

Electron Capture Probability of the Upper Copper Acceptor Level in Germanium

R. M. BAUM AND J. F. BATTEY

Electronics Division, Sylvania Electric Products, Ipswich, Massachusetts

(Received December 23, 1954)

The doping of a germanium sample is arranged so that the minority carrier lifetime is inversely proportional to the electron capture probability of the upper acceptor level introduced by copper atoms. It is found that the lifetime decreases exponentially with increasing temperature. A suggested interpretation is that only electrons of energy greater than 0.22 eV above the bottom of the conduction band can enter the second copper acceptor level.

IT is generally believed that the recombination of minority carriers in the bulk of presently produced single crystal germanium proceeds by transitions to and from intermediate energy levels in the forbidden energy gap. The statistics of the process have been described by Hall¹ and by Shockley and Read.² For low levels of minority carrier injection in a nondegenerate semiconductor where the charge in the recombination traps is neglected and a steady state with respect to injection and recombination is achieved, the lifetime, τ , of the injected carriers is given by

$$\tau = \frac{(1/C_p)(n_0 + n_1)/(n_0 + p_0)}{(1/C_n)(p_0 + p_1)/(n_0 + p_0)}. \quad (1)$$

C_p is the product of the trap density and the probability per unit time of an individual trap capturing a hole, averaged over the holes in the valence band. C_n is the product of the trap density and the probability of an individual trap capturing an electron, averaged over the electrons in the conduction band. n_0 and p_0 are the equilibrium electron and hole densities, and n_1 and p_1 are the values the equilibrium electron and hole densities would have if the Fermi level were located at the same position in energy as the recombination traps.

The bulk lifetime of most germanium samples thus far investigated increases exponentially with increasing temperature in the range where the sample is extrinsic. This is presumed to be due to the exponential variation of the carrier density in the dominant term in the numerator of (1), the denominator being virtually constant in the extrinsic range. An example of this behavior has been reported by Hall,¹ and some further illustrations of this behavior due to recombination levels of an undetermined origin are shown in Fig. 1. It is the purpose of this article to report that there is a method of preparing germanium samples so that the bulk lifetime decreases exponentially with increasing temperature. This is done by diffusing copper into an originally n -type semiconductor to such an extent that the upper acceptor levels introduced by the copper are approximately half populated. Details of sample preparation are described in a previous letter by the authors.³

¹ R. N. Hall, Phys. Rev. **87**, 387 (1952).

² W. Shockley and W. T. Read, Jr., Phys. Rev. **87**, 835 (1952).

³ J. F. Battey and R. M. Baum, Phys. Rev. **94**, 1393 (1954).

It has been shown by Burton *et al.*⁴ that the upper copper levels in germanium act as recombination levels for which at room temperature $10/C_p \approx 1/C_n$ and the diffusing in of the copper served to reduce the room temperature bulk lifetime of the samples investigated here by several orders of magnitude. For such samples as this the charge in the traps cannot be neglected, and the deviations in electron and hole densities from the equilibrium values as well as the associated lifetimes are no longer equal. Under these circumstances the steady-state electron lifetime is given as²

$$\tau_n = \frac{(1/C_p)(n_0 + n_1) + (1/C_n)[p_0 + p_1 + N_t(1 + p_0/p_1)^{-1}]}{n_0 + p_0 + N_t(1 + p_0/p_1)^{-1}(1 + p_1/p_0)^{-1}}, \quad (2)$$

where N_t is the density of recombination centers. For the sample preparation described $(1/C_p)(n_0 + n_1)$ is negligible compared to the remainder of the numerator around room temperature, and n_0 is negligible compared

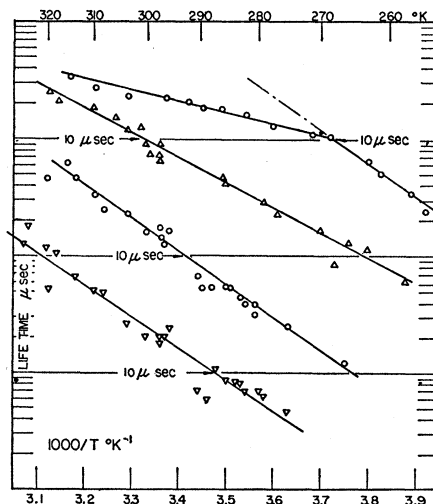


FIG. 1. Variation of bulk lifetime with temperature in n -type germanium due to recombination levels of undetermined origin. It is interesting to note that the sum of the activation energies derived from the two sections of the upper curve is approximately equal to the energy gap. This is to be anticipated if there is a transfer in dominance of the numerator of Eq. (1) from the term involving n_1 , to that involving p_1 , or vice versa.

⁴ J. A. Burton *et al.*, J. Phys. Chem. **57**, 853 (1953).

