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*In the present research, we consider nanoporous silicon filled with nematic liquid crystal (LC) *n*-pentyl-*n*'-cyanobiphenyl (5CB) as a specimen of hybrid systems with high quantum yield of fluorescence (FL). The steady-state and time-resolved FL spectra of this system excited by a nitrogen laser ($\lambda = 337$ nm) are measured. The maxima of the emission bands for porous silicon are obtained in the range 627–667 nm depending on the sample morphology. In case of porous silicon filled with 5CB, the short-wave bands of 5CB are detected along with the bands of porous silicon. The FL bands of 5CB and porous silicon were characterized by nanosecond and microsecond relaxation, respectively. It is revealed that the filling with 5CB enhances the luminescence of porous silicon by 2–3 times. Such an enhancement is due to the nonradiating energy transfer from 5CB to the porous matrix. A possible mechanism of this energy transfer is discussed.*

Keywords: liquid crystal; luminescence; *n*-pentyl-*n*'-cyanobiphenyl; porous silicon

1. INTRODUCTION

The steady scientific and technological interest in porous silicon (Si) is due to the possibilities of using this material for the production of

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light-emitting elements [1]. The properties of porous Si are especially sensitive for the influence of the environment. Organic compounds introduced in pores can essentially change both own emitting properties and properties of porous Si [2–4]. Such changes in fluorescence (FL) are due to the electronic processes running on the surface of pores, particularly, due to the high sensitivity of excitons generated in porous silicon to the permittivity of an organic filler [2,3]. The results of investigations of electronic states and resonance energy transfer in the hybrid organic-inorganic semiconductor nanostructures are presented in [5–8]. The high efficiency of non-radiating energy transfer from semiconductor nanostructures (quantum wells and quantum dots) to the organic material with overlapping electronic spectra was revealed. This happens when the time of energy transfer from excitons to the organic medium is smaller than the lifetime of excitons. These results suggest a new concept of light sources based on electrical pumping [9].

Obviously, the inverse energy transfer from the organic medium to porous silicon can substantially enhance the fluorescence of a Si matrix. The realization of this principle can lead to a new generation of light-emitting porous Si devices with substantially higher emitting efficiency. The organic filler in such devices can be pumped either electrically or optically. In the present study, the enhancement of FL of porous silicon is realized through the optical pumping of an organic filler. As a filler, we used nematic LC 5CB because of several reasons: (1) FL spectrum of 5CB is “blue”-shifted with respect to the FL spectrum of porous Si overlapping with its absorption spectrum. This makes possible the energy transfer from 5CB to the Si matrix. (2) Rod-like LC molecules can be closely packed in quasi-cylindrical pores and effectively interact with the pore walls. This assumption was based on our previous results obtained for the “5CB–porous glass” system [10,11]. Finally, FL of LC 5CB in the free state and in the porous matrices of different nature is a subject of our academic interest [11–13].

It is revealed that 5CB has high quantum yield of FL in the absorption region of porous Si. It turns out that 5CB noticeably enhances FL of porous Si due to the photoexcitation energy transfer. The underlying mechanisms of the energy transfer from 5CB to porous Si are discussed.

2. MATERIALS AND METHODS

The samples of porous Si were formed by the electrochemical etching of Si. The p-type of Si plates with a specific resistance of 10 Ohm·cm (KDB-10) and Miller indices (100) were used. The plates were covered



FIGURE 1 TEM images of porous Si samples 1 (a) and 2 (b). Magnification is 2,00,000.

by aluminum contact from outside. The porous silicon layers were formed in the fluoroplastic cell with a platinum electrode. The etching was performed in a solution of hydrofluoric acid in pure water or water doped with ethanol. The current density was $10\text{--}75\text{ mA/cm}^2$, and the etching time was varied from 1.5 to 10 min to change the morphology and, particularly, the size of silicone crystallites. The thickness of a porous layer for all samples was about $5\text{ }\mu\text{m}$. For the sake of simplicity, we will compare properties of two samples with boundary morphologies; sample 1 possessed a fine structure, while sample 2 contained much greater grains according to electron microscopy tests. The corresponding images are presented in Figure 1a and 1b.

As a liquid crystal, we used nematic liquid crystal 5CB from Merck. The 5CB has nematic phase at $22.5\text{--}35.5^\circ\text{C}$. It crystallizes at temperature less than 22.5°C and becomes isotropic at temperatures higher than 35°C [14]. Porous silicon was filled by the liquid crystal in the isotropic phase. All spectral measurements were realized at room temperature (about 24°C).

The experimental setup based on a monochromator MDR-12 was used for the spectral measurements of FL. During the measurements, a spectrometer slit width was $0.5\text{--}1\text{ nm}$. FL was excited by a pulsed nitrogen laser at the wavelength $\lambda = 337\text{ nm}$ with a pulse width of 10 ns and a pulse power of 5 kW . The FL kinetic characteristics and time resolved spectra were determined by the stroboscopic method with a strobe width of 0.1 ns . This system allowed us to record the FL spectra with different time delays t_d with respect to a laser pulse. The time resolution of the system was not worse than 0.7 ns . In measurements of the time-resolved FL spectra, the time resolution was

determined by the steepness of the leading edge of a laser pulse. The recording of the spectra and relaxation kinetics was computerized. The details of this method and the measuring system can be found in our earlier publication [12].

