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Electron paramagnetic resonance identification of the orthorhombic iron-indium pair in silicon

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A different EPR spectrum (Lu4) in silicon doped with indium and iron is reported together with an EPR spectrum previously observed by Ludwig and Woodbury. The two spectra show orthorhombic symmetry and are found to originate from the same FeIn pair. They are explained as transitions within the two Kramers doublets of an $S=\frac{3}{2}$ system with a zero-field splitting which is very large compared with the microwave energy. The ratio between the orthorhombic and axial fine-structure parameters is determined to be $E/D=0.052$, and the g values of the defect were found to be $g_z=2.09$, $g_y=2.05$, and $g_x=2.07$ ($z\parallel\langle 100\rangle$ and $x,y\parallel\langle 110\rangle$). The temperature dependence of the intensities of both spectra shows that the lower doublet corresponds to Lu4 and the upper one to the previously observed spectrum. Contrary to what has hitherto been believed, this observation implies that the axial fine-structure parameter has the same sign for the iron-indium pair as for the iron-aluminum and iron-gallium pairs.

INTRODUCTION

Pairs of transition metals and shallow acceptors in silicon have been extensively studied in recent years.[1-16] Among these, the ones consisting of a substitutional group-III acceptor and an iron atom on one of the nearby interstitial positions have drawn most attention. In particular, the observation of bistable properties has made these defects important objects of study.[7] Despite the progress that has been made in understanding the physics of such defects, questions related to the formation mechanism, the details of the electronic structure, and the observed chemical trends are still awaiting answers.

Electron paramagnetic resonance (EPR) of iron-acceptor pairs was first studied by Ludwig and Woodbury as early as 1962.[1] They reported EPR spectra of the trigonal FeB, the trigonal FeGa, and the orthorhombic FeIn pairs. In 1984 van Kooten *et al.* found two FeAl pairs, one with trigonal and another with orthorhombic symmetry.[6] Later, the orthorhombic FeGa pair was observed by Gehlhoff *et al.* who also studied new FeAl and FeGa spectra, which were attributed to transitions within excited states of the pairs.[10,11] The correspondence between the observed two deep donor levels[7,12] and the orthorhombic and trigonal configurations was demonstrated by combined EPR and DLTS experiments for FeAl.[13] Recently, the missing trigonal FeIn pair was identified by Omling *et al.*[14]

The observed defect-pair symmetries are most conveniently explained in a model where an interstitial Fe^+ ion is located in the crystal field of the negatively charged acceptor. The trigonal symmetry appears when the Fe^+ ($3d^7$) ion is located on one of the nearest interstitial (111) sites, and the orthorhombic symmetry when it is located on one of the next-nearest interstitial (100) sites. The EPR spectra of these defects are well described by an orbital singlet ground state with $S=\frac{3}{2}$ and a zero-field splitting which is very large compared with the microwave energy.[4,10,11] The EPR signals observed are often assumed to correspond to the transition within the lowest of these Kramers doublets. The axial component of the zero-field splitting is found to be positive for FeB, negative for FeAl and FeGa, and negative (trigonal) *and* positive (orthorhombic) for FeIn.[14-16] This unusual chemical trend has not been understood until now[15,16] and therefore provides a strong motivation for the present study.

In this communication we present a new EPR signal with orthorhombic symmetry which originates from FeIn. It is shown that this new spectrum is not in agreement with the previous interpretation of the electronic ground state of this defect. Evidence will be given that the new spectrum corresponds to the lower doublet state of the orthorhombic FeIn pair, and that the previously observed orthorhombic EPR spectrum corresponds to the upper one. An important consequence of this interpretation is that the previously assumed discontinuity in the chemical trend of the zero-field splitting parameter of Fe-acceptor pairs is removed.

EXPERIMENT

The samples were prepared from Czochralski-grown, indium-doped silicon crystals with a resistivity of 2 Ω cm. Iron, evaporated onto the surfaces of the crystals, was diffused at 1200 °C in a vertical furnace in an argon atmosphere for 2 h. The isotope doping was performed in a closed quartz ampoule where a piece of isotopically enriched iron metal (96% $^{57}\mathrm{Fe}$) was placed close to the silicon crystal. After diffusion, the samples were rapidly quenched in diffusion pump oil. The EPR measurements were performed at temperatures between 4 and 40 K with a $\langle 110\rangle$ axis of the silicon crystals ($\approx 0.25\times 0.25\times 1\ \mathrm{cm}^3$) oriented perpendicular to the magnetic field in a Bruker ESP 300 spectrometer, working in the X band and equipped with an Air Products helium-flow cryostat. The misalignment of the samples during g-value determination was compensated for by determination of the Euler angles in a computer minimization routine.

