

Thermally Induced Acceptors in Germanium

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When germanium is rapidly quenched from high temperature, acceptor centers are formed uniformly throughout the crystal. These centers have an energy of formation of about 2 ev. Each center is thought to contribute two acceptors, one near the valence band and one near the center of the gap. Experiments are described which indicate that these centers are either vacant lattice sites or a heretofore unidentified chemical impurity with radius smaller than that of germanium. Annealing has been studied in the temperature range 250°C–450°C. The annealing process is shown to depend markedly on both the density of dislocations and the concentration of copper. It has not been possible to ascribe a consistent physical model to conform with the observed characteristics of the annealing process.

INTRODUCTION

WHEN germanium is heated to high temperature the electrical properties become susceptible to change caused by chemical impurities¹ which readily enter the crystal by solid phase diffusion, dislocations² associated with plastic deformation, and vacancies or interstitial atoms³ which may be “frozen” into the crystal by quenching rapidly.

A heating system has been designed to minimize effects caused by chemical impurities and dislocations in hope of studying only vacancies or interstitial atoms or both. In some early studies⁴ of this effect, it was shown that, when germanium was quenched from an elevated temperature in a time of about 0.1 second, acceptor centers were introduced uniformly throughout the crystal. The present work is an investigation of the formation and annealing of these centers. The interaction of the centers with dislocations and with copper and tin impurity atoms has also been studied.

Another study of quenching of germanium has been reported by Mayburg,⁵ who quenched samples by radiation cooling. The cooling rate was considerably slower than that reported here and, in fact, was slow enough that the centers discussed here would have largely annealed during cooling.* Since Mayburg's measured acceptor density was larger by a factor of about 5, it appears that he is observing a different type of acceptor.

¹ See, for example, Fuller, Struthers, Ditzenberger, and Wolfstirn, *Phys. Rev.* **93**, 1182 (1954).

² Pearson, Read, and Morin, *Phys. Rev.* **93**, 666 (1954); R. A. Logan and M. Schwartz, *Phys. Rev.* **95**, 46 (1954).

³ Lark-Horovitz, Bleuler, Davis, and Tendam, *Phys. Rev.* **73**, 1256 (1948).

⁴ R. A. Logan, *Phys. Rev.* **91**, 757 (1953).

⁵ S. Mayburg, *Phys. Rev.* **95**, 38 (1954).

* *Note added in proof.*—This comment also applies to the experiment of Hopkins and Clarke [*Phys. Rev.* **100**, 1786 (1955)], who repeated Mayburg's experiment (with radiation cooling) but took extra precautions to keep impurities out. They observed a lower density of quenched-in acceptors than that reported here. This is to be expected from their considerably slower quenching rate and the annealing data to be presented here. It does not indicate that the present results are due to impurities.

APPARATUS AND PROCEDURE

Samples of germanium were heated and quenched using a furnace similar to that previously described.⁴ The furnace consisted basically of a vertical graphite tube heated by rf induction. This tube was contained in a quartz tube which served to insulate the carbon from the rf coil and to contain an inert gaseous ambient (helium or nitrogen). The sample was placed in the carbon tube by means of an opening supplied by a quartz ball and socket joint located directly over the furnace region, and was prevented from sliding through the carbon tube by means of a molybdenum platform which was inserted in a slot in the quartz and carbon tubes. Quenching was accomplished by removing the molybdenum platform so that the sample fell into an ethylene glycol bath about 1 inch below. The sample was protected from shock on hitting the bottom of the ethylene glycol bath by means of a glass wool pad. Castor oil was also used as a quenching fluid, but it was found to be not as effective in cooling the sample as the glycol. This is thought to be due to the mixing caused by the boiling of the glycol in the vicinity of the hot sample.

