium with a permittivity ε_2 . The local field **E**₁ inside the ball is formed by the external field **E**₀ and the field of a polarized sphere (the Lorenz field) $\mathbf{E}_d = -(4\pi/3)\mathbf{P}$, whose direction depends on the relation between ε_1 and ε_2 [2]:

$$\mathbf{E}_{1} = \mathbf{E}_{0} + \mathbf{E}_{d} = \mathbf{E}_{0} - \frac{4\pi}{3} \mathbf{P} = \frac{3\varepsilon_{2}}{\varepsilon_{1} + 2\varepsilon_{2}} \mathbf{E}_{0}, \qquad (3)$$

where

$$\mathbf{P} = \chi_0 \mathbf{E}_0 = \frac{3}{4\pi} \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} \mathbf{E}_0$$

is the polarization vector of the medium inside the ball and χ_0 is the polarizability of the sphere.

Maxwell-Garnett model. We now consider a volume V filled by a medium with the permittivity ε_2 and a few spherical inclusions with the permittivity ε_1 . The polarization vector of this volume is the sum of polarization vectors for all spherical inclusions,

$$\chi = \frac{1}{V} \sum_{i} V_{i} \chi_{0} = f_{1} \frac{3}{4\pi} \frac{\varepsilon_{1} - \varepsilon_{2}}{\varepsilon_{1} + 2\varepsilon_{2}}, \qquad (4)$$

where V_i is the volume of the *i*th particle and $f_1 = (1/V) \sum_i V_i$ is the volume filling factor. This volume is characterized by an effective dielectric permittivity ε_{eff} . If it has the shape of a ball and is surrounded by a medium with the dielectric permittivity ε_2 , then its polarizability, according to Eqn (3), is

$$\chi = \frac{3}{4\pi} \frac{\varepsilon_{\rm eff} - \varepsilon_2}{\varepsilon_{\rm eff} + 2\varepsilon_2} \,. \tag{5}$$

From Eqns (4) and (5), the Maxwell-Garnett formula follows as [13, 15]

$$\frac{\varepsilon_{\rm eff} - \varepsilon_2}{\varepsilon_{\rm eff} + 2\varepsilon_2} = f_1 \, \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} \,. \tag{6}$$

We see that the components of a composite medium are not equivalent. The Maxwell-Garnett model is considered valid when one of the materials forms a matrix and the other enters it as isolated inclusions whose volume fraction is not large (the so-called matrix media) [16]. **Bruggeman model.** In the cases where the composite medium cannot be considered a matrix with inclusions (the so-called statistical medium [17]), the model proposed by Bruggeman is often used [14]. We consider a medium formed by balls of two materials. In this model, each particle is assumed to be placed not into the matrix medium but into some effective medium with the effective dielectric permittivity ε_{eff} differing from the dielectric permittivities ε_1 and ε_2 of both components. Another assumption is that each ball is in the field that is averaged over the whole volume. Thus, the average field $\langle \mathbf{E} \rangle$ is determined by the fields \mathbf{E}_1 and \mathbf{E}_2 in the balls with ε_1 and ε_2 , respectively: $\langle \mathbf{E} \rangle = f_1\mathbf{E}_1 + f_2\mathbf{E}_2$, where f_1 and f_2 are the corresponding filling factors $(f_1 + f_2 = 1)$. With the relation between $\langle \mathbf{E} \rangle$, \mathbf{E}_1 , and \mathbf{E}_2 given by formula (3), we obtain

$$f_1 \frac{\varepsilon_1 - \varepsilon_{\text{eff}}}{2\varepsilon_{\text{eff}} + \varepsilon_1} + f_2 \frac{\varepsilon_2 - \varepsilon_{\text{eff}}}{2\varepsilon_{\text{eff}} + \varepsilon_2} = 0.$$
⁽⁷⁾

In this case, the two components forming the nanocomposite medium are equivalent. The model is often claimed to be valid under the following restriction for the filling factors, necessary for the nanoclusters to be in contact (percolation limits):

$$\frac{1}{3} < f < \frac{2}{3}$$
 (8)

In addition to these two models, the Landau–Lifshitz– Looyenga model is often used [18, 19], where

$$\varepsilon_{\rm eff}^{1/3} = \langle \varepsilon^{1/3} \rangle \,, \tag{9}$$

as well as a very efficient analytic representation proposed by Bergman [20, 21],

$$\varepsilon_{\rm eff} = \varepsilon_1 \left(1 - (1-p) \int_0^1 \frac{g(x,p)}{\varepsilon_1 / (\varepsilon_1 - \varepsilon_2) - x} \, \mathrm{d}x \right), \tag{10}$$

where p is porosity and g(x, p) is a function of the spectral density, which is independent of the properties of materials forming the nanocomposite and is determined only by the geometry. In this notation, the integrand, up to a numerical coefficient, is equal to the local field factor with the depolarization factor x.

These and other effective-medium models are extensively discussed in the literature in connection with analyzing the optical properties of nanocomposites (see [16, 17]). In particular, a detailed analysis of the optical properties of porous silicon based on effective-medium models was carried out in Refs [4, 5, 22-28]. It was shown that for mesoporous silicon (with the sizes of pores and nanocrystallites being in the range from nanometers to hundreds of nanometers) of average porosity, reliable results are given by the Bruggeman model [5, 24, 25]. At the same time, if this model is applied to microporous silicon, where the sizes of nanocrystals are of the order of nanometers, the quantum-size effect must be taken into account [24].

2.2 Taking shape anisotropy into account in effective-medium models

Laminar structure. A laminar structure, i.e., a structure formed by alternating layers with differing refractive indices, turns out to be the simplest case of a composite medium. If the electric field is orthogonal to the direction of the structure stratification, then

$$\varepsilon_{\rm eff} = f_1 \varepsilon_1 + f_2 \varepsilon_2 \,, \tag{11}$$

where f_1 and f_2 are the filling factors for each layer. If the electric field is along the direction of the structure stratification, then, because the normal components of the electric induction are equal at the boundaries, we obtain

$$\varepsilon_{\rm eff}^{-1} = f_1 \varepsilon_1^{-1} + f_2 \varepsilon_2^{-1} \,. \tag{12}$$

We note that the dielectric permittivity depends on the electric field direction [compare expressions (11) and (12)]. Thus, we are dealing with anisotropy caused by the structure of the system and the shape of the components forming the composite medium. This anisotropy is usually called the form anisotropy [2]. As can be seen from (11) and (12), a laminar structure has the properties of a negative uniaxial crystal with the optical axis coinciding with the stratification direction [2, 12]. We note that expressions (11) and (12) respectively give the upper and the lower bounds (the Wiener bounds) for all possible effective dielectric permittivities of a composite medium of any geometry [29].

Local field in an ellipsoid. The Maxwell-Garnett and Bruggeman effective-medium models can be generalized to the case where the particles composing the medium have anisotropy of shape. For example, let the medium contain rare inclusions of ellipsoidal shapes (the Maxwell-Garnett model) or completely consist of such ellipsoids (the Bruggeman model). Again, we have to solve an electrostatic problem, which is now the calculation of the local field in an ellipsoid.

Similarly to the case of a ball, the insulator polarization reduces the field inside the ellipsoid. The field E in the insulator consists of the external field E_0 and the depolarizing field E_d . The field components inside the ellipsoid are given by [30]

$$E_{1x} = E_{0x} - 4\pi L_x P_{1x},$$

$$E_{1y} = E_{0y} - 4\pi L_y P_{1y},$$

$$E_{1z} = E_{0z} - 4\pi L_z P_{1z},$$

(13)

where *L* is the depolarization factor. Thus, if the external bias field is homogeneous, the resulting field in the ellipsoid is also homogeneous, although it does not necessarily have the same direction as the external field.