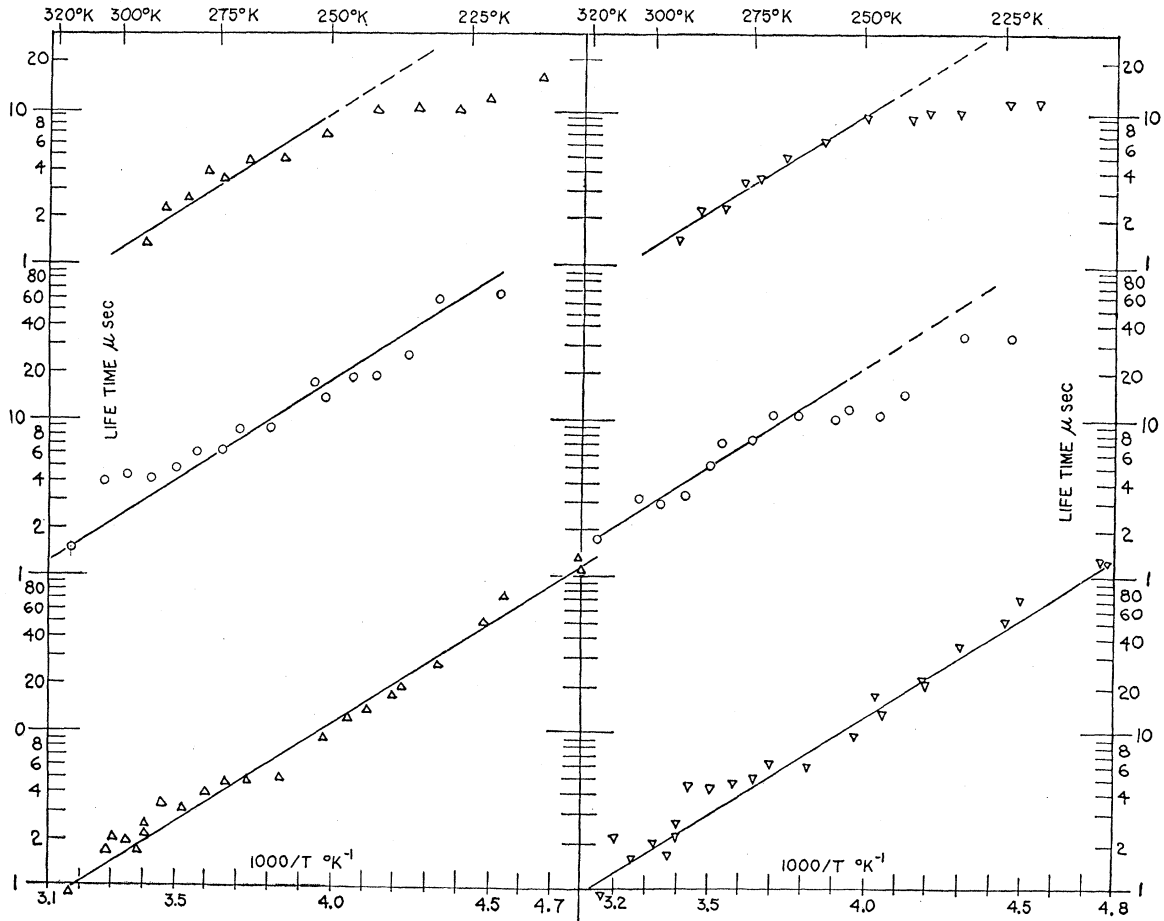


FIG. 2. Lifetime *versus* temperature in different parts of a high-resistivity copper-doped sample, wherein the lifetime is inversely proportional to the capture probability of the upper copper acceptor level for electrons.

to the other terms in the denominator for all temperatures below about 50°C. Then

$$\tau_n \approx (1 + p_1/p_0)/C_n = 1/C_n f_{pi} \quad (3)$$

where f_{pi} is the probability that a copper recombination level be empty. Equation (3) states that the minority carrier lifetime is inversely proportional to the product of the capture probability of a recombination level for an electron times the density of empty levels. Over the temperature range investigated, p_0 is small compared to N_i and f_{pi} is virtually constant for the samples used. Thus, τ_n is inversely proportional to C_n .

The lifetime measurements reported here were made at low injection levels by a diffusion length measurement using a point light source. They were corrected for surface recombination in a manner previously described by one of the authors.⁵ As might be expected for etched samples and the low values of bulk lifetime encountered, the corrections were negligible except at low temperatures, where they were still small. The data are shown in Fig. 2 in a semilogarithmic plot, which

seems to be the most significant way to display it. The data exhibited were taken on the previously described³ sample for which carrier concentrations are calculated under the tacit assumption that the traps are not degenerate. It will be noticed that within the accuracy of the data, the runs on several parts of the sample are straight lines. It is presumed that the failure of the lifetime to increase as rapidly as exponentially with decreasing temperature in other parts of the sample is due to competition from other recombination processes which become of comparable importance at lower temperatures.

