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ELECTRON PARAMAGNETIC RESONANCE OF FeFeAl COMPLEXES IN SILICON

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The observation of two new electron paramagnetic resonance (EPR) spectra in *p*-type silicon doped with aluminium and iron is reported. Both spectra, labelled Si–NL40 and Si–NL41, have monoclinic-I symmetry and can be described as a paramagnetic system with a spin $S = 1/2$ and *g*-values greatly deviating from that of a free electron, as well as by a spin $S = 5/2$ and *g*-values close to $g = 2$. The analysis of the spectra with spin $S = 5/2$ allowed to determine the relative values of the zero-field splitting parameters D and E. A good agreement with the theoretical calculation for the relationship between the components of the *g*-tensor and the value E/D is obtained. From the resolved hyperfine structure due to ^{27}Al, which is observed for some EPR orientations, and the analysis of *g*-values both centres are suggested to be FeFeAl complexes.

1. INTRODUCTION

HAVING A high solubility and high diffusion coefficient, iron is frequently present as an impurity in silicon crystals after heat treatment. Due to its low migration energy, iron is mobile even at room temperature and is readily involved in the reaction with defects and other impurities to form pairs and complexes. Electron paramagnetic resonance (EPR) studies of iron in silicon have been reported since the early sixties by Ludwig and Woodbury for the isolated iron and iron-acceptor pairs [1]. From their works, it is known that in the *p*-type material, positively charged iron ions Fe_i^+ are captured by negative substitutional shallow acceptors leading to the formation of iron-acceptor pairs. Recently, the EPR data of FeAl, FeIn and FeGa pairs [2–4] with different symmetries have become available revealing that such pairs, except the case of FeB, are described as bistable systems with the trigonal and orthorhombic configurations. From the EPR data, combined with results from electrical measurements as well as theoretical calculations [5–9], a big step in the understanding of the pairing mechanism, defect configuration and energy level structure could be achieved. The analysis of EPR data using alternative spin Hamiltonians with different values of effective spin could give a rather detailed understanding of the structure of shallow acceptor-iron pairs and complexes [10]. More recently, some more extended complexes involving two iron atoms with orthorhombic-I and monoclinic-I symmetries, which were observed in *p*-type silicon doped with boron and iron, were identified as FeFeB complexes [11–13]. In this paper, we present the analysis of the analogous spectra Si–NL40 and Si–NL41 which were observed in *p*-type, aluminium doped, iron diffused silicon. The analysis of the spectra with the effective spin $S = 5/2$ including the zero-field splitting terms shows a good agreement with the theoretical calculations for the shallow acceptor-iron complexes. The identification of the centres by using the ^{57}Fe isotope has not been made yet; however, the low symmetry of the centres and the high values of the effective spin $S = 5/2$ suggest the participation of two iron atoms in the centre.

2. EXPERIMENTAL DETAILS

Samples were prepared from Czochralski, dislocation free, *p*-type, aluminium doped silicon with the concentration of about 5×10^{15} cm^{-3}. The typical dimensions of the samples are 1.5 mm × 1.5 mm × 15 mm with the length along the [0 1 1] crystal orientation. Iron was introduced into the sample by diffusion at the temperature of 1300 °C in a closed quartz ampoule under argon atmosphere. After 2 h of diffusion, the ampoule with sample was quenched in water. A surface layer was removed mechanically.

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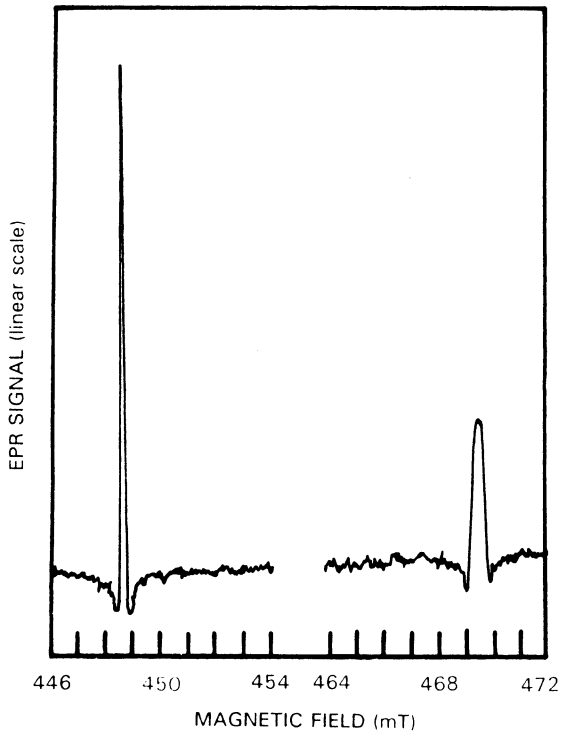

Fig. 1. EPR spectrum of Si–NL40 and Si–NL41 for magnetic field $\mathbf{B} \parallel [0\,1\,1]$ with $g_1 = 1.470$ and $g_1 = 1.404$, respectively, measured at X-band frequency.

