Neutron-Bombardment Damage in Silicon*

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Neutron-bombardment damage in silicon is compared to electron-bombardment effects which have been previously analyzed. A discrete energy level 0.27 ev above the valence band previously ascribed to the acceptor member of a defect pair having a separation greater than 50 A, is found to be produced by both neutrons and electrons. A spectrum of energy levels running from 0.16 ev below the conduction band toward the middle of the gap is ascribed to a defect pair with variable spacing, and related to the discrete level 0.16 ev below the conduction band which was found previously in electron-bombardment of silicon, and there ascribed to a close-spaced pair of defects. Lifetime effects are found to be dominated by levels near the middle of the energy gap, which may be related to the above spectrum. A very rapid decrease in mobility at low temperature is ascribed to bombardment-induced inhomogeneities.

INTRODUCTION

NEUTRON–BOMBARDMENT effects in silicon have been studied for a number of years. The optical absorption in a neutron-bombarded polycrystalline sample has been reported by Becker and Fan,[1] who found an absorption band at 1.8 microns as well as a reduction in the free-carrier absorption. The Hall effect and resistivity in these samples has been measured by Dreyfus[2] who found activation energies ranging from 0.29 to 0.19 ev. More recently the optical absorption and photoconductivity in single-crystal material has been reported by Longo.[3] He finds that the absorption band at 1.75 microns is not associated with photoconductivity indicating that it corresponds to excitation rather than ionization of a defect. With the Fermi level locked close to the middle of the gap he also reports an edge of photoconductivity at 1.45 microns (0.86 ev) and another of lower intensity at 2.25 microns (0.55 ev). He has observed the same photoconductivity in polycrystalline material after a prolonged anneal as well as in deuteron bombarded samples. Additional absorption bands have been reported by Spitzer and Fan.[4]

In an experiment designed to determine the effect of neutron bombardment on x-ray diffraction line breadth, Wood and Batterman irradiated powdered samples of silicon containing less than 10^{14} boron atoms per cc, and of silicon containing 10^{16} boron atoms per cc with about 10^{19} *nvt* thermal and 10^{18} *nvt* epicadmium. The diffraction pattern of the irradiated and unirradiated samples were recorded with a Geiger-counter diffractometer. There was no detectable difference in line breadth.[5] In a similar experiment, Wittels obtained a volume expansion of 1.7×10^{-4} after reactor irradiation with 4×10^{20} fast neutrons.[6] He did not relate this to a defect density.

Bombardment-induced electron spin resonance has been reported by a group at Purdue.[7]

In the present paper a direct comparison is made between the electrical effects of neutron and electron irradiation in samples from two crystals. Bombardment with electrons close to the threshold for the production of damage in silicon has been shown to produce two species of paired point imperfections.[8] A pair with a spacing of 2.5 A, produced in greatest density, has been tentatively identified as a vacancy-interstitial pair with the displaced atom in one of the nearest interstitial positions; electron spin-resonance experiments indicate that this position may be the second nearest, which lies in the ⟨100⟩ direction.[9] This defect gives rise to an energy level 0.16 ev below the conduction band. The other pair which is produced in much smaller density, has been found to have a spacing larger than 50 A. Its energy level lies 0.27 ev above the valence band.

Bombardment with more energetic electrons, or with heavy charged particles or neutrons, is expected to

Table I. Crystal parameters and bombardments.

	Sample No.	Bombardment	Flux (cm^{-2})	Bomb. temp. (°K)	η (cm^{-1})
Crystal 2-*n*[a]	1	fast neutrons	1.5×10^{12}	295	...
$N_d-N_a=2.2\times10^{15}$	2	fast neutrons	5.4×10^{12}	295	...
Phosphorous doped	3	fast neutrons	1.7×10^{13}	295	...
Nonrotated	4	fast neutrons	5.3×10^{13}	295	...
	5	fast neutrons	1.6×10^{14}	295	5.6
	6	fast neutrons	3.3×10^{14}	295	...
	7	1-Mev electrons	9.7×10^{15}	193	0.18
	8	1-Mev electrons	1.93×10^{16}	193	...
Crystal 2-*p*[b]	1	fast neutrons	1.5×10^{12}	295	...
$N_a-N_d=7.0\times10^{15}$	2	fast neutrons	5.4×10^{12}	295	...
Boron doped	3	fast neutrons	1.7×10^{13}	295	...
Nonrotated	4	fast neutrons	5.3×10^{13}	295	...
	5	fast neutrons	1.6×10^{14}	295	...
	6	fast neutrons	3.3×10^{14}	295	9.1
	7	1-Mev electrons	2.8×10^{17}	193	0.0098

[a] Samples cut from crystal 2-*n* vary by as much as 15% in carrier concentration.
[b] Samples cut from crystal 2-*p* vary by as much as 10% in carrier concentration.

