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## LETTER TO THE EDITOR

## An iron–phosphorus pair in silicon

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### Abstract

For n-type (phosphorus-doped) floating-zone grown silicon samples, a hitherto unreported ESR signal was detected after the samples were doped with iron and irradiated with electrons. Analysis of the hyperfine structure and the angular dependence of the resonance peak positions of the spectrum, labelled TU6, indicated that the signal originates from a defect complex of monoclinic-I symmetry containing single phosphorus and single iron atoms. The spectrum can be described in terms of a paramagnetic system with  $S = 1/2$  and  $g$  values greatly deviating from that of a free electron, as well as spin  $S = 3/2$  and  $g \approx 2$ . The spin  $S = 3/2$  may correspond to a positively charged iron atom ( $3d^7$  state) and, thus, to a doubly positive charge state of a TU6 related complex. The fact that the TU6 signal was detected only under strong external illumination for n-type samples also supports this assignment. Results obtained during isochronal annealing of the irradiated samples suggest the possible involvement of a divacancy in the formation of an iron–phosphorus pair in silicon.

### 1. Introduction

More than 30 iron-containing complexes have been detected and identified in Si during the last 40 years using various experimental methods [1]. Complexes of iron (Fe) with common shallow dopants in Si: acceptors, i.e., B, Al, Ga, In, and donors, i.e. P and As, are of special interest. This interest is related to the possibility of Fe gettering in regions with high concentrations of dopants and/or to the formation of harmful defects during the fabrication of electronic devices. The rich collection of iron–acceptor complexes (see [1–3] for reviews) make a contrast with the few experimental results reported supporting the existence of iron–donor complexes in Si. In the review [2], one can find reference to a private communication with Corbett about iron related ESR spectra labelled A25 and A26, attributed to (FeP I/V) complexes in ‘+’ and neutral charge states. Unfortunately, no further structural or formation details were given in [2] or in later publications. In [4] a decrease in the concentration of interstitial iron in iron-doped slowly cooled samples was correlated with an increase of the level of P doping. This was interpreted as a sign of the formation of stable FeP pairs with the binding energy of 0.9 eV. No FeP related signals were reported in [4]. Finally, satellite ESR lines around the signal of  $\text{Fe}_i^0$

were also reported for Si samples highly doped with donors ( $C_{P,As} \sim 10^{17} \text{ cm}^{-3}$ ) [5]. This hyperfine (HF) structure was attributed to spin–spin interaction between  $\text{Fe}_i^0$  and P (or As). However, the distribution of Fe and donor atoms was random; thus these atoms did not form pairs (complexes) of distinct structure [5]. The absence of clear evidence for the existence of iron–donor complexes was attributed to the fact that the main driving force for complex formation, i.e., electrostatic attraction, does not exist between Fe and donor atoms [1], because interstitial Fe should be neutral or positively charged and donors are positively charged in Si.

Information about iron–donor complexes may help in addressing another important problem for Si, i.e. that of the existence and properties of substitutional iron ( $\text{Fe}_S$ ). A substantial increase in iron solubility along with a decrease in the diffusivity was reported in  $n^+$ -Si ( $C_P = 1 \times 10^{20} \text{ cm}^{-3}$ ) [6]. An increase in substitutional solubility can be expected if  $\text{Fe}_S$  forms acceptor level(s) in the Si band gap. In contrast, theoretical calculations and results of Mössbauer measurements (see [7, 8] and references therein) suggest that  $\text{Fe}_S$  has no band gap state. Detection of iron–donor complexes may support the existence of acceptor states of  $\text{Fe}_S$  in Si.

Our recent investigations were related to iron–vacancy complexes in Si [9, 10]. During these investigations, a hitherto unreported ESR signal was detected after electron irradiation of  $n$ -type floating-zone (FZ) grown Si samples pre-doped with iron. The signal was labelled TU6. Results of our investigation showed that iron and phosphorus atoms are included in the structure of the defect responsible for the TU6 signal. In what follows, we report preliminary spectral characteristics and first results related to formation/annealing peculiarities of the new signal. A tentative model of the defect structure will be proposed at the end of this report.

