Recovery of Electrical Properties in 45-MeV-Electron-Irradiated *n*-Type Si from 80 to 350°K*

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Isochronal annealing from 80 to 360°K of defects induced by 45-MeV electrons in floating-zone and pulled *n*-type silicon was studied using electrical properties, namely, conductivity and carrier concentration. The results indicate that the annealing behavior in this temperature range depends on the imperfections present in the samples before irradiation. In particular, oxygen impurities are found to have a pronounced effect on the defect production and annealing process. The total numbers of silicon *A* centers produced after irradiation at 80°K and measured after anneal to 350°K yield production rates of 0.2 to 0.3 cm^{-1} which depend only slightly on the impurity concentration of the samples studied (3×10^{13} to 3×10^{15} phosphorus atoms/cm^3). The production rate of *A* centers by 45-MeV electrons is comparable for 80 and 300°K irradiations; this is different from results found in 1-MeV electron irradiation. The production of *A* centers in 15°K irradiation is found to be about one-half the value measured in 80°K irradiations. A comparison of the characteristics of defects induced by 45- and 1–4.5-MeV electrons in silicon is given.

INTRODUCTION

RECOVERY of electrical properties, carrier concentration and conductivity in irradiated *n*-type silicon in the temperature range from 80°K up to room temperature has not been explored in detail, even though there have been many experiments performed on irradiated *n*-type Si.[1,2] In this paper we report some work concerning the effect of 45-MeV electrons on the electrical properties of *n*-type Si irradiated at 80 and 15°K as well as the annealing behavior in the temperature range from 80 up to about 350°K.

One of the main purposes of the investigation reported here was to study the effects of oxygen impurities in both the damage production and in the annealing. The presence of oxygen in silicon has been shown by electron spin resonance[3] and infrared spectroscopy[4–6] to play an important role in the radiation damage process. The effect of oxygen in Co^{60} gamma-irradiated silicon annealed above 300°K was studied by Saito, Hirata, and Horiuchi,[7] and Tanaka and Inuishi[8] by means of electrical properties. Observations by Watkins[9] on vacancy motion in *n*-type silicon $\lesssim$60°K emphasize the importance of low-temperature irradiations.

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[1] R. R. Hasiguti and S. Ishino, in *Proceedings of the 7th International Conference on the Physics of Semiconductors, Paris, 1964* (Dunod Cie., Paris, 1965), p. 259. Earlier references are given in this paper.

[2] J. W. Corbett, GE Research Laboratory Report No. 65-RL-3782(B)M, 1965 (unpublished). Earlier references are given in this report.

[3] G. D. Watkins and J. W. Corbett, Phys. Rev. **121**, 1001 (1961).

[4] J. W. Corbett, G. D. Watkins, R. M. Chrenko, and R. S. McDonald, Phys. Rev. **121**, 1015 (1961).

[5] A. K. Ramdas and H. Y. Fan, J. Phys. Soc. Japan, Suppl. **18**, 33 (1963).

[6] J. C. Corelli, G. C. Oehler, J. F. Becker, and K. J. Eisentraut, J. Appl. Phys. **36**, 1787 (1965).

[7] H. Saito, M. Hirata, and T. Horiuchi, J. Phys. Soc. Japan Suppl. **18**, 246 (1963).

[8] T. Tanaka and Y. Inuishi, J. Phys. Soc. Japan **19**, 167 (1964).

[9] G. D. Watkins, in *Proceedings of the 7th International Conference on the Physics of Semiconductors, Paris, 1964* (Dunod Cie., Paris, 1965), p. 97.

