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Influence of the annealing of silicon crystals at 1200 °C on the Hall effect and magnetoresistance

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Abstract. The influence of the annealing (at $T_{anneal.}$ = 1200 °C) and different rates of cooling (from $T_{anneal.}$ to room temperature) on magnetoresistance and Hall effect of the n-Si:P monocrystals with different specific resistance, which were grown by means of various technologies, have been investigated. It means that investigated crystals had different concentrations of not only doping impurity (phosphorus) but also background impurity (oxygen atoms) in their bulk, too. It was shown that the impurity complexes (clusters) of $(SiO)_x$, $(SiO_2)_x$ or Si_xO_y types that arise in n-Si monocrystals with increased oxygen concentrations at annealing ($T_{anneal.}$ = 1200 °C) results in essential increase of magnetoresistance $\rho_H^{\perp} / \rho_0$ (approximately 2...2.5 times as much). The influence of mentioned above clusters on the magnetoresistance practically excludes its saturation in classically strong magnetic fields and forms the dependence of $\rho_H^{\perp} / \rho_0$ on magnetic field H in this region in the following form $\rho_H^{\perp} / \rho_0 \sim H^1$.

Keywords: silicon, crystal, oxygen, magnetoresistance, Hall effect, mobility, density.

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Despite the major attention that was developed by researchers during several decades to studying the magnetoresistance (MR) in semiconductors [1, 2], the heightened interest of researchers to this problem eventually is not weakened. First of all, is related to exclusive simplicity of measuring the MR effect and its high performance when studying energy-band structure and mechanisms of scattering in multivalley semiconductors [3] and, in general, in anisotropic media [4,5]. A supplementary, and not less important, stimulus to study MR, as appeared recently, is the storming and practically valid transition in physics of semiconductors to large-scale investigation of low-dimensional structures at the all-embracing microminiaturization of element basis of the modern complex microelectronic and optoelectronic systems, and also a strong dependence of manufacturing technology for these systems on requirements of heat treatment of materials on the basis of which they are created. Besides, harnessing transmutationly-doped silicon (TDS) for manufacturing devices, or search of ways to increase radiation resistance of Si using irradiation and heat treatment, also require researches of interaction of radiation, thermal and impurity defects in these crystals.

As related to mentioned above, there arises a necessity (using the study of electronic-transport phenomena, in particular Hall effects and MR) to trace both changes of MR itself and possible influence of different kinds of heat treatment (HT) [annealing (A) temperatures and time, and also cooling rates of crystals from A temperature ($T_{anneal.}$) down to room temperatures] on the most important parameters (such as concentration of major charge carriers n_e and their mobility μ) in n-Si crystals of a different technological origin. These are the questions that are the subject of this paper.

The desire to effectively minimize the influence of layered structure on the MR effect forced us to cut out explored crystals in such manner that in the samples, intended for comparative investigations, it would provided not only conformity of crystallographic orientations, but the vector of current $\vec{j}$ should be in the plane of layer growth. According to works [6,7], it releases the experimenters from necessity to take into account the influence of layers of growth on the MR effect when analyzing received results.

Having intention to concentrate a maximum attention on studying the manifestation of statistically distributed inhomogeneities, we selected the samples with different contents of the phosphorus impurity as well as the residual oxygen impurity. That is, they were selected using a principle of a similarity (or essential difference) by their specific resistances (or concentration of charge carries) from crystals grown by Czochralsky or the melted zone method, taking also into consideration some specificities of doping the phosphorus impurity through a melt, or by the method of nuclear transmutation.

For explored samples in Tables 1 and 2 for 300 and 77.4 K given are both the initial data on mobilities of charge carries (μ) and their concentrations (n_e), received

Table 1. Change of electrophysical parameters of *n*-Si:P with an increased content of residual oxygen impurity ($N_{O_i} \approx (2...5)\cdot10^{17}$cm^{-3}) as a result of heat treatments.

Growing method	T, K	Annealing	ρ_{300K} = 0.5 Ohm·cm		ρ_{300K} = 80 Ohm·cm	
			$n_e\cdot10^{-15}$, cm^{-3}	μ, cm^2/V·s	$n_e\cdot10^{-13}$, cm^{-3}	μ, cm^2/V·s
n-Si:P Czochralski-grown in argon atmosphere	300	Before A	8.76	1380	4.80	1840
		SC	8.64	1360	3.90	1680
		FC	8.46	1420	3.00	1760
	77	Before A	3.66	8050	5.38	20100
		SC	3.49	8270	4.30	19300
		FC	3.44	9580	2.64	19800

Notes. Abbreviations introdused: A – annealing; SC – slow cooling after A; FC – fast cooling (immediately after A, samples were deepened into a both with transformer oil being at room temperature).

before the annealing procedure ($T_{anneal.}$ = 1200 °C, t = 2 hours, it being carried out in vacuum), and the data received using annealed samples at different rates of their cooling ($V_{\text{cool.}}$).

