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Recombination in Plastically Deformed Germanium

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Lifetimes in plastically deformed *n*- and *p*-type germanium have been measured as a function of the amount of deformation and as a function of temperature. The results indicate that the dislocations have an electron capture radius of 3.4×10^{-8} cm. The lifetime in high-purity crystals containing 10^3 to 10^4 dislocations per square centimeter may consequently be limited by recombination at dislocations.

INTRODUCTION

The effect of dislocations on the recombination of excess carriers has recently been studied from various points of view. Gallagher[1] and Pearson, Read, and Morin[2] found the lifetime in plastically deformed germanium containing 10^7 dislocations per square centimeter to be less than a microsecond. Vogel, Read, and Lovell[3] and Okada[4] have observed recombination at lineage boundaries. Okada[4] and Kurtz, Kulin and Averbach[5] have studied the lifetime as a function of the density of naturally occurring dislocations. The recombination efficiencies of the dislocations observed by the latter two differ by a factor of about 100. More recently Kurtz, Kulin, and Averbach[6] have presented evidence that the growth rate of the crystal may change the recombination efficiency by as much as a factor of 10, probably because of the tendency of impurities to segregate on dislocations. The electrical properties of dislocations have been discussed by Read[7] and experimental evidence has been presented by Pearson, Read, and Morin[2] and by Tweet[8] that dislocations may act as acceptors but not as donors.

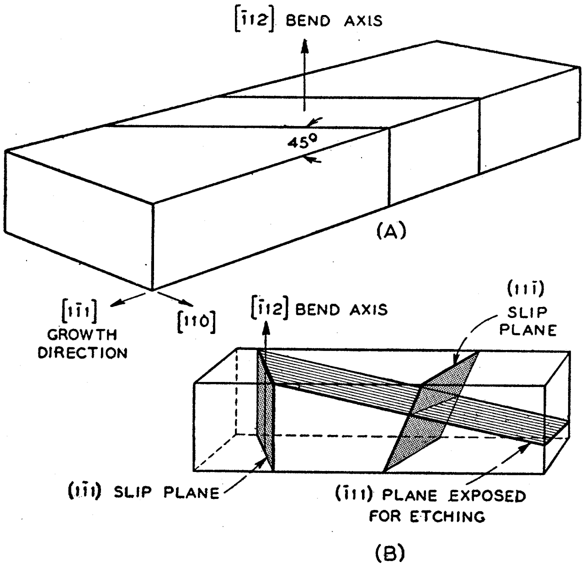

Fig. 1. Sample orientation.

Quantitative measurements of lifetime in plastically deformed material have not been feasible because the lifetimes encountered are usually less than a microsecond. If small deformations are used the effects of heating may be larger than those of the deformation. The recent development of the pulsed Van de Graaff method for lifetime measurement[9] facilitates the determination of lifetimes in the range from 10^{-8} to 10^{-6} second, and has made possible a study of recombination in plastically deformed semiconductors.

EXPERIMENTAL PROCEDURE

The crystal studied was 2.2 ohm-centimeter, indium-doped, *p*-type germanium having a bulk lifetime of 150 microseconds and an original dislocation density of 5×10^3 cm^{-2}. It was grown at a rate of 0.33 inch per hour. Limited data were taken on an 8.0 ohm-cm, antimony-doped, *n*-type crystal with comparable lifetime, and an original dislocation density of 8×10^3 cm^{-2}. It was grown at a rate of 1.0 inch per hour. Both crystals were grown in a $\langle111\rangle$ direction and rods were cut from the ingots to a size of 60 by 130 mils by 1 inch, at 45 degrees to the growth direction, as shown in Fig. 1. The rods were then cleaned in KCN solution and bent about a $\langle211\rangle$ axis in similarly cleaned germanium jaws while heated by a current passing through them according to the method of Vogel.[10] The deformation took place at a temperature of about 750°C. Examination of rods bent in this manner showed that there is a considerably higher density of dislocations on the surface of the bent rod than in the center, as has been shown by Vogel.[10] This effect was especially pronounced in slightly deformed samples. The uniformity of the dislocation densities could be improved by removing the outer, high-density layer with a chemical etch. In practice, samples were reduced to 30×100 mils with CP4.

