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CONDENSED-MATTER SPECTROSCOPY

Enhancement of Fluorescence of Porous Silicon upon Saturation by Liquid Crystal

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Abstract—The fluorescence of samples of porous silicon of various morphologies that are filled with a liquid crystal (LC), *n*-pentyl-*n*'-cyanobiphenyl (5CB), is studied. The fluorescence spectra of the sample, along with the long-wavelength band of porous silicon with a maximum in the range 627–667 nm, exhibit a short-wavelength band of 5CB with a maximum in the range 385–410 nm. The radiative relaxation times of porous silicon and 5CB lie in the micro- and nanosecond ranges, respectively. It is found that the filling of pores with 5CB enhances the fluorescence of porous silicon by two to three times. This enhancement is caused by non-radiative energy transfer from 5CB to the porous matrix as a result of efficient interactions between LC molecules and pore walls. Using IR spectroscopy, it is shown that the formation of hydrogen bonds between cyano groups of 5CB molecules and silanol groups of pore surface is the predominant type of these interactions. A transfer mechanism is suggested according to which excited associates of 5CB molecules transfer their energy via surface channels to excitons of porous silicon, enhancing its fluorescence.

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1. INTRODUCTION

Porous silicon displays its unique properties not only as an individual material [1, 2], but also in composite systems. Filling of silicon pores with various substances changes its refractive index and emission spectrum. Therefore, porous silicon can be used as a sensor of various chemical and biological compounds [3, 4]. To improve the sensitivity of porous silicon to certain compounds, the surface of its pores is frequently modified.

The formation of layers with different porosities in silicon made it possible to make silicon photonic crystals. In these structures of porous silicon liquid crystals (LCs) were used for the first time as fillers. By varying the refractive index of an LC filler by heating it [5] or reorienting it in an electric field [6, 7], the band gap width of photonic crystals based on mesoporous silicon was controlled.

It is known that, as the pore size decreases down to hundreds of nanometers, the electric control of LCs in pores becomes inefficient. A further decrease in the pore size down to a few nanometers leads to smearing of phase transitions or to the complete suppression of certain mesophases [8]. At the same time, in nanoporous media, qualitatively new size effects can occur, which are related to the fact that the volume and surface fractions of filler molecules in pores are comparable, as well as to the spatial confinement of these molecules or their associates. In previous works [9, 10], we showed that these factors affect the fluorescence spectra of LCs in nanoporous glass.

Enhancement of interface interactions in nanosized composite systems can also lead to efficient energy transfer from one component to another. Thus, in [11, 12], electronic states and resonance energy transfer in nanocomposites containing organic and inorganic semiconductor materials have been systematically studied. The possibility was described of highly efficient nonradiative energy transfer from semiconductor nanostructures (quantum wells and dots) to an organic material if spectra of their electronic states are overlapped. A transfer of this kind was observed in porous silicon saturated with a luminescent dye [13]. Based on these studies, a new concept of electrically pumped organic light sources was elaborated [14].

A reverse process, i.e., nonradiative energy transfer from an organic filler to a porous matrix, is also of indubitable interest. In this case, the enhancement of the fluorescence of an inorganic component is possible. Clearly, the implementation of this principle in the case of porous silicon increases the chances for its use in practice as a radiation source. The enhancement of the fluorescence of porous silicon was initially observed upon its filling with anthracene [15]. Recently, we observed a much more significant enhancement of the fluorescence of porous silicon when plates of this material were saturated by the LC,

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Sample	Type of silicon	Processing conditions	Layer	Color of sample	
		anodization	etching	thickness μm	Color of sample
1	KDB-10, <i>p</i> -Si	20 mA/cm^2 , 5 min with photostimulation	20 min	5	Yellow-green
2	KDB-10, <i>p</i> -Si	20 mA/cm^2 , 5 min with photostimulation	10 min	4	Orange
3	KES 001, n-Si	20 mA/cm^2 , 5 min with photostimulation	_	5	Red
4	KES 001, n-Si	20 mA/cm^2 , 5 min without photostimulation	—	5	Colorless

