Defects in Irradiated Silicon: Electron Paramagnetic Resonance of the Divacancy

G. D. WATKINS AND J. W. CORBETT General Electric Research Laboratory, Schenectady, New York (Received 19 November 1964)

Two electron paramagnetic resonance spectra produced in silicon by 1.5-MeV electron irradiation are described. Labeled Si-G6 and Si-G7, they are identified as arising from the singly positive and singly negative charged states of the divacancy, respectively. The observed hyperfine interactions with neighboring Si²⁹ nuclei and g tensors are discussed in terms of a simple molecular-orbital treatment of the defect by the method of linear combination of atomic orbitals. In addition to the anisotropy associated with the vacancyvacancy direction in the lattice, an additional distortion occurs which is identified as a manifestation of the Jahn-Teller effect. Thermally activated reorientation from one Jahn-Teller distortion direction to another causes motional broadening and narrowing effects upon both spectra in the temperature region 40-110°K. The motion is also studied by stress-induced alignment at lower temperatures, and the activation energy for the process is found to be ~ 0.06 eV for each charge state. Alignment of the vacancy-vacancy axis direction in the lattice is also achieved by stressing at elevated temperatures. The activation energy for this reorientation process is \sim 1.3 eV. The magnitude and sense of the alignment in both kinds of stress experiments are consistent with the microscopic model of the defect. It is pointed out that when the divacancy reorients its vacancy-vacancy axis, it is also diffusing through the lattice. The 1.3 eV is therefore also its activation energy for diffusion. Analysis of higher temperature annealing studies allow a lower limit estimate for the binding energy of the two vacancies as > 1.6 eV. The electrical level structure is deduced and it is concluded that the divacancy introduces one donor and two acceptor levels in the forbidden gap.

I. INTRODUCTION

HIS is the fourth in a series¹⁻³ giving detailed descriptions of defects produced by irradiation in silicon. In this paper we describe electron-paramagnetic-resonance (epr) spectra which we identify as arising from two different charge states of the divacancy. These spectra have been discussed briefly in previous publications.⁴⁻⁷ One, labeled⁸ Si-G6, we identify as arising from the singly positively charged state. The other, labeled⁹ G7, we identify as arising from the singly negatively charged state. The arguments leading to this identification will be presented along with a model of the microscopic configuration of the defect and the electronic structure in each charge state. In addition, such properties as the associated electrical-level structure in the gap, the activation energy of diffusion for the divacancy and its binding energy are estimated.

to be published).

⁸ This spectrum has previously been labeled the Si-J center (Refs. 4 and 5). The subsequent proliferation of centers found in silicon has necessitated a new labeling scheme (outlined in Ref. 7) which we will follow in this and subsequent papers in this series. For convenience in this paper, however, we will drop the prefix Si- meant to designate "silicon" since it is clear that this paper refers only to silicon.

⁹ Previously labeled the Si-C center (Refs. 4, 5, and 6).

In the paper immediately following this one,¹⁰ one of these spectra (G6) will be used as a tool to study the mechanism of the defect production by the irradiation. The information obtained there serves as strong additional confirmation of the identification as the divacancy.

II. EXPERIMENTAL PROCEDURE

The silicon samples were approximately 0.1 in. $\times 0.1$ in. $\times 0.5$ in. and were irradiated equally on opposite sides by 1.5-MeV electrons from a G.E. resonant transformer accelerator. For room-temperature irradiations the bombardment current was $\approx 2.5 \,\mu\text{A/cm}^2$, the maximum temperature rise in the sample being about 25°C. The samples were subsequently mounted with their long dimension along the axis of a TE_{011} microwave cavity and epr was studied at 20 kMc with a spectrometer which has been previously described.^{1,3}

Low-temperature irradiations were achieved in situ by introducing the beam through three 0.001-in. titanium windows, one each on the inner and outer walls of the cryostat and one on the microwave-cavity assembly. The sample was cooled by helium-gas exchange to liquid hydrogen or helium in the cryostat.

Access to the sample in the cavity from the top of the cryostat was available through a $\frac{1}{4}$ -in.-diam tube, coaxial with the cavity. For the stress experiments, a rod was inserted into this tube to transmit the force to the sample as has previously been described.¹ In the electric-field experiments, the high-voltage lead was encased in glass tubing and introduced through the same access tube in place of the stress rod. To prevent gas discharge, it was necessary to evacuate the microwave assembly. The applied voltage was 10 kV. In the

¹G. D. Watkins and J. W. Corbett, Phys. Rev. 121, 1001

<sup>(1961).
&</sup>lt;sup>2</sup> J. W. Corbett, G. D. Watkins, R. M. Chrenko, and R. S. MacDonald, Phys. Rev. 121, 1015 (1961).
⁸ G. D. Watkins and J. W. Corbett, Phys. Rev. 134, A1359

^{(1964).} ⁴G. D. Watkins and J. W. Corbett, Disc. Faraday Soc. 31, 86

^a G. D. Watkins and J. ... 211
^b J. W. Corbett and G. D. Watkins, Phys. Rev. Letters 7, 314
^c G. Bemski, B. Szymanski, and K. Wright, J. Phys. Chem. Solids 24, 1 (1963).
^r G. D. Watkins, Proceedings of the Symposium on Radiation Damage in Semiconductors, Paris, 1964 (Dunod Cie, Paris, 1965,

¹⁰ J. W. Corbett and G. D. Watkins, following paper, Phys. Rev. 138, A555 (1965).



experiments that required illumination of the sample *in situ*, a light-pipe was inserted into the access tube. The light-pipe was a $\frac{7}{32}$ -in.-diam stainless-steel tube which had been polished and gold-plated on the inside. A NaCl window was used at the entrance to the light-pipe.

The method for varying the temperature of the sample during epr study has been previously described,¹ as has been the method for applying stress at elevated temperatures.³ Annealing studies above room temperature were done in air in an oven, the samples being returned to the cavity and cryostat for epr observation after each anneal.

III. GENERAL RESULTS AND DISCUSSION

A. Experimental Results

1. General

The G6 spectrum is observed in low-resistivity p-type silicon. In boron-, aluminum-, gallium-, or indium-doped silicon it grows linearly with irradiation dose as long as the Fermi level remains locked to the acceptor level. The production rate in a room temperature radiation at 1.5 MeV is¹⁰ ≈ 0.008 defects/cm³ per electron/cm² which is an order of magnitude lower than the single-vacancy production (as monitored by the oxygen-vacancy pairs).¹⁰

The G7 spectrum is observed in high-resistivity *n*-type silicon. Starting with phosphorus-doped silicon, these defects are not observed until the irradiation has proceeded far enough that the Fermi level has receded to $\approx (E_c - 0.4)$ eV. It is thus associated with a level at this position and is observed only when this level does not contain an electron. The production rate is therefore less easy to measure, but it appears comparable to the G6 spectrum in p-type material.

The production rates of either spectrum do not appear to correlate with any known impurity (i.e., oxygen, particular donor or acceptor dopant, etc.). This suggests that each is associated with an *intrinsic* defect. Both are present after a 20.4° K irradiation, suggesting that each is a *primary* defect, i.e., not requiring annealing for formation. The fact that they are formed readily by 1.5-MeV electron irradiation indicates that they must be *simple* defect structures.