In calculating the lifetime from the measured diffusion length, the presumption is made that the minority carrier diffusion length varies as $T^{-0.6}$,⁶ which is a weak dependence compared to that of the lifetime itself. It is felt that trapping by the upper copper levels has a small effect on the diffusion coefficient, inasmuch as the relative sizes of $1/C_p$ and $1/C_n$ at room temperature indicate that once an electron is captured in the

⁵ S. Visvanathan and J. F. Battey, *J. Appl. Phys.* **25**, 99 (1954).

⁶ M. B. Prince, *Phys. Rev.* **92**, 681 (1953).

recombination level, it has a much greater probability of going to the valence band ($p_0 C_p / N_i$) than returning to the conduction band ($n_1 C_n / N_i$). Nevertheless to check against any possible unforeseen variations with temperature in the diffusion coefficient, the lifetime was also measured by a conductivity modulation technique, with substantially the same results. The conductivity modulation decays due to recombination of both electrons and holes, which do not necessarily have the same steady-state lifetime if the charge in the traps cannot be neglected. However, if it is presumed that the holes in the traps rapidly come to equilibrium with the holes in the valence band, as seems to be the case for the upper copper level, then both electrons and

holes subsequently decay with the lifetime of the electrons.

The apparent exponential increase of C_n with increasing temperature is regarded as somewhat surprising. It is the result that would be anticipated if only the electrons of energy greater than a certain critical energy above the bottom of the conduction band were allowed to enter the upper copper levels. This energy as obtained from the slopes of Fig. 2 is approximately 0.22 ev.

ACKNOWLEDGMENTS

The authors wish to give thanks to Robert Carye and George Servente for assistance with the experimental work.

PHYSICAL REVIEW

VOLUME 98, NUMBER 4

MAY 15, 1955

Ferromagnetic Resonance in Ferroxdure

M. T. WEISS AND P. W. ANDERSON
Bell Telephone Laboratories, Holmdel, New Jersey
 (Received January 28, 1955)

Ferromagnetic resonance experiments have been performed on Ferroxdure at various microwave frequencies from 9000 Mc/sec to 50 000 Mc/sec. With no externally applied field a natural resonance occurs near 50 000 Mc/sec. With magnetic field applied perpendicular to the hexagonal axis, a double resonance occurs for frequencies below 50 000 Mc/sec, while with a field applied along the hexagonal axis a single resonance occurs above 50 000 Mc/sec. A theory is developed to explain the above results.

FERROMAGNETIC resonance experiments have been performed on Ferroxdure at various microwave frequencies. Ferroxdure¹ is a ceramic permanent magnet material with high anisotropy having a hexagonal crystal structure and having essentially the composition BaFe₁₂O₁₉.

THEORY

The ferromagnetic resonance frequencies of a hexagonal crystal with high anisotropy along the hexagonal axis can be calculated as follows:

The anisotropy energy is given by $U = K \sin^2 \theta$, where θ is the angle of the magnetization with respect to the hexagonal axis. Higher order terms in $\sin \theta$ as well as anisotropy within the basal plane can be neglected for Ferroxdure at room temperature. The torque due to the anisotropy is given by

$$T = -\frac{\partial U}{\partial \theta} = -\frac{\partial U}{\partial M_{xy}} \frac{\partial M_{xy}}{\partial \theta} = -\frac{2K}{M^2} M_{xy} M_z, \quad (1)$$

or vectorially

$$\mathbf{T} = + (2K/M^2) \mathbf{M} \times \mathbf{M}_z = \mathbf{M} \times \mathbf{H}_A,$$

where \mathbf{M} is the magnetization vector, \mathbf{M}_z and \mathbf{M}_{xy} are

¹ Went, Rathenau, Gorter, and Van Oosterhaut, Philips Tech. Rev. 13, 194-208 (1952).

evident from Fig. 1, and \mathbf{H}_A is an equivalent anisotropy field which would produce the same torque. Evidently,

$$\mathbf{H}_A = (2K/M^2) \mathbf{M}_z = A \mathbf{M}_z, \quad (2)$$

so that the equivalent anisotropy field is along the hexagonal axis and is proportional to the magnetization along that axis.

In the standard equation of motion² for the magnetization $d\mathbf{M}/dt = \gamma \mathbf{M} \times \mathbf{H}$, one must take into account

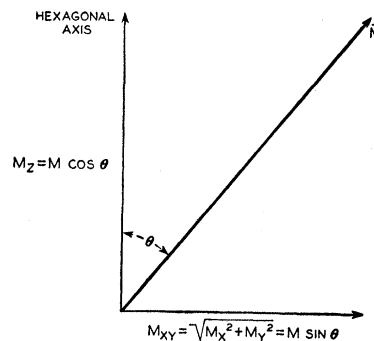


FIG. 1. Vectors used in calculating ferromagnetic resonance frequencies of Ferroxdure.

² C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1953), p. 155.