ASCERTAINMENT OF THE REASON FOR THE INCREASE IN THE ANISOTROPY PARAMETER OF THERMO-EMF FOR TRANSMUTATION-DOPED n-Si WITH INCREASING ANNEALING TEMPERATURE

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The experimental data on measuring of thermoelectromotive force (thermo-emf), tenso-thermo-emf and tensoresistance of the transmutation-doped and ordinary n-Si crystals, which subjected to annealing at $1073 \le T_{ann} \le 1473$ K during 2 h, and cooled from the annealing temperatures to the room temperature with rates of 1 and 15 K/min, were presented. On the basis of the obtained experimental data the anisotropy parameter of thermo-emf of electron-phonon drag and the anisotropy parameter of mobility were determined. It is found that in the transmutation-doped n-Si crystals the increase of the anisotropy parameter of thermo-emf $M = \alpha_{\parallel}^{ph}/\alpha_{\perp}^{ph}$ with rising of the annealing temperature was caused by the increase of the longitudinal phonon component of thermo-emf ($\alpha_{\parallel}^{ph}$), while the transversal component ($\alpha_{\perp}^{ph}$) is reduced.

Keywords: silicon; transmutation doping; annealing; thermo-emf; anisotropy parameter of thermo-emf.

Introduction

When you create the solid-state electronic devices the doping of semiconductors with necessary impurities up to predetermined values of concentrations is a major technological method. One of the fundamentally important ways to improve the quality of semiconductor crystals is the development and practical application of doping methods that could provide the homogeneous distribution of dopants by volume while keeping the structural perfection of crystal. In this connection use of the material doped by the method of nuclear transmutation under irradiation of silicon by the flux of thermal neutron is of great interest [1, 2].

As compared to silicon, doped by the ordinary method (through the melt), the transmutation doped silicon has a number of advantages: dopant is distributed uniformly over the cross section and the volume of the ingot; lack of microscopic inhomogeneities in the distribution of impurity; the possibility with high accuracy (1 % or above) to control the level of doping; is excluded the segregation of dopant at the grain boundaries in the polycrystalline silicon; the possibility to precisely control the content of impurities of heavy elements. These advantages are conditioned by the uniform distribution of the silicon isotopes within the target material and that neutrons in silicon have the considerable free path. Thus, it is possible to achieve the high precision of doping, taking into account that the concentration of phosphorus impurity is determined by the exposure time for a given neutron flux density when the neutron flux is homogeneous [3].

The transmutation-doped (TD) n-Si crystals after standard technological annealing at T = 1073 K during 2 h are characterized by the lower values both tenso-thermo-emf (measured in the region of electron-phonon drag) α_{∞}, and the anisotropy parameter of thermo-emf $M = \alpha_{\parallel}^{ph}/\alpha_{\perp}^{ph}$ (where $\alpha_{\parallel}^{ph}$ and $\alpha_{\perp}^{ph}$ are the phonon components of thermo-emf along and across the major ellipsoid axis) as compared to the ordinary (OR) n-Si crystals doped with phosphorus through the melt [4]. The effect obtained is due to the presence of residual defects. These defects are not eliminated from the volume of the transmutation-doped n-Si crystals by the use of technological annealing and make the significant corrections to the effects that occur in the electronic subsystem with long wave phonons [5]. However, in the transmutation-doped n-Si crystals the high-temperature annealing (at 1473 K) leads to increase of tenso-thermo-emf that is accompanied by 30–40 % increase in the parameter M in comparison with the ordinary crystals [4]. And the fundamental differences in the method of growth and doping of the ordinary and transmutation-doped crystals do not allow to receive the ordinary (doped through the melt) silicon with such high values of thermoelectric parameters that can be achieved on the transmutation-doped silicon, subjecting it to the high-temperature treatment.

If the increase of tenso-thermo-emf $\alpha_{\infty} = \alpha_{\parallel}^{ph} + \alpha^{e}$ (where α^{e} is the electron (diffusion) component of the thermo-emf) in the transmutation-doped n-Si crystals as a result of the high-temperature annealing can be associated with an increase in the longitudinal component of drag thermo-emf (due to the annealing of small defects, scattering long-wave phonons, satisfying of the condition $\lambda_{ph} < \lambda_{e}$, where λ_{ph} and λ_{e} is the wavelength of phonon and electron, respectively), then the question about causes of the change of the anisotropy parameter M in [4] remained open.

The aim of this study is to clarify the reason for the increase in the transmutation-doped n-Si crystals of the anisotropy parameter M as a result of the high-temperature treatment and to carry out the similar experiments on the ordinary n-Si crystals, doped with phosphorus through the melt.