Densities uniform within 50% could be obtained in

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[1] C. J. Gallagher, Phys. Rev. **88**, 821 (1952).
[2] Pearson, Read, and Morin, Phys. Rev. **93**, 666 (1954).
[3] Vogel, Read, and Lovell, Phys. Rev. **94**, 1791L (1954).
[4] J. Okada, J. Phys. Soc. Japan **10**, 1110 (1955).
[5] Kurtz, Kulin, and Averbach, Phys. Rev. **101**, 1285 (1956).
[6] Kurtz, Kulin, and Averbach, J. Appl. Phys. **27**, 1287 (1956).
[7] W. T. Read, Jr., Phil. Mag. **45**, 775 (1954).
[8] A. G. Tweet, Phys. Rev. **99**, 1245 (1955).
[9] G. K. Wertheim and W. M. Augustyniak, Rev. Sci. Instr. **27**, 1062 (1956).
[10] F. L. Vogel, Jr., J. Metals **8**, 946 (1956).

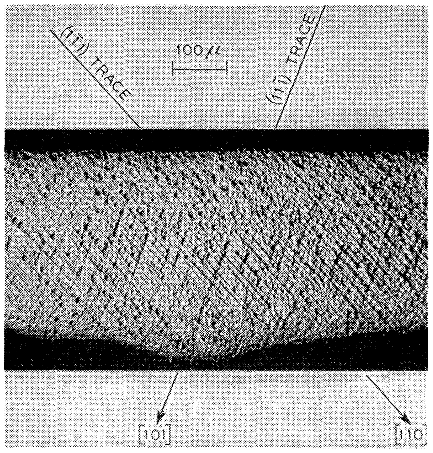

FIG. 2. Etch pits on $(\bar{1}11)$ plane of germanium rod bent to a radius of 7.5 cm about the $[\bar{1}12]$ axis.

this way for samples having a radius of curvature of 10 cm or less. The curvature was measured after bending but before etching by comparison of the sample with known curves and when necessary by an analytic method. The dislocation densities, N_d, were then obtained from the theoretical relationship between curvature and the dislocation density:

$$N_d = 1/(Rb\cos\theta), \tag{1}$$

where R is the radius of curvature in cm and b is the Burgers vector which is 4×10^{-8} cm in germanium. Where possible, etch-pit counts were also made. After the lifetime measurements had been completed, the crystal was ground to expose a $\{111\}$ plane, etched 90 seconds in CP4, and then photographed at 500 magnification. A number of 10^{-4}-cm^2 areas across the section of the crystals were counted. Figure 2 shows the appearance of a typical section of a crystal bent to a radius of 7.5 cm. The slip lines are within a few degrees of the directions expected for the orientation choosen. Good agreement between computed dislocation densities and etch-pit counts was usually obtained.

Decay times of bombardment-induced conductivity were obtained with the pulsed Van de Graaff technique.[9] Measurements were made in the temperature range from 150 to 400°K. The lower limit of measurement was 10^{-8} second. No bombardment-induced changes were observed in the samples in agreement with the low total electron flux (10^{12} cm^{-2}) used in these measurements.

RESULTS

In plastically deformed n- and p-type germanium the recombination of excess holes and electrons is thought to take place through the action of dislocation sites. It is known from the experiments of Pearson, Read, and Morin[2] and of Tweet[8] that dislocations are either neutral or partially negatively charged. Read[7] has shown that the fractional occupancy of a dislocation by electrons is limited by the Coulomb interaction of these electrons. The solution obtained by the latter is applicable in n-type material at room temperature.[11] When the occupancy is sufficiently low, Fermi statistics are used.