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[1] Becker, Fan, and Lark-Horovitz, Phys. Rev. **85**, 730 (1952).
[2] R. Dreyfus, thesis, Purdue University, 1953 (unpublished).
[3] T. A. Longo, thesis, Purdue University, 1957 (unpublished).
[4] W. G. Spitzer and H. Y. Fan, Phys. Rev. **109**, 1011 (1958).
[5] E. A. Wood and B. W. Batterman (private communication).
[6] M. C. Wittels, J. Appl. Phys. **28**, 921 (1957).
[7] Schulz-DuBois, Nisenoff, Fan, and Lark-Horovitz, Phys. Rev. **98**, 1561(A) (1955).
[8] G. K. Wertheim, Phys. Rev. **110**, 1272 (1958).
[9] Bemski, Feher, and Gere, Bull. Am. Phys. Soc. Ser. II **3**, 135 (1958).

produce more complicated damage. In particular, a damage site may contain many defects with a range of spacings, or even a grossly disturbed structure. It is unlikely that isolated vacancies or interstitials will be produced by any bombarding particle unless either the vacancy or interstitial is mobile.

EXPERIMENTAL PROCEDURE

Bridges and rods were cut from two single crystals of silicon whose parameters are given in Table I. The bridges for neutron bombardment were shielded with 1 millimeter of cadmium and exposed at room temperature to the flux from a fission plate in the Brookhaven reactor; they received fluxes ranging from 1.5×10^{12} to 3.3×10^{14} fast neutrons/cm^2 as shown in Table I. The fast flux includes all neutrons with energy greater than 100 ev, of these about 60% have an energy greater than 0.4 Mev. To avoid activation of the sample holders, these samples were mounted after bombardment; the bridges were nickel-plated in a boiling solution and attached with pure indium solder (melting point 156°C) to a copper frame. The annealing effect of this treatment on neutron-bombarded material has not been studied but it is known that no annealing occurs in room-temperature electron-bombarded material below 200°C.[10] Since no problem of activation arose in the bridges and rods for electron bombardment, they were mounted prior to irradiation.

Lifetime was measured with a time resolution of 10^{-8} sec using the pulsed Van de Graaff technique.[11] Conductivity and Hall effect were measured with conventional dc methods.

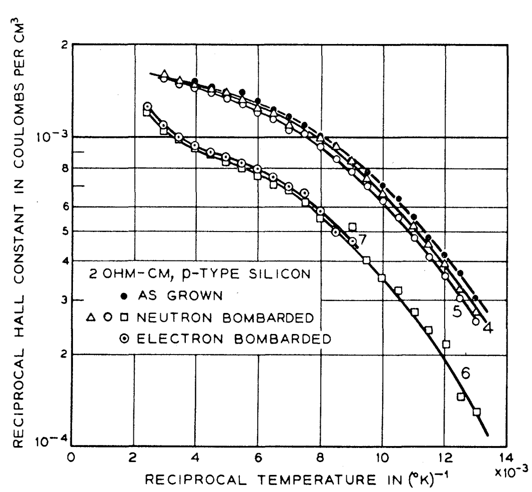

FIG. 1. Carrier concentration in 2-ohm-cm, p-type silicon as a function of temperature, following neutron or electron bombardment.

