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Properties of Thermally Treated Germanium

LEO ESAKI
Kobe Kogyo Corporation, Hyogo-ku, Kobe, Japan

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Upon heating a piece of germanium in a vacuum of 10^{-6} mm Hg, the following results have been obtained. (1) Below 350°C, the rectification characteristic is improved. Heating the specimen at a temperature between 400°C and 600°C destroys the rectification, which is not recovered completely when it is heated in vacuum. However, heating in an oxygen atmosphere leads to a slight recovery of the rectification.

(2) Treatment above 550°C makes the formation of acceptor levels detectable. With continued heating at 500°C for about 48 hours, the specimen returns again to *n* type similar to the original state. The formation and disappearance of acceptor levels were followed when the specimen was quenched from a fixed temperature to room temperature. The equilibrium concentration at the heating temperature was determined to be $A=2.5\times10^{21}\exp(-27\,000/RT)$ cm^{-3}.

(3) On the assumption that the acceptor levels produced on the surface diffuse into the interior, the data could be fairly well represented with an estimated diffusion coefficient: $D=300\exp(-37\,000/RT)$ cm^2 sec^{-1}.

(4) The resistivity and Hall coefficient from room temperature to about 200°C have been measured for several specimens.

I. INTRODUCTION

RECENTLY several investigators have suggested that quenching[1] or high energy nucleon bombardment[2] produce lattice defects which are effective for forming acceptor levels in germanium. Theuerer and Scaff especially studied phenomenologically the thermal effect upon the resistivity.

In the present paper, it will be described how the properties of pure *n* type single crystalline germanium, whose concentration of conduction electrons[3] is 1.88×10^{14} cm^{-3}, is affected by thermal treatment. A small Ge specimen was quenched or annealed arbitrarily by adjusting the heater current of a tiny vacuum furnace; and the rectification characteristic, the resistivity, and Hall coefficient of the specimen were measured at any desired temperature.

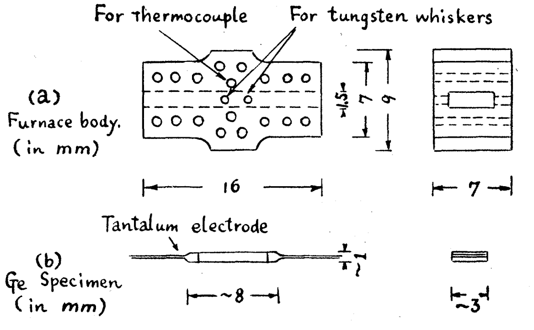

FIG. 1. Sketch of the furnace and the specimen.

2. EXPERIMENTAL APPARATUS

For the thermal treatment, a steatite furnace of small heat capacity of $7\times7\times16$ mm^3 was constructed. A schematic diagram is shown in Fig. 1(a). Along its central axis a rectangular hole of 1.5×4 mm^2 was drilled, into which a germanium specimen of $0.76\times2.65\times8$ mm^3, illustrated in Fig. 1(b), was inserted. On both sides of the specimen four tungsten whiskers, for measuring the rectification and other electrical properties, were pressed against the specimen through small holes marked in Fig. 1(a). Previously the germanium surface was lapped with 500 mesh carborundum and etched with a mixture of HF and HNO_3 for several seconds. Then tantalum ribbons of 1×0.05 mm^2 were tightly wound around both ends of the specimen as nonrectifying electrodes. Both tungsten and tantalum were chemically inert with germanium over the entire experimental temperature range. A tantalum heater wire of 0.2 mm diameter was coiled through many holes of the furnace body and a thermocouple of Pt−PtRh was also put into one of those holes.

The assembled furnace was mounted on a stem and sealed in a tube. A getter chamber was connected to the main experimental tube. The whole system was sealed off after evacuating carefully and flashing a batalum getter. The pressure remained less than 10^{-6} mm Hg throughout the experiment.

The cooling speed of the furnace could be represented by the experimental formula, $dT/dt=-T_0/(1+t)^2$, when the heater current was cut off. T and t are the temperature in °C and time in minutes, respectively, and T_0 the initial temperature. The change of the furnace temperature with time is given in Fig. 2. "Quenching" in the present paper usually means such cooling.

3. PRELIMINARY EXPERIMENTS

Prior to each thermal treatment, the dc rectification characteristic at room temperature, the specific resis-

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[1] K. Lark-Horovitz, NDRC Report, unpublished; H. C. Theuerer and J. H. Scaff, J. Metals **189**, 59 (1951).

[2] Lark-Horovitz, Bleuler, Davis, and Tendam, Phys. Rev. **73**, 1256 (1948); Davis, Johnson, Lark-Horovitz, and Siegel, Phys. Rev. **74**, 1255 (1948); N. H. Brattain and G. L. Pearson, Phys. Rev. **80**, 846 (1950); Cleland, Crawford, Lark-Horovitz, Pigg, and Young, Phys. Rev. **83**, 312 (1951); **84**, 861 (1951).

[3] That used by Cleland, Crawford, Lark-Horovitz, Pigg, and Young is 4×10^{14} cm^{-3}.

tivity, and the Hall coefficient up to 200°C were measured by the four whiskers, using the conventional method. Typical changes in the resistivity and Hall coefficient of the specimen, subjected to the treatment given in Table I and quenching, are presented in Fig. 3.

When the specimen was heated at a relatively low temperature, the rectification characteristic underwent a large change, which is illustrated in Fig. 4. The initial characteristic is curve No. 1, but it was improved to curve No. 2 by heating at 300°C for 30 minutes. On continuing to heat further, the rectification characteristic became worse at higher temperatures as indicated by Nos. 3, 4, and 11 in Fig. 4(c). The lost rectification did not recover to the original sharp characteristic by any heat treatment in vacuum; this suggests that the rectification is not always dependent upon the formation of acceptor levels. The experiment on the recovery of rectification is described in more detail in the next section.

