Infrared Absorption Spectra of Oxygen-Defect Complexes in Irradiated Silicon*

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The infrared-active localized modes of oscillation of defect-oxygen complexes in electron-irradiated and neutron-irradiated silicon containing oxygen are reported. Behavior with heat treatment and relative intensities show the existence of a large number of complexes besides the Si-*B*1 center responsible for the line at 835 cm^{-1}. Neutron-irradiated silicon exhibits satellite lines close to the 835 cm^{-1} line when such specimens are annealed above 473°K. Isochronal-annealing studies indicate that the satellite centers are not associated with the Si-*B*1 center. Multiple-vacancy centers in association with dispersed oxygen may account for the satellites.

I. INTRODUCTION

OXYGEN as an impurity can easily enter the silicon lattice, as was first shown by Kaiser, Keck, and Lange.[1] For example, concentrations up to a maximum of $\sim 2\times 10^{18}$ cm^{-3} can be introduced if silicon is grown in an oxygen ambient under optimum conditions.[2] Silicon grown in quartz crucibles by the Czochralski process normally has $\sim 5\times 10^{17}$ cm^{-3} oxygen in a dispersed form.[1] In this form oxygen is electrically neutral but its presence can be deduced from an absorption band ~ 9 μ. It has been shown[3] that this absorption band arises from the infrared-active antisymmetric mode of oscillation of the "Si-O-Si" unit, where the two nearest-neighbor silicon atoms are bonded via the oxygen atom. Oxygen can also exist in silicon in more complex forms, e.g., heat treatment ~450°C of a crystal containing dispersed oxygen produces aggregations which are donor-like complexes.[4] These complexes exhibit both vibrational[5] and electronic excitation spectra.[6,7] Heat treatment at very high temperatures ~1000°C leads to the formation of "colloidal" quartz.[8]

An interesting feature of oxygen in silicon is its ability to form complexes with other imperfections which might be simultaneously present in the crystal. For example, lithium introduced into oxygen containing silicon forms donor complexes which exhibit characteristic electronic excitation spectra.[9] Chrenko, McDonald, and Pell[10] have recently studied the localized modes of lithium-oxygen complexes in silicon. The vibration spectra of such oxygen complexes are of particular interest from the point of view of localized modes in crystals, a subject which has received much attention in recent years.[11]

One of the most striking examples of a complex formed by oxygen with an imperfection is the Si-*B*1 center[12] in electron-irradiated silicon containing dispersed oxygen. This center, first observed by Bemski, Feher, and Gere[13] in their electron-paramagnetic-resonance (EPR) studies of electron-irradiated silicon, was shown by Watkins, Corbett, and Walker[14] to be a vacancy trapped at an oxygen site. The center also exhibits an infrared active mode of oscillation with an absorption band at 12 μ.[15,16] The 12-μ band has been observed with neutron irradiated silicon also.[16] Infrared spectra of heat-treated specimens of electron-irradiated as well as neutron-irradiated silicon have revealed the formation of a bewildering variety of defect-oxygen complexes.[15–18] The formation of the Si-*B*1 center when irradiations are performed below room temperature has been previously studied using both EPR[19] and the infrared absorption line at 12 μ.[17]

The object of the present paper is to give a detailed account of the vibration spectra of the oxygen-defect complexes in irradiated silicon, with a special emphasis

