VACANCY-DONOR COMPLEXES IN GERMANIUM

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It has been assumed to date that the cause of the well-known n-p conversion of germanium following heat treatment and nuclear irradiation [1, 2] was the compensation of the n-type conductivity by the acceptor levels of the radiation or thermal defects. However, an exact comparison of the concentrations of the introduced acceptors with the number of electrons removed from the conduction band was difficult, for a number of reasons, and was never performed.

We present below results of experiments that show that the reason of the n-p conversion is not compensation, but a decrease of the concentration N_D^V of the donor states themselves of the elements of group-V atoms. It can be assumed that this is the result of the capture of free vacancies by the group-V atoms, resulting in formation of VD complexes.[1] Such complexes were observed by the EPR method in irradiated silicon doped with phosphorus [5, 6]. The authors of [5, 6] did not determine the concentration of the donor states of the phosphorus.

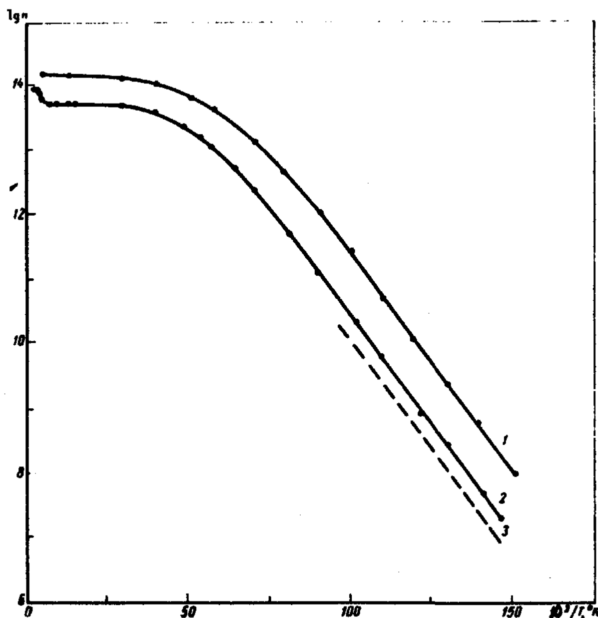

Fig. 1. Temperature dependences of the electron concentration in the conduction band for the initial sample (1) and the irradiated one (2). Curve 3 is calculated under the assumption that all the changes are due to the compensation process.

1. Decrease of N_D^V upon irradiation. We plotted the temperature dependences of the electron concentration in the conduction band in germanium doped with phosphorus, in the temperature interval 4.2 - 300°K, before and after irradiation with Co^{60} γ rays at 280°K. The irradiation dose was such that the conductivity remained of the n type. From curves 1 and 2 of Fig. 1, using the statistical methods described, for example, in [7], we determined the following: n - the concentration of the electrons in the conduction band in the region of complete ionization of the donors; $K = \Sigma N_A/N_D^V$ - the degree of compensation; N_D^V - the concentration of the phosphorus donor levels; ΣN_A - the sum of all the compensating acceptors. The results are given in Table 1. We see that although the total acceptor concentration is increased by the irradiation, the main decrease of the electron concentration is due to the decrease of N_D^V. The difference

[1] The assumed formation of VD complexes in germanium was used in [3, 4] as the basis for a model leading to good agreement between the experimental and calculated dependences of the conduction-electron concentration on the irradiation dose.

Table 1

Sample no.	State	K	$n_{T=77°K}$	N_D^V	ΣN_A	Δn	ΔN_D^V	$\Delta \Sigma N_A$	$\Delta \Sigma N_A^{exp}$
			$\times 10^{-13}$, cm^{-3}						
1,2	Initial	0.10	15.3	17.0	1.7	–	–	–	–
1	After irrad.	0.35	7.6	11.7	4.1	7.7	5.3	2.4	2.6
2	After irrad.	0.50	5.2	10.4	5.2	10.0	6.6	3.5	3.3

Table 2

Sample no.	ΔE_A, eV	K	N_D^V initial	N_A^{III}	$\Delta \Sigma N_D$
			$\times 10^{-12}$, cm^{-3}		
1	0.010	0.2	15 – 20	9	1.8
2	0.010	0.3		9	2.7
3	0.010	0.3		10	3.0
4	0.010	0.9	160	25	22.0

between the positions of the experimental curve 2 and curve 3, calculated under the assumption that the entire decrease of n is due to introduction of compensating acceptors, exceeds the limits of the experimental error.

