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Vacancies and Interstitials in Heat Treated Germanium

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Annealing experiments on the thermal acceptors quenched into germanium by rapid cooling from high temperatures are used to deduce information about vacancies and interstitials in germanium. Annealing is studied at a series of temperatures and a critical temperature is found at 516°C. Above 516°C, the annealing curves suggest a bimolecular recombination process implying that the heat treatment produces comparable numbers of vacancies and interstitials (Frenkel defects) which disappear by mutual annihilation. Below 516°C, the data can be explained by a model in which interstitials are trapped near dislocations before much recombination can occur with vacancies. As a result of these experiments and their interpretation, interstitials are believed to be more mobile than vacancies below, and possibly above, 516°C.

I. INTRODUCTION

THE introduction of defects into germanium by heat treatment was tried by many workers using a variety of heating furnaces, heating atmospheres, and quenching baths.[1] These workers found that the material becomes *p*-type after such heat treatment and the concentration of acceptors was usually in the range 10^{14} to 10^{17} per cm^3, being higher the higher the heat treatment temperature. At first glance, the "*p*" nature of the material was assumed to be caused by vacancies; however, the work of several groups at Bell Laboratories[2] established that by and large the "*p*" nature of the germanium was caused by extraneous copper which entered the germanium as an impurity during the heat treatment process. An experiment by Finn[3] demonstrated that copper can be evaporated from germanium in sufficiently good vacuum. We have been using evaporation quite successfully in order to purify the germanium before our heat treatment experiments are performed on the sample. Without such purified germanium the following studies on vacancies and interstitials would not have been possible.[4]

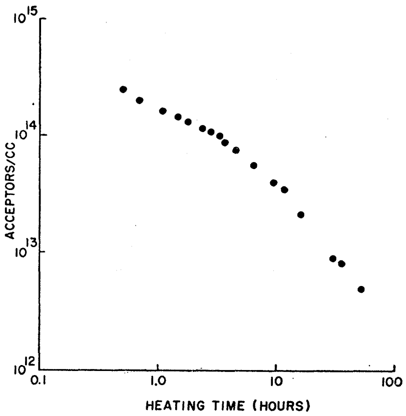

FIG. 1. The loss in acceptor concentration as a function of heating time at 636°C. These data were obtained on a sample immediately after its introduction into the vacuum system. This irreversible loss of acceptors indicates evaporation of an impurity most likely copper.

II. EXPERIMENTAL TECHNIQUES AND PROCEDURES

In a previous letter to the Editor, we briefly described the techniques used to study defects in germanium.[5] The central idea is the use of joule heating of the germanium in as good a vacuum as is conveniently obtainable which in our experiment was less than 4×10^{-7} mm of Hg. In Fig. 1, we show the evaporation of an impurity, most likely copper, from a sample immediately after its introduction into the vacuum system. This specimen was heated for various times at 636°C and quenched. In Fig. 1, we plot the number of acceptors so quenched into the germanium. We see that over a period of 40 hours at 636°C the concentration of acceptors decreases from 2×10^{14}/cm^3 to 6×10^{12}/cm^3. The evaporation from another sample where the initial heating in vacuum was performed at 750°C, took place so rapidly that it was not observed. Using evaporation we have reduced the concentration of impurity acceptors to below 3×10^{12}/cm^3 before starting our heat treatment and annealing studies.

The sample is typically a rectangular slab of germanium of dimensions 1 mm×3 mm×2 cm. The current is introduced into the germanium through tantalum leads which are welded directly to the germanium ends. Voltage probes for resistivity measurements are made of tantalum and are held by pressure contact to the narrow surface of the germanium as shown in Fig. 2. The tantalum current leads are used as supports for the germanium and they are welded to the Kovar leads in a standard vacuum tube header. The tube is attached to a kinetic vacuum system in

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[1] H. C. Theuerer and J. H. Scaff, J. Metals **189**, 59 (1951); Fuller, Theuerer, and Van Roosbroeck, Phys. Rev. **85**, 678 (1952); W. E. Taylor, Phys. Rev. **86**, 642 (1952); Colman Goldberg, Phys. Rev. **88**, 920 (1952); and G. Esaki, Phys. Rev. **89**, 1026 (1953).