EXPERIMENTAL RESULTS AND DISCUSSION

In samples co-doped with iron and indium two EPR line sets with orthorhombic symmetry were observed. The angle-dependent resonance patterns are plotted in Figs. 1 and 2. Due to instrumental limitations, the dashed line in Fig. 2 (at magnetic fields exceeding 1.5 T) was not experimentally observed. Furthermore, it should be noted that the EPR spectrum corresponding to Fig. 2 has a complex structure and, without a complete analysis, only an approximate determination of the positions of the electronic spin transitions is possible. The angular dependence of both line sets could be described with an effective spin $S'=\frac{1}{2}$ and a spin Hamiltonian which only contains the electronic Zeeman interaction $H=\mu_B(\mathbf{B}\cdot\mathbf{g}'\cdot\mathbf{S}')$. An analysis of the spectrum in Fig. 1 shows that the g' values are in close agreement with those reported by Ludwig and Woodbury,[1] i.e., $g_x'=3.80$, $g_y'=4.42$, and $g_z'=2.07$ ($z\parallel\langle 100\rangle$ and $x,y\parallel\langle 110\rangle$). A computer fit to the experimentally observed part of the angle-dependent resonance pattern shown in Fig. 2 gives the effective g' values: $g_x'=0.36$, $g_y'=0.35$, and $g_z'=6.26$. Since the first spectrum, judging from the g' values, is identical to the FeIn spectrum reported by Ludwig and Woodbury,[1] we will hereafter denote this spectrum LW. The very anisotropic spectrum in Fig. 2 has, as far as we know, not been reported before and is hereafter labeled Lu4.

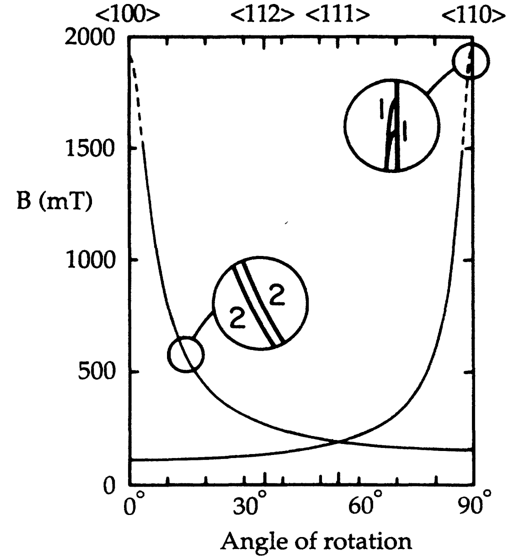

FIG. 2. Angle-dependent resonance pattern of the Lu4 spectrum. The magnetic field is in a {110} plane and the microwave frequency is 9.525 GHz. The figures along the curves indicate orientational degeneracies. Note that in the region above 1.5 T (dashed lines) no measurements could be performed.

Since no hyperfine interactions were reported by Ludwig and Woodbury,[1] it remained to be confirmed that the LW spectrum was due to an FeIn pair. In the x direction a tenfold splitting due to ^{113}In ($I=\frac{9}{2}$, 4.28% natural abundance) and ^{115}In ($I=\frac{9}{2}$, 95.72% natural abundance) was clearly observed [see Fig. 3(a)]. Since the gyromagnetic ratio of these isotopes is almost unity, only one set of lines is detected. Isotope doping experiments with ^{57}Fe ($I=\frac{1}{2}$) gave a further twofold splitting of each line [Fig. 3(b)]. This clearly shows the involvement of one In and one Fe atom in the defect. It is therefore concluded that the LW EPR spectrum originates from an FeIn pair. A complete analysis of the hyperfine splittings is in progress and will be reported elsewhere.