We have previously reported¹¹ that after a low-temperature irradiation and subsequent anneal, the G6 spectrum in p-type material is observed to increase when the isolated vacancy spectrum disappears. This is observed in vacuum-floating-zone silicon but not in pulled crystals (containing oxygen). Since oxygen is a good trap for vacancies,^{1,2} this is consistent with the identification of the G6 spectrum as the divacancy with its formation when diffusing isolated vacancies combine.

2. Spectra

In Fig. 1, we show the two spectra observed with $\mathbf{H} \| \langle 100 \rangle$ at 20.4°K. In both spectra, there is a strong central group plus weaker satellites symmetrically disposed on either side. Each spectrum can be described as arising from an anisotopic defect which has several equivalent orientations in the cubic silicon



FIG. 2. g values versus crystalline orientation with H in the (011) plane (see Fig. 3). (a) G6 spectrum, (b) G7 spectrum.

¹¹ G. D. Watkins, J. Phys. Soc., Japan, 18, Suppl. II, 22 (1963).



FIG. 3. Spin-Hamiltonian constants for the G6 and G7 spectra with axes indicated for one of the twelve defect orientations in the lattice. With the magnetic field H in the (011) plane as shown, this set of axes gives rise to the g values given by cb in Fig. 2.

lattice, and with the spin Hamiltonian

$$\mathcal{K} = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + \sum_{j} \mathbf{I}_{j} \cdot \mathbf{A}_{j} \cdot \mathbf{S}$$
(1)

with $S = \frac{1}{2}$.

The first term gives the positions of the central lines which are shown versus orientation of the crystal axes in the magnetic field¹² in Fig. 2. From this we determine the principal values of the g tensors which are given in Fig. 3 along with the principal axes for one of the equivalent defect orientations.

The second term in (1) describes magnetic hyperfine interaction with nuclei neighboring the defect. We interpret the satellites in Fig. 1 as arising from a strong hf interaction with a Si²⁹ nucleus (4.7% abundant, $I=\frac{1}{2}$) in the immediate vicinity of the defect. For both spectra, the intensity of the satellites relative to that of the central lines is twice the isotopic abundance

of Si²⁹, indicating that there are two equivalent sites which may accommodate a Si²⁹ nucleus. Study of the hyperfine satellites versus orientation demonstrates that these two sites are entirely equivalent, having identical A tensors. The principal values and axes for this hyperfine interaction are also given in Fig. 3. In the case of G6, additional partially resolved Si²⁹ hf structure, in close to the central group, is also observed. There appear to be three sets of satellites each of relative intensity corresponding to four equivalent silicon sites. It has not been possible to unravel their angular dependences, but the average magnitudes of the splittings correspond roughly to $|A| \approx 3$, 6, and 7 (10⁻⁴) cm⁻¹, respectively. These are presumably due to hf interactions with other atom sites in the vicinity of the defect. In the G7 spectrum, the lines are broader and no such structure is resolved. However, "shoulders" on the central lines suggest similar unresolved interactions of comparable magnitude for this spectrum also.

For later use, we label the transitions of Fig. 2 as referring to specific defect orientations. This has been done as follows. In Fig. 3, the four $\langle 111 \rangle$ axes are labeled "a," "b," "c," and "d." We label a defect orientation by two letters. The first letter denotes the $\langle 111 \rangle$ axis closest to g_3 and the second letter specifies the $\langle 111 \rangle$ axis closest to g_1 . The defect orientation illustrated in Fig. 3 is therefore *cb*. The corresponding spectral transitions are identified in Fig. 2.

B. Discussion

1. Model

In Fig. 4, we present a model for the defect giving rise to the two spectra. It is the divacancy with epr arising from the singly positive (G6) and singly negative (G7) charge states. In this model the two vacancies are



¹² There is one aspect of the spectra that is not understood. The amplitudes of the individual lines appear to vary somewhat depending upon the orientation of the dc (and possibly microwave) magnetic fields with respect to the corresponding defect axes. This variation is observed in both spectra but the details of the angular dependence appear to differ for the two. The magnitude of the variation may be a factor of 2. We cannot completely rule out "extraneous" causes such as subtle line shape changes, angular dependences of relaxation time, etc., but superficially it appears as though the transition matrix elements may be angle-dependent. The origin of this is not understood at present.



FIG. 5. Simple LCAO molecular-orbital model of the electronic structure of the divacancy: (a) before Jahn-Teller distortion, (b) after. The solid arrows denote the electrons, and their spins, for the singly positively charged state. The dotted arrows denote the additional electrons in the singly negatively charged state.

at adjacent atom sites, labeled c and c'. We can visualize the construction of the defect as follows: Initially, there are six broken bonds around the divacancy, one each for the six atoms neighboring it. Atoms a and d pull together to form a "bent" pair bond as do atoms a'and d'. Electron paramagnetic resonance arises from the remaining unpaired electrons in the extended orbital between atoms b and b'. For the plus-charge state there is one electron in the bb' orbital; for the negativecharge state, there are three.

Such a model explains the large hf interaction with the two equivalent atom sites b and b', the hf axis reflecting closely the $\langle 111 \rangle$ axis of the broken bonds at each site. The g tensor, reflecting somewhat more the over-all character of the wavefunction, is tilted toward the direction between the b and b' atoms (i.e., not $\langle 111 \rangle$).

A simple molecular-orbital treatment of the defect by the method of linear combination of atomic orbitals (LCAO) is shown in Fig. 5. A divacancy in the undistorted silicon lattice has D_{3d} symmetry. We construct the one-electron molecular orbitals as linear combinations of the broken-bond orbitals on each of the six neighboring atoms. The proper wave functions transforming according to the irreducible representations¹³

of D_{3d} are given in Fig. 5(a). In filling these orbitals,¹⁴ we place the first four electrons into a_{1g} and a_{1u} , paired off. The remaining electrons (one for the positive state, three for the negative) go into the e_u doublet. Because of the degeneracy associated with the partially filled e_u orbitals, a Jahn-Teller distortion takes place, lowering the symmetry to C_{2h} [Fig. 5(b)]. We deduce that the resulting shifts in the energy levels are large with respect to the original energy-level separations in D_{3d} , causing strong mixing between e_g and a_{1g} and between e_u and a_{1u} , respectively. As a result, the wave functions in C_{2h} reflect primarily the "pair" bonding (between a and d, a' and d', etc.) and only small ($\approx \lambda_{1,2}$) admixtures of the other atomic orbitals remain. Viewed this way, the "pair" bonding between a and d, a' and d', in Fig. 4 can be considered simply a manifestation of the Jahn-Teller effect.

This is still a considerable oversimplification, of course, because the electronic wave function will also spill over onto more distant neighbors. However, analysis of the hyperfine interactions in the next section shows that $\approx 70\%$ of the wave function can be accounted for on these six atoms alone, and this simplified localized "molecule" should therefore be a reasonable first approximation.