[2] C. S. Fuller and J. D. Struthers, Phys. Rev. **87**, 526 (1952); W. P. Slichter and E. D. Kolb, Phys. Rev. **87**, 527 (1952).

[3] G. Finn, Phys. Rev. **91**, 754 (1953).

[4] In a recent publication, R. A. Logan [Phys. Rev. **91**, 757 (1953)] suggests certain chemical treatments of the Ge to reduce the Cu contamination. However, we are always able to purify our samples satisfactorily by evaporating the Cu.

[5] S. Mayburg and L. Rotondi, Phys. Rev. **91**, 1015 (1953).

such a way that various constant temperature baths can be brought around the tube. The resistivity measurements used to determine the lattice defects are always taken at 195°K (dry ice and alcohol) unless otherwise specified. From the mobility data of Prince,[6] we are able to determine the concentration of acceptors minus the concentration of donors ($N_A - N_D$) as a function of heat treatment.

Once a germanium slab is mounted in the tube and the tube is attached to the vacuum system, there is no need to disassemble the sample in the course of the whole series of heat treatment studies. The germanium is heated by sending a direct current through it and for a sample of the dimensions mentioned, a current of about 12 amperes is sufficient to raise the temperature to near the melting point. The temperature of the germanium can be measured by measuring the resistivity of the germanium or by use of an optical pyrometer. We have used both and find it in general more convenient and more accurate to use the resistivity measurement to determine the temperature.[7]

The uniformity with which the sample is heated is very good. This results from the high thermal conductivity of germanium, from the low amount of power required to heat the germanium in vacuum to near its melting point (5 watts), and because the conductivity of germanium depends on temperature in such a way that a drop in temperature in a certain region results in an increase of the joule heating in that region and thus a restoration of the original temperature. In order to cut down heat losses from the specimen, it is necessary that the tantalum leads be as hot or slightly hotter than the germanium.

Stray chemical impurities present in the apparatus have little effect on the measurements reported here. The tantalum is the only foreign body in the vacuum which is raised to the temperature of the germanium. We have spectroscopically analyzed the tantalum for impurities and have not found copper or other acceptor type impurity present; we have heated tantalum strips in a good vacuum to much higher temperatures than were used in these heat treatment experiments and have found no tantalum deposited on the walls of the vacuum chamber, which is consistent with the high heat of vaporization of tantalum. Using the ideas on ionic radii, we find that tantalum will not fit interstitially into the germanium lattice; its diffusion in germanium must be substitutional.[8] The low diffusion rate of substitutional impurities makes it impossible to envision the tantalum diffusing from the welds to the probes and thereby affecting the measurements. Furthermore, an impurity would enter or leave the material irreversibly during the experiments and would thereby be detected and could be accounted for. We have detected a minor effect of this sort which seems to result from the building up of an oxide layer on the germanium.

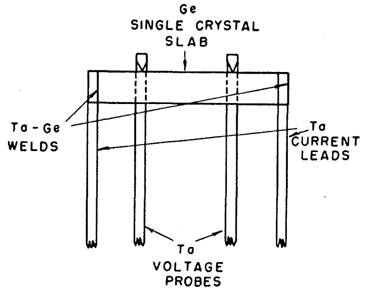

FIG. 2. The germanium single crystal specimen with tantalum current leads and voltage probes. The current leads are welded directly to the germanium and the probes are pressure contacts.

The quenching of the germanium is attained merely by switching off the heating current and allowing the germanium to cool by radiation. The cooling rate at any temperature can be estimated by noting that the power required to maintain equilibrium is equal to the radiation losses. Therefore, the cooling rate dT/dt at any temperature is equal to the power required to maintain the piece at equilibrium at that temperature divided by the heat capacity. For the samples of the dimensions mentioned above, cooling rates of 100° per second are found for temperatures near the melting point. This cooling rate is fast enough[9] to quench in the defects in the germanium.