The general feature of the Lu4 spectrum is rather complex and difficult to analyze. The complex spectrum results from the numerous overlappings of "allowed" and "forbidden" hyperfine transitions[4] as well as from the overlapping of the electronic spin transitions belonging to the different center positions and the disappearance of lines in certain directions due to mixing with lines of other

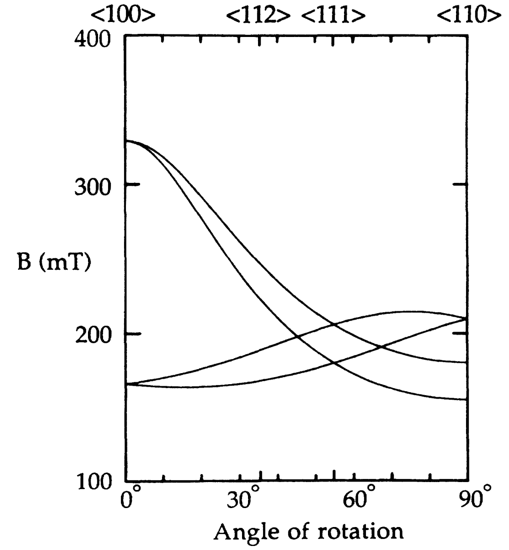

FIG. 1. Angle-dependent resonance pattern of the LW spectrum. The magnetic field is in a {110} plane and the microwave frequency is 9.525 GHz.

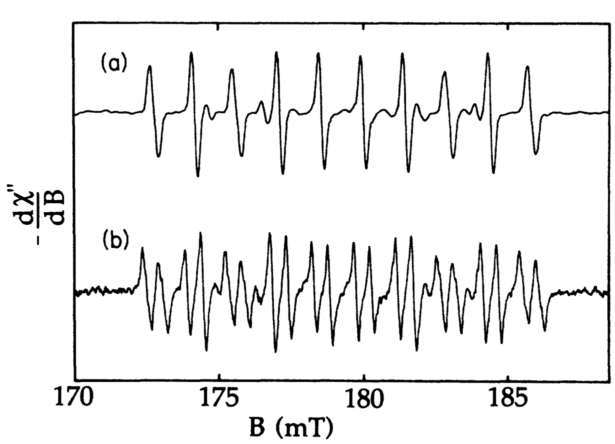

FIG. 3. Part of the LW spectrum with the magnetic field parallel to the [110] axis showing (a) the hyperfine structure due to ^{115}In ($I=\frac{9}{2}$, 95.72% natural abundance) and to ^{113}In ($I=\frac{9}{2}$, 4.28% natural abundance), and (b) the additional hyperfine splitting due to ^{57}Fe ($I=\frac{1}{2}$, enriched to 94.6% abundance).

EPR spectra. Nevertheless, the hyperfine interaction observed at some special angles indicates that one In atom is involved in the center. The small hyperfine splitting of the isotope ^{57}Fe is more difficult to observe and has not yet been confirmed. However, since Lu4 only appears in crystals co-doped with Fe we also identify Lu4 with an orthorhombic FeIn pair. The question is whether this FeIn pair is the same as the one giving rise to the LW spectrum, in analogy to the other orthorhombic Fe-acceptor pairs[10,11] or if it is a different one. To answer this question we will compare the experimental g' values with those expected from a model calculation.

The iron-acceptor pairs are considered to be well described by a substitutional, negatively charged acceptor with a closed shell and a positively charged iron atom at an interstitial position. The electronic structure of such a pair is therefore expected to be identical to that of the positively charged iron $(3d^7)$ subjected to the crystal field caused by the silicon lattice and the negatively charged acceptor. In analogy with the other iron-acceptor pairs, the measured spectra can thus be analyzed using $S=\frac{3}{2}$ and the following spin Hamiltonian:[4,10,11]

$$H=D[S_z^2-\tfrac{1}{3}S(S+1)]+E(S_x^2-S_y^2)+g_x\mu_B B_x S_x + g_y\mu_B B_y S_y + g_z\mu_B B_z S_z\,. \qquad (1)$$

Here D is the axial and E the orthorhombic fine structure parameter; S_x, S_y, and S_z are the spin components; μ_B is the Bohr magneton; B_x, B_y, and B_z are the components of the magnetic field; and g_x, g_y, and g_z are the true g values in the three main directions. Since the magnitude of the zero-field splitting $\Delta=2(D^2+3E^2)^{1/2}$ is much larger than the microwave energy, only the transitions within the two Kramers doublets of the $S=\frac{3}{2}$ system can be detected. In Fig. 4 the effective g' values in the $S'=\frac{1}{2}$ formalism are plotted against the ratio between E and D assuming that the orbital contribution to the true g values can be neglected (i.e., $g_x=g_y=g_z=2.0$). The result shows that for $E/D=0.05$, the calculated effective g' values are close to those which are experimentally observed for both the LW and the Lu4 spectra. An optimum fit is achieved for the true g values $g_x=2.068$, $g_y=2.054$, and $g_z=2.092$, and $E/D=0.0524$. This fit gives $g_x'=3.80$, $g_y'=4.42$, and $g_z'=2.07$ for the LW spectrum and $g_x'=0.33$, $g_y'=0.31$, and $g_z'=6.26$ for the Lu4 spectrum, in very good agreement with the experimentally observed values.

