Electron Spin Resonance in Neutron-Irradiated Silicon*

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Electron spin resonance produced in silicon by fast neutron irradiation was studied. The temperature of the samples during the irradiation was about 50°C. Different spectra were observed depending on the Fermi level in the irradiated sample. Samples with the Fermi level near the middle of the energy gap were studied in some detail. The observed complex spectrum was independent of the content of chemical impurities including oxygen. The spectrum simplified after annealing at temperatures $\geq$170°C. A center designated Si-*N* was identified in the spectrum of the annealed samples. The character of the **g** tensor and the hyperfine interaction suggest that at $T \leq 77$°K the unpaired electron is in a broken bond orbital on a single silicon atom. Variation of the spectrum with temperature was studied. The results may be explained by assuming that the unpaired electron has the choice of more than one broken bond orbital in the defect center.

I. INTRODUCTION

ELECTRON spin resonance studies in neutron-irradiated silicon were undertaken to investigate the nature of the lattice defects produced by the irradiation.[1,2] Prior to the initiation of these studies, radiation damage effects in silicon had been studied by observing the changes produced in the bulk properties, such as the resistivity, Hall effect, minority carrier lifetime, optical transmission, etc. These studies did not, however, provide direct information about the nature of the defects.

More recently, the use of electron spin resonance to study imperfections produced in silicon by electron irradiation has been reported by Bemski[3] and by Watkins and Corbett.[4–7] Comparatively simple defect centers may be expected in this case. From their studies, it was possible to identify centers consisting of single vacancies each associated with a foreign atom. In addition, resonance signals were observed which could be attributed to isolated single vacancies and divacancies.[6,7]

In the case of fast neutron irradiation, a different set of defect centers, possibly more complex, may be expected since it is estimated that on the average each primary knock-on produces approximately 200 secondary displacements.[8] In the work reported here, a survey of the resonance spectra was made for neutron-irradiated samples having the Fermi level at various positions in the energy gap. A detailed study was made on one type of center which gave a resonance signal in samples with the Fermi level near the middle of the energy gap.

II. DETAILS OF EXPERIMENT

Measurements were made at 9000 and 24 000 Mc/sec. The *X*-band spectrometer consisted of a frequency stabilized klystron, a magic Tee bridge and crystal detection. One side arm of the magic Tee contained the sample cavity and the other side arm contained a sliding probe which was used to adjust the mismatch of the bridge. The mismatch could be made sensitive to either the absorption or the dispersion component of the resonance signal. The magnetic field was modulated at 500 cps. The resulting audio-frequency component of the output of the crystal detector was amplifield, rectified by a phase sensitive detector and displayed on a recorder. When samples with long relaxation times were measured, the modulation of the magnetic field was replaced by audio-frequency modulation of the microwave power incident on the bridge. In the latter case, the integral signal was obtained, while in the former case, the derivative signal was obtained. The *g* value of the silicon resonance was measured relative to that of DPPH which was assumed to be 2.0036 ± 0.0002.[9]

The *X*-band sample cavity operated in the TE_{102} mode with the sample against the end wall of the cavity and completely filling the cross section of the cavity. With this simple geometry, the filling factor for the sample in the cavity could be easily calculated and an absolute determination could be made of the concentration of centers in the sample.

The *K*-band measurements were made with a balanced mixer spectrometer employing bolometer detection.[10] The klystron could be stabilized with respect to either the sample cavity or to a reference cavity. Either the absorption or the dispersion signal

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[8] K. Lark-Horovitz in *Semiconducting Materials*, edited by H. K. Henisch (Academic Press Inc., New York, 1951), p. 47.
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[10] G. Feher, Bell System Tech. J. **36**, 449 (1957).

TABLE I. Production rate of resonance centers in silicon by fast neutron irradiation. Temperature of samples during irradiation was about 50°C. Resonance measurements were made at ~9 kMc/sec.

Original resistivity (ohm-cm)		Doping impurity	Fast neutron flux (nvt)	Production rate (per neutron-cm) N/Φ	Temperature of measurement (°K)
0.01	(p)	B	2×10^{18}	0.17	4.2
0.06	(n)	As	6.4×10^{18}	0.12	4.2
0.04	(p)	B	6.4×10^{18}	0.15	4.2
23	(p)	?	7×10^{17}	0.06	300
41	(p)	?	5×10^{18}	0.08	300
35	(p)	?	1×10^{19}	0.14	4.2
				0.08	300
100	(p)	?	1.4×10^{18}	0.18	300
0.06	(n)	As	7×10^{17}	0.08	4.2

could be obtained by suitable adjustment of the phase of the microwave reference signal applied to the bolometers. The samples used almost filled the sample cavity. The geometry was such that the cavity was resonant for several frequencies in the K band. The cavity resonance with the highest Q value was normally chosen. The g values for the silicon resonance were determined by measuring both the magnetic field and the microwave frequency.

The silicon used for this investigation was obtained from a number of laboratories (Bell Telephone Laboratories, Inc., Westinghouse Electric Company, Texas Instruments, Inc., United States Semiconductors, Merck and Company). Before irradiation, the only resonance signal found in these samples was that due to the chemical donors. The fast neutron irradiations were performed either in the Graphite Reactor at Oak Ridge National Laboratory or in the CP-5 reactor at Argonne National Laboratory. The sample temperature was about 50°C in the Oak Ridge reactor and about 100°C in the Argonne reactor.