After the sample is heated long enough to remove the copper impurity to a negligible level, the sample is heated to 830°C and quenched in order to introduce about 2×10^{14} acceptors/cc, which is the equilibrium solubility for that temperature. See Fig. 3. The sample is then annealed at a lower temperature and the change in acceptor concentration is studied as a function of time at various fixed temperatures.

III. POSSIBLE ANNEALING MECHANISMS

Before discussing the experimental results it may be helpful to speculate as to possible annealing mechanisms. There has been considerable work done on the defects produced by fast particle bombardment on crystals in general and germanium in particular. James and Lark-Horovitz[10] find that the results of neutron bombardment on germanium can be explained by

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[6] M. B. Prince, Phys. Rev. **91**, 271 (1953).

[7] We have measured the intrinsic resistivity of single crystal Ge as a function of temperature, and find that a consistent error of 10°C exists in the data of Keyes (see reference 5) which we originally used. In Fig. 3, we plot the solubility of thermal acceptors as measured by Mayburg and Rotondi (see reference 5) as a function of the properly corrected quench temperature.

[8] L. W. Strock (personal communication).

[9] If the quenching rate were not fast enough, the solubility of acceptors as a function of the reciprocal of the quench temperature (Fig. 3) would show a maximum at the temperature for which the quenching rate was no longer fast enough. In the temperature range pertaining to our experiments, we observed no such maximum.

[10] H. M. James and K. Lark-Horovitz, Z. Physik. Chem. **198**, 107 (1951).

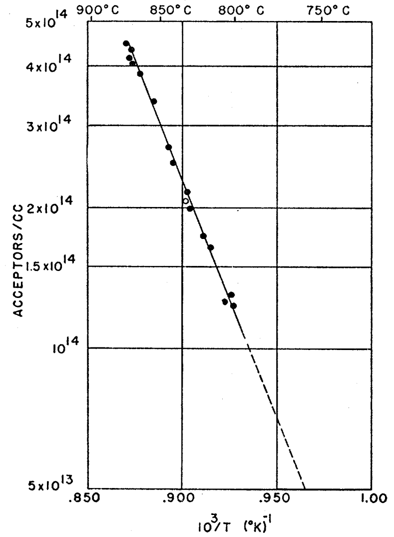

FIG. 3. The solubility of thermal acceptors in germanium as a function of the reciprocal of the heat treatment temperature from Mayburg and Rotondi (reference 5). These data have been corrected for a more accurate determination of temperature (reference 7) and are shown by the dots. The circle represents a measurement on a second specimen. The second specimen is the one used for all annealing experiments. The equation giving the concentration of acceptors, A, which are believed to equal the concentration of Frenkel defects is $A=3\times 10^{23}e^{-2.01ev/kT}(\text{cm}^{-3})$.

assuming that the bombardment produces vacancies and interstitials in roughly equal numbers and that the vacancy acts as an electron trap while the interstitial germanium atom acts as an electron donor. They further suggest that around room temperature the vacancy should trap two electrons while the interstitial would donate but one electron. Brown, Fletcher, and Wright,[11] bombarding with 3-Mev electrons, find that the vacancy-interstitial pair created in the germanium by the electron bombardment gives rise to one acceptor per pair in agreement with the suggestion of James and Lark-Horovitz.

While interstitials clearly arise as a result of particle bombardment, there is no *a priori* reason to expect that the heat treatment produces interstitial germanium. However, through studies of the annealing curves it is possible to determine whether in fact there are interstitials created by heat treatment, because the mechanism of loss of acceptors would be entirely different with or without interstitials.

If the acceptors we observe are lattice vacancies alone, the annealing process should be described by the simple diffusion of the excess vacancies out of the slab of material, either by diffusion to the surface or by diffusion to dislocations.

Esaki[12] has solved the problem of acceptor centers diffusing to the surface of a slab of material of thickness $2L$. He finds, after the early stages of annealing,[13] that the acceptor concentration, A, can be represented by the equation

$$A=A_f+(A_i-A_f)(8/\pi^2)\exp(-\pi^2Dt/L^2), \qquad (1)$$

where A_i is the initial concentration of acceptors, A_f is the final concentration of acceptors which is the equilibrium concentration at the annealing temperature, and D is the diffusion constant for the acceptors.

