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Determination of solubility of cobalt in singlecrystal silicon method neutron activation

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The possibility of instrumental neutron activation analysis is revealed for determining the solubility of cobalt in single-crystal silicon. It was shown that in *n*-Si in the diffusion temperature range of 1000−1250°C the total solubility of the ^{60}Co impurity varies within the concentration range of $2.8 \cdot 10^{14}-9 \cdot 10^{15}\,\text{cm}^{-3}$, and the electrically active concentration grows from 10^{13} to $3 \cdot 10^{14}\,\text{cm}^{-3}$. In order to reduce the error in determining the concentration of 10^{13} in doped Si samples, it is suggested to use the parent stable isotope rather than the daughter cobalt radionuclide.

Keywords: monocrystalline silicon, cobalt impurity, diffusion, neutron activation analysis, solubility, irradiation, radionuclide, concentration.

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1. Introduction

One of methods to modify properties and parameters of semiconductor materials is their doping with impurities that form deep energy levels in the band gap of the crystal [1]. Usually, these impurities are doped in the process of crystal growing from liquid phase, during ion implantation of epitaxial layer, by the nuclear transmutation method, by the diffusion annealing with applied layer of the doping agent or from gaseous medium.

The most adaptable to streamlined production, controllable and widespread method among the listed above is the method of thermodiffusion that features the technological advantage of control over the concentration and depth of the doping agent in the samples body via measurement of temperature and time of diffusion in a wide range. The most extensively studied doped semiconductor crystals include single crystal silicon. Manu studies [1–4] have been devoted to the investigation of solubility, coefficient of diffusion, behavior of different doping agents that form deep defect centers and their effect on electrophysical properties, recombinational, photoelectric and other properties of silicon. The change in the above-mentioned properties is mainly determined by concentration the doped element, and the later depends on its solubility in the crystal. The analysis of literature information on fast diffusing doping agents shows, that depending on the type of doping chemical element its solubility in silicon in the range of diffusion temperature of 800−1250°C varies within $5 \cdot 10^{13}-10^{18}\,\text{cm}^{-3}$ [3–5]. For a number of elements, depending on concentration solubility of the doping agent under study with $T_\text{D} > 1250°\text{C}$ a retrograde behavior of the change is observed [2,5]. The impurities doped into silicon manifest donor, acceptor or amorphous property changing electrophysical characteristics of the crystal, such as electrical conductivity, type of conductivity, concentration and life time of current carriers [1,3]. However, as experimental findings show, the change in the above-mentioned characteristics is determined to a significant extent by the doping agent content. The comparison of total concentrations of dissolved impurities [5–8], for example, cobalt, at identical temperatures of diffusion shows that this difference can be as high as one and a half order of magnitude or more, especially in the region of diffusion temperatures of $T_\text{D} \geq 950°\text{C}$ [3], which may be due to the use of different techniques by authors of [5–8] without taking into account features of the impurities and the dependence of detection limit on the impurity to be determined [9].

Among the existing techniques to determine concentration of dissolved elements in silicon the most sensitive and informative is the monitoring of impurity content by neutron activation analysis. Authors of [10], by optimizing the size of samples and parameters of the neutron beam, the time of exposure and conditions of the analysis, have achieved a detection limit of up to 10^{-14} mass% for some chemical elements.

In [5–9] the radioactive tracer method or activation analysis has been used to study solubility and state of Co in the silicon lattice. In these studies, depending on the method used, the concentration of ^{56}Co radionuclide was determined after high-temperature diffusion of the doping agent from the applied layer of CoCl_2 solution contained ^{56}Co [8], and in [5] the ^{60}Co radionuclide was monitored after the exposure of the doped silicon to neutron irradiation. In the first case the ^{56}Co was produced from iron by the ^{56}Fe$(p, 2n)^{56}$Co reaction (after irradiation by protons in a cyclotron), and in the second case the ^{60}Co was formed under neutron irradiation after thermodiffusion doping of the silicon from the applied metal layer of ^{59}Co, a natural stable isotope.