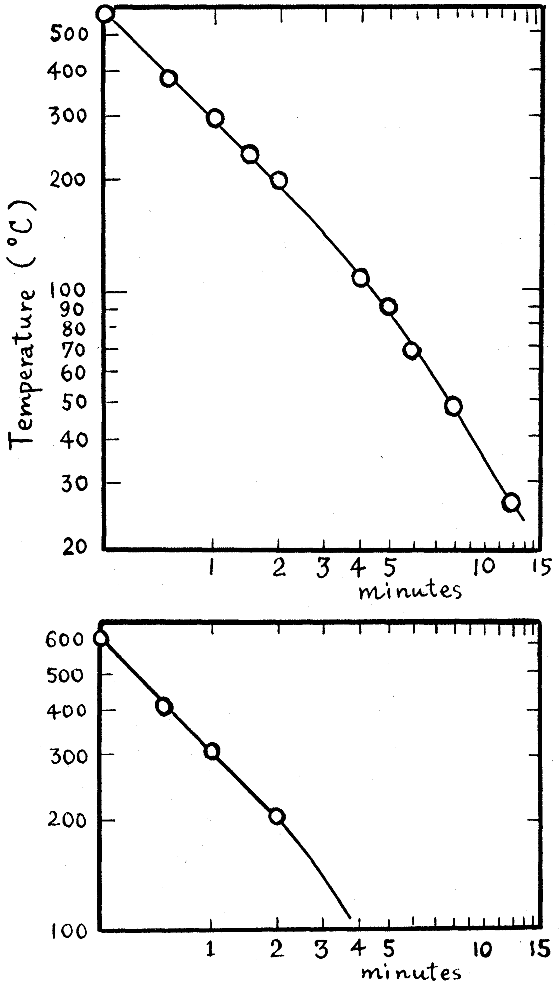

FIG. 2. Cooling of the furnace after cutting off the heater, i.e., the quenching process. Log$T$ is plotted against log $(1+t)$.

TABLE I. Conditions for thermal treatment.

Treatment conditions	Identification No. after treatment	Treatment conditions	Identification No. after treatment
——	1	550°C, 12 min	
300°C, 30 min	2	535°C, 15 min	
400°C, 30 min	3	515°C, 15 min	
460°C, 30 min	4	495°C, 15 min	
525°C, 20 min	5	480°C, 15 min	
545°C, 25 min	6	460°C, 15 min	
570°C, 20 min	7	440°C, 15 min	
585°C, 20 min	8	425°C, 15 min	16
180°C, 30 min; 15°C, several days	9	580°C, 12 min	
		550°C, 15 min	
		540°C, 30 min	
595°C, 20 min	10	530°C, 30 min	
625°C, 20 min	11	520°C, 30 min	
355°C, 20 min	12	505°C, 30 min	
535°C, 15 min	13	490°C, 30 min	
520°C, 60 min	14	475°C, 30 min	
550°C, 20 min	15	450°C, 30 min	17
		18±5°C, 3000 hr	18
		500°C, 48 hr	19

This essential feature is quite similar to the result found in the vacuum heat treatment of a silicon point contact rectifier.[4] The temperature above which rectification is completely lost was 1250°C for silicon, while that for germanium is only about 550°C. The tentative discussion for silicon may also be applied to the present case.

Moreover, it is interesting that the above-described damage of rectification has the same behavior as that due to neutron irradiation on the germanium rectifier.[5]

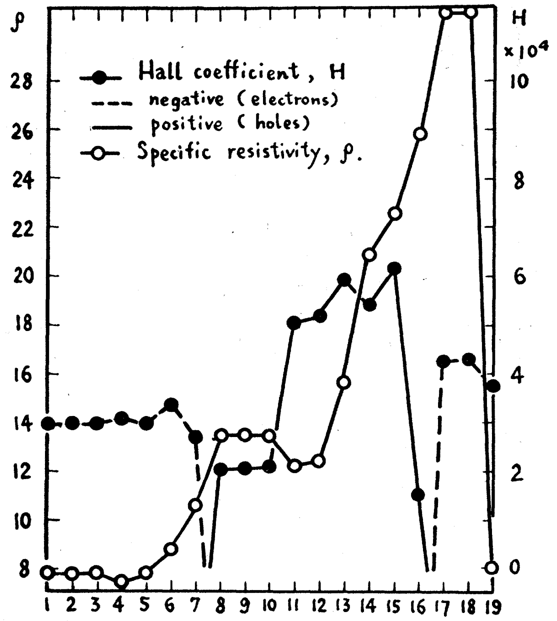

FIG. 3. The effect of miscellaneous treatments on the resistivity and Hall coefficient. The conditions for treatment are listed in Table I.

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[4] L. Esaki, Phys. Rev. 89, 398 (1953).

[5] W. E. Johnson and K. Lark-Horovitz (private communication).

