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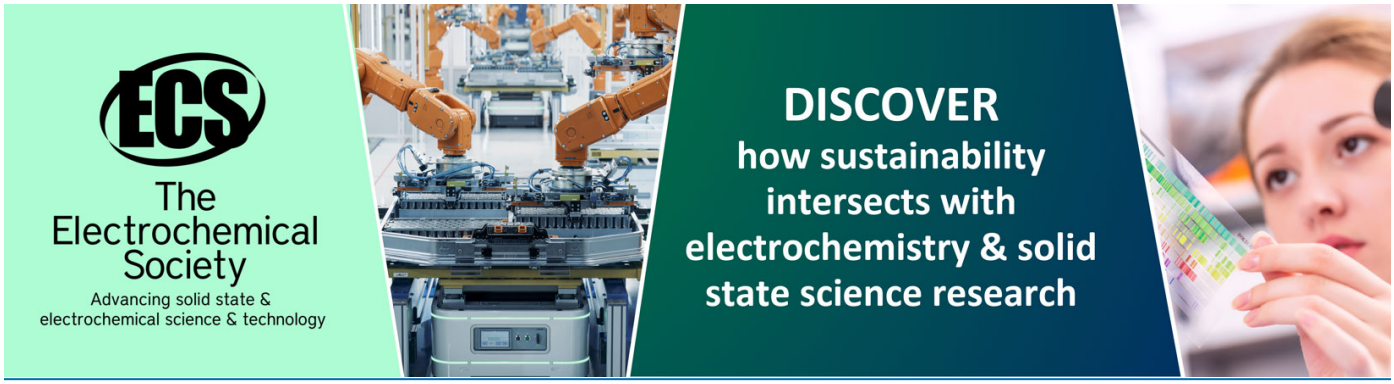

Multiphoton microscopy of mesoporous silicon

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Abstract. In this work, the behavior of the luminescence of mesoporous silicon under irradiation with a femtosecond IR laser is shown by the method of multiphoton microscopy. It was demonstrated that, along with the background photoluminescence of porous silicon, bright photoluminescence centers appear on the layer surface, and under certain conditions. Centers with a different, shorter-wavelength emission spectrum also appear.

1. Introduction

A promising area is the research of semiconductor materials and biological structures capable of emitting light in the visible range. The use of two-photon microscopy methods can help in the studying of physical principles of a photoluminescence, as well as physicochemical processes occurring in such materials.

Porous silicon is used to create new nanostructured composite materials obtained by incorporation and encapsulation [1–5]. The success of such technological operations depends on adsorption-energy characteristics of the pore surface [6–8]. Photoluminescence is an effective method for analyzing the state of pores [9–11]. However, the photoluminescence in its traditional form gives an integrating trend of luminescence over the entire volume of the sample. The informativity of confocal microscopy, and especially multiphoton microscopy, increases significantly. With a femtosecond laser, the concentration of photons increases drastically. Nonlinear effects, including two-photon absorption, are observed.

Due to its efficient photoluminescence and its ability to control electrophysical properties through a flexible manufacturing process, porous silicon is an important material for optoelectronics, energy and medicine [12–16].

Today, multiphoton microscopy is widely used to observe living tissue samples both *ex vivo* and *in vivo* [17]. New configurations of multiphoton microscopes are being developed, for example, three-photon microscopes for research scattering tissues at the depth or miniature instruments for continuous observation of tissues and neurons in freely moving animals [18, 19].

One of the main reasons for the prevalence of two-photon microscopy methods over confocal microscopy methods is that the excitation of emitting centers occurs only in the focal plane, and not in the entire volume of the sample, where the beam goes out of focus. This is due to the nature of a nonlinear optical effect called two-photon excitation, which underlies two-photon microscopy [20]. This increases the contrast of the image. In addition, the use of a beam of light at IR frequencies for excitation allows light to penetrate deeper into the tissue, with less breaking the sample (the effects of photodamage and photobleaching of the sample are reduced).