The available data on lifetime at room temperature in germanium as a function of dislocation density are given in Fig. 3. The measurements of Kurtz *et al.*[5] are based on the time required to decay to half-amplitude following optical excitation, and those of Okada[4] on measurement of the diffusion length. The present data represent the dominant time constant obtained from the analysis of the decay of bombardment conductivity. The data for the 2.2 ohm-cm p-type crystal include a point at a dislocation density of 5×10^3 cm^{-2} with a lifetime of 150 microseconds measured in the as-grown crystal. Over the range of dislocation density from 5×10^3 cm^{-2} of naturally occurring dislocations to 2×10^7 cm^{-2} introduced by plastic deformation, we find the lifetime inversely proportional to density.

p-Type

The recombination process in p-type material involves the initial capture of an excess electron by a neutral dislocation site and the subsequent annihilation with a hole from the valence band. Estimates may be made of the speed of these two processes. For electron capture, all sites are available even though only a small fraction can be occupied. For a dislocation density of 10^7 cm^{-2} and a capture time of 7×10^{-8} second (Fig. 3), one calculates a capture radius of 3.4×10^{-8} cm at room temperature [see Eq. (3)]. For 2×10^{15} holes/cm^3 and a cross section of 4×10^{-14} cm^2,[4] one obtains an annihilation time of 6×10^{-10} second. The observed decay should then consist of a single exponential having

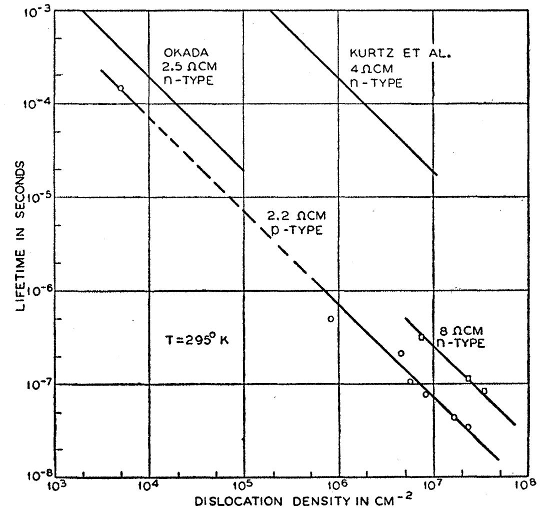

FIG. 3. Room-temperature lifetime in germanium containing known dislocation densities.

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[11] W. T. Read, Jr. (private communication).

