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Seebeck's effect in p-SiGe whisker samples

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Abstract. *p*-SiGe whisker samples with a diameter of ~40 µm, grown by chemical precipitation from the vapor phase, have been investigated. Temperature dependences of the thermal e.m.f. and conductivity within the temperature interval 20…400 K have been measured. It has been shown that the mobility of holes in $p-\mathrm{SiGe}$ whiskers upon the average is 1.5 times higher than that in bulk $p-\mathrm{Si}$ samples. $p-\mathrm{SiGe}$ whiskers possess smaller phonon scattering and larger phonon dragging in comparison with the bulk $p-\mathrm{Si}$ samples.

Keywords: whisker semiconductor crystals, Seebeck's effect, thermal e.m.f., thermoelectric effect, phonon drag, carrier scattering.

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1. Introduction

In recent years, nanotechnology achieved considerable progress in the growth of semiconductor whisker crystals [1] and creation of miniature sensors [2] that have to work not only in the aggressive media but also in high magnetic and radiation fields. Therefore, determination of radiation and magnetic-field hardness requires a reliable control of the electrophysical parameters of whisker materials and instruments based on them. It should be noted that in spite of significant experience in studying the thermal e.m.f. as well as other effects with high prospects of using $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ as thermoelectric material, the Seebeck effect of whisker semiconductors is investigated insufficiently. It is related with the fact that it is very difficult to calculate contribution of mutual dragging the quasi-particles in thermoelectric effects [3]. Difficulties exist also in measurements of the Hall effect in whisker samples. This forces to approach more correctly to measurements of thermal e.m.f. and, all the more, to calculation of the integral of collisions in the specific case. All this will make it possible to reliably determine the temperature dependence of carrier concentrations in the whisker materials and to determine the performance characteristics of sensors. In the case of bulk $p-\mathrm{Si}$ samples, measurements of the Hall effect [4] and determination of the thermal e.m.f. in these materials [5] were carried out reliably. The influence of the effects of carrier dragging by phonons, their scattering by phonons and at the boundaries of surface, and their influence on the measured temperature dependence of thermal e.m.f. were investigated.

2. Experimental details and results

Investigated in this work were $p-\mathrm{SiGe}$ whisker samples with the specific resistance $\rho = 0.018$ – 0.03 Ohm·cm grown by the method of gas transport reactions in the closed bromide system from the source materials Si and Ge. The composition of solid solutions was controlled using the method of microprobe analysis and differed within the limits no more than 3%. The crystals for investigations with the length of 10…20 mm and with the transverse sizes of approximately 20 to 30 µm were selected. Our measurements of Seebeck's coefficient was carried out using the method of the temperature gradient in whisker crystals created with the aid of current transmission through the part of the sample with the length ~0.3 to 0.5 mm. The temperature of cold end was measured by $\mathrm{Pt}-\mathrm{Au}$ thermocouple, while the temperature of the heated part of the sample was determined from the dependence $R(T)$ [6]. The accuracy of absolute thermal e.m.f. determination when measuring the e.m.f. on Pt contacts proved to be ~3%. Measurements of the conductivity with the accuracy 1% and thermal e.m.f. 3% were performed within the temperature interval 5 to 400 K with the gradient 1…3 K. The results of the carried out measurements and calculations have been depicted in Figs 1 to 5. Shown in Figs 1 and 2 are the experimental temperature dependences for the thermal e.m.f. in bulk $p-\mathrm{Si}$ samples and whisker samples of $p-\mathrm{SiGe}$. Also shown are the computed values corresponding to them and obtained with account of interaction between carriers and phonons, determined by the integral of scattering. Represented in Figs 3 and 4 are the temperature dependences of the hole concentration in the bulk and whisker samples, obtained by determining the Fermi integral of ½ degree from the temperature dependences of the thermal e.m.f., multiplied by the integral of scattering. Shown in Fig. 5 are the dependences of the hole mobility on temperature for two whisker $p-\mathrm{SiGe}$ samples.