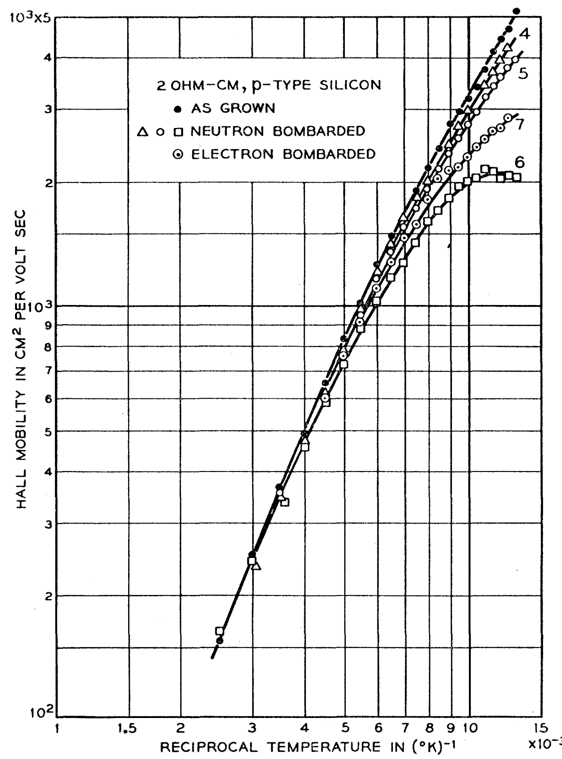

FIG. 2. Hall mobility in 2-ohm-cm, p-type silicon for the samples of Fig. 1.

RESULTS AND DISCUSSION

(a) The Lower Half of the Energy Gap

The reciprocals of the Hall constant as a function of temperature in five samples from the same p-type crystal (one unbombarded, one bombarded with electrons, and three bombarded with neutrons) are shown in Fig. 1. The data for neutron-bombarded sample 6 and those for the electron-bombarded sample are quite similar indicating that the same energy level is produced in both cases. The electron bombardment center has been identified with the acceptor member of a defect pair with spacing greater than 50 A; this spacing is sufficiently great that the energy level of the acceptor would not be perturbed by the existence of a range of spacings. The neutron bombardment defect may therefore be indentical with that produced by electrons, but it could also consist of the unpaired acceptor member of the damage site. The rate of introduction of damage by neutrons is 9.1 centers/cm^3 per fast neutron/cm^2, a value considerably greater than that observed in neutron-bombarded germanium where a value of 1.6 cm^{-1} has been obtained.[12,13]

The energy level found here in lightly bombarded[14] material may well be responsible for the activation

[10] G. Bemski and W. M. Augustyniak, Phys. Rev. **108**, 645 (1957).

[11] G. K. Wertheim and W. M. Augustyniak, Rev. Sci. Instr. **27**, 1062 (1956).

[12] Cleland, Crawford, and Pigg, Phys. Rev. **99**, 1170 (1955).

[13] Cleland, Crawford, and Pigg, Phys. Rev. **98**, 1742 (1955).

[14] "Lightly bombarded" signifies that the density of defects does not exceed the net donor or acceptor concentration.

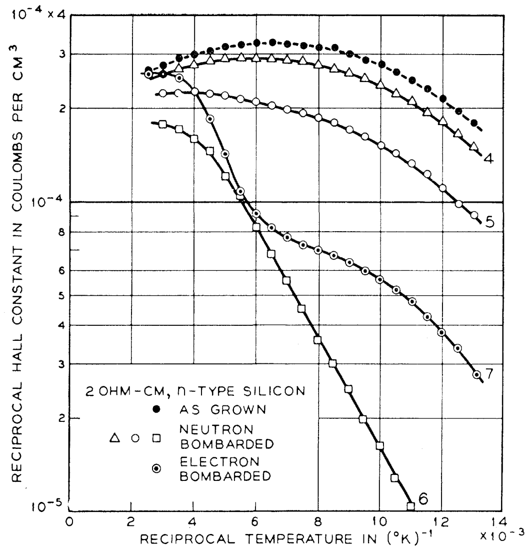

FIG. 3. Carrier concentration in 2-ohm-cm, *n*-type silicon as a function of temperature, following neutron or electron bombardment.

energies in the range from 0.29 to 0.19 ev reported by Dreyfus[2] in more heavily bombarded polycrystalline material. It is likely that the photoconductivity edge at 0.86 ev[3] corresponds to the excitation of electrons from the 0.27-ev level to the conduction band.

The mobilities in the electron and neutron case are noticeably different, Fig. 2. The Hall mobility in the neutron-bombarded material is lower than that in the electron-bombarded material containing the same density of 0.27-ev acceptors. This result is discussed later in the paper.

(b) The Upper Half of the Energy Gap

The reciprocals of the Hall constant in five samples from the same *n*-type crystal (one unbombarded, one bombarded with electrons, and three bombarded with neutrons) are compared in Fig. 3. The behavior of the electron-bombarded sample reflects the presence of the previously found discrete donor level associated with a defect pair of 2.5-A separation. The neutron-bombardment results, especially the curves for samples 4 and 5, indicate that a broad spectrum of energy levels is present.

