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Hall Effect in Germanium Doped with Different Impurities

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Abstract—The influence of different impurities on the kinetics of electronic processes in *n*-Ge⟨Sb⟩ single crystals is investigated. A substantial decrease in the charge carrier mobility in the region of predominantly impurity scattering (at 77 K) in *n*-Ge⟨Sb + Si⟩ crystals, as well as in germanium crystals doped with the rare-earth elements, is detected, and this effect is explained.

Keywords: germanium, impurities, Hall effect, Hall coefficient, charge carrier mobility

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INTRODUCTION

For most applied problems, not only is the high degree of crystal homogeneity significant, but also what impurities are contained within the crystal and what condition they are in, since both the concentration of current carriers and their mobility ultimately depend on this [1–3]. These problems can be solved by analyzing crystals in various aspects:

(a) by directly studying the influence of individual chemical elements on their electric properties;

(b) by revealing the specific features of how compensating impurities influence these semiconductor properties;

(c) by analyzing different options of complexation within crystals and its consequences.

Regarding electrically active impurities, it can be said that at least the basic properties of practically any element forming singly charged and multicharge impurity centers in germanium and silicon have been studied sufficiently by now [4–7]. This is a different situation with the problem of so-called electrically passive impurities of various elements in these crystals. If we take into account that, according to the mass spectroscopy analysis data, the oxygen content in germanium is about 2×10^{18} cm^{-3} and the hydrogen and carbon content in it is about the same [8], then a legitimate question arises: what peculiarities, e.g., of current carrier scattering may be related to these impurities, because in other experiments (e.g., in analysis of infrared radiation absorption [9]), the presence of these impurities within crystals is easily detected. The problem of the interaction of these impurities with others within *n*-Ge crystal, as well as the formation of a different sort complexes as a result, is especially interesting.

This aim of this study was to analyze the influence of an electrically passive (isovalent) silicon impurity on the Hall mobility of current carriers in *n*-Ge. The silicon atom impurities within germanium can influence the occurrence in it of transfer phenomena not only as electrically neutral elementary scatterers, but also in the form of neutral or charged complexes, which can occur when silicon atoms interact with the atoms of electrically neutral or active impurities within the crystal. This, as well as the significant lack of data directly related to the complexation problem in germanium (with respect to silicon with an isovalent Ge impurity, the situation is somewhat better [10–13]), which are important on the whole for solid state physicochemistry, have spurred investigations into certain galvanomagnetic properties of germanium doped with rare-earth elements La, Pr and Nd, which is another important objective of the present study.

ELECTRIC CONDUCTIVITY AND THE HALL EFFECT IN GERMANIUM CONTAINING ELECTRICALLY PASSIVE SILICON IMPURITY (10^{-3}–10^{-1} wt %)

It has already been shown in early works (see, e.g., [14]) that silicon is an electrically neutral impurity with respect to germanium; i.e. its atoms within germanium do not cause the formation of additional charge carriers.

It could be expected that, even in the case of electric neutrality, silicon atom impurities should affect the charge carrier mobility in the doped scattering domain. To experimentally detect the contribution of this scattering to the resulting mobility value, comparative experiments were conducted on common germa-

Table 1. Results of studying Hall effect in germanium doped with antimony and silicon