EXPERIMENTAL METHODS

The samples were made from discs cut from silicon ingots doped with phosphorus to resistivities (at 300°K) of about 1, 10, and 100 Ωcm. Eight-arm bridge samples were made from the discs using an ultrasonic cutter. The samples were polished with Durite paper, and finally etched in CP-4 solution. Nonrectifying gold contacts were put on the samples using an ultrasonic hot bonding technique. A metal cryostat capable of achieving sample temperatures of $\lesssim$10°K by conduction through a copper finger was used in the irradiations. The Hall coefficient and conductivity were measured using standard dc techniques. The samples were irradiated in the ⟨111⟩ direction with 45-MeV electrons from the variable energy (10–80 MeV) RPI linear electron accelerator. All data were taken with the sample enclosed in the light-tight vacuum container of the cryostat.

EXPERIMENTAL RESULTS

The carrier concentrations and mobilities of the *n*-type Si samples doped with different amounts of phosphorus atoms are reduced by 45-MeV-electron bombardment. A typical response of a sample during bombardment at 80°K is shown in Fig. 1, in which $1/R_He$ ($\approx$carrier concentration) and R_H/ρ (Hall mobility) are plotted versus the integrated flux of electrons, where R_H is the Hall coefficient and ρ is the resistivity. There was no significant difference in the measured carrier removal rate for all samples irradiated at $\approx$80°K with 45-MeV electrons irrespective of the initial resistivity (1, 10, and 100 Ω cm). In all cases the carrier removal rate was of order 1 cm^{-1}, even though the carrier concentrations before irradiation differed by a factor of $\sim$100. In the pulled crystals the oxygen concentrations were all of the same order of magnitude $5–10\times10^{17}$ cm^{-3} as determined by the intensity of the 9-μ infrared band.

One pair of samples (one floating-zone, 10 Ω cm, and one pulled, 11 Ω cm) was irradiated to a total integrated

flux of 3×10^{14} e/cm^2 at 15°K. Because of the high resistivity of the samples at low temperature, the measurements were only made at or above the temperature of liquid nitrogen. After irradiation, the samples were warmed up and the changes in properties of the samples due to irradiation were measured. The carrier removal rate of the pulled crystal was about the same as that of a 10-Ω cm sample irradiated at 80°K but the removal rate in the floating-zone (FZ) sample was about 30% less in comparison with the 10-Ω cm FZ sample irradiated at 80°K.

Isochronal annealing experiments were carried out between 80 and 360°K using successive temperature pulses of 10-min duration. Measurements were made at 77°K after each anneal. In most cases the irradiation was continued until the carrier concentration was reduced by 30 to 80%. After the irradiation was stopped the carrier concentration continued to increase a small amount with a lifetime of ≈100 min. Annealing experiments were started on each of the irradiated samples only after the carrier concentration reached a constant value. There were some different features observed between pulled and FZ samples, an example being that the reciprocal mobility decreased in FZ samples, but increased in pulled crystals. The cause of these changes is unknown. With the cryostat[10] used for the particular experiment it was not possible to illuminate the samples with light in order to check whether or not trapping effects were causing these changes.

The reference values of conductivity and carrier concentration were those measured at 78°K just after completion of the irradiation. In all cases the first anneal was performed on the samples two to three hours after the bombardment was stopped. In the following representation, the fraction of damage remaining in carrier concentration is defined as

$$f(n)=\frac{(n_0-n)}{(n_0-n_r)},$$

where n_0 is the carrier concentration before irradiation, n_r is the carrier concentration after the irradiation, and n is the carrier concentration after an anneal for ten minutes at temperature $T(>77°K)$. The fraction of damage remaining in reciprocal mobility is defined as

$$f(1/\mu)=\frac{(1/\mu_0-1/\mu)}{(1/\mu_0-1/\mu_r)},$$

where $1/\mu_0$, $1/\mu_r$, and $1/\mu$ are the Hall mobility before irradiation, after irradiation, and after anneal at temperature $T(>77°K)$, respectively.