At low temperatures in sample 5, between 77 and 125°K, the energy level spectrum is completely filled with electrons; beginning at 215°K the fraction of filled centers decreases slowly with rising temperature. The number of carriers removed below 125°K was used to determine the rate of introduction of damage, η, associated with the close-spaced pair of defects. It was found to be 5.6 cm^{-1}. This value is 40% smaller than that found for the 0.27-ev level but is still larger than that observed in neutron-bombarded germanium.[12,13] The emptying of the levels as a function of temperature is much slower in the region above 125°K than in the electron-bombardment case where it corresponds to a single, discrete energy level. At the highest temperature at which measurements were made a significant fraction of the centers remain filled. The Fermi level at this temperature is 0.28 ev below the conduction band; the data indicate that the spectrum of energy levels extends even further from the conduction-band edge.

These facts are in agreement with an interpretation in terms of the close-spaced donor-acceptor pair seen in the electron-bombardment case, here modified to have a spectrum of allowed spacings ranging upward from 2.5 A. The observed spectrum of energy levels is then a consequence of the fact that as the spacing of the donor-acceptor pair increases, the donor becomes a more favorable site for an electron, and consequently produces a deeper level.

A model of neutron damage may be obtained by considering the individual processes which produce the stable damage configuration observed at the end of bombardment. Under bombardment with 1-Mev electrons one expects that displacements to a range of positions greater than 2.5 A should be possible but only two types of defects are produced, those with a discrete spacing of 2.5 A and those with spacings greater than 50 A. A possible model of the damage process which accounts for this behavior, first suggested by Brown,[15] is (a) that the primary damage[8] consists of vacancy-interstitial (V–I) pairs with a range of spacings, (b) that there is a barrier for the final jump which reunites a vacancy with an interstitial; (c) that one member of the pair, say the interstitial, is mobile; (d) that diffusion carries this member either to a position close to the vacancy where it is caught producing the 0.16-ev level or else to a favorable location near some other lattice defect, in which case the 0.27-ev level is produced at the site of the stationary member of the pair. In the neutron case we take cognizance of the fact that the V–I pairs are created in a highly disturbed region, and may consequently have stable spacings greater than the one allowed in an undisturbed lattice. It follows from this model that the greater the spacing of the primary damage the more probable the production of the 0.27-ev level becomes, relative to that of the 0.16-ev level. This is in agreement with the data. In the electron case $\eta_{0.27}/\eta_{0.16}$ is 0.061, while in the neutron case it is 1.6.

The data for sample 4, which received less bombardment, are not significantly different from those just discussed, but those for sample 6 exhibit an anomalous behavior at low temperature, Fig. 4. The log of the carrier concentration plotted as a function of reciprocal temperature exhibits a slope of 0.035 ev. At first sight this suggests that there is an energy level 0.035 ev below the conduction band; however this interpretation is not tenable, since the Fermi level at the temperature where these data were taken is much deeper within the forbidden gap.

[15] W. L. Brown (private communication).

Similar behavior has been observed in silicon containing a high concentration of arsenic, but not so much as to cause degeneracy.[16] The donor concentration as well as the defect concentration in the present case are three orders of magnitude smaller, however, indicating that the processes in the two cases are not related.

It has been suggested that such behavior could arise from macroscopic fluctuations in the concentration of the chemical donor in the crystal. The effect of such fluctuations is magnified as the donor is compensated by bombardment. If this explanation were valid, the observed behavior for neutron or electron bombardment should be the same; in fact, however, sample 8, Fig. 4, which was bombarded with electrons until the density of bombardment defects exceeded the density of chemical donors does not show this effect, giving rather the slope characteristic of the 0.16-ev level.

The behavior can be best explained by ascribing it to bombardment-induced inhomogeneities. In the neutron case, each collision produces an elongated damage site, perhaps 100 A in diameter and 1000 A in length, containing a large number of defects. The resistivity of these sites tends to become high as the temperature is lowered, but the resistivity of the sample reflects chiefly the remaining low-resistivity matrix. This separation of the crystal into damaged regions of high resistivity and undamaged regions of normal resistivity is an oversimplification since the effective Debye length at room temperature is of the same order as the spacing of the damage sites, (10^3 A). If it were not for this fact the computation of Hall constants and mobilities would have little meaning. At low temperature where the breakup into high- and low-resistivity regions is accentuated the validity of these measured quantities may be questioned.

