Synthesis of Porous Silicon with Silver Nanoparticles by Low-Energy Ion Implantation

R. I. Batalov, V. F. Valeev, V. I. Nuzhdin, V. V. Vorebev, Yu. N. Osin, D. V. Lebedev, A. A. Bukharaev, A. L. Stepanov

Abstract—In this paper, a new technique is proposed for synthesis of porous silicon (PSi) layers with silver nanoparticles based on the method of low-energy high-dose metal ion implantation into Si. In order to demonstrate this technique, the implantation at room temperature of a polished Si wafer by Ag⁺ ions with the ion energy of 30 keV, ion dose of $1.5 \times 10^{17}$ ion/cm², and ion current density of 8 $\mu$A/cm² is carried out. Using methods of high resolution scanning electron and atomic-force microscopy, electron probe microanalysis, and Raman scattering, it is shown that ion implantation results in the formation, on the surface of irradiated Si, of a thin amorphous layer of PSi with the average pore size of 150–180 nm, a pore depth of about 100 nm, and wall thickness between pores of about 30–60 nm. Moreover, the PSi structure contains Ag nanoparticles 5–15 nm in size. It is established that, during the ion implantation, the sputtering of the Si surface by Ag⁺ ions takes place, which was not observed previously. Based on the data obtained, it is concluded that, in contrast to chemical techniques, the proposed physical technique for PSi formation can be integrated into the modern advanced process of fabricating and improving electronic circuits based on industrial ion implantation.

Keywords: porous silicon, silver nanoparticles, ion implantation, amorphization, surface sputtering

DOI: 10.1134/S1063739715080028

INTRODUCTION

Porous silicon (PSi) is a promising material used in micro-, nano-, and optoelectronics, which is also important for technological applications in sensorics, biosensorics, and solar batteries [1]. PSi was first discovered in 1956 as a by-product of the chemical etching of apertures in crystalline Si wafers. The discovery of PSi photoluminescence in the visible range at room temperature, which is explained by the quantum size effect for charge carriers, has drastically raised interest in PSi all over the world. Therefore, finding new ways of PSi formation and improving the presently available technologies for the synthesis of such structures offers a very interesting challenge today.

The common technique of PSi fabrication consists in the anodic electrochemical treatment of single-crystal Si in hydrofluoric acid solutions [1]. However, the technology for the formation of nanosized pores, cavities, and layers of porous materials in solids by high-dose ion implantation was also accepted a rather long time ago [2]. The effects of nanopore formation are extensively investigated especially for the metals used as the material for the first wall of fusion reactors. In semiconductor materials, particularly in Si, the effects of pore formation during ion implantation are investigated much more poorly.

As a rule, PSi was successfully formed on the surface of single-crystal Si by high-dose implantation only with inert gas ions. The solubility of inert gases in solids is very low and does not exceed the level of $10^{16}$ ion/cm³. Therefore, beginning with certain threshold doses of implantation, nanosized pores can be formed in an irradiated semiconductor by filling the local volume of the material with molecules from the implanted gas ions. In practice, the pore formation is enhanced by post-implantation thermal or laser annealing [2]. In other words, the formation of gas bubbles from ions implanted into the volume of the material results in the formation of nanopores, which are localized at the depth and on the surface of the semiconductor. Such a technique of pore formation in the near-surface region was demonstrated by implantation with Kr⁺, He⁺, and H⁺ ions [2–4]. PSi structures on the Si surface are identified with the help of a scanning electron or atomic-force microscopes. In this paper, a new technological approach for PSi formation based on metal ion implantation into Si is proposed.

Presently, a new direction in the field of nanoplasmics and nanophotonics is being intensively developed, which implies that, in order to encourage the manifestation of the optical properties of PSi (such as photoluminescence, reflectivity, and Raman scatter-
In order to form PSi layers simultaneously with the synthesis of silver nanoparticles, it is suggested here to use low-energy high-dose \( \text{Ag}^+ \)-ion implantation of single-crystal Si by analogy with the successful synthesis of the nanoparticles of various metals in dielectric matrices (inorganic glass, sapphire, or polymer) under irradiation by metal ions [9, 10].