In both cases the concentration of cobalt in silicon was monitored by measurement of the content of ^{56}Co or ^{60}Co radionuclide. However, the obtained experimental results for the solubility of cobalt in silicon are considerably different [3].

The purpose of this study is to apply the instrument neutron activation analysis to determine the total solubility of cobalt doping in the thermodiffusion-doped silicon by measurement of the content of ^{60}Co radionuclide after neutron irradiation in a WWR-SM nuclear reactor. The ^{59}Co was chosen for silicon doping due to its acceptor property, that allows producing compensated *n*-Si with different specific electrical conductivities, and the ^{60}Co radionuclide in Si is a source of gamma-radiation and can be used as a low-level reference isotope.

2. Experimental results and discussion

Samples of *n*-type single crystal silicon of KEF grade with $\rho \approx (2-10)\Omega \cdot$ cm were studied. Cobalt was injected into silicon from the metal layer of ^{59}Co sputtered in vacuum on the surface of cleaned silicon samples by heat treatment (diffusion of ^{59}Co) in the temperature range of 950–1250°C for 0.5–10 h. After removal from the metal inhomogeneous layer with a thickness of $\geq 110\,\mu$m from the surface of samples, specimens were produced from the resulted doped crystal with uniform distribution of Co in the Si body for the measurements of electrophysical parameters and cobalt concentration. Electrophysical parameters of specimens were measured by the Hall method and the ^{60}Co content was measured by neutron activation analysis (NAA).

Experimental data of the distribution of $N_{\mathrm{Co}^{60}}$ concentration profiles for samples of Si$\langle^{59}$Co$\rangle$ diffusion-doped at $T_{\mathrm{D}} = 1050$ and 1250°C for 10 h after successive removal of layers with a thickness step of $50\,\mu$m of sample depth are shown in Fig. 1. It can be seen from the obtained results, that the change in the profile of total concentration of cobalt $N(x)$ in the studied samples of *n*-Si has an *U*-shaped form and $N(x)$ in the homogeneous region within the specified temperature range varies from $2.8 \cdot 10^{14}$ to $9 \cdot 10^{15}\,\mathrm{cm}^{-3}$. The temperature dependence of current carrier concentration in doped samples of *n*-Si$\langle^{59}$Co$\rangle$ measured by means of Hall effect has shown that cobalt manifests acceptor properties forming deep centers with the ionization energy of $E_c - 0.41$ eV and $E_c - 0.53$ eV in the top half of the band gap of silicon, which is well compliant with the data of [3]. It is found that the above-mentioned centers in *n*-Si result in the capture of main current carriers and an increase in the specific resistance of the initial samples.

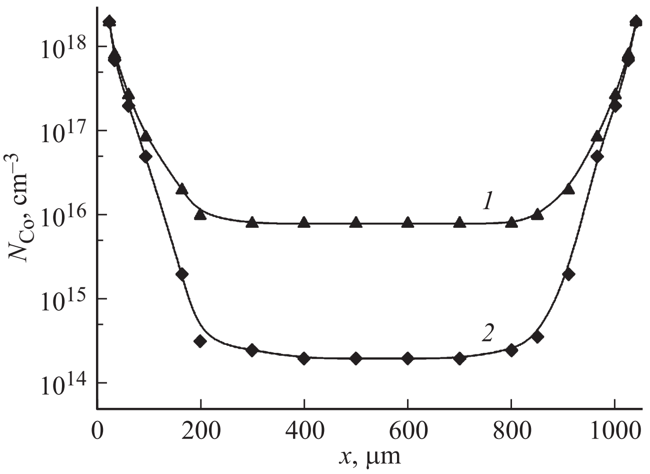

Figure 1. Distribution of the total concentration of cobalt over the depth of the doped silicon after diffusion at $T_{\mathrm{D}} = 1250$ (*1*) and 1050°C (*2*) for 10 h.