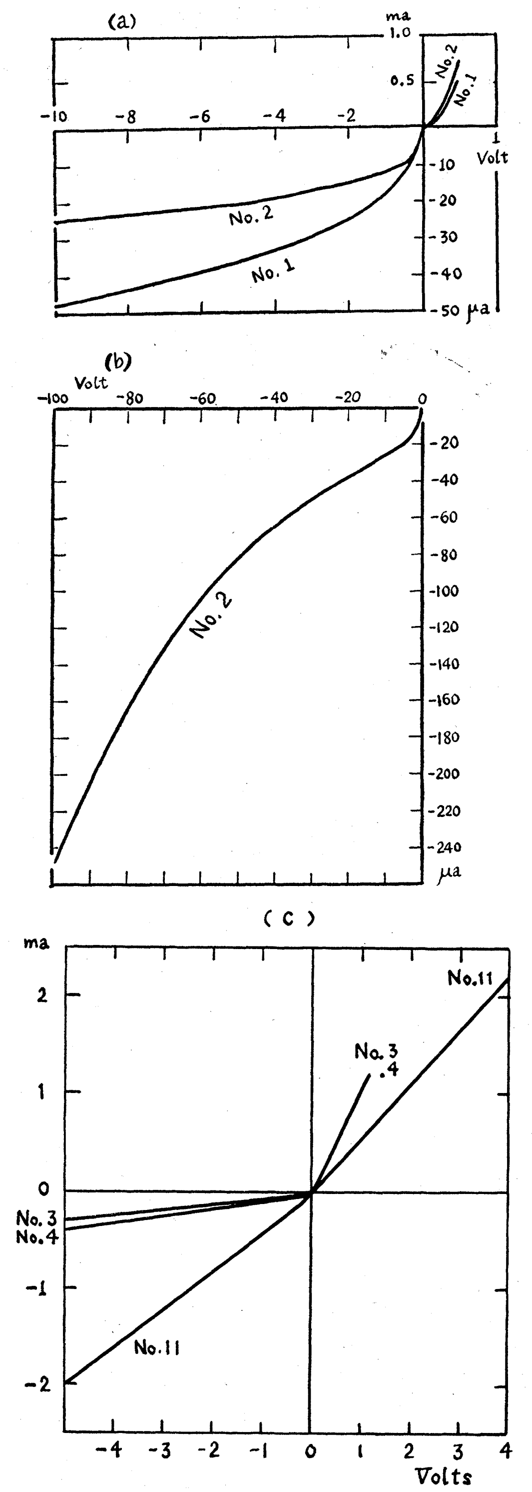

FIG. 4. The change of rectification characteristics.

After heating the specimen at about 600°C, the specific resistivity at room temperature increased gradually at first and then began to decrease, with an accompanying reversal in the sign of Hall coefficient. On subsequent heat treatment below 550°C, the specific resistivity increased to a maximum and then began to decrease. At the same time the sign of the Hall coefficient again became negative. While No. 17 was kept at room temperature for about 3000 hours, the properties remained unchanged. Finally, the specimen recovered the same properties as in the original state, except for the rectification characteristic.

The changes in the specific resistivity and Hall coefficient from room temperature up to 200°C are plotted in Fig. 5. The experimental values were satisfactorily reversible, indicating that no detectable annealing occurs in the measured temperature range. The concentration and mobility of carriers for Nos. 1 and 11 are listed in Table II together with several other quantities. The critical temperature at which the *p* type specimen converts to *n* type decreases with progressive heating at a temperature between 500°C and 600°C as seen in Table III, suggesting the gradual disappearance of acceptor levels.

4. RESULTS AND DISCUSSION

To study the behavior of thermally produced acceptors more exactly, the changes of resistivity and Hall coefficient at room temperature were observed successively for the specimen subjected to heating at a fixed temperature from 690°C to 500°C. The results are shown in Fig. 6 (1a), (2a), (3a), (4a), (5a), (6a), and (7a). In Fig. 6 (1a), (2a), (3a), and (5a), after the initial rapid increase or decrease, the resistivity finally approaches a steady value, which becomes smaller at higher temperature. The Hall coefficient indicates that the specimen is *p* type over the entire range. On the other hand, in Fig. 6 (4a), (6a), and (7a), the resistivity increases initially to a maximum and then decreases gradually to a constant value in the same way that was observed in the preliminary experiment. The Hall coefficient shows that *p-n* conversion occurs near the maximum resistivity and that the steady state is *n* type below 540°C. In general, at lower temperatures the changes are much slower.

From the observed values of the specific resistivity, ρ, or conductivity, σ, and the Hall coefficient, H, the concentration of electrons, n, and holes, p, are determined by[6]

$$\rho=\frac{1}{\sigma}=\frac{1}{e\mu_p(nb+p)}, \tag{1}$$

$$H=\frac{3\pi}{8}\frac{nb^2-p}{e(nb+p)^2}, \tag{2}$$

where μ_p is the hole mobility and b the ratio of electron mobility to hole mobility. The mobilities of electrons and holes will be assumed to be nearly independent of the acceptor concentration thermally produced. The

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[6] See W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950).

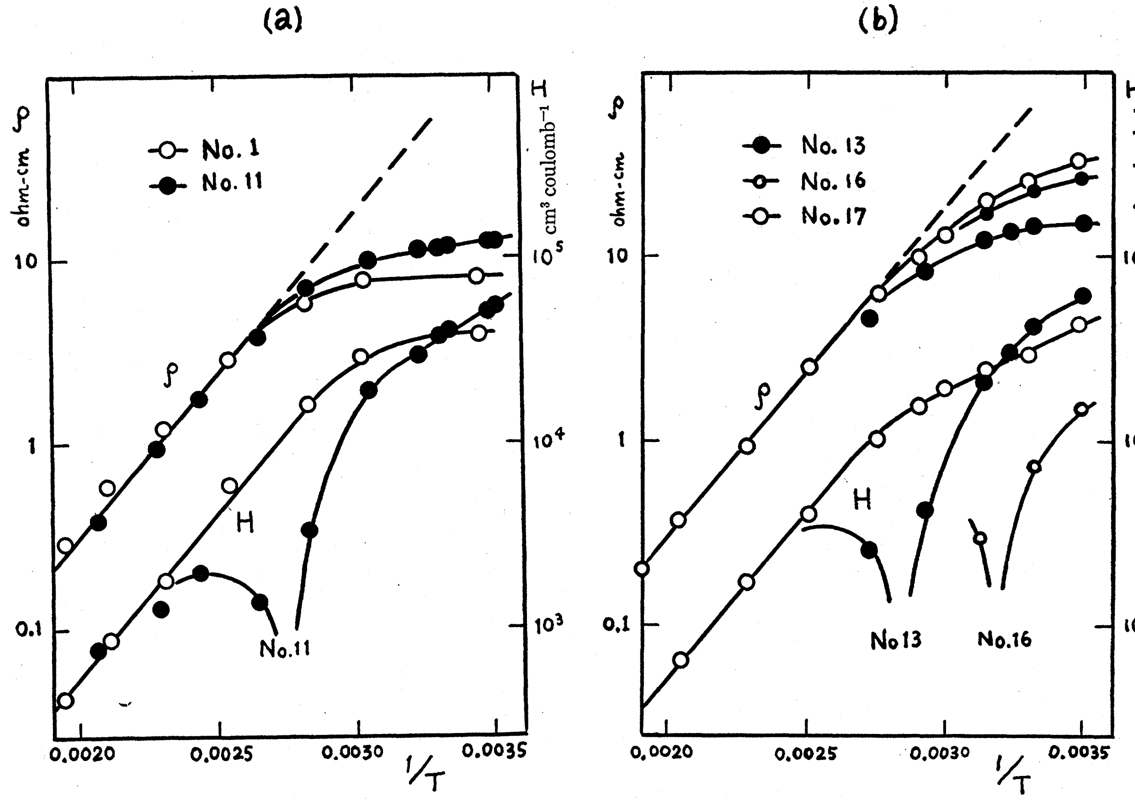

FIG. 5. Specific resistivity ρ and Hall coefficient H (logarithmic scale) *vs* reciprocal of absolute temperature.

