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Influence of neutron irradiation on elctrooptical and structural properties of silicon

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Abstract. Processes of structure defects formation, which accompanied by oxygen precipitation after a neutron irradiation ($10^{15}\div10^{19}$ n/cm^2) and high-temperature treatment (800÷1000°C) in CZ silicon, were investigated by the transmission electron microscopy. Influence of the structure defects on electrooptical properties of silicon was revealed.

Keywords: silicon, neutron irradiation, oxygen precipitates, electrooptical properties.

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For Si, grown up by CZ method, a main factor which determines changes of electrical, optical, and structural properties after heat treatment or irradiation is oxygen impurity. In the course of annealing silicon, the electrically active complexes with participation of oxygen (thermodonors) or particles of a new phase (SiO_x) are formed. The latter can getter undesirable impurities from a volume of silicon, which is used in semiconductor manufacturing techniques. With increase of requirements to the minimization of sizes of integrated circuit chips, there is a necessity for introduction of oxygen-silicon complexes (precipitates) in silicon to be controlled.

The purpose of this work was investigation of formation process of structure defects, which accompanied oxygen precipitation after a neutron irradiation and high-temperature treatment of silicon, grown up by CZ method, as well as studying these defects influence on electrooptical properties of surface layers.

Use of neutron irradiation enables to get uniformly doped or strongly compensated silicon for manufacturing microelectronic devices.

Oxygen precipitation was studied in the course of heat treating Si at 800-1000°C after irradiation by reactor neutrons with fluences $10^{15}\div10^{19}$ n/cm^2. *n*-and *p*-type silicon with a concentration of dissolved oxygen $(4\div9)\cdot10^{17}$ см$^{-3}$ was investigated. The type, size and concentration of defects were studied by the transmission electronic microscopy [1] using electronic microscope BS 613 «Tesla» with a maximal voltage 100 kV.

For investigations of electrooptical properties of silicon with oxygen-silicon precipitates, the method of the modulation spectroscopy of electroreflection was used. This method is characterized by a higher sensitivity in comparison with the classical spectroscopy [2]. Measurements of electroreflection spectra were carried out by an optical technique [3] at room temperature in unpolarized light in a spectral range of the direct absorption edge of silicon at 3–3.8 eV. Spectral resolving ability was 3 meV. Spectra of electroreflection were analyzed using low field-effect theories in combination with the threepoint method [4] for determining transition energy (width of a forbidden band) and the phenomenological parameter of extension. This parameter characterizes a scattering of charge carriers excited by light on structure defects. In case of the unipolar shape of a spectrum, it was determined from an energy position of maximum of an electroreflection signal, and Γ — from a half-width of a spectral band.

At earlier stages of annealing of unirradiated silicon at 1000°C (10÷20 hours) on electron micrographs of silicon samples, aggregate of stressed centres and dislocations accompaning them were detected. After 50 hours of annealing (Fig. 1 a, b), it was observed that these stressed centres were plate-like precipitates. Their shaping began with formation of star-shaped dendrites. The shape of plate-like precipitates was rectangular for a plane (111) or rhombic — for (110). Dislocations that accompanied precipitates arose as a result of removing mechanical

