G.P. Gaidar[1], P.I. Baranskii[2]

[1]Institute for Nuclear Research, NAS Ukraine
47, Nauky Ave., Kyiv, 03680, Ukraine;
[2]V.E. Lashkaryov Institute of Semiconductor Physics,
NAS Ukraine 45, Nauky Ave., Kyiv, 03028, Ukraine

G.P. Gaidar

P.I. Baranskii

EFFECT OF THERMAL TREATMENT ON DRAG SEEBECK COEFFICIENT ANISOTROPY PARAMETER OF TRANSMUTATION-DOPED SILICON CRYSTALS

It is shown that under the coincident (within the measurement errors) values of mobility anisotropy parameter $K = \mu_{\perp} / \mu_{\parallel}$ the values of Seebeck coefficient anisotropy parameter $M = \alpha_{\parallel}^{ph} / \alpha_{\perp}^{ph}$ in transmutation-doped n-Si samples are much lower than in n-Si crystals doped with the same phosphorus impurity, but through the melt. It has been established that high-temperature annealing performed on transmutation-doped n-Si crystals at temperature T_{anneal} = 1200 ºC, irrespective of the annealing duration (in the range of 2 ÷ 72 h) leads to an increase in the value of parameter M, and this effect was more pronounced at quick cooling (at a rate of ~ 1000 °C/min) from T_{anneal} to room temperature.

Key words: silicon, transmutation doping, thermal annealing, cooling rate, Seebeck coefficient anisotropy parameter.

Introduction

The electrophysical properties of transmutation-doped and conventional *n-Si* crystals, doped with phosphorous impurity through the melt (in the process of crystal growth by the Czochralski method), are compared in a number of works (see, for instance, [1 – 4]). Comparison of thermoelectric characteristics [5] of transmutation-doped and conventional silicon crystals was made in [6 – 9], where it is shown that with a higher homogeneity of impurity distribution in the bulk [10 – 12], as well as higher values of electron mobility measured at 77 K, the transmutation-doped *n-Si* crystals are characterized (all other factors being equal) by lower values of drag Seebeck coefficient anisotropy parameter $M = \alpha_{\parallel}^{ph}/\alpha_{\perp}^{ph}$ as compared to conventional crystals doped with phosphorous impurity through the melt. The latter is due to the fact that residual defects not eliminated from the bulk of transmutation-doped silicon crystals by standard process annealing (performed at 800 ÷ 850 ºC for 1 ÷ 2 h) and having no direct effect on the electron subsystem, introduce significant changes into effects occurring even in electron subsystem with participation of long-wave phonons. However, high-temperature annealing of transmutation-doped crystals can improve considerably their thermoelectric characteristics [8]. There is also a paper [13] where it is shown that thermal treatment of conventional *n-Si* crystals does not result in considerable change of their thermoelectric parameters.

To clarify the reasons for this difference, experiments were performed to study the influence of high-temperature annealing and cooling conditions on the thermoelectric properties of transmutation-doped silicon crystals, and that was the purpose of this work.

Results and discussion

Three types of annealing were used: process annealing (T = 800 °C, t = 2 h); high-temperature

A-type annealing (T_{anneal} = 1200 °C, t = 2 h); high-temperature *B*-type annealing (T_{anneal} = 1200 °C, t = 72 h); cooling rates after high-temperature annealing were υ_{cool} = 1 and 1000 °C/min. The object of study was conventional and transmutation-doped *n-Si* crystals. Conventional crystals were grown by the Czochralski method and were not subject to annealing (initial state). The *n-Si* crystals used later for transmutation doping were grown by zone melting technique. All transmutation-doped crystals (after silicon radiation with thermal neutrons) were first subject to process annealing at 800 °C for 2 hours (the state after such annealing will be considered to be initial for transmutation-doped crystals), and then – either to *A*-type or *B*-type annealing.