hole mobility is determined to be 3600±100 cm² volt^{-1} sec^{-1} for the various specimens in which p is much larger than n, as shown in the last column of Table IV. Therefore the ratio b is about 1.2, using the electron mobility 4340 cm² volt^{-1} sec^{-1} in the original specimen. The calculated p, n, and their product were plotted in Fig. 6 (1b), (2b), (3b), (4b), (5b), and (6b). The concentrations of holes and electrons decrease or increase, and tend to certain values corresponding to each heating temperature. By using the values of p and n, the concentration of acceptors is approximately evaluated as follows: The net charge density is given by

$$e(D-A)-e(n-p-p_a)=0, \tag{3}$$

where D and A are the concentrations of donors and acceptors, p_a that of holes bound to acceptors. The ionization energy required to excite an electron from a donor to the conduction band is so small that excess electrons bound to donors are neglected. The equation governing the relation among holes p, ionized acceptors $A-p_a$, and neutral acceptors p_a may be written

holes+ionized acceptors↔neutral acceptors.

Therefore, the equilibrium concentrations satisfy

$$p(A-p_a)=Kp_a.$$

By using Eq. 3, this is modified to

$$p(D+p-n)=Kp_a, \tag{4}$$

where D, p, and n in the left term have already been numerically determined. ($D=1.88\times10^{14}$ cm^{-3}). The equilibrium constant K is statistically given by

$$K=2h^{-3}(2\pi m_pkT)^{\frac{3}{2}}\exp\{-(E_A-E_v)/kT\},$$

where E_A and E_v are the energies of the acceptor level and the valence band, and m_p is the effective mass of a hole. The value of E_A-E_v is not yet known exactly,

TABLE II. Specific resistivity, Hall coefficient, and concentration and mobility of carriers for specimens, No. 1 and No. 11.

Specimen number	Type	Specific resist. (ohm-cm)	Hall coefficient (cm³ coulomb⁻¹)	Concentration (cm⁻³)	Mobility (cm² volt⁻¹ sec⁻¹)
1	*N*	7.7	3.93×10^{14}	1.88×10^{14}	4340
11	*P*	12.2	5.05×10^{14}	1.41×10^{14}	3600

TABLE III. *P-N* transition temperature for specimens from No. 11 to No. 16.

Specimen No.	*P-N* transition temperature
11	93°C
13	81°C
14	63°C
15	63°C
16	39°C

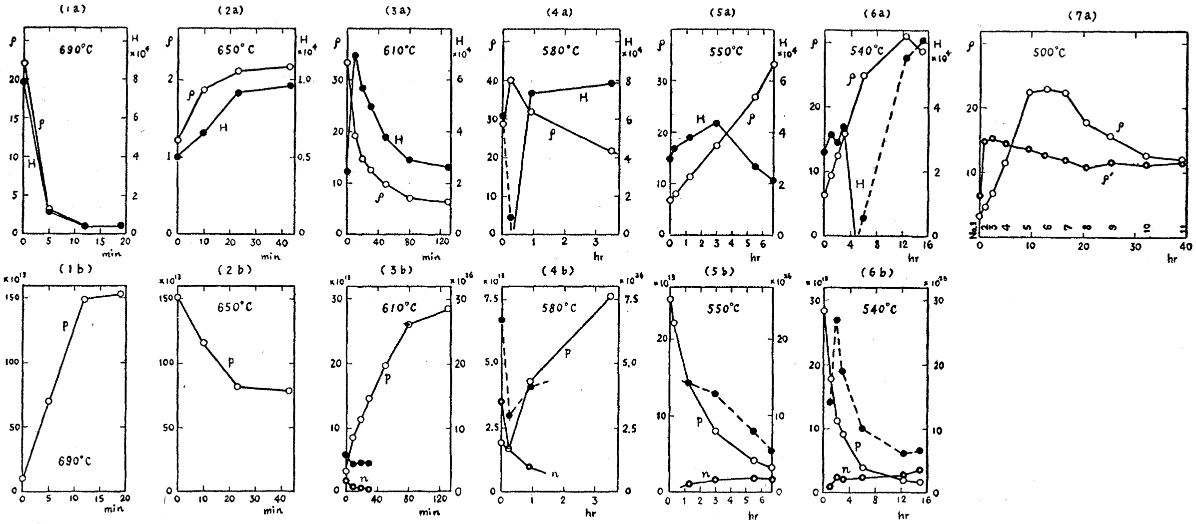

FIG. 6. (a) The changes of the specific resistivity ρ and the Hall coefficient H with heating time. Open and solid circles indicate ρ in ohm-cm on the left ordinate and H in cm^2 volt^{-1} sec^{-1} on the right ordinate, respectively. The full and dotted lines connecting the solid circles represent the positive and negative signs, respectively, in the Hall coefficient. The black circles with white centers, in (7a) give the resistivity calculated from the spreading resistance at the point contact. (b) The changes of the concentrations of electrons n and holes p and the product $p\times n$ with heating time. Open, black with white centers, and solid circles are p, n, and $p\times n$, respectively. The left and right ordinates represent the concentration in cm^{-3} and the product in cm^{-6}, respectively.

but may be assumed to be the order of 0.2 ev or less, so that K is evaluated to be 10^{16} cm^{-3} or more, if the temperature dependency of E_A-E_v is taken into consideration.[7] Comparing both terms in Eq. (4), p_a must be much smaller than p, suggesting the full ionization of acceptors. Therefore, from Eq. (3),

$$A=D+p-n. \qquad (5)$$

The plots of $\log_{10}|A-A_f|$ *vs* t at various temperatures in Fig. 7 are almost straight, where A_f is the final concentration at the corresponding temperature. Experimentally, the relationship between A and t is expressed by

$$A=A_f+(A_i-A_f)\exp(-kt), \qquad (6)$$

A_i being the initial concentration and k a function of temperature. This is the familiar first-order built-up equation, analogous to that derived in the study of neutron bombardment of germanium.[8]

TABLE IV. Acceptor concentration and diffusion coefficient as several temperatures between 500°C and 690°C, and hole mobility at room temperature.

