Investigating Structural, Electrophysical and Optical Properties of Porous Silicon Nanopowders

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Abstract: We investigated the optical and electrophysical properties of porous silicon (PS) nanoparticles in a multigranular structure. Analysis using transmission electron microscopy, Raman spectroscopy, photoluminescence and current-voltage measurements enabled us to establish that quantum size effects were more pronounced in the structure under study than in the PS layer on the substrate.

Keywords: porous silicon (PS), Raman spectroscopy, photoluminescence (PL), current-voltage characteristic (CVC), polycrystalline structure (PCS), scanning electron microscope (SEM), transmission electron microscope (TEM).

Introduction

In 1990, the discovery of new properties of porous silicon (PS), such as photoluminescence (PL) at room temperature, has predetermined the promising prospects of PS research for optoelectronic devices, gas sensors, biosensors, antireflection coatings, etc. The technology allows obtaining the nanostructured PS, which may open up new possibilities for its use [1].

Despite the interest to PS, such issues, as the physical luminescence model and actual possibilities of using PS in devices remain uncertain. One of the reasons is the volumetric complexity of PS structure, which does not allow structural and physical measurements of its elements. In our study, we attempted to increase the accessibility of PS structure for detailed investigation *via* removing its layer from the substrate and transforming it into nanopowder. The latter can be studied using the conventional methods of nano materials science.

Materials and Methods

First, a PS layer on a p-type monocrystalline silicon substrate with an electrical resistivity of 10 Ω*cm was produced *via* anodizing electrochemical method, using the technology described in [2]. Further on, the PS layer was mechanically scraped off the substrate, crushed by powerful localized ultrasound into particles, which were deposited from a suspension onto glass or metal substrate *via* the technique of self-assembly ensembles on the surface with controlled evaporation of the solvent. The nanoparticle layer was a polycrystalline structure (PCS).

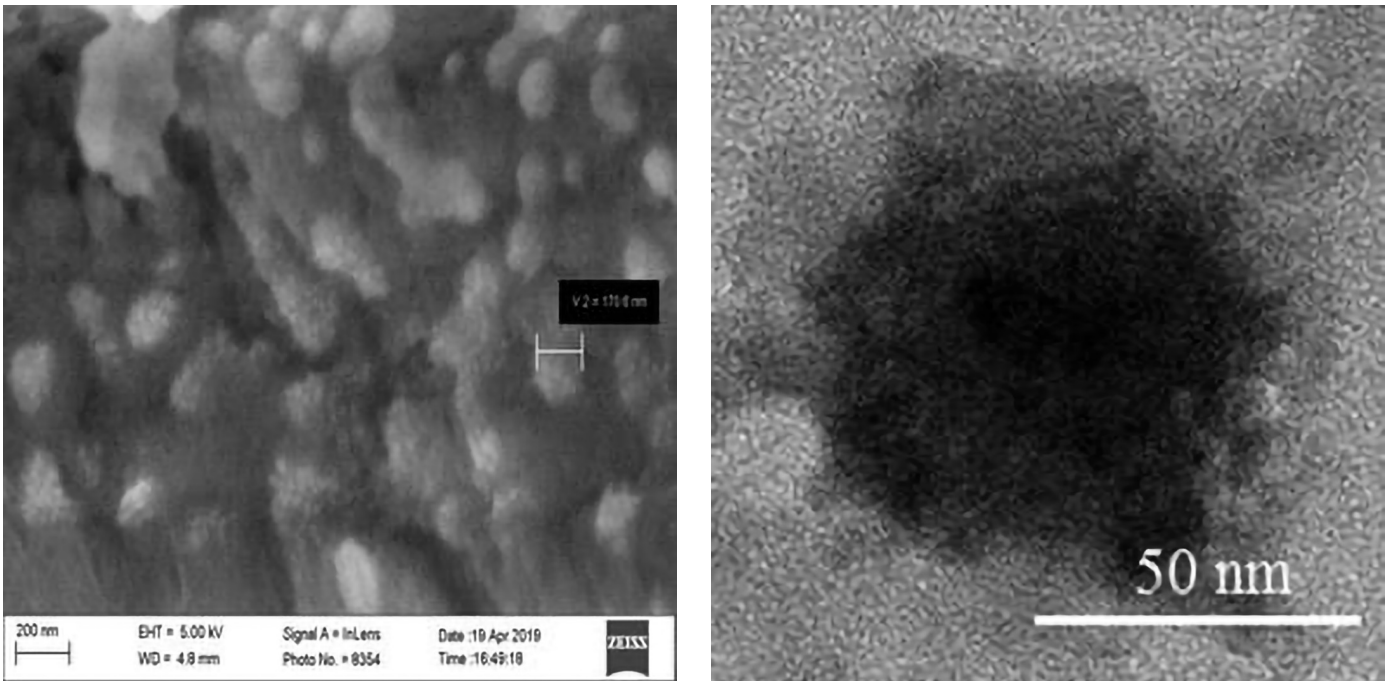

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Figure 1. Transmission electron microscopy images of porous silicon nanoparticles (a) and pore (b)