III. EXPERIMENTAL RESULTS

A. General

It is well known that the resistivity of either n- or p-type silicon increases with irradiation by high-energy particles. The Fermi level is shifted toward the middle of the energy gap. With sufficiently long irradiation, the resistivity reaches a near intrinsic value. Since the electronic occupation of the levels associated with a defect center depends on the position of the Fermi level, the resonance signal is expected to depend on the Fermi level. Such dependence was indeed observed. n-type samples with four different Fermi levels, E_D (the donor level), $E_c-0.1$ eV, $E_c-0.14$ eV, and $E_c-0.2$ eV, and p-type samples with three different Fermi levels, $E_v+0.12$ eV, $E_v+0.15$ eV, and $E_v+0.2$ eV, were measured. In addition, samples with the Fermi level near the middle of the energy gap were studied. Different resonance spectra were obtained for each of these positions of the Fermi level. None of the different signals obtained appeared to have any features in common, with the possible exception that the signals in the p-type samples with the Fermi level at $E_v+0.12$ eV and $E_v+0.15$ eV appeared quite similar. Thus, either different centers or different charge states of the same centers were responsible for the signals observed at different Fermi levels. More samples with closely spaced Fermi levels have to be studied in order to determine unambiguously the correlation between the variation of the resonance signal and the defect levels deduced from electrical and optical measurements.[11]

The observed resonance spectra differed from those obtained by Bemski[3] and Watkins and Corbett[4–7] in silicon irradiated by 1.5-MeV electrons. None of the resonance spectra reported for electron irradiation were observed in the neutron-irradiated samples with comparable Fermi levels. If the centers produced in electron irradiation were present in the neutron-irradiated samples, their signals were masked by that of other types of centers.

All of the resonance signals observed were quite complex and, in most cases, could not be resolved. All of the resonances were located quite close to $g=2.0$ and seemed to have simplest patterns for magnetic field along the ⟨100⟩ direction. The near intrinsic samples were chosen for a more detailed investigation for the following reasons. The study of the annealing of defects is more difficult for nonintrinsic material since the Fermi level shifts toward the band edges with annealing. However, nearly intrinsic material obtained with long irradiation could be subjected to considerable annealing without showing a significant shift of the Fermi level. Another advantage of working with nearly intrinsic samples is that the resistivity is sufficiently high for the resonance measurements to be extended up to slightly above room temperature.

[11] See, for example, J. Appl. Phys. **30**, 1117–1321 (1959) which contains papers and discussions presented at the Conference on Radiation Effects in Semiconductors, Gatlinburg, Tennessee, May, 1959.

B. Near Intrinsic Material

The concentration of defects was estimated from the integrated resonance signals obtained at 9000 Mc/sec. The determination is estimated to be accurate to a factor of two. The result showed that the concentration is proportional to the neutron dosage. From this we conclude that the centers were formed from the effects of individual primary events. Assuming a center with spin $\frac{1}{2}$, the production rate of centers in the near intrinsic silicon was found to be 0.1 center per cm path of a neutron. Although there is some scatter in the data, there is no systematic variation of the rate with either neutron flux or with impurity concentration (see Table I). The number is very small compared to the estimated total number of displaced atoms which is of the order of 20 per neutron-cm.[8]

The detail structure of the resonance signal could best be studied at room temperature where the relaxation time was short and it was possible to obtain the derivative of both the absorption and dispersion components of the resonance signal. A very complicated signal near $g=2.0$ was obtained. The signal was not well resolved at 9000 Mc/sec; however, adequate resolution was obtained by using 24 000 Mc/sec (see Fig. 1). The lines were Gaussian in shape with a width 4 G at half-power absorption. The resonance spectrum was found to be the same in all samples with near intrinsic resistivity irrespective of the neutron dosage. Furthermore, the same spectrum was observed in samples of high chemical purity and in samples containing different doping impurities from the III and V groups. Also, no difference was found between crucible-grown and oxygen-free samples. Thus, the spin centers produced by the irradiation did not appear to be associated with impurity atoms.

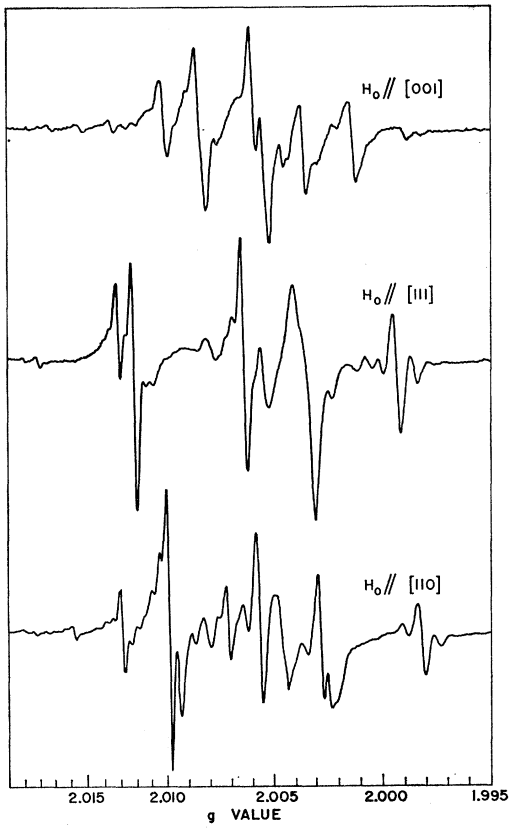

FIG. 1. Spectra of neutron irradiated silicon for three directions of the magnetic field. The temperature of the sample during irradiation was ~50°C and the sample had not been intentionally annealed. Measurements were made at room temperature and at ~24 kMc/sec.

