Electron paramagnetic resonance of new defects in heavily phosphorus-doped silicon after electron irradiation

E G Sieverts and C A J Ammerlaan

Natuurkundig Laboratorium, Universiteit van Amsterdam, Valckenierstraat 65, Amsterdam-C, The Netherlands

Abstract. Seven new EPR spectra are reported for heavily phosphorus-doped silicon $(7 \times 10^{17} \text{ phosphorus atoms/cm}^3)$ irradiated at room temperature with 1.5 MeV electrons. Three of these spectra show a hyperfine structure which reveals the formation of defect complexes with electron spin $S = \frac{1}{2}$ in which two atoms with nuclear spin $I = \frac{1}{2}$ and 100% isotopic abundance are involved. They are identified as two-phosphorus defect complexes. One of them is tentatively ascribed to the phosphorus-vacancy-phosphorus complex in its positive charge state. Simple LCAO calculations on this model are in agreement with the observed hyperfine interactions. Another spectrum appears to arise from two next-nearest phosphorus neighbours and may be described in terms of a He⁺ or H⁺₂-like effective-mass approximation. The formation by electron irradiation at room temperature of twophosphorus centres, at a rate higher than can be accounted for by a random distribution of phosphorus, is explained in terms of the slow diffusion of phosphorus-vacancy pairs (E-centres) during irradiation at 60 °C and their subsequent trapping by other phosphorus centres. For this process an ionization-enhanced diffusion mechanism is essential. Calculations of the diffusion process, based on results of a computer simulation, agree with the observed production rate.

1. Introduction

Among the large number of electron paramagnetic resonance (EPR) spectra of defects in silicon, until now only two defects (besides the phosphorus impurity itself) were found to be phosphorus-related. Watkins and Corbett (1964) thoroughly investigated the phosphorus-vacancy complex (P–V or E-centre) with EPR and ENDOR techniques; from electrical measurements, additional information on this defect is available. For the second phosphorus defect tentative models have been given by Lee *et al* (1972).

In this paper six new spectra of phosphorus defects are reported, labelled NL1-NL6. Three of them arise from phosphorus pairs. The formation of such two-phosphorus centres is explained by relying heavily upon data of the P-V complex. |EPR results of two spectra are discussed in terms of specific two-phosphorus configurations.

The present study was performed on silicon containing 7×10^{17} phosphorus atoms/cm³ irradiated with 1.5 MeV electrons. EPR experiments were carried out in a superheterodyne K-band spectrometer.

2. Experimental results

2.1. Description of spectra

A centre with electron spin $S = \frac{1}{2}$ and two nuclear spins $I = \frac{1}{2}$ can be described in its

214 E G Sieverts and C A J Ammerlaan

simplest form by a spin Hamiltonian

$$\mathcal{H} = g\mu_{\mathrm{B}} \mathrm{H} \cdot \mathrm{S} - g_{\mathrm{N}} \mu_{\mathrm{N}} \mathrm{H} \cdot (\mathrm{I}_{1} + \mathrm{I}_{2}) + A \, \mathrm{S} \cdot (\mathrm{I}_{1} + \mathrm{I}_{2}) \tag{1}$$

giving the Zeeman interactions between the magnetic field **H** and the electron spin and both nuclear spins respectively, and finally the hyperfine interaction between the electron spin and these nuclear spins. First-order energy levels are given by

$$E = g\mu_{\rm B}Hm_{\rm S} - g_{\rm N}\mu_{\rm N}H(m_{\rm I}^{1} + m_{\rm I}^{2}) + Am_{\rm S}(m_{\rm I}^{1} + m_{\rm I}^{2}). \qquad (m_{\rm S} = \pm\frac{1}{2}, m_{\rm I}^{1,2} = \pm\frac{1}{2})$$
(2)

To second-order, four of these eight levels are corrected by a quantity

$$\Delta = \frac{1}{2}A^2 / (g\mu_{\rm B}H + g_{\rm N}\mu_{\rm N}H).$$

The EPR transitions satisfy

$$\Delta E = g\mu_{\rm B}H + \Delta + A$$

$$\Delta E = g\mu_{\rm B}H + \Delta - A$$

$$\Delta E = g\mu_{\rm B}H + k\Delta \qquad (k = 0, \pm 1)$$
(3)

or

resulting in three nearly equidistant lines with an intensity ratio 1:2:1. (The correction Δ is negligible for centres with small hyperfine interaction, like NL1.)