3. Theoretical analysis

The differential thermal e.m.f. (α) for semiconductor with one type of charge carriers is defined as:

$$\alpha = \pm\frac{k}{e}\left(\frac{Q^*}{kT} - \eta\right), \quad \eta = \frac{F}{kT},$$

where the sign coincides with the sign of charge carrier, η is the reduced Fermi level, k – Boltzmann constant, T – absolute temperature, Q^* – transfer energy:

$$Q^* = kT(r+2)\frac{F_{r+1}(\eta)}{F_r(\eta)}.$$

The value r is determined by a carrier scattering mechanism. At temperatures higher than the Debye one $r = 1$. Then:

$$\alpha = \mp\frac{k}{e}\left[(r+2)\frac{F_{r+1}(\eta)}{F_r(\eta)} - \eta\right],$$

where $F_{r+1}(\eta)$ and $F_r(\eta)$ are the Fermi integrals of r degree. In the case $\eta > -1$, the Fermi integrals are equal:

$$F_{1/2} = \frac{2}{3}\left(\eta^{3/2} + \frac{\pi^2}{8}\eta^{-1/2}\right)\frac{2}{\sqrt{\pi}}; \quad F_1 = \frac{1}{2}\left(\eta^2 + \frac{\pi^2}{3}\right);$$

$$F_2 = \frac{1}{3}\left(\eta^3 + \pi^2\eta\right)\frac{1}{2}.$$

But within the interval $-1 > \eta > -\infty$ for the integral $F_{1/2}$, it is correct to use the approximation: $F_{1/2} = \left(\sqrt{\frac{\pi}{4}}\right)\exp(\eta)$.

If scattering is determined by the only one mechanism of scattering, then

$$\alpha = \frac{k}{e}\left[\frac{5}{2} + p + \ln\frac{N_V}{n}\right],$$

where p is the exponent of the energy dependence for the carrier relaxation time, n – carrier concentration in the sample, N_V – density of states in the valence band. Then, it is possible to construct a matrix and describe the dependence $F_{1/2}$ on the absolute thermal e.m.f. (Table), as the thermal e.m.f. measurements were carried out using Pt contacts.

Knowing $F_{1/2}$, we can obtain the concentration of carriers in a sample:

$$n = \frac{2}{\sqrt{\pi}}N_V F_{1/2}.$$

According to the condition of the electroneutrality of the extrinsic semiconductor, the concentration of holes in dependence on temperature is equal:

$$n(T) = \left[\left(\beta N_V(T)\exp\left(\frac{E_a}{kT}\right) + N_d\right)^2 \cdot \frac{1}{4} + \beta N_V(T) N_a \exp\left(\frac{E_a}{kT}\right)\right]^{1/2} - \frac{1}{2}\left(\beta N_V(T)\exp\left(\frac{E_a}{kT}\right) + N_d\right),$$

$$N_V(T) = 2.5\cdot 10^{19}\cdot m_p^{3/2}\cdot\left(\frac{T}{300}\right)^{3/2}\times \times\frac{1}{\left(1 + 5\exp\left(-\frac{0.01}{kT}\right)\right)}, \qquad (1)$$

where β is the degree of degeneracy of the boron acceptor level (1/2); N_a, E_a – concentration value and energy position of boron levels in $p-\mathrm{Si}$.

Within the region of mixed scattering, the high level of doping leads to the fact that the best adjustment to the temperature dependence of the carrier concentration is obtained with $r = 1$. With carrier scattering by acoustic phonons $r = -1/2$, and by ionized impurities $r = 3/2$. Interaction of carriers with phonons is determined by the integral of collisions:

$$S_{ep} = S_{ep}^e + S_{ep}^p.$$

The integral S_{ep}^e describes collisions with the equilibrium phonons. The term S_{ep}^p considers the non-equilibrium of phonons, and it is critical for drag of carriers by phonons. Scattering the holes by phonons gives not only mobility but also thermal e.m.f. to the dependence $\alpha \sim T^{-2.3}$. Within the range of low temperatures, thermal e.m.f. is proportional to the specific heat capacity per unit of volume. Since the specific heat capacity at temperatures considerably smaller than the Debye temperature is proportional to T^3, then $\alpha(T)$ will also be proportional to T^3. Therefore, we will define the integral of collisions as:

$$S_{ep} = \frac{l}{d} + g \cdot T^3 + h \cdot T^{-2.32} . \qquad (2)$$

The contribution from the phonon drag to the thermal e.m.f. of crystal should contain the parameter of l/d, where d is the transverse size of a sample, l – path length of carriers. At very low temperatures, phonon scattering on the crystal boundaries is the factor that limits the drag effect. On the other hand, in the near-surface regions of crystal, there are gradients of non-equilibrium carrier concentrations that collapse to the bulk ones at the distances of the order of diffusion length, which from the viewpoint of phonon drag should be treated as the concentration de-compensation. Phonon-phonon scattering also decreases the effectiveness of the drag effect. For this very reason, the carrier drag by phonons is negligibly small and in the experiments with thermal e.m.f. measurements is weakly pronounced near room temperatures, and at low temperatures the thermal e.m.f. is reduced with decreasing the crystal thickness.