From the experimental observations described above, and the good agreement between the calculated and measured EPR spectra, we conclude that the Lu4 spectrum originates from the same orthorhombic FeIn defect as the LW spectrum. The g values obtained ($g_x=2.07$, $g_y=2.05$, and $g_z=2.09$) are therefore considered to be the real g values for the orthorhombic FeIn pair, i.e., for both the Lu4 and the LW spectra. As a necessary consequence of the model one of the spectra has to be related to the ground doublet and the other to the excited one. In order to verify this, and to investigate which of the spectra corresponds to the ground state, the temperature dependence of the EPR signals was measured. The intensity of the Lu4 spectrum decreased monotonously with temperature, while the intensity of the LW spectrum increased up to 20 K, after which the signal started to decrease. These experiments clearly show that the LW spectrum originates from an excited state, and that the Lu4 spectrum is consistent with a ground state, thus further supporting the model. An important result of our interpretation of the experimental data is that the sign of the axial fine structure parameter becomes negative, i.e., is the same as for the other orthorhombic iron-acceptor pairs. This is in disagreement with what has been believed hitherto.[15,16]

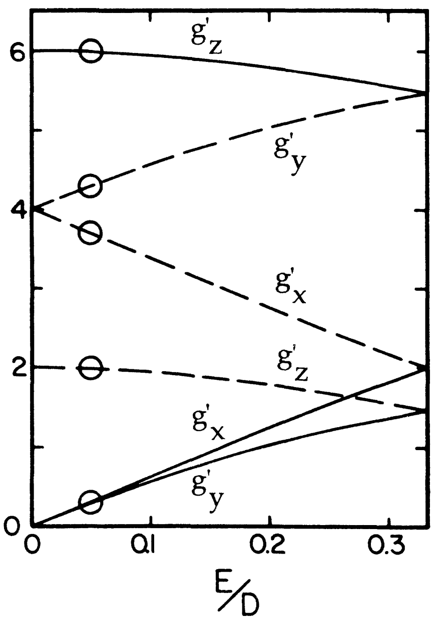

FIG. 4. Calculated apparent g values (g') as a function of the ratio of the orthorhombic (E) and the axial (D) fine structure parameters for a $S=\frac{3}{2}$ system using $g=2.0$. The solid and the dashed lines correspond to possible transitions within the two Kramers doublets. The values consistent with the experimental situation for the Lu4 and LW spectra are indicated.

For the FeIn pair in silicon one signal showing trigonal (Lu2) (Ref. 14) and two signals showing orthorhombic symmetry (Lu4 and LW) have been observed by EPR. Of the orthorhombic ones, the Lu4 spectrum is related to the ground state and the LW spectrum to the excited state. These results remove some of the problems related to the understanding of the FeIn pair in particular, and the Fe-acceptor pairs in general. The finding of the real ground state (Lu4) of the orthorhombic configuration has eliminated a discontinuity in the chemical trend of Fe-acceptor pairs. Rather, the FeIn system is very similar to the FeAl and FeGa pairs. All these pairs show the same configurational situation with one nearest-neighbor trigonal pair and one next-nearest-neighbor orthorhombic pair. The electronic structures of the orthorhombic defects are also very similar: The ground state is split into two Kramers doublets with energetic separations of similar magnitudes for the different defects.

CONCLUSIONS

We have reported a new EPR spectrum, which we identify as the ground state of the orthorhombic iron-indium pair in silicon. The previously reported orthorhombic iron-indium pair was found to be an excited state of the same center. The defect is well described by an orbital singlet state with $S=\frac{3}{2}$ and a large zero-field splitting. The ratio between the orthorhombic and axial fine-structure parameter was found to be $E/D=0.052$ and the true g values were determined to be $g_x=2.07$, $g_y=2.05$, and $g_z=2.09$. The results show, in contrast to what has hitherto been believed, that the FeIn pair is very similar to the FeAl and FeGa pairs in silicon.

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