Temp. °C	A_f cm^{-3}	D cm^2 sec^{-1}	μ_p cm^2 volt^{-1} sec^{-1}
690	180×10^{13}	152×10^{-8}	3500
650	95	82	3750
645	—	—	3540
610	50	25	3540
600	40	—	3660
580	27	12	——
550	19	7.1	——
540	17	5.5	——
500	7	1	——
A_0 or D_0*	2.5×10^{21}	3×10^2	Mean value
Q_A or Q_D*	27 kcal/g atom	37 kcal/g-atom	of μ_p
	=1.2 ev	=1.6 ev	3600±100

* $A_f=A_0\exp(-Q_A/RT)$; $D=D_0\exp(-Q_D/RT)$.

During heating at 500°C, the rectification characteristic at room temperature changed gradually, as illustrated in Fig. 8. The number designated on each curve in Fig. 8 corresponds to the number given in the lower side of Fig. 6 (7a). The spreading resistance R evaluated from the slope of the current-voltage curve in the forward direction provided that the rectification is weak, is given by[4]

$$R=\rho'/2d\ \text{ohms},$$

where d is the diameter at the point contact and ρ' the specific resistivity near the surface. Only when the specimen is uniform, is ρ' equal to ρ. For instance, the curve No. 0 in Fig. 8 for the specimen of $\rho=\rho'=3.5$ ohm-cm which was attained by prolonged heating at 645°C, gives $R=500$ ohm, resulting in $d=3.5\times10^{-3}$ cm. The same value of d was also derived for the specimen heated for a long time at any temperature. In curve No. 1, ρ' is not equal to ρ; this indicates that the specimen was unfortunately not homogeneous at the start of the treatment at 500°C. At the beginning of the treatment ρ' usually differs markedly from ρ, and finally both ρ' and ρ approach the same value, as in Fig. 6 (7a). These curves suggest that the spreading resistance changes faster in approaching the steady value than the bulk resistivity. In other words, the

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[7] V. A. Johnson and H. Y. Fan Phys. Rev. **79**, 899 (1950).

[8] Cleland, Crawford, Lark-Horovitz, Pigg, and Young, Phys. Rev. **83**, 312 (1951).

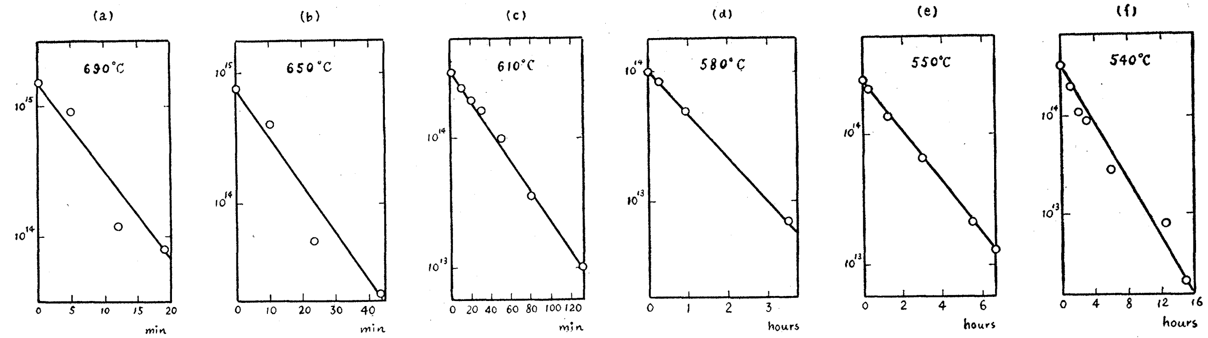

FIG. 7. $\log_{10}|A-A_f|$ *vs* heating time, where A and A_f are the acceptor concentrations at a given time and at the equilibrium state, respectively.

surface concentration of acceptors becomes constant instantly and they diffuse gradually into the interior.

As previously mentioned, the rectification is destroyed with treatment at a comparatively low temperature and is lost completely if the concentration of acceptors exceeds 3×10^{14} cm^{-3}. In p type no rectification was observed, but the lost rectification is slightly recovered as n becomes richer than p (Fig. 8). Curve No. 11 did not change even by heating at 415°C, 320°C, and 230°C, for each 8 hours. However, it was improved to curve No. 12 and curve No. 13 when the specimen was exposed to atmosphere at room temperature for several hours and when it was heated at 380°C for ten minutes in oxygen of pressure from 2×10^{-2} to 10^{-1} mm Hg, respectively.

The fact that the product of the electron and hole concentrations is not constant near the beginning of the heating in Fig. 6 (3b), (4b), (5b), and (6b), leads to an inhomogeneous distribution of donors and acceptors. According to statistical theory, in the homogeneous specimen the product is independent of impurity concentration at any temperature, having the relation:[6]

$$np=4h^{-6}(2\pi m^*kT)^3\exp\{-(E_c-E_v)/kT\},\qquad(7)$$

where m^* is the geometric mean of the effective masses of the carriers, and E_c and E_v are the energies of the conduction band and valence band. Johnson and Fan estimated this product to be 9×10^{26} cm^{-6} at 22°C.[7] In the present experiment it ranges from 3×10^{26} cm^{-6} to 3×10^{27} cm^{-6}. The wide distribution in the product will be ascribed to the inhomogeneity in the specimen. Moreover, in Fig. 6 (5b) and (6b) the product tends to 6×10^{26} cm^{-6}, indicating that the specimen becomes homogeneous with prolonged heating in agreement with the conclusion from the spreading resistance.

