SILICON DIVACANCY AND ITS DIRECT PRODUCTION BY ELECTRON IRRADIATION

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To date two defects produced in radiation damage of silicon have been identified.[1,2] These defects are a vacancy-oxygen pair and a vacancy-phosphorous pair. They were identified largely by their associated electron spin resonance spectra and have been labeled the Si-*A* and Si-*E* centers, respectively. The studies associated with these identifications demonstrated that the vacancy is mobile in a room-temperature irradiation experiment and emphasized the importance of impurities in influencing the radiation-damage processes. In this Letter we report the identification of an intrinsic defect, which is stable at room temperature, the divacancy. We also demonstrate that this defect can be produced directly in a high-energy electron irradiation (that is, the migration and agglomeration of vacancies is not required for its formation). In addition, a marked anisotropy is observed in the production rate with respect to the electron beam direction, giving insight into the detailed production process.

The divacancy is shown in Fig. 1. It consists of two vacant, nearest-neighbor, lattice sites, *A* and *B*, each surrounded by three occupied lattice sites, 1-6. The divacancy identification has been made by studies of two associated electron spin resonance spectra, previously designated the Si-*J* and the Si-*C* centers.[2] These spectra are interpreted as arising as follows: The electrons on atoms 2 and 3 and on atoms 5 and 6 each pair in molecular bonds as shown in the figure. The Si-*J* center is observed in *p*-type material and is interpreted as arising from a single unpaired electron in the extended orbital between atoms 1 and 4. In this state, the divacancy is a singly ionized donor. The Si-*C* center is observed in high-resistivity silicon and is interpreted as arising from a third electron in the antibonding orbital between atoms 1 and 4, the two bonding orbitals being filled. In this state the divacancy is a singly ionized acceptor. The Si-*C* center is not observed in low-resistivity *n*-type material, indicating that the divacancy can also accept an additional electron. It thus can act as both a single donor and a double acceptor.

Some of the arguments leading to this identification are summarized briefly as follows:

1. These spectra have anisotropic *g* tensors as shown in Table I. Both spectra exhibit resolved, axially symmetric, hyperfine interactions with two equivalent silicon atoms. The hyperfine constants are also shown in Table I. The resonance-electron orbital between atoms 1 and 4 (see Fig. 1) accounts for the simple ⟨111⟩ hyperfine interactions with the same axis for two silicon atoms, while the *g* tensor, reflecting the symmetry of the wave function as a whole, is tilted away from this direction.

2. For the divacancy shown in Fig. 1, in addi-

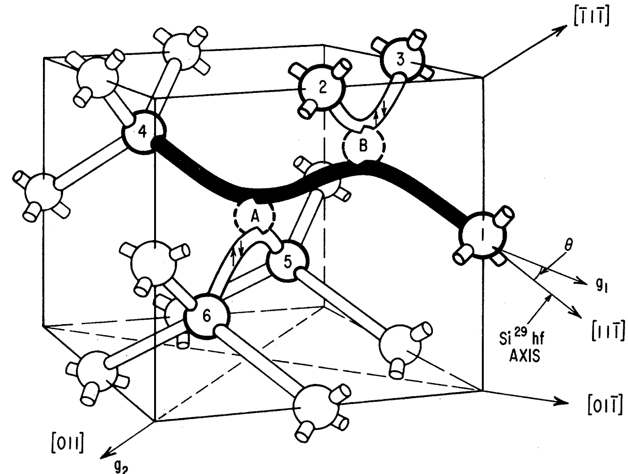

FIG. 1. The silicon divacancy. The dashed circles labeled *A* and *B* represent the two adjacent vacant lattice sites. The electrons associated with the defect can be regarded as forming the bonds shown in the figure. The axes for the spin-resonance data in Table I are indicated in the figure.

Table I. Spin Hamiltonian constants for the divacancy spectra (see Fig. 1).