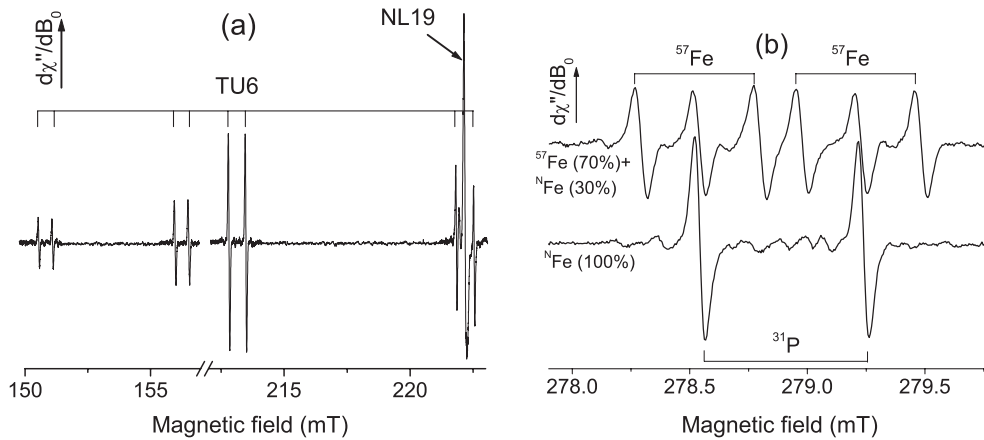
## 2. Experimental details

We used  $n$ -type FZ-Si samples doped with phosphorus with initial resistivities of 0.6 (‘R’ samples), 3 (‘M’ samples) and 1000 (‘L’ samples)  $\Omega \text{ cm}$ . Mechanically and chemically polished Si samples,  $3 \times 3 \times 12 \text{ mm}^3$  in size, were dipped into a 100 ppm  $\text{FeCl}_3$  water solution, dried and annealed at  $1200^\circ\text{C}$  in evacuated quartz capsules for iron doping. Natural iron ( $^{56}\text{Fe}$ ) or iron enriched with  $^{57}\text{Fe}$  isotope was used for  $\text{FeCl}_3$  preparation. Samples were quenched in iced water after the doping procedure and irradiated at room temperature with 3 MeV electrons (dose  $d = 4 \times 10^{17} \text{ e cm}^{-2}$ ). Isochronal 30 min annealing of irradiated samples was accomplished in an Ar flow in the  $100\text{--}550^\circ\text{C}$  range with a  $25\text{--}50^\circ\text{C}$  step in the annealing temperature.

We used a JEOL X-band ESR spectrometer equipped with a  $\text{TM}_{011}$  mode microwave (MW) resonator and a continuous helium gas-flow cryostat. The derivative of the MW field absorption with respect to the magnetic field ( $d\chi''/dB_0$ ) was measured using a lock-in amplifier and magnetic field modulation with an amplitude of 0.01–0.2 mT and a frequency of 100 kHz. The TU6 signal was detected at temperatures  $T_{\text{MEAS}} \leq 12 \text{ K}$ , under external illumination supplied through an optical window in the resonator. However, for the best signal to noise ratio, measurements were performed at  $T_{\text{MEAS}} = 6 \text{ K}$  and 0.1 mW MW power. We used an external ESR signal, i.e.  $\text{Mn}^{+2}$  in  $\text{MgO}$ , for calibration of ESR signal intensities for various samples and under various measurement conditions. The standard sample was placed in the same MW resonator at room temperature.

## 3. Results and discussion

Spectra in figure 1 were detected from the R sample annealed for 5 h at  $400^\circ\text{C}$  after iron doping and irradiation. The NL19 signal [11] from the  $(\text{FeV})^+$  pair was also strong for this sample