The basic parameters of samples under study are given in Table, where n_e and μ are charge carrier concentration and mobility, respectively, found from the Hall measurements; ρ_0 is electric resistivity in the absence of strong uniaxial mechanical stress X; ρ_∞ is resistivity at $X \geq 0.6$ GPa, $\vec{X} \parallel \vec{J} \parallel [001]$, $\vec{J}$ is current density when measuring tensoresistance (characteristic dependences ρ_X/ρ_0 are represented in Fig. 1); α_∞ and α_0 are tensothermopower ($\vec{X} \parallel \nabla T \parallel [001]$) at $X \geq 0.6$ GPa and $X = 0$, respectively (characteristic dependences α_X/α_0 are represented in Fig. 2); $\Delta\alpha = \alpha_\parallel^{ph} - \alpha_\perp^{ph}$ is thermopower anisotropy; α^e is electron (diffusion) component of thermopower calculated by the Pisarenko formula [14]:

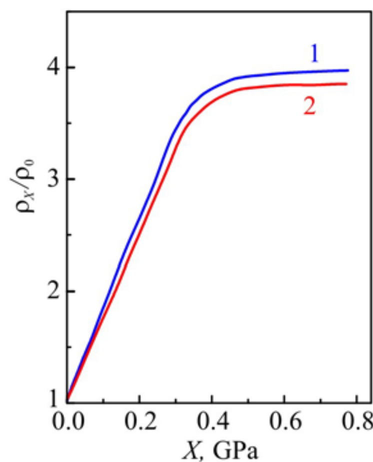

Fig. 1. Typical dependences of tensoresistance ρ_X/ρ_0 on the value of uniaxial mechanical stress $\vec{X}$ // $\vec{J}$ // [001] at T = 85 K for conventional (1) and transmutation-doped (2) n-Si crystals.

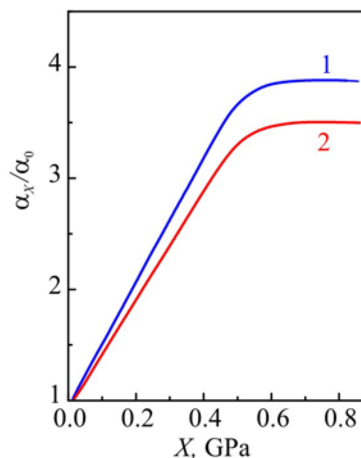

Fig. 2. Typical dependences of tensothermopower α_X/α_0 on the value of uniaxial mechanical stress $\vec{X}$ // ∇T // [001] at T = 85 K for conventional (1) and transmutation-doped (2) n-Si crystals.

Table

The basic parameters of n-Si samples under study

Conventional signs of *Si* samples; kind of thermal treatment	Symbols in the figures	υ_{cool}, °C/min	$n_e \cdot 10^{13}$, cm^{-3}	$\mu_{77\,K} \cdot 10^{-4}$, cm^2/V s	$\frac{\rho_\infty}{\rho_0}$	$\alpha_0 \cdot 10^{-3}$, $\frac{\mu V}{degree}$	$\alpha_\infty \cdot 10^{-4}$, $\frac{\mu V}{degree}$	α^e, $\frac{\mu V}{degree}$	$\alpha_\parallel^{ph} \cdot 10^{-4}$, $\frac{\mu V}{degree}$	$\alpha_\perp^{ph} \cdot 10^{-3}$, $\frac{\mu V}{degree}$	$\Delta\alpha \cdot 10^{-4}$, $\frac{\mu V}{degree}$	$K = \frac{\mu_\perp}{\mu_\parallel}$	$M = \frac{\alpha_\parallel^{ph}}{\alpha_\perp^{ph}}$
CONV	*a*	–	2.40	1.92	3.90	8.05	3.15	1220	3.03	4.70	2.56	5.35	6.45
CONV	*b*	–	5.50	1.90	3.82	7.90	3.03	1135	2.92	4.63	2.46	5.23	6.30
TD	1	–	2.90	2.22	3.86	8.00	2.85	1215	2.73	4.87	2.24	5.29	5.60
TD; 1200 °C, 2 h	1''	1000	2.40	2.00	3.87	10.2	4.90	1225	4.87	5.32	4.25	5.31	8.98
TD; 1200 °C, 2 h	1'	1	2.60	2.08	4.00	8.50	3.62	1217	3.51	4.84	3.03	5.50	7.20
TD	2	–	5.70	2.09	3.93	7.30	2.35	1132	2.24	4.66	1.77	5.40	4.90
TD; 1200 °C, 2 h	2'	1	5.50	2.14	3.95	8.40	3.57	1135	3.46	4.74	2.99	5.43	7.30
TD	3	–	5.73	2.14	3.84	7.50	2.66	1130	2.49	4.62	2.03	5.25	5.40
TD; 1200 °C, 2 h	3'	1	5.10	2.00	4.00	8.50	3.62	1140	3.51	4.84	3.03	5.50	7.20
TD	4	–	5.65	2.12	3.89	7.40	2.51	1131	2.36	4.64	1.90	5.33	5.40
TD; 1200 °C, 72 h	4''	1000	1.68	1.73	3.66	8.50	3.96	1230	3.84	4.14	3.43	5.00	9.30
TD; 1200 °C, 72 h	4'	1	3.00	2.08	3.54	8.50	3.50	1190	3.38	4.54	2.93	4.80	7.40

