Raman spectroscopy of silicon, doped with platinum and irradiated by protons

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1 Introduction

At present, single-crystal silicon is the main material for semiconductor microelectronics, optoelectronics, and power electronics, the rapid development of which determines the requirements for semiconductor devices [1].

Modern technology for the production of semiconductor microelectronic products, which is based on ion doping of the surface layer of silicon substrates, has reached the level of industrial production. An essential factor of this technology is the formation of defects under the influence of radiation exposure to protons and alpha particles and, as a result, their influence on the physicochemical characteristics of silicon substrates. The study of the structural perfection of irradiated silicon samples is an important factor in the selection of the technological mode of implantation in order to obtain controlled properties of the damaged layer for solving certain practical problems [2].
Three factors that affect the properties of semiconductors after proton irradiation are: change in the electrical properties, radiation defect formation, and the accumulation of hydrogen atoms [3].

In order to improve the efficiency of silicon photoelectronic converters, alloying elements are introduced into the composition of the functional layer. In particular, platinum forms effective recombination centers and can be used to optimize the lifetime of nonequilibrium current carriers in devices [4]. Silicon compensated with platinum has a high photosensitivity in the impurity region of the spectrum.

The aim of this work is to study the defect structure of silicon doped with platinum and irradiated with protons using Raman spectroscopy.

Raman spectroscopy is one of the most powerful non-destructive analytical methods for analyzing the chemical and phase state of various objects and their structure. The use of the method of Raman scattering of light (RSL), due to the patterns of change in their spectra, provides a wide range of parameters of the object under study. Therefore, Raman spectroscopy is an important method for determining the defect structure of single-crystal silicon, which makes it possible to estimate the size of nanocrystals, the ratio of the amorphous and crystalline phases from the shape and position of the Raman peaks, analyze the composition of crystals, and evaluate the deformation and stress in crystals [5].

2 Experimental part

The object under study was n-type silicon (n-Si) with a specific resistance of 5 ÷ 40 Ohm·cm, grown by the Czochralski method. The phosphorus dopant concentration in the initial n-Si single crystals was $8 \times 10^{13} \div 7 \times 10^{14}$ cm$^{-3}$. Doping of silicon with platinum was carried out by the diffusion method with deposition of platinum atoms on the silicon surface in evacuated quartz ampoules in the temperature range $T = 900 \div 1200 \, ^\circ$C for 2 ÷ 4 hours. Subsequent cooling of the samples was carried out at different rates [6–7].

The original (n-Si) and doped (n-Si<Pt>) samples were irradiated with protons with an energy of 600 keV at a current of 1.5 µA and a dose of $9 \times 10^{14}$ cm$^{-2}$ using the SOKOL EG-2 electrostatic accelerator at the Research Institute of Semiconductor Physics and Microelectronics.

The samples were studied using Raman spectroscopy on a CARS Raman Spectrometer manufactured by SOLAR TP in the range of 0 ÷ 3000 cm$^{-1}$. The measurements were carried out at room temperature. The elemental composition and micrographs of the studied samples were obtained using a Carl Zeiss EVO10 electron microscope (Zeiss, Oberkochen, Germany).

3 Results and discussions

Figure 1 shows the Raman spectra for single-crystal Si as a function of platinum doping and proton irradiation. The Raman spectrum of the original sample contains peaks at 304 and 522 cm$^{-1}$ characteristic of cubic silicon and a broad peak in the range of 928 ÷ 1002 cm$^{-1}$[8–12].