Table. Technique of account of $F_{1/2}$ dependence on α.

$F_{1/2}$:=	8.8442	α :=	100.6720
	7.4100		110.9355
	6.5115		118.9494
	5.4580		130.3624
	4.4876		143.7049
	3.6070		159.3120
	2.8237		177.5778
	2.1449		198.8875
	1.5756		223.5701
	1.1173		251.7649
	0.7652		283.3738
	0.5075		318.0719
	0.3278		355.3125
	0.2074		394.4944
	0.1293		435.0507
	0.0798		476.5373
	0.0489		518.6230
	0.0299		561.0935
	0.0182		603.8098
	0.00674		775.5611
	0.00034		1034.0815
	$8 \cdot 10^{-7}$		1551.1223

4. Discussion

For p-type silicon samples, the temperature dependence of the hole concentration [4] and thermal e.m.f. [5] were experimentally obtained. After describing the carrier concentration in $p-\mathrm{Si}$ depending on temperature, Fig. 3, and using the equation of electroneutrality (1), we obtained the values of the ionization energy (E_V+ 0.034 eV) and boron atom concentration ($N_\mathrm{B} = N_a = 5 \cdot 10^{18}\,\mathrm{cm}^{-3}$) in the forbidden band of silicon. Reduction in the ionization energy of boron in silicon in comparison with the value (E_V+0.046 eV) accepted attests to the fact that the impurity band is formed with this level of doping in the forbidden band of silicon. In this case, the ionization energy of the doping impurity is reduced. Formation of the impurity band is confirmed by a low value of the carrier mobility and by the fact that the thermal e.m.f. at $T < 20$ K reverses the sign to the opposite one [4, 5]. The integral of collisions is calculated by selecting the coefficients in the expression (2) in such manner that the determined values of the Fermi integral of degree ½ from its functional

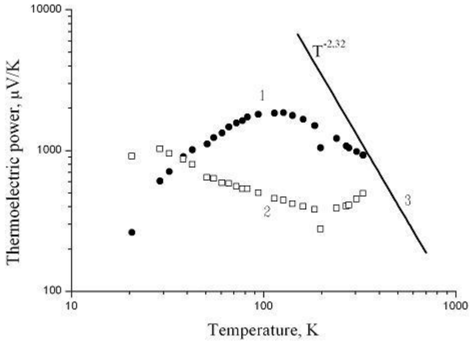

Fig. 1. Temperature dependences of the thermal e.m.f. for p-type silicon doped with boron in the samples with the sizes 0.12×0.16×1.1 cm [5]: *1* – experiment; *2* – with account of phonon drag and carrier scattering by phonons; *3* – $\alpha \sim T^{-2.32}$.

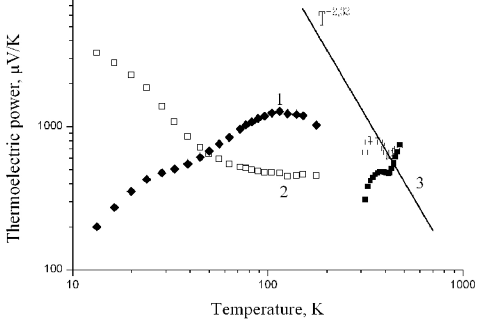

Fig. 2. Temperature dependences of the thermal e.m.f. for p–SiGe doped with boron in the samples with the sizes: d = 40 μm, l = 1 cm: *1* – experiment; *2* – with account of phonon drag and carrier scattering by phonons; *3* – $\alpha \sim 7.5\times10^{-8}\,T^{-2.32}$.

dependence on the thermal e.m.f. ($F_{1/2}(\alpha)$) make it possible to reliably determine the concentration of holes (Fig. 3), which coincides with the experimental temperature dependence [4]. The values of the coefficients: $l/d = 0.17$; $g = 1.0\cdot10^{-8}$; $h = 3.7\cdot10^{3}$ have such dimensionality that the integral of collisions is dimensionless. The effect of the integral of collisions on the experimentally determined thermal e.m.f. is shown in Fig. 1.