Due to these properties, two-photon microscopy makes possible to research the nature of the photoluminescence of a porous silicon layer at the depth, which is still poorly understood. Such

experiment could reveal new details for a better understanding of the physical phenomena underlying the photoluminescence of porous silicon. This is the purpose of this article. In addition, two-photon microscopy researches of inorganic materials are extremely rare, so this research will be of a fundamentally new nature.

2. Materials and methods

The work was performed on a Bergamo II multiphoton microscope (Thorlabs, USA). The microscope is equipped with a tunable femtosecond Ti:sapphire laser emitting at wavelengths of 720–1060 nm. The luminescence registered by the objective is divided into two beams using a dichroic mirror and delivered to two PMTs: with a range of received radiation from 320 to 525 nm (short-wavelength PMT or channel A) and with a range from 525 to 705 nm (long-wavelength PMT or channel B). The control program (ThorImageLS, Thorlabs, USA) displays an image from each of these PMTs, which can be colored in different colors. These two images are combined into one, which is generally the main source of information.

In this work, we researched the nature of the photoluminescence of mesoporous silicon obtained by electrochemical anodic dissolution of monocrystalline *p*-silicon (111) with resistivity of 1 Ω × cm in an aqueous alcohol solution of HF at a current density of 2 mA/cm^2 for 2, 4, 6, 8, and 10 min at two-photon excitation by a femtosecond laser with wavelengths of 780, 800, 900 and 1 000 nm. The porous silicon obtained under such conditions was characterized by pore sizes of the order of 10–25 nm with the characteristic dimensions of the skeleton of porous silicon on the order of a few nanometers.

The samples were passivated few days (2 or 3) in air. During these period surface oxidation occurs. It's enough for stabilization of key parameters, which are significant for correct device working. Whole photoluminescence spectrum was studied in another work [21].

As far as the laser power is set optimally for each measurement (for registration with photodetectors), the brightness of the images is not compared in this research.

3. Results and discussion

Depending on the monocrystalline silicon etching time, its surface will have a different morphology. A short etching time does not result in pore formation in the volume of the silicon wafer, whereas the surface morphology changes. At this time, the surface pattern remains practically unchanged with deeper pore formation by the increasing etching time.

Figure 1 shows two-photon microscopy images of the porous silicon surface at different etching times and the same laser wavelength of 800 nm.

It can be seen from the figures, that at an etching time of 2 minutes, the background luminescence observed on other samples is extremely small and comparable to the noise, which indicates that a sufficient layer of porous material is not formed at this stage. In this case, the luminescent centers are clearly visible, which are formed on the structured surface as a result of its etching. The same centers are visible in the images of other samples, but they are less noticeable due to the fact that the general luminescence of the porous layer overlaps the weak spots of the luminescence.

Surface thin scratches appear caused by surface roughness and scratches in existence before etching. In addition, it can appear as a result of the stressed porous layer relaxation. Such scratches are observed primarily at the surface but some of them extend deeper.

Also, a deep scratch region luminescence was studied. The scratch was made on the monocrystalline silicon wafer before etching, which was carried out at an etching time of 10 minutes. The experiment was carried out at different excitation laser wavelengths (780, 800, 900, and 1000 nm) and showed interesting results (figure 2).