After short heating again to 1300 °C a second quenching in an open ampoule followed and once again a surface layer was removed by grinding. The sample was stored at room temperature for several years before measuring.

The EPR measurements were performed on K-band (microwave frequency $\nu \approx 23$ GHz) and X-band ($\nu \approx 9$ GHz) superheterodyne spectrometers, which were tuned to observe the dispersion of the susceptibility. Sample temperature during the EPR experiment was 4.2 K.

3. RESULTS AND ANALYSIS

Besides the well known spectra of isolated interstitial iron Fe_i^0, Fe_i^+ and of trigonal and orthorhombic FeAl pairs, two new strongly anisotropic spectra were observed. For reference, they are labelled Si–NL40 and Si–NL41. Because of the low symmetry, the observed spectra look quite complicated. However, due to the differences in line intensities and line widths between the two spectra, as shown in Fig. 1, it is possible to distinguish lines between two groups, to follow line positions and make angular dependence patterns. From the rotation patterns observed in K-band and X-band measurements, the monoclinic-I symmetry is confirmed for both centres. The line

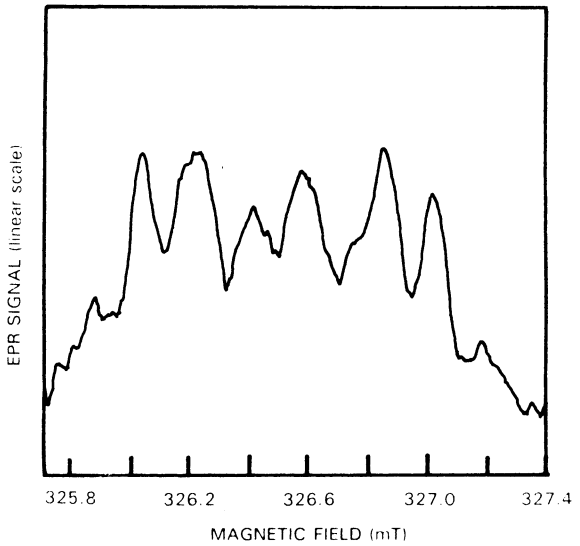

Fig. 2. EPR spectrum of Si–NL41 for magnetic field **B** 20 degrees away from [0 1 1], showing the hyperfine splitting due to ^{27}Al with nuclear spin $I = 5/2$.

intensities of both spectra are very angular dependent and are the largest in [0 1 1]. For the spectrum Si–NL41, the six-fold splitting with nearly equal intensities due to ^{27}Al, with nuclear spin $I = 5/2$, as shown in Fig. 2, is observed for one of the EPR orientations at the angle about 20 degrees away from the [0 1 1] direction. When going to the [0 1 1] direction, the outermost hyperfine lines are rapidly decreasing in intensity to vanish simultaneously with the increasing of the central component and in the [0 1 1] only one strong line is detected. The hyperfine structure with six-fold splitting is not observed for the spectrum Si–NL40 due to the overlapping of the resonances at this angle. However, a similar behaviour of hyperfine splitting is seen at other orientations of magnetic field. There is no change of the spectra after keeping the sample at room temperature for a long time. Illuminating the sample by light with different energies causes some changes in the intensity only. Probably this is related to the changing of the population by electrons or holes on the defect energy level.

The computer fits to the experimental data of the EPR spectra were made using the simple spin Hamiltonian

$$H = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S}, \qquad (1)$$

with the lowest possible value of the effective electron spin $S = 1/2$, and with the g-tensor constrained to have monoclinic-I symmetry. The fits to the X-band data are somewhat better than to those obtained at the K-band, especially for the spectrum Si–NL40. The parameters deduced from the fits are given in Table 1. The simulated angular dependence patterns of the

Table 1. Spin Hamiltonian parameters of the spectra Si–NL40 *and* Si–NL41 *obtained from the analyses with effective spin* $S = 1/2$ *and* $S = 5/2$*: principal g-values, angles* θ *between the directions of the third principal values and* [1 0 0]*, and the ratios* E/D