 Table 1. Processing conditions of silicon plates for different samples of porous silicon

e.g., *n*-pentyl-*n*'-cyanobiphenyl (5CB) [16]. This filler was chosen for several reasons. First, LC 5CB, as well as a number of other cyanobiphenyls, is characterized by a very high fluorescence quantum yield. Its fluorescence spectrum is shifted toward the short-wavelength range compared to the spectrum of porous silicon and is overlapped with the absorption spectrum of the latter. This creates possibilities for the transfer of electronic excitation energy from LC to porous silicon. Second, rodlike LC 5CB molecules are closely packed in quasi-cylindrical pores of porous silicon and align parallel to pore walls [7]. This circumstance also facilitates the efficient transfer of excitation energy. As a result, by filling porous silicon with LC 5CB, we succeeded in increasing its fluorescence intensity by several times.

In this work, we study the dependence of the fluorescence enhancement of porous silicon filled with LC 5CB on the degree of its porosity, which determines the intrinsic emission spectrum of this material. Also, we study the interface interactions in the system porous silicon–5CB and the mechanism by which excitation energy is transferred from 5CB to the porous matrix. Thus, this work is primarily aimed at elucidating the physical pattern of the effect of fluorescence enhancement of porous silicon, which was previously described in [16].

2. MATERIALS AND METHODS

Samples of porous silicon were prepared using the standard method of electrochemical etching. We used silicon plates of the p and n types with (100) Miller indices. Prior to etching, an aluminum ohmic contact was deposited on the backside of each plate. Layers of porous silicon were formed in a fluoroplastic cell with a platinum electrode. Anodization was carried out in a 1:1:2 HF: H₂O: C₂H₅ solution both in the dark and upon photostimulation (upon illumination by a 100 W incandescent lamp arranged at a distance of 10 cm from the plate). After the anodization, some samples were additionally held in the bath (the etching stage). This increased the porosity and reduced the size of silicon threads. As a result of different processing procedures, four types of samples were obtained, the parameters of which are presented in Table 1. Using electron microscopy, it was found that, in the series of samples 4-1, the porosity of the sample increases, while the size of threads decreases [16].

For filling silicon pores, we used nematic LC 5CB from Merck. This compound has a nematic phase in the temperature range $22.5-35.5^{\circ}$ C. At temperatures below 22.5° C, 5CB is crystallized. Above 35.5° C, it passes to the isotropic state. The filling of porous silicon with the LC 5CB was carried out by immersing porous plates in a 5CB isotropic melt for 1 h. After extraction, the surface of the saturated plates was carefully wiped. Spectral measurements were performed at room temperature ($22-24^{\circ}$ C).

Fluorescence spectra were measured on a spectral setup based on an MDR-12 monochromator. The spectral slit width of the monochromator was varied in the range 0.5-1 nm. The samples were excited by a nitrogen laser ($\lambda = 337.1$ nm). The excitation pulse width was 10 ns with a pulse power of 5 kW. To measure spectra with a nanosecond time resolution, we used a system based on a sampling oscilloscope with a time window of 0.1 ns. This system made it possible to record spectra with different time delays t_3 with respect to the laser pulse. The time resolution of the system was no worse than 0.7 ns (it was determined by the steepness of the leading edge of the laser pulse). The recording of spectra and relaxation kinetics was computerized. Measurements for different samples were performed under the same experimental conditions (geometry of experiment, power and duration of excitation, etc.). The method and the experimental setup were described in detail in our previous work [17].

IR spectra of the samples (pure 5CB, initial porous silicon, and porous silicon filled with 5CB) were measured on an IFS-88 Fourier transform spectrometer (Bruker). The signal-to-noise ratio was improved by programmable accumulation of signals measured by the detector during 64 scans of the spectrum. The spectral slit width was within $1-2 \text{ cm}^{-1}$. Spectra were measured at room temperature in the range 400–4000 cm⁻¹. Samples of porous silicon and porous silicon–5CB for these measurements were prepared in the same way as for fluorescence studies. Pure 5CB was placed between two KBr plates separated by a Teflon film 15 µm thick. The obtained spectral data



Fig. 1. Steady-state fluorescence spectra of samples of porous silicon: (a) pure and (b) filled with LC 5CB. The number of the spectrum corresponds to the number of the sample.

were processed (base line correction, normalization, subtraction of spectra, and determination of band maxima positions) using the standard OPUSTM software package (Bruker) for spectral data processing.