It seems quite reasonable that acceptor levels, produced on the surface, diffuse into the interior according to Fick's law, which, if the concentration of acceptors be A, is written

$$\partial A/\partial t=D\partial^2A/\partial x^2,$$

in which x is the distance and D the diffusion coefficient of acceptors. The solution, when the boundary condition is $A=A_f$ at $x=0$ and $x=l$, and $A=A_i$ at $t=0$, is given by

$$A=A_f+(A_i-A_f)\frac{4}{\pi}\sum_{n=0}^{\infty}\frac{1}{(2n+1)}\times\exp\left\{-\frac{(2n+1)^2}{l^2}\pi^2Dt\right\}\sin\left\{\frac{(2n+1)}{l}\pi x\right\},\qquad(8)$$

where the notations A_i and A_f are the same as in Eq. (6) and l is the thickness of the specimen. On integrating, we obtain

$$\int_0^l A\,dx=A_fl+(A_i-A_f)\frac{8l}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\times\exp\left\{-\frac{(2n+1)^2}{l^2}\pi^2Dt\right\}.$$

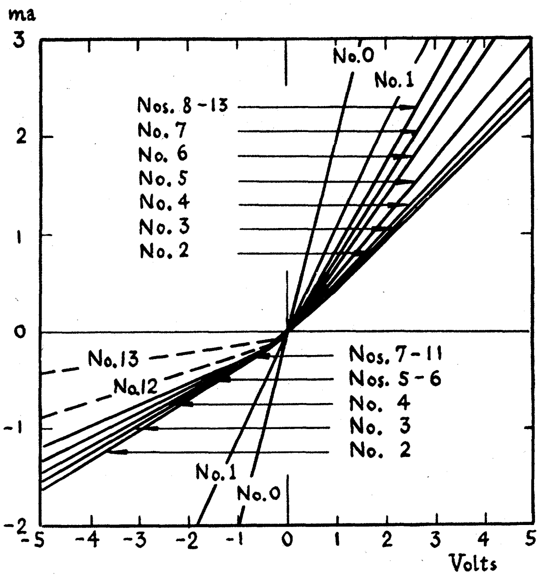

FIG. 8. Changes of the rectification characteristics.

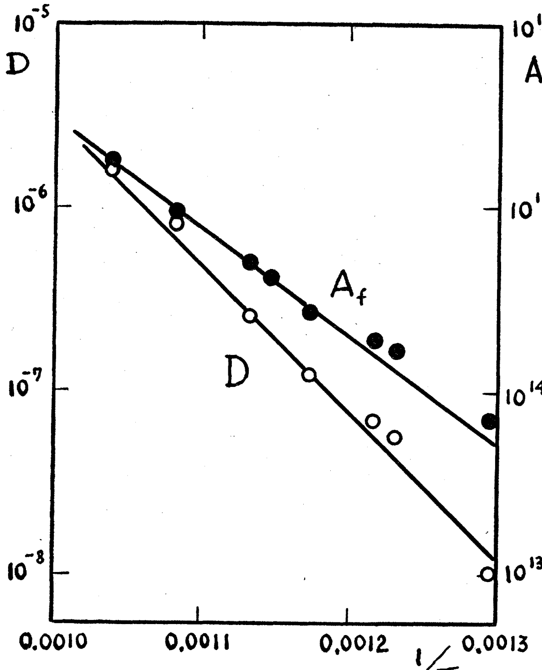

FIG. 9. The diffusion coefficient D in cm^2 sec^{-1} and the equilibrium concentration A_f in cm^{-3}, plotted *vs* reciprocal absolute temperature.

Therefore, the first approximation is given by[9]

$$\int_0^l A\frac{dx}{l}=A_f+(A_i-A_f)\frac{8}{\pi^2}\exp\left(-\frac{\pi^2}{l^2}Dt\right). \quad (9)$$

This equation is similar to the experimental equation (6); k in Eq. (6) is equal to $(\pi^2/l^2)D$ in Eq. (9). The numerical values D obtained at various temperatures are listed in Table IV together with the values A_f and the hole mobilities μ_p. In Fig. 9, D and A_f are plotted against reciprocal absolute temperature, and they are represented by[10]

$$D=300\exp(-37\,000/RT)\ \text{cm}^2\,\text{sec}^{-1},$$
$$A_f=2.5\times10^{21}\exp(-27\,000/RT)\ \text{cm}^{-3},$$

corresponding to activation energies of about 1.6 ev and 1.2 ev, respectively. The activation energy in germanium (37 kcal/g-atom) is higher than that for self diffusion in lead (28 kcal/g-atom),[11] but lower than those for silver (50 kcal/g-atom),[12] copper (45–61 kcal/g-atom), and gold (63 kcal/g-atom).

The final state of each treatment may be expected to be nearly homogeneous. Therefore, on plotting the acceptor concentration A at the last points of 500°C, 540°C, 550°C, 580°C, and 610°C in Fig. 6 against the conductivity σ, we obtain Fig. 10, in which a dotted curve represents the following equation derived from Eqs. (1), (5), and (7):

$$\sigma=\tfrac{1}{2}e[\{(D-A)+[(D-A)^2-4c^2]^{\frac{1}{2}}\}\mu_n + \{(A-D)+[(A-D)^2-4c^2]^{\frac{1}{2}}\}\mu_p], \quad (10)$$

where D, μ_n and μ_p were defined previously and are numerically known, and

$$c=np\doteqdot 6\times10^{26}\ \text{cm}^{-6}.$$

During the treatment, however, the concentrations n and p vary not only with time but also with distance from the surface, so that the basic Eqs. (1) and (2) for a homogeneous specimen should be reconsidered. If the transverse dimensions of the specimen of germanium plates are given by l and w, where w is equal to the distance between probes for the Hall voltage measurement and is much larger than l, the mean values of $n(x)$, $p(x)$, and $\sigma(x)$ may be written:

$$\int_0^l n(x)dx=\bar{n}l,\quad \int_0^l p(x)dx=\bar{p}l,$$

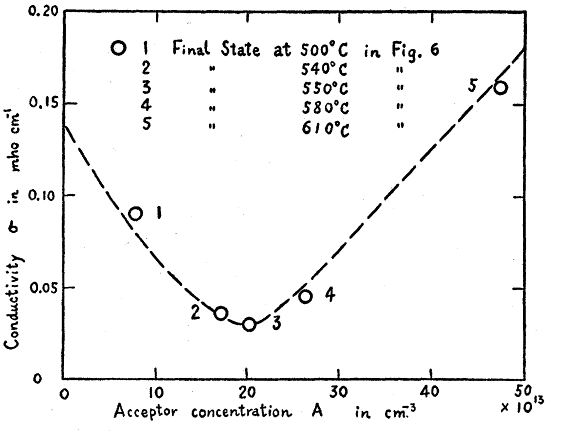

FIG. 10. Acceptor concentration *versus* conductivity. The circles designated by 1, 2, 3, 4, and 5 represent the final states at 500°C, 540°C, 550°C, 580°C, and 610°C. The dotted curve indicates $\sigma=\frac{1}{2}e[\{(D-A)+[(D-A)^2-4c^2]^{\frac{1}{2}}\}\mu_n+\{(A-D)+[(A-D)^2-4c^2]^{\frac{1}{2}}\}\mu_p]$.

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[9] In the main part of the present treatment, $(\pi^2/l^2)Dt$ is larger than 0.3. For instance, when $t=2.0$, 3.6, 11.8, 24.5, 41.3, and 53.5 minutes at 690°C, 650°C, 610°C, 580°C, and 540°C, respectively, $(\pi^2/l^2)Dt$ becomes 0.3. In this case, the approximation employed is good because the second term is only one hundredth of the first one.

The author is grateful to Dr. C. S. Fuller and Dr. van Roosbroeck for an interesting discussion on this point.

[10] While the present study was in progress, there appeared a Letter to the Editor by Fuller, Theuerer, and van Roosbroeck, Phys. Rev. **85**, 678 (1952), which has a close connection with the author's study. The values of D and A determined by Fuller *et al.* are

$$D=0.02\exp(-12\,000/RT)\ \text{cm}^2\,\text{sec}^{-1},$$
$$A=2.1\times10^{21}\exp(-27\,000/RT)\ \text{cm}^{-3}.$$

While the value of A is in a fairly good agreement with that of the author, the value of D differs significantly even though possible experimental errors are taken into consideration. These two values coincide at 1300°K. This deviation may probably be ascribed to the differences in both material and temperatures used. Fuller *et al.* used mainly polycrystalline germanium and obtained their results at high temperatures.

[11] See, for example, W. Seith, *Diffusion in Metallen* (J. Springer, Berlin, 1939).

[12] R. E. Hoffman and D. Turnbull, J. Appl. Phys. **22**, 634 (1951).

and

$$\int_0^l \sigma(x)dx=\int_0^l e(n\mu_n+p\mu_p)dx$$

$$=e(\bar{n}\mu_n+\bar{p}\mu_p)l$$

$$=\bar{\sigma}l.$$

Therefore, we get

$$\int_0^l \Delta n dx=0,\quad \int_0^l \Delta p dx=0,\quad \text{and}\quad \int_0^l \Delta\sigma dx=0, \tag{11}$$

where $n(x)-\bar{n}=\Delta n$; $p(x)-\bar{p}=\Delta p$, and $\sigma(x)-\bar{\sigma}=\Delta\sigma$. Although the formation of space charge by diffusion and recombination of electrons and holes and other effects would not be negligible, the Hall voltage V_0 induced between the probes by an uniform magnetic field B, could be tentatively expressed by

$$V_0=\frac{w}{l}\int_0^l BI(x)H(x)dx,$$

where $I(x)$ and $H(x)$ are current density and Hall coefficient at x, respectively. Using the relations

$$I(x)=E\sigma(x)=Ee(n\mu_n+p\mu_p),$$

and

$$H(x)=\frac{3\pi}{8}\frac{-n\mu_n{}^2+p\mu_p{}^2}{e(n\mu_n+p\mu_p)^2},$$

we have

$$V_0=\frac{3\pi}{8}\frac{w}{l}BE\int_0^l\frac{-n\mu_n{}^2+p\mu_p{}^2}{n\mu_n+p\mu_p}dx, \tag{12}$$

where E is the applied electric field. The total current I_0 through the specimen may be represented by

$$\begin{aligned}I_0&=w\int_0^l I(x)dx\\&=wE\int_0^l\sigma(x)dx \qquad (13)\\&=wE\bar{\sigma}l\\&=wlEe(\bar{n}\mu_n+\bar{p}\mu_p).\end{aligned}$$

Now, let us derive the Hall coefficient H_0, which is equal to V_0l/BI_0, observed for the inhomogeneous specimen in the following cases: Case 1. If $n\gg p$ or $n\ll p$, V_0 and I_0 can be simply written

$$V_0\doteqdot\frac{3\pi}{8}wBE\mu_n\quad\text{or}\quad\frac{3\pi}{8}wBE\mu_p,$$

and

$$I_0\doteqdot wlEe\bar{n}\mu_n\quad\text{or}\quad wlEe\bar{p}\mu_p.$$

TABLE V. The maximum and minimum values of the conductivity σ calculated from Eqs. (8) and (10) during the thermal treatments at 580°C, 550°C, and 540°C. The unit is mho cm^{-1}.

Time of treatment, hours	580°C		550°C		540°C	
	$\sigma_{\max}$	$\sigma_{\min}$	$\sigma_{\max}$	$\sigma_{\min}$	$\sigma_{\max}$	$\sigma_{\min}$
1	0.055	0.032	——	——	——	——
2	0.055	0.042	——	——	——	——
3	0.055	0.048	0.059	0.031	——	——
4	——	——	0.044	0.031	0.055	0.031
6	——	——	0.033	0.031	0.035	0.031

Therefore, we have

$$H_0\doteqdot\frac{3\pi}{8}\frac{1}{e\bar{n}}\quad\text{or}\quad\frac{3\pi}{8}\frac{1}{e\bar{p}}.$$

Case 2. If $|\Delta\sigma|/\bar{\sigma}$ is small throughout the specimen, Eq. (12) for V_0 becomes

$$V_0=\frac{3\pi}{8}\frac{w}{l}BE\frac{e}{\bar{\sigma}}\int_0^l(-\bar{n}\mu_n-\Delta n\mu_n{}^2+\bar{p}\mu_p{}^2+\Delta p\mu_p{}^2)\times\left(1-\frac{\Delta\sigma}{\bar{\sigma}}+\left(\frac{\Delta\sigma}{\bar{\sigma}}\right)^2-\cdots\right)dx.$$