2. Hyperfine Interactions

Let us construct the wave function for the unpaired electron as a linear combination of atomic orbitals centered on the atom sites near the defect

$$\Psi = \sum_{j} \eta_{j} \psi_{j}. \tag{2}$$

At each atom site j, we approximate ψ_j as a hybrid 3s3p orbital given by

$$\psi_j = \alpha_j(\psi_{3s})_j + \beta_j(\psi_{3p})_j. \tag{3}$$

For the atoms adjacent to the vacancy, we take the p function as directed approximately along the $\langle 111 \rangle$ direction from the site to the center of the nearest vacancy. To a good first approximation, the hyperfine interaction at the *j*th nuclear site is determined solely by ψ_j , i.e., that part of the wave function close to the nucleus. In this approximation, the hyperfine interaction is axially symmetric along the *p*-orbital axis and can be written

$$A_{11} = a + 2b,$$

$$A_{1} = a - b.$$
(4)

Here the isotropic term a arises from the Fermi contact interaction

$$a_{j} = (16\pi/3) \left(\mu_{j}/I_{j} \right) \beta \alpha_{j}^{2} \eta_{j}^{2} |\psi_{3s}(0)|_{j}^{2}, \qquad (5)$$

¹³ In D_{3d} , there is an ambiguity in the labeling of the a_u states that arises from the fact that the group can be generated by either $C_{3v} \times i$ or $D_3 \times i$. The labeling in Fig. 5 corresponds to that for $C_{3v} \times i$. For $D_3 \times i$, which is often used in the literature, a_{1u} in the figure should be replaced by a_{2u} .

¹⁴ The ordering in energy of these orbitals indicated in Fig. 5 was deduced considering the kinetic energy associated with the nodes in the wave functions. Such a consideration leaves some uncertainty in the relative ordering of the e_a and e_u orbitals. However, the arguments that follow are not sensitive to this initial ordering.

TABLE I. Hyperfine parameters $(a_i \text{ and } b_i)$ and the corresponding molecular wavefunction coefficients $(\alpha_i^2, \beta_i^2, \eta_i^2)$ calculated from the observed hyperfine-interaction constants for the atom sites in the vicinity of G6 and G7 centers.

Spec- trum	Sites	Equiv. No.	<i>aj</i> (10 ⁻⁴ cm ⁻¹)	b_i (10 ⁻⁴ cm ⁻¹)	$lpha_j^2$	β_{i^2}	η_j^2
G6	b,b'	2	(-)49.3	(-)9.3	0.11	0.89	0.31
	?	4	(-) 7	•••	(0.25)	(0.75)	0.02
	a,d,a',d'	4	(-) 6	•••	(0.25)	(0.75)	0.02
	?	4	(-) 2	•••	(0.25)	(0.75)	0.01
G7	b,b'	2	(-)64	(-)7.7	0.17	0.83	0.27
	a,d,a',d'	4	(-)10	•••	(0.25)	(0.75)	0.03

where μ_j is the magnetic moment and I_j the spin of the *j*th nucleus. The anisotropic term *b* results from the dipole-dipole interaction averaged over the electronic wave function and is given by

$$b_j = \frac{4}{5} (\mu_j / I_j) \beta \beta_j^2 \eta_j^2 \langle r_{3p}^{-3} \rangle_j.$$
(6)

We have previously³ estimated for silicon, $|\psi_{3s}(0)|^2 = 31.5(10^{24} \text{ cm}^{-3})$ and $\langle r_{3p}^{-3} \rangle = 16.1(10^{24} \text{ cm}^{-3})$. Using these values, we can solve Eqs. (5) and (6) for α_j^2 , β_j^2 and η_j^2 at the *b*-*b'* sites, using the hyperfine constants given in Fig. 3. The results are given in Table I. Equations (5) and (6) predict that a_j and b_j should have the same sign as μ_j . With this assumption, there is no ambiguity in determining a_j and b_j from (4) even through the absolute values of A_{11} and A_1 were not determined. The signs of the a_j 's and b_j 's in Table I are in parentheses to indicate that they were not determined experimentally.

We see that for both spectra $\sim 60\%$ of the wave function can be accounted for on the two principal sites alone (b and b' of Fig. 4). In the case of G6, much of the remainder of the wave function can be accounted for by the partially resolved hf interactions observed in close to the central lines. The exact amount of the wave function involved is very sensitive to the anisotropic part b, which could not be determined. However, if we make a guess¹⁵ of 25% s and 75% p, we obtain the values given in Table I. Since there are four equivalent sites for each of these, they account for an additional $\approx 20\%$ of the wave function. The remaining wave function is presumably spread out over more distant sites, contributing to the remaining unresolved breadth.

In the absence of a detailed analysis of these weaker interactions, it is not possible to identify the specific sites in the model of Fig. 4 associated with each interaction. However, we will find in Sec. IV A that the interaction on sites a, d, a', and d' of Fig. 4 can be indirectly estimated from another experiment. There we find that for the G6 spectrum, a is $6(10^{-4})$ cm⁻¹ for these sites. We have therefore made this identification in Table I. For the G7 spectrum, the corresponding satellite structure for these weaker hf interactions was not resolved. However, again we will find that in Sec. IVA we can estimate the hyperfine constant a for the a, d, a', d' sites. The value determined is $10(10^{-4})$ cm⁻¹, and this is included in the table, along with estimates for the other corresponding quantities. The shoulders seen on the central lines are consistent with an interaction of this magnitude.

From Table I, we see that $\approx 70\%$ of the wave function is located on the six atoms surrounding the two vacancies and the localized molecule considered in Figs. 4 and 5 should represent a reasonable approximation.

3. g Tensor

We have previously³ considered the g tensor expected for an electron in a single broken-bond orbital in silicon. There we concluded that $\Delta g_{11} \approx 0$ and $\Delta g_1 \approx +0.01$ -0.02, where "parallel" and "perpendicular" refer to the broken-bond axis. This conclusion was based partially on a simplified theoretical treatment of the problem and partially upon the general consistency of g values found experimentally for centers that we have identified as made up of such dangling bonds.

Because the broken bonds at the two primary sites (b and b') of Fig. 4 have the same axis, we might also expect the g tensor for these centers to display the same behavior. We note that this appears to be the case for the G7 spectrum, with g_1 close to the freeelectron value and with Δg_2 and Δg_3 positive by the expected amount. The agreement is not as good however for the G6 spectrum, although the ordering, i.e., $\Delta g_3 > \Delta g_2 > \Delta g_1$, remains the same.

Of course, the wave functions are not localized solely on these two silicon atoms. Approximately 40% of the wave function is localized on other nearby atoms in the vicinity. A detailed treatment of the g shift would have to consider the contribution from this part of the wave function also. This contribution could well be large and of somewhat unpredictable sign because of the possibility of *interatomic currents* arising from the overlapping of the wave functions on these neighboring sites.¹⁶ We will not attempt a detailed treatment of these effects in this paper but simply note that apparently for the G6 spectrum, at least, these effects may be important.

IV. MOTIONAL EFFECTS

In the previous sections we have presented a model for the spectra and have shown that it is compatible

¹⁵ This corresponds to the normal admixture for sp^3 tetrahedral bonding, as was found to be the case for the more distant atomic sites of the oxygen-vacancy center (Ref. 1).