3. RESULTS

3.1. Fluorescence of Pure Porous Silicon

Prior to filling with LC, the steady-state and timeresolved fluorescence spectra were measured for all the samples of porous silicon (Table 1). In the steady-state spectra of all samples (Fig. 1a), a broad structureless band is observed in the long-wavelength range ($\lambda >$ 500 nm). The position of the maximum and intensity of this band depend on the morphology of the sample.

For samples 1, 2, 3, and 4, the fluorescence band maximum is located at 603, 614, 627, and 667 nm, respectively. This behavior of the fluorescence spectrum in relation to the morphology of porous silicon is caused by quantum size effects in silicon nanocrystallites (threads) [2, 18]. The smaller the size of silicon threads formed during etching, the more the fluorescence band of porous silicon is blue shifted. The shape of the fluorescence band of porous silicon is determined by the size distribution function of its silicon threads.



Fig. 2. Time-resolved spectra of sample 3 of porous silicon: (1, 2) pure and (I', 2') filled with LC 5CB. The time delays between the spectrum excitation and measurement are (1, I') 0.2 and (2, 2') 15 µs.

According to Fig. 1a, the fluorescence intensity of porous silicon increases in the series samples 1-3, i.e., with increasing thread thickness. Most likely, this is related to the formation of a nonluminescing oxide layer (SiO₂) on the surface of threads, which is confirmed by the results of IR spectroscopy experiments (Section 3.3). The volume ratio SiO₂/Si in thin threads is greater than that in thick threads, which may explain the enhancement of the fluorescence emission in the series of samples 1-3. The weak fluorescence of sample 4, which was obtained without illumination during anodization, is evidently related to the fact that the porosity of this sample is weak and, therefore, its structure approaches that of ordinary crystalline silicon.

The measurement of the time-resolved spectra of the samples of porous silicon showed that the steadystate spectra consist of a set of time-resolved bands. As the delay time between the excitation and recording increases, the fluorescence band is shifted toward longer wavelengths. As an example, Fig. 2 shows the time-resolved fluorescence spectra of pure sample 3 recorded for the delay times 0.2 and 15 µs (curves 1 and 2). The wavelengths of the fluorescence band maxima of this sample for the series of the delay times $t_{\rm d}$ are given in Table 2. The redshift of the fluorescence spectrum with increasing t_d is explained by different lifetimes of excited states in threads with different diameters. The excitation lifetime increases with an increase in the thread diameter [2, 18]. This means that, after the photoexcitation, fluorescence initially arises in threads with smaller diameters and then, in thicker threads. A decrease in the fluorescence intensity for long-wavelength components is evidently related to a rather narrow size distribution of threads and to the dependence of the fluorescence efficiency on the thread size.

3.2. Fluorescence of Porous Silicon Filled with the LC

The steady-state fluorescence spectra of composites porous silicon-5CB have bands of both porous sil-

Table 2. Fluorescence band maxima wavelengths (λ_{max} , nm) of pure porous silicon and of porous silicon filled with LC 5CB and formamide (data for sample 3 are given in Table 1)

Type of sample t_d , μ s	0.2	1	3	6	9	12	15
Porous Si	605	611	619	620	630	636	642
Porous silicon–5CB, λ_{max} , nm	614	617	621	627	633	636	642
Porous silicon–formamide, λ_{max} , nm	602	608	612	616	621	625	628



Fig. 3. Fluorescence spectra of LC 5CB in a (1, 2, and 3) macrolayer and (1', 2') dispersed state in sample 3 of porous silicon. Spectrum 3 is steady-state, and spectra 1, 2, 1', and 2' are time-resolved. The time delays between the spectrum excitation and measurement are (1, 1') 0.7 and (2, 2') 10 ns.

icon and LC contained in pores (Fig. 1b). Fluorescence bands of 5CB lie in the short-wavelength range (they are peaked at 390–400 nm). A comparison of Figs. 1a and 1b shows that, upon introduction of LC into porous silicon, the fluorescence intensity of the matrix increases by a factor from two to three and the fluorescence spectrum itself is somewhat shifted toward longer wavelengths. At the same time, the intensity of short-wavelength bands of 5CB proportionally decreases. This behavior indicates that excitation energy is efficiently transferred from the LC to threads of porous silicon. Energy transfer mechanisms will be discussed in detail in Section 4.