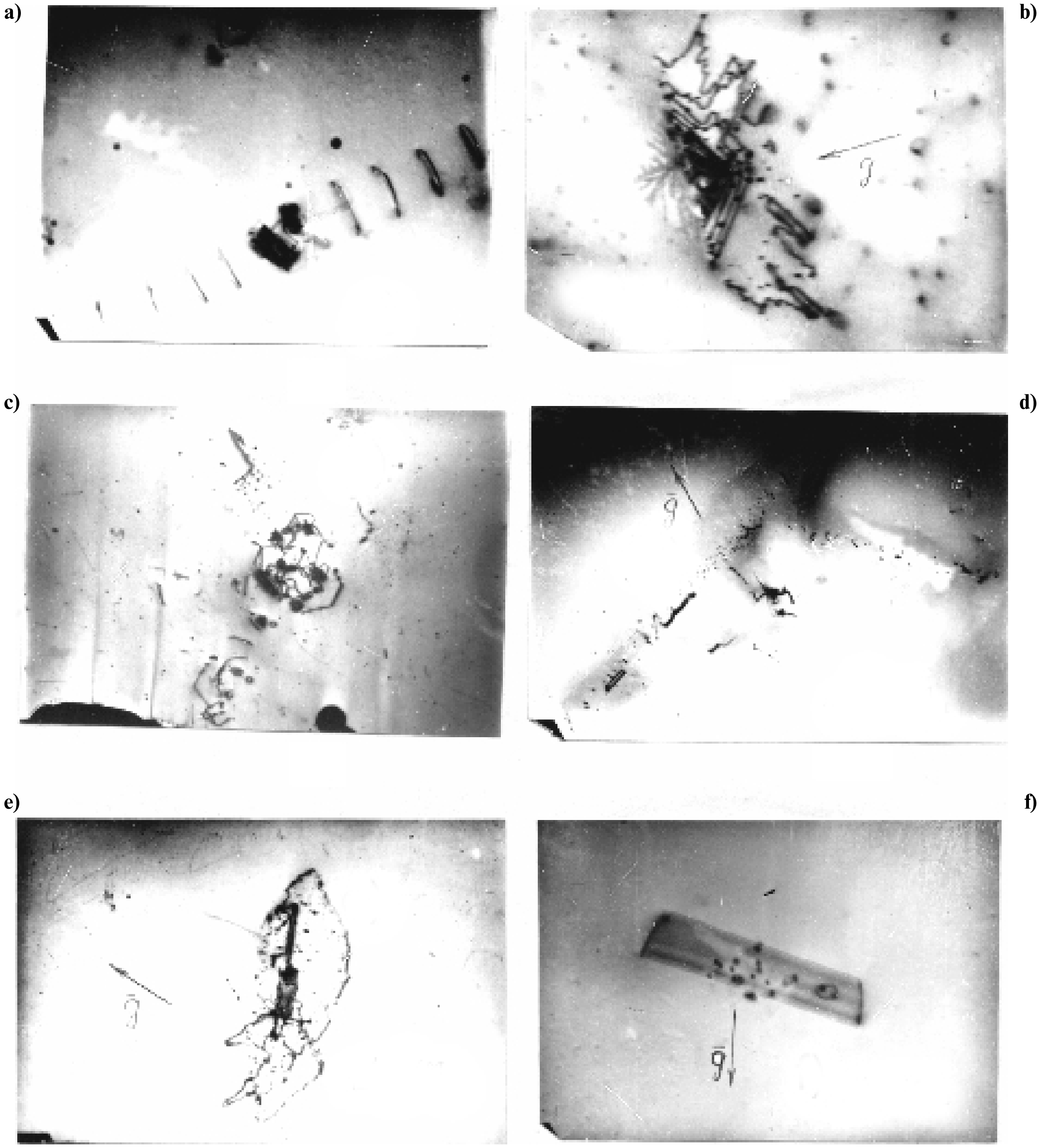

Fig. 1. Electron microphotographs of defects in silicon after annealing at 1000°C during 50 hours. (a, b), 120 hours (c, d) and after irradiation by the neutron fluence of $\Phi = 2\times10^{19}$n/cm^2 and annealing at 1000°C for 1 hour (e, f).

stresses caused by the difference in volumes comprised by SiO_x phase (plate-like precipitates) and silicon matrix. The volume of SiO_x ($x \le 2$) phase is greater than that of a silicon matrix, therefore there are internal mechanical strains in Si [5]. At this duration of annealing, except of plate-like precipitates, formation of a new type of defects– colonies of microprecipitates and segments of dislocation loops which enclosed them (Fig. 1b) were observed. After 70 hours of annealing increasing sizes of microprecipitate colonies and partial dissolution of plate precipitates were observed. At places of the latter we observed colonies of microprecipitates. Annealing for 120 hours at 1000°C leads to increasing sizes of colonies up to ~ 10÷12 micrometers (Fig. 1 c, d).