**EXPERIMENTAL**

In order to obtain a structured composite PSi material, a wafer of single-crystal Si with \( \text{p} \)-type conductivity and crystallographic orientation (100) is used. The \( \text{Ag}^+ \)-ion implantation is performed with the energy of 30 keV, ion dose of \( 1.5 \times 10^{17} \) ion/cm\(^2 \), and ion current density of 8 \( \mu \)A/cm\(^2 \) on an ILU-3 ion accelerator. In order to estimate the sputtering or swelling of the surface, an additional experiment is carried out, in which a grid Ni-mask with square cells 20 \( \mu \)m in size is deposited on the Si wafer in the process of ion implantation to form a step between the radiation-irradiated and nonirradiated areas of the Si surface.

The examination of the surface morphology and the energy-dispersive X-ray (EDX) analysis of the implanted Si are carried out with the help of a Merlin (Carl Zeiss) high-resolution scanning electron microscope (SEM). An Aztec X-MAX energy-dispersive spectrometer (Oxford Instruments) is used for the elemental analysis in the SEM. The cross-section profile of PSi is measured with the help of Solver P47 (NT MDT) and FastSkan (Bruker) atomic-force microscopes (AFMs). The crystallinity of the implanted Si is estimated by Raman spectra, which are excited by a LGN-502 continuous argon laser (at the wavelength of 448 nm with the radiation power of 50 mW), and recorded at room temperature in the photon-counting mode of a DFS-52 spectrometer.

**RESULTS AND DISCUSSION**

Ion implantation is widely used in practice for the controlled doping of various metals, dielectrics, and semiconductors when energy-accelerated ions of various chemical elements are embedded into them [1]. Due to the specificity of this technique, in the process of irradiation, the ions implanted into the material being irradiated are distributed nonuniformly over the depth of a sample, which affects the localization of ion-synthesized nanoparticles [10]. Therefore, using the SRIM-2013 software package [11], the distribution profile of the silver ions implanted into Si for the acceleration energy of 30 keV is simulated. It is found that, at the initial period of irradiation, the accumulation of silver atoms takes place with the maximum statistical distribution of the concentration along the Gaussian curve being at the depth of \( R_p \sim 26.3 \) nm and the ion range straggling from \( R_p \), being \( \Delta R_p \sim 8 \) nm. However, as can be seen below, a long-term irradiation accompanied with the formation of PSi and by the segregation of silver at the surface results in the sputtering of Si.

Figure 1 shows the SEM images of the Si surface implanted with silver ions, which is demonstrated at different scales. As is seen from Fig. 1, in contrast to the original polished wafer, the morphology of the irradiated Si is characterized by the presence of a pronounced PSi structure. The PSi layer formed by ion implantation seems to be homogeneous over a large area (tens of micrometers) of the sample (see Fig. 1a), which is an importation characteristic (scalability) for a number of technological applications [1]. The magnified image of the surface fragment (Fig. 1b) allows one to estimate the average size of the pores (black regions), which is \( \sim 150–180 \) nm (see the size distribution histogram in Fig. 2), and the thickness of pore walls (gray regions), which is \( \sim 30–60 \) nm. The next magnified image (Fig. 1c) shows the ion-synthesized nanoinclusions with the average size of \( \sim 5–10 \) nm in the structure of PSi walls (light spots on the gray background of the PSi matrix). Since heavier (in terms of mass) chemical elements, which are recorded by the detector of backscattered electrons, appear in the SEM images in a lighter tone, it can be concluded that, for the composite material being analyzed (which consists only of Si atoms and implanted silver), the light (bright white) regions on the dark background (signal from Si) are due to the metallic silver in the form of nanoparticles. Note that silver atoms and Si together do not form any chemical compounds such as metal silicides (with cobalt, iron, etc.).