If the acceptors are vacancies they can be absorbed on dislocations. Actually the only place along a dislocation where a single vacancy or interstitial can lose its identity is at a "jog".[14] Any place else along the body of the dislocation the defect retains its identity and must be annihilated by the opposite defect. As we shall see later, it appears unlikely that at high temperatures the body of the dislocation can even trap the defects.

Let us now see the effect of the absorption of vacancies at jogs on the diffusion process. Suppose the concentration of jogs per cc is j. The recombination of vacancies with jogs will proceed with a rate per unit volume

$$(1/\tau)(j/N)(n-n_f),$$

where τ is the jump time for a vacancy, j/N is the probability that a vacancy is making a jump will land on a jog instead of on the other $N\text{-}j$ lattice points, n is the concentration of vacancies, and n_f is the equilibrium concentration at the annealing temperature. Under these circumstances the usual diffusion equation becomes:

$$D\partial^2n/\partial x^2-(1/\tau)(j/N)(n-n_f)=\partial n/\partial t. \qquad (2)$$

The solution to Eq. (2) is identical with Eq. (1), except the time dependence becomes

$$\exp[-(\pi^2D/L^2+j/\tau N)t].$$

Thus, if we include the effect of the jogs on dislocations in annihilating vacancies, Eq. (1) can be written in the form,

$$\log(A-A_f)=-(\pi^2D/L^2+j/\tau N)t+\text{const.} \qquad (3)$$

Therefore, if only vacancies are present as a result of the heat treatment, the acceptor concentration should vary with time according to Eq. (3) during the annealing process. All "monomolecular" processes have the same time dependence as Eq. (3).

An appreciably different time dependence from that given by Eq. (3) can be obtained for the acceptor concentration only if there are a number of interstitials comparable with the number of vacancies. (This situation corresponds to a bimolecular process.) For

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[11] Brown, Fletcher, and Wright, Phys. Rev. **92**, 591 (1953).

[12] G. Esaki, Phys. Rev. **89**, 1032 (1953).

[13] Neglect of the "higher modes" in the solution of the diffusion equation amounts to an error of 22 percent in acceptor concentration at $t=0$. This error is negligible when compared with the annealing curves which show changes of acceptor concentration of factors of 10 and 100.

[14] F. Seitz, Acta Metallurgica **1**, 365, (1953).

the purpose of this argument let us assume that the high-temperature heat treatment produces Frenkel defects, i.e., equal numbers of interstitials and vacancies. The recombination of interstitials with vacancies will now determine the annealing process. The measured acceptor concentration, A, which is the number of holes contributing to the conductivity, is the difference between the number of acceptors N_A and the number of donors N_D; i.e.,

$$A = N_A - N_D.$$

As was mentioned previously, from the analysis of the bombardment experiments by James and Lark-Horovitz we know that each Frenkel defect gives rise to one acceptor. Hence, A is the concentration of vacancies or of interstitials if Frenkel defects are the sole defects or impurities present.

The annealing of Frenkel defects has been studied extensively in connection with radiation damage experiments.[15] For our purpose, the rate of loss of defects can be expressed by the equation

$$dA/dt = -(A^2 - A_f^2)/\bar{\tau}N, \tag{4}$$

where A_f is the equilibrium concentrations of vacancies or interstitials at the annealing temperature, N is the concentration of lattice positions, and $\bar{\tau}$ is an appropriate average jump time for the defects. In the case when only one of the defects is mobile, τ represents the jump time for that defect.

Equations (3) and (4) represent two different simple mechanisms for annealing. In the next section we shall see which mechanism best describes the experimental annealing curves.