We can find L by solving the Laplace equation in elliptical coordinates. Different principal axes correspond to different values of L, the depolarization factors for the three principal ellipsoid axes (x, y, and z) being related as

$$L_x + L_y + L_z = 1. (14)$$

For an ellipsoid of rotation (a spheroid), the situation simplifies because two of the three depolarization factors are equal in this case. We let L_{\parallel} denote the depolarization factor for the field directed along the rotation axis and L_{\perp} denote the depolarization factor for the field orthogonal to that axis. The value of L_{\parallel} is determined by the ratio $\xi = a/b$ of the polar semi-axis *a* and the equator semi-axis *b* [31],

$$L_{\parallel} = \frac{1}{1 - \xi^2} \left(1 - \xi \, \frac{\arcsin\left(\sqrt{1 - \xi^2}\right)}{\sqrt{1 - \xi^2}} \right),\tag{15}$$

$$L_{\parallel} + 2L_{\perp} = 1. \tag{16}$$



The dependences of L_{\parallel} and L_{\perp} on the semi-axis ratios are shown in Fig. 1. The condition a/b < 1 corresponds to a squashed ellipsoid of rotation, a/b > 1 to a stretched one, and a/b = 1 to a ball. In the last case, $L_{\parallel} = L_{\perp} = 1/3$. The ratio $a/b = \infty$ corresponds to an infinite cylinder ($L_{\parallel} = 0$, $L_{\perp} = 1/2$) and a/b = 0 to a plane ($L_{\parallel} = 1$, $L_{\perp} = 0$).

The polarization vector components \mathbf{P}_1 are related to the field \mathbf{E}_1 as

$$P_{1i} = \chi_{ii} E_{1i} = \frac{\varepsilon_{1,ii} - 1}{4\pi} E_{1i}, \qquad (17)$$

where χ_{ii} are the components of the dielectric susceptibility tensor and *i* labels a Cartesian coordinate. From (13), we obtain

$$E_{1i} = E_{0i} \left(1 + \frac{\varepsilon_{1,ii} - \varepsilon_{2,ii}}{\varepsilon_{2,ii}} L_i \right)^{-1}.$$
 (18)

Generalization of the Maxwell-Garnett and Bruggeman models to the case of anisotropy. In the Maxwell-Garnett model, we consider inclusions to have ellipsoidal shapes. The modified relation then becomes [16, 32]

$$\frac{\varepsilon_{\rm eff} - \varepsilon_2}{L(\varepsilon_{\rm eff} - \varepsilon_2) + \varepsilon_2} = f_1 \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_2 + L(\varepsilon_1 - \varepsilon_2)} \,. \tag{19}$$

In the Bruggeman model, we assume that a medium with some effective dielectric permittivity contains ellipsoids with permittivities ε_1 and ε_2 . The generalized Bruggeman relation takes the form [16, 17]

$$f_1 \frac{\varepsilon_1 - \varepsilon_{\text{eff}}}{\varepsilon_{\text{eff}} + L(\varepsilon_1 - \varepsilon_{\text{eff}})} + f_2 \frac{\varepsilon_2 - \varepsilon_{\text{eff}}}{\varepsilon_{\text{eff}} + L(\varepsilon_2 - \varepsilon_{\text{eff}})} = 0.$$
(20)

Various directions of the field correspond to various depolarization factors and, as a result, various values of the effective dielectric permittivity. This allows taking the anisotropy into account in terms of the effective-medium model. We note that for spherical nanoparticles (L = 1/3), formulas (19) and (20) become (6) and (7), respectively.

3. Formation of nanocomposite materials

In the present work, we focus on the optical properties of porous semiconductors and dielectrics. We briefly discuss the methods of their formation.

3.1 Electrochemical methods

Electrochemical etching of solids, leading to the growth of nanometer-sized pores and the formation of nanocrystals, has become a method of creating semiconductor media with new properties. An important parameter of such media is their porosity, the ratio of the volume of pores to the whole volume of the composite medium. The porosity p is often measured gravimetrically (by weighing the sample before and after the creation of pores, as well as after removing the porous layer). It is defined as

$$p = 1 - \frac{\rho}{\rho_0} \,, \tag{21}$$

where ρ and ρ_0 are the respective densities of the porous layer and the original material.

In addition to the porosity, important characteristics of porous layers are the sizes of pores and remaining nanocrystals, the distances between them, and their morphology. These parameters essentially determine the physical properties of porous layers. According to the classification of the International Union of Pure and Applied Chemistry (IUPAC) [33], there is a distinction between micro-, meso-, and macroporous materials. The first group includes materials with the typical sizes of pores and nanocrystals being less than 2 nm, the second includes materials with pore sizes between 2 and 50 nm, and the third includes materials with pores larger than 100 nm.

Pores are formed during various regimes of electrochemical processing (etching) of semiconductors, in which a positive potential is applied to the semiconductor and a negative potential to the electrolyte. Such anode etching is determined by the exchange of charge carriers between the semiconductor and the electrolyte and, which is extremely important, requires at least a single positive charge carrier (a hole) for the process to start. Generation of holes is nonuniform over the surface of a semiconductor monocrystal, and this forms a system of pores growing into the depth of the crystal. Thus, although the surface of a semiconductor crystal is initially uniform, it later splits the front of the electrochemical reaction into many separate microscopic domains, which are stable even at large depths.

Pore formation has been observed for Si and Ga with various types of conductivity, while for GaAs, InP, GaP, and CdSe, only in n-type samples. No pore formation was registered in more narrowband III–V binary compounds: InAs, InSb, or GaSb. The creation of holes in the near-surface area in n-type semiconductors is caused by electrolyte electrons tunneling through the space-charge domain or by the generation of electron–hole pairs due to illumination.

We note that there are still no models that can adequately describe specific electrophysical and chemical mechanisms of porous structure formation in semiconductor crystals. There is no complete clarity in understanding the origin of pore formation and the relation between the directions of their growth and the directions of semiconductor crystallographic axes. Finally, it is not understood why the sizes and shapes of etched nanometer-scale canals are stable, even as deep as dozens or hundreds of microns into the bulk of the crystals.

Porous silicon. Silicon is the basic material of modern electronics. The study of silicon-based photonic materials is therefore of large practical importance, which, in turn, attracts researchers from all over the world to investigations in this field.



Figure 2. Results of studying the PS structure with the original (110) surface orientation by means of transmission electron microscopy (a, b) and X-ray diffraction (c, d): (a) the transverse section of a macro-porous silicon layer, with the image in the ($\overline{1}12$) plane [3], (b) the image of a meso-porous silicon surface [42], (c) crystalline silicon, and (d) meso-porous silicon.

PS was first obtained by Uhlir, an American researcher, as early as 1956 [34]. But the study of the physical properties of PS was not active enough for a long period of time. Research mostly focused on the insulating properties of PS and oxidized PS [35-37]. As regards the optical properties of PS, they attracted some interest only in connection with using PS as an anti-reflection coating [38]. However, starting from 1990, when Canham, a British researcher, found a relation between the photo-luminescence of PS and the quantum-size effect in silicon nanocrystals [39], the situation changed considerably. PS and, in particular, its optical properties became the focus of numerous studies (see, e.g., review [3]).

In most cases, PS films are manufactured through the anodic electrochemical etching of monocrystalline silicon (c-Si) plates, with various values of the specific resistance and various orientations of the surface, in an alcohol solution of hydrofluoric acid. The thickness of the PS layer is determined by the etching time, while the porosity depends on the etching current density *j*, the electrolyte chemical composition, and the specific resistance of the original c-Si plate. Because etching requires holes, illumination is required in the case of n-type silicon for creating charge carriers. Typical thicknesses of PS films are between a few microns and hundreds of microns. The sizes of nanocrystals and pores depend considerably on the type and amount of impurities. As a rule, current densities up to 200 mA cm⁻² are required for forming PS. Increasing the current density allows switching the etching process from the regime of pore formation to that of electropolishing. This fact is used for preparing free (detached from any silicon substrate) PS films; for this, the current density is rapidly increased up to values above 500 mA cm^{-2} .