In Fig. 2 is shown a comparison of the annealing of

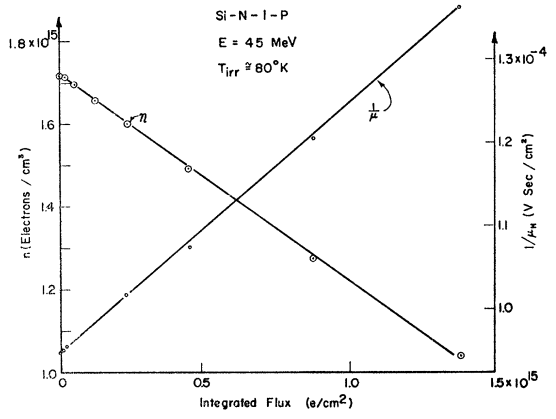

FIG. 1. Flux dependence of carrier concentration n and reciprocal Hall mobility $1/\mu$ for a phosphorous-doped (~1-Ω cm) silicon sample irradiated at 80°K with 45-MeV electrons.

[10] For experiments to detect trapping effects, light was introduced on the sample by a small flashlight bulb inserted inside the cryostat. The light would have caused a ≈10°C temperature rise in the sample and hence some possible annealing, and for this reason the light was not turned on.

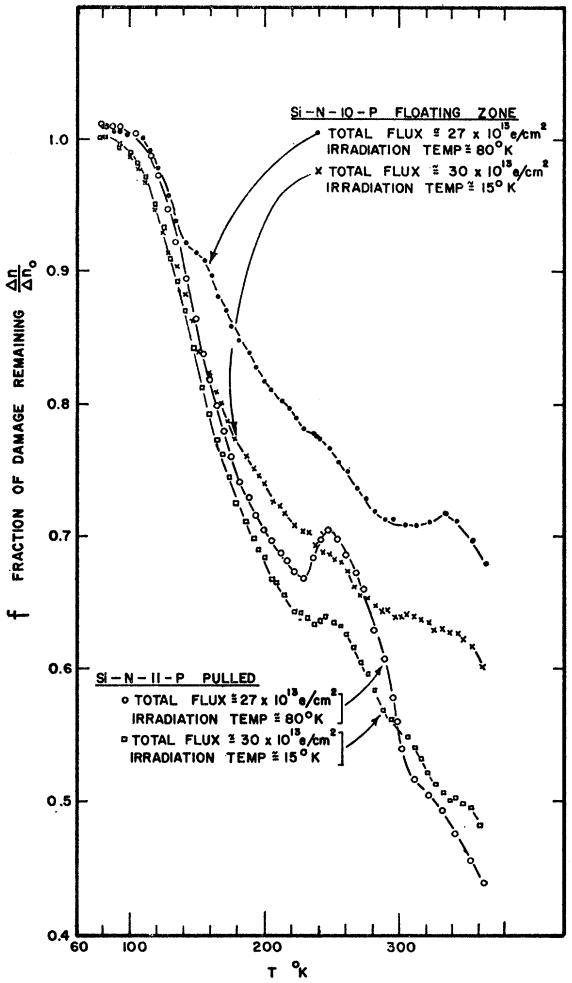

FIG. 2. Isochronal annealing of carrier concentration (fraction of damage remaining) $f(n)$ versus temperature for ~10-Ω cm pulled and floating-zone phosphorus-doped silicon after irradiation by 45-MeV electrons at 80°K and at 15°K.