The samples of germanium used in these experiments were in the form of rods of dimension 0.060 in.×0.1 in.×1 in. The rods were cleaned⁴ and carefully inserted into the furnace through the opening provided by the ball and socket joint. The rods were then heated as follows: The sample was heated in about 1 minute to the temperature T , from which it was to be quenched, and maintained at that temperature for 1 minute. The sample was then either quenched by removing the molybdenum platform or cooled slowly by shutting off the rf power. In quenching it is estimated by considerations of heat conduction that the sample cooled to near room temperature in about 0.1 second. In slow cooling, the sample reached 500°C in about 15 seconds and room temperature in about 2 minutes.

The resistivity of the sample was measured before and after the heating process by the two-point probe technique. These measurements were generally performed at room temperature, but some were also made at dry ice temperature. In both cases, the change in

acceptor concentration was calculated from the resistivity change.

It is, of course, essential to the experiment that control samples can be heated to the temperature from which they are quenched, and cooled slowly without any significant change in room temperature resistivity. This can sometimes be accomplished in a furnace of this kind, without any special cleansing of the components. However, usually the furnace contains extraneous volatile chemicals that contaminate the specimen. To eliminate these, the following cleansing procedures were used:

(1) The quartz tube was soaked in concentrated hydrofluoric acid (48% HF), rinsed in de-ionized water and fire polished to the softening point in an oxygen-hydrogen flame.

(2) The molybdenum platform was degreased with solvents, soaked in concentrated hydrochloric acid (37% HCl), rinsed in de-ionized water, soaked in an aqueous KCN solution, and finally rinsed in de-ionized water.

(3) The carbon tube was heated for 25 minutes at about 1800°C in a vacuum of about 10^{-5} mm Hg to evaporate out the impurities which it contained.

RESULTS

A. Temperature Dependence of the Quenched Centers

Samples of germanium of various resistivities were heated to various temperatures and quenched as described above. After quenching, the change in density of filled acceptors was deduced from the change in room temperature resistivity. If these concentrations were determined from resistivity measurements at dry ice temperature, the concentrations in *n*-type samples were raised by about 20%, and those in the *p*-type samples were lowered by the same percentage. These results are consistent with Hall effect measurements by F. Morin that will be discussed below. Either measurement is a consistent approximation to the actual concentration of centers. For convenience, all measurements were subsequently made at room temperature.

The added acceptors due to quenching were found to be uniformly distributed throughout the samples. In Fig. 1 the logarithm of the increase in acceptor density is plotted *versus* the reciprocal of the temperature of quench. In the limit of $T \rightarrow \infty$, the curves have been made to pass through the value 1.3×10^{24} per cc as computed theoretically.⁶ The energy for formation of a center is calculated from the slope to be about 2 ev.

⁶ The coefficient of the exponential changes with temperature due to entropy effects which may be calculated [see C. Zener in *Imperfections in Nearly Perfect Crystals* (John Wiley and Sons, Inc., New York, 1952), p. 289]. These calculations for germanium were made as in reference 1 using the temperature dependence of the modulus of rigidity measured by Bond, Mason, McSkimin, Olsen, and Teal, *Phys. Rev.* **78**, 176 (1950); H. J. McSkimin, *J. Appl. Phys.* **24**, 988 (1953); and M. E. Fine, *J. Appl. Phys.* **24**, 388 (1953).

It is noted in Fig. 1 that the concentration of acceptors in *n*-type samples is about double that found in *p*-type samples quenched from the same temperature. This suggests that the quenched center has two electronic energy levels, one near the valence band and the other near the center of the energy gap. Further support was given to this explanation by the annealing data. It was found that, in a given time of annealing, the same percentage of acceptors annealed in both *n*- and *p*-type samples, which indicates that both acceptors were formed by the same defect. The annealing data will be discussed in more detail later. The Hall effect studies described in the following section are also consistent with this interpretation.