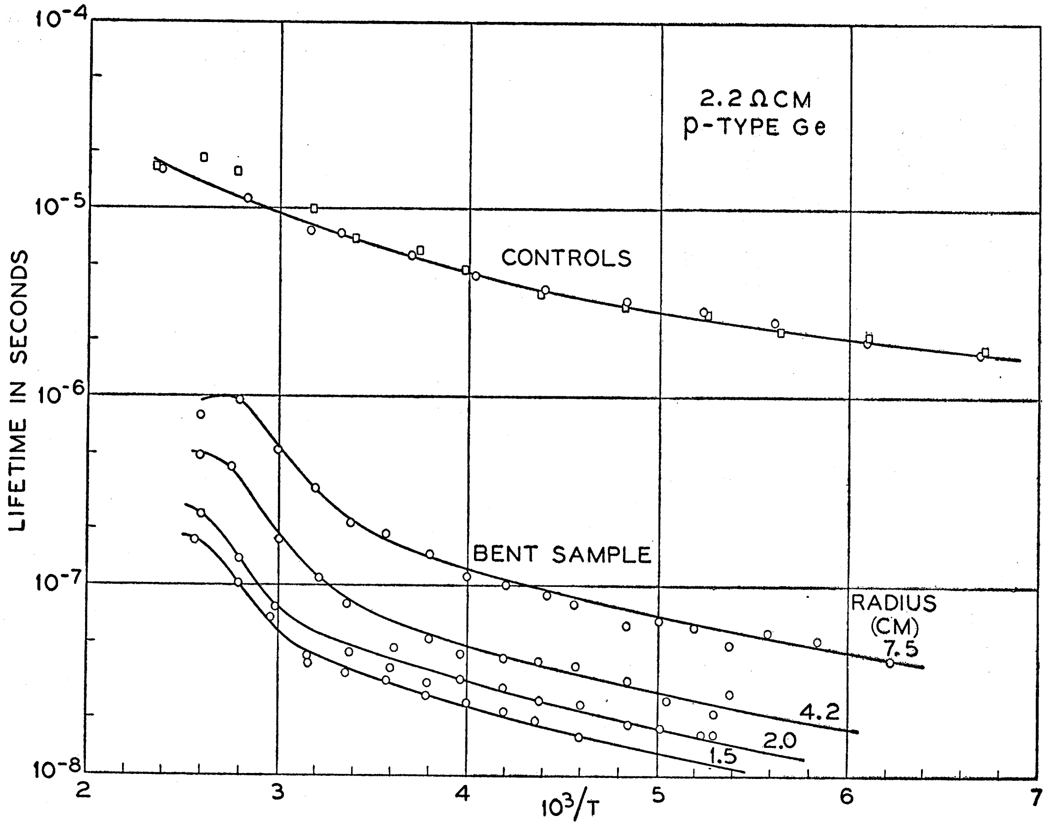

FIG. 4. Temperature dependence of lifetime in plastically deformed germanium.

the time constant of the slower process, i.e., electron capture, and no significant fraction of the injected carriers should accumulate on the dislocations.

The temperature dependence of the principal decay mode in four bent crystals and in two controls is given in Fig. 4. One control was cut and etched to size; the other was cut, heated, and etched. In general, some deterioration of the bulk lifetime would be expected in a heating cycle such as the one employed here. The two controls indicate, however, that the changes produced by bending are much greater than those of heating. The computed surface recombination velocity in a 30-mil rod with a lifetime of 8 microseconds is 4.8×10^3 cm/sec. This is somewhat higher than expected for a clean etched surface[12] but indicates that the lifetime in the controls is dominated by surface recombination.

The temperature dependence of the decay time in *p*-type germanium follows from the assumption that the dislocation energy level lies somewhat above the middle of the gap in accordance with the results of Pearson, Read, and Morin.[2] At low temperature the dislocation sites are all empty, so that the temperature dependence of the lifetime represents the change in the capture radius with temperature. As the temperature is raised toward the intrinsic range, the capture time increases because some dislocation sites are now normally occupied by electrons and are not available for electron capture.

The decrease in lifetime below $10^3/T=3.5$ is associated with a temperature dependence of the capture radius. The data in Fig. 4 are consistent with a lifetime of the form

$$\tau=KT^{2.5}. \tag{2}$$

The additional temperature dependence introduced by the thermal velocity in the equation

$$\rho(T)=\frac{1}{2N_d v(T)\tau(T)\sqrt{\frac{2}{3}}}, \tag{3}$$

results in a capture radius of the form

$$\rho=CT^{-3}. \tag{4}$$

In Fig. 5 the lifetimes of Fig. 4 have been multiplied by $T^{-2.5}$, resulting in a normalized lifetime constant below room temperature. This shows that the T^{-3} temperature dependence is followed accurately below room temperature.

The dependence above room temperature, Fig. 4, is

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[12] W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, New York, 1950), p. 324.

