Energy levels of Se in Ge

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The positions of the energy levels of Se in Ge are studied by a new method.

An impurity selenium atom in germanium is generally regarded[1] as being a divalent donor with levels 0.14 and 0.28 eV from the bottom of the conduction band (E_c). This understanding, however, seems to be contradicted by some experimental data. In particular, it is asserted in Refs. 1 and 2 (with citation of an unpublished study by Tyler) that Se introduced into Ge either by diffusion or by addition to the melt gives rise to two levels, at 0.14 and 0.28 eV, in the energy gap of the Ge. The concentration of the centers with the 0.28-eV level, however, is several times higher than that of the center with the 0.14-eV level, in contradiction of the understanding of Se as a divalent donor. It may be that different states of Se in the Ge lattice are associated with different levels.[1,2]

We have attempted to experimentally resolve the question by studying Se as it is produced in Ge by thermal-neutron bombardment.[3–5] Natural Ge consists of the isotopes Ge^{70}, Ge^{72}, Ge^{73}, Ge^{74}, and Ge^{76}. After capturing a thermal neutron, the isotopes Ge^{70}, Ge^{74}, and Ge^{76} undergo the conversions

$$Ge^{70}(n,\gamma)\,Ge^{71}\xrightarrow[12\ \text{days}]{K\text{-capture}}Ga^{71}, \tag{1}$$

$$Ge^{74}(n,\gamma)\,Ge^{75}\xrightarrow[82\ \text{min}]{\beta\text{-decay}}As^{75}, \tag{2}$$

$$Ge^{76}(n,\gamma)Ge^{77}\xrightarrow[12\ \text{h}]{\beta\text{-decay}}As^{77}\xrightarrow[38.8\ \text{h}]{\beta\text{-decay}}Se^{77}. \tag{3}$$

The final concentrations of Ga^{71}, As^{75}, and Se^{77} are in the proportions[6] 1:0.26:0.01. Reaction (1) describes the appearance of Ga^{71} acceptors. After capturing a neutron, the isotope Ge^{70} converts into Ge^{71}, which then converts into Ga^{71} through K capture with a decay half-life of 12 days. The appearance of shallow donors (As^{75}) and deep donors (Se^{77}) is described by reactions (2) and (3); the Se^{77} appears as a result of a more complicated process. The As^{75} donors appear essentially immediately after the bombardment. The Ga^{71} acceptors appear slowly, and not until 6 days after the bombardment does their concentration (N_{Ga}) become comparable to the As^{75} concentration (N_{As}). At this time, the Se^{77} concentration (N_{Se}) in the crystal is $\sim 85\%$ of its final value [i.e., nearly all the decay events (3) have already occurred]. In the time interval (~ 6 h long) during which the inequality

$$N_{As} < N_{Ga} < N_{As} + kN_{Se} . \qquad (4)$$

holds, and over a broad temperature range, electrons are excited into the conduction band only from Se levels. The coefficient k in (4) is 1 or 2, depending on whether the Se is a monovalent or divalent donor. By studying the temperature dependence of the electron density in the band during the time interval (4), we can determine the positions of the Se energy levels.

In the present experiments, ultrapure samples of n-type Ge ($n \sim 2 \times 10^{11}$ cm^{-3}) were bombarded. We chose a bombardment dose to put the final Ga^{71} concentration at $\sim 3 \times 10^{14}$ cm^{-3}. After bombardment, the samples were annealed at 450 °C (No. 1) and 500 °C (No. 2) for 12 h and then slowly cooled. This annealing eliminates the radiation defects. We measured the Hall effect and determined the carrier density in the band, assuming a unit Hall factor. Figure 1 shows the time evolution of the carrier density in the band at 77 K. The "dip" corresponds to condition (4) (the temperature of 77 K is not high enough to excite electrons from the deep levels). Figure 2 shows the temperature dependence of the electron density at various times. The experimental points are labeled for assistance in determining the measurement time from Table I. The slopes of the curves recorded in the time interval from 7 to 9 h (all times are reckoned from the beginning of the 6 days) do not correspond to a definite activation energy. We believe that this circumstance stems from levels distributed over a certain energy interval in the upper half of the energy gap. These levels may be associated with unannealed defects. Compensation of these levels by the Ga^{71} acceptors which appear occurs in 2 h, and from 9 h on the curves in Fig. 2 correspond to an activation energy of 0.28 eV from the bottom of the conduction band, E_c. At our bombardment dose over the 6

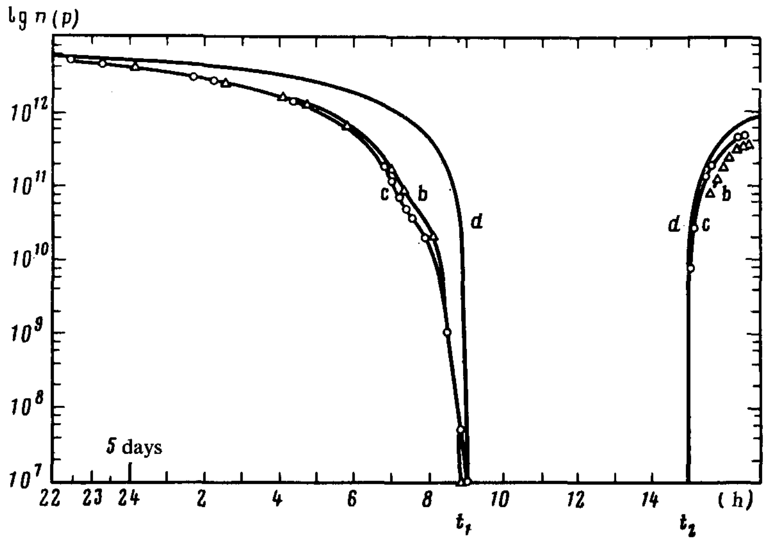

FIG. 1. Time evolution of the carrier density in the bands at 77 K. c, b—Experimental curves for samples No. 1 and No. 2, respectively; d—calculated from Eqs. (1)–(3), which describe the radioactive decay. The parts of the curves at the left show the electron density, while the parts at the right show the hole density.