Impurity	Specimens	$T = 300$ K				$T = 77$ K				Si impurity, wt %
		ρ, Ω cm	R_H, cm^3/C	n_e, cm^{-3}	μ, cm^2/V s	ρ, Ω cm	R_H, cm^3/C	n_e, cm^{-3}	μ, cm^2/V s	
Sb	1'	25.0	9.04×10^4	8.05×10^{13}	3070	3.14	1.08×10^5	6.82×10^{13}	29200	–
	2'	22.5	8.09×10^4	8.99×10^{13}	3050	2.91	9.69×10^4	7.60×10^{13}	28300	–
	3'	22.8	6.87×10^4	1.06×10^{14}	2560	2.56	8.15×10^4	9.03×10^{13}	27000	–
Sb + Si	1	29.6	1.02×10^5	7.13×10^{13}	2940	5.94	1.06×10^5	6.96×10^{13}	15130	10^{-3}
	2	32.3	1.15×10^5	6.33×10^{13}	2980	4.73	1.46×10^5	5.04×10^{13}	26200	10^{-2}
	3	45.8	1.32×10^5	5.51×10^{13}	2440	9.33	2.80×10^5	2.63×10^{13}	25500	10^{-2}
	4	14.6	5.10×10^4	1.43×10^{14}	2960	1.72	4.68×10^4	1.57×10^{14}	23100	5×10^{-2}
	5	11.8	3.73×10^4	1.95×10^{14}	2680	1.58	3.65×10^4	2.02×10^{14}	19600	10^{-1}
	6	7.60	2.86×10^4	2.54×10^{14}	3200	1.05	2.54×10^4	2.90×10^{14}	20500	2.1×10^{-1}

nium specimens doped with antimony and on germanium specimens doped with antimony and silicon.

As far as it is known, there is very little information in the scientific literature [15–18] on research of electron gas kinetics in crystals grown under combined doping (i.e., when doping more than one impurity).

To studying the influence of an isovalent silicon impurity on the electrophysical properties of n-Ge doped with electrically active antimony (Sb) impurity, ingots were used, some of which were doped with Sb impurity only (single doping), while others, in addition to Sb impurity, were also doped with Si impurity with approximately the same concentration (double or multiple doping). Two groups of specimens were fabricated from these ingots, which were intended to measure the resistivity and Hall effect both at room and liquid nitrogen temperature. All measurements were conducted in a magnetic field $H = 2340$ Oe.

Before the current contacts and contacts to the measuring probes were soldered, the specimens were polished and etched for about 2 min in a boiling solution of 30% hydrogen peroxide, then they were rinsed with distilled water. The contacts were soldered with pure tin (Sn), after which the specimens were again etched. Before measurement, the resistance of the current contacts was tested at the values of currents, which several times exceeded the values used in experiments.

Table 1 gives the measurement results for the germanium specimens both at 300 and 77 K.

It is seen from Table 1 that when the dominant scattering for lattice oscillations (i.e. under 300 K) in the singly doped and doubly doped specimens, the mobility value μ_{300K} is typical of n-Ge with a charge carrier concentration 10^{13}–10^{14} cm^{-3}: ~ 2700–3000 cm^2/V s.

However, in the domain of predominantly impurity scattering (i.e., under 77 K) in the doubly doped crystals (n-Ge⟨Sb + Si⟩), the charge carrier mobility values $\mu_{77\,K}$ were evidently understated compared with the $\mu_{77\,K}$ values typical of conventional specimens (n-Ge⟨Sb⟩). Thus, the isovalent Si atom impurity, which was not electrically active, significantly reduces the mobility of charge carriers in Ge crystals doped with the electrically active Sb impurity due to manifestations of additional scattering of charge carriers by neutral centers [19].

The result can be caused by a certain difference in the tetrahedral radii of Si and Ge ($r_{Si} = 1.17$ Å; $r_{Ge} = 1.22$ Å), and hence by the occurrence of internal local stresses of the lattice around Si atoms. However, the observed violations of monotonicity in the reduction of the charge carrier mobility with increasing silicon concentration within germanium (see Table 1, for 77 K) may be a manifestation of a Ge lattice irregularity with the Si impurity caused, in turn, by nonuniformity in the distribution of silicon impurity within the studied crystals. This is also confirmed also by the sharply expressed, in the case of the Ge–Si system, phenomenon of intracrystalline segregation, which makes the fabrication of homogeneous ingots very difficult [8, 20].