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[1] W. Kaiser, P. H. Keck, and C. F. Lange, Phys. Rev. **101**, 1264 (1956).
[2] W. Kaiser and J. Breslin, J. Appl. Phys. **29**, 1292 (1958).
[3] H. J. Hrostowski and R. H. Kaiser, Phys. Rev. **107**, 966 (1957).
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[5] W. Kaiser, H. J. Hrostowski, and C. D. Thurmond, Bull. Am. Phys. Soc. **5**, 61 (1960).
[6] H. J. Hrostowski and R. H. Kaiser, Phys. Rev. Letters **1**, 199 (1958).
[7] R. L. Aggarwal and A. K. Ramdas, Bull. Am. Phys. Soc. **9**, 61 (1964).
[8] W. Kaiser, Phys. Rev. **105**, 1751 (1957).
[9] R. L. Aggarwal, P. Fisher, V. Mourzine, and A. K. Ramdas, Phys. Rev. **138**, A882 (1965).
[10] R. M. Chrenko, R. S. McDonald, and E. M. Pell, Phys. Rev. **138**, A1775 (1965).
[11] See, for example, W. Hayes, Phys. Rev. **138**, A1227 (1965).
[12] G. D. Watkins, *Proceedings of the Symposium on Radiation Damage in Semiconductors, Paris, Royaumont, 1964.* (Dunod Cie., Paris, 1965), p. 97. It should be pointed out that the author has changed the designation of the oxygen-vacancy complex from Si-*A* in Ref. 14 to Si-*B*1 in Ref. 12.
[13] G. Bemski, G. Feher, and E. Gere, Bull. Am. Phys. Soc. **3**, 135 (1958). See also G. Bemski, J. Appl. Phys. **30**, 1195 (1959).
[14] G. D. Watkins, J. W. Corbett, and R. M. Walker, J. Appl. Phys. **30**, 1198 (1959). See also G. D. Watkins and J. W. Corbett, Phys. Rev. **121**, 1001 (1961).
[15] J. W. Corbett, G. D. Watkins, and R. M. Chrenko, Bull. Am. Phys. Soc. **5**, 25 (1960); J. W. Corbett, G. D. Watkins, and R. S. McDonald, *ibid.* **5**, 197 (1960); J. W. Corbett, G. D. Watkins, R. M. Chrenko, and R. S. McDonald, Phys. Rev. **121**, 1015 (1961).
[16] A. K. Ramdas and H. Y. Fan, Bull. Am. Phys. Soc. **5**, 197 (1960); H. Y. Fan and A. K. Ramdas, *Proceedings of the International Conference on the Physics of Semiconductors, Prague, 1960* (Academic Press Inc., New York, 1961), p. 309.
[17] A. K. Ramdas and H. Y. Fan, J. Phys. Soc. Japan **18**, Suppl. II, 33 (1963).
[18] J. W. Corbett, G. D. Watkins, and R. S. McDonald, Phys. Rev. **135**, A1381 (1964).
[19] G. D. Watkins, J. Phys. Soc. Japan **18**, Suppl. II, 22 (1963).

on the evolution and annealing of the complexes with heat treatment.

II. EXPERIMENTAL PROCEDURE

Silicon samples containing dispersed oxygen were irradiated with fast neutrons or with 4.5-MeV electrons. Fast-neutron irradiations have been performed at various times at the Oak Ridge National Laboratory, the Argonne National Laboratory or the Brookhaven National Laboratory. It was ensured that the sample temperature during irradiations in the reactor did not exceed ~50°C in order to prevent any inadvertent annealing during the irradiation itself. The electron irradiations were carried out at the Purdue Linear Accelerator which provides 4.5-MeV electrons, the sample being maintained at 273°K during the irradiations. The transmission measurements have been made with a double-pass Perkin-Elmer 112 spectrometer equipped with NaCl prism and a 112G spectrometer equipped with Bausch and Lomb gratings blazed at 8.5 μ and 12 μ, respectively. A glass optical cryostat[20] was employed for measurements with either liquid nitrogen or liquid helium as the coolant. The heat treatment for annealing studies were carried out in a vacuum furnace.

III. EXPERIMENTAL RESULTS

A. Results Prior to Heat Treatment

In Fig. 1 are presented the absorption spectra of an electron-irradiated crucible-grown silicon (curve B), neutron-irradiated crucible-grown silicon (curve C) and electron-irradiated floating-zone silicon (curve A). These measurements were made with a prism monochromator, using NaCl prism. The absorption peaks in B and C, collectively labeled "9-μ band," are observed even in unirradiated silicon crystals which have dispersed oxygen; the fine structure is observed at low temperatures.[21] The curve A, for floating-zone irradiated silicon, is characterized by the absence of the 9-μ band, a consequence of the absence or the near absence of dispersed oxygen. The broad absorption bands exhibited by the floating zone silicon are due to the multiphonon lattice bands observed in unirradiated specimens also.[22] As can be seen in Fig. 1, sharp lines