Experiment

The experiment was performed on the samples made from two ingots one of which is the transmutation-doped with phosphorus ($n_e = 5.8 \times 10^{13}$ cm^{-3}) and the other ingot (ordinary) doped with phosphorus through the melt ($n_e = 8 \times 10^{13}$ cm^{-3}). After taking the orientation, which provide in what follows the preparation of samples with the long axis in direction [001], the samples, made from both ingots, were simultaneously annealed under identical conditions at T_{ann} = 1173, 1273, 1373, 1473 K during t = 2 h. The samples, made from both ingots, were cooled from each annealing temperature to room temperature using a two cooling rates $\upsilon_{cl} = 1$ and 15 K/min. Before the carrying out of the above-mentioned thermal annealing, the transmutation-doped and ordinary n-Si crystals were subjected to the technological annealing at T = 1073 K during 2 h (in what follows these crystals will be called as «initial»). In all the figures presented below, the marks with a cross inside will indicate the experimental data for the samples in the initial state.

Results and Discussion

On the transmutation-doped and ordinary samples, prepared as described above, every time at T = 77 K, $0 \le X \le 0.7$ GPa the dependences of the resistivity on the pressure $\rho = \rho$ (X) were measured. At T = 85 K the dependences of thermo-emf on the pressure $\alpha \equiv \alpha^{ph} + \alpha^{e} = \alpha$ (X), X = 0.7 GPa were measured, where X is the mechanical stress of compression (used for the directed deformation of crystal), applied in the current direction J (when measured ρ (X)) or ∇T (when measured $\alpha = \alpha$ (X)), i.e. $\vec{X} \,//\, \vec{J}$, ∇T // [001]. For ρ (X) and α (X) were taken subscripts ∞ or 0: the functions were measured at values X deducing these functions on saturation ($X \to \infty$), or in the absence of stress on the crystal (X = 0). On the basis of experimental data the anisotropy parameter of mobility K and the anisotropy parameter of thermo-emf M were calculated by the formulas in [4]:

$$K = \frac{\mu_\perp}{\mu_{||}} = \frac{3}{2}\frac{\rho_\infty}{\rho_0} - \frac{1}{2}, \quad M = \frac{\alpha_{||}^{ph}}{\alpha_\perp^{ph}} = \frac{2K}{\left(2K+1\right)\dfrac{\alpha_0 - \alpha^e}{\alpha_\infty - \alpha^e} - 1},$$

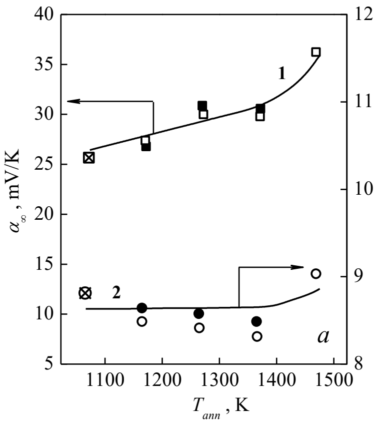
where $\mu_{||}$ and $\mu_\perp$ are the mobility of charge carriers along and across the major axis of isoenergetic ellipsoid, respectively; $\alpha(X) = \begin{cases} \alpha(0) \equiv \alpha_0 = \alpha^{ph}(0) + \alpha^e, \\ \alpha(\infty) \equiv \alpha_\infty = \alpha_{||}^{ph} + \alpha^e. \end{cases}$

To calculate the diffusion component of thermo-emf α^e (practically independent on the compression stress X) by the formula $\alpha^e = \frac{k}{e}\left[2 + \ln\frac{2\left(2\pi m^* kT\right)}{n_e h^3}\right]$, the values of charge carrier concentration n_e, obtained for the samples studied using Hall measurements (according to the expressions from [6]), were used.

For the transmutation-doped n-Si samples the values obtained α_0, α_∞, M and K depending on the thermal treatment conditions were presented by the corresponding curves in Fig. 1.

Comparison of the results obtained for the transmutation-doped and ordinary silicon samples, first of all, indicates an extremely high sensitivity of the tensoresistance effect in transmutation-doped n-Si crystals, annealed at 1473 K, to the conditions of their cooling. It was found that the cooling rate $\upsilon_{cl} = 15$ K/min provides the appearance of the strong dependence of the total charge carriers concentration in the conduction band (c-band) of these crystals on the value of mechanical stress X. This fact practically eliminates the possibility of obtaining ρ_∞ and others parameters (such as K, M et al.), directly connected with ρ_∞. However, the reasons for such «anomalous» behaviour of ρ_X/ρ_0 are of independent interest and require additional experiments, the results of which will be described hereinafter.

In contrast to α_∞ and M parameters (practically weakly dependent on annealing conditions), characterizing the ordinary samples, in the transmutation-doped samples these parameters with increasing T_{ann} from 1073 to 1473 K monotonously and continuously increase (Fig. 1a, curves 1). Taking into account that $\alpha_\infty = \alpha_{||}^{ph} + \alpha^e$ and $\alpha^e \approx$ const in the investigated range of the annealing temperatures $1073 \le T_{ann} \le 1473$ K with an accuracy of not less than 4 %, on the basis of [4] we can conclude that the observed growth of curve 1 in Fig. 1a is directly related to an increase in the efficiency of removal of small defects (acting as scatterer of long-wave phonons) with increasing T_{ann}.



