just gp_1. This is shown schematically in the right hand position of Fig. 5. It was necessary to make this correction only at the highest temperature (62°C) at which the cross section of the β traps was measured.

For the α traps, it is not necessary to measure l and r independently in order to obtain S, for their ratio can be obtained directly from the oscillogram, Fig. 1, as described in the text.

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Precipitation of Copper in Germanium

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The density of dislocations is shown to have a marked effect on the rate of anneal of copper in germanium. At 500°C samples containing high dislocation density ($\sim 10^6$/cm^2) anneal in about 1 hour in contrast to material of low dislocation density ($\sim 10^4$/cm^2) which requires about 24 hours. When copper-doped germanium is cooled from a high temperature in regions of high dislocation density, significant precipitation occurs in a cooling cycle of only a few seconds. In this case, in order to prevent precipitation the sample must be quenched from the high temperature in a time of the order of 0.1 second.

INTRODUCTION

WHEN germanium is heated to high temperature without precaution to prevent chemical contamination, impurities diffuse into the crystal. Copper has an appreciable solubility and high diffusivity in germanium[1] and is generally the principal contaminant in most heating procedures. Copper is an acceptor in germanium with an energy level[2] 0.04 ev above the valence band and a higher energy level[3] near the center of the energy gap.

When germanium is heated at a given temperature in the presence of copper at equilibrium, the concentration of the solid solution is characteristic of the temperature only. Except for the temperature range near the melting point where retrograde solubility occurs,[4] the solubility increases with increasing temperature. Hence except for retrograde solubility effects, as soon as the temperature is lowered from this equilibrium temperature, the copper solution immediately becomes supersaturated; and the copper concentration, as inferred from resistivity measurements, will drop from the high-temperature value to that characteristic of the lower temperature. A study[1] of this annealing process with techniques using radioactive copper showed that the copper precipitated at various places in the crystal. The extent to which this copper precipitates depends mainly on the cooling cycle and the density of nucleation sites.

In the experiments reported here, it is shown that precipitation of copper is extremely rapid in regions of the crystal of high dislocation density ($\sim 10^6$ dislocations/cm^2). In such samples significant precipitation occurs in a few seconds, and in order to prevent precipitation the sample must be quenched from the high temperature in a time of the order of 0.1 second. In addition, complete annealing at 500°C will occur in about 1 hour in contrast to a time of about 24 hours in material of low dislocation density ($\sim 10^4$ dislocations/cm^2).

In these experiments, dislocations associated with plastic deformation are introduced into germanium by bending at high temperature. The copper solubility in these samples, determined from resistivity measurements, shows a marked dependence on the density of dislocations. In regions of high dislocation density ($\sim 10^6$/cm^2), the density of acceptors due to copper is much lower than in regions of low dislocation density ($\sim 10^4$/cm^2). This phenomenon gives rise to an apparent decrease in copper solubility (as inferred from resistivity measurements) in regions of high dislocation density.

EXPERIMENTAL PROCEDURE

In these experiments, rods of dimension 0.06 in.×0.1 in.×1.0 in. were cut from a single crystal of germanium which had a room temperature resistivity of about 0.8 ohm-cm, n-type. The rods were bent about the (111) crystal axis, without introducing chemical contamination, by a method devised by Pearson.[5] This method consists of (1) cleaning the rod,[6] (2) clamping it between molybdenum electrodes, (3) heating it by the joule heat developed by passing current through the rod, and (4) deforming the rod by bending at a high temperature ($\sim$800°C). The bent rods were then dipped in an

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[1] Fuller, Struthers, Ditzenberger, and Wolfstirn, Phys. Rev. **93**, 1182 (1954).

[2] F. J. Morin and J. P. Maita, Phys. Rev. **90**, 337 (1953).

[3] Burton, Hull, Morin, and Severiens, J. Phys. Chem. **57**, 853 (1953).

[4] C. D. Thurmond and J. D. Struthers, J. Phys. Chem. **57**, 831 (1953).

[5] Pearson, Read, and Morin, Phys. Rev. **93**, 666 (1954).

[6] R. A. Logan, Phys. Rev. **91**, 757 (1953).

aqueous solution of $CuSO_4$ and heated for 5 minutes at 750°C to diffuse the copper into the crystal. At this temperature the diffusion constant of copper[1] is 2.8×10^{-5} cm^2/sec, and in 5 minutes copper will thus diffuse a mean distance of about 40 mils.