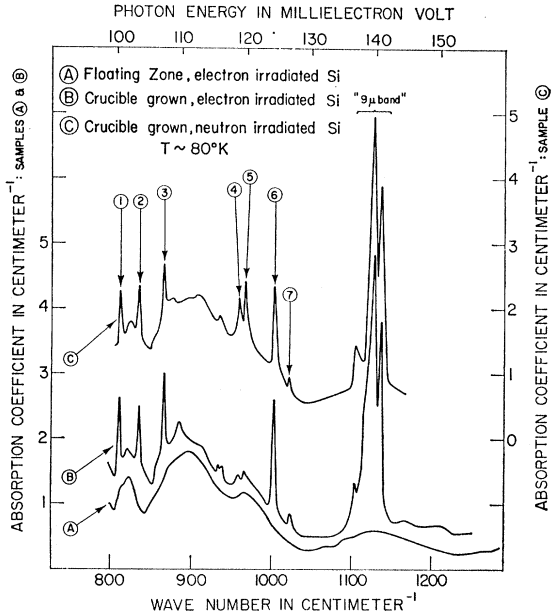

FIG. 1. The infrared active vibrations of defect-oxygen complexes in irradiated silicon. The samples B and C were obtained from the same ingot which was antimony-doped, crucible grown with a room temperature Hall coefficient in the range -30 cm³/C to -5 cm³/C. The sample B received a flux of 1.2×10^{18} electrons/cm² of 4.5-MeV electrons. The sample C received a fast neutron flux of 8×10^{17} neutron/cm² at the Oak Ridge National Laboratory. The sample A was obtained from a high resistivity floating zone silicon [$\rho(300°K)=8800\ \Omega$ cm] and received a flux of 6×10^{17} electrons/cm² of 4.5-MeV electrons.

labeled 1–7 are observed for *both* the electron- and the neutron-irradiated samples which also show the 9-μ band. They stand out clearly above the background due to the multiphonon lattice bands. The line 2, first reported by Corbett *et al.*,[15] has been designated by them as the 12-μ band since the maximum of absorption occurs at that wavelength at room temperature. In this paper we refer to the lines by their positions in wave numbers at the temperature of the measurement.

We have examined a large number of crucible-grown silicon samples obtained from various sources and subjected to either neutron or electron irradiation. The absorption spectra have been measured at room, liquid-nitrogen, and liquid-helium temperatures. The following comments may be made regarding the lines observed: (1) The lines are observed even at room temperature. They sharpen on lowering the temperature, but their intensities remain unaltered. The observation of the lines does not appear to depend on the position of the Fermi level in the irradiated samples. This is in contrast to the absorption bands of electronic origin observed in irradiated silicon.[23] These features strongly indicate a vibrational origin for these lines. (2) The lines shift to higher frequencies when the temperature is lowered, say from room temperature to liquid-nitrogen temperature; this shift becomes very

[20] P. Fisher, W. H. Haak, E. J. Johnson, and A. K. Ramdas, *Proceedings of the Eighth Symposium on the Art of Glassblowing* (The American Scientific Glassblowers Society, Swinhurst, Wilmington, Delaware, 1963), p. 136.

[21] (a) H. J. Hrostowski and B. J. Alder, J. Chem. Phys. **33**, 980 (1960). (b) The work of R. C. Newman and J. B. Willis [J. Phys. Chem. Solids **26**, 373 (1965)] has been recently called to our attention. These authors have observed an absorption peak at 1104 cm^{-1} in silicon specimens containing both oxygen and carbon. They have suggested the possibility of carbon being a constituent in some of the defect-oxygen complexes in irradiated silicon. The irradiated specimens whose spectra are shown in Fig. 1, Curves B and C, do exhibit a line ~1104 cm^{-1}. The importance of electrically neutral impurities besides oxygen cannot be overemphasized in radiation-damage studies.