The study of the PS microstructure has shown that in the course of c-Si electrochemical etching, the growth of pores occurs presumably in the (100) directions (Fig. 2a, b) [41]. This is caused by the anisotropy of etching rates with respect to the crystallographic direction. This anisotropy of pore growth is clearly seen for layers on strongly doped p-type silicon $(p^{++}-Si)$ substrates or for silicon with electron-type conductivity (n-Si). In PS layers obtained on weakly doped ptype silicon (p^{-} -Si), pores are developed with less ordering. As we know from the experimental results on X-ray and electron diffraction, pore formation does not disturb the short-range order of silicon atoms, i.e., the PS layers preserve the crystalline structure of silicon [3, 40] (Fig. 2c, d). When PS is formed, the dangling chemical bonds are terminated by hydrogen; further, as a result of external effects, $Si-H_x$ bonds are replaced by $Si - O_x$ bonds.

Oxidized porous silicon. The most efficient way of oxidizing PS films is their thermal heating [43]. Oxidization in air at the temperature 950 °C for 2.5 h suffices for the full oxidization of PS [44]. This kind of processing, leading to the creation of oxidized porous silicon (OPS), allows making films that are transparent in the visible range, in contrast to PS. The results of X-ray diffraction in OPS suggest that this material is amorphous.

Porous gallium phosphide. Layers of porous GaP (PGP) are formed through the electrochemical etching of n-GaP doped by Te or S, in solutions of H_2SO_4 and HF. From the atomic-force-microscope images of PGP, the sizes of inhomogeneities (pores and nanocrystals) are between 0.05 and 1 μ m [9–11] (Fig. 3).

Porous aluminum oxide. Layers of porous aluminum oxide (PAO) are formed through the electrochemical etching of



Figure 3. Atomic-force-microscopy images of PGP surfaces with orientations (110) (a) and (111) (b) [10].

aluminum-foil substrates in various acids [45]. The resulting porous layer is a system of hexagonal oxide cells with a hollow canal at the center [46-50]. The inter-pore distance increases linearly with an increase in the bias voltage. The pore diameter is determined by the rate of aluminum oxide chemical dissolving, which depends on the electrolyte used. Depending on the acid contained in the electrolyte and its concentration, the pore diameter can vary within a broad range: it is about 0.01-0.03 µm for sulfuric acid, 0.02- $0.07 \,\mu\text{m}$ for oxalic acid, $0.05 - 0.2 \,\mu\text{m}$ for orthophosphoric acid, and $0.1-0.5 \mu m$ for tartaric acid. After a PAO layer is formed, it is separated from the substrate by dissolving the latter in a 0.05 M CuCl₂: HCl (50%) solution. The quality of PAO formation can be further improved by means of socalled 'nanoimprinting' technology, in which special pits are formed on the surface before etching, using a special microscopic press, and these pits seed the etching process [49].

3.2 Photonic-crystal structures

Photonic crystals are composite materials with periodically ordered inhomogeneities, with the period being comparable to the wavelength [51]. Propagation of light in such materials is similar to the motion of an electron in the periodic potential of a crystal. In particular, for some spectral range, the interference of waves forbids the propagation of light in some directions. By analogy with solid-state physics, we can speak about a photonic band gap (PBG) [52]. Photonic crystals can be successfully manufactured using porous semiconductors. Because porosity and refractive indices are determined by the electrochemical etching current density, structures with alternating layers of different porosity and, hence, with different refractive indices can be obtained by periodically varying the current density. This way, a onedimensional PS-based [5, 23, 53] or PGP-based [54] photonic crystal is formed. Based on PS, lateral periodic structures can be formed using the photosensitivity of the etching process and the interference pattern of two laser beams [55].

In n-type silicon, macro-porous structures can be created given by two- or three-dimensional photonic crystals with the PBG in the infrared range. For this, using photolithography, the locations where pores are to be formed are marked, and then, by means of alkali etching, pits are created, to become seeds for the pores. Macropores are formed during electrochemical etching. This way, two-dimensional photonic crystals are created with the PBG in the spectral range from 8 to $1.3 \,\mu\text{m} [56-61]$. Periodic variation of the illumination intensity, leading to the variation of the pore diameter, allows creating a three-dimensional photonic crystal [57, 58]. It is also possible to manufacture structures with broken periodicity, that is, with defects [60]. Photolithography and subsequent anisotropic etching allow creating so-called 'slit structures,' which are alternating layers of monocrystalline silicon and slits with thicknesses typically of the order of several microns [62]. PAO with hexagonally ordered pores can also be viewed as a photonic-crystal structure [49].

Meso-porous photonic-crystal structures are often created based on ordered polymer spheres [63-66] or silicon oxide spheres [67]. Porous structures can also be manufactured by intensive evaporating of a polymer solution in a volatile solvent [68].

4. Birefringence in nanostructured semiconductors and insulators

4.1 Methods of study

Refractive indices are often measured from the transmission or reflection spectra in the IR and visible ranges. A convenient way to determine refractive indices is the analysis of oscillations in transmission (reflection) spectra caused by wave interference in a film made of the material under study. Typical transmission spectra are shown in Fig. 4. In the absence of optical dispersion, refractive indices can be calculated using the simple formula

$$n = \frac{1}{2d\Delta v}, \qquad (22)$$

where *n* is the refractive index, *d* is the film thickness, and Δv is the difference in wave numbers corresponding to two neighboring maxima or minima in the spectrum. But in the presence of optical dispersion, calculation using Eqn (22) leads to a considerable over-estimation of refractive indices (see Ref. [23] for a typical example and Ref. [69] for a discussion). Therefore, for the correct measurement of the refractive index, the order of the interference extremum must be taken into account. Knowing this order, we can easily find the refractive index as

$$n = \frac{m\lambda}{2d} \quad \text{(for a maximum)},$$

$$n = \frac{(m+1/2)\lambda}{2d} \quad \text{(for a minimum)},$$
(23)



Figure 4. Transmission spectra of a PS birefringent film in the visible and near-IR ranges for incident radiation polarization parallel and orthogonal to the optical axis [26].

where *m* is the order of the interference maximum and λ is the corresponding wavelength. In this case, the following procedure of finding the exact value of *n* is used. First, formula (22) is applied in the IR range, where the dispersion is minimal and, hence, the error in the refractive index calculated from Eqn (22) is also minimal, and preliminary values of refractive indices *n'* are found. Further, the number of the interference peak is found as

$$m_{\rm o,e} = \left[\frac{2dn'_{\rm o,e}}{\lambda}\right],\tag{24}$$

where the square brackets denote the integer part of the number and the 'o' and 'e' indices respectively relate to the ordinary and extraordinary waves. After finding the interference order for the largest wavelength possible, we can set all interference extrema, up to the visible range, in correspondence with their orders of interference and easily calculate the refractive indices for the ordinary and extraordinary waves according to formulas (23) [26].

To measure the birefringence, the sample under study is often placed into the waist of a focused light beam and oriented such that its optical axis is at 45° with respect to the polarization plane of the radiation [61, 70]. After the sample, an analyzer is placed, which transmits radiation polarized parallel or orthogonal to the incident radiation. Then the intensity *T* of the transmitted light scales as

$$T \sim 1 \pm \cos\left(\frac{2\pi}{\lambda} \Delta nd\right),$$
 (25)

where $\Delta n = |n_o - n_c|$ is the birefringence, n_o and n_e are the respective refractive indices for the ordinary and extraordinary waves, d is the sample thickness, and the '+' sign corresponds to parallel polarizers and the '-' sign to orthogonal polarizers. A similar scheme is used for dichroism measurements [26].