$$\alpha^e = \frac{k}{e}\left[2 + \ln\frac{2\left(2\pi m^* k T\right)^{3/2}}{n_0 h^3}\right], \tag{1}$$

where n_0 is charge carrier concentration; e is electron charge; k is the Boltzmann constant; T is temperature; h is the Planck constant; $m^* = N^{3/2}\sqrt[3]{m_{\parallel} m_{\perp}^2}$ is density-of-state effective mass; N is the number of isoenergetic ellipsoids; $m_{\parallel}$ and $m_{\perp}$ are effective masses of charge carriers lengthwise and crosswise the long axis of isoenergetic ellipsoid, respectively.

The value of mobility anisotropy parameter K is known to be experimentally obtained (see, for instance, [15]) from the data on tensoresistance with the use of relationship

$$K = \frac{\mu_{\perp}}{\mu_{\parallel}} = \frac{3}{2}\frac{\rho_{\infty}^{[001]}}{\rho_0} - \frac{1}{2}, \tag{2}$$

where $\mu_{\parallel}$ and $\mu_{\perp}$ are charge carrier mobilities lengthwise and crosswise the long axis of isoenergetic ellipsoid, respectively.

The phonon drag thermopower anisotropy parameter will be found through use of the following expression [8]:

$$M = \frac{\alpha_{\parallel}^{ph}}{\alpha_{\perp}^{ph}} = \frac{2K}{\left(2K+1\right)\dfrac{\alpha_0 - \alpha^e}{\alpha_{\infty} - \alpha^e} - 1} = \frac{2K}{\left(2K+1\right)\dfrac{\alpha_0^{ph}}{\alpha_{\infty}^{ph}} - 1}, \tag{3}$$

where $\alpha_{\parallel}^{ph}$ and $\alpha_{\perp}^{ph}$ are phonon components of thermopower lengthwise and crosswise the long axis of isoenergetic ellipsoid found from the formulae

$$\alpha_{\infty}^{ph} \equiv \alpha_{\infty} - \alpha^e = \alpha_{\parallel}^{ph}, \tag{4}$$

$$\alpha_0^{ph} = \alpha_0 - \alpha^e, \tag{5}$$

$$\alpha_{\perp}^{ph} = \alpha_{\parallel}^{ph} / M. \tag{6}$$

For the interpretation of the results we used the concentration dependence of drag thermopower anisotropy parameter M (Fig. 3, curve L), borrowed from [16].

Anisotropy parameters K and M, measured on silicon single crystals doped with phosphorous impurity by nuclear transmutation and in the process of growth by the Czochralski method were compared. It turned out that the values of drag thermopower anisotropy parameter M of crystals doped with phosphorous impurity through the melt (Fig. 3, dots a and b) obtained in this paper for comparison with transmutation-doped crystals of similar concentration exactly fall on curve L. And the values of parameter M for transmutation-doped crystals (with about the same carrier concentration n_e) are arranged much lower of this curve (Fig. 3, dots 1 – 4).