Measuring the optical Raman spectra of the irradiated and nonirradiated Si (see Fig. 3) shows that the peak, which is recorded at the frequency of \( \sim 520 \) cm\(^{-1} \) and is known [12] to be related to the optical phonon scattering of the crystalline Si matrix, completely disappears after ion implantation, thus characterizing the formed PSi layer as amorphous.

The EDX analysis of the PSi surface with two different phases (see the dark and light regions in Fig. 1c) shows that there are characteristic spectra with peaks from silver in the energy interval of 2.5–3.5 keV, which were not observed in the EDX spectrum of the nonirradiated Si. These data are consistent with the conclusion (from the SEM observation) about the formation of a two-phase system consisting of a Si matrix and silver nanoparticles.
The additional information confirming the formation of PSi in the process of the Ag⁺-ion implantation of Si is obtained from the AFM measurements. Figure 4 shows the AFM images of the PSi surface fragment, which are obtained in the imaging and phase contrast modes; these images seem to be typical for PSi structures [1]. The cross-section profile of the individual pores, which is measured in the direction marked in Fig. 4a, is presented in Fig. 4d. It allows one to estimate the depth of the pores, which is \( \approx 40–50 \) nm. Thus, it can be concluded that, as a result of the Ag⁺-ion implantation of Si, the typical pores are formed that are comparable with the relatively shallow pores in the PSi formed by the electrochemical method in highly dilute solutions of hydrofluoric acid [1]. The AFM image taken at the lateral illumination (see Fig. 4b) clearly shows that the silver nanoparticles are formed by ion implantation in the PSi structure. It should be noted, however, that, due to the convolution effect [13], the sizes of the nanoparticles in the AFM images seem to be somewhat overstated compared to their real sizes shown in the SEM images (Fig. 1).

In order to estimate the step which is formed at the interface between the irradiated and nonirradiated areas due to the sputtering or swelling of the surface in the process of ion implantation (particularly, when forming pores in semiconductors, for example, in Ge under irradiation by Ge⁺ ions), the method of mask ion implantation is traditionally used [14]. Figure 5 shows the SEM image of the Si surface, which contains fragments of the PSi microstructure formed by Ag⁺-ion implantation through a mask. It can be seen (Fig. 5) that, after ion implantation, rectangular areas of PSi (light regions) are formed on the Si surface; these PSi areas are bounded by the tracks (dark regions) of nonirradiated single-crystal Si.

Figure 6 shows the magnified image of the sample fragment in the corner region of the square mask cell at the Si–PSi interface. Obviously, in the process of Ag⁺-ion implantation and the formation of a porous structure, the effective sputtering of the Si wafer surface takes place. As a result, a cavity, which is a step at
Formerly, the sputtering and erosion of the Si surface were observed under irradiation by accelerated argon ions in the energy range of 50–140 keV, but without reporting about the formation of pores [15]. However, in this paper, it is shown that the Ag⁺-ion implantation results in the formation (in the irradiated area of Si) of a cavity and step due to the sputtering at the Si–PSi interface. This is important for determining the mechanism of PSi formation. At the same time, it is somewhat unexpected, since it is known that the opposite effect (swelling of the surface) was observed in the process of pore formation in the semiconductors (Ge) being implanted [9]. Therefore, the mechanism of pore formation in the germanium being implanted, which is based on the generation of vacancies in the irradiated semiconductor (which, in turn, unite into pores), cannot be simply applied to the Si matrix implanted with silver ions.
A new technique for forming PSi layers with silver nanoparticles on the surface of single-crystal Si by low-energy high-dose ion implantation is demonstrated. Ion implantation is now one of the basic technologies used in industrial semiconductor microelectronics for fabricating various types of Si-based microdevices and processors. For this reason, the proposed new physical technique of PSi formation, in contrast to chemical techniques, offers the advantage of easy integration into the modern advanced process of fabricating and improving electronic circuits.

For the first time, PSi structures with silver nanoparticles are formed by a nonchemical procedure. It is obvious that the next steps in improving such types of composite materials must involve optimizing the fabrication process, and in particular, finding the correlation between structural parameters and optical, plasmonic, photoluminescent, and sensory characteristics of the new porous structures.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 13-02-12012_ofi) and the Russian Science Foundation (project no. 14-13-00758).