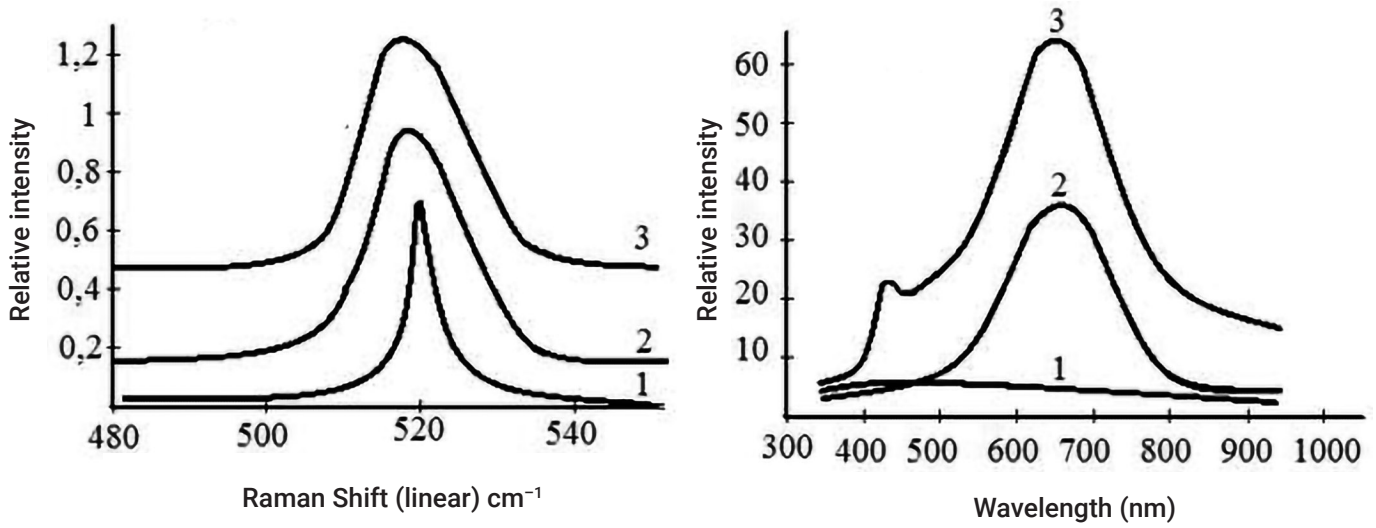

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Figure 2. Raman shift (a) and photoluminescence (b): 1 – substrate, 2 – porous silicon layer, 3 – porous silicon nanoparticles

The shape and size of the particles was monitored with electron microscopes: scanning electron microscope (SEM) ZEISS SIGMA VP and transmission electron microscope (TEM) LIBRA® 120. Most of them were flattened petals 30-500 nm in diameter and several nanometers thick (Figure 1).

The structural features were investigated by the method of Raman scattering spectroscopy (RSS). The half-width of the main Raman peak of the nanopowder was 6.25 cm^{-1}, which was three times as much as for the original silicon (1.95 cm^{-1}) and 1.5 times greater than for PS on monocrystalline