Annealing Experiments

Since the complex signal might be produced by several different kinds of centers, a series of annealing experiments were performed in order to simplify the signal if possible. The initial anneal of 2 h at 170°C produced very drastic changes in the resonance pattern. Some of the lines in the spectrum disappeared and some of the remaining lines appeared to have shifted slightly, indicating that a part of the defects annealed out and the remainder underwent some transformation. The samples in question were irradiated in the Oak Ridge reactor. It is interesting to note that the samples irradiated at Argonne, where the sample temperature was raised to 100°C by the high power level of the reactor, gave a somewhat simplified signal without the annealing. After the first two hours, further annealing at 170°C for a total of 15 h produced no additional change.

Silicon samples which become nearly intrinsic after irradiation show an infrared absorption band at 1.8 μ. The band decreases with annealing at 170°C.[12] However, the rate of decrease is too slow, a decrease by a factor of 2 in 10 h, as compared with the rate of those resonance lines which disappeared after 2 h. On the other hand, the infrared band can be annealed out completely at 170°C, therefore it is not associated with the remaining resonance signal.

No additional changes were observed with annealing at temperatures less than 300°C. After 1-h anneal at 300°C, an additional part of the signal annealed out but the strong lines in the spectrum remained. Further annealing for periods of time up to 8 h at temperatures as high as 500°C produced no additional changes in the resonance pattern. The signal obtained after the 300°C anneal could be divided into a set of fairly intense lines associated with one type of center and a number of less intense lines associated with one or more additional types of centers. This division was supported by the temperature dependence of the resonance signal as a function of temperature below room temperature. The set of relatively intense lines showed definite saturation behavior when the tempera-

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

ture was lowered below room temperature while the less intense lines showed little or no saturation effects. This saturation behavior and other details of the temperature variation of the resonance signal were used to identify that portion of the spectrum at a given temperature which was due to the same center as was responsible for the more intense portion of the room-temperature signal.

The more intense portion of the signal designated as Si-N center was studied in detail. Measurements made at two different frequencies, 9000 and 24 000 Mc/sec, showed that the magnetic field for each of the observed lines was proportional to the microwave frequency, indicating that the splitting between the lines was neither due to zero-field splitting nor due to hyperfine interaction. The spectrum may be analyzed using a spin Hamiltonian of the form

$$\mathcal{H}=\beta\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S}, \tag{1}$$

where $S=\frac{1}{2}$, β is the Bohr magneton, and $\mathbf{g}$ is a tensor. The resonance condition is given by

$$h\nu=g\beta H, \tag{2}$$

where

$$g=(g_1^2\cos^2\theta_1+g_2^2\cos^2\theta_2+g_3^2\cos^2\theta_3)^{1/2}, \tag{3}$$

θ_1, θ_2, and θ_3 being the angles between the direction of the applied magnetic field and the directions of the principal g values g_1, g_2, and g_3, respectively. There are 192 equivalent positions in the silicon lattice which give 24 different expressions of the form (3), for a given direction of the magnetic field. Hence, the resonance spectrum for a defect in the silicon lattice may have as many as 24 lines. Some of the lines should coincide when the magnetic field is applied along crystallographic directions of symmetry, e.g., the possible number of different lines is 3 for $H\|\langle 100\rangle$, 4 for $H\|\langle 111\rangle$, and 6 for $H\|\langle 110\rangle$. Depending on the particular $\mathbf{g}$ tensor, the resonance spectrum may have less than the maximum possible number of lines. Figure 2 shows the g values of the various lines in the N-center spectrum as functions of the magnetic field orientation. There is a single line for $H\|[001]$, indicating that all three possible different lines coincide. In the [111] direction, two of the four lines coincide giving three lines of intensity 2-1-1. In the [110] direction two pairs of the six lines coincide giving four lines of intensity 1-2-2-1. Analysis of the spectrum gives

$$g_1[1\bar{1}0]=2.0125,\quad g_2=2.0046,\quad g_3=2.0091,$$

where g_2 and g_3 are both in the $(1\bar{1}0)$ plane. The direction of g_2 makes an angle of 19° with the [111] direction and an angle of about 16° with the [110] direction.