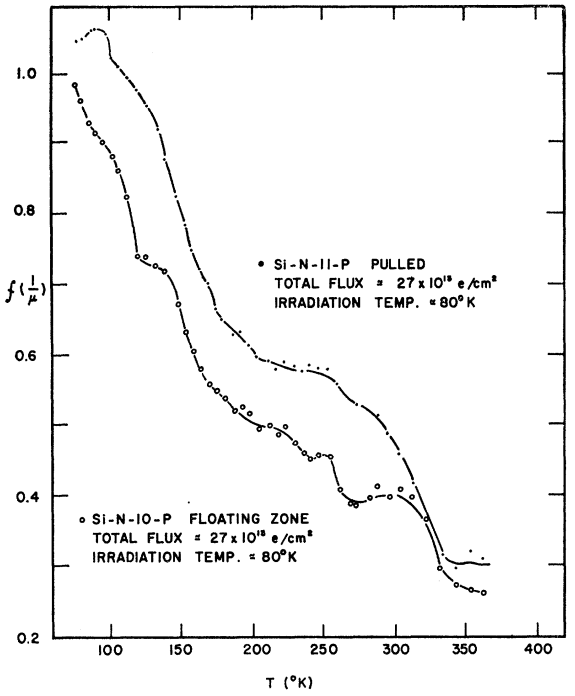

FIG. 3. Isochronal annealing of reciprocal Hall mobility (fraction of damage remaining) f $(1/\mu)$ versus temperature for $\approx$10-Ω cm pulled and floating-zone phosphorus-doped silicon after irradiation by 45-MeV electrons at 80°K.

the fraction of damage remaining in carrier concentration $f(n)$ versus temperature for two pairs of samples. In each pair, there is one floating-zone and one pulled silicon sample, both doped with roughly the same concentration of phosphorus ($\sim 3\times 10^{14}$ cm^{-3}). One pair was irradiated at a temperature of 80°K, and the other pair was irradiated at 15°K, both with approximately the same total integrated flux of electrons. The fraction of damage remaining in reciprocal mobility of one pair of samples irradiated at 80°K versus annealing temperature is shown in Fig. 3. The main differences between these two samples are the larger oxygen concentration in the pulled samples (factor $\sim$100) as mentioned above, and the higher density of dislocations in floating-zone crystals than in pulled crystals.

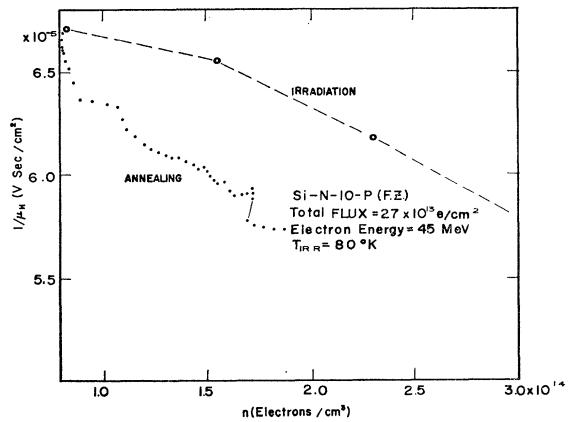

FIG. 4. Reciprocal Hall mobility $1/\mu$ versus carrier concentration n, during irradiation by 45-MeV electrons at 80°K and after 10-min anneals of 10-Ω cm phosphorus-doped floating-zone silicon.

In floating-zone samples, the annealing curves of the sample irradiated at 80°K have some structure which appears more pronounced in the sample irradiated with lighter dose. From Fig. 2 it can be seen that there appear to be three recovery stages in the 10-Ω cm floating-zone crystals irradiated at 80°K. These stages are located at 125, 160, and 260°K. However, there is no corresponding structure on the annealing curves of the 10-Ω cm floating-zone sample irradiated at 15°K. An annealing experiment with a 1-Ω cm floating-zone (P-doped) sample irradiated to a higher dose (14×10^{15} e/cm^2) showed only two annealing stages; one broad recovery stage from 100 to 200°K, and another at 260°K.

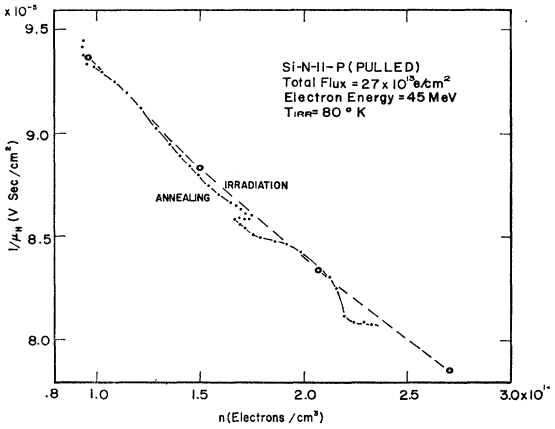

FIG. 5. Reciprocal Hall mobility $1/\mu$ versus carrier concentration n during irradiation by 45-MeV electrons at 80°K and after 10-min anneals of 11-Ω cm phosphorus-doped pulled silicon.