In electron micrographs of neutron-irradiated Si samples just after the first hours of annealing at 1000°C, we observed that the main defects were colonies of microprecipitates and stacking faults (Fig. 1e, f). Plate-like precipitates were not observed. Investigations of absorption spectra in the region of 1000-1300 cm^{-1} on the samples of silicon annealed at 1000°C, after the precipitation process completion (when the concentration of interstitial oxygen reached saturation) [6] have shown that in the thermally treated samples of Si irradiated by fluences $< 10^{16}$ n/cm^2, the major phase was cristobalite, and in the samples irradiated with higher fluences $> 10^{19}$n/cm^2 – amorphous silica was dominant. As for unirradiated Si structure of observed phases was more manifold. The comparison of optical and electron microscopical data enabled us to assume that plate-like precipitates are cristobalite phase, and colonies of microprecipitates are amorphous silica phase.

The time necessary for the defect concentration to reach saturation in the irradiated and annealed silicon was 30÷40 hours, in unirradiated ones it was 90 hours. This fact confirms that the neutron irradiation accelerates precipitation of oxygen in silicon.

In Fig. 2 represented is the dependence of different type defects concentration in silicon after annealing at 1000°C for six hours on the fluence of neutron irradiation. It is obvious that general concentration of defects increases with a fluence up to its value 10^{16} n/cm^2 and does not vary further. Defect concentration has increased from 10^7 up to 10^8 cm^{-2}, and concentration of stacking faults increase from $2.5{\cdot}10^6$ cm^{-2} up to $8.5{\cdot}10^7$ cm^{-2}. Thus, we think that stacking faults are main defects in common defect concentration in irradiated silicon.

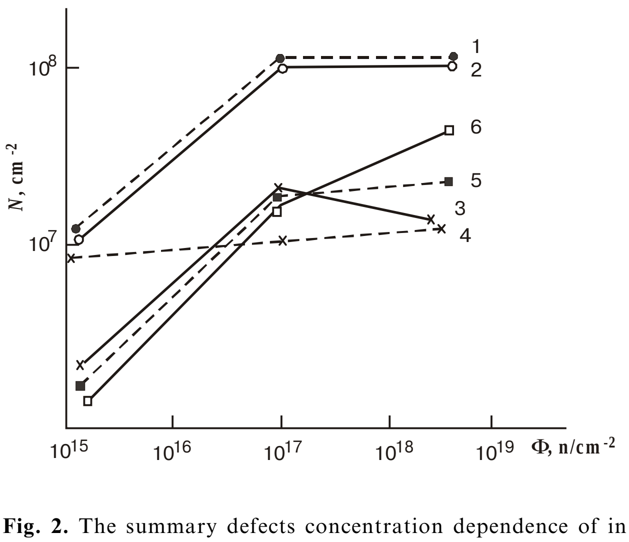

Fig. 2. The summary defects concentration dependence of in silicon with oxygen content (7-8)×10^{17} cm^{-3}(1) and 9×10^{17} cm^{-3}(2) after annealing at 1000°C for 6 hours on the value of a neutron fluence. 1,2-summary defects concentration; 3,4-microprecipitate colonies concentration; 5,6-stacking faults concentration.

The electrooptical investigations have shown that unirradiated Si samples have another polarity of electroreflection spectrum signals, which corresponds to the spectrum of *p*-type silicon with parameters E_g = 3.41 eV and Γ = 220 meV. After annealing unirradiated samples at 800°C (170 hours), the spectrum shape remained of another polarity, nevertheless parameters were changed: E_g = 3.39 eV and Γ= 110 meV, which corresponds structurally more perfect surface and to twice increasing of charge carriers mobility [7].

When the fluence of irradiation has reached the value of 10^{15} n/cm^2, the unipolar shape of the electroreflection spectrum of with the positive phase ($\frac{\Delta R}{R} > 0$) was observed. After annealing a sample, the unipolar shape of the spectrum was kept, and the parameter of extension decreased (from 120 down to 115 meV). Energy of transition also varied in comparison with the initial one (unirradiated and unannealed) and was 3.36 eV and 3.38 eV for samples unannealed and annealed after irradiation, respectively. Decreasing a forbidden band of samples testifies to presence of interior mechanical stresses of a tension, which arise during irradiation due to occurrence of vacancy complexes, and after heat treatment relax partly due to occurrence of precipitates SiO_x which caused stress pressure.