[22] R. J. Collins and H. Y. Fan, Phys. Rev. **93**, 674 (1954) and F. A. Johnson, Proc. Phys. Soc. (London) **73**, 265 (1959).

[23] H. Y. Fan and A. K. Ramdas, J. Appl. Phys. **30**, 1127 (1959).

small at the lower temperatures. For example, line 2 shifts from 829 cm^{-1} at 300°K to 835 cm^{-1} at 80°K, but the shift is negligible on going to liquid-helium temperatures. (3) The appearance of the irradiation-induced lines seems to occur at the expense of the 9-μ band. A decrease in the 9-μ band on neutron irradiation was first reported by Vavilov, Plotnikov, and Zakhvatkin.[24] It is, however, difficult to assess quantitatively the decrease in the 9-μ band, and hence this comment is only qualitative. (4) The relative intensities of the various lines are not the same for all the samples, clearly showing they are due to independent centers. For example, line 3 at 865 cm^{-1} is not observed in many samples. As can be seen in Fig. 1, the relative strengths of the lines 1–7 are not the same for the neutron-irradiated sample on the one hand and the electron-irradiated sample, on the other. Both the samples were obtained from the same original ingot.

Apart from the fact that oxygen in a dispersed form is essential for the irradiation-induced lines discussed above, it has not been possible to establish the constituents which make the various centers different from one another.[21(b)] The only center which appears in all the samples examined is the one which gives rise to the 12-μ line, i.e., line 2 in Fig. 1. Corbett *et al.*[15] have shown that this is due to the vibrational mode of the "Si-O-Si" molecule in the Si-$B1$ center and is a transformation of the 9-μ band.

That the presence of dispersed oxygen is an essential prerequisite for the appearance of all the above vibrational lines can be established in a very simple manner. When silicon containing dispersed oxygen, i.e., exhibiting the 9-μ band is subjected to a heat treatment ~1000°C, the absorption band disappears[8] due to the formation of long chain SiO_2 complexes. Electron irradiation of a sample subjected to such a heat treatment failed to produce any of the above vibrational bands. It is also known[4] that donor-like complexes are produced in samples subjected to a prolonged heat treatment ~450°C. A lack of correlation between the presence of these donors and the appearance of the irradiation-induced oxygen-defect complexes giving rise to the infrared lines appears to rule them out as playing any role in the formation of the latter. Thus evidence is very strong that the oxygen-defect complexes involve dispersed oxygen as an essential constituent. A most direct evidence in this connection has been given for the Si-$B1$ center by Corbett *et al.*[15] who showed that the line 2 exhibits an "isotope shift" when O^{18}-enriched silicon sample is irradiated.

The structures of the defects giving rise to the lines other than the one at 835 cm^{-1} have still to be determined. The lines at 811 cm^{-1} and 865 cm^{-1} are sufficiently close to the vibrational mode of the Si-$B1$ center. It is therefore tempting to suggest that they can be attributed to the same vibrating unit, i.e., "Si-O-Si" molecule where the two silicons are at next-nearest-neighbor sites along ⟨110⟩. The shift in frequency from 835 cm^{-1} is then presumably due to a slightly different environment in which the vibrating unit is located. The additional constituents which would convert Si-$B1$ centers into those giving the shifted frequencies have yet to be identified.[17] The production of the Si-$B1$ centers on the one hand and the 865 cm^{-1} centers on the other, during a low-temperature irradiation is interesting in this context.[17] Though the Si-$B1$ centers, as judged by the strength of the 835 cm^{-1} line, appear to be produced as copiously at liquid-nitrogen temperature as at 300°K, the 865 cm^{-1} line makes its appearance only if the sample is warmed to 300°K. The strength of the line then is the same as it would have been had the irradiation been carried out at 300°K.

[24] V. S. Vavilov, A. F. Plotnikov, and G. V. Zakhvatkin, Fiz. Tverd. Tela **1**, 976 (1959) [English transl.: Soviet Phys.—Solid State **1**, 894 (1959)].