4.2 Porous silicon

4.2.1 Birefringence in porous silicon. Silicon has a high-symmetry diamond-type lattice (with the *m*3*m* symmetry) and, as a result, a negligibly small birefringence. For crystal-line silicon, the largest birefringence is achieved for a light wave propagating along the [110] crystallographic direction and is $\Delta n = n_{(110)} - n_{(100)} = 5 \times 10^{-6}$ [72].

During electrochemical etching of strongly doped crystalline silicon with hole-type conductivity (p^{++} -Si), pores mostly grow along the $\langle 100 \rangle$ crystalline axis (Fig. 5), and therefore the symmetry of porous silicon is reduced compared to crystalline silicon. This is manifested in the so-called 'form



Figure 5. Schematic diagram of pores in PS obtained on substrates with (100) and (110) surface orientations.

birefringence' [2]. For PS layers on substrates with the (100) surface orientation, the optical axis is along the [100] crystallographic direction and birefringence becomes noticeable only when incident radiation is tilted with respect to the normal [22, 73]. In the case of substrates with low surface symmetries, for instance (110) and (211) [42, 70, 74], the layers of meso-porous silicon have the properties of a uniaxial crystal with the optical axis parallel to the surface.

It is known that birefringence can be caused by tensions in many materials. However, the X-ray analysis of PS nanocrystals shows that PS preserves the diamond-type structure. Estimates based on elasto-optical constants show that birefringence caused by deformations of the crystal lattice is negligible in this case [75], i.e., each silicon nanocrystal is optically isotropic. Therefore, the observed effect is only due to the anisotropy of pores and nanocrystals.

PS layers formed by the above method have the properties of a negative uniaxial crystal (Fig. 6). The optical axis of a birefringent PS crystal manufactured on a p⁺⁺-Si substrate with the (110) surface orientation is parallel to the surface plane and coincides with the crystallographic direction [001]. Indeed, when the sample is rotated around the [110] axis, the refractive index is practically constant for the radiation polarized parallel to this axis, as it indeed should be for an ordinary wave. On the contrary, for radiation polarized in the plane of the [001] axis, the refractive index depends on the angle of incidence on the sample. The dependence of the extraordinary-wave refractive index on the angle θ between the optical axis and the wavevector direction is

$$n_{\rm e}(\theta) = \frac{n_{\rm e}n_{\rm o}}{\sqrt{n_{\rm e}^2\cos^2\theta + n_{\rm o}^2\sin^2\theta}},$$
(26)

where θ is related to the angle of radiation incidence on the sample θ_0 as

$$\cos\theta = \frac{1}{n_{\rm e}(\theta)}\sin\theta_0.$$
⁽²⁷⁾

As can be seen from Fig. 6a, there is indeed a good agreement between the experimental data and the results of calculations with Eqns (26) and (27). The difference between the measured refractive index and the calculated one is probably caused by the divergence of the IR radiation beam at a distance comparable to the sample size and, possibly, by the inhomogeneity of the sample itself.

Birefringence considerably depends on porosity, which, in particular, is determined by the etching current density. As can be seen from Fig. 7, an increase in porosity is accompanied by a decrease in the effective refractive indices for ordinary and extraordinary waves, as well as an increase in the birefringence $\Delta n = n_o - n_e$, which for highly porous layers can be as high as 0.24 in the IR range, the mean value of the refractive index being $(n_o + n_e)/2 = 1.3$ [76]. We note that this value of Δn exceeds the analogous parameter for Iceland spar, a highly birefringent material ($\Delta n = 0.15$).

The type of birefringence and the direction of the optical axis depend on the morphology of the porous layer, which is in turn determined by the amount of doping of the initial crystalline silicon, the orientation of its surface, and the etching current density. If crystalline silicon with the same surface orientation (110) but lower doping (p⁺-Si, 20–100 m Ω cm) is used, then the optical axis coincides with the crystallographic direction [110], although it still lies in the



Figure 6. Dependences of the refractive indices in the IR range on the radiation angle of incidence on a film (a, b) and on the angle between the optical axis and the wavevector direction in the layer (c, d) for a PS obtained on substrates with orientations (110) (a, c) and (100) (b, d). The symbols \Box and \blacksquare and solid lines denote an ordinary wave, and the symbols \circ and \bullet and dashed lines denote an extraordinary wave.



Figure 7. Dependences of (a) refractive indices for ordinary and extraordinary waves (\bigcirc and \bullet , respectively), (b) birefringence (\blacksquare) and porosity (\triangle) on the etching current density *j*.

plane of the surface. Such a structure also exhibits the properties of a negative birefringent crystal. It is interesting

to note that here, in contrast to the p^{++} -Si case, an increase in the etching current density and, hence, an increase in the porosity, leads to a decrease in the value of birefringence [27]. This is because pores in PS obtained from p^+ -Si are less ordered.

In PS layers obtained on substrates with the (100) orientation, pores are normal to the surface (see Fig. 5). Therefore, birefringence in such layers is of the positive type. Refractive indices for the ordinary and extraordinary waves in PS formed on a (100)-oriented substrate with the specific resistance 15 m Ω cm are shown in Fig. 6c as functions of the radiation angle of incidence on the sample. Indeed, this PS film exhibits the properties of a positive crystal, in agreement with the predictions of the theory [2, 22].

It is also worth noting that the birefringence value can be controlled by filling the pores with insulating liquids. In particular, this idea was used for detecting the condensation of liquids in pores [71].

4.2.2 Dispersion of optical parameters and modeling of optical anisotropy in porous silicon. Using the generalized Bruggeman model in (20), we can calculate refractive indices for PS. In this case, PS is considered an ensemble of ellipsoids of rotation with parallel axes; the direction of the rotation axes then coincides with the optical axis direction. This model is chosen according to the shapes of silicon nanocrystals, which were observed using electron and atomic-force microscopy (see Ref. [42]). The dielectric permittivity of crystalline silicon was calculated using the known dependence of the refractive index on the wavelength [77]. The imaginary part of the dielectric permittivity for crystalline silicon was approximated from the data in Ref. [78].

In such calculations, the depolarization factor and porosity play the role of fitting parameters. It turns out that



Figure 8. Depolarization factors (a) (symbols \bullet and \circ for L_{\parallel} and L_{\perp} , respectively) and the aspect ratios of the ellipsoids of rotation (b) calculated for the generalized Bruggeman model as functions of porosity. The orientation of the ellipsoid of rotation is shown schematically.

the porosity values measured gravimetrically and determined from the refractive-index analysis differ by not more than the measurement accuracy. The depolarization factors and the spheroid aspect ratios obtained from the analysis of refractive indices in the IR range (see Fig. 7) are shown in Fig. 8.

It is very important to study the dependence of refractive indices on the wavelength. These data are useful for testing the validity of the effective-medium model for the description of PS birefringence, as well as for the study of nonlinear phase matching in PS layers [80, 81].

Figure 9 shows the wavelength dependencies of n_0 and n_e for PS films with the porosity about 60% and 74% obtained through the etching of (110)-oriented p^{++} -Si substrates. Normal dispersion of refractive indices is well pronounced. As follows from comparing the experimental data with the results of calculations, generalized Bruggeman model (20) used here is a good approximation for describing the optical properties of samples with medium porosity. But for higher porosities, the Bruggeman effective-medium model does not describe the PS properties so well (Fig. 9b). In addition, the differences between the measured and calculated values of refractive indices become more pronounced in the long-wave and short-wave ranges. In the first case, this is because calculations do not take absorption by free carriers into account and in the second case because the wavelength approaches the size of a nanocrystal and, hence, the static effective-medium theory loses its validity. A more exact analysis requires including the so-called 'dynamic depolarization,' i.e., the size of nanocrystals and the finite time of wave propagation through them, as well as radiation damping [82-84]. Taking the dynamic depolarization into account in the framework of the effective-medium model



Figure 9. Refractive index dispersion in PS grown on a p^{++} -Si substrate with the orientation (110): (a) porosity 60% [79], (b) porosity 74% [26]. Ordinary and extraordinary refractive indices measured in experiment are shown by \Box and \circ symbols, respectively. Solid lines show the results of calculations in accordance with generalized Bruggeman model (20).

provides a better approximation of experimentally obtained refractive indices [85].