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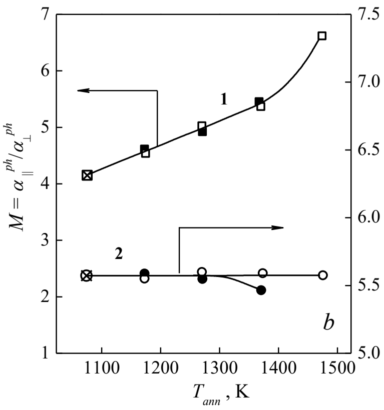


b

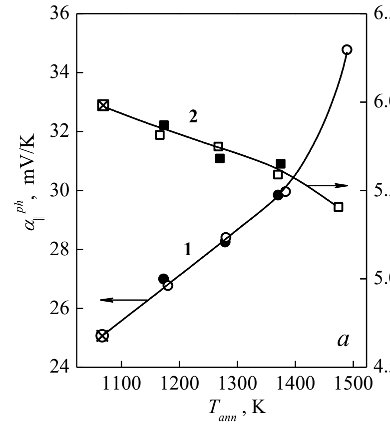
Fig. 1. Dependences for the transmutation-doped n-Si crystals: *a* – $\alpha_\infty = \alpha_\infty(T_{ann})$ (1), $\alpha_0 = \alpha_0(T_{ann})$ (2); *b* – $M = M(T_{ann})$ (1), $K = K(T_{ann})$ (2). Open symbols – for $\upsilon_{cl} = 1$ K/min; close – for $\upsilon_{cl} = 15$ K/min

The values of each of the components were calculated on the basis of experimental data (for the transmutation-doped and ordinary samples and the specific conditions of thermal treatment) by the following formulas

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

$$\alpha_\perp^{ph} = \frac{1}{2K}\left[\left(2K+1\right)\left(\alpha_0 - \alpha^e\right) - \alpha_{||}^{ph}\right].$$

Subsequently they can be presented as the corresponding curves in Fig. 2.



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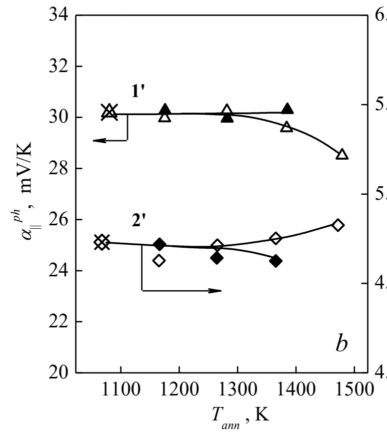

b

Fig. 2. Dependences $\alpha_{\parallel}{}^{ph} = \alpha_{\parallel}{}^{ph}$ (T_{ann}) (1, 1') and $\alpha_{\perp}{}^{ph} = \alpha_{\perp}{}^{ph}$ (T_{ann}) (2, 2') for the transmutation-doped (a) and the ordinary (b) n-Si crystals. Open symbols – for υ_{cl} = 1 K/min; close – for υ_{cl} = 15 K/min

Analysis of the results obtained shows that:

1) observed in the transmutation-doped n-Si crystals the increase of the anisotropy parameter of thermo-emf $M = \alpha_{\parallel}{}^{ph}/\alpha_{\perp}{}^{ph}$ with rising of the annealing temperature (Fig. 1b, curve 1) caused by the increase $\alpha_{\parallel}{}^{ph}$ (Fig. 2a, curve 1) while reducing the $\alpha_{\perp}{}^{ph}$ (Fig. 2a, curve 2) with increasing T_{ann};

2) the longitudinal phonon component of thermo-emf ($\alpha_{\parallel}{}^{ph}$) in the transmutation-doped n-Si crystals in the initial state is significantly below of this value in the ordinary crystals, however, the high-temperature annealing (at cooling rate υ_{cl} = 1 K/min) changes the relation between these components on reversed, i.e. provides $\alpha_{\parallel}{}^{ph}$ (TD) > $\alpha_{\parallel}{}^{ph}$ (OR) (Figs. 2a and 2b, curves 1, 1');

3) at all investigated thermal treatments (and other similar conditions) $\alpha_{\perp}{}^{ph}$ (TD) > $\alpha_{\perp}{}^{ph}$ (OR) (Figs. 2a and 2b, curves 2 and 2').

Conclusions

It is shown that in the transmutation-doped n-Si crystals the increase of the anisotropy parameter of thermo-emf M with increasing of the annealing temperature caused by the rise of the phonon component of thermo-emf along the major axis of the isoenergetic ellipsoid $\alpha_{\parallel}{}^{ph}$ while reducing $\alpha_{\perp}{}^{ph}$. The transmutation-doped and ordinary n-Si crystals were characterized by the ratio $\alpha_{\parallel}{}^{ph}$ (TD) < $\alpha_{\parallel}{}^{ph}$ (OR) before the annealing, and after the annealing – by the ratio $\alpha_{\parallel}{}^{ph}$ (TD) > $\alpha_{\parallel}{}^{ph}$ (OR) at υ_{cl} = 1 K/min. The ratio $\alpha_{\perp}{}^{ph}$ (TD) > $\alpha_{\perp}{}^{ph}$ (OR) was observed in all the cases studied.

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