TABLE I. Infrared active lines of defect-oxygen complexes in neutron-irradiated silicon.[a]

Before anneal[b]	Anneal #1 473°K for ½ h	Anneal #2 473°K for 1 h	Anneal #3 473°K for 4 h
811 (1)	...	...	...
835 (2)	835	835	835
...	...	856	856
865 (3)	865	865	865
876	876	876	876
...	886	886	886
...	...	913	913
...	952	952	952
960 (4)	960	960	...
966 (5)	966	966	...
...	973	973	973
1003 (6)	...	...	...
1021 (7)	...	...	...

[a] The numbers represent the positions of the lines in wave numbers at 80°K.
[b] The numbers in parentheses correspond to the labeling of the lines in Fig. 1.

B. Changes Produced by Heat Treatment

When irradiated silicon exhibiting vibration spectra of oxygen-defect complexes is subjected to heat treatment, the lines decrease in intensity due to annealing of the centers and new lines appear due to the evolution of new defect complexes. Table I summarizes the result for the neutron-irradiated sample whose spectrum before heat treatment is given as curve B in Fig. 1. As can be seen, lines 1 and 6 disappear with as little heat treatment as ½ h at 473°K. The lines 4 and 5 steadily decrease in intensity and two other lines at 952 cm^{-1} and 973 cm^{-1} appear instead. As pointed out in an earlier paper,[17] the average frequency of 4 and 5 is close to the average frequency of the new lines—a feature suggestive of coupled oscillators with a stronger coupling after annealing. The lines 2 and 3 remain unaltered up to 573°K. The annealing behavior of the different centers responsible for the lines 1–7 in Fig. 1 also demonstrates that one is here dealing with a multiplicity of centers.

TABLE II. Positions of lines observed with heat treatment[a] in neutron-irradiated crucible-grown silicon.

Before anneal	Anneal #1	Anneal #2 to 7	Anneal #8 and 9	Anneal #10	Anneal #11 to 13	Anneal #14 to 16	Anneal #17 to 20
835	835	835	835	835	835	835	835
	842	842	842	842	842	842	842
			833				
			829	829	829	829	829
				895	895	895	895
	923	923	923	923	923	923	923
	937	937	937				
	964	964					

[a] Annealing steps #1 to #20 correspond to 30-min isochronal anneals at 10°K intervals, beginning with 483°K. The numbers represent positions of lines in wave numbers at liquid-helium temperature.

In order to follow the annealing of the Si-$B1$ center responsible for the line at 835 cm^{-1} (line 2) under the least complicated situation we deliberately chose a neutron irradiated specimen which exhibited only this line most prominently. For example, the line 3 at 865 cm^{-1} was undetectable in the sample. The annealings were isochronal of 30-min duration, at 10°K intervals starting with 483°K. Measurements of the spectra were made with the grating monochromator and with liquid helium as the coolant in the optical cryostat. Table II lists the lines observed at various stages of anneal and Figs. 2, 3, 4, and 5 show the absorption spectra at the annealing stages where significant qualitative changes were most clearly manifested. The intensities of the various lines as a function of the annealing temperature are given in Fig. 6.

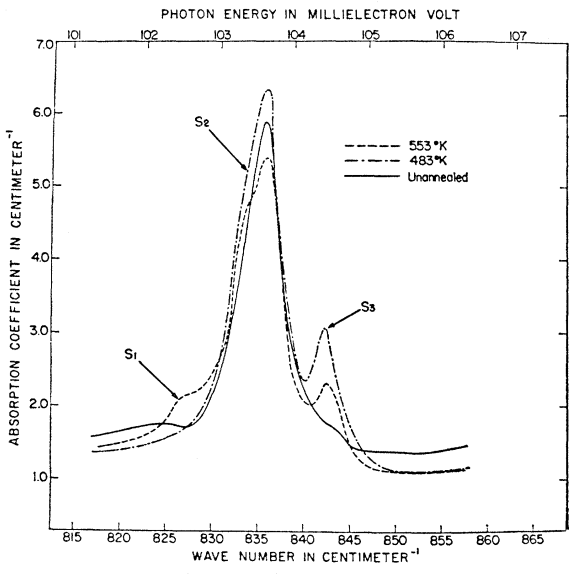

FIG. 2. The "satellites" near the 835 cm^{-1} line produced in neutron-irradiated silicon subjected to heat treatment. The spectrum was measured with liquid helium as the coolant. The sample was obtained from a high-resistance undoped crucible grown ingot and received a flux of 1.6×10^{19} neutrons/cm^2 at the Argonne National Laboratory. Measured with liquid helium as the coolant.