B. Studies of Hall Effect, Carrier Trapping and Lifetime in Quenched Samples

Samples of germanium were prepared in the form of the conventional bridges used in Hall effect studies. These bridges were heat treated in the same manner as the samples described above. Hall effect studies were then made on these bridges by F. J. Morin. In the *p*-type quenched samples, the only acceptors found (in addition to the ordinary group III acceptors) had an activation energy 0.04 ev above the valence band and were indistinguishable from copper.

However, a new acceptor with activation energy 0.1 to 0.2 ev below the conduction band was observed in a quenched *n*-type sample. The temperature dependence of the carrier concentration in this sample is shown in Fig. 2. For comparison, similar data are shown for a control sample which was heated but not quenched;

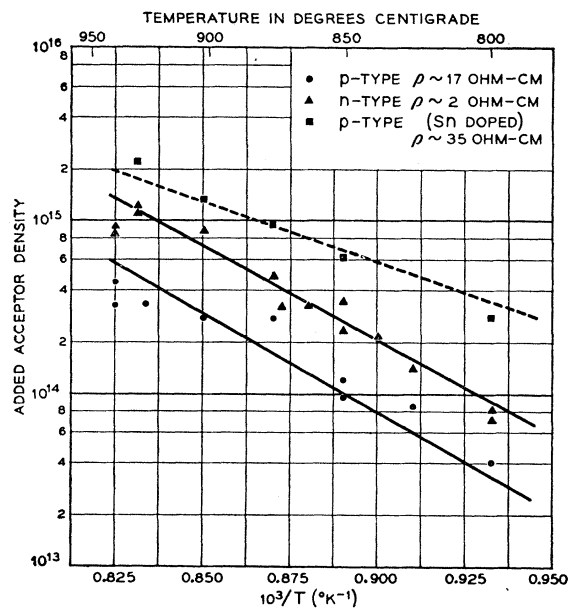


Fig. 1. The temperature dependence of the acceptor concentration in quenched germanium samples. The dashed curve was obtained with samples which contained 6×10^{19} atoms of tin per cc.

the heat treatment did not introduce any detectable change in impurity concentration. It is seen that the acceptors introduced on quenching become ionized at 150 to 250°K. At this temperature the Fermi level is in the range 0.1 to 0.2 ev below the conduction band, indicating that this is also near the position of the acceptor energy level. However, it is not possible to fit the data in this region by using an acceptor of a single activation energy.

It is evident in Fig. 2 that the number of filled acceptors introduced on quenching (the difference between the two curves) is about 20% greater at dry ice temperature than at room temperature. This is in agreement with the resistivity measurements described above.

Shulman has examined quenched *n*-type bridges to observe the effects of trapping of conducting holes.⁷ The quenched centers did not act as hole traps; the only trapping observed was due to copper. For example, in the above bridge which contained about 10^{15} quenched acceptors per cc, Shulman identified a copper concentration of 5×10^{13} cm⁻³. This is in good agreement with other measurements of the level of copper contamination in control samples heated in the quenching apparatus at that time.

Measurement of the lifetime of minority carriers by the Haynes and Hornbeck⁸ photodecay technique indicate that recombination centers are introduced into the sample by quenching. For example, quenching from 850°C reduced the lifetime in typical sample rods from the initial value of 150 μsec to about 15 μsec. In the control rods the heat treatment without quenching reduced the lifetime to about 70 μsec.

C. Quench of Tin-Doped Crystals

Interesting results which help to clarify the nature of the quenched centers were obtained using specimens of single-crystal germanium doped with 6×10^{19} tin atoms per cc. Since tin is a group IV element and forms an electrically neutral impurity in germanium,⁹ it would be expected that the atoms of tin in solid solution in germanium would be in substitutional positions. However, the tetravalent radius of a tin atom is about 20% larger than the germanium atom; so some stress is exerted by the tin atom on the adjacent germanium atoms. At elevated temperature this strain could be reduced by inserting either a small impurity or vacancy adjacent to the tin atom. The observed increase in acceptor density produced on quenching tin doped crystals is shown in Fig. 1 (dashed curve) and is taken as evidence that the quenched centers are formed adjacent to tin atoms. As before, in the limit of $T \rightarrow \infty$, the curve has been made to pass through the computed⁶ value 5.6×10^{20} per cc. The slope indicates that the