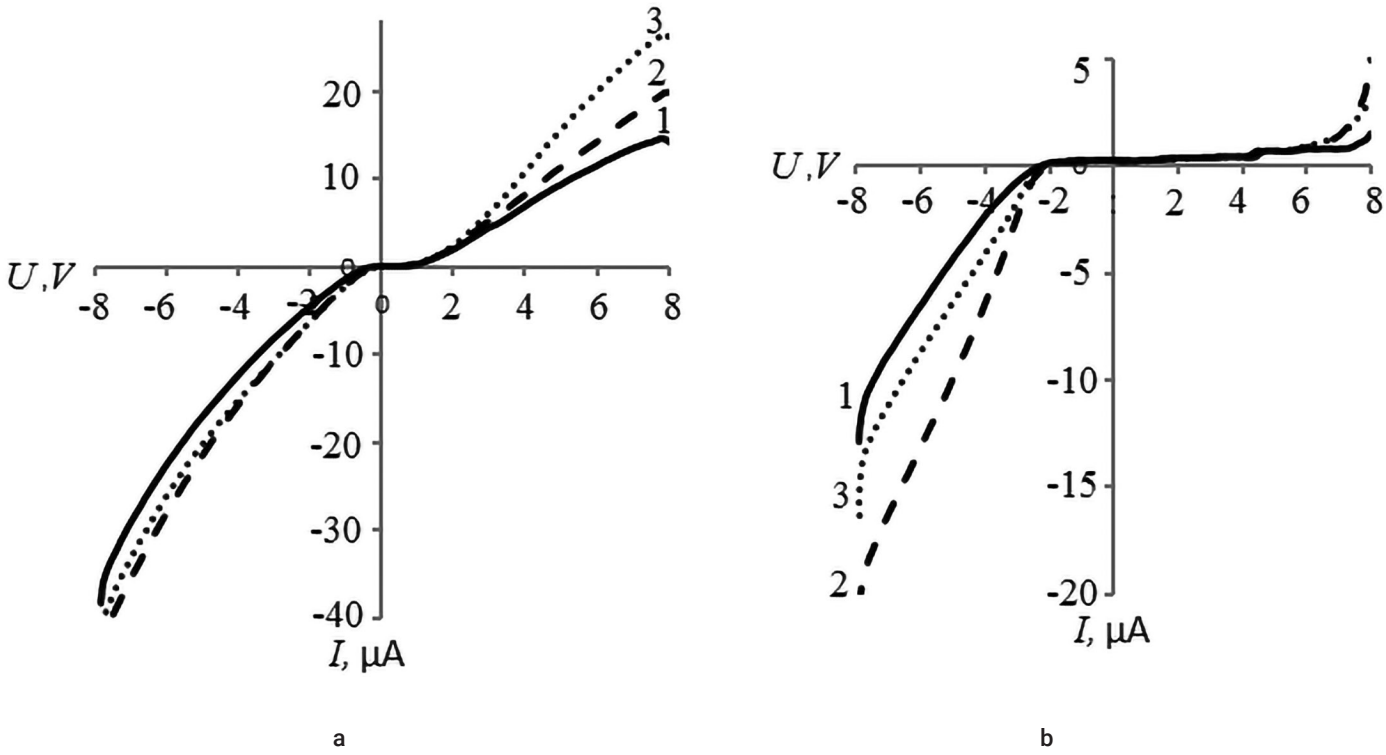

Figure 3. Effect of light on current-voltage characteristics of porous silicon nanoparticles: 1 – without light, 2 – filament lamp, 3 – violet (405 nm)

substrate (4.64 cm^{-1}). This means that there was an effect provided by a decrease in the quantum size of PS nanoparticles, as compared to its layer on the substrate.

Current-voltage characteristics (CVC) of the PCS-PS were investigated. For measuring the CVC of PCS, we used a non-standard generator of unipolar low-frequency pulse sawtooth voltage up to 300 V, pulse duration of 500 μs, and a duty cycle of 128. The parameters of the circuit elements and the regimens were selected, taking into account the absence of impact of the reactive components on the CVC. The parameters of the circuit elements and modes were selected taking into account the lack of influence on the CVC of the reactive components, and the transients were monitored by oscillograms. The methodology was described in detail in our earlier publication [3].

Results

Figures 3 and 4 show the current-voltage characteristics in linear and characteristic coordinates. The CVC were nonlinear, they depended on illuminance, and varied greatly after the storage in open air. After a carefully conducted procedure of approximation in Microsoft Excel, it has been established that, at voltages up to 5 V, CVC approached the power function $I \sim V^c$ with the exponent value c~2.1 (Figure 4a), whereas in the interval (5-15) V, CVC approached the expression $I \sim \exp[-b/V]$ (Figure 4*b*). These results disagree with the data of [4, 5] for a PS layer on a silicon substrate, in which the current-voltage characteristics were inferred by the dependences $I \sim \exp[aV]$ and $I \sim \exp[cV^{1/2}]$. We explain the difference by the fact that, in our case, as well as for nanoparticles of other materials, intergranular tunneling processes through the near-surface barrier ($I \sim \exp[-b/V]$) and current limitation by the surface charge of nanoparticles are limiting factors for electron transport [3].

PL spectra (Figure 2b) were recorded on the MDR-41 monochromator with interchangeable diffraction gratings. A halogen lamp was used as a source of exciting radiation in the visible and near-infrared ranges, while photomultiplier tube PMT-62 served a photodetector. The measurements were carried out step by step: for PS in suspension and for PS on a substrate with multiple measurements as the solvent was drying out. As the solvent was drying, the PL quantum yield was growing almost tenfold. In

