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ON THE PRODUCTION OF PARAMAGNETIC DEFECTS IN SILICON BY ELECTRON IRRADIATION

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Monocrystalline silicon samples of different impurity contents have been irradiated with 1.5 MeV electrons in order to produce divacancies in their negative charge state. In these samples different combinations of defects have been observed with electron paramagnetic resonance. The conditions for production and observation of these defects are compared. For two new EPR spectra, labelled (Si-) NL11 and (Si-) NL12, the spin Hamiltonian parameters are reported. For NL11, which arises from an $S = 1$ spin state, the obvious identification with the neutral charge state of the divacancy can not be confirmed.

1. INTRODUCTION

BY THE USE of electron paramagnetic resonance (EPR), during the past 15 years a remarkable number of irradiation defects in silicon has been found. Well over 80 different EPR spectra have been recognized. They are associated with intrinsic lattice defects or with more complex defects in which also impurity atoms are involved. For about half of the spectra a defect model has been proposed. The identifications are mainly based on the symmetry properties of the defect and on prominent hyperfine interactions, both as deduced from EPR, together with the correlation between defect production and the impurity concentrations in the silicon. Among the identified defects the divacancy is the prominent intrinsic defect present after room temperature irradiation. In behalf of a study on its negative charge state by means of electron-nuclear double resonance [1, 2] silicon samples with different impurity contents have been irradiated. In all cases series of defect spectra have been observed. In this letter the productions of these spectra are described and compared. The new spectra, labelled NL1 to NL7, which appeared in heavily phosphorus doped silicon have already been described elsewhere [2, 3]. Two other new spectra, labelled NL11 and NL12, will be reported here. One of these, NL11, arises from an $S = 1$ paramagnetic state. This spectrum is observed in *p*-type samples when the position of the Fermi level is such that neither the positive nor the negative charge state of the divacancy can be observed. Arguments for a possible identification with the triplet state of the neutral divacancy are explored.

2. EXPERIMENT

For the present study four different kinds of floating zone, monocrystalline silicon samples have been used. A specification of their properties is given in Table 1. Samples were given dimensions of $2 \times 2 \times 20\ \text{mm}^3$ with an $[0\bar{1}1]$ crystal direction parallel to their long edges. Irradiation with 1.5 MeV electrons from a Van der Graaff accelerator took place at room temperature. Fluences, which reached a maximum of 3.3×10^{18} electrons per cm^2, were measured with two Faraday cups. The temperature of the samples during the irradiation was kept below 70°C. Spin resonance experiments were carried out in a superheterodyne *K*-band spectrometer, adjusted to observe the dispersion part of the signal. Most EPR spectra were recorded under circumstances of adiabatic slow passage. The magnetic field could be varied in the $(0\bar{1}1)$ plane of the sample.

3. DEFECT PRODUCTION

3.1. *Samples A*

The defects produced in type A samples have already been reported [2, 3]. Upon irradiations between 3×10^{17} and 1.2×10^{18} electrons per cm^2 defect spectra appeared, in which pairs of phosphorus atoms (spectra NL1 to NL3), or single phosphorus atoms (spectra NL4 to NL6) were present. Besides these spectra also other resonances could be observed, which had phosphorus hyperfine interactions larger than 550 MHz. They were too weak however to be analyzed. The original spectrum from the neutral phosphorus donors was no longer present at fluences above 6×10^{17} electrons per cm^2. After 9×10^{17} electrons per cm^2 a similar

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Table 1. Specification of the samples

Sample type	Conductivity type	Dopant impurity	Resistivity at room temperature (Ohm-cm)	Impurity concentration (cm^{-3})	Dislocation density (cm^{-2})
A1	*n*	*P*	0.026	1.0×10^{18}	Zero
A2	*n*	*P*	0.031	7.0×10^{17}	6000
B	*n*	*P*	0.116	9.0×10^{16}	Zero
C	*n*	*P*	0.34	2.2×10^{16}	Zero
D	*p*	*B*	0.87	1.8×10^{16}	Zero

*Table 2. The magnitude of the spectra observed in type A samples, as a function of electron fluence. Small: *; moderate: **; large: ***; very large: *****

	1.5 MeV electron fluence (10^{17} electrons per cm^2)									
Spectrum	1.5	3	6	9	12	15	18	24	27	33
Phosphorus	**	**	**	**[a]						
G7				**	**	**	***	***	***	****
NL1			**	*	*					
NL2				**						
NL3			**	**						
NL4				**						
NL5				*	*					
NL6				**						
NL7			*	*	**	***	***	***	**	**
G8								*[b]	*[b]	*[b]
B1				*	*					

[a] Hyperfine splitting 108 MHz instead of 117.5 MHz.