The change of the electroreflection spectrum shape is caused by a change of electronic properties of silicon after neutron irradiation. Both *n*- and *p*-type samples had conductivity close to intrinsic silicon after its neutron irradiation [8], spectra of electroreflection of intrinsic semiconductor show the unipolar shape, as it was observed earlier [9]. The parameter of widening was essentially decreased even before annealing in comparison with an initial sample, which testifies to ordering the defect structure. It is bound with the nonuniform distribution of oxygen in silicon ingots.

With increasing neutron fluence from 10^{16} up to 10^{18} n/cm^{-2}, signals of electroreflection were not observed. They were visible only after annealing of irradiated samples, and it had the unipolar spectrum shape with an opposite phase ($\frac{\Delta R}{R} < 0$) in comparison with a sample irradiated with the fluence 10^{15} n/cm^{-2} (Fig. 3). Absence of a signal testifies to high disorder structures of silicon and occurrence of density-of-states tails after irradiation, which were decreased due to heat treatment [10]. From Fig. 3 we can see that fluence increasing causes electroreflection signal decreasing in the case of annealed samples. The change of a signal phase and decrease of its intensity are bound with an increase of SiO_x precipitate sizes and, as a consequence, with an enrichment of silicon by electrons on the interface of Si-SiOx [11-12].

The dependence of parameter of extension (a half-width of electroreflection band) on fluence of an irradiation after annealing is given in Fig. 4. It is easy to see that the parameter of extension decreases donn to 80 meV with increasing fluence of irradiation. It means that the

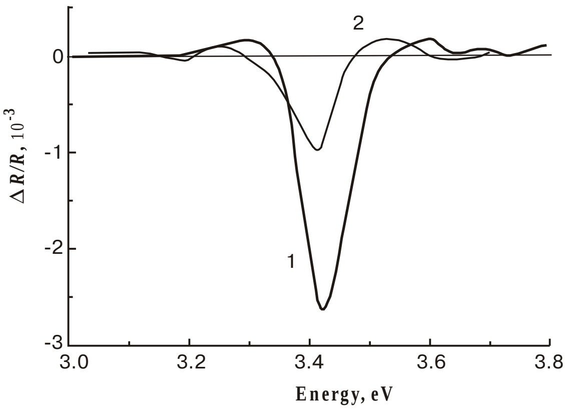

Fig. 3. Spectra of electroreflection for neutron irradiated and annealed at 800°C silicon samples: 1 – fluence of 10^{16} n/cm^2; 2 – fluence of 10^{18} n/cm^2.

increase of charge carriers mobility takes place due to a decrease of a silicon surface defectiveness [13]. It is also obvious that the decrease of extension parameter reaches saturation with irradiation fluence growing up to 10^{16} n/cm^2. The forbidden band almost does not vary with increasing irradiation fluence (3.4 eV and 3.41 eV) and reaches value which is typical for an initial sample. Nevertheless, as to initial unirradiated sample, another polarity is observed of the electroreflection spectrum. The width of a forbidden band almost does not vary at the high fluences. It is possible that mechanical stresses of another sign due to defect formation compensate each other, the deformation potential decreases, and therefore the extension parameter decreases.

Thus, the main features of defects formation which accompany oxygen precipitation in the irradiated silicon after high-temperature treatment are the following: a) a decrease of defect formation time in comparison with that of unirradiated silicon; b) plate-like precipitates are not detected in irradiated silicon for irradiation fluences above 10^{16} n/cm^2; c) formation of the microprecipitate colonies in the first hours of irradiated silicon annealing; d) dominant formation of stacking faults, its concentration increase with annealing time and increasing irradiation fluence.