4.2.3 Dichroism in porous silicon. Measurements of the absorption coefficient in the range 0.54-0.82 µm for PS films manufactured on p++-Si substrates with the orientation (110) have shown that absorption is higher for radiation polarized along the $[1\overline{10}]$ crystallographic direction than for radiation polarized along [001] [86]. As the wavelength decreases, the value of dichroism, $\Delta \kappa = \text{Im} n_0 - \text{Im} n_e$, increases (Fig. 10) [26, 86]. This fact is also well described by the above model (compare the experimental data and the calculation results for wavelengths above 0.6 µm). But for wavelengths below 0.52 μ m, $\Delta \kappa$ decreases as the wavelength increases. This nonmonotonic dependence on the wavelength is apparently due to the inapplicability of the effectivemedium static approximation in some ranges and to a partial depolarization of radiation transmitted through the PS film, caused by scattering by nanoparticles. Indeed, the wavelength in silicon corresponding to the 0.5 µm wavelength in the vacuum is only 0.15 μ m, which is comparable to the sizes of nanocrystals and pores in meso-porous silicon (0.02-0.05 µm).

Absorption by $Si - H_x$ bands in the IR range also exhibits noticeable dichroism caused by the form anisotropy of pores and nanocrystals. This fact allows reaching conclusions about the fine structure of the vibrational modes of $Si - H_x$ bonds and about the distribution of Si - H groups, such as monohydrides, monohydride dimers and dihydrides, on the surface of nanocrystals [86, 87].



Figure 10. Dispersion of dichroism in (110) PS with the porosity 74% [26]. Solid line shows the result of calculations according to Bruggeman generalized model (20).

4.3 Oxidized porous silicon

4.3.1 Birefringence of oxidized porous silicon. To obtain transparent OPS layers of high optical quality, the effect of various regimes of thermal oxidization on the optical properties of PS was studied.

When a PS film is heated to $100 \,^{\circ}$ C, its refractive index is practically constant (the water removed due to the heating is rather quickly absorbed from the surrounding atmosphere). Heating in the air to $350 \,^{\circ}$ C leads to the desorption of hydrogen from the inner PS surface and to the oxidization of the surface of nanocrystals, which, in turn, leads to a decrease in the refractive indices. Further oxidization of the samples at the temperature $600 \,^{\circ}$ C allows reducing the refractive index, but the samples remain nontransparent in the visible range. Transparency of the samples can be achieved by heating them at $950 \,^{\circ}$ C for 2.5 h.

Refractive-index anisotropy of OPS films in the visible and near-IR ranges was determined from the spectra of their transmission between crossed and parallel polarizers (see Section 4.1). A typical spectrum is shown in Fig. 11a. As the anisotropy of the films increases, interference maxima and minima in their spectra are shifted towards the IR range. Analysis of the spectra enabled the measurement of birefringence in OPS samples (Fig. 11b). It can be seen that birefringence was still present after thermal oxidization, although its value decreased by an order of magnitude. We recall that according to the results of structure measurements, OPS is an amorphous material, and the observed optical anisotropy is the anisotropy of form. Birefringence of OPS increases with the increase in the etching current density, i.e., with the increase in the porosity of the original PS samples. The maximal value of the OPS birefringence is achieved for the sample with the largest porosity and is $\Delta n = 0.025$, which is more than twice as large as the anisotropy of crystalline quartz [89, 90].

We note that in contrast to the PS case, the OPS birefringence dependence on the current density is essentially nonlinear (compare Figs 7 and 11b). This is because the OPS porosity depends on the etching current more strongly than the PS porosity. This can probably be explained by the fact that oxidization of low-porosity samples of PS leads to the 'closing' of pores. On the contrary, in samples with high



Figure 11. (a) Transmission spectrum of oxidized porous silicon (950 °C, 2.5 h) placed between crossed polarizers normalized to the transmission spectrum of the same material placed between parallel polarizers. The values of birefringence (Δn) and the phase difference ($\Delta \phi$) between ordinary and extraordinary waves after their propagation through the layer are shown on the plot. (b) Birefringence of oxidized porous silicon layers plotted versus the current density [89, 90].

porosity, the pores persist after oxidization, and their ordering causes form birefringence.

4.3.2 Optical dispersion in oxidized porous silicon. It follows from Fig. 11a that the value of Δn in OPS increases as the wavelength decreases. This result is related to the normal dispersion of silicon oxide, which constitutes the OPS nanoclusters. More detailed information about the refractive-index dispersion can be obtained by analyzing transmission spectra for polarized IR radiation. The dispersion dependences of the refractive indices for ordinary and extraordinary waves in the IR range are shown in Fig. 12.

The obtained dispersion dependences were analyzed in a similar way, using the generalized Bruggeman model. Both pores and silicon-oxide nanoclusters formed through the oxidization of silicon nanocrystals were assumed to have the shapes of squashed spheroids. We can therefore expect the OPS layer formed from PS with the orientation (110) to exhibit the properties of a negative uniaxial crystal, its optical axis coinciding with the [001] direction. Indeed, when the radiation was polarized along the [001] crystallographic axis of the original crystalline-silicon plate, refractive indices were smaller than when the radiation was polarized along the [110] crystallographic axis, which does not contradict the above assumption.



Figure 12. Measured and calculated refractive-index dispersion dependences for ordinary (\bigcirc and the dashed line) and extraordinary (\blacksquare and the solid line) waves in an OPS sample. The inset shows the dependence of birefringence on the wavelength, calculated in the Bruggeman model (solid line) and measured experimentally (\blacktriangle) [89].

The dispersion dependences of OPS were extrapolated in accordance with the modified Bruggeman formula (20) using the refractive-index dispersion of fused silica [77]. As the extrapolation fitting parameters, the porosity p and depolarization factors L_{\parallel} and L_{\perp} were used. A satisfactory agreement between the calculated refractive-index dispersion for ordinary and extraordinary waves and the experimental data was obtained at p = 0.3, $L_{\perp} = 0.210$, and $L_{\parallel} = 0.58$ (see Fig. 12).

4.4 Porous gallium phosphide

The ordering of pores in PGP also leads to optical anisotropy. Indeed, Ref. [88] reported a birefringence of $\Delta n = 0.24$ achieved in a PGP layer formed on a crystalline GaP substrate with the surface orientation (111). In this case, the pores are normal to the surface, and the PGP layer has the properties of a positive crystal with the optical axis parallel to the [111] crystallographic direction.

Similarly to the PS case, if GaP porous layers are formed on low-symmetry surfaces like (110), then the optical axis of the porous optically anisotropic material is in the plane of the surface.

It follows from IR reflection measurements that a PGP layer formed on a substrate with the (110) orientation is indeed birefringent. Figure 13b shows the PGP refractive indices and their dispersion calculated from reflection spectra with interference peaks (Fig. 13a). We can see that the refractive index is maximal for polarization along the [001] direction, and is minimal for the [110] direction. Thus, the refractive-index anisotropy in the studied PGP layer is $\Delta n = 0.04$ [11].