In a more general case, g and A must be replaced by tensors representing anisotropic interactions. The spectra NL1–NL3 are analysed in terms of such a Hamiltonian. NL1 moreover shows two resolved hyperfine interactions with magnetic ²⁹Si nuclei. Such interactions can be described by additional terms ($\mathbf{S} \cdot \mathbf{A}_j \cdot \mathbf{I}_j - g_N \mu_N \mathbf{H} \cdot \mathbf{I}_j$) where j enumerates neighbouring lattice positions. The largest of the ²⁹Si hyperfine interactions has nearly (111) axial symmetry. The P hyperfine interaction, within experimental error, seems to approximate to (011) axial symmetry. The various aspects of NL1 are illustrated in figure 1. NL2 (figure 2) shows nearly isotropic g and A values; beyond its linewidth no ²⁹Si hyperfine satellites are present.

The spectra NL4-NL6 are provisionally analysed in terms of a familiar onephosphorus Hamiltonian, although the absence of a 1:2:1 structure is only certain for NL4. NL7 involves no phosphorus. Parameters of all spectra are presented in table 1.

2.2. Occurrence of spectra

With increasing electron dose the initial neutral phosphorus concentration decreases. This is monitored by the central part of its EPR spectrum, which arises from clusters of interacting donor atoms (Maekawa and Kinoshita 1965). Spectra NL2 and NL7 emerge at 6×10^{17} electrons/cm²; after 9×10^{17} electrons/cm² neutral phosphorus has disappeared completely; in turn NL4, NL6, and especially NL2 are present, while the negative divacancy G7 arises as well. Prolonged irradiation further lowers the Fermi level. Successively NL3 and NL2, NL4, and NL6 disappear (1.2×10^{18} electrons/cm²); G7 and NL7 increase. Only after persistent electron bombardment (> 3.3×10^{18} electrons/cm²) or by infrared illumination during EPR does the P–V complex assume the neutral charge state (spectrum G8).

EPR of new defects in heavily phosphorus-doped silicon



Figure 1. EPR dispersion trace of NL1 showing hyperfine interactions with ³¹P and with ²⁹Si (T = 4.2 K, H [111]). Nearly out of phase, the single phosphorus impurity spectrum is faintly visible. The angular dependences of g and hyperfine interactions, with H in the (011) plane, are inset.



Figure 2. EPR trace of NL2 (T = 5 K, H # [100]) and angular dependences of g and A. Spectra NL3, NL6 and NL7 are also visible.

An isochronal (15 min) annealing experiment shows the reverse course. In a first stage (130–140 °C), many electrons are released from dissociating P–V complexes; NL2–NL6 reappear (whether NL5 was present before annealing is not yet clear) and G7 disappears. Upon further annealing all these spectra vanish and, together with a low concentration of neutral phosphorus, only NL1 is present (170–200 °C). Careful examination, however, shows the presence of NL1, more or less obscured by other spectra, in all EPR traces, as long as NL2 or phosphorus are visible.

216 E G Sieverts and C A J Ammerlaan

Table 1. EPR parameters of the new spectra NL1-NL7. Principal values of **g** and **A** tensors are given, together with their values for symmetry directions. Uncertainty in g values is ± 0.0001 , in A values ± 0.5 MHz (unless mentioned otherwise). Temperatures of largest dispersion signal at magnetic field modulation frequency of 19 Hz are given (165 Hz for NL4).

No.	g values				Hyperfine interactions A (MHz)					Temp.
	<i>g</i> ₁ , <i>g</i> ₂ , <i>g</i> ₃	[100]	[111]	[011]	nucleus	A_{1}, A_{2}, A_{3}	[100]	[111]	[011]	(K)
NL1	2.0128 2.0026 2.0047	2.0077 2.0047	2.0101 2.0033	2.0128 2.0062 2.0026	2 × ³¹ P ²⁹ Si _I	$ \begin{array}{r} 13.7 \pm 0.2 \\ 13.3 \\ 13.2 \\ 514.8 \\ 464.6 \\ 463.0 \\ \theta = 40^{\circ} \\ 69+2 \end{array} $	13.4 13.2 479.0 484.4	13·3 13·5 471·2 514·4 466·4	13.3 13.3 13.7 464.6 499.8 463.8 493.4 nobserved	4.2
NL2	1·9992 1·9974 1·9978	1·9982 1·9978	1∙9987 1∙9975	1·9992 1·9980 1·9974	⁵⁴ 1 2 × ³¹ P ‡	276·5 275·0 272·0	275·5 272·0	275·0 274·0	276·5 274·0 275·0	5
NL3	1.9949 2.0000 1.9991 $\theta=23^{\circ}$	1∙9984 1∙9975	1·9995 1·9977 1·9945	2·0000 1·9992 1·9968 1·9949	2׳¹P †	149.5 148.1 151.5 $\theta = 27^{\circ}$	151·1 149·0	149·1 149·6 151·1	148·1 149·5 150·6 149·9	9
NL4	1·9957 1·9988 1·9988	1.9978	1∙9985 1∙9957	1∙9988 1∙9968	³¹ Р †	251.4	anisot	ropy u	nresolved	5
NL5	1.9986				³¹ P†	545.5				11
NL6	1.9982	anisotropy unresolved			³¹ P†	420 ± 2				12
NL7	2·0059 1·9987 2·0032	2.0032 2.0023	2∙0050 2∙0002	2·0059 2·0027 1·9987	†					6-80

