5,10,15,20-tetraphenylporphyrin photoluminescence on nanoporous silicon substrates

M O Koroleva¹, M A Elistratova², I B Zakharova¹, G V Li² and O M Sreseti²

¹St. Petersburg State Polytechnical University, 29 Polytechnicheskaya Street, St. Petersburg 195251, Russia
²Ioffe Institute, 26 Polytechnicheskaya Street, St. Petersburg, 194021, Russia

E-mail: qomu@ya.ru

Abstract. Photoluminescence of 5,10,15,20-tetraphenylporphyrin (H₂TPP) on nanoporous silicon substrates has been studied. Used nanoporous silicon has a visible PL in the region of H₂TPP absorption. Reradiation of porous silicon photoluminescence to the tetraphenylporphyrin long-wavelength peak of the photoluminescence spectrum is observed. The substrate microrelief plays a major role in the formation of tetraphenylporphyrin crystalline structures. The microrelief size of porous silicon was controlled by changing the technological parameters of electrochemical etching.

1. Introduction
The search for new materials to create light-emitting devices continues in modern industry. This niche may be occupied by organic semiconductors with an ability of self-organization. The scope of their usage in the case of gaining control over the self-organization process may be very wide: light-emitting devices (OLED), photosensitizers, solar cells, etc. can be created on their basis [1,2]. Materials from the porphyrin group are very promising for this application. Self-organization means the independent formation of supramolecular structures during crystallization, which happens only under the influence of internal factors. However, the absence of external influence, in the general, means the inability to control the final result. Thus, works devoted to the study of the possibility of controlling the crystallization of such materials are of great importance. The self-organization of tetraphenylporphyrins was mainly studied in supersaturated solutions and monolayers [3,4]. However, solid-state structures and thin films are of the greatest interest for creating organic semiconductor devices. One of successful methods for managing self-organization is the use of substrates with a microrelief. Porous silicon is proposed as such a substrate. The ability to vary the etching parameters makes it possible to obtain microstructures with different porosities, which ensures a microrelief with the required roughness size.

2. Methods and materials
5,10,15,20-tetraphenylporphyrin (H₂TPP, Sigma-Aldrich 99%) was chosen as a material for this study. Coating of tetraphenylporphyrin on substrates was carried out from a toluene solution. The concentration of the solution was significantly lower than the solubility limit in order to avoid the aggregation of porphyrin in the solution observed for this material. Samples of nanoporous silicon obtained from wafers of monocrystalline polished boron-doped silicon with conductivity 1-4 Ω·cm
and 12 Ω-cm, respectively, were used as a substrate. Electrochemical etching was performed in a commonly used electrolyte with an HF:Ethanol composition of 1:1, at a current density of 5-20 mA/cm², and the etching time was 5-30 min. This process leads to the formation of nanoporous silicon with a pore size of 3 - 5 nm, which has PL in the visible spectral region. Porous silicon powder was made from polycrystalline Si powder (Vesta Ceramics, Si: 99%, O: 0.2-1%, Al: 0.07%, Fe: 0.07%) with an average particle size of ~ 3 - 11 mkm by chemical etching in a mixture of hydrofluoric and nitric acids - HF:HNO₃:H₂O/4:1:20 [5]. Porous silicon powder consists of crystallites of 20 - 30 nm in size and does not have visible PL. In order to avoid oxidation of the porous layer, which leads to decrease in the adhesion of tetraphenylporphyrin, the coating was applied immediately after the manufacture of the substrates. To increase the thickness of the self-organized crystalline film, the coating was repeated 2 or more times. Samples were also prepared by mixing a H₂TPP solution and porous silicon powder, followed by co-drying. The structure of the samples was controlled with a Nikon LV150 optical microscope. The photoluminescence (PL) spectra were measured in the pulsed mode (the excitation radiation wavelength was 337 nm and the pulse duration was 8 ns) using a monochromator, a photomultiplier, and a stroboscopic voltage converter. The PL spectrum of nanoporous silicon has fast and slow components (with short and long lifetimes, respectively). At the same time, H₂TPP photoluminescence is characterized by short times of luminescence, therefore the total PL was measured only at the excitation pulse maximum. PL spectra were measured at room temperature.

3. Results and discussions
It was previously noted that H₂TPP has the ability to self-organize into various nanostructures [6], which is appeared in the growth of nonplanar crystalline structures – nanoroads, nanowiskers. Wherein, it is possible to influence the shape of such crystals by changing the technological growth conditions and using orienting substrates.

Figure 1. Surface image obtained in an optical microscope for H₂TPP samples on (a) nanoporous silicon with a 3-5 nm pore size, (b) with porous silicon powder.