The shape of a time-resolved fluorescence spectrum of the porous silicon–5CB composite substantially depends on the resolution time with which this spectrum was measured. The spectra measured with a nanosecond resolution time show only the shortwavelength band of 5CB. The long-wavelength band of porous silicon is only contained in the spectra measured with a microsecond time resolution.

Using sample 3 as an example, we consider the microsecond fluorescence spectra of this sample measured with different microsecond delay times t_d . Figure 2 shows the time-resolved fluorescence spectra of this sample for the delay times 0.2 and 15 µs (curves *I*' and *2*'). The wavelengths of the corresponding fluorescence band maxima for the series of the delay times t_d are given in Table 2. It can be seen from Fig. 2 that the

shape of the fluorescence band of porous silicon changes little upon its filling with LC. At the same time, fluorescence spectrum of porous silicon is shifted, especially at small t_d (0.2–9 µs). Therefore, 5CB in pores of silicon affects the character of exciton luminescence of the latter.

The effect of a filling compound on the spectrum of a nanostructured matrix in semiconductor nanocomposites depends on the relation between the dielectric permittivities of the matrix ε_m and filler ε_f [11, 18]. This is related to the influence of the polarizability of the environment on the binding energy of excitons in nanocrystallites. At $\varepsilon_f \le \varepsilon_m$, the binding energy of excitons remains sufficiently large to prevent them from decay at room temperature. At the same time, at $\varepsilon_f > \varepsilon_m$ the interaction between electrons and holes in excitons decreases, and these quasiparticles are formed in considerably smaller numbers because of destabilizing thermal motions.

The average dielectric permittivity of LC 5CB is $\langle \epsilon_{LC} \rangle = 9.63$. According to [19], the permittivity of porous silicon ϵ_m depends on the diameter of threads and is varied from 11.7 to 4 for silicon threads with diameters from 6 to 2 nm. Consequently, in porous silicon filled by the LC 5CB, $\epsilon_f \leq \epsilon_m$.

The case where $\varepsilon_f > \varepsilon_m$ was implemented using formamide as a filler. The dielectric permittivity of this compound is $\varepsilon \approx 200$, which is by an order of magnitude higher than that of porous silicon. Upon excita-



Fig. 4. IR absorption spectra of samples of porous silicon with different porosities: (solid curve) sample 3 and (dashed curve) sample 4. Vibrations of associated groups are denoted by the index "as."

tion by a nitrogen laser, formamide fluoresces in a short-wavelength spectral range, and its spectrum can be observed only if it is recorded with a nanosecond resolution time. Therefore, in the microsecond range, this spectrum is completely unobservable, and only the fluorescence of porous silicon is observed. As was expected, the fluorescence intensity of porous silicon filled with formamide substantially decreases. In addition, filling with this compound leads to a significant shift of the fluorescence bands of porous silicon (Table 2). As can be seen, unlike LC 5CB, upon filling porous silicon with formamide, the fluorescence spectrum of the matrix is considerably shifted toward shorter wavelengths. Therefore, if, in filled porous silicon, $\varepsilon_m \ge \varepsilon_f$, then, upon filling, the fluorescence bands of porous silicon are shifted toward longer wavelengths. In turn, if $\varepsilon_m < \varepsilon_f$, the fluorescence spectrum of porous silicon is shifted toward shorter wavelengths. This result is consistent with the data of [20].