^{+ 29}Si hyperfine interaction not yet observed.

‡ No ²⁹Si hyperfine interaction resolvable in EPR.

Infrared illumination during EPR, in the stage where NL2 disappears under annealing, restores this spectrum. A slight electron reirradiation of an annealed specimen likewise brings back NL2 and NL3–NL7 with former intensity. This clearly demonstrates that the disappearance of these spectra under annealing is due to a Fermi-level shift.

3. Discussion

3.1. Formation of two-phosphorus centres

For a random distribution of phosphorus atoms in a 7×10^{17} phosphorus atoms/cm³ sample, the concentration of nearest-neighbour and next-nearest-neighbour pairs is less than 10^{14} cm⁻³. However, from the observed pair spectra a much higher concentration (well over 10^{15} cm⁻³) is inferred. An explanation can be given in terms of diffusion of the P–V complex until it is trapped by another phosphorus. Diffusion occurs by P–V

interchange combined with reorientation of the P-V axis of the defect. Watkins and Corbett (1964) gave a characteristic time for this reorientation. In their low-temperature G8 EPR spectrum they observed redistribution over the four different P-V directions as a result of room temperature uniaxial stress. High-temperature relaxation gave

$$\tau^{-1} = 1.6 \times 10^{13} \exp(-0.93 \, \text{eV}/kT) \,\text{s}^{-1}$$

for reorientation of neutral P–V. (For the negative charge state Watkins and Corbett (1964) and Kimerling *et al* (1971) give an activation energy of about 1.3 eV.) For P–V interchange a much lower activation energy is likely.

Our experiments showed that P-V|almost always retained the nearly immobile negative charge state. During electron irradiation, however, the formation of twophosphorus centres occurs by ionization-enhanced diffusion (Bourgoin and Corbett 1975). Electron-hole pairs are created by the irradiation and, as a result of preferential hole capture, a substantial fraction of P-V will acquire the neutral charge state. For a calculation of this fraction the majority carrier concentration as a function of irradiation dose, the electron-hole pair production, the hole lifetime τ_p , and the cross section ratio σ_p/σ_n for hole and electron capture (Hirata *et al* 1966, Kimerling and Carnes 1971) were estimated. For a 1.5 MeV irradiation for 330 min, with 5×10^{13} electrons/ cm²s, this resulted in the fraction increasing from about 15 to 60%.

For the trapping process of P–V we assume that a next-nearest-neighbour configuration with a phosphorus atom is required. The probability of finding a phosphorus atom is determined by the mean number of different next-nearest neighbours passed by a diffusing P–V. A computer simulation of this specific diffusion process was carried out to determine that number. After large numbers of steps (4000–20 000 reorientations) an average of about 1.8 'new' next-nearest neighbours per orientation was found. With a P–V production rate of 0.5 P–V/electron cm, in agreement with our irradiation results, we calculated (for a 10^{18} electrons/cm² irradiation at 60 °C) a production of about 2×10^{15} two-phosphorus centres/cm³. (The uncertainty of τ_p and σ_p/σ_n implies lower and upper limits of 3×10^{14} and 10^{16} .) This gives a reasonable explanation for the observed quantities.

3.2. Defect models

The first model suggested by the trapping of P–V by a phosphorus atom, as described in §3.1, is the phosphorus-vacancy-phosphorus complex, denoted PVP. Figure 3 gives the structure of this defect, exhibiting C_{2v} symmetry; a, b, c, and d denote the neighbours of the vacancy in the directions [$\overline{111}$], [$11\overline{1}$], [$1\overline{11}$], and [$\overline{111}$] respectively. A defect with phosphorus atoms on a and c is labelled ac.

