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SOME THERMOELECTRIC FEATURES OF CONVENTIONAL AND TRANSMUTATION DOPED SILICON CRYSTALS

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• *In this paper, we have determined the anisotropy parameter of the drag thermoEMF M in n-Si single crystals ($\rho_{300K} \cong 150 \div 170$ Ohm·cm) doped with phosphorous impurity from the melt and transmutation doped samples, nondeformed and uniaxially elastically deformed. It turned out that in transmutation doped n-Si <P> samples $M^{TD}=\alpha_{\parallel}^{ph} / \alpha_{\perp}^{ph} \approx 5$, and in conventional silicon samples $M^{Conv}=\alpha_{\parallel}^{ph} / \alpha_{\perp}^{ph} \approx 6.8$. Components of the thermoEMF tensor in a thermoelectrically anisotropic plate with temperature gradient oriented along the normal to its longitudinal axis and deflected by angle φ from the anisotropy axis of this plate have been described in detail, and the expression for maximum efficiency of anisotropic thermoelement (on evidence derived from the literature) has been given. The piezoresistance and piezothermoEMF have been obtained for the conventional and transmutation doped crystals that were measured (at temperature T = 85 K) under conditions X // J // [001] and X // ∇T // [001], respectively.*

Introduction

A drastic increase of requirements to quality of silicon crystals is related not only to growing automation rate of production and social spheres in any technically advanced country, but is also due the emergence and fast improvement in semiconductor engineering of different- purpose charge coupled devices, very large-scale integral circuits of superhigh performance, super powerful high-voltage thyristors, etc. All this motivates an urgent necessity of search for new technological processes of getting enhanced quality silicon crystals. One of basically important ways for quality improvement of semiconductor crystals is development and mastering of their doping techniques that would assure homogeneous bulk distribution of doping impurities on retention of crystal structural perfection.

Phosphorous is known to be the most widespread doping impurity in the manufacture of *n*-type silicon single crystals (*n-Si* <*P*>). However, many years' experience shows that such doping methods as introduction of phosphorous from gaseous phase or as a hard alloy directly into a crucible for Czochralski-grown crystals or into a polycrystalline billet for crucible-free zone melting, etc, do not allow to obtain under conditions of large-scale production single crystals with resistivity spread in the bulk less than 10 ÷ 20 % and in the cross section less than 5 ÷ 7 % [1].

Due to the foregoing, one of important technological lines in the manufacture of silicon crystals with a homogeneous phosphorous distribution, namely transmutation doping method, is worthy of attention. The essence of this method comes down to the fact that in the process of irradiation with thermal neutrons silicon isotope ^{30}Si first goes over to ^{31}Si, and then – to phorphorous ^{31}P in conformity with a nuclear reaction [2 – 4]

$$^{30}Si\left(n,\gamma\right)\,^{31}Si \xrightarrow{\beta^-} {}^{31}P\,. \qquad (1)$$

The half-life of the intermediate product (that is, β-radioactive isotope ^{31}Si) is 26 hours. Note that transmutation reaction (n, γ) at interaction of thermal neutrons with silicon, is realized for all its

natural isotopes: ^{28}Si (92.18 %), ^{29}Si (4.70 %) and ^{30}Si (3.12 %), however, only reaction (1) results in the formation of impurity phosphorous atoms.

The homogeneity of resistivity in the bulk of transmutation doped silicon single crystals of diameter ~ 80 mm and length 600 mm is on the average ± 5 % of the given value [5]. In so doing, typical bulk spread is within 3 ÷ 10 %, and in the ingot radius it does not exceed 1 %.

As the sources of thermal neutrons (with the energy $E_n \leq 100$ keV), research nuclear reactors or nuclear reactors of atomic power stations that are always characterized by the availability of high density thermal neutron flows, are used. Silicon irradiation with thermal neutrons is also accompanied by irradiation with fast neutrons and γ-component of reactor spectrum. As a result, silicon single crystals are obtained that are saturated with all currently known radiation defects, which is aided by extremely intensive integral neutron fluxes (~ $10^{18} \div 10^{19}$ n/cm^2) in nuclear reactor channels. So, irrespective of the initial type of material and its parameters, as-irradiated transmutation doped silicon has *p*-type conduction with the resistivity $\rho \approx 10^5 \div 10^6$ Ohm·cm and very short lifetime of minority carriers. Moreover, after silicon irradiation with nuclear reactor neutrons, ^{31}Si atoms (that spontaneously go over to ^{31}P) are found, as a rule, in the interstitial position which is known to correspond to electrically inactive state. Thus, for annealing of radiation defects and for activation of ^{31}P atoms which in the bulk of silicon show donor properties only in lattice sites, transmutation doped silicon should be subject to thermal treatment.

