

Characteristics of Neutron Damage in Silicon

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The production and annealing behavior of the divacancy and the A center in fission-neutron-irradiated silicon was studied by infrared absorption, using the 1.8-, 3.9-, and 12- μ bands. The production rate of the divacancy was found to be high, about 5.7 cm^{-2} , and to be enhanced by the presence of boron ($\sim 2 \times 10^{17}$ atoms per cm^3), but not by the presence of oxygen ($\sim 1 \times 10^{18}$ atoms per cm^3). The annealing of divacancies in neutron-irradiated Si required an activation energy of 1.25 eV, as in electron-irradiated Si, indicating that most of the divacancies were removed by diffusion to sinks. The annealing results also indicate that the local defect concentrations in the damaged regions can be as high as $\sim 10^{20}$ defects cm^{-3} , in which the divacancies still retain their individual properties as far as their infrared absorption and annealing properties are concerned. The production rate of the A center was found to be extremely low. The near-edge absorption band was also studied. About 95% of the near-edge band disappeared upon annealing in the same broad temperature range as did the divacancies. From these results, it was concluded that the majority of the total volume in localized damage regions produced by the fission-neutron irradiation of silicon is rich in divacancies and is still crystalline.

INTRODUCTION

FAST-NEUTRON damage of silicon is expected to introduce localized damage regions because of the high energy of the primary knock-ons. Many experiments have been carried out on this subject. One interesting experimental observation from electrical property studies^{1,2} of fast-neutron-irradiated silicon was a rapid decrease in carrier mobility. This was ascribed to large disordered regions caused by fast neutrons. Truell's ultrasonic attenuation measurements³ on fast-neutron-irradiated silicon were consistent with the presence of damaged regions having radii between 100 and 2700 Å. Stein⁴ found that the introduction rate of neutron damage as monitored by carrier lifetime did not exhibit the temperature dependence expected for close pair production. He also found that the annealing extended over a broad temperature range from 60 to 220°C with no distinct annealing stage. A growth of the 12- μ band (associated with the A center) in neutron-irradiated pulled silicon upon annealing to 275°C was reported by Whan.⁵ She attributed the growth of the band to evolution of additional vacancies from defect clusters produced by neutrons. She also mentioned that the production rate of the A center was extremely low in neutron-irradiated silicon. Curtis⁶ reported that no observable dependence of lifetime degradation on oxygen and n -type dopants was found in neutron-irradiated silicon. Recently, Nakashima and Inuishi⁷ reported that the carrier removal rate in p -type silicon measured by the Hall effect was independent of oxygen and dopants during neutron irradiation. The above experimental results are consistent with the concept of

localized damage regions produced in silicon by neutrons, but they do not disclose the structure of the damaged region.

There have been some experimental results concerning the structure of the damaged regions in silicon. By using electron microscopy, Parsons⁸ observed similar damaged regions in both silicon and germanium after 100-keV oxygen ion bombardment. In addition, the damaged regions in germanium were amorphous⁹ and the average diameter of the images was about 30 Å in silicon compared with 65 Å in germanium. Recently, Bertolotti¹⁰ reported that the etch pits in neutron-irradiated silicon were different in structure from those in silicon bombarded with 40-keV antimony ions. From this, he suggested that the damaged regions in neutron-irradiated silicon might still be crystalline.

The range of primary knock-ons in a crystal indicates the extent of the damaged regions. Since the average energy of fission neutrons is about 2 MeV, the average energy transmitted to a silicon atom per neutron collision is about 100 keV.¹¹ The range of this energetic silicon atom estimated from Lindhard's theory¹² is about 2000 Å. With such a large range, it seems likely that the primary knock-on produces a damage region which may have a relatively high defect density but which still remains crystalline. This is consistent with Bertolotti's suggestion. Therefore, a study of simple defects in neutron-irradiated silicon may give important information about the structure of the damaged regions.

The divacancy in electron-irradiated silicon has been extensively studied by electron paramagnetic resonance and infrared absorption.^{13,14} It may be produced directly

⁸ J. R. Parsons (private communication).

⁹ J. R. Parsons, *Phil. Mag.* **12**, 1159 (1965).

¹⁰ M. Bertolotti, in *Radiation Effects in Semiconductors*, edited by F. L. Vook (Plenum Press, Inc., New York, 1968), p. 311.

¹¹ H. J. Stein, *J. Appl. Phys.* **38**, 204 (1967).

¹² J. Lindhard, M. Scharff, and H. E. Schiøtt, *Kgl. Danske Videnskab. Selskab, Mat. Fys. Medd.* **33**, No. 14 (1963).