Neglecting terms of order $(\Delta\sigma/\bar{\sigma})^2$, $\Delta n(\Delta\sigma/\bar{\sigma})$, $\Delta p(\Delta\sigma/\bar{\sigma})$, and of higher order, and using Eq. (11), we get

$$V_0\doteqdot\frac{3\pi}{8}wBE\left(\frac{-\bar{n}\mu_n{}^2+\bar{p}\mu_p{}^2}{\bar{n}\mu_n+\bar{p}\mu_p}\right).$$

This leads to

$$H_0\doteqdot\frac{3\pi}{8}\frac{-\bar{n}\mu_n{}^2+\bar{p}\mu_p{}^2}{e(\bar{n}\mu_n+\bar{p}\mu_p)^2}\quad\text{or}\quad\frac{3\pi}{8}\frac{-\bar{n}b^2+\bar{p}}{e(\bar{n}b+\bar{p})^2}.$$

The condition for Case 1 may be fulfilled both in the main ranges of treatment at 690°C, 650°C, and 610°C, and in the beginning of those at 550°C and 540°C, as seen from Fig. 6(a). By using Eqs. (8) and (10), the maximum and minimum values of σ are obtained as written in Table V. In such a state as listed, the mean value of $(\Delta\sigma/\bar{\sigma})^2$ relative to x is less than 0.02. Therefore, it is found that Case 2 may be applicable both to the main range of treatment at 580°C, and to those at 550°C and 540°C except for the initial few hours. Thus, the values of n and p determined in the present study from Eqs. (1) and (2) may indicate approximately ordinary mean values, so that the results may be fairly understandable.

It is difficult in the present study to determine the type of lattice defects forming acceptor levels. However, it is noteworthy that nearly all of the effect of lattice defects which were produced by neutron bombardment could be removed merely by heating up to 400°C, and also some of them could be considerably annealed even at room temperature,[8] in contrast to the behavior of lattice defects produced thermally. Therefore, these two kinds of defect may be considered to be different in type;[13] it may be that the defect produced by bombardment is Frenkel type, while the thermally produced defect is Schottky type.

5. SUMMARY

The changes in some properties of germanium, subjected to heating, are explained quite well by assuming that acceptor levels are formed by the lattice defects produced on the surface and diffusing into interior. When germanium is quenched from a high temperature in a vacuum furnace at a rate given by $dT/dt \doteqdot -T_0/(1+t)^2$ °C min^{-1}, it contains a fairly large number of lattice defects "fronzen in." These defects are not easily annealed up to 200°C.

On heating in vacuum, the rectification characteristic is improved at comparatively low temperatures, but is destroyed at higher temperatures, perhaps not only because lattice defects are produced but also because the surface becomes free from adsorbed gas. No theory satisfactorily explains all the phenomena of rectification.

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Note added in proof:—(1) Lately Fuller and Struthers (Phys. Rev. **87**, 526 (1952)) have reported that copper may be an impurity responsible for thermal acceptors in germanium. The diffusion constant at 825°C obtained by them, 1.3×10 cm^2 sec^{-1}, is in a very good agreement with the value, 1.36×10 cm^2 sec^{-1}, calculated from the above-derived equation, $D=300\exp(-37\,000/RT)$. (2) The recent results published by Goldberg [Phys. Rev. **88**, 920 (1952)] have several points of agreement with the present study.

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[13] See N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystal* (Oxford University Press, London, 1940), p. 36.

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Vapor-Liquid Equilibria in He^3-He^4 Solutions

J. C. MORROW
Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina

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Recent measurements of the vapor pressures of He^3-He^4 liquid solutions by Daunt and Heer and by Sommers are used to evaluate the solution non-ideality, for the calculation of which the large deviations of the vapor from ideality are taken into account. Estimation of the standard chemical potential of normal He^4 at temperatures below the lambda-point is discussed. Agreement of excess chemical potentials of He^4 above the lambda-point and the values obtained from the simple theory demonstrates the usefulness of the theory in discussions of effect of nonideality on the shift of the lambda-point with He^3 concentration.

I. INTRODUCTION

MEASUREMENTS of vapor-liquid equilibria can be used successfully to study thermodynamic properties of He^3-He^4 solutions, particularly the deviations from solution ideality, as has been pointed out previously.[1] These results are especially valuable since they can be used above the lambda-point, for which condition speculations about superfluid and its influence are not limitations. Recently some measurements of solution vapor pressures both above and below the lambda-point have been made by Daunt and Heer[2] and by Sommers.[3] The results above the lambda-point can be used to give direct information about the magnitude of solution nonideality and about the relative likeness of a simple solution model[1] and the real solution. From these equilibrium measurements one can calculate the model nonideality parameter a, which, for a binary mixture of nonelectrolytes, gives the excess chemical potential of component j as $V_j a f_i^2$, where ${}_jV$ is the molar volume of pure j and f_i is the volume fraction of i. One of the features of such experimentally evaluated parameters which one would immediately subject to scrutiny is concentration dependence, since the model parameter is independent of concentration. The results of Sommers must be used in such an instance since the measurements by Daunt and Heer refer to a single liquid concentration.

II. EQUILIBRIUM ABOVE THE LAMBDA-POINT

Following Sec. III of reference 1, one has for the chemical potential of component i in the binary liquid mixture

$$\mu_{il}{}^0(P_i{}^0, T)+\bar{V}_{il}(P-P_i{}^0)+RT\ln x_i+\mu_i{}^E,$$

where the first term is the standard chemical potential of the pure component at temperature T and pressure equal to the vapor pressure of the pure component at T; $\bar{V}_{il}$ is the partial molal volume of liquid i; P is the

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[1] J. C. Morrow, Phys. Rev. **84**, 502 (1951).
[2] J. G. Daunt and C. V. Heer, Phys. Rev. **86**, 205 (1952).
[3] H. S. Sommers, Jr., Phys. Rev. **88**, 113 (1952).