It can be assumed that substantial underrating of the values of parameter M for transmutation-doped crystals (as compared to standard curve obtained in the experiments with conventional crystals) is related to the emergence of lattice violations, i.e. residual defects. Such defects arise in huge concentrations in the process of transmutation doping and are not eliminated completely under conditions of relatively low-temperature (800 ^{o}C) process annealing of relatively short duration (2 h).

It should be noted that process annealing is a final and absolutely necessary stage of transmutation doping process. Silicon radiation with thermal neutrons is also accompanied by radiation with fast neutrons and γ - component of reactor spectrum. This results in silicon single

crystals saturated with all currently known radiation defects, which is promoted by extremely intensive integral neutron fluxes ($\sim 10^{18} \div 10^{19}$ n/cm^2) in nuclear reactor channels. Therefore, irrespective of the initial material type and its parameters, the as-irradiated transmutation-doped silicon is characterized by *p*-type conductivity with resistivity $\rho \approx 10^5 \div 10^6$ Ω·cm and very low lifetime of minor carriers. Moreover, after silicon irradiation with nuclear reactor neutrons the ^{31}Si atoms (which spontaneously go into ^{31}P according to nuclear reaction $^{30}Si\left(n,\gamma\right)\,^{31}Si \xrightarrow{\beta^-} {}^{31}P$) are as a rule found in the interstitial position. Such position corresponds to electrically inactive state. Therefore, for annealing of radiation defects and for activation of phosphorous atoms ^{31}P showing donor properties in the bulk of silicon only in lattice nodes, the transmutation-doped silicon must be subject to thermal treatment.

As shown by experiment, residual defects that were not eliminated during process annealing did not demonstrate marked influence on the electron subsystem of samples under study (mobility anisotropy parameter *K* remained practically unchanged), but changed essentially the effects occurring with participation of long-wave phonons.

Therefore, one could try to eliminate the underrating of parameter *M* values relative to standard curve *L* (Fig. 3) observed in the experiments with transmutation-doped silicon by annealing these crystals at higher temperatures than those (800 °C) used for process annealing. In all probability, annealing at higher temperatures will be able to transform, at least partially, the residual defects into such (point) defects on which phonons will be scattered less efficiently. Such process should have been accompanied by increase in parameter *M*, which was confirmed experimentally.

From Table it is seen that mobility anisotropy *K* is practically independent (within measurement error) of doping method or the employed thermal treatment modes, whereas drag Seebeck coefficient anisotropy parameter *M* is essentially responsive to annealing with subsequent cooling.

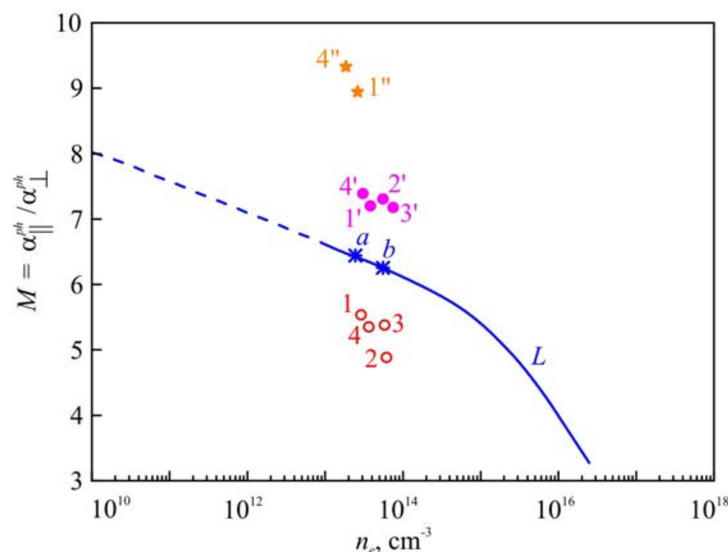

Fig. 3. Dependence of drag Seebeck coefficient anisotropy parameter $M = \alpha_{\parallel}^{ph}/\alpha_{\perp}^{ph}$ on electron concentration n_e: 1) in conventional (doped with phosphorous impurity from the melt) n-Si crystals at T = 85 K: solid curve L; 2) in transmutation-doped crystals, subject to low-temperature process annealing at 800 ºC for 2 h: dots 1 – 4; 3) in transmutation-doped crystals, annealed at high temperature (1200 ºC) and cooled at different rates (1 and 1000 ºC/min): dots 1' – 4' and 1", 4", respectively.