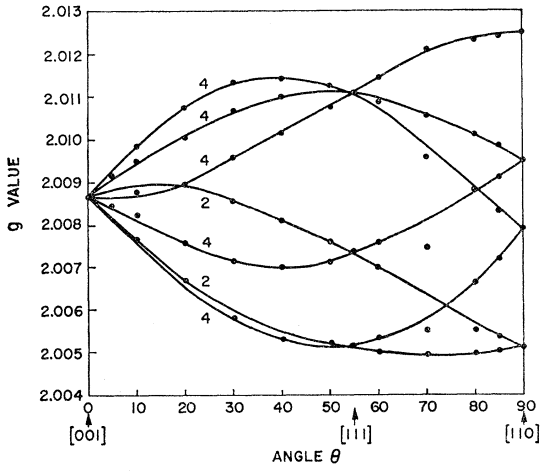

FIG. 2. Variation of the g values with direction of the magnetic field for the Si-N center at room temperature. Measurements were made at ~24 kMc/sec.

Low-Temperature Measurements

At liquid-nitrogen temperature, the relaxation time of the N-center spectrum had become comparable to the period of the audio-frequency (500 cps) modulation used for the magnetic field. Under these conditions, the absorption and dispersion signals have components in-phase and in-quadrature with the modulation. The two components can be observed separately by suitable adjustment of the phase of the reference voltage supplied to the phase sensitive detector in the detection system. The absorption signal, both the in-phase and in-quadrature components saturated with increasing microwave power. But the dispersion signals did not saturate. From the saturation behavior of the absorption signal, the relaxation time for the center was estimated to be of the order of 10^{-4} sec at 77°K.

Figure 3 shows the anisotropy of the dispersion signal of the Si-N center obtained at 77°K. The following principal g values were obtained from the analysis:

$$g_1[1\bar{1}0]=2.0117,\quad g_2=2.0020,\quad g_3=2.0104,$$

where g_2 and g_3 are in the $(1\bar{1}0)$ plane and g_2 makes an angle of about 2.5° with the [111] direction and an angle of 32.5° with the [110] direction. Thus, the g tensor has nearly axial symmetry about $\langle 111\rangle$, the normal tetrahedral bond direction.

At liquid-nitrogen temperature, weak satellite lines were observed which were identified as hyperfine lines due to Si^{29} nuclei associated with the N center. The identification was based on the following observations. (1) The saturation behavior of the satellite lines was the same as that for the fine structure spectrum of the N center; (2) the separation between the lines is independent of magnetic field for measurements made at 20 and 24 kMc/sec; (3) the anisotropy of these lines was consistent with that of hyperfine lines arising from the interaction with a nucleus of spin $I=\frac{1}{2}$; (4) the intensity of these lines was consistent with the natural abundance, 4.7%, of Si^{29}; this observation indicated that the hyperfine lines of a center arose from the

interaction of the spin with a single silicon nucleus. The anisotropy of the hyperfine structure is shown in Fig. 4. The low-field branch of the spectrum could not be obtained reliably as it was obscured by the more intense fine structure pattern. The spin Hamiltonian can be written in the form

$$\mathcal{H}=\beta\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S}+\mathbf{I}\cdot\mathbf{A}\cdot\mathbf{S}, \quad (4)$$

where the second term represents the hyperfine interaction. The anisotropy of the hyperfine structure showed axial symmetry along the ⟨111⟩ direction. The

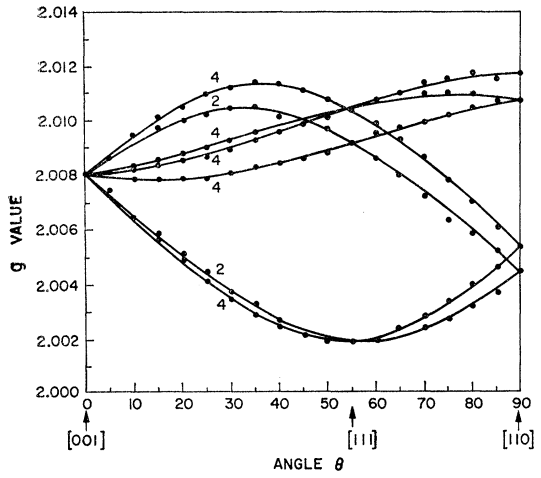

FIG. 3. Variation of the g values with the direction of the magnetic field for the Si-N center at 77°K. Measurements were made at ~24 kMc/sec.

two principal values of $\mathbf{A}$, $A_{\parallel}$ for field along the ⟨111⟩ direction and $A_{\perp}$ for field perpendicular to the ⟨111⟩ direction are given in Table II.

Measurements made at 4°K gave essentially the same $\mathbf{g}$ tensor and hyperfine interaction as found at 77°K. The measurements were made at very low microwave power levels to avoid complications arising from the very long relaxation times found at these temperatures. Therefore, the measurement of the hyperfine structure was not too reliable but the indications were that the hyperfine structure was the same as at 77°K. Thus, it