All pulled crystals exhibited three other annealing processes, located at about 100–200, 240, and 290°K, for both 80 and 15°K irradiations. However, the fraction of damage annealed out at the 240 and 290°K stages was smaller in the case of the 15°K irradiation than in that of the 80°K irradiation. The recovery stage at 240°K appears as a small reverse annealing process and is not a carrier trapping effect which has been found in irradiated p-type germanium. This was determined by illuminating with white light at 78°K, which would have indicated the presence of traps, if they existed. The recovery stage at 290°K in the pulled crystals was one of the main annealing processes for 80°K irradiation, in which about one-fifth of the total defect concentration was removed in 11-Ω cm samples. The two annealing stages at 240 (reverse annealing) and 290°K appear to be related to the oxygen atoms, since they have no counterpart for floating-zone silicon containing less dispersed oxygen.

In general, the number of defects annealed as determined from measurements of the carrier concentration in the pulled crystals appears to be higher than that in the floating-zone crystals in the temperature range 80–360°K, but the percent recovery in the Hall mobility is nearly the same for both FZ and pulled crystals. The experimental results given in Figs. 4 and 5 also show that the annealing curve is close to the irradiated curve for the pulled crystal, but this is not the case for the floating-zone sample in which the mobility anneals at a faster rate at lower temperature.

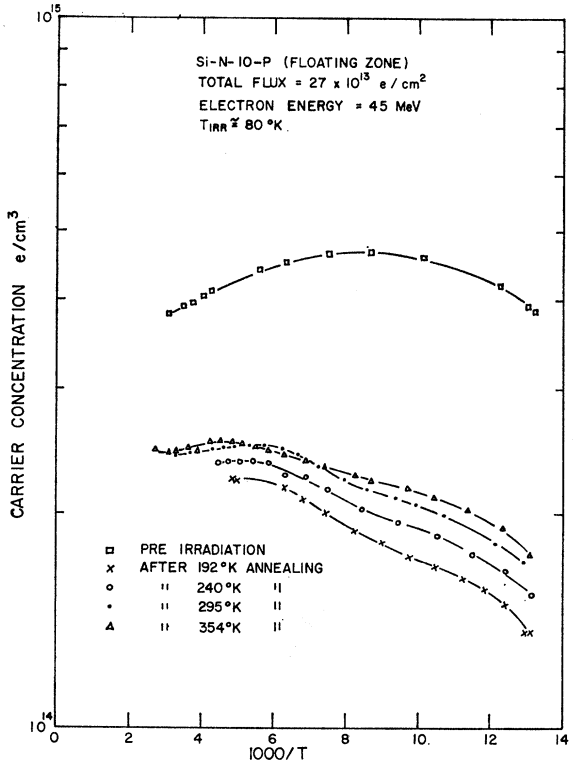

FIG. 6. Temperature dependence of carrier concentration of irradiated 10-Ω cm phosphorus-doped floating-zone silicon after various 10-min anneals at the temperatures indicated.

The temperature dependence of the carrier concentrations of one floating-zone sample and one pulled crystal after various anneals are plotted in Figs. 6 and 7, respectively. For the pulled crystal, there is a defect energy level located about 0.17 eV below the conduction band, which is associated with the oxygen vacancy complex (A center).[3,4] The method of Kitovskii, Mashovets, and Ryvkin[11] was used to compute the value of the energy level. The production rates of the A center during 80°K irradiations, estimated from the temperature dependence of carrier concentration after annealing to

[11] N. A. Kitovskii, T. V. Mashovets, and S. M. Ryvkin, Fiz. Tverd. Tela 4, 2849 (1962) [English transl.: Soviet Phys.—Solid State 4, 2088 (1964)].