Thermal annealing after transmutation doping

Mechanisms of origination of radiation defects and the specificity of their thermal annealing, as well as the reasons assuring their thermal stability in the irradiated crystals have been detailed in specialized literature [6 – 10] and in a number of reference books [11, 12].

It is considered that defects that appear in transmutation doped *Si* crystals irradiated with thermal neutrons can be almost completely removed from the bulk of the crystal by annealing at $T = 800 \div 850$ °C within 1 ÷ 2 hours (the so-called technological thermal annealing).

Transmutation doped *Si* crystals due to radiation with thermal neutrons differ from conventional *Si* crystals doped with phosphorous impurity through the melt, not only in the improved homogeneity of doping impurity distribution in the bulk of the crystal [13 – 15], but also in higher mobility μ values, all other factors being equal.

The question arose as to whether similar advantages become apparent in transmutation doped *Si* crystals (as compared to conventional crystals) even when the effects related to phonon, rather than electron scattering, will be used as trial ones. Such methodical approach (in case of its efficiency) will be equivalent, in principle, to expansion of the heuristic opportunities of this procedure, since the de Broglie wavelength of phonons satisfies the inequality $\lambda_{ph} < \lambda_e$.

Indeed, when it comes to scattering of certain quasiparticles, such as electrons or phonons, obstacles to their motion in crystals can be conveniently estimated by comparing the size of these obstacles to the de Broglie wavelength characterizing the respective objects. In this connection it should be noted that technological thermal annealing experienced by transmutation doped *n-Si* <*P*> crystals removes from the bulk of the crystals the radiation defects comparable in their size to the electron de Broglie wavelength, and current carrier mobility in such annealed crystals is essentially increased. However, it does not mean that such a kind of technological annealing eliminates absolutely all radiation defects: defects of much smaller size can remain, and the electron de Broglie wavelength propagating in crystal will just “take no notice” of them, bypassing easily. To reveal smaller-size

defects, it is necessary to use much shorter waves. If the electron de Broglie wavelength in a crystal overlaps a hundred or several hundreds of interatomic distances, then phonons that are responsible for the formation of the electron-phonon drag thermoEMF (in the temperature range of $T \approx 20 \div 80$ K in the case of *Si* and *Ge*), have the wavelength $1.5 \div 2$ orders smaller than the electron de Broglie wavelength.

Research on the electron-phonon drag thermoEMF

The results of works [16 – 18] testify to the effect that under given polarization of long-wave phonons (*l* or *t*) the electron-phonon drag in the direction of a long (principal) axis of isoenergetic ellipsoid is decisive, that is

$$\alpha_{\parallel}^{(l,t)} >> \alpha_{\perp}^{(l,t)},$$

and under the assigned direction relative to ellipsoid axes, the primary role in the electron-phonon drag is played by longitudinally polarized phonons, that is

$$\alpha_{\parallel,\perp}^{(l)} >> \alpha_{\parallel,\perp}^{(t)}. \tag{2}$$

Because of this, the thermoelectric properties of different samples (doped, for instance, by different methods) should be compared exactly to component $\alpha_{\parallel}^{(l)}$, which is why, according to the results obtained in [16],

$$\frac{\alpha_{\parallel}^{(l)Conv}}{\alpha_{\parallel}^{(l)TD}} \approx 1.7. \tag{3}$$

Hence it follows that longitudinal phonons (which preferably determine the phonon component of the electron-phonon drag thermoEMF along the long axis of isoenergetic ellipsoid $\alpha_{\parallel}^{ph} \sim \alpha_{\parallel}^{(l)}$) are more efficiently scattered in transmutation doped crystals (that have been subjected only to technological annealing) than in conventional silicon crystals doped with phosphorous impurity in the same concentration from the melt.