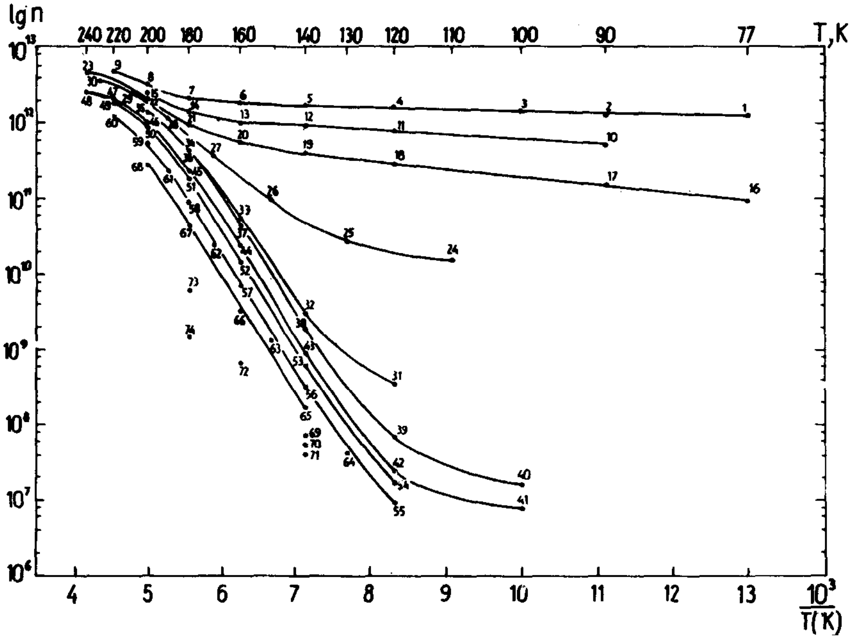

FIG. 2. Temperature dependence of the electron density in the band. These curves were recorded near the time of the conversion from an n-type material to a p-type material.

TABLE I. The times (reckoned from the beginning of the 6 days after the bombardment) at which the experimental points in Fig. 2 were measured.

N°	1	2	3	4	5	6	7	8	9	10
t	4^{45}	4^{51}	4^{54}	5	5^{07}	5^{15}	5^{25}	5^{33}	5^{40}	6^{30}
N	11	12	13	14	15	16	17	18	19	20
t	6^{32}	6^{37}	6^{42}	6^{45}	6^{55}	7^{20}	7^{25}	7^{30}	7^{33}	7^{36}
N	21	22	23	24	25	26	27	28	29	30
t	7^{40}	7^{48}	7^{55}	8^{15}	8^{20}	8^{25}	8^{30}	8^{35}	8^{40}	8^{45}
N	31	32	33	34	35	36	37	38	39	40
t	9^{10}	9^{15}	9^{20}	9^{25}	9^{30}	9^{35}	9^{40}	9^{43}	9^{46}	9^{50}
N	41	42	43	44	45	46	47	48	49	50
t	9^{55}	10^{10}	10^{17}	10^{20}	10^{25}	10^{30}	10^{35}	10^{50}	11	11^{04}
N	51	52	53	54	55	56	57	58	59	60
t	11^{07}	11^{13}	11^{20}	11^{24}	11^{45}	11^{55}	12	12^{05}	12^{10}	12^{15}
N	61	62	63	64	65	66	67	68	69	70
t	11^{21}	11^{28}	11^{34}	11^{37}	12	12^{06}	12^{13}	12^{21}	12^{50}	13
N	71	72	73	74						
t	13^{20}	13^{30}	13^{40}	14						

days, the Ga concentration in the sample increases by $\sim 10^{12}$ cm^{-3} in 2 h, so that the concentration of centers with levels distributed in the interval $[E_c, E_c - 0.28$ eV] is also 10^{12} cm^{-3}. These centers retard the decrease in the electron density in Fig. 1 in the time interval from 7 to 9 h. During the dip in Fig. 1, i.e., from 9 to 15 h, the electrons are excited into the band from the 0.28-eV level. The duration of the dip can also be used to determine the concentration of centers with this level: $\sim 3 \times 10^{12}$ cm^{-3}. The same value is found from the curves in Fig. 2. According to this model for neutron doping,[3] the 0.28-eV level should belong to Se. Consequently, it follows from our results that Se in Ge is a monovalent donor with a level of 0.28 eV. If there were two levels associated with Se, at 0.14 and 0.28 eV, we would see an activation energy of 0.14 eV in the first half of the dip and an activation energy of 0.28 eV in the second half. The Se introduced during neutron bombardment is apparently at Ge lattice sites, and the 0.14-eV level[1,2] corresponds to either a complex involving Se or a Se atom in an interstitial position.

In conclusion, we note that the method used here, involving a motion of the Fermi level from the upper part of the energy gap to the lower part, could be used to advantage for the spectroscopy of local centers in Ge.

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