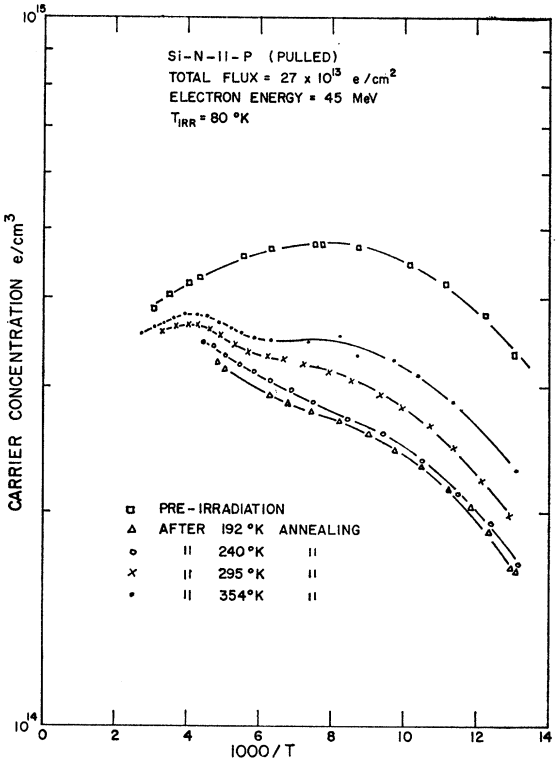

FIG. 7. Temperature dependence of carrier concentration of irradiated 11-Ω cm phosphorus-doped pulled silicon after various 10-min anneals at the temperatures indicated.

300°K, are about 0.2, 0.23, and 0.32 cm^{-1} for 1, 11, and 100 Ω cm, respectively, for pulled crystals. The production rate of the A center in the 11-Ω cm pulled crystal irradiated at 15°K is about 0.1 cm^{-1}. The production rates of deep levels (>0.2 eV from conduction band) in the pulled sample irradiated at 15°K were about 0.3 cm^{-1} but only ~0.1 cm^{-1} in the same resistivity sample irradiated at 80°K.

DISCUSSION OF RESULTS AND CONCLUSIONS

We can give some reasonable arguments to explain the difference between the annealing behavior of the pulled crystals and floating-zone crystals. Since the oxygen concentration in the pulled crystals is at least two orders of magnitude higher than in floating-zone crystals, one would expect that some influence of oxygen impurity on annealing behavior should appear from a comparison of the annealing results of two kinds of samples. The experimental data in Figs. 2, 3, 4, and 5 show that there were some clearly discernable differences in the recovery of electrical properties from 80 up to 350°K.

One may inquire whether there is some effect of oxygen impurity on the formation of defects at 80°K or whether there is only an effect on annealing. This dif-

ference cannot be determined from our data since the number of carriers removed and the number of scattering centers produced are roughly the same for both types of crystals. From G. D. Watkins'[9] spin resonance work, it is known that the negatively charged single vacancy in n-type Si becomes mobile below about 60°K. Also the formation rate of A centers for 4.5-MeV-electron irradiation at 80°K is the same as that at 273°K.[5] From these results, one may expect that there would be some difference between the radiation data of the two kinds of crystals. The possible explanation for the failure to observe a marked difference in our data is that the measurements of electrical properties are macroscopic in which only total carrier removal and scattering center change can be measured and no information about the nature of the individual defects can be obtained. Also the radiation-induced defects associated with oxygen impurity are only part of the total induced damage. If we also include the information gotten from the 15°K irradiation, (see Fig. 2) it seems reasonable to conclude that the oxygen impurity affects the formation of defects in an 80°K irradiation.

