КРАТКИЕ СООБЩЕНИЯ

НАУЧНЫЙ

ОТДЕЛ

Nanostructured Porous Silicon Layers Formation at Low Doses of γ-Radiation

O. Ya. Belobrovaya, V. V. Galushka, A. L. Karagaychev, E. A. Zharkova, V. P. Polyanskaya, V. I. Sidorov, D. V. Terin, A. A. Mantsurov

Olga Ya. Belobrovaya, https://orcid.org/0000-0002-9160-8702, Saratov State University, 83 Astrakhanskaya St., Saratov 410012, Russia, lab32@mail.ru

Victor V. Galushka, https://orcid.org/0000-0002-0980-7826, Saratov State University, 83 Astrakhanskaya St., Saratov 410012, Russia, gwiktor@mail.ru

Andrey L. Karagaychev, https://orcid.org/0000-0002-3010-7648, State Health Institution “Regional Clinical Oncology Dispensary”, Saratov 410001, Russia, carandleo@gmail.com

Elvira A. Zharkova, https://orcid.org/0000-0002-6501-5479, Saratov State University, 83 Astrakhanskaya St., Saratov 410012 Russia, lab32@mail.ru

Valentina P. Polyanskaya, https://orcid.org/0000-0002-4773-527X, Saratov State University, 83 Astrakhanskaya St., Saratov 410012, Russia, lab32@mail.ru

Vasiliy I. Sidorov, https://orcid.org/0000-0002-8955-2105, Saratov State University, 83 Astrakhanskaya St., Saratov 410012, Russia, lab32@mail.ru

Denis V. Terin, https://orcid.org/0000-0003-2850-4406, Saratov State University, 83 Astrakhanskaya St., Saratov 410012, Russia, lab32@mail.ru

Anton A. Mantsurov, https://orcid.org/0000-0002-8416-682X, Saratov State University, 83 Astrakhanskaya St., Saratov 410012, Russia, lab32@mail.ru

We present results of experimental study of nanoporous Si (SiNP) structure formation by using the method of metal-stimulated chemical etching upon irradiation with small doses of γ-radiation directly in the process of production (*in situ*). It is shown that the radiation leads to an increase of the crystallization of SiNP structures obtained on previously irradiated substrates. Apparently, this can be explained by a decrease in the initial defectiveness of the silicon substrate due to irradiation with small doses of γ-radiation.

Keywords: porous silicon, metal-stimulated chemical etching, nanostructures, X-ray diffractometry, morphology, *in situ*, γ-irradiation, radiation dose, microstresses, scanning electron microscope, pores, crystallite size, control.

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Recently there has been an increase in interest in porous silicon (SiNP) nanowires which are obtained by the method of metal-stimulated chemical etching (EE method) [1–3]. This is due to the use of nanostructured porous silicon in modern electronics, optoelectronics, biomedicine as the materials for creating active substrates for giant Raman spectroscopy (SERS) [4–7], as well as for elaborating multifunctional resistive and capacitive devices [8, 9].

The morphology of nanostructures and their sizes can be controlled by selecting technological parameters, modifying the initial silicon or the final structure. Studying the influence of gamma radiation on the properties of crystalline materials has shown that there is a so-called effect of small doses ($D = 10^3 - 10^5$ R), in which, in contrast to large doses, the structure is ordered and, accordingly, the properties of the material are modified [10–12].

The explanation of this effect assumes the crucial influence of the initial crystal defect on the processes which are caused by radiation exposure. At the same time, it is supposed that at the first stage of exposure, point defect transformations prevail and result in a decrease in the initial defect. At the next stage of radiation exposure, the concentration of radiation defects grows and, as a result, they predominantly influence the semiconductor properties [9–18].

According to [11–18], the radiation treatment of the final nanostructures was carried out at the stage of substrate preparation and after the formation of a porous silicon layer. Taking into account that the substrate structure in SiNP is repeated for almost the entire formed layer, it is advisable to carry out a modification by irradiating both the substrate and the SiNP layer during its formation. This issue has not been considered in the literature known to us.