[b] Only observable during or after illumination.

spectrum with a significantly smaller hyperfine interaction could be observed however.

After fluences larger than 1.2×10^{18} electrons per cm^2 all phosphorus related spectra had disappeared as a consequence of the drop of the Fermi level upon irradiation. Another new spectrum, NL7, did not exhibit a phosphorus hyperfine interaction. The spectra NL7 and G7 associated with the negative divacancy [4] remained the prominent ones. Spectrum G8, associated with the neutral phosphorus-vacancy complex [5], was only visible after illumination with light for fluences larger than 2.4×10^{18} electrons per cm^2. For some fluences spectrum B1, arising from negatively charged oxygen-vacancy complexes [6], was present in low intensity. A summary of the appearance and disappearance of spectra upon irradiation is presented in Table 2.

By annealing at about 140°C of high fluence samples the spectra NL1 and NL6 reappear. In this way the spectra NL1 to NL4 could be made visible with at least four times larger intensity than before anneal. Upon annealing at higher temperature the spectra NL2 to NL6 disappear. However a slight re-irradiation of an annealed sample restores the spectra to their former intensity. The behaviour of these spectra upon anneal until at least 200°C turns out to be only a Fermi level effect [3].

A difference in defect production between the A1 and A2 samples, attributable to their different dislocation content, was never observed.

3.2. *Samples B*

In type B samples after irradiation with fluences of 6×10^{17} to 1.5×10^{18} electrons per cm^2 the EPR spectra G7, G8, and G16 [7, 8] could be observed. After a 15 min anneal at 150°C these spectra disappeared, while NL7 and B1 arose.

3.3. *Samples C*

In type C samples four different spectra appeared upon irradiation with fluences ranging from 3×10^{17} to 2×10^{18} electrons per cm^2. One spectrum could only

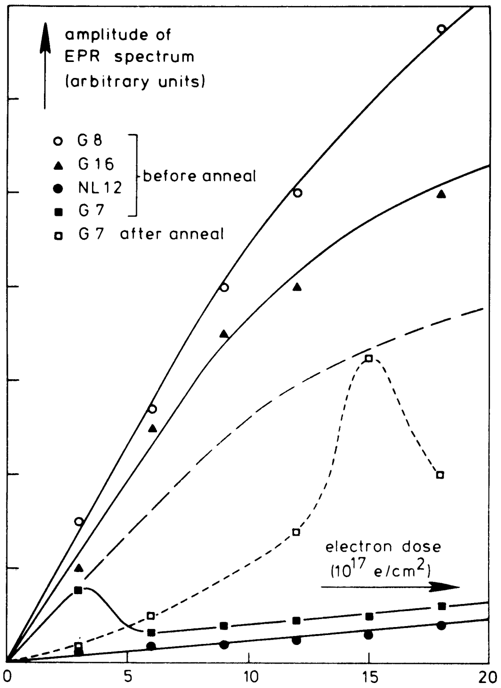

Fig. 1. The observation of paramagnetic defects in phosphorus doped silicon (samples type C) after 1.5 MeV electron irradiation.

be observed at temperatures below 4.5 K. Resonance signals were in phase with respect to the magnetic field modulation at a frequency $\omega_m = 120$ Hz. This is indicative for a spin–lattice relaxation time much shorter than the modulation period of $\simeq 10^{-2}$ sec [9]. This spectrum, first observed by Van der Linde (private communication), was labelled NL12, as it exhibited significant differences with all known spectra. The production of this spectrum was roughly proportional to the irradiation fluence. The other observed spectra were G7, G8, and G16. All spectra were visible during the whole range of electron irradiation fluences, as shown in Fig. 1. After a one hour 150°C anneal G8 and NL12 have disappeared, G7 has grown, and a glimpse of B1 is present. Spectrum G16 is hardly affected by 150°C nor by 300°C anneal.