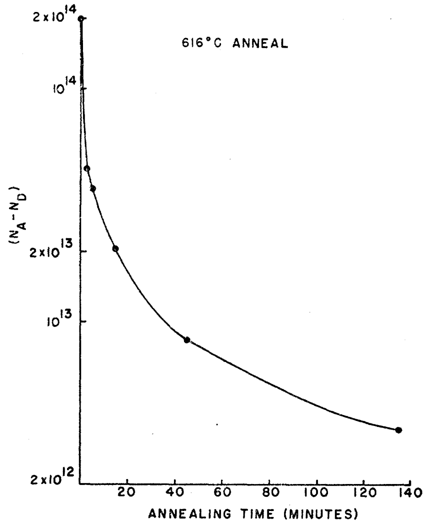

FIG. 4. The concentration of acceptors, $N_A - N_D$, as a function of annealing time at a temperature 616°C. The initial concentration of acceptors was 2×10^{14}/cc. Notice the extremely fast initial drop in acceptor concentration.

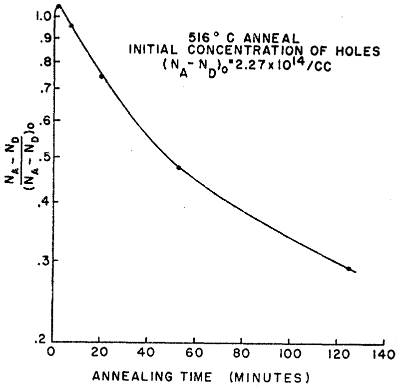

FIG. 5. The relative concentration of acceptors $(N_A - N_D)/(N_A - N_D)_0$ as a function of annealing time at a temperature of 516°C. For convenience, the concentration has been normalized to one at the start of the annealing process ($t=0$). Note the initial increase in acceptor concentration in the first minute of the annealing process.

IV. COMPARISON OF EXPERIMENTAL RESULTS WITH THEORY

In Fig. 4, a typical annealing curve taken at 616°C is presented. We have plotted as a function of time the net number of holes, which is equal to the number of ionized acceptor centers, N_A, minus the number of ionized donor centers N_D. The data are plotted on the semilog scale.

Notice the extremely fast drop in concentration at the beginning of the annealing process. In the first 2.5 minutes, the concentration of holes has decreased by a factor of more than 4. These data, which are representative of many such annealing curves, cannot be represented by Eq. (3) which describes the simple diffusion mechanism. If they were representable by Eq. (3), Fig. 4 would be a straight line. Rather, Eq. (4) gives a far better description of Fig. 4. For let $A \gg A_f$. Then Eq. (4) becomes

$$d\ln A/dt = -A/\bar{\tau}N,$$

and we see immediately that $-d\ln A/dt$ is large when A is large and is small when A is small, in agreement with Fig. 4. It therefore seems highly plausible that the heat treatments have introduced comparable numbers of vacancies and interstitials into the germanium (in other words, Frenkel defects).

A strikingly different annealing behavior is obtained if the annealing temperature is lowered to 516°C or below. Instead of the fast drop in the hole concentration as typified by Fig. 4, there is a rise in hole concentration and then a drop. Data taken at 516°C, 490°C, 447°C, and 402°C are typical of this stage of the annealing process and are presented in Figs. 5 and 6. A possible mechanism to explain the difference in anneal ing behavior above and below 516°C can be found in Cottrell's ideas concerning the strain energy interaction

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[15] A. W. Overhauser, Phys. Rev. **90**, 393 (1953); R. C. Fletcher and W. L. Brown, Phys. Rev. **92**, 585 (1953).

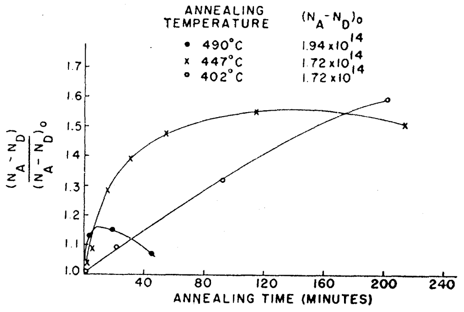

FIG. 6. The relative acceptor concentration $(N_A-N_D)/(N_A-N_D)_0$ as a function of annealing time at 490°C, 447°C, and 402°C. Note that the acceptor concentration increases before it decreases and that the maximum occurs earlier the higher the temperature.