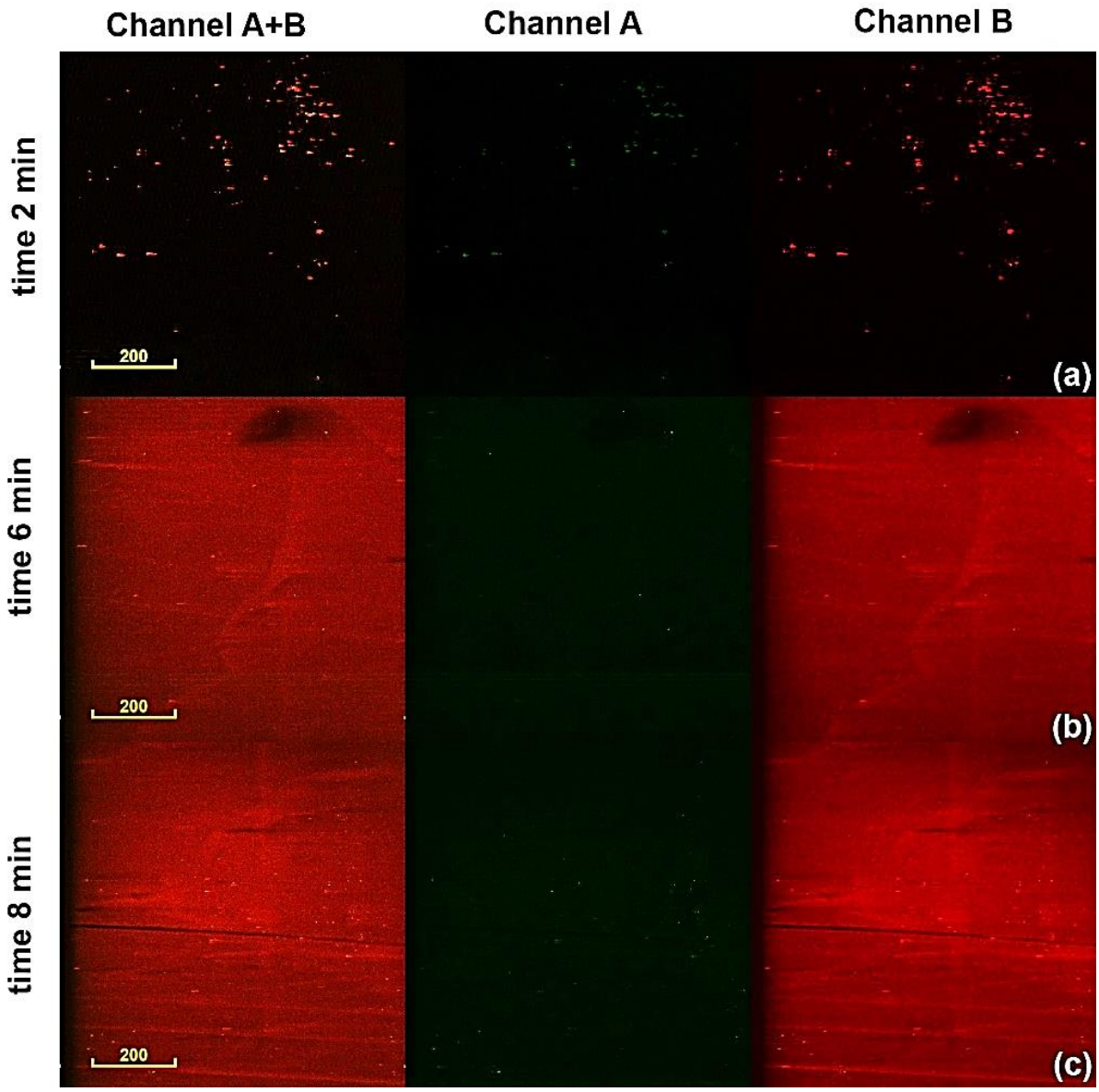

Figure 1. Two-photon microscopy images of the porous silicon surface at the 800 nm laser irradiation. Etching time: (a) 2 min, (b) 6 min, (c) 8 min. Scale size in μm.

There is irregular electric field intensity distribution at scratch boundaries. Intensity arises and changes anodization conditions. It causes structural and componential differences, what can be the reason of stronger photoluminescence at boundaries.

Interestingly, the number of luminous centers in the short-wavelength region (channel A) changes, as well as the total number and brightness of the centers depending on the wavelength.

Figure 2 shows that there are fewer luminous centers at 800 nm than at other wavelengths. The increase in the number of centers at 780 nm can be explained by the fact that at a shorter wavelength, the distinguishability of structural elements (including luminous ones) is better due to the higher resolution (diffraction limit enhancement). However, the reason why a large number of centers are visible at 900 and 1000 nm remains to be seen.