The fluorescence spectrum of LC 5CB also changes upon the introduction of this compound into porous silicon. The fluorescence spectra of this LC in the bulk and in porous silicon are presented in Fig. 3. Curves 1 and 2 correspond to the time-resolved fluorescence spectra of a macroscopic LC layer 50 μ m thick. The resolution times of spectra 1 and 2 are 0.7 and 10 ns, respectively. Curve 3 is the steady-state spectrum of this sample. Spectra 1 and 2 of the macrovolume correspond to spectra 1' and 2' of 5CB in nanopores (sample 3). The fluorescence of 5CB in pores is quenched, and its spectrum broadens. Simultaneously with this, fluorescence of porous silicon increases. At the same time, the position of the band maximum pertaining to excimer radiation of 5CB ($\lambda \approx 400$ nm) [17] does not significantly change.

The fact that the spectrum of the macrovolume of the 5CB differs from the spectrum of this LC dispersed in porous silicon may indicate that, apart from clustering of LC in pores, it efficiently interacts with the matrix. This conclusion is confirmed by results for the LC dispersed in other porous media [8–10, 21]. Interface interactions in the system porous silicon–5CB were studied by IR spectroscopy.

3.3. IR Spectra of the System Porous Silicon–LC 5CB

Figure 4 presents the IR absorption spectra of samples of porous silicon with different porosities (samples 3 and 4). As can be seen from this figure, the absorption spectra of the samples of initial porous silicon show the band of vibrational modes of the silicon skeleton Si–Si, whose maximum is at 614 cm⁻¹. The spectrum also exhibits bands that are characteristic of oxidized and hydroxylated states of silicon, which can occur at its surface. First of all, these are the bands of stretching and bending vibrations of siloxane groups Si–O–Si, whose maxima are located at 1080, 1120, and 458 cm⁻¹, respectively. In addition, the band of stretching vibrations of associated (bound by hydrogen bonds) silanol groups Si–OH is clearly seen in the



Fig. 5. Fragments of IR absorption spectra of (1) initial porous silicon, (2) pure 5CB, and (3) porous silicon filled with LC 5CB recorded in the range of stretching vibrations of the CN group. Differential spectrum 4 that results from the interaction of the corresponding part of 5CB with pore walls was obtained by subtracting the spectrum of pure 5CB from the spectrum of filled porous silicon. The data correspond to sample 3 of porous silicon.

high-frequency range of the IR absorption spectrum of the studied samples of porous silicon; the maximum of this band is at 3623 cm⁻¹. It should be noted that the intensity of the band of silanol groups in the absorption spectrum of the samples of porous silicon decreases with decreasing sample porosity. This indicates that oxidized and hydroxylated silicon is localized on pore walls or, equivalently, on the surface of silicon threads.

The IR absorption spectra of the samples of initial porous silicon exhibit a clearly pronounced broad band at 3410 cm⁻¹, which corresponds to stretching vibrations of hydroxyl groups of adsorbed water. Weak absorption bands at 2268 and 2140 cm⁻¹ correspond to stretching vibrations of SiH(O₃) and SiH(SiO₂) groups [22]. Therefore, the surface of pores adsorbs hydrogen and hydroxyl groups.

The spectra also show weak bands of C–H stretching vibrations of CH_2 and CH_3 groups, which are located at 2980, 2923, and 2849 cm⁻¹. Most likely, these bands correspond to residues of ethanol, which was used for washing the samples.

The spectra of the samples of porous silicon-5CB were analyzed using the interpretation of the vibrational spectrum of LC 5CB, which was previously obtained in [23] based on quantum-chemical calculations. Initially, we considered the spectral range 3000–4000 cm⁻¹, which contains stretching vibrations of

OH groups located on the surface of porous silicon. It was observed that the broad band at 3410 cm^{-1} attributed to these vibrations experiences substantial changes upon filling with 5CB. Two new components appear in the range of this band, which are located at $3450 \text{ and } 3623 \text{ cm}^{-1}$. It is likely that these components correspond to stretching vibrations of OH groups that are located on the pore surface of porous silicon and that are involved in the formation of hydrogen bonds with 5CB molecules.