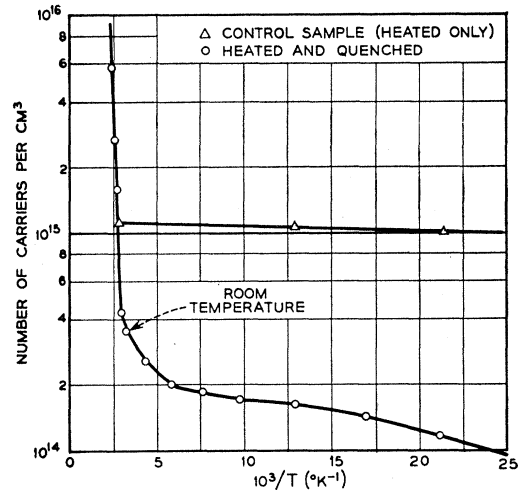


Fig. 2. The temperature dependence of the carrier concentration in *n*-type germanium which has been heated to about 900°C and quenched. The control sample was also heated to 900° but cooled to 500° in about 15 seconds, to room temperature in about 2 minutes. At lower temperature both curves approach the slope characteristic of the donor impurity atoms ($E=0.0115$ ev).

energy of formation of the center adjacent to a tin atom is 1.3 ev. The acceptor density in the tin-doped crystals is about five times as large as in pure samples. This implies that the quenched-in center is either a vacancy or a small chemical impurity, heretofore unidentified.

D. Annealing of the Quenched-In Centers

The annealing in air of the quenched-in centers was studied over a temperature range from 250°C to 450°C. The usual procedures were used to avoid extraneous chemical contamination.⁴ The furnace consisted of a cleaned quartz test tube immersed in a lead-tin bath. The cleaned sample was dropped into the tube at the beginning of the anneal. At the end of the anneal the test tube was removed from the lead-tin bath and quenched in water. Annealing times were thus determined to within a few seconds and the temperature of the lead-tin bath was maintained within 1% of the nominal value of the anneal temperature.

Resistivity was measured at room temperature using the 2-point probe technique. The change in acceptor density was calculated from the measured resistivity change. The annealing data is presented in Fig. 3 where the percent of quenched-in acceptors that remain in the quenched sample is plotted against the time of annealing at various anneal temperatures. The solid curves in Fig. 3 were obtained with samples which contained about 10^{14} quenched-in acceptors per cc. The *p*-type samples were all cut from the sample crystal; the *n*-type samples, except those annealed at 400°C, were also cut from a single crystal. These samples were heated in helium and quenched from about 850°C in castor oil. Each sample was annealed

⁷ R. G. Shulman, Phys. Rev. (to be published).

⁸ J. R. Haynes and J. A. Hornbeck, Phys. Rev. **90**, 152 (1953).

⁹ F. A. Trumbore, private communication.

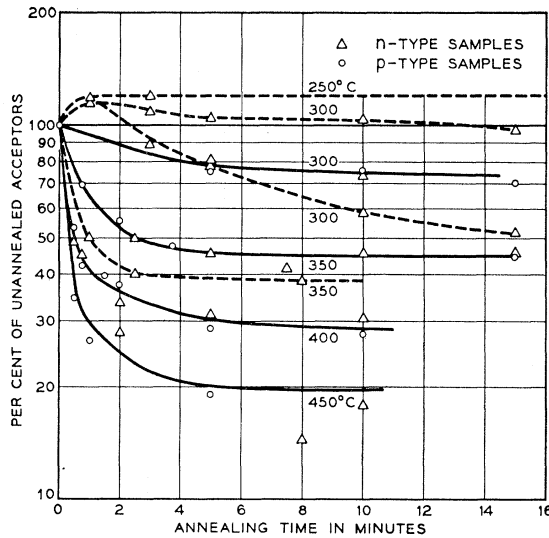


FIG. 3. The percent of quenched-in acceptors that remain in the sample plotted against the time of annealing for various temperatures of annealing. The solid curves were obtained with samples which had $\sim 10^{14}/\text{cc}$ quenched-in acceptors whereas the dashed curves were obtained with samples having $\sim 10^{15}/\text{cc}$ quenched-in acceptors.