The rods were then cleaned and heated in a furnace designed to heat and quench germanium.[7] In this and subsequent heatings precautions were taken[6] so that no further chemical contamination was introduced into the samples. The heating cycle employed was as follows: The sample was heated to 900°C in 1 minute and was maintained at this temperature for 1 minute. The sample was then cooled by one of two possible cycles. In the first cycle the power to the furnace was simply shut off, and the sample cooled to 500°C in about 15 seconds and to room temperature in about 2 minutes. In the other cycle the sample was quenched by dropping it out of the furnace into a bath of ethylene glycol. In the quench, it is estimated by considerations of heat conduction that the sample cooled to near room temperature in about 0.1 second.

Two rods of germanium were bent to radii of curvature of 2.5 cm and 20 cm, introducing dislocation densities of about 10^7/cm^2 and 10^6/cm^2, respectively.[8] The rods were n-type with $N_D - N_A \sim 2 \times 10^{15}$/cm^3 so that acceptors associated with the added dislocations[5] would have a negligible effect on $N_D - N_A$. The rods were then cleaned[6] and heated to 900°C in the two-minute cycle as described above, followed by either a quench or a "slow" cool.

Resistivity measurements were then made along the length of the rod by the 2-point probe technique, using points separated by 0.010 in. Resistivity readings were recorded at steps of 0.0052 in., so that a resistivity profile of the rod was obtained. The resistivity type (n or p) was determined from the sign of the thermoelectric voltage (thermal probe technique).

RESULTS

The resistivity profile of the rod bent to $R = 2.5$ cm is shown in Fig. 1. Curve (a) shows the resistivity profile obtained after heating the rod to 900°C followed by a "slow" cool. Curve (b) shows the profile of the same rod obtained after quenching from 900°C.

It is evident that after quenching, the resistivity along the rod is nearly uniform, and the impurity concentration deduced from the resistivity measurements varies less than 15% from the mean value. However, in the case of the "slow" cool there is a marked resistivity variation along the length of the rod, and the associated impurity concentration varies by more than an order of magnitude. It will be shown in a subsequent paper that no acceptors associated with defects are introduced by the quench since the high dislocation density prevents the formation of these defects.

From the resistivity measurements the increase in acceptor density can be calculated.[9] In the region of maximum deformation more acceptors are found after quenching than after the "slow" cool. This effect is reversible in that heating to 900°C followed by either a quench or a "slow" cool will cause the acceptor density in the deformed region to cycle back and forth to the values characteristic of the quench and "slow" cool, respectively. This effect is presented in Fig. 2 where a plot is made of the added acceptor concentration measured after heat cycles which end with either a quench or "slow" cool. In this case, the room temperature resistivity was measured at the region of maximum deformation by the 2-point probe technique using points separated by 0.150 in.

Studies of low-temperature annealing at 500°C in plastically deformed germanium indicate that again the dislocation density has a marked influence on the rate of copper precipitation. Figure 3(a) shows the resistivity profile of the rod bent plastically to an $R = 20$ cm. This rod was heated 5 min at 750°C in the presence of copper and cooled to room temperature in about 1 minute. The rod had an initial resistivity of 0.8 ohm-cm, n-type, and after bending and introducing copper into the crystal, the crystal remained n-type in the region of the deformation. The ends of the rod which were held by the clamp type electrodes used to support the rod while bending remained cool and hence undeformed during the bending. In these regions of low dislocation density the rod converted to low resistivity, p-type.

This rod was annealed at 500°C in a nichrome furnace in an H_2 atmosphere. The heating was inter-

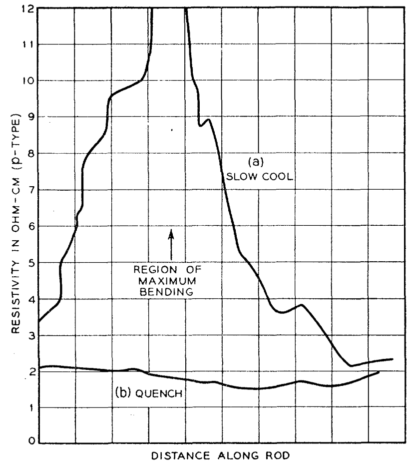

FIG. 1. Curve (a) is a plot of 2-point probe resistivity measurements along the copper doped bent rod ($R = 2.5$ cm) after heating to 900°C and "slow" cooling to 500°C in about 15 sec; to room temperature in about 2 min. Curve (b) shows 2-point probe resistivity measurements along the same rod after heating to 900°C and quenching in about 0.1 sec.

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[7] This furnace is very similar to that described in 6.

[8] W. T. Read, Jr., *Dislocations in Crystals* (McGraw Hill Book Company, Inc., New York, 1953), p. 38.