This work presents studies of the SiNP nanostructure formation upon irradiation with γ-radiation directly in the process of production (*in situ*).

P-type mono-crystal silicon with a resistivity of 4.5 Ω cm and a crystallographic direction of <111> was used to form porous silicon by the two-stage EE method on unirradiated and γ-irradiated substrates. The substrates were irradiated with bremsstrahlung-radiation of the electron accelerator of the SGU betatron at a maximum energy of $E_{\gamma\max} = 25$ MeV. Samples were placed in the beam center at the distance of 75 cm from the platinum inhibitory target. The exposure dose for substrate irradiation was 10, 20, 30, and 40 kR. SiNP structures were obtained by irradiating with bremsstrahlung-radiation from the Varian Unique medical linear electron accelerator of the Saratov Regional Oncology Center at an electron energy of 6 MeV. The radiation dose was 24 kR. The first stage of production consisted in the chemical deposition of silver on the surface of various substrates. The substrates were immersed in an aqueous solution of 0.01 $MAgNO_3$ and 5 MHF (1 min). Cuvettes with several unirradiated and irradiated substrates were placed in the irradiation chamber.

At the second stage, the treated samples were placed in an etching aqueous solution of 5 MHF, 0.5 MH_2O_2 and were irradiated. After processing, the samples were etched in a concentrated nitric acid for an hour. The surface morphology and the cleavage of SiNP samples were studied. The SiNP structural properties were studied on the base of measurements performed on the analytical complex MIRA 2 LMU scanning electron microscope (SEM) and the DRON-4 diffractometer using an X-ray tube with a copper anode (Cu-K_α), and the corresponding results were presented.

The PCPDFWIN database (v. 2.02, 1999, International Center for -Diffraction Data (JCPDS)) was used to analyze the diffraction patterns. The X-ray diffractometry allows to track changes in the crystal structure of samples and evaluate the effectiveness of γ-radiation. Fig. 1 shows a typical surface morphology of a SiNP sample which is obtained using the EE method on an irradiated substrate with dose of 30 kR (the etching time is 60 minutes).

The increase in the etching time leads to a better identification of the surface structure of the studied samples. While the diameter of the SiNP in their array was varied from about 40 to 300 nm, the diameter for each individual SiNP did not change significantly along the nanowire. The SEM measurement data processing enabled us to obtain a dependence of the etching depth of the SiNP on the etching time (Fig. 2).

The etching depth of the SiNP depends on the etching time. For the etching time from 20 to 50 minutes, the layer thickness of the SiNP did not depend on the radiation dose within the measurement error. When the etching time increased, the height of the SiNP pillars was increased sharply with growing radiation dose. The X-ray diffraction analysis of the substrates and nanosilicon samples without exposure and after exposure with γ-rays at the angle range of $2\theta \approx 28°$, 59°, 95° showed that the changes in the intensity for each angle were manifested individually. Diffraction patterns of irradiated with γ-radiation and unirradiated silicon substrates are shown in Fig. 3.

On the unirradiated substrate, a “bifurcation” of the diffraction peak is observed at $2\theta \approx 28°$ of the crystallographic direction Si <111> (Fig. 3, *a*, curve *1*) and thus indicates the presence of microstresses. If we assume that the splitting of the Si <111> peak is due to a disturbance of the crystallinity of monosilicon, it is removed by irradiating the substrate (Fig. 3, *a*, curve *2*). As a result of radiation treatment, the crystallization in the SiNP sample increases. Fig. 3 illustrates this situation.