The measurement of electrophysical parameters of samples after diffusion doping of silicon (Si$\langle^{59}$Co$\rangle$) in the temperature range of 950–1250°C has shown that the specific resistance (ρ) increases and at $T_{\mathrm{D}} = 1250$°C it reaches the value of $\sim 120\,\Omega \cdot$ cm, and in undoped samples after annealing at the above-mentioned temperature of T_{D} the ρ remains nearly unchanged. This shows, that the cobalt doping in silicon mainly manifests itself as an acceptor property, not as an amorphous property as it is shown in [8], and results in a decrease in concentration of electrons in *n*-Si. The manifestation of acceptor property of Co in Si has been noted in [3–8] as well, where the change in electrophysical parameters of silicon is connected with the capture of electrons by deep levels located in the top half of the band gap of Si with the ionization energy of $E_c - 0.41 \pm 0.02$ eV and $E_c - 0.53 \pm 0.02$ eV. However, according to some data [4,6], the doping of Si with Co can form a donor center as well with $E_c - 0.21 \pm 0.02$ eV, depending on the rate of cooling of samples after the thermodiffusion of the doping agent. At the same time, it has been found that the total concentration of electrically active centers of Co in Si is not greater than 0.02% of the total solubility of the doping agent in silicon.

The study of the total solubility of Co in silicon by the method of instrument neutron activation analysis was carried out after the irradiation in the channel of reactor up to a neutron fluence of $2 \cdot 10^{19}\,\mathrm{cm}^{-2}$. For the irradiation, 4 sets of Si$\langle$Co$\rangle$ samples doped in the temperature range of 1000–1250°C with a step of 100°C and reference samples of Al:Co alloy with a metal cobalt content of 0.01 by weight were prepared. Sizes of the irradiated Si$\langle$Co$\rangle$ samples were $12 \times 4 \times 0.8$ mm and density of the thermal neutron flux was $8.8 \cdot 10^{12}\,\mathrm{n/cm}^{-2} \cdot \mathrm{s}$. Temperature of samples during the irradiation was not more than 60°C. The intensity of gamma-line of irradiated samples was measured by a semiconductor gamma-spectrometer with a DGDK-100 AUP-1 K8 „Aspekt“ detector equipped with the „Angamma“ software that allows for direct comparison to the spectrum of the reference target irradiated in parallel.