For this model, symmetry-allowed linear combinations of wavefunctions are constructed, starting with four sp³-hybridized electron wavefunctions on each of the two phosphorus atoms and one sp³-orbital on the eight silicon atoms of the types 1, 2, and 3 as labelled in figure 3. This results in 16 so-called symmetry orbitals. According to the four irreducible representations of the point group C_{2v} they can be classified into four different symmetry types, denoted A_1 , A_2 , B_1 , and B_2 . Four of the orbitals can be interpreted in terms of extended bonding and antibonding orbitals between phosphorus atoms and between type-1 silicon atoms. By suitable symmetric and antisymmetric





Figure 3. Model of the PVP complex (see text).

combination of pairs of the other twelve symmetry orbitals within each symmetry type, one can represent the six covalent bonds between the phosphorus atoms and their direct neighbours. The six bonding orbitals are thought to have lowest energy, the six antibonding highest. In between remain the energies of the extended bonds between both next-nearest-neighbour pairs where the bonding orbitals have lower energy than both antibonding. In the paramagnetic singly positive charge state of PVP, 17 electrons must be accommodated in these levels. All bonding orbitals will be filled with 16 of them; the 17th will occupy the lowest of the P–P or type-1 Si–Si antibonding orbitals.

The chosen linear combination of atomic orbitals (LCAO), centred on the ten atoms considered above, will be reflected in the experimental hyperfine interactions. Selecting atomic 3s and 3p orbitals, the linear combination

$$\psi \stackrel{\bullet}{=} \sum_{j} \eta_j \left(\alpha_j \psi_{3s}^{(j)} + \beta_j \psi_{3p}^{(j)} \right)$$

results in axially symmetric hyperfine tensors whose principal values can be written as $a_i + 2b_i$, $a_j - b_j$, and $a_j - b_j$. In this case the Fermi contact interaction is given by

$$a_{j} = \frac{8}{3} \pi g \mu_{\rm B} g_{\rm N} \mu_{\rm N} \alpha_{j}^{2} \eta_{j}^{2} |\psi_{3s}^{(j)}(0)|^{2}, \tag{4}$$

and the anisotropic part, from the dipole-dipole interaction, is given by

$$b_{j} = \frac{2}{5} g \mu_{\rm B} g_{\rm N} \mu_{\rm N} \beta_{j}^{2} \eta_{j}^{2} \langle r^{-3} \rangle_{3p}^{(j)}.$$
(5)

Using the values $|\psi_{3s}^{Si}(0)|^2 = 31.5$, $|\psi_{3s}^{P}(0)|^2 = 41.6$, $\langle r^{-3} \rangle_{3p}^{Si} = 16.1$, and $\langle r^{-3} \rangle_{3p}^{P} = 24.2$ (10²⁴ cm⁻³), estimated by Watkins and Corbett (1964), localization (η_j^2) and s- and p-character (α_j^2/β_j^2) on relevant atoms can be derived.

For spectrum NL1 the symmetry, as determined from the angular dependence of the g value, agrees with PVP symmetry. The prominent hyperfine interaction is with a ²⁹Si atom which lowers the defect symmetry to C_{1h}. Together with EPR intensity considerations this leads to type-1 or type-3 silicon atoms as candidates. About 60% of the electron wavefunction is localized on both the Si neighbours of the correct type $(\eta^2 = 0.3, \alpha^2 = 0.4, \beta^2 = 0.6)$. Combining this result with the possible symmetry orbitals of the paramagnetic PVP electron, one finds that for orientation ac (figure 3) this electron can only be accommodated between b and d (type 1). Moreover, the hyperfine interaction is nearly (111) axially symmetric in accordance with the bond directions.

EPR of new defects in heavily phosphorus-doped silicon

Figure 1 is labelled according to this identification. The only phosphorus symmetry orbital allowed to admix with the B₂ orbital b-d by configuration interaction has $\langle 110 \rangle$ axial symmetry perpendicular to the PVP plane. The observed phosphorus hyperfine interaction likewise seems to have this symmetry. Only 0.17% of the electron is found on each phosphorus atom. Whether the second ²⁹Si hyperfine interaction (3% of the electron on each Si) originates from the two neighbours of type 3 or from the four of type 2 is not clear from EPR results. Only type 2, however, has symmetry orbitals of required B₂ symmetry. All the above arguments are in accordance with an identification of NL1 with PVP. Moreover, a consideration of the g-shift criteria of Lee and Corbett (1973) points to a bent-bond defect, probably positively charged.