for only one period of time so that each experimental point is obtained with a different quenched sample. Since the measured changes in concentration were small, this was done to eliminate cumulative effects and errors. The dashed curves in Fig. 3 were obtained with samples which contained about 10^{15} quenched-in acceptors per cc. These samples were heated in nitrogen and quenched from about 900°C in ethylene glycol, which is a more effective quenching fluid than the castor oil. For these samples a whole annealing curve is obtained from a single sample. This was found to introduce no extraneous effects since a sample which was heated for a given interval of time was found to anneal to the same extent as a sample which was annealed in a series of short intervals for the same total time.

The data presented in Fig. 3 for the samples with $\sim 10^{15}/\text{cc}$ quenched-in acceptors agrees at the higher temperatures (350°C) with that obtained with the samples containing only $\sim 10^{14}/\text{cc}$ quenched-in acceptors. Similar results were also obtained using samples from the tin-doped crystals. At lower temperatures, however, the results indicate that even more acceptors are "annealed" into the crystal than the concentration initially quenched-in. This effect, although not understood, is similar to that observed by Mayburg.⁵

At a given temperature, the rate of annealing decreases markedly after a fast initial rate. For example, samples containing $\sim 10^{14}$ quenched-in acceptors per cc annealed to the same extent in 60 minutes at 300°C as those heated only 10 minutes at this temperature. Other samples which contained $\sim 10^{15}$ quenched-in

acceptors per cc retained 30% of these acceptors after heating for 22 hours at 350°C compared to the plateau at 40% reached in a few minutes by similar samples, as shown in Fig. 3.

After annealing for a long time at low temperature (300°C or 350°C), further annealing occurs if the samples are heated at higher temperature (400°C or 450°C). These samples annealed to the same extent as control samples which had not been previously annealed at the lower temperature. In the experiments where samples were annealed at 350°C and then at 400°C , the results were not changed if the samples were heated slowly ($\sim 1^\circ$ per minute) in going from 350°C to 400°C .

In estimating the precision of the annealing data, several factors have to be considered:

(1) The copper concentration in the heated samples as deduced from measurements on control samples was always at least an order of magnitude smaller than quenched-in acceptor densities. For example, when $10^{14}/\text{cc}$ quenched-in acceptors were observed, $10^{13}/\text{cc}$ of these may possibly be due to copper and no corrections were applied for this.

(2) The percentage error ascribed to the resistivity measurements is about $\pm 5\%$ so that for most measurements the room temperature concentration of filled acceptors is uncertain by about $2 \times 10^{13}/\text{cc}$. Hence the precision in the annealing data is poor at the high temperatures (as is evidenced, for example, by the scatter in the experimental points obtained when annealing at 450°C).

(3) The concentration of quenched-in centers was deduced from room temperature resistivity measurements. As shown in Fig. 2, this estimate is about 25% too low. Such a discrepancy should not greatly affect a qualitative study of the anneal process.