In Fig. 3, dots 1' – 4' and 1", 4" represent the data of experiments (see also Table) performed on transmutation-doped crystals annealed at 1200 °C. The results (irrespective of annealing duration

in the range of 2 ÷ 72 h) exceeded expectations, since the values of parameter M measured on annealed crystals not just "moved up" to position of curve L (as might be expected), but all without exception were well above this curve. In so doing, the values obtained with fast (υ_{cool} = 1000 °C/min) cooling of transmutation-doped crystals after annealing at 1200 °C proved to be so large (dots 1" and 4") that even with conditionally accepted linear change of function $M = M(n_e)$ (along a line segment in the form of strokes) they could be observed only at such values of $n_e \leq 10^8$ cm^{-3} which in the framework of existing technology of fabrication (and doping) of conventional silicon crystals are certainly unattainable.

What critical weaknesses of the method for growing (and doping) conventional crystals prevent from obtaining on them so high values of thermopower anisotropy parameter (and other thermoelectric characteristics) which are relatively easily obtained at comparable n_e on transmutation-doped silicon crystals annealed at higher temperatures?

The reason is probably as follows. In transmutation-doped crystals, the values of parameter M are transferred from positions 1 – 4 to positions 1' – 4' (and 1", 4") only due to high-temperature annealing, exempting the annealed crystal from the defects on which long-wave phonons are scattered that are responsible for the appearance of drag thermopower. Therefore, it is natural to believe that the process of conventional crystals growth and their doping with phosphorous impurity through the melt is accompanied by the emergence of stable and rather efficient scatterers for long-wave phonons in the form of impurity clusters which satisfy the condition $d_{clust} \sim \lambda_{ph} / 4$, which inevitably complicates formation of drag thermopower in such crystals. Indeed, under conditions of growth (and doping) of conventional crystals the emergence of small-size impurity clusters [17] is promoted by high temperature $T_{cryst}^{Si} \approx 1400\,^{\circ}\mathrm{C}$ strongly violating mutual correlation of impurity centres [18]. At such temperature, impurity atoms are introduced into silicon lattice, whereas under conditions of neutron transmutation the atoms of doping impurity will only statistically uniformly appear in lattice nodes in the entire volume of irradiated crystal.

By the example of obtaining a material with high thermoelectric figures (M, $\Delta\alpha$, α_∞ and others; see Table) through high-temperature annealing of transmutation-doped silicon crystals one can make certain in the relative character of what is often called the quality of semiconductor material. Indeed, seeking to improve by this method the thermoelectric characteristics of transmutation-doped silicon crystals, we inevitably get in these crystals sufficiently low lifetime values of minor carriers τ (within several units or tens of microseconds). Resting upon low-temperature process annealing, i.e. showing proper care about lifetime, we, naturally, will not be able to obtain on the basis of transmutation-doped silicon crystals high-quality material designed for thermoelectric applications. Similar statements remain correct regarding other characteristics of semiconductor materials (such as the dislocation density, the content of related impurities, etc.).

For these reasons, the quality of semiconductor materials should be considered as intimately linked with the specific tasks that must be solved, using these or other materials, showing special care about parameters governing realization of functional capabilities of specific semiconductor instruments and devices.

Conclusions

1. It was discovered that for silicon samples doped with phosphorous by nuclear transmutation the thermopower anisotropy parameter is considerably lower than for the samples doped through the melt in the process of growth by the Czochralski method, with practically coincident values of

mobility anisotropy parameter *K*. It was concluded that these changes are caused by residual defects on which long-wave phonons are strongly scattered, producing no effect on electron subsystem.

2. It was established that high-temperature annealing (T_{anneal} = 1200 °C; t = 2 ÷ 72 h) in transmutation-doped *n-Si* crystals increases Seebeck coefficient anisotropy parameter, this effect being more pronounced at quick cooling of samples. It was revealed that mobility anisotropy parameter *K* is practically independent either of doping method or of thermal treatment used.

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