To answer the question of which groups of 5CB molecules participate in the formation of hydrogen bonds with the pore surface, it is necessary to analyze the IR spectra of the filled samples in the range of stretching vibrations of the cyano group C=N of 5CB $(2100-2300 \text{ cm}^{-1})$ (Fig. 5). The differential spectrum presented in this figure was obtained by subtracting the absorption spectrum of pure 5CB from the spectrum of porous silicon filled with 5CB. The differential spectrum contains information on the structure and dynamics of 5CB molecules in the near-surface layer. Compared to the spectrum of the initial 5CB, the differential spectrum shows a new band, which is shifted toward the high-frequency spectral range and whose maximum is at a frequency of 2258 cm⁻¹. This band corresponds to the weakly pronounced inflection that is observed in the spectrum of filled porous silicon on the high-frequency wing of the band of stretching C=N vibrations at 2248 cm⁻¹ (curve 2 in Fig. 5). As was

shown in our previous works [23, 24], this additional absorption band is attributed to stretching vibrations of cyano groups involved in the formation of hydrogen bonds with surface hydroxyl ($C \equiv N...H-O-H$) or silanol ($C \equiv N...H-O-Si$) groups. These experimental facts indicate that CN groups of 5CB molecules efficiently interact with OH groups located on the surface of pores in porous silicon.

4. DISCUSSION OF RESULTS

In this section, we will discuss the mechanisms by which energy is transferred from 5CB to porous silicon and by which porous silicon saturated with LC 5CB fluoresces. First, consider the mechanisms of fluorescence of the components of the system, i.e., unfilled porous silicon and LC 5CB.

The fluorescence spectra of LC 5CB were previously studied by several groups of researchers [25-27] and, in recent years, in our works [17, 28]. It was shown that the complicated structure of the fluorescence spectrum of this compound is related to the combination of monomer and excimer radiations, with the latter radiation being determined by several types of excimers.

Two radiation mechanisms are possible in crystalline silicon, i.e., the radiative recombination of free electrons and holes and the annihilation of excitons. Since silicon is a nondirect-gap semiconductor material, the probability of a direct radiative recombination of carriers in it is very small; i.e., it is smaller by an order of magnitude than the probability of radiation by exciton annihilation. However, the efficiency of the exciton annihilation in macroscopic silicon samples is also low. This is determined by the low binding energy of charge carriers in the exciton (on the order of 14 meV) and, therefore, the low concentration of electron—hole pairs at room temperature [29]. These reasons explain why the fluorescence quantum yield of crystalline silicon is low.

The situation cardinally changes as the size of crystalline particles decreases to 1-10 nm, which is achieved in porous silicon. In this case, the radius of Wannier–Mott excitons is restricted by the size of nanoparticles, which leads to a considerable increase in the binding energy of carriers in an electron-hole pair. The binding energy of excitons is very sensitive to the state of the surface of nanothreads and to the polarization of the surrounding medium. Under favorable conditions, the binding energy of excitons in silicon threads 1.5-3 nm in diameter can achieve 60-140 meV [30]. An increase in the binding energy leads to an increase in the concentration of excitons and, therefore, to an increase in the intensities of absorption and fluorescence. In addition, a decrease in the size of crystallites to a few nanometers leads to a quantum size effect, namely, to the quantization of energies of electrons and holes and an increase in the band gap. This manifests itself in the short-wavelength shift of the fluorescence spectrum.

The fluorescence spectra of porous silicon that we obtained in this study (Figs. 1a and 2) can be well understood in terms of these notions. The radiation of porous silicon observed in the yellow-red spectral range is caused by the formation of nanocrystallites (threads) in the surface region of samples. An increase in the blue shift of the fluorescence spectrum with increasing porosity of samples is related to a decrease in the size of nanocrystallites. The broad fluorescence spectrum is due to the distribution of threads over the diameter. Steady-state fluorescence spectra are determined by the radiation from the entire set of threads. In turn, time-resolved spectra correspond to the radiation of threads of a certain diameter; the longer the delay time t_d , the thicker the threads for which radiation is experimentally detected. In the limit of long $t_{\rm d}$, one can observe the radiation of crystalline silicon. Consequently, excitons are inhomogeneously distributed over energies and relaxation times in porous silicon. Therefore, it is difficult to spectrally separate the fluorescence of excitons with certain energies [20].