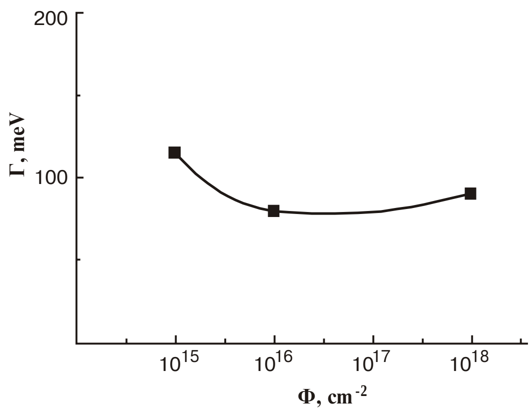

Fig. 4. Dependence the Γ parameter of electroreflection spectra extension of silicon samples annealed at 800°C on the value of irradiation fluence.

In this work the method of the modulation spectroscopy of electroreflection is applied firstly for determining electrooptical properties of neutron irradiated silicon with oxygen-silicon precipitates. It is shown that spectra of electroreflection correlate with transformation of structural defects in irradiated and annealed silicon which has an effect on width of a forbidden band and value of phenomenological parameter of extension.

References

1. P.G. Litovchenko, M.I. Starchik and K.M. Shevtsov-Kazmirchuk, The kinetics of accumulation of structural defects in neutron irradiated silicon at high-temperature treatment. In: *XI All-Union conference on an electronic microscopy,* Suzdal, pp. 88–89 (1990)
2. M.C. Kardona, *The modulation spectroscopy,* Mir, pp. 416 (1972).
3. V.A. Tyagay and O.V. Snitko, *Electroreflection of light in semiconductors*, Naukova dumka, pp. 302 (1980).
4. D.E Aspnes , Third-derivative modulation spectroscopy with low field electroreflectance // *Surf. Sci.* **37**(2), pp. 418–442 (1973).
5. A. Borgesi, Oxygen precipitation in silicon//*J. Appl. Phys.*, **77**(9), pp. 4169–4224 (1995)
6. A.A. Groza, V.I. Varnina, P.G. Litovchenko, L.G. Nikolaeva and G.G. Shmatko, Structural - phase transformation at heat treatment of the irradiated silicon and their influence on physical properties and radiation resistance // *Radiative Materiology*, **4,** Kharkov, pp. 127–133 (1990).
7. T.Ya Gorbach, R.Yu. Holiney, I.M. Matiyuk, L.A. Matveeva, S.V. Svechnikov and E.F. Venger, Electroreflectance spectroscopy and scanning electron microscopy study of microrelief silicon wafer with various pretreatment // *Semicon. Phys., Quant. Electron. and Optoelectron,* **1**(1), pp. 66–70 (1998).
8. V.D. Tkachev *The doctoral thesis,* the Byelorussian university edition, Minsk (1967).
9. I.P. Garbar, L.A. Matveeva, V.F. Mitin, Yu.A. Tkorik and Yu.M. Schwarts Strongly doped and strongly compensated heteroepitaxial germanium film // *Phys. Tech. Poluprovodnikov*, **21**(3), pp. 393–399 (1987).
10. A.A. Groza and V.I. Khivrich, Near edge adsorption in the silicon irradiated by neutrons and by 1.5 MeV electrons // *Phys. Tech. Poluprovodnikov*, **13**(5), pp. 870–874 (1979).
11. E.F. Venger, T.Ya. Gorbach, L.A. Matveeva and S.V. Svechnikov, The spectroscopy of electroreflection, electronic bound structure and the mechanism of a visual photoluminescence of anisotropically etched silicon // *Jour. Experimentalnoy Theor. Phys,* **116**(5(11)), pp. 1750–1761(1999).
12. R.Yu. Holiney, L.L. Fedorenko, L.A. Matveeva, I.Yu. Strilchenko, E.F. Venger and N.M. Yusupov, Electroreflectance of porous layers obtained by stain etching of laser modified silicon // *J. Phys. Appl. Phys. D.*, **33**, pp. 2875–2879(2000).
13. R.Yu. Holiney, L.A. Matveeva and E.F. Venger, Investigation of the undersurface damaged layers in silicon wafer // *Semicond. Phys, Quant. Electron. and Optoelectron*, **2**(4), pp. 10–12(1999).