We thank N.V. Kurbatova for her assistance in taking the Raman spectrum measurements.

REFERENCES

1. Izhenko, A.A., Fetisov, G.V., and Aslanov, L.A., Nanokremniy: svoystva, poluchenie, primenenie, metody issledovaniya i kontrolya (Nanosilicon: Properties, Formation, Application, Investigation and Control Methods), Moscow: Fizmatlit, 2011.

2. Kozlovskiy, V.V., Kozlov, V.A., and Lomasov, V.N., Modification of semiconductors by proton beams. A review, Semiconductors, 2000, vol. 34, no. 2, p. 123.

3. Lehmann, V. and Gosele, U., Porous silicon formation: A quantum wire effect. Appl. Phys. Lett., 1991, vol. 58, pp. 856–868. doi: 10.1063/1.104512

4. Stein, H.J., Myers, S.M., and Follstaedt, D.M., Infra-red spectroscopy of chemically bonded hydrogen at voids and defects in silicon, J. Appl. Phys., 1993, vol. 73, pp. 2755–2764. doi: 10.1063/1.353050

5. Amran, T.S., Hashim, M.R., Al-Obaidi, N.K., Yazid, H., and Adnan, R., Optical absorption and pho-
toluminescence studies of gold nanoparticles deposited on porous silicon, *Nanoscale Res. Lett.*, 2013, vol. 8, pp. 35–41. doi: 10.1186/1556-276X-8-35

6. Wang, Y., Liu, Y.P., Liang, H.L., Mei, Z.X., and Du, X.L., Broadening antireflection on the silicon surface realized by Ag nanoparticle-patterned silicon, *Phys. Chem. Chem. Phys.*, 2013, vol. 12, pp. 2345–2350. doi: 10.1039/C2CP44406B

7. Panarin, A.Y., Chirvony, V.S., Kholostov, K.I., Turpin, P.-Y., and Terekhov, S.N., Formation of SERS-active silver structures on the surface of mesoporous silicon, *J. Appl. Spectrosc.*, 2009, vol. 76, pp. 280–287.

8. Kreibig, U. and Vollmer, M., *Optical Properties of Metal Clusters*, Berlin: Springer, 1995.

9. Stepanov, A.L., *Ion-Synthesis of Metal Nanoparticles and Their Optical Properties*, New York: Nova Science, 2010.

10. Stepanov, A.L., *Fotonnie sredy s nanochastitsami sintezirovannymi ionnoi implantatsiey* (Photonic Media with Nanoparticles Synthesized by Ion Implantation), Saarbrücken: Lambert Academic, 2014.

11. Ziegler, J.F., Biersack, J.P., and Littmark, U., *The Stopping and Range of Ions in Solids*, New York: Pergamon, 1985.

12. Tyschenko, I.E., Popov, V.P., Talochkin, A.B., Gutakovsky, A.K., and Zhuravlev, K.S., Formation of nanocrystalline silicon layers by high dose H⁺ implantation into silicon layers on isolator and subsequent rapid thermal annealing, *Semiconductors*, 2004, vol. 38, p. 107.

13. Bukharaev, A.A., Nurgazizov, N.I., and Sugonyako, A.V., Wet etching of ion-implanted silicon dioxide monitored by atomic-force microscopy, *Russ. Microelectron.*, 2002, vol. 31, no. 2, pp. 103–109.

14. Romano, L., Impellizzeri, G., Tomassello, M.V., Gianazza, G., Spinella, C., and Grimaldi, M.G., Nanostructuring in Ge by self-ion implantation, *J. Appl. Phys.*, 2010, vol. 107, pp. 084314-1–084314-5. doi: 10.1063/1.3372757

15. Gerasimenko, N.N. and Parkhomenko, Yu.N., *Kremniy — material nanoelektroniki* (Silicon as Nanoelectronics Material), Moscow: Tekhnosfera, 2007.

*Translated by Yu. Kornienko*