Now, let us consider processes that occur in porous silicon filled with LC. Energy can be transferred both radiatively and nonradiatively from 5CB to porous silicon. To model the process of radiation, unfilled and filled samples of porous silicon were excited in the range of efficient fluorescence of 5CB by radiation from a He–Cd laser ($\lambda = 442$ nm). However, the fluorescence efficiency of porous silicon upon excitation by laser light at the wavelength of efficient radiation of 5CB was significantly lower compared to samples excited by radiation with $\lambda = 337$ nm. This allows us to conclude that the main mechanism by which energy is transferred from 5CB to porous silicon is nonradiative. The nonradiative transfer is also favored by the fact that, upon placing LC 5CB in pores, its fluorescence bands broaden (Fig. 3, spectra 1' and 2'). This inhomogeneous broadening of spectral bands is characteristic of systems with an efficient nonradiative energy transfer [13, 15]. In the short-wavelength range, the excitation spectrum of porous silicon overlaps with the long-wavelength part of the radiation spectrum of 5CB, which is responsible for excimer radiation. In this case, at the interface LC-porous silicon, molecular excitations in 5CB can hybridize with Wannier-Mott excitons in porous silicon, ensuring nonradiative energy transfer from LC to porous silicon. This energy transfer reduces the radiation intensity of the LC in the range of excimer radiation. Since the excimer radiation occurs via the excitation of monomers in predimer pairs, we can assume that the energy transfer rate constant from the LC to porous silicon is comparable with the rate constant of formation of excimers from predimer states.

As was shown in Section 3.3, an effective interaction in the system under study arises mainly as a result of the formation of hydrogen bonds between polar $C \equiv N$ groups of 5CB molecules and silanol groups of the partially oxidized silicon surface. It is not excluded that hydroxyl groups of water molecules adsorbed on pore walls also form hydrogen bonds with 5CB molecules. Therefore, the formation of interphase hydrogen bonds of the C≡N...H−O type, along with the favorable relation between energy levels of porous silicon and 5CB are very important conditions of the energy transfer from LC 5CB to porous silicon. Taking into account predominant absorption of 5CB molecules in associated states and exciton radiation in porous silicon, we assume that energy is transferred from excited associates of 5CB molecules to porous silicon via interphase hydrogen bridges, increasing the intensity of excitation of carriers and, therefore, the intensity of formation of electron-hole pairs and of their radiative relaxation.

In conclusion, we note that LC 5CB proved to be an extremely good filler for nanostructured porous silicon not only from the viewpoint of the fluorescence spectrum position, but also from the viewpoint of the dielectric properties. As was noted above (Section 3.2), the properties of excitons near the surface of a nanostructured semiconductor strongly depend on the dielectric properties of the environment. The dielectric permittivity of porous silicon is comparable with the permittivity of LC 5CB. As a result, filling porous silicon with LC weakly affects the binding energy of excitons and, therefore, the intensity and spectral position of exciton fluorescence.

5. CONCLUSIONS

We studied the fluorescence and IR absorption spectra of porous silicon filled with LC 5CB. It was revealed that the filling of pores with LC 5CB leads to a considerable increase (by two to three times) in the radiation of porous silicon under the UV excitation $(\lambda = 337 \text{ nm})$. This effect is due to nonradiative energy transfer from 5CB to porous silicon for the following two reasons: (i) the favorable relation between the absorption and emission spectra of the components (the emission spectrum of 5CB is overlapped with the absorption spectrum of porous silicon) and (ii) the efficient molecular interaction of 5CB with silicon pore walls by the formation of hydrogen bonds.

We proposed an energy transfer mechanism in the composite according to which molecular excitation energy of 5CB is nonradiatively transferred to nanocrystallites of porous silicon via interphase associates 5CB...H–O–Si, enhancing its fluorescence by means

of generation and radiative recombination of additional electron-hole pairs.

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