We note that up to the present time, no cubic crystals with high optical nonlinearity, such as GaP, GaAs, and InP, have been used in nonlinear optics, because these crystals are optically isotropic. The discovery that a PGP layer on a (110)-oriented surface exhibits birefringence with the optical axes parallel to the surface opens new perspectives for GaP applications in nonlinear optics. In particular, it becomes possible to achieve exact phase matching for frequencyconversion processes under normal incidence of a pump (the 90° phase matching). This regime of phase matching is attractive because, first, it is less sensitive to the divergence of the pump and the converted radiation, which reduces the



Figure 13. Reflection spectrum (a) and refractive-index dispersion (b) for light polarized along the $[1\overline{10}]$ (solid line and \bigcirc) and [001] (dashed line and \blacksquare) directions [11].

conversion efficiency and, second, it allows using beams with smaller diameters and materials with larger thicknesses [91].

4.5 Porous aluminum oxide

For PAO layers obtained under certain conditions, the average inter-pore distance is much shorter than the wavelength in the visible range. If the sample is considered a homogeneous optical medium with an effective refractive index, then, because the pores in PAO are normal to the film surface, form birefringence should be expected: there should be a difference between refractive indices for light polarized along the pores (extraordinary wave) and orthogonally to the pores (ordinary wave). In this case, the PAO layer must exhibit the properties of a positive uniaxial crystal ($\Delta n = n_e - n_0 > 0$) [2, 45, 92–95].

To determine the optical anisotropy of PAO, transmission spectra of PAO films have been measured, with the films placed between two crossed or parallel polarizers and the varied incidence angle θ of the probe radiation. Figure 14a – e shows the transmission spectra of a PAO film placed between crossed polarizers normalized to the transmission spectra of the same film placed between parallel polarizers, I_{\perp}/I_{\parallel} , at various angles of incidence of the probe radiation, within the spectral range 0.5–0.95 µm. The structure period for this sample is about 0.09 µm and the pore diameter is about 0.03 µm.

From the positions of maxima and minima in the transmission spectra at various incidence angles θ , the angular dependence of the refractive-index anisotropy Δn for the PAO sample under study was calculated. The dependence is shown in Fig. 14f. It can be seen that as the probe radiation angle of incidence increases, the refractive-index difference for the ordinary and extraordinary waves increases from zero to $\Delta n = 0.018$ at $\theta = 70^{\circ}$. This confirms the assumption that the optical axis is directed normally to the surface.

For a uniaxial crystal, the angular dependence of the refractive-index anisotropy is given by formula (26), which was used for fitting the experimental dependence of the birefringence of a PAO layer on the radiation incidence angle (Fig. 14f). The refractive index principal values corresponding to the best fit are $n_0 = 1.59$ and $n_e = 1.65$. Thus, the refractive-index anisotropy for the PAO sample under study is $\Delta n = 0.06$. The obtained values satisfy the



Figure 14. (a-e) Transmission spectra of a PAO sample placed between crossed polarizers normalized to transmission spectra of the same sample placed between parallel polarizers, for various angles of incidence of radiation. (f) Dependence of the PAO birefringence on the radiation incidence angle [92].

generalized Bruggeman model with the pores assumed to have cylindrical shapes and the porosity 16% [92, 95].

5. Photonic crystals based on porous semiconductors

Optically inhomogeneous materials are, in a sense, the opposite of materials described in the framework of the effective-medium approximation. By optically inhomogeneous materials, we refer to composite materials in which either the sizes of the components or the distances between them are comparable to the optical wavelength. Such systems include, on the one hand, disordered media, causing considerable scattering and, on the other hand, materials where domains with different refractive indices alternate in a regular manner, for instance, periodically (photonic crystals). A common feature of such systems is the necessity to take the interference of scattered (in the first case) or reflected (in the second case) waves into account. In this section, we consider the linear optical properties of one- and twodimensional photonic-crystal structures formed from porous semiconductors and insulators.

5.1 One-dimensional photonic-crystal structures based on porous silicon and oxidized porous silicon

5.1.1 Reflection and transmission spectra. One-dimensional photonic-crystal structures based on PS were obtained by

periodically varying the current density in the course of electrochemical etching of crystalline silicon. The main way of characterizing the obtained multilayer structures is to measure their reflection or transmission spectra. The shape of such a spectrum can be calculated, e.g., using the matrix method [2]. The position of PBG in such systems is determined by the thicknesses and effective refractive indices of PS layers (i.e., eventually, by their porosity), as can be seen in Fig. 15a-c. In a multilayered system formed by alternating layers with the respective effective refractive indices n_1 and n_2 and thicknesses d_1 and d_2 , the condition for the existence of a first-order PBG centered at a wavelength λ is

$$n_1 d_1 + n_2 d_2 = \frac{\lambda}{2} \,. \tag{28}$$

We note that the reflection coefficient, as well as the steepness of the borders for the resulting PBG, is determined by the number of periods in the multilayer structure (Fig. 15d-f). Periodicity breaking is analogous to a defect in a solid and leads to the appearance of narrow transmission bands in the spectra.

Using birefringent PS layers, one can form a onedimensional photonic crystal with the positions of photonic band-gaps depending on polarization (Fig. 16) [80, 96-98]. Similar multi-dimensional structures can be useful for manufacturing dichroic mirrors and filters.

The above features restricting the applications of PS (nontransparency in the visible range and slow oxidization in the air) are apparently also valid for multi-layer structures manufactured from it. Similarly to the case of PS films, a possible solution is oxidization of such structures [99]. Transmission spectra of the original structure formed by alternating layers of PS with different porosities and the structure prepared from it by heating at 950 °C for 2 h are shown in Fig. 17. Because the OPS refractive indices are smaller than the PS refractive indices, the PBG position is shifted towards the blue side of the spectrum (from 3000 to 4500 cm^{-1}). The structure undergoes no noticeable reduction in quality: transmission in the PBG remains extremely low and the spectrum maintains transmission resonances outside the PBG.

5.1.2 Dispersion properties. Due to the periodicity, photoniccrystal structures have special dispersion dependences. As a result, there is an interesting possibility of using them for controlling the propagation of ultra-short pulses, providing the absence of their spreading or even their compression.

For a one-dimensional infinite structure, the electric and magnetic fields can have the form of Bloch functions [12]. A multilayer structure consisting of a finite number of layers can also be characterized by the effective refractive index $n_{\text{eff}} = Kc/\lambda$ (where K is the effective wavevector determined by the dispersion of the structure as a whole and c is the speed of light in the vacuum) and the first-order dispersion parameter $u = \partial \omega / \partial K$ and the second-order one $k_2 =$ $\partial^2 K / \partial \omega^2$. These parameters have been calculated for a real structure consisting of 12 alternating pairs of PS layers of low and high porosity; the reflection spectrum of this structure is shown in Fig. 18a. The measured values of the refractive indices and layer thicknesses were corrected by fitting of the real spectrum by the calculated one and were found to be $n_1 = 1.42$, $d_1 = 110$ nm, $n_2 = 1.22$, and $d_2 = 127$ nm. For



Figure 15. (a-c) Reflection spectra of PS-based multi-layer structures with various periods (the layer thickness increases from (a) to (c) [80]. (d-f) Reflection spectra for PS-based multi-layer structures with various numbers of periods: 3 (d), 6 (e), 12 (f).



Figure 16. Reflection spectra of a multi-layer structure based on anisotropic porous silicon [80].

determining the effective refractive index, the field transmission coefficient t of a multilayer structure of thickness L was calculated using the matrix method [2]. (The intensity transmission coefficient is related to t as $T = |t|^2$.) Then, arg $t = \Delta \phi$, where $\Delta \phi$ is the phase difference for waves incident on the structure and transmitted through it. Hence, we can find the real and imaginary parts of the effective refractive index as

$$\operatorname{Re} n_{\rm eff} = \frac{\Delta \phi \lambda}{2\pi L} \,, \tag{29}$$

$$\operatorname{Im} n_{\rm eff} = -\frac{\lambda}{2\pi L} \ln |t| \,. \tag{30}$$



Figure 17. Transmission spectra of PS-based multi-layer structures: the original one (solid line) and the spectrum obtained by its thermal oxidization (dashed line).