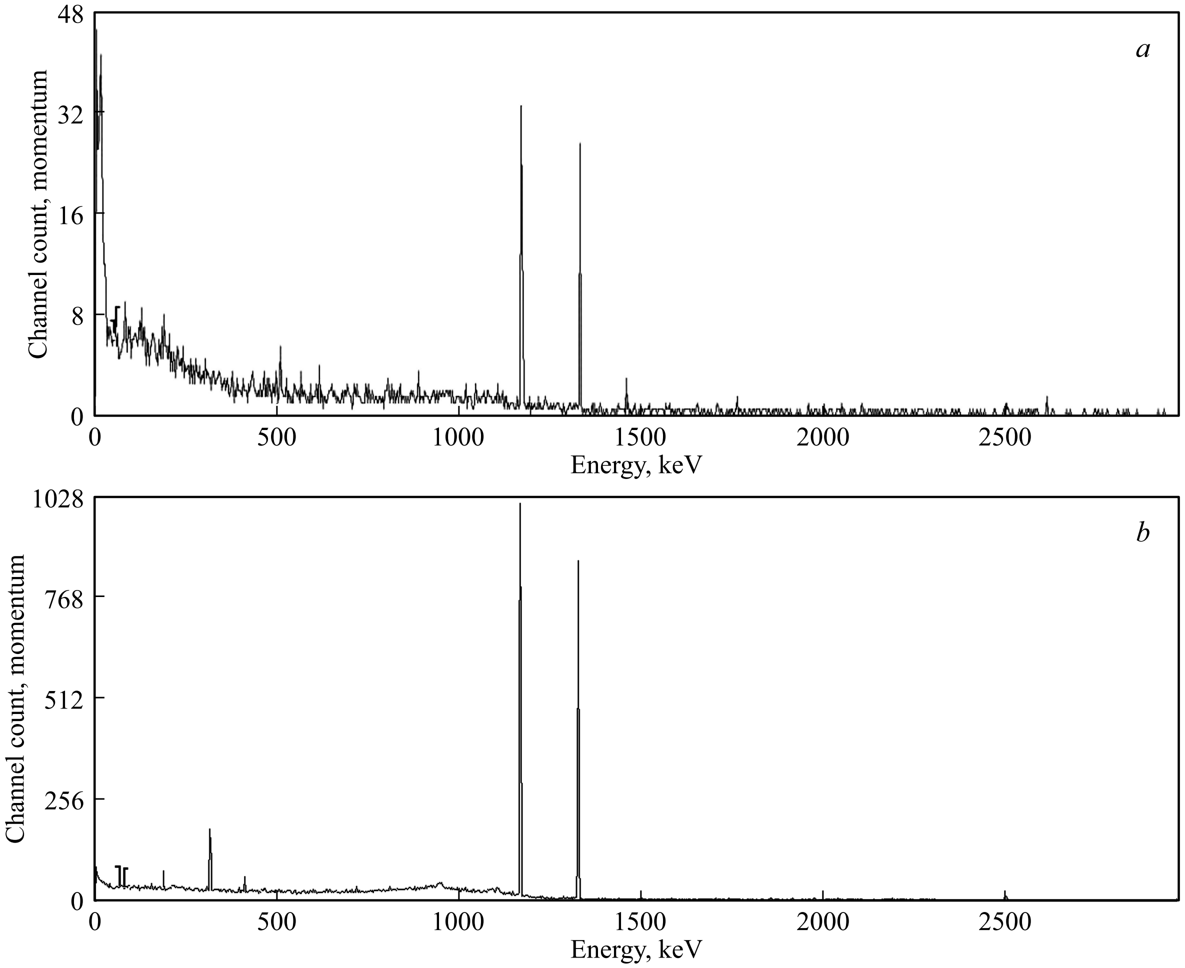

Figure 2. Spectra of samples of ^{59}Co-doped *n*-type silicon after irradiation by neutrons with a fluence of $1.03 \cdot 10^{19}\,\text{cm}^{-2}$, doping temperature — 1000°C (*a*), 1250°C (*b*).

Time of the gamma-spectrum measurement was 300 s. It is known that the presence of ^{59}Co doping in silicon samples and in the reference target under irradiation results in formation of the ^{60}Co radionuclide by the $^{59}\text{Co}(n, \gamma)$ reaction with half-life of $T_{1/2} = 5.24$ year and thermal neutron capture cross section of 34.8 barn.

Spectra of gamma-lines of two neutron-irradiated samples with different content of ^{59}Co in the doped Si are shown in Fig. 2. It can be seen from the figure that after the neutron irradiation two gamma-lines of ^{60}Co are observed in the spectrum in the region of 1173 and 1332 keV with gamma-line amplitude determined by the content of the formed ^{60}Co radionuclide in samples of $\text{Si}\langle^{59}\text{Co}\rangle$.

From the comparison of gamma-lines of $\text{Si}\langle^{60}\text{Co}\rangle$ samples to the spectrum of reference target taking into account their sizes and masses, neutron flux density, duration of the irradiation and cross-section of the $^{59}\text{Co}(n, \gamma)^{60}\text{Co}$ nuclear reaction, the content of cobalt in the neutron-irradiated samples was determined by the relationship of [11], connected to the induced activity I

$$I = m_x\,\frac{0.6 f\sigma}{M}\,(1 - e^{-\lambda t})e^{-\lambda\tau},$$

where m_x is the content of element of interest, σ is nuclear reaction cross-section for the given stable isotope, f is neutron flux density; $\lambda = \frac{0.693}{T}$ is decay rate of the produced radioactive isotope; t, T, τ are duration of irradiation, half-life and duration of cooling, respectively, M is atomic weight of the irradiated stable isotope.