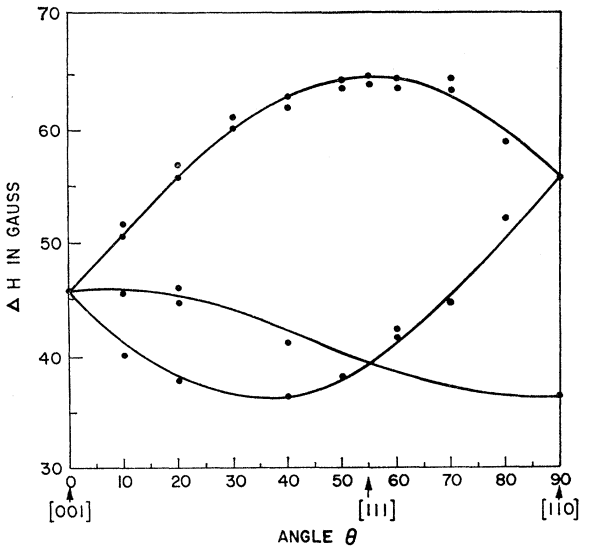

FIG. 4. Variation of the hyperfine interaction with the direction of the magnetic field for the Si-N center at 77°K. The value ΔH plotted is the separation between the hyperfine line and the corresponding fine structure line.

appears that at low temperatures the spin is localized on a single silicon atom. The wave function is axially symmetric about the ⟨111⟩ direction near the nucleus, according to the hyperfine tensor A, but is, over all, slightly distorted from the axial symmetry as indicated by the $\mathbf{g}$ tensor. A broken or dangling bond along the normal tetrahedral bond direction is suggested.

Recently, Watkins and Corbett[6] reported a spin center, Si-B, in silicon irradiated by 1.5-MeV electrons. The $\mathbf{g}$ tensor and the hyperfine $\mathbf{A}$ tensor of the resonance signal have qualitatively similar characteristics as in our case. The author discussed the hyperfine interaction on the following basis. The wave function of the electron was approximated by $3s$ and $3p$ orbitals localized at various sites j

$$\Psi=\sum_j \eta_j(\alpha_j\Psi_{3s}{}^j+\beta_j\Psi_{3p}{}^j),$$

where α_j and β_j were normalized according to

$$\alpha_j{}^2+\beta_j{}^2=1.$$

TABLE II. A and g tensors for Si-N and Si-B centers.[a] The hyperfine interaction constant $A_{\parallel}$ and $A_{\perp}$ are for the magnetic field parallel and perpendicular to the [111] direction. θ is the angle between the direction of the principal g value g_2, which lies in the $(1\bar{1}0)$ plane between [111] and [110], and the [111] direction.

Center	Temperature (°K)	$g_1[1\bar{1}0]$	g_2	g_3	θ (deg)	$A_{\parallel}$ (10^{-4} cm^{-1})	$A_{\perp}$ (10^{-4} cm^{-1})
	350	2.0126	2.0048	2.0090	23.5		
	300	2.0125	2.0046	2.0091	16		
Si-N	200	2.0120	2.0040	2.0100	13		
	77	2.0117	2.0020	2.0104	2.5	138	75
Si-B	Probably 20	2.0085	2.0026	2.0107	1.3	130	71

[a] The data for the Si-B center are taken from Watkins and Corbett (reference 6). Note that the designation of the principal g values given above differ slightly from that used in reference 6.

The factor η_j^2 gives the proportion of contribution from the site j and the ratio α^2/β^2 gives the relative weight of s to p orbitals. The values of η_j^2 and α_j^2/β_j^2 can be calculated from the **A** tensor

$$(A_{\parallel}{}^i+A_{\perp}{}^i)/3=(16\pi/3)\gamma\beta_e\beta_n\alpha_j^2\eta_j^2|\Psi_{3s}(0)|^2,$$
$$(A_{\parallel}{}^i-A_{\perp}{}^i)/3=(4/5)\gamma\beta_e\beta_n\beta_j^2\eta_j^2\langle r^{-3}\rangle_{3p},$$

where γ is the gyromagnetic ratio, β_e is the Bohr magneton, and β_n is the nuclear magneton. Using the value, $|\Psi_{3s}(0)|^2/\langle r^{-3}\rangle_{3p}=1.4$, estimated from the tabulated Hartree functions, and the value, $|\Psi_{3s}(0)|^2=24\times10^{24}$ cm^{-3}, obtained from previous work on Si-A centers, Watkins and Corbett calculated for the Si-B center:

$$\eta^2=0.64, \quad \beta^2/\alpha^2=6.1.$$

The value of η^2 was taken to indicate that 64% of the wave function was accounted for by the orbitals localized at one site. The enhancement of the p character of the wave function, i.e., β^2/α^2 is larger than the value of 3 for a (sp^3) tetrahedral orbital, was taken as an indication that the orbital was associated with an atom in the neighborhood of a vacancy. The p character of the wave function would be enhanced if the atom was pulled away from the vacancy to approach the plane of its three neighboring atoms. Similar analysis gives for the Si-N center

$$\eta^2=0.63, \quad \beta^2/\alpha^2=6.4.$$

The considerations pertaining to the Si-B center are evidently applicable also to the Si-N center and support the suggestion that the latter involves a dangling bond.