The dependences of the effective refractive index on the wavelength are shown in Fig. 18b [100]. We note that as the wavelength increases, n_{eff} tends to the refractive index of a laminar structure [Eqn (12)].

The possibility of controlling the dispersion of a multilayer structure gives us more freedom in controlling the parameters of ultra-short laser pulses. In particular, if the wavelength of laser radiation is near the edge of the photonic band gap, the group velocity of the laser pulse can be made very small, which leads to an increase in the local field (Fig. 18c) and, hence, to the enhancement of many nonlinear-optical processes. We can calculate the k_2 spectrum for



Figure 18. (a) Reflection spectra of a PS-based multi-layer structure; (b) the spectra of the real and imaginary parts of the effective refractive index for such a structure, the dashed line corresponding to the refractive index of a laminar structure [Eqn (12)]; (c) the value of $u = \partial \omega / \partial K$ normalized to the speed of light; (d) the value of k_2 in a one-dimensional PS-based photonic crystal [100].

such structures (Fig. 18d). The obtained high values of k_2 indicate that the phase control and compression of such a pulse can be performed at comparably small distances, which allows creating PS-based compact optical compressors and other devices for phase-modulated pulses [100].

5.2 Two- and three-dimensional photonic-crystal structures 5.2.1 Macro-porous silicon. As we have already mentioned, two-and three-dimensional photonic crystals based on silicon can be created. We note that the shape of reflection (transmission) spectrum of such structures depends on the crystallographic direction of the photonic crystal. In particular, the creation of a high-quality three-dimensional photonic crystal with a cubic structure and the period 2 µm was reported in [58]. Although a complete PBG does not appear in such a structure, the propagation of light there is prohibited for a broad range of frequencies and wavevector directions. The reflection spectrum of such a photonic crystal contains a broad range with the reflection coefficient close to unity; the results of experiments are in good agreement with the calculation. Similar structures can be very useful for the engineering of laser media.

Birefringence in the IR range. Due to its high ordering of pores and silicon elements, a photonic crystal should manifest the properties of a highly birefringent medium. Indeed, in a

two-dimensional photonic crystal with the pore radius 0.644 µm and inter-pore distance 1.5 µm, the birefringence is 0.366. The largest birefringence should be achieved in a structure formed by parallel silicon layers separated by empty spaces (slits) [62]. Indeed, a large value of birefringence in slit structures was reported in [102]. Detailed measurements in a broad frequency range (up to 2000 µm) carried out in Ref. [103] allowed determining the values of refractive indices and birefringence; the latter was found to be $\Delta n = 0.77$, in full agreement with the above model.

Elements of light control based on photonic-crystal structures. Together with the development of novel laser media, one of the most promising applications of photonic-crystal structures is the development of optical devices for the control of light. Here, a principal role is played by the possibility of generating carriers in a semiconductor through its illumination. In slit structures, this leads to an increase in absorption by three orders of magnitude [103]. As shown in Ref. [101], variation in the refractive index due to the generation of charge carriers under a femtosecond laser pulse can lead to a shift in the PBG position; the duration of this process is determined by the life-time of nonequilibrium carriers. Much hope lies also in experiments on filling the slits with liquid crystals, which will also provide control over the birefringence of such a composite system [104].

5.2.2 Porous aluminum oxide. The technology of PAO production allows the pore sizes and the inter-pore distances to be varied within a large range, from dozens to hundreds of nanometers. This also leads to a variation in the optical properties of such structures. Layered PAOs with periods close to the visible-range wavelength exhibit photonic-crystal properties.

This is confirmed by the transmission spectra of PAO films, which demonstrate noticeable changes under variation in the radiation angle of incidence [92, 105-107]. At incidence angles of 40° and larger, a dramatic reduction in the transmission coefficient in the $0.5-0.7 \,\mu m$ range is observed, which is well explained by the existence of a PBG in PAO. According to the results of structure studies, pores in a PAO layer are oriented normally to its surface. Therefore, a PAO layer does not have periodicity along the normal to the surface, while in any other direction the refractive index changes periodically on a mesoscopic scale. Correspondingly, the photonic band gap is absent for radiation that is normally incident on a PAO film. If a PAO film is rotated around an axis parallel to its surface, a photonic band gap appears in the transmission spectrum, shifting toward larger wavelengths with the increase in the angle of incidence. We note that the band gap appears for wavelengths comparable to the period of the refractive-index variation. As the incidence angle increases, the changes in the transmission coefficient in this spectral range become more noticeable, which is apparently because the wavevector component parallel to the pores decreases for the s-polarized light used here. PAO is of great interest as a possible matrix for various organic and inorganic compounds to be embedded into its pores. In particular, CdSe can be embedded into PAO pores [107], such that a spatially periodic source of light is formed. Due to the photoniccrystal properties of this structure, this opens new possibilities for the formation of laser media. This structure can also be used for nonlinear transformations of light, for instance, harmonic generation.

6. Disordered optically inhomogeneous systems based on porous semiconductors

6.1 Localization effects in the scattering of light

The scattering of light is a statistical process in which both the amplitude and the phase of the incident wave are subject to random changes. For an ensemble of scatterers, an important parameter is the average free path l, the average distance a photon travels between consecutive acts of scattering. When the scattering by different scatterers is independent, i.e., when the density of scatterers ρ is sufficiently low, the average free path is related to the density and to the scattering cross section σ as

$$l = \frac{1}{\rho\sigma} \,. \tag{31}$$

For Rayleigh scattering by spheres with a diameter a and filling factor f, the free path is [108]

$$l = \frac{9}{2f} \left(\frac{\lambda}{2\pi}\right)^4 \frac{1}{a^3} \frac{1}{\left(\varepsilon_2 - \varepsilon_1\right)^2} \,. \tag{32}$$

For a sufficiently large number of scatterers, we can use the approach based on the energy transfer in the scattering medium. The interference of scattered waves is ignored in this model. Then the energy density U of the scattered waves satisfies the diffusion equation [108]

$$\frac{\partial U}{\partial t} - D \frac{\partial^2 U}{\partial^2 z} = I_0 \delta(z - z_d) - \frac{1}{\tau} U.$$
(33)

This equation takes into account that a plane wave incident on a medium becomes almost completely scattered after traveling the distance $z_d \sim l$. Therefore, a plane wave is replaced in Eqn (33) by a diffuse light source with the intensity I_0 placed in the sample at the depth z_d . This equation also takes absorption into account (τ is the absorption time). Equation (33) is valid under the condition that the inequality $\lambda/l \ll 1$ holds. An increase in the number of scatterers ($\lambda/l < 1$) leads to slowing down the diffusion; in this case, we can speak of a weak localization of light. Finally, when $\lambda/l \sim 1$, diffusion of light is stopped, and light is scattered back. In this case, we speak of the Anderson localization of light.

In electron systems, the transport properties and their dependence on the crystal-lattice disordering are well studied. The effect of carrier localization was theoretically predicted by Anderson in 1958 [109, 110] and was observed experimentally in amorphous semiconductors and metal films [111]. Because the localization effect is based on interference, it occurs for all wave processes, including the propagation of light [112–114]. The transition from diffuse propagation to localization is recognized using the Ioffe–Regel criterion, which was derived for the motion of electrons in strongly doped semiconductors [115],

$$kl \lesssim 1$$
, (34)

where, in the case of light waves, $k = 2\pi n/\lambda$ is the wavevector in matter. This condition can be satisfied for strong scattering, i.e., at a large contrast of dielectric permittivities, which is the case, for instance, in porous semiconductors [116]. At first sight, materials with negative dielectric constants (metals) seem to be most attractive for observing the Anderson localization, because they provide huge cross section values for resonance scattering and hence small values of *l*. But strong absorption suppresses the Anderson localization and hinders the experimental detection of the signal. Good candidates for light localization are media containing semiconductor particles with a high refractive index and transparent within a broad wavelength range.