between impurity atoms and dislocations.[16] The Cottrell argument depends on the fact that the impurity atoms strain the lattice in their neighborhood. The region around an edge dislocation is one of both lattice expansion and lattice contraction. Therefore, the dislocation will act as an attractive center for any atom which strains the lattice. The interaction energy between the impurities and the dislocation varies inversely with distance and has been estimated to be of the order of tenths of electron volts.[16] This interaction has no clear cut range but can be felt over large regions of the crystal depending on the temperature. According to the Cottrell model, a critical temperature occurs which is essentially the temperature at which kT becomes comparable to the elastic strain energy, u, of interaction between the impurity atoms and the dislocation. Below this critical temperature the impurity atoms form a condensed atmosphere around the dislocation with a distribution of concentration, C, according to the equation

$$C=C_0e^{u/kT}.$$

Above the critical temperature the impurity atoms are little influenced by the strain attraction u and therefore they are free to move throughout the crystal lattice. The dislocation is freed of its atmosphere, and far less force is required to move it.

Cottrell's ideas have been applied to the problem of impurities in germanium by Kurtz and Kulin[17] at the Lincoln Laboratory. They have focused their interest on the interaction between the dislocations in germanium and impurity atoms such as copper in order to explain phenomena similar to that originally found by Theuerer and Scaff[18] who reported that copper acceptors could be annealed out of germanium at 500°C or below while above that temperature the copper atoms remained as acceptors.

Plastic deformation in germanium is found to be critically dependent on temperature.[19] Deformation does not become important until 500°C. Seitz[20] has discussed these experiments and suggests that the Cottrell type of mechanism must be used in order to make a start toward explaining the experiments.

In order to have Cottrell's mechanism operative for a lattice defect rather than an impurity atom, all that is required is that the defect create a region of strain in the lattice surrounding it. And once such a region of strain is created there automatically will be an attractive force between the defect and the dislocation. However, this attractive force which arises from the strain energy, u, is only operative if we are below some critical temperature T_c such that u is greater than kT_c. Our annealing experiments display such a critical temperature, and our results can be explained by assuming that below this critical temperature the dislocations are able to trap interstitial germanium atoms before the interstitials have been able to make sufficient jumps to alter appreciably the concentration of vacancies. It is reasonable to expect that the dislocations prefer to trap interstitials than vacancies because in general the strain introduced in the lattice by an interstitial is larger than that produced by a vacancy and hence u will be larger for interstitials than vacancies.[21] Also, since we notice that the acceptor concentration increases in these low-temperature annealing experiments, we expect that the donor, not the acceptor, is leaving the bulk of the material.

In this connection, it is important to realize that the accumulation of the interstitials at the dislocations does not mean an annihilation of the interstitials.

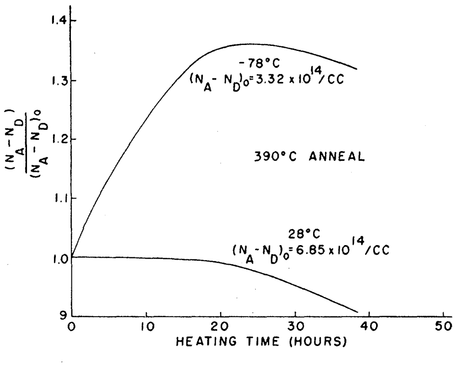

FIG. 7. The relative acceptor concentration measured both at −78°C and at 28°C as a function of annealing time at 390°C. Notice that the acceptor concentration at room temperature does not increase as does the acceptor concentration measured at dry ice temperatures. However, after 20 hours of annealing both curves show a decrease in concentration.

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[16] For a general discussion and other references see A. H. Cottrell, *Dislocations and Plastic Flow in Crystals* (Oxford University Press, London, 1953), p. 134.

[17] A. D. Kurtz and S. A. Kulin, Acta Metallurgica **2**, 354 (1954).

[18] H. C. Theuerer and J. H. Scaff, J. Metals **189**, 59 (1951).

[19] G. J. Gallagher, Phys. Rev. **88**, 721 (1952).

[20] F. Seitz, Phys. Rev. **88**, 722 (1952).