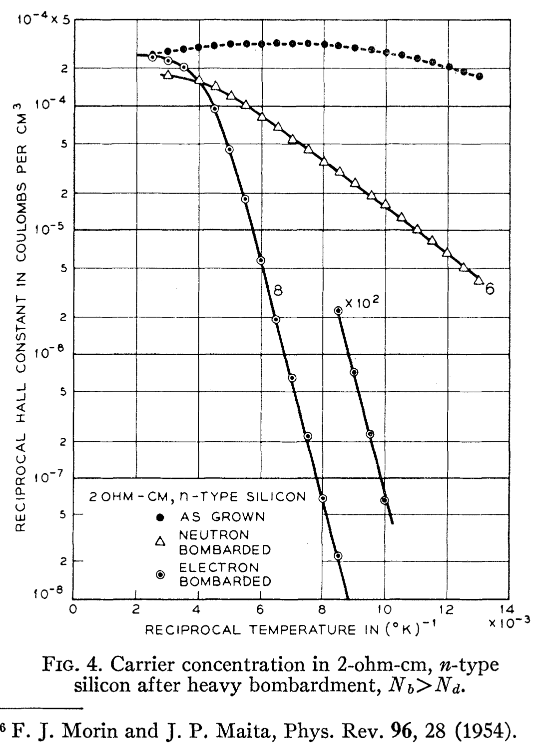

FIG. 4. Carrier concentration in 2-ohm-cm, n-type silicon after heavy bombardment, $N_b > N_d$.

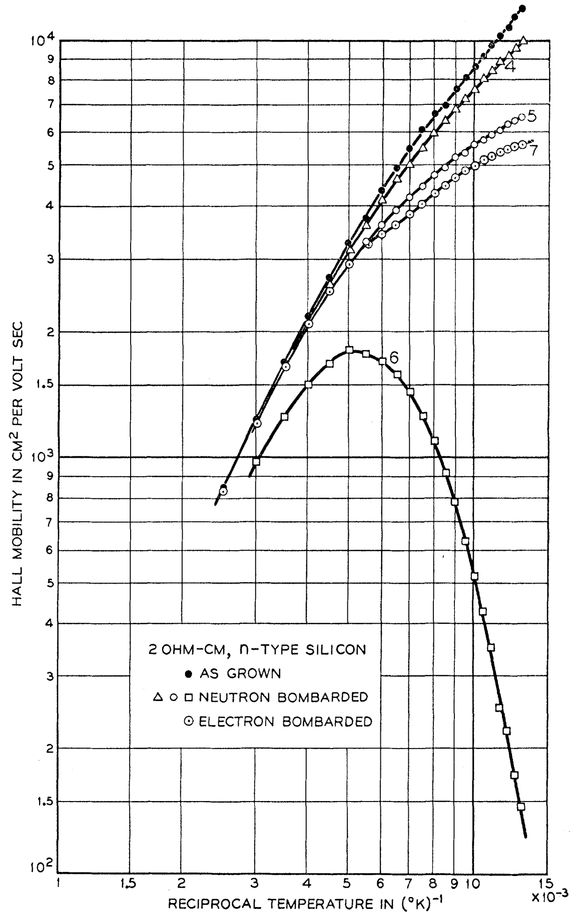

FIG. 5. Hall mobility in 2-ohm-cm, n-type silicon for the samples of Fig. 3.

The anomalous mobility behavior expected for a crystal containing such defects has also been observed and is shown in Fig. 5. The drop in the Hall mobility with decreasing temperature is much faster than that expected on the basis of charged-center scattering, which indicates that another mechanism is acting. Similar mobility behavior has been seen following neutron bombardment of germanium,[13] in nickel-doped germanium,[17] as well as in unbombarded silicon containing a high density of chemical donors or acceptors.[16] In the first two cases it was ascribed to inhomogeneities in the crystal, and in the last impurity-band conduction. It is apparent that this behavior in sample 6 cannot be attributed to the latter process, since the sites produced by bombardment occupy only a small fraction of the volume, and since the effect persists to high temperature. Impurity-band conduction within

[16] F. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1954).

[17] Tyler, Newman, and Woodbury, Phys. Rev. **98**, 461 (1955).