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

¹⁴ L. J. Cheng, J. C. Corelli, J. W. Corbett, and G. D. Watkins, *Phys. Rev.* **152**, 761 (1966).

¹ G. K. Wertheim, *Phys. Rev.* **111**, 1500 (1958).

² E. Sonder, *J. Appl. Phys.* **30**, 1186 (1959).

³ R. Truell, *Phys. Rev.* **116**, 890 (1959).

⁴ H. J. Stein, *J. Appl. Phys.* **37**, 3382 (1966).

⁵ R. E. Whan, *J. Appl. Phys.* **37**, 3378 (1966).

⁶ O. L. Curtis, Jr., *IEEE Trans. Nucl. Sci.* **NS-13**, 33 (1966).

⁷ K. Nakashima and Y. Inuishi, in *Radiation Effects in Semiconductors*, edited by F. L. Vook (Plenum Press, Inc., New York, 1968), p. 162.

TABLE I. Production of the absorption bands by neutrons at 50°C.

Sample	Dopant and its concentration (atoms/cm ³)	Oxygen content (atoms/cm ³)	Total neutron flux (10 ¹⁶ ·n/cm ²)	Absorption coefficient at peak (cm ⁻¹)				I ^c
				1.8μ ^a	3.9μ ^a	12μ ^b	Near-edge ^a at 1.8μ	
Si-N-500 (FZ)	P, ~1×10 ¹⁸	~10 ¹⁶	0.34 1.03	0.28 0.73			0.44	
Si-P-43 (pulled)	Ga, ~1×10 ¹⁴	~1×10 ¹⁸	2.05 3.08 4.10	1.48 2.25 2.94		0.23	1.15 1.75 2.17	
Si-P-10 (FZ)	B, ~5×10 ¹⁴	~10 ¹⁶	3.08 4.10	2.24 2.88			1.55 1.99	
Si-P-10-0 (pulled)	B, ~5×10 ¹⁴	~3×10 ¹⁷	4.10	2.89		0.10	1.89	
Si-P-0.1 (FZ)	B, ~2×10 ¹⁷	~10 ¹⁶	1.03 2.05 3.08 4.10	0.33 0.66 2.42 3.26	~1.7 ^d ~1.5 ^d			~1.2 ~1.4 2.58 3.30

^a Measured at 300°K.^b Measured at 77°K.^c Defined as (absolute coefficient)_{1.8μ} + (absolute coefficient)_{3.9μ} (width of 3.9-μ band/width of 1.8-μ band).^d The uncertainty is due to inaccuracy in determination of the background absorption caused by free carriers.

as a multiple-displacement defect in a radiation damage event, or indirectly by the combination of two vacancies. In electron-irradiated silicon the divacancies are removed by diffusion to sinks, which requires an activation energy of 1.25 eV.¹⁴ It is known that the 1.8-, 3.3-, and 3.9-μ bands in silicon are associated with the divacancy¹⁴ and that their appearance depends on the position of the Fermi level. According to Fan and Ramdas,¹⁵ the Fermi level must be below $E_c - 0.21$ eV, above $E_c - 0.21$, and below $E_v + 0.25$ eV for the appearance of the 1.8-, 3.3-, and 3.9-μ band, respectively.

Another well-known defect in irradiated silicon is the *A* center (also designated Si-Bl center) which is formed when a vacancy is trapped by an oxygen atom.¹⁶⁻¹⁸ The vibration of the oxygen atom in the *A* center causes an absorption band at 12μ.¹⁹ This defect is relatively stable and disappears upon annealing above 573°K.¹⁸⁻²⁰ Since interstitial oxygen in silicon acts as an effective trap for mobile vacancies, the *A* center can be used as a monitor for the production of single vacancies capable of long-range motion during room-temperature irradiation. Also, it can be used to monitor the vacancies either as they are evolved from other defects or become mobile during heat treatment.

There is another important but less known radiation-induced band in silicon, namely, the near-edge absorption.^{14,15} The intensity of this absorption decreases monotonically with increasing wavelength above the absorption edge. The origin of the absorption is unknown. Fan and Ramdas¹⁵ first suggested that the absorption was due to the modification of the band edge

caused by the presence of defects. From their photoconductivity experiments on 1.5- and 45-MeV electron-irradiated *n*-type silicon, Kalma and Corelli²¹ concluded that the near-edge absorption arose only from the defect complexes produced by 45-MeV electrons. They suggested that the complexes were clusters of vacancies, interstitials, and impurity atoms which locally destroy some of the lattice periodicity thereby creating a continuum of allowed energy states in the forbidden gap. Therefore, a study of the near-edge band in neutron-irradiated silicon may give some information the defect clusters.