¹⁶ The g shifts arise from orbital angular momentum induced into the wave function by the spin-orbit interactions at the several atomic cores. The sense of the circulation of the electrons around the atomic cores may differ from that of the associated interactomic electronic circulation, and the sign of the effective spin-orbit interaction can then be reversed. Such effects have been observed in the color centers in alkali halides. [F. Luty and J. Mort, Phys. Rev. Letters **12**, 45 (1964); D. Y. Smith and W. B. Fowler, Bull. Am. Phys. Soc. **9**, 240 (1964); D. C. Krupka and R. H. Silsbee, Phys. Rev. Letters **12**, 193 (1964).]



with the observed hyperfine interactions and g tensors. There is always the question, however, as to whether this model is unique. Are there other possible microscopic configurations that might also be compatible with these quantities? In this section we will present other tests of the validity of the model.

The model of Fig. 4 predicts a number of motional effects. For instance, for the particular vacancyvacancy direction shown in the figure, there are two other entirely equivalent configurations, corresponding to (i) bonding a to b and a' to b', leaving the unpaired electron on d and d', or (ii) b to d and b' to d', with the unpaired electron on a and a'. These together with the configuration depicted in Fig. 4 represent the three equivalent Jahn-Teller distortions of Fig. 5. The barrier for reorientation for one distortion direction to another should not be large and we expect thermally-activated reorientation to manifest itself at relatively low temperatures. This motion can be studied in the resonance in two ways: (i) If the correlation time for the reorientation process is short enough ($\tau \leq 10^{-7}$ sec), the individual lines in the epr spectrum become lifetimebroadened and give a direct means of studying the nature and kinetics of the motion. Such a study is described in Sec. IV.A; (ii) in Sec. IV.B, the motion is revealed by studying the preferential alignment of the defects induced by the application of uniaxial stress to the crystal. In addition to revealing the nature and kinetics of the reorientation process, the magnitude and sense of the stress-induced alignment also confirms other important features of the model.

The vacancy-vacancy direction is another "degree of freedom" that can be probed by stress. In Sec. IV.C, preferential alignment of this axis of the defect is achieved by stress at elevated temperatures. The study of the magnitude and sign of the alignment plus the kinetics of its recovery gives a further test of the model.

All of these motional effects have been previously studied on a similar center, the phosphorus-vacancy pair.³ In that paper a detailed treatment of these effects was given. Rather than repeat this, the analysis in the following sections will rely heavily upon the formalism developed in this preceeding paper. The interested reader should refer to it for the details.

A. Low-Temperature Linewidth Studies

In the temperature region $\approx 40-110$ °K, both spectra are observed to change drastically as shown for the G6 spectrum in Fig. 6. Initially some of the lines broaden and disappear as the temperature is raised, and at higher temperatures a simplified spectrum emerges.

This behavior suggests thermally activated reorientation of the defects. Because of the anisotropy in the g value, each time a defect reorients, its resonance position changes abruptly, giving rise to a lifetime broadening of the multiplets in the spectrum. In the initial stages of the broadening, the width of the multiplets gives a direct measure of the lifetime τ of the random jump motion. As the temperature is raised, eventually motional *narrowing* will occur (the anisotropy will be averaged out) and a new set of lines will emerge at the *average* position of the original multiplets.

The effect of this motion can be understood directly from Fig. 2, which shows the variation of the g value versus crystalline orientation for the differently oriented defects of each spectrum. We note by reference to Figs. 3 and 4 that the labels of Fig. 2 have a simple interpretation in terms of the model of the defect. Considering a vacancy site at c' (the center of the unit cell shown in Fig. 4), the first letter denotes the position of the other vacancy and the second letter denotes the site (and its primed partner) for the unpaired electron. Therefore, in exciting the thermally activated reorientation from one Jahn-Teller distortion direction to



FIG. 7. Lifetime τ of the Jahn-Teller reorientation versus temperature for both spectra.

another, the second letter of the orientation designation changes, but its first does not. The corresponding g value changes can be read directly from Fig. 2.

Figure 6 is for $\mathbf{H} \| \langle 111 \rangle$, and the three lines observed at low temperatures correspond to the three distinguishable g values (labeled A, B, C) in Fig. 2(a). We note that for multiplet C, the reorientation has no effect because each of the three Jahn-Teller distortions gives rise to the identical g value (da, db, dc, in Fig. 2). (This multiplet arises from the defects for which the magnetic field is pointing along the vacancy-vacancy direction.) In Fig. 6, this multiplet stays sharp throughout this temperature region, confirming this expectation of the model. The other multiplets are altered by the motion and broaden as expected. Also, as expected, at elevated temperatures, a new line emerges at the weighted average position of A and B.

Proceeding as in our previous treatment,³ we have studied these effects versus temperature for both spectra and have deduced the lifetime τ of the reorientation process. This can be done in both the initial broadening and final narrowing regions, and the results are shown in Fig. 7. As discussed previously,³ there are some uncertainties in these determinations, as evidenced by the scatter of the points, but one can still make a reasonably good estimate of τ and its activation energy for each spectrum because the points span about two decades. However, we will defer this until the next section, where additional experimental data allow a more accurate estimate. We note only that the activation energies are ≈ 0.06 eV, which we feel is a reasonable value for such an electronic "bond-switching" motion.

That this motion is "electronic" and not a reorientation of a molecular unit as a whole is clearly demonstrated in Fig. 8. Here the G6 spectrum is shown both at 20°K and in the motionally averaged state at 108°K, with $\mathbf{H} || \langle 100 \rangle$. We note that the hf satellites for the motionally averaged spectrum are \approx three times as intense relative to the central group but with a splitting reduced to 22.4 G. This is just what we expect because in the motionally averaged state, the defect becomes a *six* silicon center. That is, in the model of Fig. 4, the



FIG. 8. The G6 spectrum (a) at 20.4°K and (b) in the motionally averaged state at 108°K, with H|| $\langle 100\rangle$.



FIG. 9. Change in the G6 spectrum (H||[011]) under [011] compressional stress at 30°K. The insets show a typical defect orientation for each multiplet.

unpaired electron is hopping between the aa', bb', and dd' site pairs so fast as to be indistinguishable from a defect in which the electron is in a LCAO molecular orbital spread over all six. The hyperfine interaction is now given by

$$\begin{array}{l} 4'(\langle 100 \rangle) = \frac{1}{3} A_{bb'}(\langle 100 \rangle) \\ + \frac{1}{3} A_{aa'}(\langle 100 \rangle) + \frac{1}{3} A_{dd'}(\langle 100 \rangle), \quad (7) \end{array}$$

where $A_{bb'}$ is the interaction for the configuration of Fig. 4 when atom b or b' is Si²⁹ and $A_{aa'}$ and $A_{dd'}$ are the correspondingly smaller terms when a, a', d or d', are Si²⁹. Equation (7) simply expresses the fact that if one of the six silicon sites surrounding the divacancy contains a Si²⁹ nucleus, there is an interaction of $A_{bb'}$ for the third of the time the electron is in an orbital located mostly on the atom pair which includes this site, but there is also $A_{aa'}$ and $A_{dd'}$ for each of the other one-thirds when the electron is located primarily on the other two silicon atom pairs.