Poor sensitivity of changes μ and n_e to spent in the given operation A with the relevant cooling rates, – in comparison with the thermoelectromotive force and piezo-termoelectromotive force, which are measured in the conditions of the electron-phonon drag [8-10], – was to some extent overlapped in the given work by essential expansion of assortment of investigated crystals that were too much differed between themselves both by a level and method of their doping, as well as conditions of growing them (see Tabs 1 and 2). This circumstance, and also use of the data on the MR effect that was measured using crystals not only cooled but also annealed under conditions of two different modes, – have provided carrying out of comparative experiments and enabled (using MR as an example) to analyze a role of those relatively small, but qualitatively different, changes of μ and n_e in the crystals that were grown and doped in different ways. However, the method of doping and growing the explored crystals completely depends not only on concentration of dopants and residual impurities (in particular, impurities of oxygen and carbon), but also a state in which these impurities are in their bulk.

As against the tendency to decrease n_e under annealing (with slow and rapid cooling), which is indicative of low-resistance ($\rho_{300K} \cong 0.5$ Ohm·cm) and high-resistance ($\rho_{300K} \cong 80$ Ohm·cm) samples (see Tab. 1), changes of μ values at the same A of named crystals are oppositely directed: μ of the low-resistance samples at the A displays the tendency to increase, and μ of the high-resistance ones – distinctly drops.

In the group of samples with increased contents of residual oxygen impurity ($N_{O_i} \cong (2–5)\cdot10^{17}$cm^{-3})) the characteristic for a low-resistance crystal appeared presence of an energy level of the more deep deposition and in comparison with that was in low-doped (by the same phosphorus impurity) crystal. The evidence on it is the strong decrease (approximately by 2.5 times) in concentrations n_e with transition from measurements at 300 K to those at 77 K, which is not present in the case of more high-resistance crystal.

Even less apparent appeared changes with A n_e in crystals with the reduced contents of a residual impurity of oxygen ($N_{O_i} \approx 5\cdot10^{15}–10^{16}$cm^{-3}, see Tab. 2). As the doping level of crystals in Tab. 2 does not coincide with n_e of high-resistance and low-resistance crystals in Tab.1, by viewing Tab. 2 there is a sense to compare each other taking data for the crystals that figure only in this table. It was found that tendencies in changes of mobility after A in the crystals doped in an ordinary way and by transmutation are oppositely directed: in the common crystals the tendency of μ to fall down is displayed (as shown in Tab. 2), whereas in transmutationally doped samples – μ

Table 2. Electrophysical characteristics of n-Si:P crystals with reduced content of residual oxygen impurity (N_{O_i} = (5...10)$\cdot10^{15}$cm^{-3})

Method of crystal growing and doping	T, K	Annealing	$\rho_{300K} \cong$ 15 Ohm·cm	
			$n_e\cdot10^{-14}$, cm^{-3}	μ, cm^2/V·s
n-Si:P BKEF-15 (FZM) in argon atmosphere	300	Before A	2.10	1790
		SC	2.49	1710
		FC	2.68	1670
	77.4	Before A	2.78	18400
		SC	2.51	18050
		FC	2.54	17350
n-Si:P doped by the method of nuclear transmutation	300	Before A	2.28	1670
		SC	2.67	1730
		FC	2.60	1700
	77.4	Before A	2.38	17100
		SC	2.30	17950
		FC	2.20	17800

Notes. For abbreviations see Table 1.

displays the tendency to slight increase. This statement, as shown in Tab. 2, remains valid both for experiments carried out at 300 K and at 77.4 K.

The investigations carried out using electron microscopy of high resolution have shown that precipitates, which are gained in the crystals Si with a residual impurity of oxygen at the A, have amorphous $(SiO)_x$ structure [11, 12]. The formation of plate precipitates is observed before $T_{anneal.}$ = 1000 °C. With the rise in $T_{anneal.}$ from 600 °C up to 1000 °C their concentration decrease from 10^{11} down to 10^7 cm^{-3}, but in the case their sizes grow from 1.5 up to 1000 nm [11, 13]. At higher $T_{anneal.}$ = = 1200 °C, large plate precipitates that consist of amorphous $(SiO)_x$ phase, grow. Formation of oxygen precipitates lead to rise of mechanical tensions, owing to a difference of molecular volumes of Si oxide and matrix. These tensions may partially decrease due to emission of interstitial Si atoms from precipitate into a matrix. So, degree reduction of oversaturated solid solution of oxygen in silicon (due to oxygen precipitation) lead to oversaturation of silicon matrix with natural interstitial atoms. The amount of silicon atoms, introdused into intersticials of a crystal lattice due to emission, as a result of connection to the precipitate of an oxygen atom, may be calculated by the formula [11]:

$$\beta = \frac{d_{\mathrm{Si}} - d_{\mathrm{SiO_2}}}{2d_{\mathrm{SiO_2}}} \cong 0.5$$

where d_{Si} and $d_{\mathrm{SiO_2}}$ – the molecular densities of Si and SiO_2.