3.4. *Samples D*

The type D samples were the only of *p*-type material which were investigated. Upon the initial electron irradiation positive divacancies were formed. Together with the corresponding spectrum G6 [4] also spectrum B4 [10] was observed. As a result of the rather low boron content, the Fermi level which was originally pinned upon the boron level rises upon electron irradiation. After 9×10^{17} electrons per cm^2 spectrum G6 has disappeared. At 1.2×10^{18} electrons per cm^2 a new spectrum arises, which has been labelled NL11. Spectrum B4 has disappeared at 1.8×10^{18} electrons per cm^2, but after higher fluences it may be generated by illumination with infrared light. Spectrum NL11 is still visible after a fluence as high as 3×10^{18} electrons per cm^2. After this fluence samples are still *p*-type. Spectrum G7 has not been observed.

4. ANALYSIS OF SPECTRA

Most paramagnetic defects in silicon have an electron spin $S = 1/2$, and their spectra can be described by the simple spin Hamiltonian

$$\mathcal{H} = \mu_B \mathbf{H}.g.\mathbf{S} + \sum_i (\mathbf{S}.A_i.\mathbf{I}_i - g_N \mu_N \mathbf{H}.\mathbf{I}_i)\,.$$

This operator comprises an electronic Zeeman interaction and a sum of hyperfine interactions and nuclear Zeeman interactions from ^{29}Si nuclei (isotopic abundance 4.7%, nuclear spin $I = 1/2$). Summation is over neighbouring lattice sites, which carry label *i*. In most cases only hyperfine interactions with one or two shells of neighbouring lattice sites can be resolved in EPR. Among others the spectra B1, B4, G6, G7, G16, NL7, and NL12, mentioned here, can be described in this way. The parameters of spectrum NL12 are given in Table 3. The presence of one (G8, NL4 to NL6) or two (NL1 to NL3) phosphorus atoms (^{31}P isotope 100% abundant, $I = 1/2$) gives rise to additional hyperfine and nuclear Zeeman interaction terms [3].

If a spectrum has to be described with an electron spin $S = 1$, a spin Hamiltonian can be written

$$\mathcal{H} = \mu_B \mathbf{H}.g.\mathbf{S} + \mathbf{S}.D.\mathbf{S}\,,$$

where the second term represents the electronic spin–spin interaction and where nuclear terms have been omitted. EPR transitions between the triplet states are in first order given by [11]

$$\Delta E = \mu_B H g_{\mathrm{eff}} \pm 3/2 D_{\mathrm{eff}}\,.$$

Spectrum NL11 is analyzed using this spin Hamiltonian. Its parameters are given in Table 3.

5. DISCUSSION

5.1. *Samples A*

The occurrence of the two-phosphorus spectra NL1 to NL3, only in type A samples can be understood as their formation will be roughly proportional to the square of the phosphorus concentration. The fact that NL4 to NL6, involving one phosphorus nucleus, are also present only in type A samples may be an indication that they are formed as secondary defects only in observable quantities if the phosphorus concentration is high enough to make this impurity the main trapping center for nearly all primary defects.

Table 3. Spin Hamiltonian parameters of new defect spectra observed after electron irradiation

Spectrum	Spin	Tensor	Principal values[a]	$H \parallel [100]$	$H \parallel [111]$	$H \parallel [011]$	Temp. (K)
NL11	1	g	$g_1 = 1.9991$	2.00565	2.00815	2.00945	4.2–20
			$g_2 = 2.00945$	2.0055	2.00705	2.0086	
			$g_3 = 2.0083$		1.9991	2.0026	
			$\theta = 33.2 \pm 1°$			2.00185	
		D (MHz)	$D_1 = -5.9$	$+62.8$	$+25.3$	$+23.2$	
			$D_2 = -50.8$	-27.9	$+9.9$	$+11.7$	
			$D_3 = +63.7$		-13.0	-4.9	
			$\theta = 6.8 \pm 1°$			-50.8	
NL12	1/2	g	$g_1 = 2.0088$	2.0067	2.0090	2.0103	2–4.5
			$g_2 = 2.0103$	2.0065	2.0076	2.0092	
			$g_3 = 2.0007$		2.0007	2.0040	
			$\theta = 57.5 \pm 1°$			2.0030	
		A (MHz)	$a = 38 \pm 1$	(Probably four ^{29}Si nuclei involved)			

[a] The axes of g_2 and D_2 are along $\langle 110 \rangle$, g_1 is in a $(1\bar{1}0)$ plane and makes an angle θ with $\langle 001 \rangle$; errors in principal g values are ± 0.00005.