With $A'(\langle 100 \rangle) = 22.4$ G, $A_{bb'}(\langle 100 \rangle) = 54.2$ G, we can solve (7) for $A_{aa'}$ and $A_{dd'}$ which must be equal by symmetry. This gives

$$A_{aa'}(\langle 100 \rangle) = A_{dd'}(\langle 100 \rangle) = \pm 6.5 \text{ G} = \pm 6(10^{-4}) \text{ cm}^{-1},$$

where the sign is the same as $A_{bb'}(\langle 100 \rangle)$. A similar study for the G7 spectrum reveals the same behavior with $A'(\langle 100 \rangle) = 30.2G$ and $A_{bb'}(\langle 100 \rangle) = 69.5G$. Equation (7) therefore gives for this spectrum

$$A_{aa'}(\langle 100 \rangle) = A_{dd'}(\langle 100 \rangle) = \pm 10.5 \text{ G} = \pm 10(10^{-4}) \text{ cm}^{-1};$$

again of the same sign as $A_{bb'}$. The intensity of the hf satellites in the averaged spectrum was not adequate to study the anisotropy of A' and hence $A_{dd'}$, etc.,

TABLE II. Comparison of observed and calculated energy differences (in °K) for the differently oriented defects under stress at low temperatures. The stress is 865 kg/cm² and is applied along a $\langle 110 \rangle$ direction.

Spectrum	T_{i}	Observed (°K)	Calculated (°K)
G6	T_{α} T_{θ}	 —135	+16 $\Gamma - 1357$
G7	$ \begin{array}{c} T_{\alpha} \\ T_{\beta} \end{array} $	+30 - 176	+21 [-180]

for either spectrum. The values determined above represent averages along the three perpendicular cubic axes and therefore give to a first approximation the isotropic part a of these interactions. These values have been included in Table I.

B. Low-Temperature Stress Studies

All of the possible orientations of the divacancy are equally probable in the cubic silicon lattice, and at thermodynamic equilibrium we have equal numbers of defects in each of these orientations. If we now strain the crystal, and distort it from cubic symmetry, the various orientations are no longer equivalent and, if the defects are free to reorient, they will do so, tending to seek out the lowest energy configuration.

In Fig. 9, the effect on the G6 spectrum of applying a uniaxial compressional stress along a (110) axis of the crystal at 30°K is shown. Referring to Fig. 3, the stress is along the [011] direction and the magnetic field is along the [011]. Representative defects associated with each of the multiplets are identified in Fig. 9 along with their corresponding letter designations. It is seen that the stress produces a large effect, the ab, and ac orientations being strongly suppressed, with the ad being proportionately enhanced. We note at the outset that this is the sense that we might expect from the model in that the defect prefers to align in such a way that the applied compression serves to push the two pairs of bonding silicon atoms closer together. Stated another way, the preferred alignment is such that the applied stress aids the Jahn-Teller distortion of Fig. 5. Similar results are also found for the G7 spectrum. We will return to the magnitude and sense of the alignment but first let us consider the kinetics.

Upon removal of the stress the recovery of each spectrum is observed to follow a simple exponential law with a time constant that depends upon temperature. For the G6 spectrum at 20.4°K, the time constant τ was measured to be $1.9(10^5)$ sec; at 30°K, τ was 2.1 sec. This τ is the same characteristic reorientation time as that involved in the linewidth studies, and these points are therefore also plotted in Fig. 7. Together with the linewidth estimates these points span fourteen decades in τ . Fit to a straight line on this semilog plot, we therefore obtain a highly accurate estimate of the

activation energy and pre-exponential factor as shown in the figure.

Similar studies were also performed on the G7 spectrum, and these results are also shown in the figure.

The magnitude of the alignment has also been studied quantitatively in terms of the model. As has been shown previously,³ the [011] stress creates three nonequivalent sets of orientations. With a Boltzmann distribution between these sets, this gives two energy differences kT_{α} and kT_{β} defined in terms of the populations of the sets by¹⁷

 $n_{bc}/n_{bd} = \exp(-T_{\alpha}/T)$,

 $n_{ad}/n_{ab} = \exp(-T_{\beta}/T)$

$$n_{bc} = n_{cb}; n_{ad} = n_{da},$$

 $n_{bd} = n_{db} = n_{ba} = n_{ab} = n_{cd} = n_{dc} = n_{ca} = n_{ac}.$

In Table II, the measured values for these quantities are given at a stress of 865 kg/cm². (For G6, only T_{β} could be determined because for it the *bc*, *cb* multiplets were not sufficiently well resolved.)

To interpret these, we take a very simple view of the defect. We assume that the change in energy of a particular defect orientation is determined solely by the component of strain along the line joining the two pairs of "bonding" silicon atoms (a and d, a', and d' of Fig. 4). As before³ we define the change in the defect energy per unit strain along this direction as

$$M = (dE/d\epsilon)_{\rm Si-Si}.$$
 (9)

(8)

Using the measured value for T_{β} in Table II, and following our previous procedure,³ we obtain for the G6 spectrum

$$(M)_{G_6} \cong +24 \text{ eV/unit strain},$$
 (10)

and for G7,

$$(M)_{\rm G7} \cong +32 \, {\rm eV/unit \ strain}$$
. (11)

The values of T_{α} determined using these estimates of M are also given in Table II. For G7, where T_{α} could also be measured experimentally, the agreement is fairly good, considering the simplified model.¹³

The positive value of M means that the energy is lowered when the atoms of the bonding pairs are pushed together, as we noted earlier. Since there are four electrons involved in these bonding orbitals (see Fig. 5), Eqs. (10) and (11) mean that, *per electron*, there is $\approx +6$ eV/unit strain for G6 and $\approx +8$ eV/unit strain for G7. We argue that these values are reasonable

 $^{^{17}}$ See Fig. 14(a) in Ref. 3. The defect labeling scheme has been chosen here so that the formulas developed in Refs. 1 and 3 can be used directly.

used directly. ¹⁸ In previous studies of the phosphorus-vacancy pair (Ref. 3) and the oxygen-vacancy pair (Refs. 1 and 2) a more detailed study was made including stress along the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions. For these it was found that the simplified analysis outlined here accounted quite satisfactorily for the complete behavior of the defects.

being similar to the value $\approx +8$ eV/unit strain per electron found for the similar bonding orbitals in the vacancy-oxygen pair^{1,2} and the phosphorus-vacancy pair.³

C. High-Temperature Stress Studies

There is another "degree of freedom" for the defect, the vacancy-vacancy axis, which has not been probed as yet. In the low-temperature studies this axis remained fixed. In terms of the model, it should be more difficult for this axis to change because *atoms* must rearrange rather than the easier *electronic* rearrangement involved in the low-temperature motion.

This vacancy-vacancy axis reorientation can be revealed by stress alignment at elevated temperatures. For this the crystals were compressed along a $\langle 110 \rangle$ axis to $\approx 1870 \text{ kg/cm}^2$ at 160°C in an external squeezing apparatus for ≈ 1 h, then cooled to room temperature with stress on, removed and inserted into the microwave cavity, and then cooled to 20.4°K for study. A significant alignment was achieved, as can be seen in Fig. 10 for the G6 spectrum. By reference to Figs. 2, 3, and 4, we see that the preferred direction for the vacancyvacancy axis is in the plane perpendicular to the stress direction.