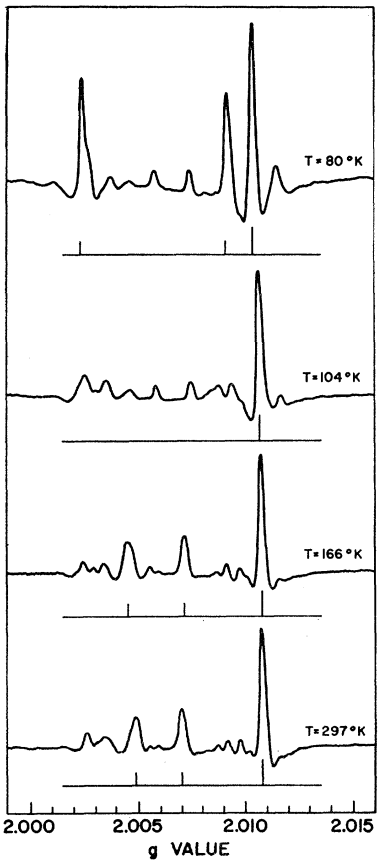

FIG. 5. Spectra of the Si-N center for $H\|[111]$ at temperatures between 77 and 300°K. Measurements were made at ~24 kMc/sec. The line drawings under each spectrum shows the positions and relative intensities of the lines of Si-N center according to the interpretation given in the text.

Variation of Si-N Center Spectrum with Temperature

As the temperature is raised above 77°K, the intensities of the hyperfine lines decrease and these lines are no longer observable at 100°K, having decreased by a factor of at least 10. The single fine-structure line in the spectrum for $H\|\langle100\rangle$ associated with the N center remained unchanged. However, for the other directions, certain of the fine structure lines had decreased in intensity and disappeared. The changes in the spectra for the $\langle111\rangle$ direction can be seen by comparing the two upper traces in Fig. 5. As the temperature is raised above 100°K, new lines begin to appear near the positions of the lines which had disappeared. The intensity of these lines increase as the temperature is raised and saturates by 160°K. (See third trace from top, Fig. 5). As the temperature is raised above 160°K, there are no additional drastic changes in the nature of the spectrum but slight changes in the position of the line were observed (compare the two lower traces in Fig. 5).

Throughout the temperature range studied, the single intense line in the $\langle100\rangle$ spectrum could be followed continuously. The intensity of this line was constant, taking into account the $1/T$ temperature dependence and saturation effects. In the temperature range slightly above 100°K, the lines which had not disappeared could not be fitted to a **g** tensor. Furthermore, those lines which had disappeared when the temperature was raised obviously could not be fitted to a **g** tensor either since there had been no changes in the $\langle001\rangle$ spectra. Therefore, the observed behavior is not consistent with an assumption that the spectrum obtained at 77°K was really due to two distinct centers and that the disappearance and reappearance of certain fine structure lines was due to the thermal excitation of the electron from one of these centers to a third nonequivalent center.

The observed temperature dependence of the resonance spectra of the N center can be explained by assuming a mechanism of electron "hopping" or exchange between crystallographically equivalent sites within the given defect center. The N-center spectrum at 77°K indicates that the electron is localized at one of the twelve energetically and crystallographically equivalent sites. As the temperature is raised above 77°K, the electron acquires sufficient thermal energy so that it is no longer localized at one site but is capable of hopping to another equivalent site in the given defect center. In this simplified model, it will be assumed that,

for a given orientation of the magnetic field, if the electron hops between two equivalent sites which give rise to different resonance lines each of these lines will decrease in intensity. In addition, if the hopping occurs between sites which give rise to the same resonance line, there will be no decrease in the resonance line. Strictly speaking, the lines broaden and decrease in intensity when the hopping or exchange rate become comparable to the linewidth of the fine structure lines, when the linewidth is expressed in units of reciprocal time. Experimentally, the lines were observed to decrease in intensity without noticeable broadening. However, the signal had to be observed in dispersion due to the long relaxation times found in this temperature range and it is not obvious how motional broadening should effect an inhomogeneously broadened line observed under these conditions.

From the analysis of the N-center spectrum at 77°K, the principal g values were found to be along the following directions:

$$g_1[1\bar{1}0],\quad g_2[11h],\quad g_3[hh\bar{2}],$$

where

$$h=\sqrt{2}\,\tan^{-1}(32.5°).$$

The 12 equivalent $\mathbf{g}$ tensors are given in Table III.

A schematic representation of the spectrum of the N center at 77°K for the field along the [001], [111], and [110] directions is given in Fig. 6. Each line is labeled to indicate which of the 12 equivalent $\mathbf{g}$ tensors listed in Table III give rise to the line. The spectrum for the field along the [001] direction is not labeled since all 12 sites give rise to the single line found in this direction.

Let us consider the effect of hopping between sites. Assume that the electron at a given site, for example, site A, is permitted to hop to any one of the eleven equivalent sites B, C, $\cdots$, J. For $H\|[111]$; if the electron at site A hops to either site B or site C, line ABC will not decrease in intensity. However, if the electron at site A hops to sites D, H, L, E, etc., the line ABC will decrease in intensity. It can easily be seen that under this assumption line ABC will decrease in intensity to 2/11 of its original intensity. Similar arguments for line DHL and line $E\cdots J$ show that line DHL will also decrease to 2/11 of its original intensity and line $E\cdots J$ will decrease to 5/11 of its original intensity. These results are contrary to the experimental observation that lines ABC and DHL disappeared completely while line $E\cdots J$ remained unchanged. For $H\|[110]$, under the mechanism assumed above, lines AD and GJ will decrease in intensity to 1/11 of its original intensity while lines $BCEF$ and $HLKI$ will decrease to 3/11 of their original intensity. Experimentally, lines AD and GJ have constant intensity while lines $BCEF$ and $HLKI$ disappear. Thus, the assumption of unrestricted hopping is not consistent with the observed behavior.