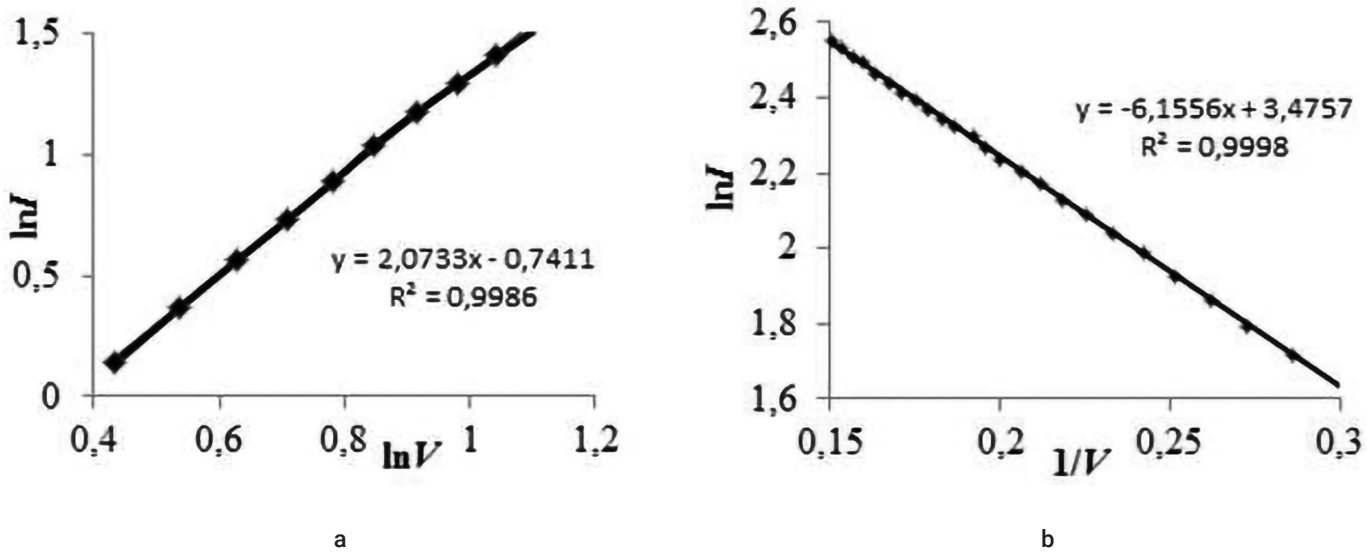

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Figure 4. Current-voltage characteristics of polycrystalline structure in typical coordinates

the nanopowder, the PL intensity was several times higher than in the PS film (Figure 2b), from which it was obtained. In the nanopowder, the PL intensity was several times higher than in the PS film (Figure 2b), from which it was obtained.

The wavelength of the PL spectrum maximum of the PC λ_{max}~657 nm, which corresponds to the calculated value of the band gap E_g~1.89 eV [5], the spectrum half-width $\Delta\lambda$~215 nm. For the PCS-PS, λ_{max}~649 nm (slightly shifted to the shortwave region), E_g~1.91 eV, and the half-width is slightly increased ($\Delta\lambda$~223 nm). Calculations of crystallite sizes corresponding to λ_{max}, according to the formulas presented in [5], gave values of 2–2.5 nm. For PCS-PS, we observed the short-wavelength 477-nm shoulder with a half-width of 121 nm (Figure 2b). According to [5], the size of nano-crystallites in that case was ~1 nm, and E_g~2.6 eV. The observed reduction in the size of nano-crystallites due to PL correlates with the data obtained from RSS.

Discussion

Thus, all obtained results indicate that PS in the nanopowder form has somewhat better size quantization properties. This finding can be explained by the fact that, in the layer on the substrate, the dimensional restriction for an electron acts only in one coordinate direction – perpendicular to the surface of the nanopore; whereas in a crushed version, it acts in all three directions. In this case, the smaller the nanoparticle size, the better the effect should manifest itself. These considerations can be confirmed by the following model representation.

Porous silicon is a layer up to tens of microns thick on a monocrystalline substrate, comprising submicron pores. The latter are separated by nanoscale monocrystalline septa coated with a reaction product, mainly silicon oxides, and a medium of molecular gas layer surrounding the sample. In such structure, electron-hole processes occur precisely in a silicon septum.

In this case, the surface boundary and the sorbed layer will influence the electron trapping centers, as well as a limiting shell of the quantum-size layer and process. The silicon septum itself luminesce only if it has quantum-size properties. For this reason, it is possible to have photoluminescence in a relatively simple and reliable way virtually solely on a single variant of the substrate (p-type with a with an electrical resistivity of several Ω*cm). Also, this makes the transition energies twice as large as for the monocrystalline silicon substrate.

Conclusion

There is just one direction of dimensional limitation of charge carriers in a nanoscale septum: perpendicular to the septum plane. When a layer is crushed into the nanopowder, nanoparticle boundaries start additionally restricting the carrier movement to some extent. Therefore, the studied quantum effects are more pronounced in the structure with nanoparticles.

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