Having used the experimentally measured (at $T \approx 80 \div 85$ K) thermoEMF values in the nondeformed α_0 and deformed α_∞ transmutation doped *n-Si* samples (with the resistivity values at room temperature $\rho_{300\,K} \approx 150 \div 170$ Ohm·cm), and having freed this data from the contribution of the electron (diffusion) component of thermoEMF $\alpha^e = 1170$ μV/K, one can obtain the value of thermoEMF related to demonstration of the electron-phonon drag effect, namely: $\alpha_{\parallel}^{ph} = 29200$ μV/K and $\alpha_{\perp}^{ph} = 5830$ μV/K ($\alpha_{\parallel}^{ph}$, $\alpha_{\perp}^{ph}$ are phonon components along and across the long axis of isoenergetic ellipsoid, respectively). Hence we find the anisotropy parameter of the drag thermoEMF *M* that characterizes phonon subsystem:

$$M^{TD} = \frac{\alpha_{\parallel}^{ph}}{\alpha_{\perp}^{ph}} \cong 5.02. \tag{4}$$

It turns out that while reducing considerably (for the reason mentioned above) the anisotropy parameter of the drag thermoEMF $M^{TD} \approx 5$ as compared to $M^{Conv} \approx 6.8$, the above defects (that are not removed completely in the course of technological thermal annealing) do not reduce, however, the mobility values in transmutation doped samples (μ^{TD}), as demonstrated by the fulfillment of inequality

$\mu^{TD} > \mu^{Conv}$. This result is in good agreement with the data obtained in work [16].

Note that the anisotropy parameter of the drag thermoEMF M can be determined both directly (according to $\alpha_{\parallel}^{ph}$ and $\alpha_{\perp}^{ph}$ data) and through use of formula [19]:

$$M = \frac{2K}{(2K+1)\dfrac{\alpha_0 - \alpha^e}{\alpha_\infty - \alpha^e}} = \frac{2K}{(2K+1)\dfrac{\alpha_0^{ph}}{\alpha_\infty^{ph}} - 1}\ , \tag{5}$$

where $\alpha^e = \dfrac{k}{e}\left[2 + \ln\dfrac{2\left(2\pi m^* kT\right)^{3/2}}{n_0 h^3}\right]$ is the electron (diffusion) component of thermoEMF (the Pisarenko formula) [20]; n_0 is charge carrier concentration; e is electron charge; k is the Boltzmann constant; T is temperature; h is the Planck constant; $m^* = N^{2/3}\sqrt[3]{m_{\parallel} m_{\perp}^2}$ is the effective mass of density of states; N is the number of isoenergetic ellipsoids, in particular for *n-Si* $N = \begin{cases} 6 \text{ for } X = 0, \\ 2 \text{ for } X = 12\,\text{t/cm}^2 \end{cases}$; $m_{\parallel}$, $m_{\perp}$ are the effective masses along and across the long axis of isoenergetic ellipsoid, respectively; $K = \dfrac{\mu_{\perp}}{\mu_{\parallel}} = \dfrac{3}{2}\dfrac{\rho_\infty^{<001>}}{\rho_0} - \dfrac{1}{2}$ is the anisotropy parameter of the electron mobility in the framework of one isoenergetic ellipsoid taken separately, parameter K characterizes electron subsystem; $\mu_{\parallel}$, $\mu_{\perp}$ are charge carrier mobilities along and across the long axis of isoenergetic ellipsoid, respectively; ρ_0, $\rho_\infty^{<001>}$ is resistivity of nondeformed $\rho(X = 0) \equiv \rho_0$ and uniaxially elastically deformed $\rho(X \to \infty) \equiv \rho_\infty$ (which corresponds to saturation area $\rho = \rho(X)$ of *Si* crystal in crystallographic direction <001> (that is, under condition of $X \,//\, J \,//\, [100]$, where X is mechanical stress, J is current); α_0^{ph}, α_∞^{ph} are phonon components of the thermoEMF without pressure ($X = 0$) and in saturation ($X \to \infty$) which are equal to experimental data (α_0 and α_∞) without the electron component:

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

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

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

Symbol (∞) is used to designate the values obtained at the values of mechanical stress X which bring the respective parameter to saturation.