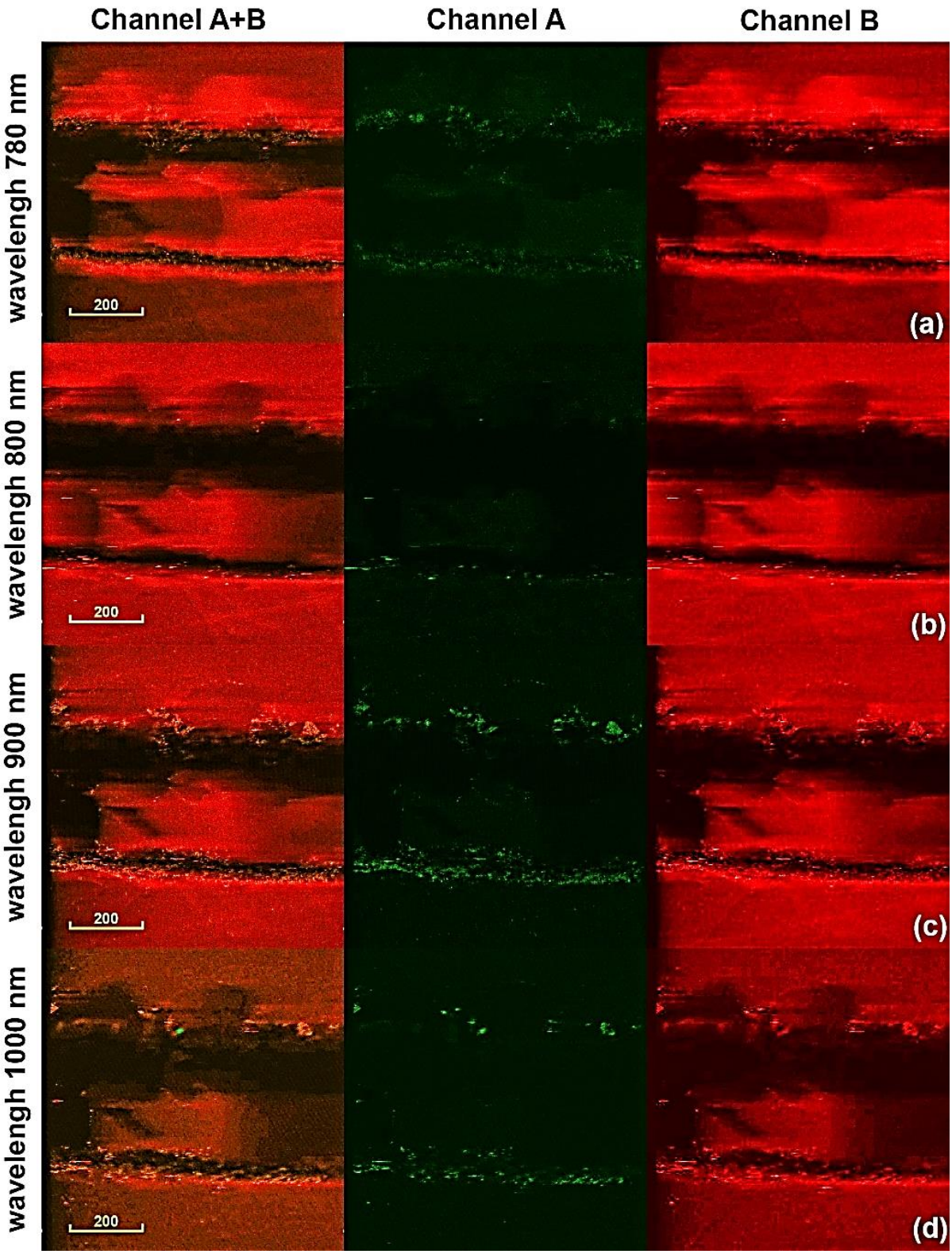

Figure 2. Two-photon microscopy images of the porous silicon surface at the etching time 10 min. Laser irradiation wavelength: (a) 780 nm, (b) 800 nm, (c) 900 nm, (d) 1 000 nm Scale size in μm.