H₂TPP samples obtained by coating from a toluene solution on two types of porous silicon (porSi) are shown in figure 1. Structures with the form of a nanoroad/nanowire growing at an angle of 60° to the substrate were observed on nanoporous silicon (see figure 1(a)), which is typical for non-orienting substrates. Nanoporous silicon with a smaller pore diameter (up to 5 nm) has a smaller effect on the growth of tetraphenylporphyrin, and H₂TPP crystallites have a preferred growth direction. In a previous work [6] on mesoporous silicon, H₂TPP crystals exhibit a greater degree of self-organisation due to the greater influence of the substrate relief. In comparison, porous silicon powder allows to obtain planar three-dimensional crystals by coating from a solution (figure 1(b)) with a significantly greater degree of crystallinity. Crystallinity influence on photoluminescence of tetraphenylporphyrins on various type of substrates was studied in a previous work [6]. It was shown that high crystallinity
samples might be obtained on substrates of mesoporous silicon. Difference between meso- and nanoporous silicon is crystallite sizes. Mesoporous silicon does not have visible PL due to the large crystallite size – about 20 nm. It is well known that nanoporous silicon with 3-5 nm crystallite sizes has a visible photoluminescence in the region of 550-650 nm, which is a region with strong tetraphenylporphyrin absorption. The influence of PL of a nanoporous silicon substrate on the tetraphenylporphyrin PL has not been previously studied.

The PL spectra of three types of samples were measured: nanoporous silicon before and after the coating of tetraphenylporphyrin, and tetraphenylporphyrin on monocrystalline polished silicon. The results are presented in figure 2. As it is known, the PL spectrum of H$_2$TPP consists of two maxima that correspond to two excited transitions in the energy structure of tetraphenylporphyrin - the electronic transition (PL peak $\lambda = 650-670$ nm) and the electron-vibrational (vibronic) one (PL peak $\lambda = 710-730$ nm) [7]. A “red” shift of the spectrum by 10 nm to the long wavelength side is observed after depositing a tetraphenylporphyrin coating on a porous silicon substrate. This indicates an increase in the crystallinity degree of samples obtained on nanoporous silicon. In comparison with previous work [6], the PL spectrum of H$_2$TPP on nanoporous silicon has a lower “red” shift than on mesoporous silicon. A decrease in the PL intensity of the nanoporous silicon substrate is observed in the spectral region 550 - 650 nm. This is accompanied by reradiation to the long-wavelength maximum of the tetraphenylporphyrin photoluminescence spectrum at a wavelength of about 730 nm. This fact is explained by the partial absorption of PL of nanoporous silicon by tetraphenylporphyrin. The absorption of additional radiation leads to an increase in the probability of only vibronic transitions in tetraphenylporphyrin molecules and subsequent reradiation to the corresponding maximum of the spectrum.

![Figure 2](image_url)

**Figure 2.** PL spectral dependences of H$_2$TPP samples obtained from a solution on (1) monocrystalline polished silicon and (2) nanoporous silicon; (3) PL of a nanoporous silicon substrate.

4. **Conclusions**

The photoluminescence of H$_2$TPP on nanoporous silicon substrates with visible PL in the region of strong H$_2$TPP absorption is studied and discussed in the present work. Absorption of nanoporous silicon photoluminescence by crystalline tetraphenylporphyrin was observed. The absorption of additional radiation leads to reradiation and an increase in the probability of electron-vibrational transitions in the energy spectrum of H$_2$TPP at 730 nm. Artificial surface microrelief allows obtaining samples with a high degree of crystallinity. It is proposed to use porous silicon as substrates with a microrelief which allows one to get H$_2$TPP with a given type of crystallinity and PL.
References

[1] Jeon I S, Kim S J, Bae G, Lim Y R, Song W, Myung S, An K S 2018 Thin Solid Films 649 1
[2] Kubát P, Henke P and Mosinger J 2019 Colloids Surf., B: Biointerfaces 176 334
[3] Udal’tsov A V, Tosaka M and Kaupp G 2003 J. Mol. Struct. 660 15
[4] Boeckl M, Bramblett A, Hauch K D, Sasaki T, Ratner B D and Rogers J W 2000 Langmuir 16 5644
[5] Limaye S 2007 Phys. Status Solidi A 204 1297
[6] Elistratova M A, Zakharova I B, Li G V, Dubrovin R M and Sreseli O M 2019 Semiconductor 53 51
[7] Harriman A 1980 J. Chem. Soc., Faraday Trans.1: Physical Chemistry in Condensed Phases. 76 1978