Results of the total solubility and the concentration of electroactive doping of cobalt in *n*-type silicon in the diffusion temperature range of 1000–1250°C obtained on the basis of instrument neutron-activation analysis and Hall effect are shown in Fig. 3 (lines *1* and *2*, respectively). As can be seen from the figure the total concentration of ^{60}Co radionuclide (dependence *1*) in thermodiffusion-saturated samples of n-$\text{Si}\langle\text{Co}\rangle$ in the above-mentioned temperature range varies in the range from $2.8 \cdot 10^{14}\,\text{cm}^{-3}$ to $9 \cdot 10^{15}\,\text{cm}^{-3}$ and can be described by the following relationship

$$N_{^{60}_{\text{Co}}} = 2.76 \cdot 10^{20} \exp\left(-\frac{2.78 \pm 0.04)}{kT}\right),$$

and electrically active concentration (dependence 2) varies from $10^{13}\,\text{cm}^{-3}$ to $3 \cdot 10^{14}\,\text{cm}^{-3}$, which is much lower and

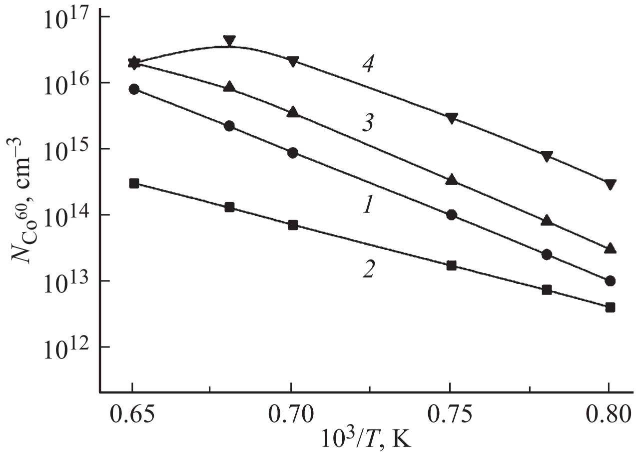

Figure 3. Temperature dependence of cobalt doping content in n-Si: *1* — total concentration of cobalt; *2* — electrically active concentration of cobalt; literature data *3* — [5], *4* — [8].

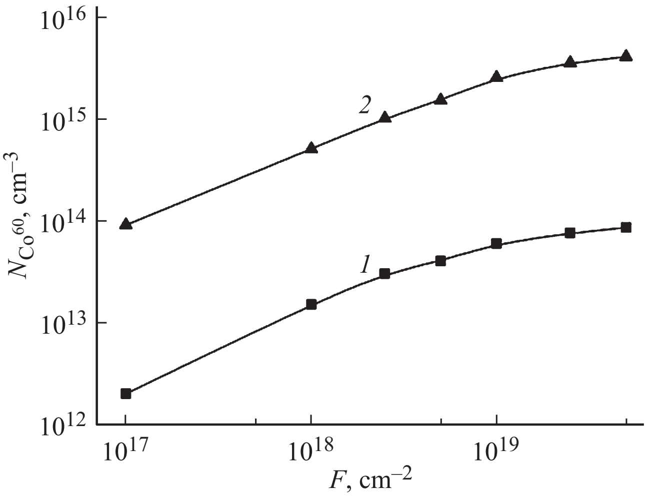

Figure 4. Calculated dependence of ^{60}Co radionuclide concentration in the doped silicon from the fluence of neutron irradiation at the following content of ^{59}Co in Si: *1* — $1.70 \cdot 10^{-4}$%; *2* — $3.35 \cdot 10^{-4}$%.

is not consistent with the data of [5,8]. It is worth to note, that the determination of the electrically active component of the cobalt doping in the reference and irradiated samples of Si took into account the efficiency of the ^{31}P stable isotope formation in Si$\langle^{60}$Co$\rangle$ under neutron transmutation through the following reaction:

$$ {}^{30}\mathrm{Si}(n,\gamma)^{31}\mathrm{Si}\,\frac{\beta^{-1}}{2.62h} \rightarrow {}^{31}\mathrm{P}, $$

which is a donor impurity in silicon and results in a change in the concentration of current carriers in samples [12].