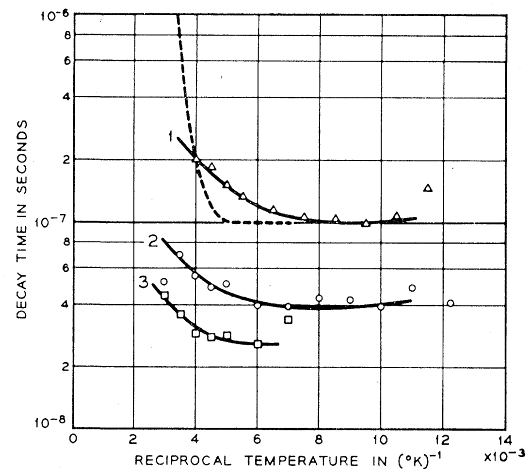

FIG. 6. Lifetime as a function of temperature in 2-ohm-cm, neutron-bombarded n-type silicon. The injection level is held constant. The dotted line shows the lifetime observed after electron bombardment.

the sites where the defect density may be greater than 10^{18} cm^{-3} cannot account for the observed behavior since no more than 10^{-3} of the crystal volume is contained in the sites. The most reasonable explanation is that the effect is due to the scattering by neutron damage sites with dimensions comparable to the electron wavelength. The effect is sufficiently great so that a determination of the density of charged scattering sites cannot be made at any temperature. The same effect accounts for the low mobility in the p-type crystal mentioned above and in the less heavily bombarded n-type specimens.

(c) Lifetime Measurements

The transient-recombination lifetime in the neutron-bombarded samples differs significantly from the behavior observed after electron bombardment. The temperature dependence of the lifetime is not compatible with an interpretation in terms of either of the two defects found to act as recombination centers in electron-bombarded crystals. The absence of a discrete activation energy, Figs. 6 and 7, and the observed dependence of the magnitude of the lifetime on injection level can best be explained on the basis of a spectrum of recombination centers near the middle of the energy gap.

Let us examine the transient lifetime in a sample containing a fixed density of centers as a function of their location in the forbidden gap. The solution for moderately large injection[18] may be written

$$\tau=\frac{\tau_{p0}(N^0+n_0+n_1+\delta n)+\tau_{n0}(N^-+p_0+p_1+\delta p)}{n_0+p_0+N^0N^-/N+\delta nN^-/N+\delta pN^0/N},$$
$$N^0=Nn_1(n_0+n_1)^{-1},$$
$$N^-=Np_1(p_0+p_1)^{-1}. \tag{1}$$

[18] G. K. Wertheim, Phys. Rev. **109**, 1086 (1958).

This solution is invalid when δn and δp dominate in any term. Nonexponential decay and injection-level-dependent behavior are then to be expected, since the differential equations of recombination can no longer be treated as having constant coefficients.

Equation (1) may be specialized for recombination centers located at least $3kT$ below the Fermi level in n-type material, to obtain

$$\tau\approx\frac{1}{\sigma_pv_pN}+\frac{1+(p_1+\delta p)/N}{\sigma_nv_n(n_0+\delta n)}. \tag{2}$$

We note that nonlinear or large-signal effects may occur for $\delta n\ll n_0$ provided only that p_1, N and δp are of the same order; that is, they are found when the density of recombination centers is small and when these centers are located far from the minority-carrier band. Under these conditions one finds τ increasing with injection level as is usually observed in crystal as grown. It should also be noted that the smallest lifetime for a given density of recombination centers is obtained when $p_1\ll N$.

In the samples under discussion n_0 is 2.2x10^{15} cm^{-3} and the injection level is 10^{12} cm^{-3}. At room temperature p_1 is less than δp for recombination centers more than 0.41 ev from the valence band. The density of close-spaced pair centers in sample 1 is 8.7×10^{12} cm^{-3} as determined from carrier-removal rates in more heavily bombarded samples. Of these only a small fraction is expected to lie near the middle of the gap. As a result the criteria for large-signal behavior are readily met. The analysis of the p-type data leads to the same conclusion. The deep-lying levels which dominate recombination in these samples may be those producing the photoconductivity at 2.25 microns observed by Longo,[3] and are tentatively identified with the pairs which produce the spectrum of levels extending from 0.16 ev below the conduction band toward the middle of the gap.