The cubic structure of diamond-type silicon (space group $O_{h}^{7}$) is known to allow the presence of one Raman-active first-order phonon corresponding to a wave number of 520 ± 1 cm$^{-1}$ (LTO), as well as additional, less intense peaks as a result of long-range translational symmetry [10,11]. According to [13,14], the vibration found at 304 cm$^{-1}$ in the Raman spectra of silicon is attributed to the longitudinal acoustic mode. A broad peak in the range of 900 ÷ 1100 cm$^{-1}$ was found experimentally for nanocrystalline [11,13,14] and single-crystal [12] silicon. This vibration is due to the scattering of several transverse optical phonons (2TO) and their overtone state [10,15,16]. As a result of the decomposition of the peak in the range of 900 ÷ 1100 cm$^{-1}$, a new peak at 981 cm$^{-1}$ was identified in [17].
using the Lorentz function, shown in Fig. 2a, three vibrations were found at 940, 955, and 982 cm\(^{-1}\), which is consistent with theoretical calculations [10].

Fig. 1. Raman spectra of single-crystal silicon. Further doping of Si single crystals with platinum leads to minor changes and the appearance of new vibrations in the Raman spectra. The intensity of the main silicon peak at 521 cm\(^{-1}\) decreases by a factor of 1.6, while its FWHM practically does not change and is about 4.0 cm\(^{-1}\). Such a decrease in the intensity of the peak is probably due to the weakening and breaking of bonds in the structure of the silicon crystal lattice due to the incorporation of Pt atoms. The vibration intensity at 304 cm\(^{-1}\) decreases by a factor of 1.8, and its FWHM decreases from 9.7 to 7.2 cm\(^{-1}\). As a result of the decomposition of the peak at 928–1002 cm\(^{-1}\) using the Lorentz function, three vibrations at 939, 950, and 981 cm\(^{-1}\) were also detected (Fig. 2b). The shift of these oscillations towards the smallest wave numbers compared to the initial silicon reaches 5 cm\(^{-1}\), with the largest shift undergoing vibration at 950 cm\(^{-1}\).
Fig. 2. Fragments of the Raman spectra of single-crystal silicon, approximated by the Lorentz function.

- a) initial Si single crystal;
- b, c) silicon doped with platinum;
- d) silicon doped with platinum after proton irradiation.