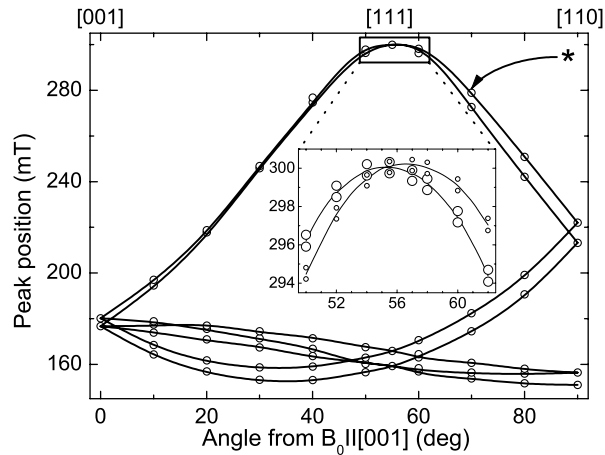


**Figure 1.** Experimental ESR spectra from the Fe–P complex in an n-type FZ-Si sample, pre-doped with Fe, annealed at 400 °C for 5 h after electron irradiation. Measurement conditions:  $T_{\text{MEAS}} = 6$  K,  $P_{\text{MW}} = 0.1$  mW,  $f_{\text{RES}} = 9.047$  GHz, external illumination. (a) The sample doped with  $^{56}\text{Fe}$ ,  $\mathbf{B}_0 \parallel [110]$ ; (b) the isotope content of Fe used for doping is indicated beneath the curves; the orientation and branch are indicated by ‘\*’ in figure 2.

(see figure 1(a)). However, for  $T_{\text{MEAS}} \approx 6$  K the NL19 signal intensity is suppressed [12] and it becomes possible to separate the TU6 and NL19 signals even for  $\mathbf{B}_0 \parallel [110]$  orientation at around  $B_0 = 224$  mT. The TU6 signal was not observed in reference, i.e., for non-irradiated samples subjected to similar doping and annealing procedures. The NL19 and TU6 signals were not observed for the sample cooled in the dark from above 50 K. The TU6 signal intensity strongly correlated with that of the external illumination (band gap energy photons), yet saturated for very large illumination intensities. As distinct from the TU6 signal, the NL19 signal persisted with suppressed intensity at  $T_{\text{MEAS}} < 18$  K after the external illumination was turned off.

In figure 1 the 1:1 HF splitting of the TU6 related signals is clearly seen. It is natural to suppose that this HF splitting is related to a nuclear spin with  $I = 1/2$  of  $^{31}\text{P}$  atoms (abundance  $A = 100\%$ ). The absence of the TU6 signal for the L sample and the smaller intensity for the M sample, i.e., about  $\sim 20\%$  of that for the R sample, supported such a supposition. However, the change in the charge state of the defect due to the variation in donor concentration may be another reason for the observed differences for the R, M and L samples. Further, hydrogen with similar  $A$  and  $I$ , unintentionally introduced into the sample during high temperature annealing from the walls of a quartz capsule, may cause similar HF splitting. To check the possibility of H involvement in the defect structure, we performed intentional doping of Fe-doped samples with H and H/D mixtures before electron irradiation (see [13] for doping details). The shape of the TU6 signal was not affected by the presence of H(D) atoms in the sample. This unambiguously excludes the possibility of hydrogen atoms affecting the HF structure of the TU6 signal. Moreover, the intensity of the TU6 and NL19 signals were suppressed in the H-doped samples and several new ESR spectra, presumably from  $\text{Fe}_X$ ,  $\text{FeH}_X$  and  $\text{FeH}_X\text{P}$  ( $X \geq 1$ ) complexes, appeared upon annealing of irradiated samples. The results related to these spectra will be reported elsewhere. The presence of other elements with similar  $A$  and  $I$  compositions ( $^{89}\text{Y}$ ,  $^{103}\text{Rh}$  and  $^{169}\text{Tm}$ ) can be ruled out. Thus, single P atoms remain the only possible cause of the 1:1 HF splitting of the TU6 signal.

To check the number of Fe atoms in the TU6 signal related complex, we analysed samples doped with iron enriched in the  $^{57}\text{Fe}$  isotope. A sample spectrum from a