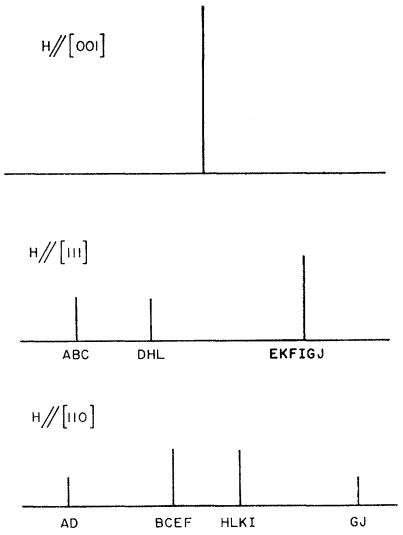

FIG. 6. Schematic representation of the resonance spectra for Si-N center for three crystallographic directions. The letters under each of the resonance lines indicate which of the twelve equivalent sites, which are enumerated in the text, contribute to the given line. The spectrum for $H\|[00\bar{1}]$ is not labeled as all twelve equivalent sites contribute to the single resonance line.

TABLE III. Directions of the principal g values for the twelve equivalent $\mathbf{g}$ tensors describing the Si-N center. The factor h is related to angle θ described in the text by the equation $h=\sqrt{2}$ arc tan θ.

Center	Direction of principal g values g_1	g_2	g_3
A	$1\bar{1}0$	$11h$	$hh\bar{2}$
B	$10\bar{1}$	$1h1$	$h\bar{2}h$
C	$01\bar{1}$	$h11$	$\bar{2}hh$
D	$1\bar{1}0$	$11\bar{h}$	$hh2$
E	101	$1h\bar{1}$	$h\bar{2}\bar{h}$
F	011	$h1\bar{1}$	$\bar{2}h\bar{h}$
G	110	$\bar{1}1\bar{h}$	$\bar{h}h2$
H	$10\bar{1}$	$\bar{1}h\bar{1}$	$h2h$
I	011	$\bar{h}1\bar{1}$	$2\bar{h}\bar{h}$
J	110	$1\bar{1}\bar{h}$	$\bar{h}h2$
K	101	$1\bar{h}\bar{1}$	$h2\bar{h}$
L	$01\bar{1}$	$h\bar{1}\bar{1}$	$2hh$

The observed behavior can be obtained if certain restrictions are placed on the sites between which hopping occurs. For the field along the [111] direction, it must be assumed that an electron at site A can hop only to sites D, H, or L. In the [110] spectrum if an electron on A hops to D, line AD will not decrease in intensity which is consistent with the experimental results, while if an electron at site A hops to either site H or L, line AD would decrease. Thus, it would be consistent with experiment to have hopping of an electron on site A only to site D.

If the electron were originally on site D, hopping of the electron to which of the equivalent sites would be consistent with experiment? For the [111] direction, an electron on D can hop only to A, or B or C. For the [110] direction, an electron on D can hop to A but not to B or C. Hence, the restriction must be imposed that an electron at A can hop only to D and that an electron at D can hop only to A.

By extending similar considerations to all the other equivalent sites, it is easily seen that hopping should be restricted to following pairs of sites. AD, BH and/or

BL, *CH* and/or *CL*, *EK* and/or *EI*, *FI*, *GJ*. It will be noted that six of the pairs consists each of two sites with the same direction for g_1. The pairs *EI*, *CH*, and *BL* are exceptions. They are optional and can be ruled out. With this restriction on the hopping, the observed disappearance of some of the lines is accounted for satisfactorily.

In summary, the observed disappearance of certain of the fine structure lines can be explained if it is assumed that at $T>77°$K, the electron, which had been localized at a single silicon atom at 77°K and below, begins to hop between equivalent sites within the defect center but that the hopping can occur only between certain pairs of these equivalent sites, that is, hopping can occur only between those equivalent sites whose **g** tensors has the principal g value g_1 along the *same* ⟨110⟩ crystallographic direction. As the temperature is raised above 100°K, the hopping rate will increase and the electron will be shared by the two sites and new lines will grow in corresponding orbitals associated with two silicon atoms. By symmetry, the **g** tensor might be expected to be of the following type:

$$g_1[1\bar{1}0],\ g_2[110],\ g_3[001].$$

Experimentally, the **g** tensor at ∼160°K, when the newly emerging lines have reached their full intensities, had g_1 along $[1\bar{1}0]$, and g_2 at an angle of 22° from [110] and 13° from [111]. However, with g_1 remaining along $[1\bar{1}0]$, g_2 turned toward [110] with increasing temperature. At 350°K, the highest temperature at which measurements were made, g_2 was about 11.5° away from the [110] direction. See Table II for summary of data.