The lack of information in the literature on the dependence of the Hall coefficient on magnetic field strength in germanium with silicon impurity is not only technically inconvenient when processing Hall data, it also significantly prevents the obtaining of sin-

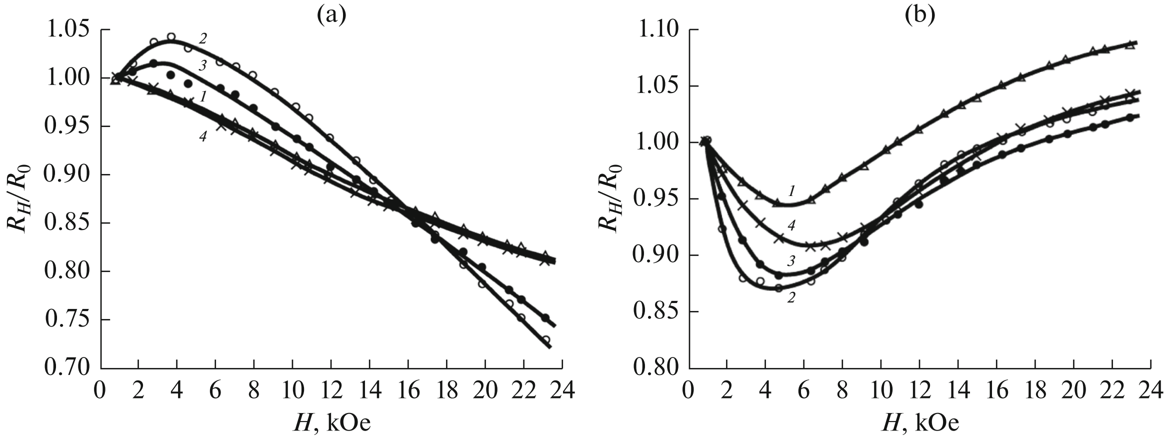

Fig. 1. Dependences $R_H/R_0 = f(H)$ obtained in experiments with n-Ge crystals doped with Si at $T \approx 300$ K (a) and at $T \approx 77$ K (b): curves (*1*) specimen no. 5 ($\rho_{300\ K} = 11.8\ \Omega$ cm); curves (*2*) specimen no. 3 ($\rho_{300\ K} = 45.8\ \Omega$ cm); curves (*3*) specimen no. 2 ($\rho_{300\ K} = 32.3\ \Omega$ cm); curves (*4*) specimen no. 6 ($\rho_{300\ K} = 7.6\ \Omega$ cm (see Table 1).

gle-valued results on the Hall mobility of charge carriers in such crystals.

In this regard, the dependences of the Hall coefficient R_H on the magnetic field strength were measured on the germanium specimens doped with antimony and silicon. It was revealed that the results of these experiments conducted both at room temperature and at 77 K (see Fig. 1) are essentially typical of n-Ge without silicon impurity and should be studied under such conditions [21]. A somewhat peculiar behavior of curves *2* and *3* in the $R_H/R_0 = f(H)$ diagram (Fig. 1a), detected at 300 K; the presence of an insignificant maximum in weak magnetic fields ($H \approx 3$–4 kOe) is apparently related to the influence of heterogeneities. The resulting effect in the case of high-resistance specimens should be the most perceptible, and the experiment confirms this.

ELECTRIC CONDUCTIVITY AND THE HALL EFFECT IN GERMANIUM WITH THE IMPURITY OF RARE-EARTH ELEMENTS La, Nd, Pr

It is known that doping of metals with rare-earth elements purifies them from impurities such as oxygen, nitrogen etc.; solubility, the segregation coefficient, the donor nature of impurities of lanthanum (La), neodymium (Nd), and praseodymium (Pr) in germanium are also known [22]. However, there almost no attention has been given directly to the Hall effect in the literature.

In this regard, we studied the Hall effect in single germanium crystals (containing traces of antimony) doped with rare-earth elements La, Nd, Pr, which can interact with other (including gas) impurities within it.