3. RESULTS

3.1. Fluorescence of Porous Silicon

The steady-state and the time-resolved FL spectra of porous Si samples are presented in Figures 2 and 3, respectively. From Figure 2, one can see that FL is practically absent in the short-wave region. According to [1], the FL in this region mainly corresponds to SiO_x layers formed on the pores' walls due to the oxidation. The weak FL in the short-wave region determined mainly by the oxidized surface layers [1] suggests that SiO_x layers are very thin, and so Si probes are poorly oxidized.

In the long-wave spectral region ($\lambda > 500$ nm), one can see a wide structureless band for each sample (Fig. 2). The spectral position and intensity of this band is determined by the sample morphology. For samples 1 and 2, the maxima of the band are at 627 nm and 667 nm, respectively. Such a character of the FL of porous Si is due to quantum dimensional effects in Si nano-crystallites ("threads") of a variable profile [1,2,15,16]. The smaller the diameter of Si

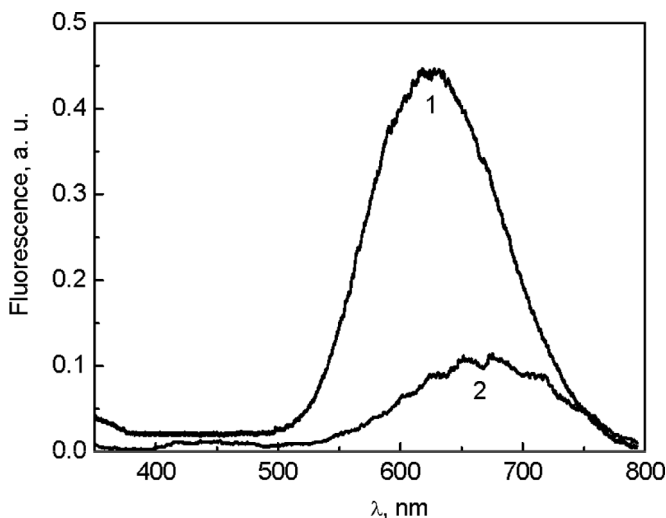


FIGURE 2 Steady-state fluorescence spectra of porous Si for sample 1 (1) and sample 2 (2).

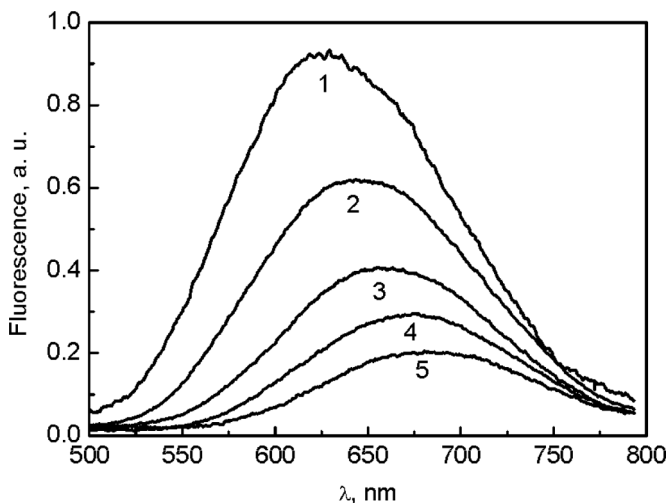


FIGURE 3 Time-resolved fluorescence spectra of porous Si (sample 2) measured with different time delays: (1) 0.1 μ s, (2) 6 μ s, (3) 9 μ s, (4) 12 μ s, and (5) 20 μ s.

crystallites formed in the etching process, the shorter is the spectral maximum of the FL band [15].

The time-resolved fluorescence spectra with microsecond resolution uncover that the steady-state spectra analyzed above consist of a continuous set of bands shifted with respect to one another in the long-wave region. For example, in Figure 3, the shift of the band for sample 2 occurs from 627 nm ($t_d = 0.1 \mu$ s) to 687 nm ($t_d = 20 \mu$ s). This behavior can be explained by the different lifetimes of excited states for the threads of different diameter; the lifetime increases with the diameter of a thread [15]. This means that, after the photoexcitation, the FL first occurs from the threads of small diameters and then from the thicker threads.

3.2. Photoluminescence of Porous Silicon Filled with Liquid Crystal

In the steady-state, the FL spectra of porous Si filled with LC 5CB along with the long-wave spectral bands, which are typical of porous Si, short-wave bands corresponding to the excitation of 5CB occur (Fig. 4). The spectra in Figure 4 are normalized to long-wave bands in order to better observe a band profile and to compare it with the spectra of non-filled porous Si (Fig. 2).