Formation of dislocation loops using the interstitial Si atoms is accompanied by reduction of the local mechanical tensions in a crystal lattice.

If oxygen-containing Si crystal before the high-temperature A was given in the previous low-temperature A (or tested it during the growing) in such crystal there will be already exist the rudimentary crystallization centers. This circumstance at the high annealing temperatures will have an essential influence on the change of morphology of precipitates that causes change of their shapes from lamelliforms up to a view of volumetric polyhedrons (as a rule, as the cut off octahedrons [13] with sides parallel to planes $(111)_{\mathrm{Si}}$ [11, 12]). The medial size of precipitates that grow at the A in the field of 1200 °C have scattering on their sizes in limits from 15–20 nm up to 0.1 microns. So, there are all bases to consider these precipitates (with their local media as mechanically intense crystal lattice with gettered atoms of impurities) as statistically dispersed inside the crystal bulk as inhomogeneities of the Herring type [6].

Using crystals of different technological origin we have analyzed above the influence of A on the change n_e and μ only at two fixed temperatures ($\approx$ 300 and 77 K), while the influence of similar A on change of parameter μ in a wide interval $40 \le T \le 300$ K was interrogated in [14]. Authors of this paper showed that, for the description of $\mu = \mu(T)$ in the range $T \le 40$ K in annealed Si samples with oxygen the account of only three basic mechanisms of scattering (scattering on phonons, ionized and neutral impurities) is not sufficient. It is also necessary to take into account scattering of free charge carriers on the oxygen precipitates grown at A of n- and p-types Si at $T_{anneal.} \ge 450$ °C as well as scattering on space charge regions in annealed p-Si, which occur due to inhomogeneous allocation of interstitial oxygen and, accordingly, to the nonuniform overcompensation of p-Si in n-type material due to thermodonors.

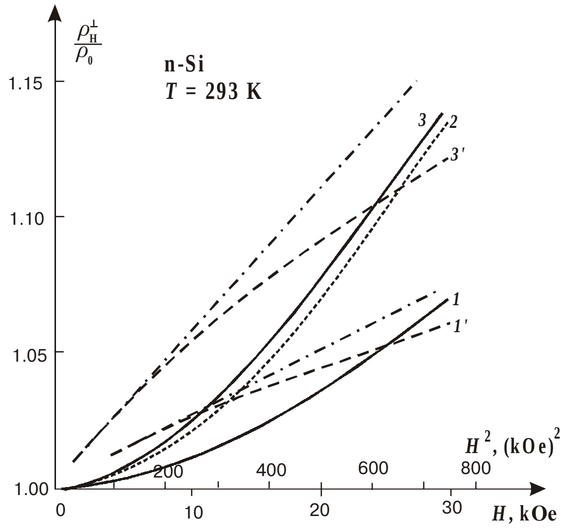

Fig. 1. Dependences $\rho_H^{\perp}/\rho_0 = f(H)$: *1* – for the sample in its initial state (before annealing); *2* – after annealing at T = 1200 °C for t = 2 hours; *3* – after annealing at T = 1200 °C for t = 72 hours. *1′* and *3′* – dependences $\rho_H^{\perp}/\rho_0 = f(H^2)$ for curves *1* and *3*, respectively. Crystals were grown in [001] direction that coincided with the magnetic field strength direction $H \parallel [001]$, while the current vector was oriented in the perpendicular to H direction [010] that is the plane perpendicular to growth axis of the crystal.

According to results, previously obtained by us and other authors, it was possible to expect that lattice imperfections in the form of complexes considered above, and caused by high-temperature A, as statistically distributed defects of the Herring type will have considerable effect on the value and field dependences of the MR effect. It is this statement that is confirmed with the observed MR data, both at 300 (Fig. 1), and at 77 K (Fig. 2). The investigations were carried out using Cz-Si crystals; ($\rho_{300\mathrm{K}} \cong 80$ Ohm·cm), annealed at 1200 °C during different time (t = 2 and 72 hours). The samples were cooled with different rates from $T_{anneal.}$ = 1200 °C, namely: $V_{\mathrm{cool.}}$ = 1, 15 and 1000 °C/min.