By comparing the data from 15 and 80°K irradiations, some conclusions may be made. The number of the defects causing the 240°K reverse annealing and 290°K annealing in pulled crystals are smaller during 15°K irradiation than during 80°K irradiation. Also the total number of A centers in the sample after irradiation at 15°K and anneal to 350°K in a 15°K irradiation is about a half of the value in an 80°K irradiation after 350°K anneal. The number of the defects associated with deep levels after 350°K annealing is higher for the lower temperature irradiation. In FZ samples the annealing rate of damage as measured by carrier concentration is more rapid in 15°K irradiation than in 80°K irradiation (see Fig. 2). These experimental facts suggest that the formation rates of some defects have temperature dependence, and/or indirectly, they suggest that some primary defects are mobile below 80°K.

It is possible that the defects which correspond to the annealing stage of 290°K in pulled crystal are formed by oxygen atoms and some primary radiation-induced defects, which are mobile below 80°K. The possibility that the 290°K annealing stage is related to oxygen-enhanced annealing is ruled out, since there is no corresponding annealing stage in the floating-zone samples.[12,13]

There are several possible explanations for the reverse annealing at about 240°K. One is that the dissociation of some complex defects produced favorably by 80°K irradiation occurs around 240°K, with the fragments individually forming stable defects with some imperfections (most probably oxygen atoms) existing in the pulled crystal only, which are able to trap carriers at liquid-nitrogen temperature. The dissociating defects might exist in the floating-zone crystal but there are not enough oxygen atoms to form the stable defects to trap carriers, such as the A center. Other different explanations are still possible, such as follows; this behavior may occur in the case of annealing of donors whose levels lie in the forbidden band close to bottom of the conduction band. These centers are then completely ionized in the sample at the temperature of liquid nitrogen and their annealing reduces the carrier concentration. Also this kind of defect has to be associated with oxygen atoms.

For comparison between the annealing behavior of low-energy- (e.g., 1 MeV) and high-energy- (e.g., 45 MeV) electron-irradiated n-type silicon, we can mention the annealing studies on the 80°K irradiation of silicon by low-energy electrons which can be found in the literature. Hill[14] observed in n-type Si irradiated with 4.5-MeV electrons at liquid-nitrogen temperature that (1) there were three recovery stages for 0.24-Ω cm crystal which were the same as we found, and (2) the annealing features observed in one sample with high resistivity (69 Ω cm) were similar to our data in FZ samples (see Fig. 2). Hill did not quote the oxygen concentration in his samples, so detailed comparisons are not possible. Wertheim and Buchanun[15] reported an annealing of mobility at 120°K in 1-MeV-electron-irradiated phosphorus-doped silicon (floating-zone crystal) with an integrated flux of 6.0×10^{14} e/cm^2. In our experiment, one annealing stage located at about 125°K was found, in which the damage recovery amounted to 10% in carrier concentration, but about 30% in $(1/\mu)$. This agrees qualitatively with the data of Wertheim and Buchanun. Novak[16] observed three annealing stages in 1-MeV-electron-irradiated N-type arsenic-doped Si (quartz crucible-high oxygen content), which were the same as we found. The percentage of recovery of damage in his samples in the temperature range 100 to 220°K was about 10% and is small in comparison with our result (see Fig. 2). This difference may suggest that some of the defects annealed out in this temperature range are caused by the high-energy electrons only.

Watkins found in his spin resonance work that (1) the divacancy with a nearby defect (possibily an interstitial) anneals out around 130°K,[9] (2) the number of E centers increases around 120°K and also around 280°K,[17] (3) the number of A centers increases around 200°K,[18] and (4) some unidentified spectra anneal out around 140°K.[17] His samples were irradiated at 4 or

[12] J. C. Corelli, Rensselaer Polytechnic Institute Progress Report 1965 (unpublished), from work sponsored by the National Aeronautics and Space Administration under Grant No. NsG-290.

[13] G. D. Watkins and J. W. Corbett, Phys. Rev. **138**, A543 (1965).

[14] D. E. Hill, Ph.D. thesis, Purdue Univerisity, 1959 (unpublished).