E. Effect of Dislocations and of Copper

It was not possible to quench acceptors into samples in which about 10^6 dislocations/ cm^2 had been introduced

TABLE I. The effect of copper on the anneal process.^a

Sample number	Initial value				
	ρ (ohm-cm)	$ N_D - N_A /\text{cc}$	ΔC_u	Δ_{quench}	Δ_{anneal}
N-type samples from crystal GeII-1073					
1	5.32	3.3×10^{14}	1.13×10^{14}	1.76×10^{14}	1×10^{13}
2	8.35	2.1×10^{14}	1.28×10^{14}	$\sim 10^{14}$	1×10^{13}
3	5.63	3.1×10^{14}	(controls)	2.1×10^{14}	1.07×10^{14}
4	4.83	3.54×10^{14}		1.75×10^{14}	1.15×10^{14}
P-type samples from crystal GeVIII-528					
5	13.55	2.8×10^{14}	0.65×10^{14}	1.75×10^{14}	4×10^{13}
6	13.65	2.8×10^{14}	0.5×10^{14}	2.1×10^{14}	4.5×10^{13}
7	10.44	3.6×10^{14}	(controls)	1.6×10^{14}	6×10^{13}
8	11.86	3.2×10^{14}		1.7×10^{14}	9×10^{13}

^a ΔC_u is the concentration per cc of copper added by heating the samples at 550°C in the presence of copper. Δ_{quench} is the concentration per cc of acceptors added by quenching the samples from 850°C . Δ_{anneal} is the concentration per cc of acceptors removed by annealing the samples for 5 minutes at 400°C .

by plastic deformation at high temperature. Apparently the dislocations so increase the rate of annealing that the centers anneal during the quench. In addition, copper markedly affects the process of annealing. About 10^{14} copper atoms per cc (added by diffusion at 550°C) had no effect on the quenched-in acceptor concentration, which was also about 10^{14} per cc. However, the copper-doped samples annealed to a lesser extent than control specimens, as is shown in Table I.

DISCUSSION AND CONCLUSIONS

Germanium samples have been heated and rapidly quenched under conditions where the thermal treatment introduces negligible effects due to chemical impurities and plastic deformation. Rapid quenching introduces acceptor centers with two energy levels, one near the valence band and the other near the center of gap. The enhanced effects obtained on quenching samples heavily doped with tin are taken as evidence that the quenched-in center is either a vacancy or an impurity with smaller radius than a substituted germanium atom.

The annealing of the centers has been studied in the temperature range 250°C – 450°C . The low temperature at which annealing occurs indicates a low activation energy for the annihilation of the quenched-in centers. After the fast initial rate at a given temperature, the annealing progresses very slowly. This slow rate can be increased by heating the sample at a higher temperature than that at which it has been previously annealed. At the high temperatures from which the samples are quenched, the rate of annealing is markedly increased in the presence of high dislocation density. At lower temperatures, the extent of annealing decreases with increased copper concentration in the sample. These interactions of the centers with dislocations and copper make the data both difficult to obtain consistently and to interpret. Although the observed characteristics of the centers does not permit an unambiguous identification or detailed understanding of the process of formation and anneal, certain possible explanations can be excluded.

The simple processes of annealing can be shown to be incompatible with the observed characteristics of the annealing. Two such processes are as follows:

(1) The temperature dependence of the rate of anneal may be expressed in terms of an activation energy or a spectrum of activation energies.

(2) The centers may anneal by interacting with another species or compete with another species for the sites at which they are annihilated.

The observations described above rule out these mechanisms by using the following arguments:

(1) Some of the centers that do not anneal in 22 hours at 350°C anneal in about 100 seconds at 400°C . If this is a thermally activated process, then the activation energy is 5 eV, or the jump time is 10^{24} seconds at 400°C . Thus the centers could not possibly anneal in 100 seconds at 400°C by a thermally activated process.

(2) If the centers anneal by interacting with another species or compete with another species for the sites where they anneal, then as the species or anneal sites are used up at each temperature of annealing, the rate of annealing will decrease with time. Such a model is consistent with many of the observations but is contradicted by some of the data. For example, after annealing a quenched sample for a long time so that the anneal rate becomes very small, further annealing at high temperature should not annihilate centers, since according to this model the competing species or the anneal sites are used up. However, as described above, samples did anneal further at 400°C after being annealed for a long time at 300 or 350°C .

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