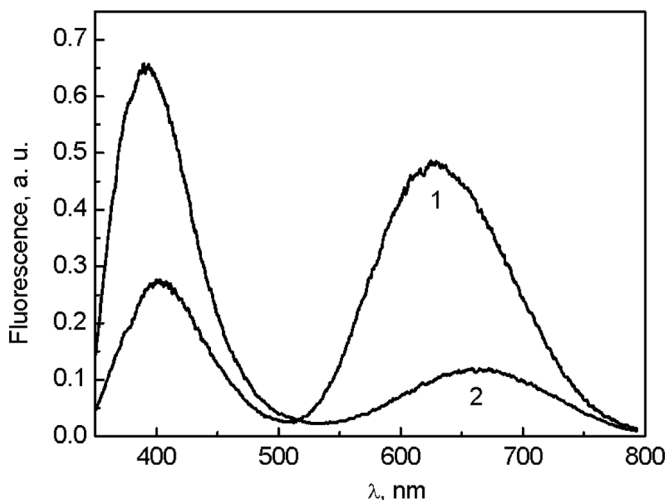


FIGURE 4 Steady-state fluorescence spectra of porous Si filled with liquid crystal 5CB for sample 1 (1) and sample 2 (2).

The time-resolved spectra of this probe strongly depend on the resolution time. The short-wave 5CB band is presented only in the spectra measured with the nano-second resolution. The long-wave band corresponding to porous Si is presented only in the spectra measured with the microsecond resolution times.

It is revealed that the insertion of 5CB in Si pores enhances the intensity of the long-wave FL of porous Si by 2–3 times. The maximum of the long-wave band slightly shifts to longer waves in comparison with that for the non-filled porous Si. At the same time, the intensity of the short-wave fluorescence corresponding to 5CB confined to the Si pores decreases. These results imply the excitation energy transfer from 5CB to the Si matrix, which is discussed in the following section.

4. DISCUSSION

The energy transfer from 5CB to porous Si can be radiating or nonradiating. To model the radiating process, the neat porous Si and 5CB porous Si probes were pumped with the 442-nm irradiation of a He-Cd laser corresponding to the range of the effective FL of 5CB (Figure 4). However, the efficiency of FL was much less than that of the 5CB filled porous Si probe pumped with a 337-nm irradiation. This leads us to the conclusion that the major channel of the energy transfer is nonradiating one.

It is well-known that the major energy carriers in porous silicon are excitons, whose properties substantially depend on the state of pore walls, because of the small diameters of Si threads [1–5]. According to [17,18], the properties of excitons near the surface of a semiconductor are strongly influenced by the environment. In the case where the permittivity of the environment is much higher than that of a semiconductor, the binding energy of excitons is small, and excitons dissociate without luminescence. In the opposite case, when the permittivity of a semiconductor is considerably higher than that of the environment, a rise of the exciton energy is possible [19]. The selection of an appropriate semiconductor and a dielectric allows one to change the binding energy of excitons in a wide range.

The average permittivity of LC 5CB is $\langle\epsilon\rangle = 9.63$. According to [20], the permittivity of Si nanoparticles decreases from 11.7 down to 4 with decrease in the size of nanoparticles from 6 to 2 nm. Such changes in the permittivity were due to the dielectrical environment (SiO_x) of Si threads. When the diameter of a Si thread tends to the Bohr radius of an exciton, the permittivity becomes close to that typical of crystalline Si. In any case, the permittivity of porous Si probes is comparable with that of LC 5CB, so that the binding energy of excitons is not changed considerably and the corresponding FL of porous Si is not considerably modified.

In the spectra of 5CB, the long-wavelength components prevail which correspond to the radiation of molecular associates, primarily excimers of 5CB [12,13] and associates of 5CB molecules with the fragments from pore walls [11]. The latter sort of associates can occur due to the formation of hydrogen bonds between 5CB molecules and OH groups from a SiO_2 layer covering the surface of silicon threads. This mechanism was earlier experimentally proved for 5CB introduced into porous glass [10].

The arguments above give us the ground to believe that the excitation energy of 5CB associates transfers to the Si matrix due to the effective 5CB–matrix interaction giving rise to excitons in silicon threads. The most effective channel of energy transfer seems to be formed by the surface associates of 5CB with pore walls. The effective energy transfer suggests that the excitation rate of the pre-excimer molecules of 5CB is comparable with the rate of energy transfer from 5CB to porous Si. Of course, the proposed model needs to be better argued and, on this stage, it should be considered as a hypothesis which agrees well with the previous results and allows one to explain the FL data for the 5CB–porous Si system.

CONCLUSIONS

The FL spectra of porous Si filled with liquid crystal 5CB are investigated. It is revealed that the filling of porous Si with 5CB results in a

significant enhancement of FL in the wavelength region corresponding to porous Si. This effect is caused by the nonirradiating energy transfer from 5CB to porous Si. The model of this energy transfer is proposed. According to this model, the excitation energy of 5CB associates (excimers, etc.) transfers to porous Si giving rise to excitons and the enhancement of the FL of porous Si. The revealed effect is of great interest for applications, since it shows the effective way of the enhancement of the FL of porous Si.

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