In the present experiments, the production and annealing behavior of the divacancies and the *A* centers in fission-neutron-irradiated silicon was studied by infrared absorption using the 1.8-, 3.9-, and 12-μ bands. In addition, the near-edge absorption was monitored. The results indicate that the majority of the total volume in localized damage regions produced by the fission neutron irradiation of silicon is rich in divacancies and is still crystalline.

EXPERIMENTAL PROCEDURE

Rectangular samples ($\frac{3}{4}$ in. × $\frac{3}{8}$ in. × $\frac{1}{4}$ in.) were cut from commercially available silicon crystals which had been grown by pulling or by the floating-zone technique. The properties of the samples are listed in Table I. The oxygen concentrations were estimated from the intensities of the 9-μ absorption band caused by the vibration of interstitial oxygen atoms.²² The sample surfaces which transmitted the infrared light were polished with diamond compound.

A Perkin-Elmer model No. 21 infrared spectrometer was used to measure the absorption spectra. Most of the measurements were carried out at room tempera-

¹⁵ H. Y. Fan and A. K. Ramdas, *J. Appl. Phys.* **30**, 1127 (1959).¹⁶ G. D. Watkins, J. W. Corbett, and R. M. Walker, *J. Appl. Phys.* **30**, 1189 (1959).¹⁷ G. Bemski, *J. Appl. Phys.* **30**, 1195 (1959).¹⁸ G. D. Watkins and J. W. Corbett, *Phys. Rev.* **121**, 1001 (1961).¹⁹ J. W. Corbett, G. D. Watkins, R. M. Chrenko, and R. S. McDonald, *Phys. Rev.* **121**, 1015 (1961).²⁰ J. C. Corelli, G. Oehler, J. F. Becker, and K. J. Eisentrant, *J. Appl. Phys.* **36**, 1787 (1965).²¹ A. H. Kalma and J. C. Corelli, in *Radiation Effects in Semiconductors*, edited by F. L. Vook (Plenum Press, Inc., New York, 1968), p. 153.²² W. Kaiser and P. H. Keck, *J. Appl. Phys.* **28**, 882 (1957).

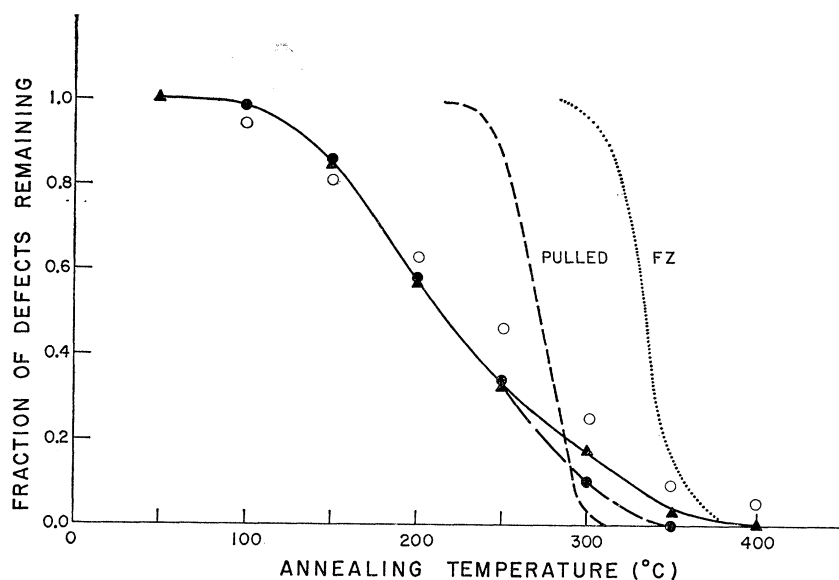


FIG. 1. 15-min isochronal annealing of the 1.8- μ band in pulled (\bullet) and in floating-zone (\blacktriangle) silicon, and of the near-edge absorption (\circ) in floating-zone silicon irradiated with a total flux of 4×10^{16} fast neutrons per cm^2 . The dashed and dotted lines represent the isochronal annealing of the divacancy in pulled and in floating-zone Si after electron irradiation (Refs. 13 and 14).

ture. For the measurements at liquid-nitrogen temperature, a glass cryostat was used. The annealing experiments were done in a temperature-controlled oil bath for temperatures below 250°C and in an oven for higher temperatures.