The comparison of our results for solubility to the literature data [5,6,8] with identical diffusion temperature (1250°C) shows that the total concentration of cobalt differs by 2–4 times and the concentration of electrically active cobalt is 0.04% of the total concentration of cobalt. Such a low concentration of electroactive state of cobalt in Si$\langle$Co$\rangle$ samples as compared to the total concentration may be due to the formation of different passive low-size defect complexes in the body of silicon with the participation of its own structural inhomogeneities and accompanying process impurities, such as oxygen and carbon [3].

It is necessary to note that to decrease errors in determination of the total solubility of cobalt in Si, diffusion-saturated Si$\langle^{59}$Co$\rangle$ samples were used, which then were exposed to neutron irradiation, and dose of the neutron irradiation was pre-calculated taking into account density of neutron flux, concentration, degree of Si sample saturation with the ^{59}Co doping under the thermodiffusion and cross-sections of thermal neutron capture by cobalt. Calculated changes in the concentration of ^{60}Co radionuclide caused by the neutron irradiation fluence at a limited content of ^{59}Co in Si are shown in Fig. 4. As can be seen from the figure the increase in content of ^{59}Co in doped samples results in a non-linear change in concentration of ^{60}Co radionuclide as the irradiation fluence varies (curves *1, 2*). This allows selecting required duration of the irradiation taking into account the density of neutron flux in the presence of different concentrations of ^{59}Co in the doped samples of silicon.

When determining the concentration of ^{60}Co, the error of gamma-line measurement by semiconductor spectrometer was not more than 2–4% and was corrected by the duration of measurement of the irradiated Si$\langle^{59}$Co$\rangle$ samples. Thus, the difference found between the total solubility of cobalt in silicon in [8] and in our data is by 2–4 times (Fig. 3) and may be related to improper choice of ^{56}Co radionuclide for thermodiffusion by the authors. It is known that ^{56}Co radionuclide is produced via irradiation in cyclotron by high-energy protons through $^{56}\mathrm{Fe}(p,n)^{56}\mathrm{Co}$ and $^{57}\mathrm{Fe}(p,2n)^{56}\mathrm{Co}$ reactions with 77.2-day half-life of ^{56}Co [13], which further transforms to the stable parent isotope of iron, i.e. the presence of difference in solubility of cobalt doping in n-Si suggests that the cobalt solubility determined in [8] highly likely refers not to the Co doping but to the ^{56}Fe or the ^{57}Fe parent isotope, from which the ^{56}Co radionuclide has been extracted and $\mathrm{CoCl_2}$ chloride salt and its solution has been produced for the diffusion.

The cobalt solubility obtained in [5] differs by (1.5–2) times from our results, which may be due to the improper choice of the diffusion duration and insufficient removal of the ^{59}Co metal layer from the surface of doped samples after the thermodiffusion, i.e. the content of ^{60}Co is measured in an inhomogeneously distributed region of samples.

3. Conclusion

Based on the study of cobalt solubility in doped single crystal silicon the possibility is found to use the reactor neutron activation analysis to determine concentration of the injected cobalt doping in the solid solution of Si$\langle^{59}$Co$\rangle$ of about 10^{-12} mass%.

Main requirements are established for the samples under study, that are based on the choice of the doping natural isotope, temperature, duration of diffusion and homogeneously saturated layer in doped samples. It is shown that in the diffusion temperature range of 1000−1250°C the total solubility of ^{60}Co doping in *n*-Si varies in the concentration range of $2.8 \cdot 10^{14}-9 \cdot 10^{15}\,\text{cm}^{-3}$ and the electrically active concentration varies in the range from 10^{13} to $3 \cdot 10^{14}\,\text{cm}^{-3}$ and is equal to 0.04% of the total solubility. At the same time, cobalt in *n*-Si manifests the acceptor property forming mainly deep centers with levels of $E_c - 0.41\,\text{eV}$, and $E_c - 0.55\,\text{eV}$ in the top half of the band gap of silicon.

An assumption is made that to determine the absolute solubility of doping agents in doped semiconductors by the reactor neutron activation analysis, it is necessary to use as ligature the stable parent isotope, that forms after irradiation a daughter radionuclide with a long half-life and not the radionuclide of the foreign chemical element.

Conflict of interest

The authors declare that they have no conflict of interest.

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