From Fig. 10, we estimate the degree of alignment

$$\frac{n_{1}}{n_{11}} = \frac{n_{da} + n_{db} + n_{dc}}{n_{ba} + n_{bc} + n_{bd}} \cong 1.5.$$
(12)

Studies for the G7 spectrum give similar results again with a value ≈ 1.5 . We note that in the low temperature studies of the previous sections, small differences between the behavior of the G6 and 67 spectra under stress were observed. Indeed, although being associated with the same defect, we would expect the detailed properties of the defect to depend somewhat upon its charge state. However, at elevated temperatures, whether in high resistivity *n*-type silicon for studying



FIG. 10. G6 spectrum (20.4°K, H||[011]) (a) before and (b) after 1870 kg/cm² [011] compressional stress at 160°C.



FIG. 11. Recovery of the stress-induced divacancy axis polarization during a (15-min) isothermal anneal. (See Ref. 17.)

the G7 spectrum, or lower resistivity p type for the G6 spectrum, the Fermi level recedes toward the middle of the gap and the divacancy in either material will tend to approach the same charge state. It is to be expected then that in measurements such as these that reflect the *elevated-temperature properties* of these defects the properties monitored by either spin resonance center will tend to become the same.

Analysis of Eq. (12) similar to that in the previous section where we consider only the strain along the bonding silicon pairs and with an average value¹⁹ of $M \cong +28 \text{ eV/unit strain predicts}$

$$(n_{\rm I}/n_{\rm II}) = 1.44$$

The close agreement of this with the observed value of ≈ 1.5 demonstrates that the major consideration in the alignment of the vacancy-vacancy axis is again the desire of the two bonding silicon atom pairs to be pushed together, as predicted by the model.

We can now study the kinetics of the reorientation of the vacancy-vacancy axis by studying the recovery of the stress-induced alignment. This is shown in Figure 11 for 15-min isochronal annealing studies of each spectrum. Here we note again the similarity of the two spectra both in the magnitude of alignment²⁰ as before and also in the recovery versus temperature. Detailed kinetic studies have not been made, but if we assume first order kinetics with a characteristic frequency factor of 10¹³, we obtain from Fig. 11 and activation energy for the process of 1.3 eV, as shown in the figure.

It is interesting to inquire as to how this reorientation takes place. Referring to Fig. 4, we note that when the divacancy reorients, it also moves one lattice spacing in the lattice. For instance, atom b may hop into c'and then over to c, leaving the divacancy with a new

¹⁹ Average of the values determined from the low-temperature studies of each spectrum given by Eqs. (10) and (11).

²⁰ The two values plotted for G6 represent two different ways of estimating the alignment from the spectrum. The difference in these two estimates gives some indication of their absolute accuracy. The accuracy for G7 may be somewhat better due to the better resolution of the spectral multiplets.



FIG. 12. Disappearance of the divacancy spectra in (15-min) isochronal annealing studies.

axis and displaced to sites *b-c'*. In studying the kinetics of the reorientation, we are therefore also studying the kinetics of migration, or *diffusion* of the divacancy. We have thus determined in a rather simple way that the activation energy for diffusion of the divacancy is ≈ 1.3 eV.

The two vacancies have had to separate one lattice spacing (atom b hopping into c' leaves the vacancies at b and c) and then reunite (atom b then hopping into c) in order for the divacancy to reorient-or diffuse. The activation energy for this process therefore reflects the binding energy that must be overcome between the two, as well as the activation energy for single vacancy motion. We have previously determined the activation energy for single-vacancy motion to be $\approx 0.3 \text{ eV}$,¹¹ which suggests a substantial binding energy ≈ 1.0 eV between the two vacancies. Actually it must be even greater than this in that we do not observe any loss of divacancies in the annealing studies of Fig. 11. There must still be substantial binding even with the vacancies in their first separated position. We can make a further estimate of the binding energy by annealing studies to be described in the next section.

V. OTHER EXPERIMENTS

A. Annealing Studies

The results of 15-min isochronal annealing studies of the disappearance of the G6 and G7 spectra are shown in Fig. 12. In "pulled" crystals (containing oxygen to $\approx 5 \cdot 10^{17}/\text{cm}^3)^{21}$ both spectra follow similar annealing curves with the 1/e point ≈ 290 °C. With the single jump rate given in Fig. 11, we calculate that the divacancy has made $\sim 10^4$ diffusional jumps after 15 min at that temperature. Since the fractional oxygen concentration is $\sim 10^{-5}$, we must consider the possibility that the divacancy has still not dissociated but only run into oxygen and become trapped. That this is apparently the case is demonstrated in Fig. 12 by a study in floating zone silicon of the G6 spectrum anneal.²² In this lowoxygen-content material, the divacancies require higher temperatures ($\approx 350^{\circ}$ C) to anneal out. We still do not know whether the divacancy has finally dissociated or not, but if we assume that it has, we can estimate a lower limit for the binding energy.

After 15 min at 350°C, we estimate from the single jump rate given in Fig. 11 that the divacancy has reoriented $\approx 2(10^5)$ times. We argue then that each time the two vacancies separate one lattice jump, the probability at 350°C of return must be $\geq 2(10^5)$ that of separation. We equate this to a Boltzmann factor weighting the return and dissociation processes in this first separated position

$$\alpha \exp(+\Delta E/kT) > 2(10^5)$$
,

where α is a geometric factor (≈ 1). Taking $\alpha = 1$, we obtain $\Delta E \ge 0.65$ eV. This quantity is not strictly equal to a binding energy at this site but rather gives a difference in barrier heights as shown in Fig. 13.

Figure 13 summarizes schematically what has been learned from these annealing and high-temperature stress studies. We have plotted the interaction between the two vacancies versus their separation. The abscissa denotes schematically the different atom positions for one vacancy neighboring the other. They are not necessarily in a straight line. We don't know the exact shape to be expected, but it seems reasonable to assume it is something as shown. The height of the first maximum is determined to be ~ 1.3 eV from the stress orientation studies (Fig. 11). The $\Delta E > 0.65$ eV comes from the annealing studies (Fig. 12). The similarity of the G6 and G7 center behavior in these studies suggest that the properties being monitored are either relatively insensitive to the charge state of the defect, or, more likely, that they refer to the intermediate, i.e., neutral, charge state. We therefore tentatively conclude that the values given in Fig. 13 refer to the neutral charge state of the divacancy.

We have also included in Fig. 13 the activation energy 0.33 eV previously determined for the motion



FIG. 13. The potential energy (in eV) of one neutral vacancy in the vicinity of another, as deduced from the high-temperature annealing studies of the divacancy. The abscissa denotes the various neighbor positions in order of increasing separation, which are not necessarily in a straight line.

center (Ref. 3) and it anneals at a lower temperature, the material, therefore, returning to low resistivity prematurely.

²¹ As determined by the intensity of the 9μ infrared band.

²² A similar study of the G7 anneal in floating zone material was not possible because of the requirement that the material remain high-resistivity n type for accurate monitoring of the spectrum. In floating-zone n type silicon, the dominant defect is the E

where

or

FIG. 14. Electrical levels associated with the divacancy. The level positions (in eV) are given to the nearest band edge. The charge states giving rise to the G6 and G7 spectra are indicated.

of the neutral isolated vacancy.²⁸ With this, we can deduce a lower limit for the binding energy of the two vacancies >1.6 eV, as shown. This is a lower limit because we do not know whether the divacancy is dissociating in the floating zone sample of Fig. 12 or whether it is still being trapped by impurities.