Irradiations were done inside a water-cooled annulus of enriched uranium fuel at 50°C in the *E-3* hole of the NRX reactor at Chalk River Nuclear Laboratories. The fast-neutron flux was $5.7 \times 10^{12} n \text{ cm}^{-2} \text{ sec}^{-1}$, measured by the $\text{Ni}^{58}(n,p)\text{Co}^{58}$ reaction using an effective cross section of 90 mb for fission neutrons.²³

EXPERIMENTAL RESULTS

A. Defect Production

The peak absorption for the 1.8-, 3.9-, and 12- μ bands of neutron irradiated silicon is listed in Table I. The intensity of the 1.8- μ band at room temperature increased linearly with fluence in all samples except those with high boron content. The presence of oxygen had no significant effect on the intensity of the band. This agrees with previous results of Fan and Ramdas. From the known divacancy concentration (measured by EPR)²⁴ and the intensity of the 1.8- μ band (measured at room temperature)¹⁴ in samples irradiated with 45-MeV electrons at room temperature, it was possible to relate the magnitude of the absorption to the divacancy concentration. The measured increase in absorption with fission neutron irradiation corresponds to a divacancy production rate of 5.7 cm^{-1} , or 38 divacancies per scattered neutron, assuming a scattering cross section of 3 b.²⁵ It should be noted that the absolute value of this production rate may be in error

²³ A. W. Boyd, H. W. J. Connor, and J. J. Pieroni, Atomic Energy of Canada Ltd. Report No. AECL 2203 (1965).

²⁴ J. W. Corbett and G. D. Watkins, Phys. Rev. **138**, A555 (1965).

²⁵ R. J. Howerton, University of California, Lawrence Radiation Laboratory Report No. UCRL-5351, Part II, 1958 (unpublished).

by as much as 50%, because of the inaccuracy of the flux measurements in both electron and neutron irradiation. However, the relative values among all the measurements reported in this paper are only in error by about 5%. The intensities of the 1.8- and 3.9- μ bands in the samples of high boron content were not linearly dependent on the fluence because of the change in Fermi level, as has previously been reported.^{14,15}

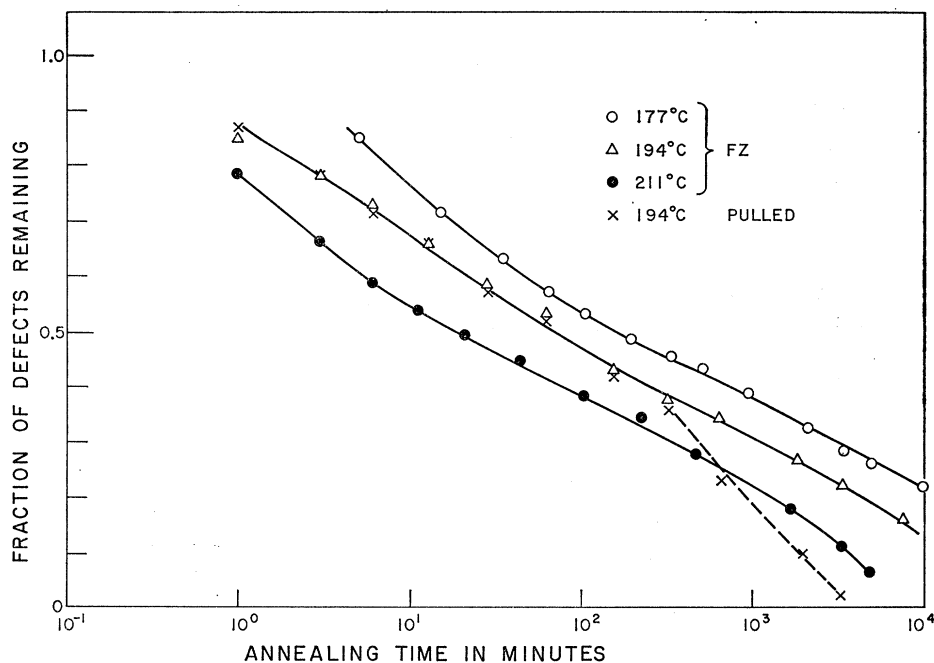
The production rate of the *A* center in silicon by irradiation depends on the oxygen content. From Table I it is noticed that the production rate of the 12- μ band by the neutron irradiation of pulled silicon is extremely low, which agrees with the previous results of Whan.⁵ Assuming the same oscillation strength for oxygen at an *A* center (12- μ band) as for oxygen at an interstitial site (9- μ band), the production rates of the *A* center by fission neutrons in the pulled samples with 3×10^{17} and 1×10^{18} oxygen atoms cm^{-3} were estimated to be 0.14 and 0.43 cm^{-1} , respectively. The corresponding ratio of production rates of divacancies to that of *A* centers is 40 and 13. These numbers are remarkably higher than the value 0.3 measured by EPR in pulled silicon irradiated with 52-MeV electrons.²⁴