The radiation treatment leads to an increase of the crystallization of SiNP structures which are obtained on previously irradiated substrates. The intensity of

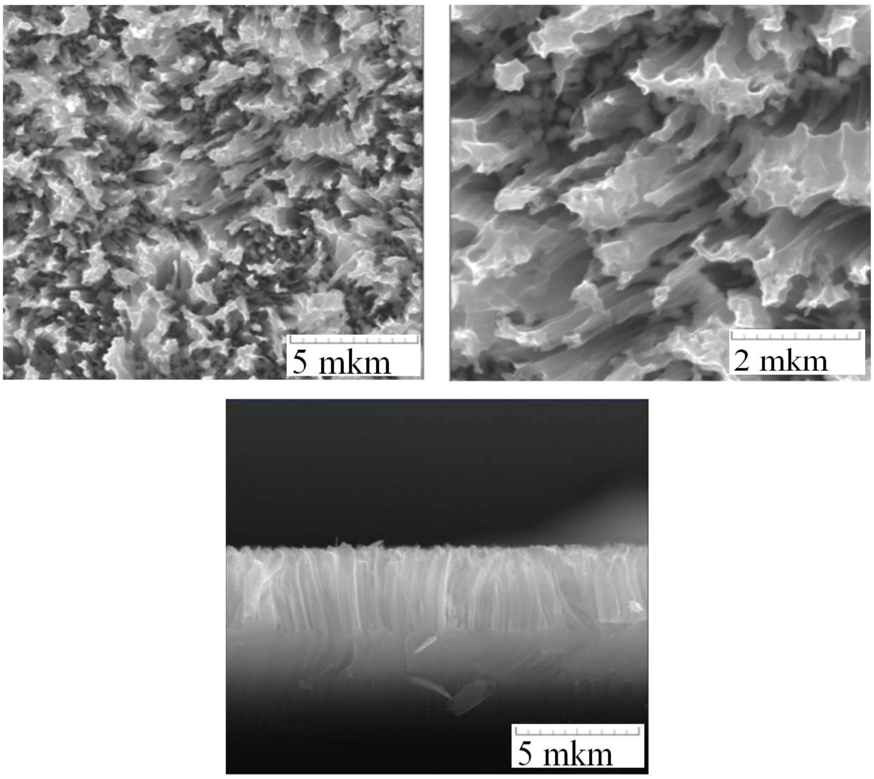

Fig. 1. Surface morphology and cleavage of a SiNP sample

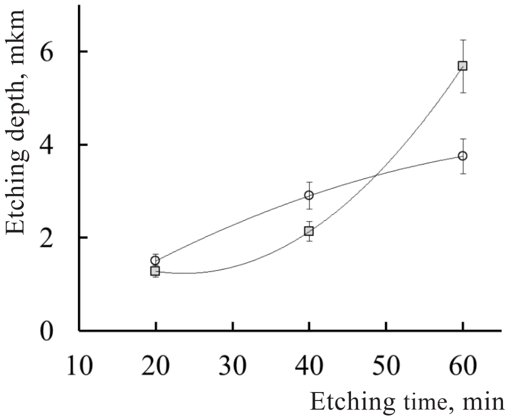

Fig. 2. Dependence of the etching depth of the SiNP on the etching time (irradiation of the substrate with γ-rays of 30 kR (circles) and 40 kR (squares))

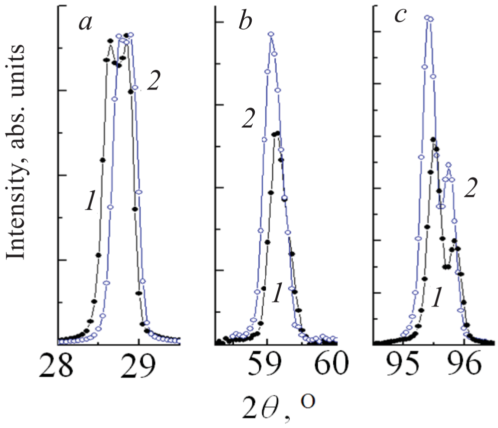

Fig. 3. X-ray diffraction patterns of SiNP samples of Si peaks <111> (*a*), <222> (*b*), <511> (*c*) obtained *in situ* on unirradiated (*1* – black circle) and irradiated (*2* – blank circle) substrates