Spectra	Spin	Principal g-values			Direction θ (°)	E/D	Remarks
		g_1	g_2	g_3			
Si–NL40	$S = 1/2$	1.470	2.836	8.907	36.6		$g_1 \parallel [0\,1\,1]$
	$S = 5/2$	2.064	2.064	2.064		0.1475	
Si–NL41	$S = 1/2$	1.404	2.661	9.027	64.6		$g_1 \parallel [0\,1\,1]$
	$S = 5/2$	2.066	2.066	2.066		0.1590	

spectra using these parameters are given in Figs. 3 and 4. For both spectra, thus, the analysis with $S = 1/2$ is possible to match the experimental data and gives a unique set of parameters for the centres. It is remarkable that the g-values of both centres are unusually high at some directions compared with the free electron value $g = 2$. For the low-symmetry centres, one would expect no significant contribution of the orbital momentum to the magnetism. The high g-values in these cases then indicate that the true spins of the centres are larger than 1/2. As known from the analysis of the iron-impurity complexes [10], such high g-values can well be explained by using an effective spin higher than 1/2 or 3/2. Following this way of

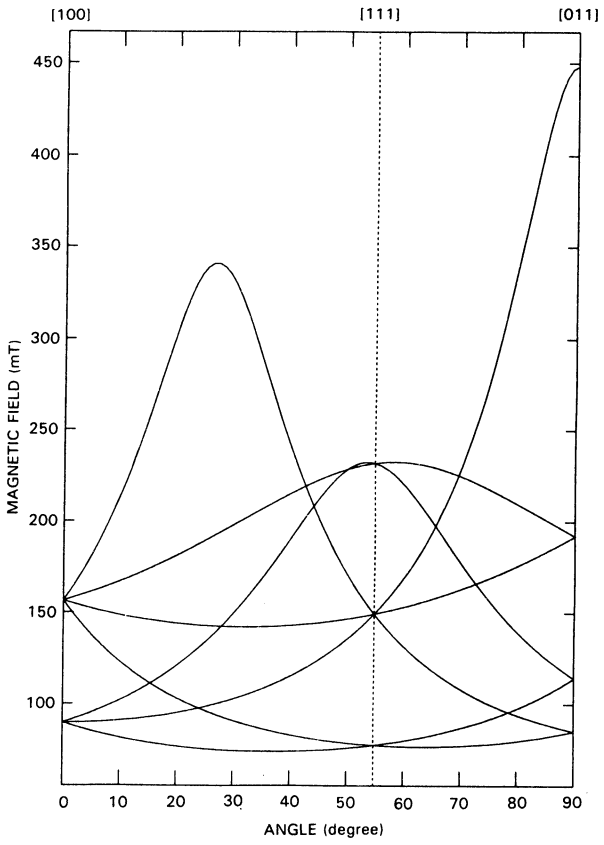

Fig. 3. The angular dependence pattern of the EPR spectrum Si–NL40; microwave frequency ν = 9.2277 GHz.

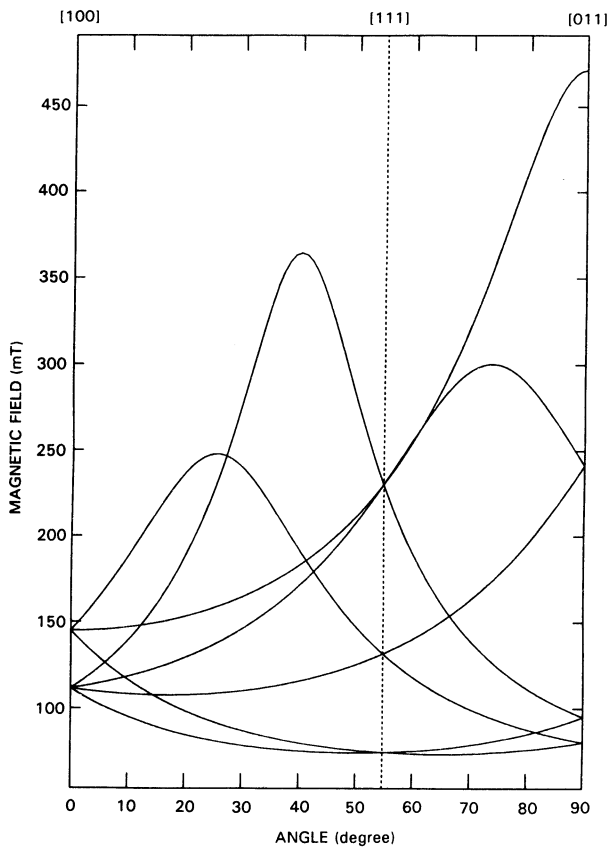

Fig. 4. The angular dependence pattern of the EPR spectrum Si–NL41; microwave frequency ν = 9.2277 GHz.