Spectrum	$g(\pm 0.0003)$	θ (See Fig. 1)	Si^{29} hf (10^{-4} cm^{-1})
Si-*C*	$g_1 = 2.0012$		
	$g_2 = 2.0135$	$6 \pm 1°$	$A_{\parallel} = 79 \pm 2$
	$g_3 = 2.0150$		$A_{\perp} = 56 \pm 2$
Si-*J*	$g_1 = 2.0004$		
	$g_2 = 2.0020$	$7.7 \pm 0.5°$	$A_{\parallel} = 67.8 \pm 0.5$
	$g_3 = 2.0041$		$A_{\perp} = 40.0 \pm 0.5$

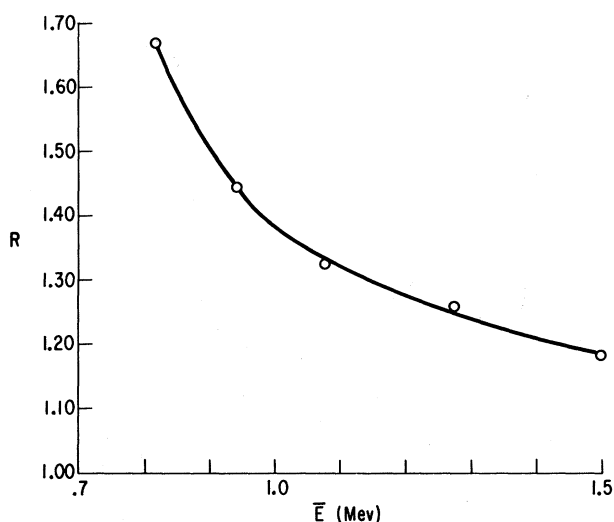

FIG. 2. R vs the average energy of the incident electron beam, $\bar{E}$. R is the ratio of the number of divacancies with the vacancy-vacancy direction along the incident beam ⟨111⟩ direction (say the [$\bar{1}1\bar{1}$] of Fig. 1) to the number along one of the other three equivalent ⟨111⟩ directions (the [$11\bar{1}$]).

tion to the orbital between atoms 1 and 4, as shown, equally likely configurations involve the orbital being between atoms 2 and 5 and between atoms 3 and 6. For both the Si-C and Si-J centers, motion between these configurations has been detected both by stress-induced alignment and by linewidth studies, confirming this prediction of the model. The activation energy for this motion is ~0.06 ev for both centers.

3. Preferential alignment of the vacancy-vacancy direction has been quenched in by stressing at elevated temperatures. The magnitude of the alignment as well as the kinetics of reorientation is identical as monitored by both centers. The activation energy for this motion is ~1.3 ev.

4. Both spectra are observed after an in situ irradiation at 20°K, showing that they are due to a primary defect, which does not require annealing for formation.

That the divacancy is produced as a primary process has also been demonstrated in an informative way as follows:

Oriented samples 0.010 in. × 0.1 in. × 0.6 in. were cut from p-type (~3×10^{16} B/cc) pulled silicon with the thin dimension a ⟨110⟩ direction. For convenience we will consider this thin dimension to be the [$01\bar{1}$] of Fig. 1. These samples were irradiated at room temperature with a high-energy electron beam incident along the [$\bar{1}1\bar{1}$] direction, and the Si-J center resonance observed. By observing the relative intensities of the multiplets of the spin resonance spectrum it is possible to count the divacancies in each of the possible orientations. The ratio, R, of the number with the vacancy-vacancy axis along the beam direction ([$\bar{1}1\bar{1}$]) to the number in one of the other three equivalent ⟨111⟩ directions (i.e., [$11\bar{1}$]) is shown in Fig. 2 as a function of bombarding energy. As can be seen, there is a substantial anisotropy in the production rate, which increases with decreasing bombarding energy.

This behavior can be qualitatively understood in terms of a conventional model for divacancy production: A high-energy electron collides with the nucleus of an atom and imparts a recoil energy to the atom. The recoiling atom collides with a nearest neighbor atom, causing it to be displaced into the lattice as an interstitial. In addition the initial recoil atom must retain enough energy so that it too becomes an interstitial. In this way, two adjacent vacancies, a divacancy, are created. The energy the primary recoil atom receives in the collision with a high-energy electron, and the direction of recoil are correlated, being determined by the Mott-Rutherford scattering formula. The highest energy recoil is along the beam direction. Consequently as the beam energy is reduced, a point is ultimately reached where sufficient recoil energy is available to produce a divacancy along the beam direction but not in the ⟨111⟩ direction 70° 32′ away from the beam direction, which suggests the tendency seen in Fig. 2.

There are several considerations which make the data in Fig. 2 provisional (e.g., local heating of the lattice during the defect production process, finite sample thickness, and the fact that the irradiation was at a temperature where single vacancies could aggregate). However, all of these would reduce the observed anisotropy, so that it is at least as large as shown in Fig. 2.

In summary we observe the divacancy as the result of the direct production process. It is produced at a rate ~5% of the vacancy production rate, as monitored by the Si-A center, for a 1.5-Mev irradiation,[3] and plays an important part in room-temperature radiation-damage processes.