The intensity of the near-edge absorption at 1.8 μ measured at room temperature increased linearly with fluence (see Table I). There was no significant difference between the measurements at 1.8 μ and at other wavelengths as far as their fluence dependences were concerned. The presence of oxygen had no significant effect on the intensity of this absorption, which differs from the electron irradiation case.¹⁴

B. Defect Annealing

Figure 1 shows the 15-min isochronal annealing of the 1.8- μ band and the near-edge absorption in neutron-irradiated silicon in comparison with the annealing of the divacancies in electron irradiation studies. There

FIG. 2. Isothermal annealing of the 1.8- μ band in floating-zone silicon irradiated with a total flux of 4×10^{16} neutrons cm^{-2} and in pulled silicon ($\sim 1 \times 10^{18}$ oxygen atoms cm^{-3}) irradiated with a total flux of 2×10^{16} neutrons cm^{-2} .



was always a small amount (3~5%) of the near-edge band remaining after the complete annealing of the divacancies. This remainder was reduced slightly after annealing 15 min at 500°C.

It was found also that the 12- μ band in a pulled sample (Si-P-10-0) irradiated with 4.1×10^{16} neutrons cm^{-2} increased gradually up to a factor of about 4 during the annealing up to 250°C, which agrees with the results of Whan.⁵ The 12- μ band then disappeared upon annealing at a temperature around 340°C.

Figure 2 shows the isothermal annealing of the 1.8- μ band in neutron-irradiated floating-zone samples (Si-P-10) at 177, 194, and 211°C. The kinetics of the annealing were found to be complicated, which differs from the simple exponential decay with time that was observed in electron-irradiated Si.¹⁴ It was found, by using the cross-cut method,²⁶ that the activation energy for the last 85% of the annealing process was between 1.23 and 1.28 eV. This value agrees closely with the value (1.25 eV) obtained from electron irradiation studies.¹⁴ Figure 2 also shows an isothermal annealing of the 1.8- μ band at 194°C for a pulled sample (Si-P-43). At first, the annealing followed closely the corresponding annealing of the 1.8- μ band in the floating-zone sample. Then the annealing rate in the pulled samples became markedly larger when the fraction of defects remaining was about 0.4. It was found that the later part of the annealing in the pulled sample did have an exponential decay in time.

²⁶ A. C. Damask and G. J. Dienes, *Point Defects in Metals* (Gordon and Breach, Science Publishers, Inc., New York, 1963), p. 146.

DISCUSSION AND CONCLUSIONS

A. Divacancy Production

For a 100-keV primary knock-on in silicon, only about 40 keV is spent in displacement events with the remainder lost to electron excitation.¹¹ Assuming that the production of each displacement requires twice the threshold energy of 13 eV,²⁷ as in the Kinchin and Pease model,²⁸ the total number of displaced atoms per primary knock-on is 1540. This number will be too high since neither the effect of crystal structure nor the spontaneous recombination of defects has been included. However, the effect of spontaneous recombination has been estimated for metals by Beeler²⁹ using the computer-simulation method. According to his results, the average probabilities that displacements caused by 5–20-keV primary knock-ons in α -iron, tungsten, and copper are stable against recombination at 0°K are 0.13, 0.15, and 0.10, respectively. These estimates are consistent with the experimental results of Swanson and Piercy,³⁰ who reported that the number of Frenkel pairs produced in Al per scattered fission neutron at 4°K was about 130. Because the atomic number of aluminum is similar to that of silicon, the spontaneous recombination is expected to reduce the total number of displacements in silicon to about 150–300 per neutron collision. For room-temperature irradiation, the simultaneous annealing of single vacancies and interstitials

²⁷ J. J. Lofenski and P. Rappaport, *Phys. Rev.* **111**, 432 (1958).

²⁸ G. H. Kinchin and R. S. Pease, *Rept. Progr. Phys.* **18**, 1 (1955).

²⁹ J. R. Beeler, Jr., *Phys. Rev.* **150**, 470 (1966).

³⁰ M. L. Swanson and G. R. Piercy, *Can. J. Phys.* **42**, 1605 (1964).

which are mobile³¹ should reduce this number considerably. Since the room-temperature irradiation produced 38 divacancies per scattered neutron, it is clear that a significant fraction of the defects produced in silicon during fission neutron irradiation are in the form of the divacancies.