Previous studies[17] have shown that heat treatment of a neutron-irradiated silicon at 523°K gave rise to sharp lines at 842, 833, and 829 wave numbers, respectively. Like the 865 cm^{-1} line but all the more, these appear to be due to centers which have the same vibrating unit as the one which Si-$B1$ possesses. These have been designated as "satellites." These satellites are peculiar to neutron damage since they do not appear in samples irradiated with 4.5-MeV electrons and subjected to the same heat treatment. Nor have they been reported by Corelli *et al.*[25] who have made similar studies with samples irradiated with 60-MeV electrons.

As can be seen from Fig. 6, the appearance at 483°K of S_3, the most prominent of the satellites, is not accompanied by any corresponding decrease of the Si-$B1$ center; if anything, a slight initial increase is noticed. Also, in the temperature range 483–553°K the satellite S_3 decreases somewhat in intensity though Si-$B1$ is stable in the same temperature range. The centers responsible for S_3 thus are not related to the Si-$B1$ centers. Similar remarks apply to S_2 in that its occurrence too does not take place at the expense of

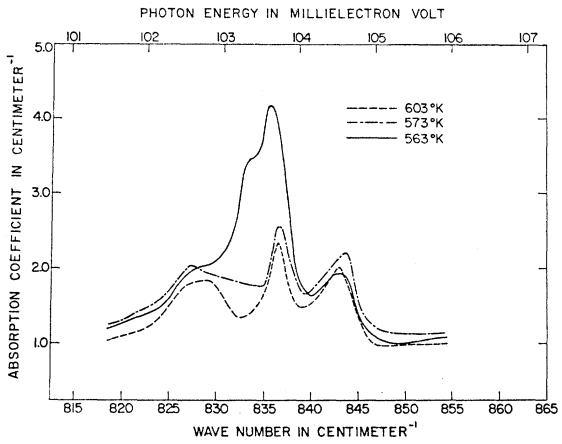

FIG. 3. The evolution of the satellites near the 835 cm^{-1} line on further heat treatment. Measured with liquid helium as the coolant.

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

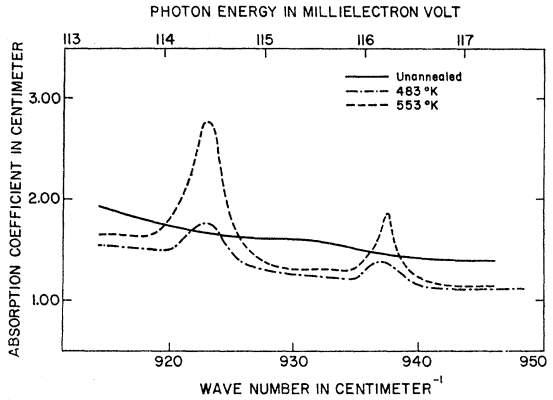

FIG. 4. The evolution of oxygen-defect vibration lines on annealing neutron-irradiated silicon. This spectrum represents an extension of Fig. 2 to the higher wave numbers. Measured with liquid helium as the coolant.

Si-$B1$ center. The appearance of S_1 and a pronounced decrease in Si-$B1$ center takes place around the same temperature. This could be interpreted as the S_1 centers being produced by a transformation of the Si-$B1$ centers. However, this satellite has been observed previously[17] simultaneously with S_2 and S_3 in a sample which was annealed for 30 min at 523°K without the anneals at the lower temperatures; the appearance of all the three satellites occurred in that sample without any corresponding decrease in the Si-$B1$ center. Thus it is not possible to deduce a definite relationship between S_1 and Si-$B1$.