The observed variation of the resonance spectrum in the temperature range above 160°K cannot be explained on the basis of the model of hopping proposed above. From the separation of the fine structure lines which undergo motional broadening, an estimate was made that, when motional narrowing sets in, the hopping frequency was of the order of 10^8 per sec. This hopping frequency was slow enough so that any distortion in the defect should average out and a **g** tensor with the expected symmetry, principal g values along the [001], [110], and $[1\bar{1}0]$ axes should have been obtained after motional narrowing had been completed at $T\sim160°$K. Thus, an additional mechanism must be proposed. For example, large regions of damage are produced by neutron irradiation and it would be reasonable to assume that there are distortions of the lattice in the vicinity of the *N* center, and that the thermal averaging of these distortions are responsible for the **g**-tensor variation above 160°K. The existence of such distortions, however, is just speculation until further experiments have been performed.

Discussion on the Si-*N* Center

The Si-*N* center was found in neutron-irradiated silicon which had the Fermi level near the middle of the energy gap. The *N*-center spectrum has been definitely identified in samples which had been annealed at temperatures $\gtrsim$170°C. Recent studies by Jung and Newell of this laboratory[13] have shown that the Si-*N* resonance is actually absent from the resonance signal in samples which had been irradiated at ∼50°C and had not been annealed. Thus, annealing was necessary for the formation of the *N* center. The defect responsible for the *N*-center resonance probably does not have a foreign impurity atom associated with it as the *N*-center spectrum was observed in annealed samples which had different amounts of various impurities including oxygen.

The character of the **g** tensor and of the hyperfine interaction for the *N* center suggests that, at $T\leq 77°$K, the unpaired electron is associated with a single silicon atom and is in an orbital approximately symmetrical about the direction of the tetrahedral bond. Table II shows that the **g**-tensor and hyperfine interaction constants are qualitatively similar to those of the Si-*B* center observed by Watkins and Corbett[6] in electron-irradiated silicon. The Si-*B* center was reported to be formed by room-temperature irradiation and did not require annealing above room temperature for its formation.[14] Furthermore, the *B* center did not undergo any motional broadening or narrowing in the temperature range up to room temperature. Therefore, despite the fact that the *N* center at 77°K and the *B* center are both assumed to be dangling bonds associated with a single silicon atom, they are definitely not due to the same radiation produced imperfection.

The observed variation of the spectrum with temperature indicated that the unpaired electron has the choice of more than one crystallographically equivalent orbitals within the defect. However, with the resonance data available to date, it is not possible to specify unambiguously the physical nature of the defect center. A variety of models can be proposed for the *N* center. The motional behavior requires that the defect have at least two dangling bonds and that the **g** tensors of two of these dangling bonds have a certain relation to one another. The simplest defect which has the necessary orbitals is the single isolated vacancy shown in Fig. 7(a). A strong objection to assuming such a vacancy is that the work of Watkins and Corbett has shown that single vacancies are mobile even at temperatures below room temperature and that they diffuse through the crystal until they are trapped by some imperfection. The resonance data do not show the presence of any imperfection in the neighborhood of the *N* center, but this does not rule out the possibility that a nonparamagnetic imperfection is present. A multiple vacancy defect such as the divacancy

[13] Wun Jung and G. S. Newell, Bull. Am. Phys. Soc. **7**, 186 (1962).
[14] G. D. Watkins (private communication).

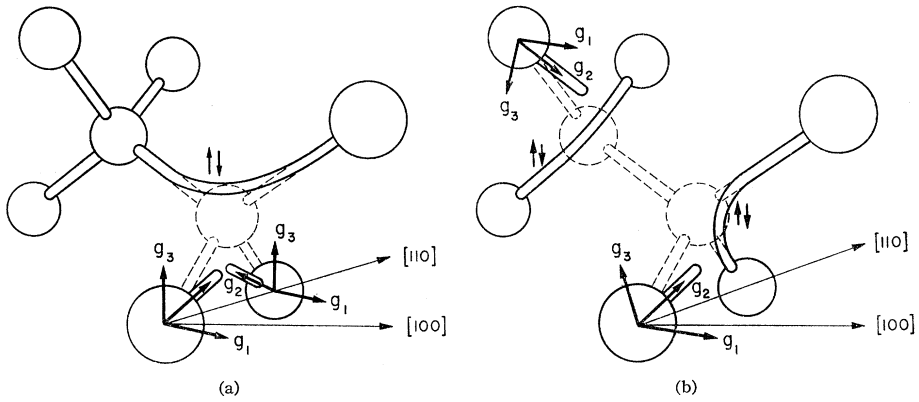

FIG. 7. Possible models for the Si-*N* center. Either the single vacancy shown in (a) or the divacancy shown in (b) would be consistent with the observed resonance behavior.

shown in Fig. 7(b) would also have the requisite orbitals to satisfy the motional behavior observed. The two silicon orbital formed after motional narrowing would not be coplanar and would be much more complicated than the simpler coplanar divacancy proposed by Watkins and Corbett to explain the Si-*C* and Si-*J* centers in electron-irradiated silicon. More complex clusters of vacancies will also be satisfactory; however the data thus far obtained do not justify speculations about such centers. Clustering of defect would be expected to occur in the case of neutron irradiation. Additional experimental observation are needed to determine definitely the nature of the defects including the *N* center.

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