The performed annealing procedures (with different cooling rates) at unessential decrease of electrically active centre concentration and rather nonessential but sizable decrease of charge carrier mobility, resulted in the quantitative and qualitative changes of MR effect. These are as follows:

– the values of $\rho_H^{\perp}/\rho_0$ measured both at 300, and at 77 K (Figs 1 and 2) grew by 2 to 2.5 times;

– deviation of field MR dependence from the square-law one in annealed samples took place (in the range of weak magnetic fields) at much smaller values of H than in experiments with samples in the initial state (compare curves 1′ and 3′ of Fig. 1);

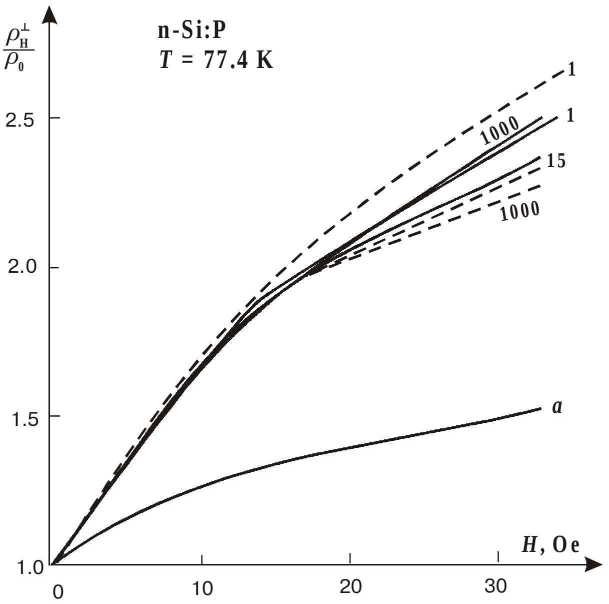

Fig. 2. Dependences $\rho_H^{\perp}/\rho_0 = f(H)$: *a* – measurements made on the sample before annealing (in the initial state). The rest curves were obtained after annealing at T = 1200 °C for t = = 2 hours (dashed lines) and t = 72 hours (solid lines). After annealing the samples were cooled with rates V_{cool} = 1, 15 or 1000 °C/min. The same figures stand near respective curves.

– a slope of dependences $\rho_H^{\perp}/\rho_0 = f(H)$, measured at 77.4 K in the range of display Herring inhomogeneities (at $H \geq 13$ kOe, if $\frac{\mu \times H}{c} \geq 2.5$) – in annealed samples greater than proper slope obtained in investigations with initial crystals (Fig. 2). It is typical that value of a slope of the dependences for these samples undergone to two-hour annealing progressively grew (concerning to a slope of the samples, annealed during 72 hours) with reduction of their cooling time from $T_{anneal.}$ = 1200 °C in a direction from $V_{\mathrm{cool.}}$ = 1000 up to 1°C/min. It is interesting to note (and to compare to the data upon an anisotropy of thermoelectromotive force of drag [9]) that near $V_{\mathrm{cool.}} \cong 15$ °C/min these slopes (as apparent from Fig. 2) almost coincide between themselves. That is $V_{\mathrm{cool.}} \cong 15$ °C/min rate is found somewhere close to inversion points in the relative arrangement of curves $\rho_H^{\perp}/\rho_0 = f(H)$ received for crystals annealed at 1200 °C during different time (t = 2 and 72 hours). The difference in slopes of the curves depicted in Fig. 2 in the range of $\frac{\mu \times H}{c} > 1$ is relatively small and essentially depends not only on annealing time and cooling rate of crystals but also on a concentration and type of doping and residual impurities. That is why this difference may not be interpreted so fully and identically without supplementary investigations.

Summarizing the discussion of results above, we can conclude that:

– the impurity complexes (clusters) gained as $(\mathrm{SiO})_x$ $(\mathrm{SiO}_2)_x$ or as $\mathrm{Si}_x\mathrm{O}_y$ in oxygen-containing crystals at the annealing procedure in the range of $T_{anneal.}$ = 1200 °C (when well-known electrically active thermodonors TD-1 and TD-11 will be practically destroyed [13,15]) lead to an essential increase of the MR effect $\rho_H^{\perp}/\rho_0$, showing themselves as heterogeneities of the Herring type, which are chaotically distributed in the crystal bulk. At the practically invariable mobility of current carriers μ (or, even, its some decrease) the magnetoresistance measured both at 300, and 77.4 K, in the Cz-Si monocrystals, annealed at $T_{anneal.}$ = 1200 °C, grows by 2 to 2.5 times;

– the influence of mentioned clusters of $(\mathrm{SiO})_x$, $(\mathrm{SiO}_2)_x$ or more generally $\mathrm{Si}_x\mathrm{O}_y$ on the MR effect practically excludes saturation of their field dependence in the range of classically strong magnetic fields and forms this dependence (for $\frac{\mu \times H}{c} > 1$) as $\rho_H^{\perp}/\rho_0 \sim H^1$.

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