Because the 1.8- and 3.9- μ bands were simultaneously observed in the samples (Si-P-0.1) with high boron concentration, both these bands, which are thought to arise from different charge states of the divacancy, should be considered in estimating the concentration of divacancies. Assuming the oscillator strengths of the two bands are the same and the total absorption is equal to their peak-absorption coefficient times their bandwidth, the sum of the total absorption of the two bands should correspond to the total number of divacancies produced. In the last column of Table I, the "equivalent" absorption is given, which corresponds to the peak absorption of the 1.8- μ band if all the divacancies in the high boron samples absorbed energy of this band. The bandwidths used to obtain the "effective" absorption coefficient were 0.16 and 0.076 eV for the 1.8- and 3.9- μ bands, respectively. It is clear, from Table I, that the equivalent absorption coefficient in the samples of high boron concentration was larger than the coefficient of the 1.8- μ band in all the other samples with the same neutron dose. Thus, the presence of boron atoms enhances the production rate of the divacancy. Also, the increase due to the presence of 2×10^{17} boron atoms per cm^3 was about 2.7×10^{16} divacancies per cm^3 , for the dose of 3.08×10^{16} , and $4.1 \times 10^{16} n \text{ cm}^{-2}$. It seems to be a saturation effect with increasing neutron dose, although the error in the increments is large. From his EPR experiments, Watkins has suggested that interstitials in *p*-type silicon can be trapped by substitutional group-III impurities.³¹ This trapping would explain both the greater divacancy production due to the presence of boron and the saturation effect. The result implies that the interstitials produced in silicon by neutron irradiation can escape from the locally damaged regions and a significant portion of the "free" interstitials are trapped by boron atoms. Assuming that the saturation effect occurs at the dose of $3 \times 10^{16} n \text{ cm}^{-2}$ at which every boron atom has trapped one interstitial, and one extra divacancy is present for every two trapped interstitials, the measured saturation value of the enhancement implies that about one-third of the total vacant sites are in the form of divacancies. This estimate is very rough, but it does support the argument mentioned in the last paragraph, that a significant fraction of the defects in neutron-irradiated silicon are in the form of divacancies. At present, it is very difficult to argue how large the frac-

tion really is. It is believed that there should also be an appreciable fraction of the vacant sites in groups larger than divacancies.

Because the presence of oxygen has no significant effect on the production rate of the divacancies, it is likely that oxygen is not an effective trap for the interstitials at room temperature.

B. A Center Production

The extremely low production rate of *A* centers during neutron irradiation implies that few vacancies are able to migrate far enough to meet the oxygen atoms. A significant portion of the defects formed during neutron irradiation should be single vacancies. The single vacancies are highly mobile at room temperature and the binding energy of the divacancy in silicon is quite high, $\lesssim 1.7$ eV. Therefore, the result indicates that neutron irradiation produces a localized vacancy concentration which is significantly higher than the oxygen concentration.

C. Annealing Behavior

From Fig. 1 it is clear that the number of divacancies in neutron-irradiated silicon starts to decrease when annealing at a much lower temperature than is required for the electron-irradiated case. Also the annealing in the neutron case extends over a broad temperature range from 100 to 350°C, in contrast to the distinct stage observed in the electron case.^{13,14} However, from the isothermal experiments, it is found that the activation energy for the annealing of the divacancies in neutron-irradiated silicon is the same as that for electron-irradiated silicon. Therefore, it is concluded that most of the divacancies in neutron-irradiated silicon diffuse to sinks or possibly cluster together. The number of jumps required for the divacancies to meet a sink can be estimated from the recovery rate by using the measured migration energy of 1.25 eV and the measured jumping frequency factor of $\sim 8 \times 10^{12} \text{ sec}^{-1}$ from electron irradiation studies.¹⁴ The "effective sink concentration," which is the product of the sink concentration per cm^3 and the effective capture volume in units of atomic sites, is approximately equal to $(J)^{-1} \times 5 \times 10^{22}$, where *J* is the number of jumps required for a particular divacancy to reach a sink. In Fig. 3, the estimated values for the effective sink concentration obtained from the data shown in Fig. 2 were plotted against the fraction of the divacancies remaining after annealing in comparison with the values obtained from electron irradiated studies.^{13,14} It is clear that the effective sink concentrations for the early part of the annealing in neutron-irradiated Si are much higher than those in electron-irradiated Si. The presence of oxygen enhances the annealing of all the divacancies in electron-irradiated

³¹ G. D. Watkins, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors; III, Radiation Damage in Semiconductors* (Dunod Cie., Paris, 1965), p. 97.