The specimens of germanium doped with La, Nd and Pr impurities used in the experiments were cut so

Table 2. Results of studying Hall effect in germanium doped with rare-earth elements

Specimens of germanium with impurity	$T = 300$ K				$T = 77$ K			
	ρ, Ω cm	R_H, cm^3/C	n_e, cm^{-3}	μ, cm^2/V s	ρ, Ω cm	R_H, cm^3/C	n_e, cm^{-3}	μ, cm^2/V s
La	1.15	4.02×10^3	1.83×10^{15}	2970	0.19	3.79×10^3	1.94×10^{15}	17400
La	1.83	6.41×10^3	1.15×10^{15}	2980	0.27	5.27×10^3	1.40×10^{15}	16600
Pr	1.36	4.97×10^4	1.48×10^{14}	3100	1.51	4.25×10^4	1.73×10^{14}	23900
Nd	1.58	5.47×10^3	1.35×10^{15}	2930	0.24	5.19×10^3	1.42×10^{15}	18300
Nd	2.49	8.94×10^3	8.23×10^{14}	3050	0.33	8.29×10^3	8.88×10^{14}	21100
Sb	15.40	5.70×10^4	1.29×10^{14}	3140	1.72	5.64×10^4	1.30×10^{14}	27900

that the current vector (in each of them) was in the (101) plane and perpendicular to the [111] crystallographic direction; and magnetic field strength vector $\vec{H}$ coincided with the [110] direction. At room temperature (300 K) and the temperature of liquid nitrogen (77 K) the resistivity ρ and Hall coefficient R_H were measured at these samples. All measurements were implemented with the magnetic field strength $H = 2340$ Oe.

The results are listed in Table 2, the last row of which contains the data obtained in experiments with the specimens of germanium doped with antimony.

Comparison of the data obtained in the experiments at 300 K with these specimens and with the specimens of germanium doped with La, Nd, Pr show that the value of the Hall mobility for a concentration of rare-earth element impurities of $n_e \approx 10^{14}–10^{15}$ cm^{-3} within germanium does not differ at all from values of mobility obtained in the experiments with germanium doped with the same quantity of the usual impurity (in this case, it is Sb).

However, the values of the charge carrier mobility obtained at 77 K in the experiments with germanium doped with rare-earth element impurities are significantly lower than in the case of germanium doped with antimony. This is probably related to the fact that in the presence (and with the participation) of rare-earth element impurities, electrically passive impurities such as oxygen can form complexes that are effective scatterers of charge carriers. It may also be related to the influence of germanides (such as $LaGe_2$) of rare-earth elements [23], which are probably formed within the crystal in the course of it growth.

These questions are quite interesting and require more careful consideration; clearly, unambiguous answers can be only obtained by special physical and chemical research.

CONCLUSIONS

We studied the influence of isovalent Si impurity on the electric conductivity and Hall effect in *n*-Ge single crystals doped with electrically active Sb impurity. It was shown that in the domain of predominantly impurity scattering (at $T \approx 77$ K), the presence of electrically passive silicon impurity within germanium significantly reduces the mobility of charge carriers. This is the result of manifestation of both additional carrier scattering by neutral centers and change in scattering during the oscillations of the crystal lattice due to imperfections in its structure owing to some difference in the covalent radii of atoms of the (Ge) matrix and isovalent (Si) impurity.

It was revealed that at room temperature, the value of the Hall mobility of charge carriers for the concentrations of rare-earth element impurity of $n_e \approx 10^{14}–10^{15}$ cm^{-3} within Ge does not differ from those obtained in experiments with germanium doped with the same quantity of common impurity (*n*-Ge⟨Sb⟩). However, the mobility values obtained at 77 K in the experiments with germanium doped with La, Pr and Nd impurities are noticeably lower than for germanium doped with antimony. The detected effect is probably related to an increase in the complexation of electrically passive impurities in the presence of rare-earth element impurities.

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