The disappearance of neutral substitutional phosphorus after a fluence of 6 x 10^{17} electrons per cm^2 is in agreement with the formation of phosphorus vacancy complexes in their diamagnetic negative charge state, at the generally assumed introduction rate of 0.5 cm^{-3} per electron per cm^2. It is not known what effects the spectrum with the smaller hyperfine interaction at slightly higher fluences.

Spectrum G7 is observed already after much lower electron fluences than spectrum G8 which moreover requires illumination. This indicates that the level of $V_2^{=}$, below which the spectrum G7 associated with V_2^- can be observed, is considerably higher than the level of PV$^-$ at about $E_c - 0.4$ eV, below which G8 is visible. The results of Kimerling [12] and of Evwaraye and Sun [13] who report an energy level at $E_c - 0.23$ eV for $V_2^{=}$ are consistent with the present EPR results. This value disagrees with that originally reported by Watkins and Corbett [4].

5.2. *Samples A, B, and C*

It is not clear why spectrum NL7 is present in type *A* and *B* samples, but not in type *C*, even after annealing at 150°C. The presence of other, unknown, impurities may be important however.

The presence of spectrum G16 at high intensities, comparable to G8 (Fig.1), in floating zone material (B and C) excludes that oxygen is involved in the associated center. Therefore the tentative model of Lee *et al.* [14] as the negative charge state of the CVO-complex, whose positive charge state is associated with spectrum G15, has to be rejected. Spectrum G15 in turn has never been observed in floating zone *p*-type silicon.

5.3. *Samples C*

By the irradiation of *n*-type phosphorus doped silicon the Fermi level drops below the shallow donor level. In type C samples the occurrence of G8 already after an irradiation fluence of 3 x 10^{17} electrons per cm^2 is an indication that the Fermi level is at about $E_c - 0.4$ eV after that small fluence. The fluence dependence of the intensity of G7, shown in Fig. 1, indicates that V_2^- has an energy level just below PV^-. This implies a different order of the levels than was reported recently from deep level transient spectroscopy (DLTS) [12]. It is known however that a number of different defects exhibits energy levels near $E_c - 0.4$ eV, generally producing a huge DLTS peak around this energy. Therefore it tends to be difficult to assign accurate energy values in that region. The occurrence of G7 even after 2 x 10^{18} electrons per cm^2 points out that the Fermi level is still at about the same position. It is clear that in this case the observed EPR intensities are not an accurate measure for the defect production. Due to local inhomogeneities part of both defects may assume a nonparamagnetic charge state.

For the new spectrum NL12 no defect model can yet be proposed. Its monoclinic I symmetry, its approximate $\langle 111 \rangle$ axial g tensor and its deviations from the free electron g value make it probable that it would belong to the family of defects with one-broken-bond or parallel-pair-bonds [2, 15].

5.4. *Samples D*

Although Corbett and Watkins have reported the observation of spectrum G7 in *p*-type pulled silicon after prolonged irradiation [16], we did not succeed to do so in the floating zone type D samples. On the other hand, the G7 spectrum could be produced by electron irradiation of type D samples in which oxygen was diffused [17]. For the required *p*- to *n*-type conversion the presence of oxygen seems to be essential. This is reminiscent to type conversion by heat-treatment of oxygen-rich silicon [17]. Spectrum B4, originally observed in crucible grown silicon [10], is here reported for floating zone material.

The presence of the $S = 1$ spectrum NL11 in samples where G6 is no longer present and G7 has not (yet) appeared, suggests it to be related to the neutral charge state of the divacancy. In the following some arguments pro and con will be explored.

The monoclinic I symmetry, the nearly ⟨111⟩ axial *g* tensor and the deviations from the free electron *g* value [2, 15] agree with a divacancy-like defect. On the other hand spectrum NL11 does not appear immediately upon the disappearance of G6 although it can be generated by light. It can not be conceived however how the position of the Fermi level should influence whether the triplet or the singlet state is the ground state. Also the intensity of this EPR spectrum is too low to account for the total number of divacancies present in the samples. A last interesting feature is a comparison of the observed spin–spin interaction with calculated values for the dipole–dipole interactions of two electrons in broken bonds at different neighbour distances. From a comparison with the results of Brower [18] and Lee and Corbett [19] it turns out that the experimental values found for the present D-tensor, correspond to broken bonds between which four lattice sites are present.

From these considerations it has to be concluded that an identification of spectrum NL11 with the V_2^0 triplet state in the ordinary atomic configuration can not be justified. Hyperfine interactions with ^{29}Si nuclei were observed, but could not yet be analyzed.

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