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[1] G. D. Watkins and J. W. Corbett, Phys. Rev. 121, 1001 (1961); J. W. Corbett, G. D. Watkins, R. M. Chrenko, and R. S. McDonald, Phys. Rev. 121, 1015 (1961).

[2]G. D. Watkins and J. W. Corbett, Discussions Faraday Soc. (to be published).

[3]Analysis of the absolute production rates vs bombarding energy for the Si-J center indicates a considerably higher threshold energy for divacancy production than that for the single vacancy, as is to be expected. This is in agreement with work by Bemski (to be published), who similarly reports a higher threshold energy for the Si-C center formation. As a result of this observation, Bemski independently concluded that the Si-C center was to be associated with a multiple defect, suggesting the divacancy as a possibility.

BOUND EXCITON COMPLEXES

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Exciton complexes in which excitons are bound to neutral or charged donors or acceptors have been described by Haynes[1] and Lampert.[2] In crystals with a direct band gap, such states are observable as sharp absorption and emission lines occurring at wavelengths longer than that of the lowest energy intrinsic exciton state. This Letter shows that the Zeeman effect of these impurity complex states can be used to identify which type of center a given absorption line represents. In this way, the g values of donors and acceptors, the binding energies of the various complexes, and even information about the energy levels and g values of excited states of donors and acceptors can be obtained. The electron-hole spin-spin (exchange) interaction can be measured in some of these states. The experimental results discussed are for CdS, but the method of investigation seems to be promising for a wide class of semiconducting crystals. Previous work has established the energies of the intrinsic exciton lines[3] in CdS, but the explanation of the lines occurring at lower energies has remained unsatisfactory.[4,5]

Excitons can be bound to neutral donors or acceptors to form molecular states, or to ionized donors or acceptors to form molecular ion states, as illustrated in Fig. 1. The neutral donors and acceptors are doublet states ($S=\frac{1}{2}$), and this is also true for the complexes formed from these states since the "bonding" electrons or holes must have antiparallel spins. (It is well known that for molecular hydrogen, if the "bonding" particles have parallel spins an unstable system results. Precisely the same considerations apply to the exciton complexes discussed here.) The states considered here are ground states and so have no orbital angular momentum. In a magnetic field the states derived from the neutral centers will split, as shown in Fig. 1, with a g value equal to that of the odd particle in the particular complex. This four-level system gives rise to two pairs of lines, one with a separation controlled by $|g_u - g_l|$ and the other controlled by $|g_u + g_l|$, where u and l refer to the upper and lower states, respectively.

In hexagonal CdS free electrons occupy an S-like $J=\frac{1}{2}$ Γ_7 band, and free holes (from the top valence band) a P-like $J=\frac{3}{2}$ Γ_9 band.[3] The free electron has an almost isotropic g value of -1.7_8. Because the conduction band is simple, this g value will be almost independent of the binding of the electron in a center. Symmetry requires that the g

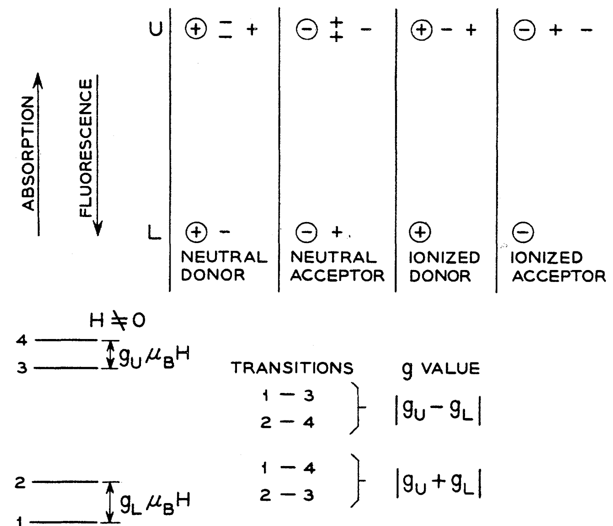

FIG. 1. Schematic diagram illustrating the ground and excited states of the various transitions discussed in the text. The g values of the states arising from the neutral centers are determined by the g value of the odd particle, and the splittings of these states are as illustrated. The ionized centers show no splitting in the ground states; the splitting of the excited states of these centers with $c \perp H$ is complicated by the presence of a spin-spin interaction energy. The charges within a circle indicate a chemical center.