Figs. 1 and 2 represent typical dependences of piezoresistance and piezothermoEMF on the mechanical stress X, respectively. Measurements were made at $T = 85$ K in a wide range of X. In so doing, one should take into account essential dependence of the values of respective α and K on the thermal history of samples under investigation, as it was shown in paper [21]. On high-temperature treatment which is inevitably experienced by crystal even in the course of growing, the observed complexes are formed with the interaction of residual atoms of carbon, oxygen (and possibly other electrically neutral impurities) with point defects of the type of vacancies and interstitial atoms. The more so that concentration of point defects is largely governed by the content of both doping and residual impurities in a crystal.

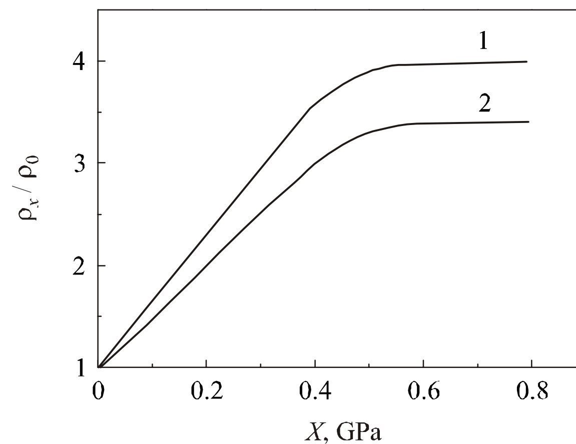

Fig. 1. Dependences of piezoresistance ρ_x/ρ_0 *on the value of uniaxial mechanical stress X // J // [001] at T = 85 K for conventional (1) and transmutation doped (2) n-Si.*

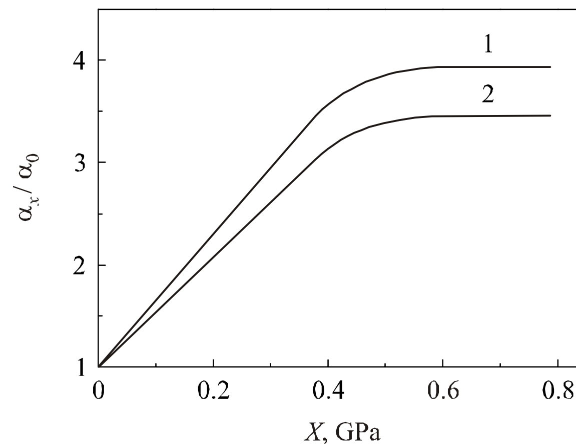

Fig. 2. Dependences of piezothermoEMF α_x/α_0 *on the value of uniaxial mechanical stress X // ∇T // [001] at T = 85 K for conventional (1) and transmutation doped (2) n-Si.*

Thermoelectrically anisotropic media

Of all the problems thermoelectricians are concerned with, one should primarily emphasize three which to our opinion are most relevant, namely:

– fundamental problems of physics of thermoelectric phenomena;

– problems of material research aspect, that is the tasks related to technology of preparation of thermoelectrically efficient materials with preset properties, as well as

– issues of optimal design of thermoelectric devices of various functional purpose.

One of the topical problems in this field is actual absence of thermoelectrically anisotropic materials suitable for practical use in the range of cryogenic temperatures. In this context, the problem related to possible application of multi-valley semiconductors (of *Ge* and *n-Si* type) in the field of thermoelectric instrument making can be considered little investigated and practically important, while being, no doubt, worthy of attention.

Really, consider a thermoelectrically anisotropic medium (such as directionally deformed *n*-type *Ge* or *Si* crystal), the thermoEMF tensor of which in crystallographic axes (*x, y*) is of the form

$$\hat{\alpha} = \begin{pmatrix} \alpha_{\perp} & 0 \\ 0 & \alpha_{\parallel} \end{pmatrix}. \tag{6}$$

If a plane-parallel plate is made of such thermoelectrically anisotropic material so that its thermoelectric axis makes an angle ϕ with the direction of temperature gradient (grad T or ∇T), oriented along the normal to its longitudinal axis (axis a in Fig. 3), then the thermoEMF tensor will be as follows

$$\hat{\alpha} = \begin{pmatrix} \alpha_{\parallel}\cos^2\phi + \alpha_{\perp}\sin^2\phi & \left(\alpha_{\parallel} - \alpha_{\perp}\right)\sin\phi\cos\phi \\ \left(\alpha_{\parallel} - \alpha_{\perp}\right)\sin\phi\cos\phi & \alpha_{\parallel}\sin^2\phi + \alpha_{\perp}\cos^2\phi \end{pmatrix}. \tag{7}$$