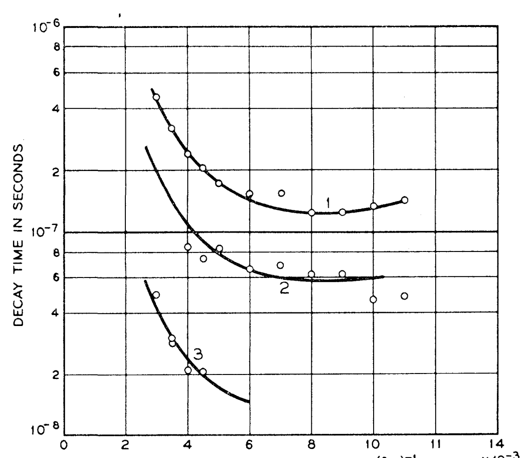

FIG. 7. Lifetime as a function of temperature in 2-ohm-cm, neutron-bombarded, p-type silicon.

Room-temperature lifetimes in these samples are given by the following equations for an injection level of 10^{12} cm^{-3}:

$$n\text{-type } \tau \approx \frac{3.9\times 10^5}{\varphi} \text{(sec)},$$

$$p\text{-type } \tau \approx \frac{4.3\times 10^5}{\varphi} \text{(sec)},$$

where φ is the neutron flux. In the region studied the lifetime varies approximately as the square root of the injection level.

CONCLUSIONS

The effect of low-integrated-flux neutron bombardment on the carrier concentration in silicon is similar to the effect of low-flux electron bombardment. Of the two species of defect produced, one appears identical in both cases, and the other differs only insofar as it is produced with a range of spacings rather than with one discrete spacing. Such similarities in the energy level scheme after gamma and neutron bombardment of germanium have been reported by Cleland *et al.*[19] Mobility effects in the neutron and electron cases are similar at high temperature, but at low temperature a very rapid drop in the mobility occurs in the former. This has not been observed in the electron case, and is in agreement with the notion that neutrons produce localized inhomogeneities containing a high density of centers. The lifetime in neutron-bombarded material is dominated by centers near the middle of the forbidden gap.

ACKNOWLEDGMENTS

The author is indebted to J. W. Easley for the neutron bombardments made in the Brookhaven reactor, and to D. N. E. Buchanan for assistance with the measurements.

[19] Cleland, Crawford, and Holmes, Phys. Rev. **102**, 722 (1956).

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Effect of Anisotropy on the Temperature Dependence of Elastic Constants

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We suggest that an important part of the temperature dependence of the elastic constants of perfect crystals arises from the elastic anisotropy itself without reference to the features of any model of the interaction between the atoms. The intrinsic effect of the anisotropy is introduced via the local oscillatory rotations produced in a crystal by transverse acoustic vibrations. The elastic properties belonging to different directions are thereby mixed, in proportion to the temperature. A linear temperature dependence of the elastic constants and a partial averaging out of the anisotropy results. Application is made to the elastic constants of β brass.

INTRODUCTION

THE temperature dependence of the elastic constants of perfect crystals is usually considered[1,2] to be determined by the coefficients of the cubic terms in the displacement-energy function of the atoms or ions about equilibrium. These coefficients derive from some model of the interaction between the atoms, or ions and electrons. In the present paper we suggest, however, that an important part of the temperature dependence of the elastic constants of anisotropic crystals arises from the anisotropy itself, independently of the features of any particular model.

The intrinsic role of the anisotropy is introduced via the local oscillatory rotations produced in a crystal by transverse acoustic vibrations. As a consequence the elastic stiffnesses belonging to different crystalline directions are mixed, in proportion to the mean square rotation and hence to the temperature. This effect contributes a linear dependence of the elastic constants on temperature and on the anisotropy constant $C_{44}-\frac{1}{2}(C_{11}-C_{12})$, and produces a partial thermal averaging-out of the anisotropy. For example, the smallest shear stiffness of the crystal is increased and the largest shear stiffness decreased by increasing temperature.

We shall give estimates of the magnitude of the temperature dependence to be expected from this effect. For simplicity we shall consider only cubic crystals, although the treatment of other kinds of symmetry is entirely analogous. Application will be made to the anomalous behavior of β brass,[3,4] *viz.*, the smallest shear stiffness, $\frac{1}{2}(C_{11}-C_{12})$, increases with increasing temperature.

[1] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, Oxford, 1954), Chap. VI.
[2] C. Zener, *Elasticity and Anelasticity of Metals* (University of Chicago Press, Chicago, 1948), Chap. III.
[3] J. S. Rinehart, Phys. Rev. **58**, 365 (1940); **59**, 308 (1941).
[4] C. Zener, Phys. Rev. **71**, 846 (1947).