[21] G. J. Dienes, Phys. Rev. **86**, 228 (1952), has shown that in copper the interstitial copper atom strains the lattice and contributes far more toward increasing the elastic constants than the vacancies.

In Fig. 7 we have compared annealing curves similar to those shown in Fig. 6, where we have measured the change in acceptor concentration at room temperature as well as at dry ice temperature. The interesting result from this experiment is that very little change in the room temperature concentration occurs while the interstitials are moving toward the dislocations. Thus the room temperature concentration stays initially constant while the dry ice concentration increases by a considerable amount. Not until we reach the maximum in the dry ice concentration curve do we see any appreciable decrease in the room temperature concentration curve.

These data must mean that in moving to the dislocations the interstitials do not annihilate any vacancies, as otherwise we could expect a change in the room temperature concentration. Therefore the difference between the room temperature and dry ice concentrations must arise from changes in electrical properties of interstitials clustered around dislocations, such changes being detectable at dry ice temperatures but not at room temperature. When we reach the peak in the dry ice concentration curve, we have reached the point where the vacancies are beginning to diffuse out of the bulk toward the dislocations. In the process, some of these vacancies will begin to recombine with the interstitials which are congregated around the dislocations. The recombination involves a direct annihilation of the acceptor center and the donor center. We therefore reasonably may expect that both the dry ice concentration and the room temperature concentration should decrease at this stage of the annealing process.

V. THE CRITICAL EXPERIMENT

In order to test the idea of interstitials segregating at dislocations, we performed the following experiment. The sample had quenched in it an original concentration of about 1.7×10^{14} acceptors per cc. It was then annealed for several days at 370°C. The concentration of acceptors at dry ice temperatures was thereby increased to 4.1×10^{14} acceptors per cc. The sample was then annealed at 585°C and the annealing curve is shown in Fig. 8. For comparison, in Fig. 8 we show an annealing curve taken at the same temperature with an initial concentration of quenched in acceptors of 1.8×10^{14}. As we readily see from Fig. 8, within the first minute of annealing the interstitials have been evaporated back into the bulk of the material from the dislocations. Thereafter, the annealing curve obtained is essentially the same as the annealing curve obtained with no anneal at 370°C. The fact that the first annealing curve lies below the second at long times can be explained because the starting point was slightly lower and because, even during the 370°C anneal, a few of the vacancies were annihilated by the interstitials. If the dislocations were not acting as storage places for interstitials, but rather as a place for the annihilation of the interstitial, the nature of the annealing curves with and without the 370°C anneal would have been entirely different.

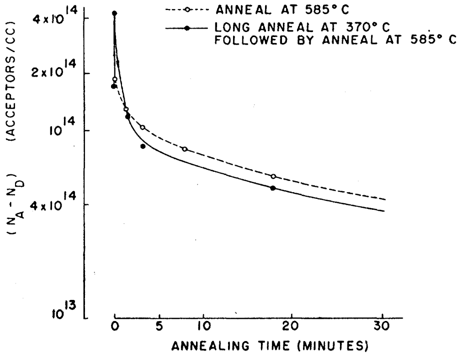

FIG. 8. The acceptor concentration as a function of annealing time at 585°C. The solid curve represents a treatment in which the sample was annealed at 370°C before being annealed at 585°C. The dashed curve represents an anneal in which the sample received no previous treatment after the initial non-equilibrium number of acceptors were quenched in. Notice that, after the early stages of annealing, the two annealing curves have the same essential features.

VI. CONCLUSIONS

In the foregoing discussion we have established certain qualitative conclusions about the nature of the defects produced in germanium by heat treatment.

1. The defects are most likely Frenkel defects, i.e., equal numbers of vacancies and interstitials.
2. Below a temperature of 516°C, the dislocations begin to preferentially trap the interstitials before the interstitials are annihilated by direct recombination with vacancies. Above 516°C, the direct recombination of interstitials with vacancies determines the annealing behavior.
3. Up to 585°C, the interstitials are more mobile than the vacancies. Above 585°C, we have no data to show which defect is more mobile.

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