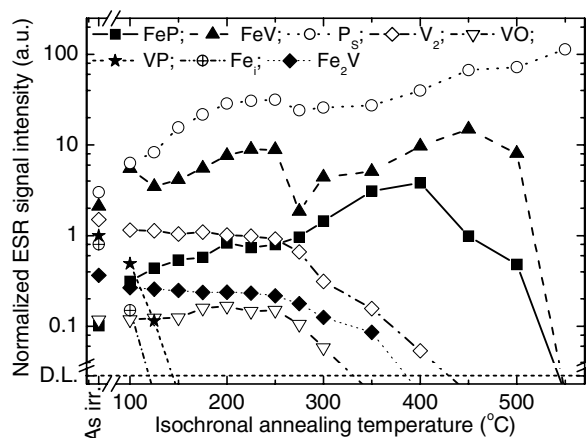
**Figure 2.** The angular dependence of the ESR peak positions (symbols) related to the TU6 spectra in the  $B_0$  range 70–550 mT. Curves show the fitted dependence for  $S = 1/2$  and the parameters of the Zeeman interaction indicated in the text. The inset shows the detailed dependence near  $B_0 \parallel [111]$  with symbol size indicating peak intensity. The measurement conditions were the same as indicated in figure 1; sample was rotated in the  $(\bar{1}10)$  plane.

$^{57}\text{Fe}$  (70%) +  $^{58}\text{Fe}$  (30%) co-doped sample is presented in figure 1(b). The results prove the participation of single Fe atoms in the TU6 signal related complex. The possibility of participation of intrinsic defects, i.e., vacancies and/or interstitials, in the TU6 related defect complex cannot be excluded and will be discussed later. However, for the sake of simplicity we will use the label ‘FeP pair’ for the complex.

The angular dependence of the TU6 related ESR peak positions for the range of magnetic fields investigated, i.e., 70–550 mT, is presented in figure 2. An analysis of the angular dependences obtained with spin  $S = 1/2$  of the centre gives the following parameters of Zeeman interaction:  $g_1 = 4.073$ ,  $g_2 = 2.153$ ,  $g_3 = 4.280$  with the angle between the [001] crystal axes and the  $g_2$  axis equal to  $\theta \approx 57^\circ$ . The symmetry of the centre is monoclinic-I. A large difference of the parameters obtained from these reported for the A25 and A26 spectra (see [2]) should be emphasized.

For the low symmetry centre, a significant contribution of the orbital momentum to the magnetism cannot be expected. Therefore, large deviations of  $g_1$  and  $g_3$  from  $g = 2$ , the value for a free electron, suggest that the effective spin of the centre  $S$  is  $> 1/2$  [2]. The analyses of low symmetry iron related centres in silicon [2] suggest for the TU6 centre a value  $S = 3/2$  and  $E/D \approx 0.9$ , where  $D$  is the axially symmetric part and  $E$  is the asymmetry parameter of the fine structure interaction term in the spin Hamiltonian. From the value of  $E/D$ , one can estimate  $g_i$  values, using expressions from [2], that are fairly close to that of a free electron.

The HF interactions related to P and Fe atoms show similar monoclinic-I symmetry and nearly isotropic nuclear Zeeman interaction. On the assumption that  $S = 3/2$ , the HF interaction parameters can be estimated as  $A_1 = 4.93$ ,  $A_2 = 6.21$ ,  $A_3 = 4.89$  for  $^{57}\text{Fe}$  and  $A_1 = 5.24$ ,  $A_2 = 7.47$ ,  $A_3 = 5.11$  for  $^{31}\text{P}$  in units of  $10^{-4} \text{ cm}^{-1}$ . The relatively small value for the  $^{31}\text{P}$  related HF interaction term suggests small density of the paramagnetic wavefunction on the P nucleus. Therefore, the spin value  $S = 3/2$  is apparently related to three spins localized on the Fe atom and coupled in parallel. This is the well known  $(3d)^7$  electronic configuration, i.e., three holes in a 3d shell, of the positively charged Fe atom. The total charge state of the FeP pair, responsible for the TU6 signal, should thus be ‘2+’. Such a charge state explains why the TU6 signal could be observed for n-type Si samples only under strong external illumination. Insufficient intensity of the TU6 signal, obscuring signals from the NL19 spectra and limitations of measurements on X-band ESR spectrometers, prevented us from explicitly describing the HF structure of the TU6 spectra at this stage. In particular, the HF structure related to the  $^{29}\text{Si}$  isotope was unclear. However, no  $^{29}\text{Si}$  related HF peaks could be observed



**Figure 3.** Variations in the intensities of ESR signals from various defects upon 30 min isochronal annealings of the electron-irradiated samples. The attribution of the symbols is indicated in the figure and explained in the text. Symbols are connected to guide the eye. 'DL' stands for detection limit.

with intensities corresponding to more than two atoms positioned in the equivalent Si atom shells around the paramagnetic centre.