[15] G. K. Wertheim and D. N. Buchanun, J. Appl. Phys. **30**, 1232 (1959).

[16] R. Novak (private communication).

[17] G. D. Watkins (private communication).

[18] G. D. Watkins, J. W. Corbett, and R. M. Walker, J. Appl. Phys. **30**, 1198 (1959).

20°K with ~1- and 45-MeV electrons. It is not easy to correlate a macroscopic measurement with Watkins' measurements because there are so many different defect centers observed in the latter, even in the case of low-energy electron irradiation.

In FZ samples, the annealing of damage as measured by the reciprocal mobility is more rapid than in carrier concentration. The source causing this is unknown. It is possible that the dislocations in the samples play an important role for this phenomena, since the dislocations belong to one kind of the major imperfections in FZ crystals.

The production rate of the A center which we obtain in pulled crystals irradiated by 45-MeV electrons at 80°K is comparable to that measured by Watkins[17] from spin resonance using the same energy electrons at room temperature. Ramdas and Fan[5] also have reported that the production rate of the 12-μ band (A center) at 80°K is not significantly different from the production rate at 300°K in 4.5-MeV electron irradiations. These findings are different from the results[15,17] of 1-MeV electron irradiation, in which the production rate of the A center at liquid-nitrogen temperature is about an order of magnitude less for pulled silicon irradiated at room temperature. Because of the close similarity of our data and the results of Hill,[14] Novak,[16] and Wertheim,[15] we conclude that a large number of defects produced by 45-MeV electrons at lower temperatures are similar to the defects found in low-energy electron irradiations. In other words, low-dose 45-MeV electron irradiations will not produce a larger number of high-order defects, such as clusters, as was originally anticipated; but instead, larger numbers of simple defects are produced.

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Fine Structure of the Infrared Absorption and Emission Spectra of Cu^{2+} in ZnS and CdS Crystals

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Near-infrared absorption and emission spectra of Cu^{2+} as a substitutional impurity in ZnS and CdS crystals recorded at low temperatures are found to exhibit a pronounced fine structure. The optical transitions occur between energy levels which result from a splitting of the Cu^{2+} ground state by a crystal field of tetrahedral symmetry and the spin-orbit interaction. A small contribution of lower symmetry—possibly produced by Jahn-Teller effect—and an interaction of the center with vibration modes of the host lattice account for the occurrence of numerous lines. Crystal field and spin-orbit parameters were calculated for Cu^{2+} in ZnS and CdS crystals.

IT is well known, that copper can act as an activator for luminescence in ZnS and CdS phosphors. Several emission bands in the visible[1] and near-infrared[2] spectral regions could be correlated to centers containing at least one Cu ion. Particularly detailed experiments have been performed to understand the chemical and electronic structure of the center leading to the emission bands near 1.5μ and to the corresponding absorption peaking at about 1.3μ.[3–6] There is evidence by both chemical[5] and radioactive[6] methods that the incorporation of uncompensated copper on cation sites causes these infrared emission and absorption bands. As uncompensated copper forms a doubly charged ion with electron configuration $3d^9$ the system of electronic levels as well as the radiative transitions between them should be explainable by means of crystal field theory. This has been shown already for absorption in copper-

[1] N. Riehl, Ann. Physik **29**, 636 (1937). S. Rothschild, Trans. Faraday Soc. **42**, 635 (1946).
[2] G. F. J. Garlick and M. J. Dumbleton, Proc. Phys. Soc. (London) **B67**, 442 (1954); P. F. Browne, J. Electron. **2**, 1 (1956).
[3] I. Broser and H.-J. Schulz, J. Electrochem. Soc. **108**, 545 (1961).
[4] H.-J. Schulz, Phys. Status Solidi **3**, 485 (1963).
[5] E. F. Apple and J. S. Prener, J. Phys. Chem. Solids **13**, 81 (1960).
[6] I. Broser and K.-H. Franke, J. Phys. Chem. Solids **26**, 1013 (1965).