The change in the Raman spectrum of Si<sub>Pt</sub> in the range of 60–280 cm<sup>-1</sup> (Figure 2c) is due to the presence of elemental Pt and the formation of PtSi [17, 18, 20]. In [17], to quantitatively characterize the formation of PtSi at the interface between platinum and Si(100), multichannel Raman spectroscopy was used, where spectra were obtained from PtSi layers up to 10 Å thick and from <40 Å PtSi at 140 Å from Pt. According to this work, characteristic vibrations for PtSi appear at 82–85 and 140 cm<sup>-1</sup>. In [11], Raman modes near 90 and 140 cm<sup>-1</sup> from PtSi are also reported, where the latter mode is due to the formation of a disordered mixed phase of Pt and Si. The authors of [17] also noted that a more intense vibration of PtSi at 82 cm<sup>-1</sup> can hide a weak signal at 88 cm<sup>-1</sup> from a small amount of Pt<sub>2</sub>Si, provided that it is formed. It is shown that the FWHM of the Raman peak of fully reacted PtSi is less than 6 cm<sup>-1</sup>, while their initial reaction at room temperature shows wider Raman bands (more than 20 cm<sup>-1</sup>). The first value of FWHM is typical for well-ordered crystallized materials, while the second value is typical for materials in which there is a short-range/local order, but no long-range order [17,19]. The Raman vibration for Pt<sub>2</sub>, according to theoretical calculations, is at 218/225.59 cm<sup>-1</sup>[20,21]. This Raman peak corresponds to the stretching mode between two platinum atoms. In [20] and [22], the Raman spectrum of platinum in an argon matrix was obtained and single vibrations were observed at 234 and 217.2 cm<sup>-1</sup>, respectively. Pt<sub>3</sub> is characterized by Raman vibrations at 140.76/147 and 187.36/228 cm<sup>-1</sup>[20], where the first mode is due to stretching of two Pt–Pt bonds, while the third bond remains immobile. Another vibrational mode corresponds to the valence mode of three bonds in the ground state of the Pt<sub>3</sub> cluster. An <em>ab-initio</em> study [21] obtained vibrational modes for Pt<sub>3</sub> at 145, 215, and 290 cm<sup>-1</sup>. For Pt<sub>4</sub>, the Raman spectra exhibit vibrations at 27.66/29, 46.21/49, 172.71, 172.73, and 190.88/198 cm<sup>-1</sup>[21]. The lowest frequency vibrations for Pt<sub>5</sub>, Pt<sub>6</sub>, Pt<sub>7</sub>, Pt<sub>8</sub>, Pt<sub>9</sub>, and Pt<sub>10</sub> are observed at 18.76, 18.78, 11.43, 17.63, 26.08, and 33.48 cm<sup>-1</sup>, 199.94 and 202.68 cm<sup>-1</sup>, respectively [21]. Raman vibrations for Pt<sub>4</sub>, Pt<sub>5</sub>, Pt<sub>6</sub>, Pt<sub>7</sub>, Pt<sub>8</sub>, Pt<sub>9</sub>, Pt<sub>10</sub> were reported in [20] in the range of 10–215 cm<sup>-1</sup> with intense vibrations at about 240, 163, 240, 238, 170, and 160 cm<sup>-1</sup>, respectively. From the above, it can be assumed that the vibrations in the obtained Raman spectra of Si<Pt> at 86 and 146 cm<sup>-1</sup> are associated with PtSi, and at 71 cm<sup>-1</sup>, with elemental Pt (Figure 2c), while the FWHM of vibrations is about 86 and 146 cm<sup>-1</sup> is more than 20 cm<sup>-1</sup>, which may indicate the initial stage of PtSi formation [17, 18]. Raman vibrations at 108 cm<sup>-1</sup> (TA) and 249 cm<sup>-1</sup> (2TA (L)) can be associated with...
cubic Si, since it was noted in [17] that the signal from the silicon substrate and the PtSi surface layer is significantly reduced due to the attenuation of the unreacted platinum [10]. The presence of platinum in single crystals is also confirmed by X-ray spectral analysis, according to which the content of platinum in the samples is 2 at.% or 12 wt.%. The energy-dispersive spectra presented in Figure 3 indicate the presence of only platinum in the composition of the studied samples, no other impurity elements were found.

**Fig. 3.** X-ray spectral microanalysis of a silicon single crystal doped with platinum.

Micrographs of the surface of silicon doped with platinum clearly show the presence of nanostructures of a spherical shape, in the form of drops (Figure 4b). According to the maps of the distribution of elements over the surface, shown in Figure 5, the detected nanostructures correspond to the element platinum. As can be seen from the micrographs, when the Pt droplets are close enough to each other, they react and combine into larger formations [23]. At the same time, the morphology of the silicon wafers themselves did not change after the doping process (Figure 4a and b).

**Fig. 4.** Micrographs of the surface of Si single crystal wafers before (a) and after doping with Pt (b).
Fig. 5. Micrographs of the surface of a Si single crystal after doping with Pt with distribution maps.

The Raman spectrum for irradiated Si<Pt> samples has a form close to that of the initial single crystal. The fundamental vibration of silicon at 520 cm⁻¹ is characterized by a slight increase in intensity and a narrowing of FWHM to 3.3 cm⁻¹. FWHM fluctuations at 304 cm⁻¹ are 9.5 cm⁻¹, which is greater than for Si<Pt>, before irradiation. As a result of the decomposition of the peak at 928–1002 cm⁻¹ using the Lorentz function, three vibrations at 940, 951, and 979 cm⁻¹ were also detected (Fig. 2d). The existence of other vibrations in the obtained spectra was not found. For example, it was noted in [10] that vibrations at 430 and 830 cm⁻¹ in the Raman spectra of single-crystal Si, caused by the LO background at L critical points, may indicate its amorphous state or the existence of some kind of disorder, respectively.