The satellites S_1, S_2, and S_3 have been observed with all the neutron-irradiated annealed specimens we have examined, though the measurements have not been as extensive as for the unannealed specimens. They are observed irrespective of the presence or absence of the 865 cm^{-1} center. Thus the satellite centers appear to represent, unlike the 865-cm^{-1} center, a more complex defect than just an isolated vacancy produced by neutron irradiation and trapped at an oxygen site. The

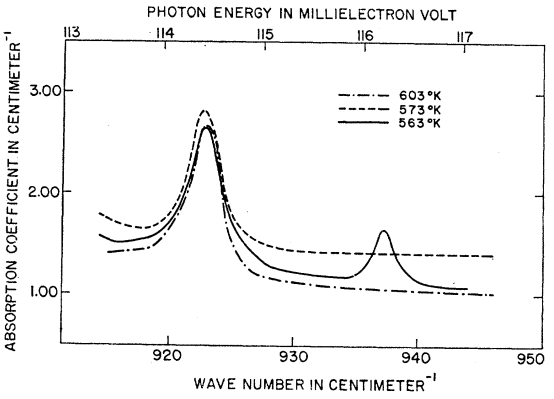

FIG. 5. The evolution of oxygen-defect vibration lines on annealing neutron-irradiated silicon. This spectrum represents an extension of Fig. 3 to the higher wave numbers. Measurements were made with liquid helium as the coolant.

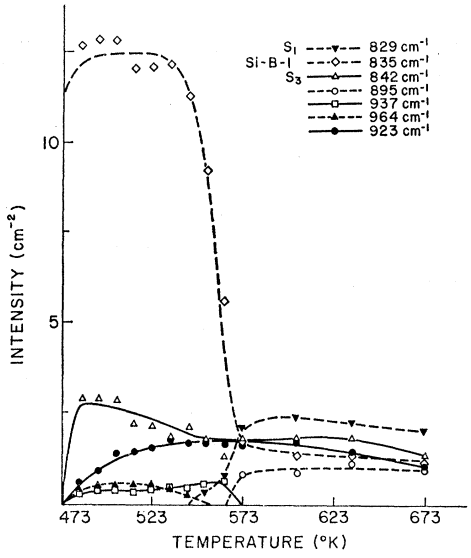

FIG. 6. Annealing and evolution of oxygen-dependent lines on isochronal annealing of neutron-irradiated crucible grown silicon whose spectra have been presented in Figs. 2, 3, 4, and 5.

fact that the satellites are produced on heat treatment without any corresponding increase in the Si-$B1$ center and their absence in electron-irradiated annealed samples, seems to rule out a modified Si-$B1$ type of defect. One possible candidate is a defect with a multiple vacancy trapped at an oxygen site. For example, consider the model for an isolated divacancy $G6$ or $G7$ as proposed by Corbett and Watkins,[26] with A and B as the vacant sites as shown in Fig. 7. If now oxygen is incorporated such that it bridges the silicon atoms 5 and 6 or 2 and 3, one would indeed have a vibrating unit similar to that in the Si-$B1$ center but in an environment sufficiently different to give frequencies shifted from 835 cm^{-1}. It is interesting to note in this context that the satellites are formed in a temperature range in which the divacancy center observed by Cor-

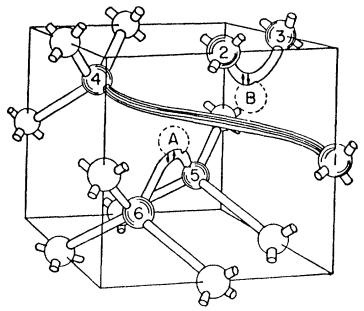

FIG. 7. The model proposed by Watkins and Corbett (Ref. 27) for the divacancy center, Si-$G6$, observed in EPR of electron irradiated silicon. Oxygen, if incorporated between the silicon atoms 2 and 3 or 5 and 6, can lead to a vibrating unit similar to the one in the Si-$B1$ center.