B. Electrical Level Structure

The suggested level structure is shown in Fig. 14. From production rate studies in *n*-type silicon, we have previously noted that the G7 spectrum is associated with a level at $\approx (E_e - 0.4)$ eV and is observed when this level does not contain an electron. Since $S = \frac{1}{2}$ in the G7 spectrum, the defect must be in an odd charge state consistent with the identification as the single negative charge state in Fig. 14. This requires the double negative charge state above this level.

The G6 spectrum is seen in low $\rho \not p$ -type silicon and, because $S=\frac{1}{2}$, we have identified it with the single positively charged state. We know that the level associated with this donor state is above $(E_v+0.16)$ eV because the G6 spectrum is still the stable charge state in indium-doped silicon, for which the Fermi level is at $(E_v+0.16)$ eV. We have estimated the level position more accurately by the following optical-bleaching experiment.

A p-type silicon sample ($\approx 10^{16}B/\text{cm}^3$) was irradiated at room temperature to a total dose of $\approx 2 \cdot 10^{18} el/cm^2$ at 1.5 MeV. With such heavily irradiated material, the electronic equilibration time in the absence of light at 20.4°K was essentially infinite. The sample was illuminated at this temperature first with unfiltered light to generate a large intensity of the G6 spectrum and then the light was turned off. Subsequently, the sample was illuminated by light from a Perkin Elmer Model 83 monochromator, which was slowly scanned with increasing energy. At ≈ 0.25 eV, the onset of bleaching of the G6 spectrum was clearly observed. From this we deduce that the donor level is at $\approx (E_v + 0.25)$ eV, as shown in Fig. 14, and that bleaching arises from the optical excitation of a hole from the defect level to the valence band edge.²⁴

The divacancy therefore introduces three levels in the gap, with four possible charge states. It can act either as a single donor or double acceptor.

C. Electric Field Effect

Because of the small overlap between the b and b' orbitals of Fig. 5, we might expect the symmetric (a_g) and antisymmetric (b_u) orbitals made up from them to be close in energy. One experiment that we have performed to try to measure this separation was to study the effect on the G6 spectrum of the application of a large dc electric field to the sample. These two states, being of opposite parity, are connected by the electric field. First-order perturbation theory gives for the orbital in the presence of an electric field **E**

$$\psi \to 2^{-1/2} [(b+b') + \lambda(b-b')], \qquad (13)$$

$$\lambda = \frac{1}{\Delta E} \left\langle \frac{b+b'}{\sqrt{2}} \middle| e\mathbf{r} \cdot \mathbf{E} \middle| \frac{b-b'}{\sqrt{2}} \right\rangle \cong \frac{e\mathbf{R} \cdot \mathbf{E}}{2\Delta E} \,. \tag{14}$$

Here **r** is the position vector of the electron in the molecular orbital, **R** is the vector distance between the b and b' sites and ΔE is the energy spacing between the two states. In Eq. (13) the equivalence of the b and b' sites has been destroyed and we would expect to observe a *splitting* in the hf structure as a result.

An electric field of 8 kV/cm was applied along the $\langle 100 \rangle$ axis of the crystal and no detectable splitting was observed. From this, we estimate that $\lambda < 0.02$, giving

$$\Delta E > 0.007 \text{ eV} \tag{15}$$

$$\Delta E/k > 80^{\circ} \mathrm{K}$$
.

In the neutral charge state of the divacancy this energy ΔE should correspond closely to the triplet (S=1)-singlet (S=0) separation. Equation (15) explains why no spectrum is observed at low temperatures for the neutral divacancy. Equation (15) does not rule out the possibility of thermal excitation of triplet states at room temperature however. Several $\bar{S}=1$ centers have been reported in room temperature studies by Jung and Newell²⁵ in neutron-irradiated silicon. As pointed out by these authors, one of these centers (II, III) has much of the expected characteristics of the divacancy. However, as they noted, the lack of low-temperature motional effects and the instability of that center above $\approx 185^{\circ}$ C rules out this possibility. We have searched in electron irradiated silicon at room temperature and have so far found no

²³ As discussed in Ref. 7, this value (determined in Ref. 11) is believed to be associated with the neutral charge state of the vacancy.

²⁴ In such an experiment there is always the alternative explanation that ionization of an electron has occurred at an entirely different defect site and that bleaching of the G6 spectrum results

when the electron released to the conduction band is trapped at the divacancy site. This would require a donor level at $(E_e - 0.25)$ eV. To our knowledge no such level in irradiated silicon has been reported in the literature. This, combined with the fact that a level has been reported [G. K. Wertheim, Phys. Rev. 110, 1272 (1958)] at $(E_v+0.27)$ eV, makes us tentatively rule out this alternative possibility.

²⁵ W. Jung and G. S. Newell, Phys. Rev. 132, 648 (1963).

S=1 center of sufficient intensity to be a candidate for the divacancy.

VI. SUMMARY AND CONCLUSIONS

We conclude that the divacancy introduces a single donor and two acceptor levels into the forbidden gap and can therefore exist in four different charge states. We identify two epr spectra, G6 and G7, as arising from the singly positive and the singly negative charge states of the divacancy, respectively.

The model of the divacancy deduced from the studies in this paper is one in which the two vacancies are at adjacent atom sites. Four of the six silicon atoms adjacent to the divacancy bond together by pairs and the remaining electrons are spread over the other two atoms, which are separated from each other across the divacancy. For the G6 spectrum there is one electron shared between these two atoms; for the G7, there are three. This pulling together of the other atom pairs can be viewed as a manifestation of the Jahn-Teller effect. The primary confirming features in the epr studies for both spectra are summarized as follows:

(1) Both spectra are produced in a 20.4°K irradiation with 1.5-MeV electrons (as well as room temperature irradiations), suggesting that they arise from a simple defect which can be produced as a primary event. Their production rates depend only upon Fermi level and show no correlation with any known impurity such as oxygen, particular acceptor or donor, etc. Also, the G6 spectrum is observed to grow upon annealing when single vacancies (also observable by epr) disappear, suggesting vacancy-vacancy pairing to form divacancies.

(2) Analysis of the Si²⁹ hf interactions indicates that $\approx 60\%$ of the wave function is located on the dangling bonds of two equivalent silicon atoms. Another $\approx 20\%$ is accounted for by partially resolved hyperfine interactions with ≈ 12 nearest neighbors, with the remaining $\approx 20\%$ presumably spread out over more distant sites.

(3) The general magnitude of the g shifts is consistent with those expected for a defect made up of dangling broken bonds around vacancies. Also, the symmetry of the g tensor is consistent with the symmetry of the model. A detailed treatment of the g shift, however, has not been given.

(4) Motional broadening and narrowing effects are observed in the spectra in the temperature region 40-110°K and are attributed to the thermally activated reorientation from one Jahn-Teller distortion direction to the other. Analysis confirms that the motion is that of an electronic "bond switching" (not atom motion) and that the motion is around the vacancy-vacancy axis as predicted by the model.