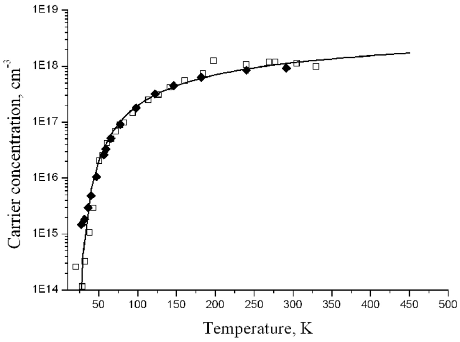

Fig. 3. Temperature dependences of the hole concentration in the silicon sample doped with boron: ● – taken from the work [4]; solid line – calculation of $p(T)$ according to the equation (1); □ – $p(T) \sim N_V(T)\cdot F_{1/2}$.

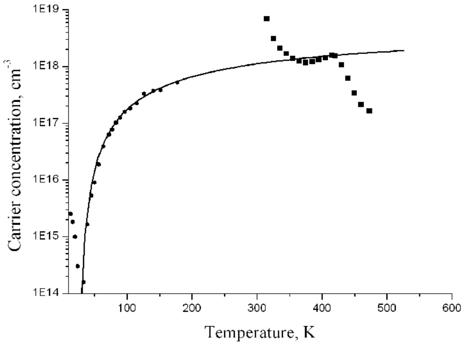

Fig. 4. Temperature dependences of the hole concentration in the p–SiGe whisker samples doped with boron: solid line – calculation of $p(T)$ according to Eq.(1); ●, □ – $p(T) \sim N_V(T)\cdot F_{1/2}$.

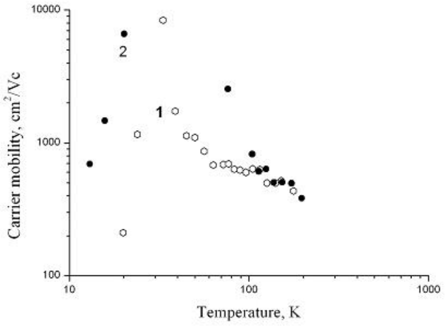

Fig. 5. Temperature dependences of the hole drift mobility in the boron doped p–SiGe whisker samples with the specific resistances: 0.03 Ohm·cm (*1*), 0.018 Ohm·cm (*2*).

Unfortunately, measurements of the Hall-effect in $p-\mathrm{SiGe}$ whisker samples are not currently possible. Therefore, after being certified in the reliability of the function $F_{1/2}(\alpha)$, and after determining the coefficients in the integral of collisions: $l/d = 0.21$; $g = 3.5\cdot10^{-8}$; $h = 6.5\cdot10^{3}$, the temperature dependence of the hole concentration in $p-\mathrm{SiGe}$ (Fig. 4) was calculated. The influence of the integral of collisions on the experimentally measured thermal e.m.f. is shown in Fig. 2. The temperature dependence of the calculated concentration of holes was described using the equation (1). With the boron atom concentration $N_a = 5\cdot10^{18}\,\mathrm{cm}^{-3}$ and concentration of the shallow compensating centers $N_d = 5\cdot10^{15}\,\mathrm{cm}^{-3}$, the ionization energy of boron atoms is equal ($E_V + 0.038$ eV). An increase of the ionization energy of boron atoms in $p-\mathrm{SiGe}$ whisker samples indicates the smaller energy extent of impurity band in the whisker samples in comparison with that in bulk $p-\mathrm{Si}$ samples. In the whisker samples, in comparison with the bulk ones, the coefficients in the integral of collisions have increased. This only can mean that in the whisker samples, as compared with the bulk $p-\mathrm{Si}$ ones, the lower value of the maximum thermal e.m.f. due to the lower cross-section of samples is observed. An increase of g in the whisker samples does testify that phonons transfer high energy to charge carriers, and thus they strengthen the phonon drag. The increase of h in the whisker samples testifies about the decrease of carrier scattering by phonons. Actually, in the whisker $p-\mathrm{SiGe}$ samples, in comparison with bulk $p-\mathrm{Si}$, the mobility of holes is increased, which indicates the decrease of charge carrier scattering by phonons in the whisker samples (Fig. 5).

5. Conclusion

The concentration of boron atoms and mobility of charge carriers in the whisker $p-\mathrm{SiGe}$ samples have been determined. It is shown that on the average the mobility of holes is ~1.5 times higher in the whisker $p-\mathrm{SiGe}$ samples in comparison with the bulk $p-\mathrm{Si}$ ones. Using selection of coefficients in the integral of collisions, values of the thermal e.m.f. corresponding to the charge carrier concentration have been calculated. The great magnitude of the integral of collisions in the whisker samples, in comparison with that in the bulk $p-\mathrm{Si}$ samples, is indicative of a decrease in carrier scattering by phonons and increase in the phonon drag in $p-\mathrm{SiGe}$ whisker samples.

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