It will be made clear subsequently (Sec. 2) that the Fermi level is shifted by the irradiation process over the entire width of the forbidden band (from E_c - 0.012 to E + 0.010 eV). From the plots of n and p against 1/T at different stages of the irradiation it is then possible to determine separately the concentrations of all the introduced acceptor levels. The value of $\Delta\Sigma N_A^{exp}$ determined in this manner and listed in Table 1 coincides approximately with $\Delta\Sigma N_A$. Since this sum is smaller than $\Delta\Sigma N_D^V$, it is apparently impossible to set the complexes VD in direct correspondence with some levels in the forbidden band.

2. <u>"Limiting" position of the Fermi level</u>[2]. After the n-p conversion the Fermi level tends to the valence band and reaches a certain limiting value, which does not change no matter how much the irradiation dose is increased. It turns out that this limiting position coincides at 0°K with the group-III acceptor levels which are partly filled with electrons. The concentration N_A^{III} is close to that previously determined from the degree of compensation of the initial material, and the number of electrons in the system does not exceed several percent of their initial concentration (see Fig. 2 and Table 2).

[2] An investigation of the "limiting" state was carried out not only for germanium doped with phosphorus, but also for germanium with another donor impurity [3, 4] and subjected to both irradiation and heat treatment.

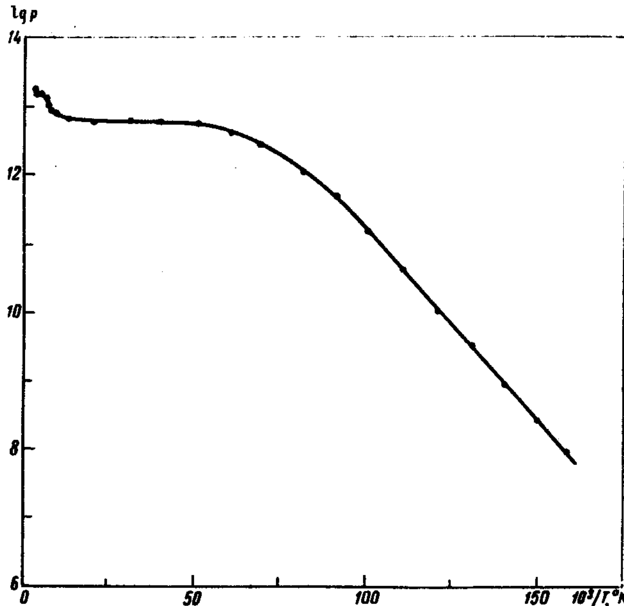

Fig. 2. Temperature dependence of the hole concentration for the irradiated sample in the "limiting" state.

Thus, even if the sum of the states appearing in the forbidden band $\Delta\Sigma N_A$ were to equal or exceed N_D^V, the "limiting" state of the system at 0°K can be obtained only if the bulk of the group-V donors are bound into complexes whose electronic states lie in the valence band.

It is possible that the localization of these states is one of the conditions that determine the difference in the "limiting" position of the Fermi level, in n-type germanium and silicon, since the levels of the complexes in silicon lie near the middle of the forbidden band [5, 6].

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[1] V.S. Vavilov and N.A. Ukhin, Radiatsionnye effekty v poluprovodnikakh i poluprovodnikovykh priborakh (Radiation Effects in Semiconductors and Semiconductor Devices), Atomizdat, 1969.
[2] A. Seeger and K.P. Chik, Phys. Stat. Sol. 29, 455 (1968).
[3] N.A. Vitovskii, M. Maksimov, and T.V. Mashovets, Fiz. Tekh, Poluprov. 4, 1030 (1970) [Sov. Phys.-Semicond. 4, 880 (1970)].
[4] N.A. Vitovskii, M. Maksimov, and G.T. Mashovets, ibid. 4, 2276 (1970) [4, 1960 (1971)].
[5] G.D. Watkins and J.W. Corbett, Phys. Rev. 134, A1359 (1964).
[6] G.D. Watkins, Proceedings of the Santa Fe Conference on Radiation Effects in Semiconductors, p. 67, Plenum Press, New York, 1968.
[7] J.S. Blakemore, Semiconductor Statistics, Pergamon, 1961.

OBSERVATION OF THE HIGH-TEMPERATURE QUANTUM SIZE EFFECT IN A SEMICONDUCTING CuS FILM

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We investigated semiconducting quantizing CuS films. The dispersion law in the subband is $\varepsilon = \varepsilon_n(\vec{P}_\perp)$ (n = 1, 2, 3, ..., $\vec{P}_\perp$ is the quasimomentum with components P_x and P_y) [1, 2]. The distance between the subbands is given by

$$\Delta\epsilon_{n,n+1} = \frac{\pi^2\hbar^2}{2m^*}\,\frac{2n+1}{L^2}$$

where m* is the effective mass in the direction normal to the film, and depends on the masses in the bulky sample [3].

The conditions for the appearance of superconductivity in a semiconducting film, according to [4], differs from the conditions in a bulky sample. This is