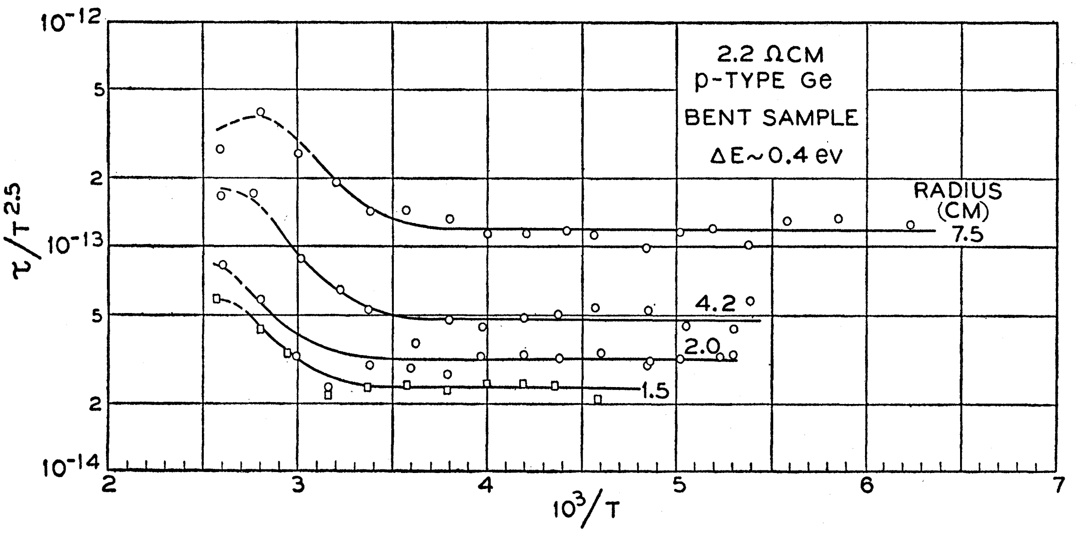

FIG. 5. Temperature dependence of the normalized lifetime.

consistent with an activation energy of about $\frac{1}{2}$ the energy gap. This is in agreement with other evidence[2] which indicates that the acceptor level of the dislocation lies slightly above the middle of the gap.

In highly bent specimens the decay consists of a single exponential from room temperature down to the lowest temperature at which measurements could be made. This is consistent with the theory outlined above. In less severely bent samples additional, longer components were also obtained. These had apparent time constants 6 times longer than the dominant one. These longer time constants dominate the decay in slightly deformed specimens.

It appears that the longer decay-time components are associated with inhomogeneities in the distribution of dislocations. This is consistent with the facts that (1) the longer components have the same temperature dependence as the dominant decay, (2) the longer components are more important in slightly deformed crystals where a low dislocation-density central region was observed, and (3) the decay time of the longer component is inversely proportional to the dislocation density.

Four alternative mechanisms have been considered and rejected for the following reasons: (1) The longer time constants are not associated with the annihilation of trapped electrons on dislocations since the speed of this process would be proportional to the hole density rather than to the dislocation density as observed. (2) It does not involve a competing recombination process since such a process would result in a single faster decay rather than in a two-time-constant decay. (3) It is not due to a competing trapping process in which hole capture is the limiting process since the decay time depends on the dislocation density rather than the hole density. (4) Nonlinear processes may be ruled out on the observation that the amplitude ratios and time constants are independent of the magnitude of the carrier injection.

n-Type

The discussion of *n*-type material is complicated by the space-charge cylinder surrounding the dislocation. The decay process here should involve the capture of an excess hole by a normally charged dislocation site, resulting in a neutral site, and the subsequent recharging of the same or another site by an electron from the conduction band.

In the material under consideration approximately 4% of the dislocation sites are charged, making the spacing between electrons 10^{-6} cm and the energy of interaction 0.01 ev. On the other hand, the radius of the space-charge cylinder is 10^{-4} cm. Recombination in *n*-type material must consequently be interpreted in terms of the analysis given by Morrison,[13] extended to the transient case.

The room-temperature data for the 8 ohm-cm *n*-type crystal are given in Fig. 3. The decay of conductivity could in general be represented by three exponentials. Only one of these persisted at all temperatures. It has the largest amplitude and the intermediate length. The longer time constant was observed at low temperature and the shorter one only at high temperature in the less severely bent samples. Figure 3 shows the intermediate time constant. The data are in good agreement with those of Okada[4] obtained for dislocation densities of 10^3 to 10^5 cm^{-2}.

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[13] S. R. Morrison, Phys. Rev. **104**, 619 (1956).