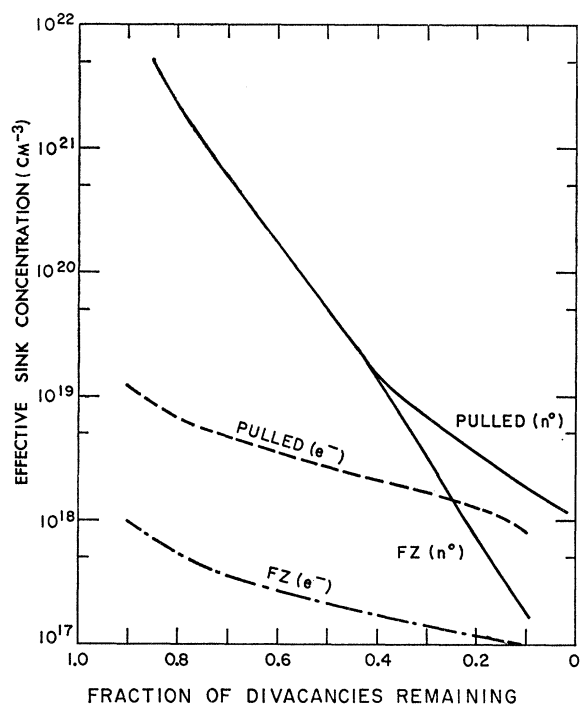


FIG. 3. The effective sink concentration per cm^3 plotted against the fraction of the divacancies remaining after successive anneals for electron- and neutron-irradiated Si.

silicon, but only affects the later part of the annealing in neutron-irradiated silicon. The effect of oxygen on the annealing of the divacancies becomes detectable when the local effective sink concentration is equal to the effective sink concentration of oxygen. From Fig. 3, the effective capture volume of oxygen for divacancies was found to be about 4 to 8 atomic sites. It is reasonable to say that the local sink concentrations can represent the local defect concentration in the damage regions as far as the divacancy annealing is concerned. Thus, from Fig. 3, it seems likely that the local defect concentration in certain portions of the damaged regions may be as high as about 10^{20} defects per cm^3 . In spite of this high concentration, the divacancies still retain their individual properties as far as infrared absorption and diffusion are concerned. Therefore they must be in regions that are still crystalline.

The growth of the $12\text{-}\mu$ band can be attributed to the evolution of vacancies from the damaged regions⁵ or to the migration of divacancies with their subsequent trapping at oxygen atoms.¹⁴ The gradual increasing intensity of the $12\text{-}\mu$ band is not inconsistent with the previous discussion, since the total measured concentration of A centers is about one order of magnitude smaller than the divacancy concentration. If a small fraction of the divacancies go to oxygen atoms at lower temperatures ($\approx 200^\circ\text{C}$), it will not appreciably influ-

ence the divacancy recovery kinetics but will be a measurable effect for the much lower A -center concentration.

About 95% of the near-edge band disappears upon annealing in the same broad temperature range as does the divacancy (see Fig. 1). Some enhancement of the latter part of the annealing of the near-edge band due to the presence of oxygen was also observed. If the annealing of the near-edge band represents the annealing of all the defect clusters including divacancies, the results indicate that most of the defect clusters produced by neutron irradiation disappear upon annealing in the temperature range from 100 to 350°C .

From the results of the present experiments, it is concluded that the majority of the total volume in localized damage regions produced by the fission neutron irradiation of silicon is rich in divacancies and is still crystalline. However, this conclusion does not exclude the existence of an amorphous structure in other parts of the damaged region produced by neutron irradiation of silicon.

D. Comparison with Electrical Properties

It is worthwhile to compare the present results with the data obtained from the measurements of electrical properties. Nakashima and Inuishi⁷ reported that a predominant defect in neutron-irradiated p -type Si had an energy level at $E_v+0.3$ eV. The singly positively charged divacancy also had an energy level at $E_v+0.3$ eV.³² If the divacancy were the main defect responsible for carrier removal, the carrier removal rate in Si by fission neutrons should be about 11.4 cm^{-1} in n -type Si and 5.7 cm^{-1} in p -type Si, according to the present result. The assumption that the divacancies in n -type Si are doubly negatively charged was used.³¹ However, the experimental value is $3\text{--}5$ cm^{-1} in n -type Si³³ and 9.1 cm^{-1} in p -type Si.¹ The presence of a space charge around the damage region may cause some of the difference, but it can only reduce the removal rate. In addition, the isochronal annealing curves on neutron-induced electrical property changes and lifetime degradation in n -types Si reported by Stein^{4,11,34} are different from the annealing of the divacancies and of the near-edge band in the present experiments. Therefore the production and annealing of the divacancies in neutron-irradiated silicon do not closely correlate with the change of electrical properties. It should be noted that presumably there are two kinds of divacancies in neutron-irradiated Si, one within the space-charge

³² L. J. Chang, in *Radiation Effects in Semiconductors*, edited by F. L. Vook (Plenum Press, Inc., New York, 1968), p. 143.