It is also interesting to explore the possibility of fitting NL2 with PVP. This spectrum also corresponds to C_{2v} symmetry, though difficult to observe from the nearly unresolved anisotropy. Also the large phosphorus hyperfine interaction is nearly isotropic. Analysing this hyperfine interaction as above, a localization of the electron of only 3% on each phosphorus atom, in an almost s-like orbital, is obtained. Further, no resolved hyperfine interaction is present. From this we conclude that, although not a shallow level, the electron of NL2 is not accommodated in sharply localized bent or broken defect bonds, such as for instance those of PVP. This means that NL2 is most probably related to a centre which hardly disturbs the periodicity of the lattice. From this point of view we propose two substitutional next-nearest phosphorus atoms (PSiP) as bringing about spectrum NL2. Such a centre is expected to act as a double donor, only visible with EPR in its positive charge state.

An analogy with the sulphur donor is obvious. Using a helium-like effective-mass approximation, Ning and Sah (1971) calculated energy levels of S^+ and S^0 in silicon in agreement with experimental values. Although there is still disagreement about identification of some of the observed levels (Milnes 1973) they seem to be roughly comparable to those of PSiP⁺ and PSiP⁰, estimated to be about 0.4 eV and 0.1-0.2 eV below the conduction band respectively, as could be deduced from the occurrence of NL2 in relation to other spectra.

This analogy suggests adopting classical effective-mass theory (Kohn 1957) for a rough description of PSiP⁺. One can calculate the value of the electron wavefunction with 'central cell corrections' (Kohn and Luttinger 1955) using the experimental and theoretical ionization energies of 0.4 eV and 0.116 eV ('He⁺') respectively. For a He⁺-like model this results in a value for $|\psi(0)|^2$ which is seven times as large as for P in Si. A further correction can be made by taking a H⁺₂-like model. From calculated wavefunctions of H⁺₂ as a function of internuclear distance (e.g., Slater 1963) a correction factor $|\psi(0)_{H^+_2}|^2/|\psi(0)_{He^+}|^2$ can be deduced. For an internuclear distance of 3.83 Å expressed in units of a corrected 'Bohr radius' of 11 Å, as derived from ionization energy, this factor equals 0.5. The resulting theoretical ratio 3.5 of the hyperfine interactions of PSiP⁺ to P is in as good agreement with the experimental value of 2.35 for NL2 compared to P as can be expected from the present crude calculation. Nevertheless it is a clear indication that an identification of NL2 in terms of this PSiP model is probably correct.

4. Conclusions

The first remarkable result of this study is that, although phosphorus is one of the most

220 E G Sieverts and C A J Ammerlaan

important dopants in silicon, a new series of phosphorus-related defects has been detected. A second result is that in heavily P-doped material just above room temperature, diffusion of the P–V complex during irradiation causes formation of phosphorus pairs. For two of the pair spectra a model is suggested, originating from different theoretical descriptions. Whether or not for one of the other spectra the possibility of interstitial phosphorus has to be considered is left to future research.

Acknowledgments

We thank Dr S H Muller and Dr C L Vlaanderen for participating in different stages of this work, which formed part of the research programme of the 'Foundation for Fundamental Research on Matter' (FOM).

References

Bourgoin J C and Corbett J W 1975 Lattice Defects in Semiconductors 1974 (Inst. Phys. Conf. Ser. 23) p149
Hirata M, Hirata M and Saito H 1966 J. Appl. Phys. 37 1867
Kimerling L C and Carnes C P 1971 J. Appl. Phys. 42 3548
Kimerling L C, DeAngelis H M and Carnes C P 1971 Phys. Rev. B3 427
Kohn W 1957 Solid St. Phys. 5 257 (New York: Academic Press)
Kohn W and Luttinger J M 1955 Phys. Rev. 97 883

Maekawa S and Kinoshita N 1965 J. Phys. Soc. Japan 20 1447

Lee Y H and Corbett J W 1973 Phys. Rev. B8 2810

Lee Y H, Kim Y M and Corbett J W 1972 Radiat. Effects 15 77

Milnes A G 1973 Deep Impurities in Semiconductors (New York: Wiley) p32

Ning T H and Sah C T 1971 Phys. Rev. B4 3482

Slater J C 1963 Quantum Theory of Molecules and Solids vol 1 (New York: McGraw-Hill) p6

Watkins G D and Corbett J W 1964 Phys. Rev. 134 A1359