(5) This motion is also studied by stress-induced alignment at lower temperatures. Combined with the linewidth studies, the kinetics of the reorientation

processes can be obtained with very high precision. The observed activation energies ≈ 0.06 eV appear reasonable for this process. The sense of the alignment is consistent with the natural preference of the defect to align so that the applied stress aids the Jahn-Teller distortion. The degree of alignment can be accounted for by a simple model that only considers the change in energy per unit strain along the axis joining the bounding Si-Si pairs. The magnitude deduced for this parameter is reasonable, being of the order of observed deformation potentials.

(6) Stress-induced alignment of the vacancy-vacancy axis is also studied for both spectra. The sense and magnitude can also be accounted for in terms of the model. The kinetics of this process, with an activation energy of 1.3 eV, appear reasonable for the atom rearrangements required by the model.

It is pointed out that the divacancy, in reorienting, is also diffusing through the lattice, and the 1.3 eV is also the activation energy for diffusion for the defect. Annealing studies show that the divacancy can diffuse large distances in the lattice without dissociating and an estimate can be made for its binding energy of ≶1.6 eV.

These elevated temperature stress and annealing experiments give identical results when monitored by either of the two spectra. This tends to confirm that both spectra are associated with the same defect. It also leads us to conclude that the measured binding energy and activation energy for motion refer to the neutral charge state of the divacancy.

We may compare the results with recent calculations of Scholz and Seeger.²⁶ They calculated the binding energy of the neutral divacancy in silicon by considering the neighboring atoms to reform bonds by pairs, using a Morse function to describe the bond strength. (This is similar to the approach used by Swalin,²⁷ Scholz,²⁸ and Scholz and Seeger²⁹ in calculations on the isolated vacancy, although the divacancy calculation was somewhat less detailed in that they did not allow for lattice distortions.) One of the bondpairing configurations they considered corresponded to the model of Fig. 5 and they calculated for it a binding energy of 1.16 eV. Considering the simplicity of the calculation, this agreement is perhaps adequate. The marksmanship is about as good as their calculations of the formation energy for the isolated vacancy²⁶ which give 2.78 eV as compared to our recent experimental estimate,³ of 3.6 ± 0.5 eV. It is interesting to note, however, that they calculate a greater stability $(\sim 0.1 \text{ eV})$ for a different pair bonding configuration then the experimentally observed one of Fig. 5. The

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²⁶ A. Scholz and A. Seeger, Proceedings of the Symposium on Radiation Damage in Semiconductors, Paris, 1964 (Dunod Cie, Paris, 1965, to be published).
 ²⁷ R. A. Swalin, J. Phys. Chem. Solids 18, 290 (1961).
 ²⁸ A. Scholz, Phys. Stat. Solidi 3, 42 (1963).
 ²⁹ A. Scholz and A. Seeger, Phys. Stat. Solidi 3, 1480 (1963).

failure to detect such a configuration in the epr studies suggests that this result is not correct.

In the following paper,¹⁰ the detailed mechanism by which the divacancy is formed in the damage event will be studied. There it is found that the threshold for production of these spectra is greater than that for the single vacancy. Also a preferential alignment of the defects with respect to the bombarding beam direction is achieved. These serve as strong additional confirmation of the model.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge the assistance of W. Colliton in all phases of the measurements. We are indebted to Dr. R. W. Redington for the use of the monochromator.

PHYSICAL REVIEW

VOLUME 138. NUMBER 2A

19 APRIL 1965

Production of Divacancies and Vacancies by Electron Irradiation of Silicon

J. W. CORBETT AND G. D. WATKINS General Electric Research Laboratory, Schenectady, New York (Received 19 November 1964)

A study is described of the dependence of the room-temperature production of divacancies and vacancies in silicon upon the energy of the bombarding electrons over the range 0.7-56 MeV. For the divacancy, the Si-G6 electron-paramagnetic-resonance spectrum associated with the singly positively charged state of the defect was monitored. As a monitor for single-vacancy production, the Si-B1 center due to the oxygenvacancy pair was used. Over the energy range 0.7-1.5 MeV, the divacancy production rate rises a factor of 7 while the single-vacancy rate rises only a factor of 1.5, reflecting a higher threshold for divacancy production, as expected. Also presented are data on the dependence of the divacancy production rate on the orientation of the crystal axes with respect to the incident beam and on the resulting anisotropy of the divacancy orientation in the lattice. The results of the anisotropy studies are shown to be consistent with a simple microscopic model of the damage event.

I. INTRODUCTION

N this paper, we present measurements of the de-**L** pendence of the \hat{direct} production of divacancies in silicon at room temperature upon the energy of the incident electrons. We also present data on the dependence of this production rate on the orientation of the crystal axes with respect to the incident beam, and on the resulting anisotropy of the divacancy orientation in the crystal lattice.¹

For this study, the epr spectrum associated with the singly positively charged state of the divacancy (Si-G6)² was monitored. In order to assure that only divacancies produced as a primary damage event were observed, the study was performed in oxygen-doped (pulled) silicon. The oxygen is a good trap for mobile single vacancies,^{3,4} inhibiting their agglomeration to form additional divacancies.

Also reported are measurements of the energy dependence of the room-temperature production of the oxygen-vacancy pairs. For this, the associated Si-B1⁵ epr spectrum was monitored. Since oxygen is a dominant trap for mobile vacancies in pulled silicon, the oxygenvacancy pairs should serve as a reliable monitor of the single-vacancy production at room temperature.

It is found that the energy dependence for divacancies and oxygen-vacancy pairs are significantly different. reflecting a higher threshold energy for divacancy formation, as expected. In addition, the studies of the anisotropy of the divacancy production give insight into the details of the damage process.

II. EXPERIMENTAL

The Si-G6 spectrum, used as the divacancy monitor, is observed when the Fermi level is below $(E_r + 0.25)$ eV2; as a result, these measurements were performed on p-type (boron $\sim 2 \times 10^{16}$ /cm³) pulled silicon.⁶ The Si-B1 spectrum, used as the oxygen-vacancy pair monitor, is observed when the Fermi level is above $(E_c+0.17)eV^3$; for these studies, *n* type (phosphorus $\sim 2 \times 10^{15}$ and 5×10^{16} /cm³) pulled silicon⁷ was used. For all samples, production-rate studies were performed at low enough irradiation doses such that the Fermi level stayed locked to the original values. Under these conditions a linear production rate of spectra was observed versus integrated irradiation flux. This is a necessary feature of production-rate measurements and was always checked by at least two successive

¹ A preliminary report of this work was given in J. W. Corbett and G. D. Watkins, Phys. Rev. Letters 7, 314 (1961). ² G. D. Watkins and J. W. Corbett, preceding paper, Phys.

Rev. 138, A543 (1965).

 ³ G. D. Watkins and J. W. Corbett, Phys. Rev. 121, 1001 (1961).
 ⁴ J. W. Corbett, G. D. Watkins, R. M. Chrenko, and R. S. McDonald, Phys. Rev. 121, 1015 (1961).

⁶ This center was originally labeled the Si-A center and is discussed in Refs. 3 and 4. The new labeling scheme has been outlined in G. D. Watkins, Proceedings of the Symposium on Radiation Damage in Semiconductors, Paris, 1964 (Dunod Cie, Paris, 1965, to be published).

⁶ Purchased from DuPont Company.

⁷ Kindly supplied by Dr. R. O. Carlson.