³³ J. W. Cleland, P. F. Bass, and J. H. Crawford, Jr., in *Proceedings of the Seventh International Conference on the Physics of Semiconductors; III, Radiation Damage in Semiconductors* (Dunod Cie., Paris, 1965), p. 407.

³⁴ H. J. Stein, *Phys. Rev.* **163**, 801 (1967).

region and the other outside of it. Both can be observed by means of absorption, but only the latter is observable in the electrical property measurements. In addition, it should be mentioned that the neutron fluences used in the present experiments were about three orders of magnitude higher than those used in the electrical measurements.

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Energy Dependence of Damage Recovery in *n*-Type Ge Electron-Irradiated at 4.2°K

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Damage produced in *n*-type Ge by electron irradiation partially anneals in two stages centered near 35 and 65°K. A small but constant reduction in conductivity is produced by bombardment with electrons with energies from 0.7 to 1.2 MeV. The fraction of the radiation-induced conductivity change recovered in each stage is observed as a function of electron energy for a sample with little residual damage and for one with large residual damage. The 65°K defect recovery increases with energy in both cases. This result is explained on the basis of radiation modification of 65°K defects. The 35°K defect recovery versus energy peaks in both cases. The dropoff at low energy is explained as being due to radiation annealing. The dropoff at high energies is explained as being due to the decrease in the modification of 65°K defects to 35°K defects in the sample with little residual damage. In the sample with considerable residual damage it is suggested that production of 35°K defects as primary defects decreases with increasing energy. Results are consistent with the model proposed by MacKay and Klontz with the addition that the 65°K defect can be modified to the 35°K defect by ionization of one of the two electrons trapped by the 65°K defect.

INTRODUCTION

STUDIES at Purdue University of heavily doped germanium bombarded with electrons at helium temperatures indicated no detectable damage in *p*-type specimens although, under the same conditions, damage was observed in *n*-type specimens. Annealing experiments on *n*-type specimens indicated prominent stages centered near 35 and 65°K with no further annealing up to 120°K. These and other observations led to the postulation of a model with the following characteristics¹⁻⁵:

(1) The 65°K defect is the primary one and consists of a close interstitial-vacancy (I-V) pair which must capture an electron to stabilize; there is further evidence for the capture of a second electron.^{2,4-6}

(2) The 35°K defect is produced by modification of 65°K defects and as a primary defect when permanent defects are present.

(3) Permanent defects are described as those which do not anneal below 120°K.

(4) Radiation annealing at helium temperatures was shown to exist and to increase in efficiency with decreasing incident electron energy.¹

Recent studies of isothermal annealing of the 65°K stage by Zizine⁷ shows an impurity dependence of the annealing rate. This is inconsistent with the close I-V pair model. An alternative is to allow for the mobility of the interstitial at low temperatures and its trapping at impurity sites.⁸ Details of such an alternative model remain to be evolved.

On the basis of the model of close I-V pairs, it was anticipated that the recovery in the combined stages would decrease with increasing electron energy since the probability of production of more widely separated I-V pairs would increase with energy. MacKay and Klontz's results were opposite to this, which was explained by the existence of radiation annealing.⁴ Call-

¹ J. W. MacKay and E. E. Klontz, *J. Appl. Phys.* **30**, 1269 (1959).

² J. W. MacKay and E. E. Klontz, *Radiation Damage in Solids*, (International Atomic Energy Agency, Vienna, 1963), Vol. III, p. 27.

³ E. E. Klontz and J. W. MacKay, *J. Phys. Soc. Japan* **18**, Suppl. III, 216 (1963).

⁴ J. W. MacKay and E. E. Klontz, in *Proceedings of the Seventh International Conference of the Physics of Semiconductors, Paris 1964*, edited by P. Baruch (Academic Press Inc., 1964), Vol. III, p. 12.

⁵ T. A. Callcott and J. W. MacKay, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors, Paris, 1964*, edited by P. Baruch (Academic Press Inc., 1964), Vol. III, p. 3.

⁶ T. A. Callcott and J. W. MacKay, *Phys. Rev.* **161**, 698 (1967).

⁷ J. Zizine, in *Proceedings of the Toulouse Symposium on Radiation Effects in Semiconductor Devices*, Toulouse, France, 1967 (to be published).

⁸ J. W. MacKay and E. E. Klontz, in *Proceedings of the Sante Fe Conference on Radiation Effects in Semiconductors, October 3-5, 1967*, edited by Frederick L. Vook (Plenum Press, Inc., New York, 1968).