Due to the practical difficulties in creating three-dimensional random media with high scattering efficiency, the experimental observation of strong localization for electromagnetic waves is difficult. There are only few papers where localization of electromagnetic waves is considered. In Ref. [117], localization of microwave radiation in a suspension of aluminum and teflon spheres was studied. The Anderson localization of near-IR light in GaAs powders was mentioned in connection with the analysis of light distribution in a scattering cone ('curving' of the peak) and the dependence of the transmitted intensity on the layer thickness [118]. At the same time, it was shown that the results in Ref. [118] could be explained by taking the absorption of light in the medium into account [119]. The ambiguity of the obtained results makes one turn to different materials and methods for registering the localization of light.

6.2 Light scattering in porous gallium phosphide

Porous GaP is characterized by a high refractive index (3.1 at the wavelength 1.2 μ m and 3.46 at the wavelength 0.6 μ m [120]), transparency in the visible range (for waves longer than 0.55 μ m), and one of the highest values of the quadratic dipole susceptibility $\chi^{(2)}$ among inorganic materials, 0.2 nm V⁻¹ [122]. As was already mentioned, pores and nanocrystals in PGP have sizes of hundreds of nanometers. All this makes PGP one of the most attractive materials for the study of scattering and localization of light.

The samples of PGP have considerable scattering in the visible range, which is confirmed by the scattering spectra shown in Fig. 19. The observed dependence of the scattered light intensity on the wavelength has the form $I_{\text{scat}}(\lambda) \sim \lambda^{-\alpha}$, where $\alpha = 2.5$ and 2.8 for different samples. For wavelengths less than 0.55 µm, deviations from these dependences are observed, caused by the absorption in GaP. The obtained dependences $I_{\text{scat}}(\lambda)$ indicate a non-Rayleigh type of scattering.



Figure 19. Scattering spectra of PGP samples. Thin dashed and dotted lines show the dependences $I_{\text{scat}} \sim \lambda^{-\alpha}$ for $\alpha = 2.5$ and 2.8, respectively [11].

In Ref. [121], the curving of the backscattering peak for porous GaP in the absence of absorption was caused by the beginning of the Anderson localization. The dynamics of light scattering in PGP layers were studied using the optical heterodyne scheme based on the Michelson scanning interferometer and a femtosecond-pulsed laser system.

Optical heterodyne method. This method allows registering deviations from the usual diffusion transport of photons and to quantitatively distinguish between elastic scattering and absorption processes [123]. The optical heterodyne method is based on the same principles as the Fourier spectroscopy, where the autocorrelation function of the radiation is measured with the help of a scanning Michelson interferometer with an oscillating mirror, and the radiation spectrum is found by means of the Fourier transformation. A photodetector scans a time-averaged intensity (where the averaging time is determined by the response time of the photodetector) of the resulting light wave,

$$I(t) = I_{\rm ref} + I_{\rm probe} + C(\tau) + C^*(\tau), \qquad (35)$$

where I_{ref} and I_{probe} are the intensities of the reference wave and the wave reflected from the sample, which describe the background contribution (constant in time) to the heterodyne signal. The last two terms, $C(\tau)$ and $C^*(\tau)$, are in fact the cross-correlation functions for waves propagating in different arms of the interferometer, and τ is the time delay determined by the position of the moving mirror in the interferometer.

Determination of the parameters of light scattering in PGP. The results of measuring the I(t) function for samples of different porosities are shown in Fig. 20a. It follows that the signal contains a high-frequency component (see the inset in Fig. 20a). The oscillation frequency is determined by the speed v of the mirror motion and is $v = 2v/\lambda$. On the other hand, the interval between the two maxima corresponds to a single optical cycle duration (for 1.25 µm, which is the wavelength of a Cr: forsterite laser, the optical cycle duration is 4.1 fs), which provides the relation between the time scale t of the signal registration and the delay time τ of the scattered light pulse.

As can be seen from Fig. 20a, the function $C(\tau)$ takes nonzero values within a considerable range of time, which much exceeds the laser pulse duration (50 fs). As the porosity increases, there is also an increase in the correlation time between the probe and scattered pulses, i.e., the time at which the cross-correlation function is nonzero.

We use the Fourier transformation to select the signal at a frequency v and plot its power P as a function of the time delay τ (Fig. 20b). For a sample with 12% porosity, we can easily see peaks corresponding to the reflection from the back boundary between porous and crystalline GaP. For samples with higher porosity, where scattering is stronger, no such peaks are observed. Small frequent peaks in the $P(\tau)$ dependence correspond to speckles.

When the heterodyne signal of light backscattered by a strongly scattering medium is measured as a function of the time delay, three ranges can be observed in the dependence [125]. The first is an intense front caused by the scattering at the boundary; its length is comparable to the duration of the probe femtosecond pulse. The second, the fast-decaying part, corresponds to the transition between the regimes of single scattering and multiple scattering. The third is a long exponential 'tail' caused by multiple scattering in the medium. The rate of the exponential is determined by the



Figure 20. (a) Signals I(t) observed in the optical heterodyne scheme for samples of different porosities. The inset shows the high-frequency component of I(t) at the frequency $v = 2v/\lambda$. (b) Time dependence of the signal power at the frequency $v = 2v/\lambda$ for PGP samples (solid line for p = 12%, dashed line for p = 55%). (c) Dependence of the free path on the porosity [124].

lifetime of a photon inside the sample. In the diffusion approximation, the exponential decay for a medium without absorption is [125]

$$P(t) \propto \exp\left(-\frac{t}{\tau_0}\right) = \exp\left(-\frac{\pi^2}{L^2}Dt\right),$$
 (36)

where L is the sample thickness and D is the diffusion coefficient for the photons. The obtained values of D allow estimating the average free path l for the photons [116],

$$l = \frac{3D}{v} \approx \frac{3Dn_{\rm eff}}{c} \,. \tag{37}$$

Here, the energy transfer rate was estimated using the phase speed c/n_{eff} , where n_{eff} is the effective refractive index calculated in the effective-medium approximation and c is the speed of light.

The free paths determined for PGP samples of various porosities are shown in Fig. 20c. It follows that the increase in porosity leads to a reduction of the free path of a photon and to an increase in the photon lifetime in the porous layer. We note that the lifetime of a photon in a porous layer depends on the layer thickness, while the free path is determined only by the layer scattering properties. At the same time, although the value of kl reduces from kl = 67 to kl = 6 as the porosity increases from 12% to 55%, the strong-localization regime is apparently not achieved.

We note that due to the increase in the local field, the efficiency of second- and third-harmonic generation, as well as of sum- and difference-frequency generation, in porous semiconductors is by orders of magnitude higher than the efficiencies of these processes for bulk semiconductors [9, 11, 124, 126-128].

7. Conclusion

By analyzing the optical properties of porous semiconductors, we see that the ordered structure of pores leads to a form birefringence emerging in such materials. In the cases where the sizes of pores and nanocrystals are small compared to the wavelength, form birefringence can be described in the framework of the effective-medium approximation. At the same time, for inhomogeneous photonic systems whose typical sizes are comparable to the wavelength, the processes of light scattering and localization play a crucial role.

Anisotropic etching of semiconductors leads to their optical anisotropy. The parameters of the anisotropy are determined by the structure and shape of the pores and the nanoclusters (nanocrystals) remaining after the etching. Models have been developed in which the birefringence and dichroism of porous semiconductors are related to the form anisotropy of the nanocomposite components. On the basis of porous semiconductors, one can efficiently manufacture photonic-crystal systems. In disordered inhomogeneous optical materials based on porous semiconductors, the free path of a photon increases as the porosity increases, which manifests itself as weak localization of light.

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