If in a plate there exists one-dimensional temperature field, grad T of which is oriented towards uniaxial stress, then, as shown by the authors of [22],

$$V = \frac{a}{b}\left(\alpha_{\parallel} - \alpha_{\perp}\right)\left(T_1 - T_0\right)\sin\phi\cos\phi, \tag{8}$$

where $\alpha_{\parallel} - \alpha_{\perp} = \Delta\alpha$ is plate thermoEMF anisotropy; V is thermoelectric voltage.

The issue of anisotropic thermoelement efficiency was detailed in works [23, 24], and here we give only its maximum value according to the results of these works:

$$\eta_{\max} = \eta_C \frac{1}{1 + \dfrac{2\left(1 + \bar{M}\right)}{Z\,T_1}},$$

where $\eta_C = \dfrac{T_1 - T_0}{T_1}$ is the Carnot efficiency; $\bar{M} = \sqrt{1 + Z\,\bar{T}}$; $\bar{T} = \dfrac{T_1 + T_0}{2}$; and $Z = \dfrac{\alpha_{12}^2}{\chi_{22}\,\rho_{11}}$ is the figure of merit of anisotropic thermoelement; α_{12}, χ_{22}, ρ_{11} are components of thermoEMF, thermal conductivity and resistivity tensors, respectively.

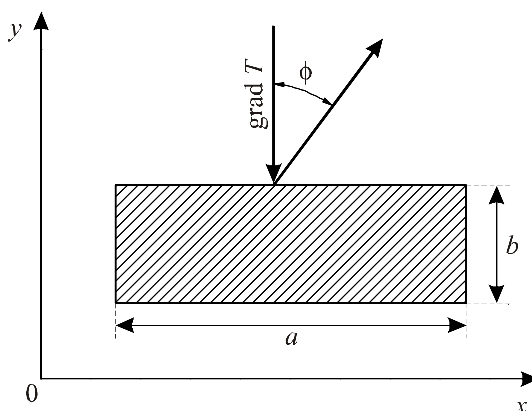

Fig. 3. Location of grad T relative to anisotropy axis in thermoelectrically anisotropic crystal (schematic of anisotropic thermoelectric converter).

In conclusion, it should be noted that, as was shown in [25], the longitudinal phonon component $\alpha_{\parallel}^{ph}$ of transmutation doped *n-Si* crystals (unlike $\alpha_{\perp}^{ph}$) is more sensitive to thermal annealing in the region of 800 ÷ 1200 ^{o}C, and its absolute value increases with a rise in annealing temperature almost 1.4 times, whereas $\alpha_{\perp}^{ph}$, with the same rise in thermal annealing temperature, shows only a weak tendency to reduction. In conventional (rather than transmutation doped) *n-Si* crystals these changes are insignificant even at the highest thermal annealing temperatures.

Conclusions

This paper deals with a mechanism of transmutation doping of silicon crystals with phosphorous impurity and subsequent technological thermal annealing which is the inseparable component of this doping technique.

We have investigated the anisotropy of the electron-phonon drag thermoEMF and the phonon component of piezothermoEMF of *n-Si* crystals conventionally doped with phosphorous impurity from the melt and transmutation doped, and the general view of thermoEMF tensor is represented in thermoelectrically anisotropic medium in which capacity there were considered directionally deformed *n*-type *Si* or *Ge* crystals.

The numerical value of the electron-phonon drag thermoEMF ($M^{Conv} = \alpha_{\|}^{ph} / \alpha_{\perp}^{ph} \cong 5$) has been found in directionally deformed transmutation doped *n-Si* crystals with $\rho_{300\,K} \approx 150 \div 170$ Ohm·cm, and the value of this parameter has been compared to a similar parameter obtained in experiments with the conventional (melt-doped) crystals ($M^{Conv} = \alpha_{\|}^{ph} / \alpha_{\perp}^{ph} \approx 6.8$).

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