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

bett and Watkins[26] disappears. The disappearance, moreover, occurs at a lower temperature in an oxygen-containing specimen as against a floating-zone specimen. They interpret this fact to imply an undissociated divacancy getting trapped by an oxygen atom. Their results are thus consistent with the model proposed for the satellites. The divacancy model proposed by Jung and Newell[27] to explain the spin-1 EPR center (II, III) can also, together with oxygen, possess the necessary Si-O-Si units to produce a satellite. Indeed, Jung and Newell have also reported oxygen dependent spin-1 centers in neutron irradiated silicon. As has been emphasized earlier, the absence of the satellites in electron-irradiated annealed samples is striking. Its significance is presumably that complex defects like multiple vacancies are produced more abundantly with neutron irradiation. This is to be expected since fast neutrons produce many more secondaries per primary than do electrons.[28]

The lines at 923, 937, and 964 wave numbers, Figs. 4 and 5, are also observed during annealing above 483°K. There appears to be no correlation between any of them and the Si-$B1$ center. None of these have been observed by Corbett *et al.*[18] in their annealing studies of electron-irradiated silicon.

Figure 6 shows that the decrease in Si-$B1$ occurs in the same temperature range in which 895 cm^{-1} line appears. Corbett *et al.*[18] have reported a line with its peak at 887 cm^{-1} at room temperature. The 895 cm^{-1} line observed at liquid-helium temperatures in the present studies appears at 887 cm^{-1} when measured at room temperature. Therefore the lines observed by us and by Corbett and coworkers appear to be identical. The latter have proposed that it represents the vibration of a Si-$B1$ center which is captured at another oxygen site; the new defect then has two oxygen atoms at the vacancy.

IV. CONCLUDING REMARKS

The results of the infrared studies reported in this paper as well as those of other workers have succeeded in revealing numerous species of defect-oxygen complexes that are produced in irradiated silicon. It is rather intriguing that the same centers are observed with both electron irradiation and neutron irradiation in unannealed specimens, in spite of the significant differences in the types of damage produced by them. In this context it should be emphasized that the number of defects revealed by their infrared active lines is much smaller than the total number of defects produced. For example, a flux of 10^{18} electrons/cm^2 of 4.5 MeV electrons produces $\sim 10^{19}$ defects/cm^3 as assessed by the removal rates of carriers.[29] On the other hand, the number of Si-$B1$ centers for an equivalent irradiation is of the order of $10^{17}/cm^3$ as assessed by the strength of the 835 cm^{-1} line. Thus it appears that the formation of a defect-oxygen complex is a rather rare event and it is reasonable then to expect them to be formed both with neutron and electron irradiations.

The production of Si-$B1$ center with increasing flux can be followed using the 835 cm^{-1} line as the monitor. Unlike the observation of the EPR signal for which the Fermi level has to be within 0.16 eV of the conduction band,[14] the 835-cm^{-1} line can be observed even if the specimen becomes intrinsic, as it will on sufficient irradiation. Such a study reveals that the production of the Si-$B1$ center shows saturation with neutron or electron flux.[17] This occurs even though only a fraction of dispersed oxygen is used up. This suggests that vacancies are unable to reach oxygen sites with increasing irradiation, being trapped by, say, interstitials. More investigations are necessary to obtain an insight into this phenomenon. It also appears that the long-range motion of vacancies at 300°K occurs even at 80°K, as judged by the production of the 835 cm^{-1} line at the two temperatures.[17] On the basis of the EPR studies on the Si-$B1$ center, on the other hand, one would have expected a lower production at 80°K. Watkins[12] has found that the activation energy for vacancy migration depends upon whether the specimen is n-type or p-type; it is lower for the former. The specimen used in the infrared studies was originally high-resistance p type, and as such should have become intrinsic with very little irradiation. This aspect of the problem needs more experimental work.

Finally, attention should be drawn to the defect-oxygen complexes in electron or neutron irradiated germanium as studied by both infrared[30–33] and EPR techniques.[34,35] The existence of a defect which is the analog of the Si-$B1$ center has been inferred on the basis of these measurements. Infrared studies of specimens irradiated at low temperatures show that germanium too, like silicon, has a low activation energy for vacancy migration.[32]

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