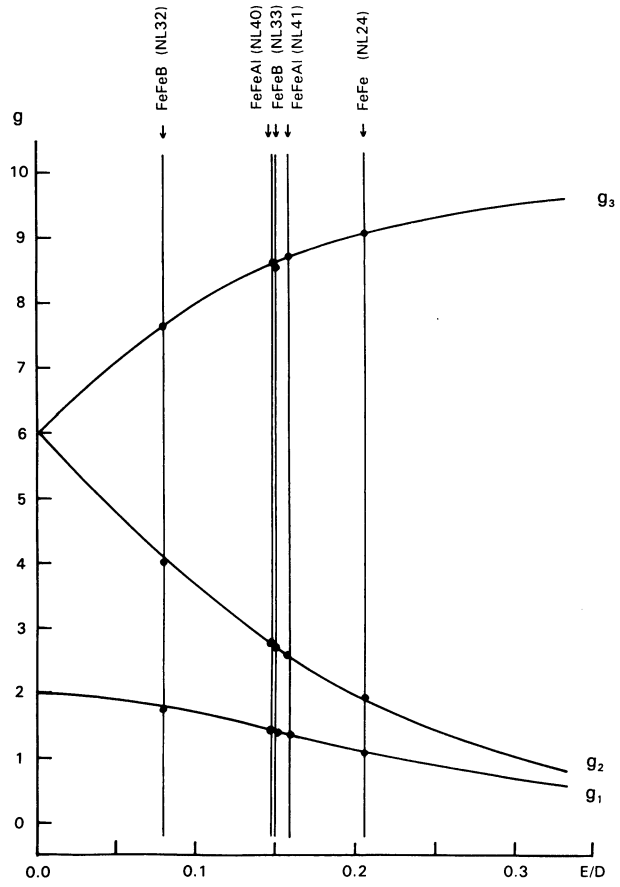

Fig. 5. Principal g-values in the doublet ground state of a true spin $S = 5/2$. The solid curves are the calculated ones taken from [10]; in the plot, the experimental data of some similar centres are also given.

analyzing, for our case, the spin Hamiltonian is written as:

$$H = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + D[S_z^2 - (1/3)S(S+1)] + E(S_x^2 - S_y^2), \quad (2)$$

with $S = 5/2$. The g-tensor is considered to have cubic symmetry with the value close to $g = 2$. The interaction between spins is represented by the second and the third terms which are the axial and orthorhombic crystal field terms, respectively. A number of fits with different starting values of D and E were made and it is clear that for both spectra, satisfactory fits could be obtained and the ratios E/D are well determined. The parameters deduced from these fits are also given in Table 1. As shown in Fig. 5, the results are in good agreement with the calculated dependence of the g-components on the parameter E/D for the ground state doublet of the $S = 5/2$ spin system given in [10]. The g-values of the centres given in this analysis are also very close to $g = 2.070$, which is the g-value for the neutral interstitial iron atom. It is very similar to the cases of the monoclinic and orthorhombic FeFeB centres, involving two iron atoms, and to the FeFe complex. From this analysis, it can be concluded that the true spin for both centres is $S = 5/2$. To account for this value of spin, the participation of two iron atoms in the centre is required. A possible electronic model is $Fe^+ Fe^0 Al^-$, with one Fe^+ ($S = 3/2$), one Fe^0 ($S = 1$) and Al^- ($S = 0$). Ferromagnetic coupling between iron spins then gives total spin $S = 5/2$. With only symmetry information from the g-tensor, it is not possible to suggest an exact model of the centre. Several geometrical arrangements of atoms in the centre are conceivable satisfying the monoclinic-I symmetry. It is known that in all complexes, iron is on interstitial sites and shallow acceptors occupy a substitutional site. A probable atomic model for these centres is the one in which the acceptor is on a substitutional site and the two iron atoms occupy tetrahedral and hexagonal interstitial sites on one $\{0\,1\,1\}$ plane through the acceptor site.

4. CONCLUSION

Our observation of two new spectra, together with the previously reported pairing and complexing reactions, reveals that the interaction between iron and shallow acceptors can at the same time lead to the formation of different complexes with various sizes. Both centres are stable at room temperature and this behaviour is apparently different from the iron cluster defects such as FeFe pairs. Similar to other complexes involving two iron atoms, these centres can be described as paramagnetic systems with spin $S = 1/2$ and unusually high g-values, or by spin $S = 5/2$ and g-values close to that of the neutral interstitial iron. From the analysis of the spectra the true spin $S = 5/2$ is confirmed for both centres.

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