It should be noted that the broad peak in the range of 60–280 cm⁻¹ associated with Pt and PtSi disappears in the Raman spectra of irradiated Si<Pt>. However, the presence of platinum on the surface of silicon single crystals is confirmed by scanning electron microscopy in combination with X-ray spectral microanalysis. According to the element distribution maps shown in Figure 6, the surface of irradiated Si<Pt> also contains nanostructures in the form of droplets caused by platinum. However, the size of some droplets is increased compared to non-irradiated samples (Figure 4b) and a porous structure is characteristic (Figure 7, inset). In addition, from the micrograph presented in Figure 7, changes in the surface morphology of silicon platinum plates after their irradiation with protons are clearly visible. Cracks and pores appear on the surface, and its smoothing occurs as a result of heating the material [26].
Fig. 6. Micrograph of the surface of a single crystal Si<Pt> after irradiation with protons with a map of the distribution of elements.

Fig. 7. Micrograph of the surface of Si<Pt> single crystal plates after proton irradiation.

In [24], a review of radiation defect formation in silicon carbide is presented. The authors noted that a change in the properties of semiconductor materials as a result of exposure to proton irradiation can occur due to radiation defect formation, the formation of new impurities as a result of nuclear reactions (radiation modification) and the accumulation of hydrogen atoms. When the surface of samples is bombarded with protons with energies up to 50 MeV, a large number of initially displaced atoms can be created due to elastic scattering by atoms and nuclei of the substance. At the same time, at proton energies above 50 MeV, the process of transmutation doping of semiconductors due to nuclear reactions can occur [24]. In addition, simple defects are formed in the initial sections due to the inhomogeneous distribution of defects over the depth of the material along the proton path, and at the end of the path, clusters are formed or electrons are captured with transformation into a hydrogen atom [24]. It was noted in [25] that some of the defects in the irradiated material can combine to form clusters of dislocation loops, stacking fault tetrahedra, and pores.

The presence of platinum atoms in silicon significantly affects both the rate of introduction and the temperature stability of the dominant radiation defects (vacancy–oxygen pairs, divacancies, and vacancy–oxygen–hydrogen complexes) [27]. The disappearance of vacancy–oxygen pairs and vacancy–oxygen–hydrogen complexes during annealing and an increase in the platinum content in silicon is accompanied by the generation of a number of new electrically active and more stable defects [27]. In this case, as the silicon irradiation...
dose increases, the degree of activity of doped Pt atoms decreases [28]. This is due, on the one hand, to the fact that diffusing platinum in the interstices is transformed into a replacement configuration on the way to the area of maximum damage. On the other hand, high-dose irradiation can lead to the formation of V\textsubscript{Pt} complexes whose activity differs from that of the substituting Pt. It was noted in [28, 29] that the amount of platinum induced by radiation due to defects at a low dose of proton irradiation increases with an increase in the irradiation dose. But when the dose of proton irradiation is high enough, the peak concentration of gettered platinum tends to saturate.

In our case, using Raman scattering, no changes were detected in the crystal structure of Si<Pt> single crystals after irradiation with protons at a dose of 9 \times 10^{14} \text{cm}^{-2} with an energy of 600 keV, except for the disappearance of the Raman band 60–280 cm\textsuperscript{-1} associated with Pt and PtSi.

4 Conclusion

An analysis of the results obtained using Raman spectroscopy shows that the introduction of Pt atoms into the Si lattice leads to insignificant changes and the appearance of new vibrations in the Raman spectra of the samples. The decrease in the intensity of the peaks belonging to silicon is probably due to the weakening and breaking of bonds in the structure of the silicon crystal lattice due to Pt atoms. The appearance of new vibrations in the range 60–280 cm\textsuperscript{-1} in the spectra of Si<Pt> is associated with the presence of elemental Pt and the formation of PtSi. Further irradiation of Si<Pt> samples with 600 keV protons leads to a change in the Raman spectra, and the peaks from Pt and/or PtSi disappear. However, the presence of platinum on the surface of irradiated Si<Pt> is confirmed by scanning electron microscopy and X-ray spectral microanalysis. However, the size and structure of platinum nanoformations are changed.

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References

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