the diffraction pattern peaks increases. The broadening of the peaks remains almost unchanged. The interplanar spacings of the samples for each crystallographic plane shown in Fig. 3 also differ. Moreover, for the <111> plane, the largest interplanar distance is observed in the sample which was not subjected to radiation treatment, while the smallest distance is evident for the sample obtained by irradiation on an irradiated substrate. The sizes of crystallites, which were defined from the diffraction patterns, are large enough and increase for the samples obtained *in situ*. The largest sizes were determined for a SiNP sample on an irradiated substrate.

Thus, the studies of the Si nanostructures formation under irradiation with gamma radiation directly in the production process (*in situ*) are presented. The X-ray phase analysis of the studied substrates before and after irradiation and the SiNP samples obtained *in situ* by the EE method revealed the removal of microstresses in the SiNP structure. Evidently, this is related to a decrease in the initial defectiveness of the silicon substrate due to irradiation with small doses of γ-radiation [12–18]. Due to the influence of γ-rays in the irradiation chamber and change *in situ* properties of the hydrofluoric acid aqueous solution, the rate of radiation-induced oxidation of samples also changed [10].

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Формирование слоев наноструктурированного пористого кремния при облучении малыми дозами γ-радиации

О. Я. Белобровая, В. В. Галушка, А. Л. Карагайчев, Э. А. Жаркова, В. П. Полянская, В. И. Сидоров, Д. В. Терин, А. А. Манцуров

Белобровая Ольга Яковлевна, ведущий инженер лаборатории микроэлектроники факультета нано- и биомедицинских технологий, Саратовский национальный исследовательский государственный университет имени Н. Г. Чернышевского, olgabel50@yandex.ru

Галушка Виктор Владимирович, научный сотрудник ОНИНС и БС, Саратовский национальный исследовательский государственный университет имени Н. Г. Чернышевского, gwiktor@mail.ru

Карагайчев Андрей Леонидович, начальник отдела медицинской физики, ГУЗ «Областной клинический онкологический диспансер», г. Саратов, carandleo@gmail.com

Жаркова Эльвира Александровна, старший научный сотрудник лаборатории микроэлектроники факультета нано- и биомедицинских технологий, кандидат физико-математических наук, Саратовский национальный исследовательский университет имени Н. Г. Чернышевского, lab32@mail.ru

Полянская Валентина Петровна, ведущий инженер лаборатории микроэлектроники факультета нано- и биомедицинских технологий, Саратовский национальный исследовательский государственный университет имени Н. Г. Чернышевского, polvalpet@gmail.com

Сидоров Василий Иванович, заведующий ЛЯФ и У, Саратовский национальный исследовательский государственный университет имени Н. Г. Чернышевского, lab32@mail.ru

Терин Денис Владимирович, доцент кафедры материаловедения, кандидат технических наук, Саратовский национальный исследовательский государственный университет имени Н. Г. Чернышевского, lab32@mail.ru

Манцуров Антон Андреевич, аспирант факультета нано- и биомедицинских технологий, Саратовский национальный исследовательский государственный университет имени Н. Г. Чернышевского, lab32@mail.ru

Приводятся результаты экспериментального исследования формирования структур нанопористого Si (SiNP) методом металл стимулированного химического травления при облучении малыми дозами γ-радиации непосредственно в процессе получения (*in situ*). Показано, что радиационное излучение приводит к увеличению кристаллизации структур SiNP, полученных на предварительно облученных подложках, и может быть связано с понижением исходной дефектности подложки кремния.

Ключевые слова: пористый кремний, металлстимулированное химическое травление, наноструктуры, рентгеновская дифрактометрия, морфология, *in situ*, гамма радиация, доза облучения, микронапряжения, дефекты, сканирующий электронный микроскоп поры, размеры кристаллитов.

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