With increasing wavelength, the number of emitting centers and their brightness in the short-wavelength part of the spectrum increase. Moreover, at a wavelength of 800 nm (figure 3(a)) only centers emitting predominantly in the long-wavelength region of the visible spectra are visible. This centers luminescence spectra partially cover the short-wavelength half (figure 2). At a wavelength of 1000 nm (figure 3(b)) centers are clearly luminesce only in a short spectral region (flashes at channel A).

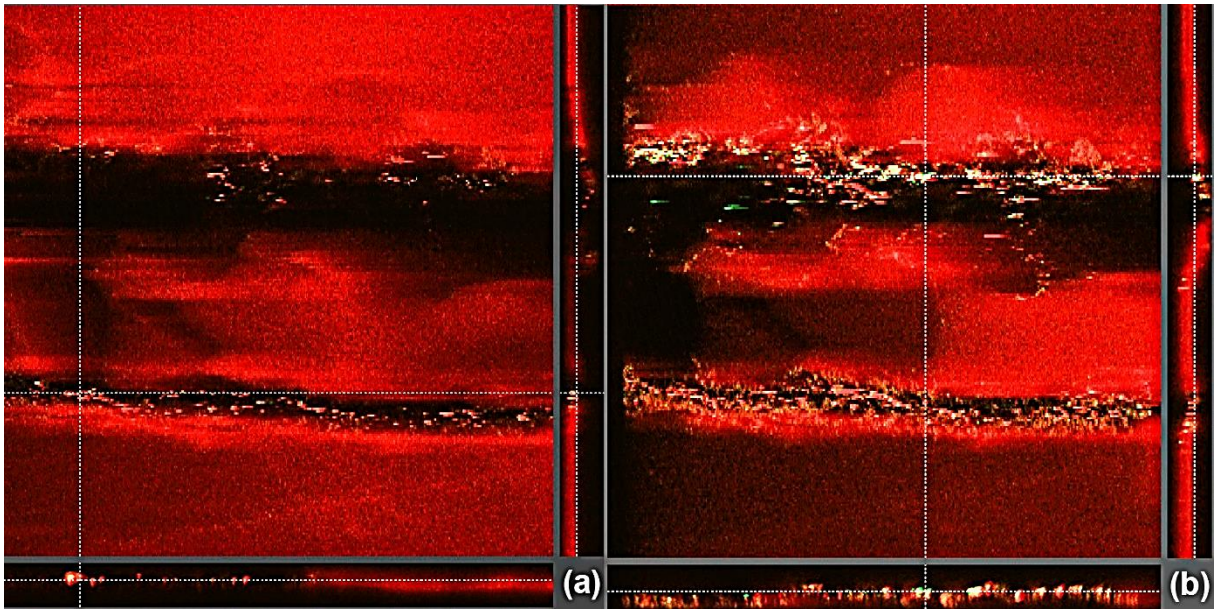

Figure 3. Two-photon microscopy projection images along the *xy* (center). *xz* (bottom) and *yz* (side) planes of the porous silicon surface at the etching time 10 min. Laser irradiation wavelength: (a) 800 nm, (b) 1 000 nm.

4. Conclusion

Multiphoton microscopy analysis of the mesoporous silicon obtained under different anodization time reveals the presence of different types of photoluminescence centers located differently on the surface of the porous layer and excited at different wavelengths. Separate nonuniform photoluminescence regions (spots size is about 15–25 μm) are predominantly formed at short anodizing times (up to 2–3 min) under the certain technological conditions. With an increase in the anodization time, the entire porous silicon layer exhibits a fairly uniform photoluminescence. In this case, both types of photoluminescence are simultaneously observed at inhomogeneities of the surface of the porous layer (edges, scratches). Study of the wavelength affection of exciting laser radiation in the range of 780–1000 nm made it possible to excite photoluminescence centers of various natures with a higher spectral accuracy. It was found, that the number of emitting centers and their brightness in the short-wavelength part of the spectrum increases with the increasing wavelength of the exciting radiation, which are not excited when irradiated with shorter-wavelength light.

Acknowledgements

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