[9] M. B. Prince, Phys. Rev. **92**, 681 (1953).

rupted after 5, 20, and 60 minutes, and room temperature resistivity profiles were obtained. These are shown in Figs. 3(b), 3(c), and 3(d), respectively. Two features of this anneal are noteworthy. In the region of maximum dislocation density ($\sim 10^6/\text{cm}^2$), essentially complete anneal has occurred in about 1 hour, whereas in the undeformed region, little annealing has occurred in this time. Secondly, although it is not understood, it is evident that in the first few minutes of anneal, more acceptors are present in the deformed region than at the beginning of the anneal.

DISCUSSION AND CONCLUSIONS

The results presented above show that the rate of precipitation of copper in germanium is increased markedly in the presence of large dislocation density. Although the actual mechanism of precipitation was not ascertained, it seems reasonable that copper atoms become attached to dislocations and act as centers of nucleation for precipitation of other copper atoms. The rate of anneal would also be markedly increased if copper atoms diffused along dislocations much faster than they diffuse in the pure crystal.

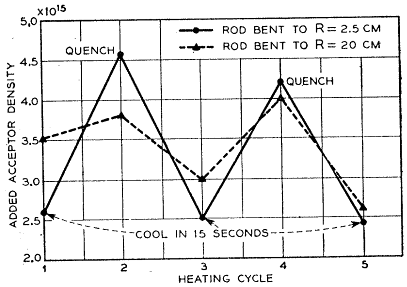
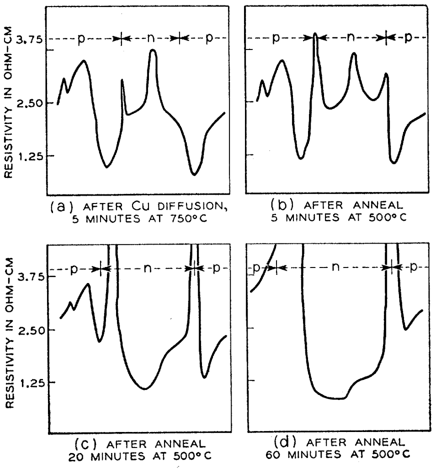


FIG. 2. The added acceptor concentration in the copper doped bent rods plotted after successive heat cycles as follows: 1, 3, and 5—heated to 900°C and cooled to 500°C in 15 sec; to room temperature in about 2 min. 2 and 4—heated to 900°C and quenched in about 0.1 sec.

These results suggest an explanation to some early experiments on annealing of copper in germanium. It was observed[10] that specimens obtained from multicrystalline cast ingots annealed much faster than specimens of equal resistivity obtained from single crystals grown by conventional crystal-pulling techniques. For example at 500°C about 20 hours was required to anneal the single-crystal specimens whereas specimens from the cast ingots would anneal to the same extent in about 1 hour. The multicrystalline ingot would be expected to contain high dislocation density due to the strains introduced on freezing. In addition, the imperfections associated with the grain boundaries in these ingots might also stimulate precipitation.



(a) AFTER Cu DIFFUSION, 5 MINUTES AT 750°C
(b) AFTER ANNEAL 5 MINUTES AT 500°C
(c) AFTER ANNEAL 20 MINUTES AT 500°C
(d) AFTER ANNEAL 60 MINUTES AT 500°C

FIG. 3. Resistivity profiles of the copper doped bent rod ($R = 20$ cm) showing stages of anneal at 500°C.

In the determination of copper solubility using resistivity measurements, a considerable variation in acceptor concentration is encountered from sample to sample at any given temperature.[1] It is quite reasonable to suppose that this variation may be largely due to precipitation during the cooling cycle. This point of view is supported by the results obtained with radioactive copper,[1] which measures the total amount of copper in the crystal, including that which precipitates as the crystal is cooled from the high temperature. Solubilities determined by radioactivity have been in general higher than those deduced from resistivity measurement.

As shown in Fig. 3, a copper-doped sample containing 10^6 dislocations/cm^2 annealed completely in about 1 hour at 500°C. However, in the first few minutes of the anneal the acceptor concentration actually increases before the rapid decrease due to precipitation became the dominant effect. This process, which is not understood, is very similar to that observed by Mayburg[11] in his studies of the annealing of quenched germanium at 500°C.

ACKNOWLEDGMENTS

I would like to thank Miss A. D. Mills who measured the resistivity profiles in the deformed samples. It is also a pleasure to acknowledge the many suggestions and informative discussions with W. T. Read, Jr. throughout the course of this work.

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[10] C. S. Fuller (private communication).

[11] S. Mayburg, Phys. Rev. **95**, 38 (1954).