CONCLUSIONS

Measurements of lifetime in plastically deformed *p*-type germanium yield an electron capture radius of $3.4\times10^{-8}(300/T)^3$ cm. The room-temperature lifetime is given by

$$\tau=0.7\times N_d^{-1}. \tag{5}$$

This suggests that the lifetime in high-purity *p*-type crystals may be limited by the dislocations introduced in the crystal-growing. Measurements on *n*-type germanium indicate that, at room temperature,

$$\tau=2.5N_d^{-1}. \tag{6}$$

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Definition of Energy Bands in the Presence of an External Force Field

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It is shown that for an electron moving in a periodic potential perturbed by a weak electric field the "physical energy bands" differ from the energy bands in the absence of the perturbing field. By means of a wave-packet treatment it is shown that for very weak fields the modified bands are those suggested earlier by Wannier and by Adams and Argyres. In stronger fields, no such treatment can be given, and the functions defined by Wannier for that case do not represent "physical energy bands" in the same sense.

INTRODUCTION

It is well known that the energy levels of an electron in a perfectly periodic potential group themselves into "bands," which are sometimes separated by "forbidden bands." The modern theory of solids predicts that an electron in one of these energy bands, when perturbed by certain kinds of weak perturbing field, accelerates under the perturbing force in somewhat the same manner as would a free particle of rather peculiar inertial properties. It is an outstanding success of the modern theory of solids that it can account quantitatively for many otherwise puzzling phenomena by recourse to the expected properties of these "effective free electrons."

The theory of electronic transport properties in metals and semiconductors assumes that the chief effect of a very weak and slowly varying perturbing field is to accelerate the effective electron about in its allowed energy band. This assumption is used in both semiclassical treatments of electronic motion and quantum-mechanical treatments of the electronic energy levels in a perturbed periodic potential, and with considerable success.

In order to understand the ordinary "effective electron" treatment of the effect of perturbing fields it is necessary to answer a perplexing question of a fundamental nature, *viz.*, what is the status of the energy-band concept in the presence of an external perturbation that destroys the crystalline periodicity. As far as this writer is aware, there has nowhere been given a systematic discussion of how this question is to be answered in principle. However, various authors, when addressing themselves to specific problems,[1–3] have assumed an answer to the question sufficient for their immediate purposes.

Recently Wannier[4] and Adams and Argyres[5] have discussed this problem of definition of the bands in the presence of an external field. They have given definitions of field-dependent Bloch functions which seem to have some of the properties that we might expect for the energy states in the presence of the field. However, their discussions are not complete in that they do not show in what way the functions they construct correspond to a *physical definition* of the "energy bands in the presence of the field."

In the first section we will show that the case of a weak electric field, the field-dependent Bloch functions defined by Wannier and by Adams and Argyres correspond to the physical energy states of an electron accelerating slowly in the electric field. The method of attack is to find the motion of a narrow wave packet, initially in a single energy band, as an electric field is slowly turned on. We find that the wave packet always behaves as though it consisted of a packet of functions from a single energy band of the field-dependent sort. Our results show that the motion of such a packet takes place without any transitions between bands only if

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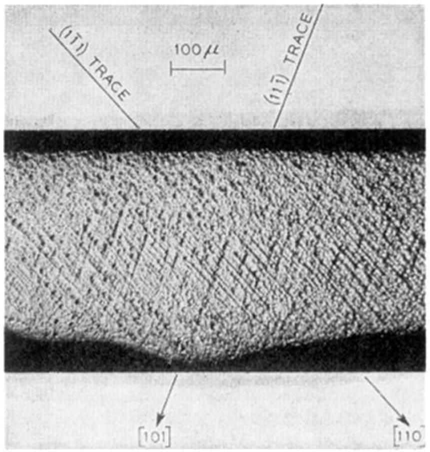
[1] A. H. Wilson, *The Theory of Metals* (Cambridge University Press, New York, 1936).

[2] E. N. Adams, Phys. Rev. **89**, 633 (1953).

[3] R. Karplus and J. M. Luttinger, Phys. Rev. **95**, 1154 (1954).

[4] G. H. Wannier, Phys. Rev. **100**, 1227 (1955); **101**, 1835 (1956).

[5] E. N. Adams and P. N. Argyres, Phys. Rev. **102**, 605 (1956).



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