Before discussing a model for the structure of the FeP pair, we would like to present results related to its formation. Changes in the ESR signal intensities of various defects in irradiated R samples after isochronal annealing steps are presented in figure 3. Besides the TU6 and NL19 signals, the behaviours of the signals from P ( $P_S^0$ ), the excited states of vacancy–oxygen pairs ( $VO^*$ ), vacancy–P pairs ( $VP^0$ ), divacancies ( $V_2^-$ ) and 2Fe vacancies ( $Fe_2V^-$ ) were analysed (for descriptions of and references on related ESR spectra, see [2, 14]). It should be emphasized that, due to the influence of passage conditions during ESR measurements, due to the variations in charge state of the defects and due to the variations in concentrations of recombination centres upon annealing, it becomes impossible to estimate absolute concentrations of the defects in the samples. Moreover, the named factors may strongly affect even estimates for the relative change in the concentrations. Therefore, the results presented in figure 3 are of qualitative character; yet these results are able to supply some clues about formation processes for the FeP pairs.

Probably the most striking peculiarity of the results presented in figure 3 is the 'mirror-like' annealing behaviours of the FeP pair and  $V_2^-$  in the 250–400 °C temperature range. Decreases in the ESR signal intensities from  $P_S^0$ , FeV,  $Fe_2V^-$  and VO at 275–300 °C accompany the increase in the TU6 signal. These facts lead one to suppose that the inflow of vacancies due to the annealing of  $V_2^-$  and VO affects the formation of FeP pairs from  $P_S^0$ , FeV and  $Fe_2V^-$ . Moreover, the decreases in PV, FeV and  $Fe_2V^-$  signal intensities at around 100–125 °C are also accompanied by increases in the TU6 signal intensity. The detection of a weak TU6 signal for as-irradiated samples may be related to the heating of the sample under irradiation (the actual temperature of the water-cooled sample during irradiation is in the 50–100 °C range). As reported in [9], the increase in the FeV related signal strength after 300 °C may be attributed to the simultaneous dissolution of  $V_2^-$  and  $Fe_2V^-$ . The annealing out of FeP pairs after 400 °C is accompanied with increases in FeV and  $P_S^0$  strengths. All discussed peculiarities made it possible to suppose that  $P_S^0$ , FeV and vacancy (vacancies) are species involved in the formation and structure of FeP pairs.

The exact microscopic structure of the defect should be determined, employing measurements with K or Q-band ESR spectrometers and the ENDOR technique. At present, we will discuss only a tentative model of the microscopic structure. The model is based on the spectroscopic and defect formation results. First, various interstitial positions for the Fe atom

in the pair may be excluded on the basis of the absence of the TU6 signal for the reference samples, i.e., samples not subjected to irradiation. Therefore, pair structures, similar to that proposed for  $C_iP_S$  [15] will not be considered. Nearest-neighbour (NN)  $Fe_S P_S$  pair structure can probably also be excluded, from symmetry considerations and the small value of the HF splitting related to the P atom. A structure where the  $P_S$  atom is next to a NN site from the Fe atom would be consistent with the observed symmetry and HF interaction terms. However, the questions to be addressed are those of the possible participation of vacancies and the exact position of the Fe atom, i.e., in a substitutional site or displaced, as in the case of FeV [11].

Formation peculiarities of FeP pairs suggest the possibility of vacancy incorporation in the microstructure of the defect. The simplest possible structure is the  $FeVP_S$  complex. The structure would be like that of the known  $P_SVP_S$  defect in Si [16], with Fe instead of one of the  $P_S$  atoms. Monoclinic-I symmetry allows the Fe atom to be displaced from the exact substitutional position, remaining in the same (110)-type plane with the  $P_S$ . Moreover, the absence of equivalent Si atom shells with more than two atoms suggests that the Fe is not exactly on the substitutional site. Interestingly, we did not detect an isotopic shift in the values of the spin Hamiltonian terms for the TU6 signal, like that reported for the FeV defect [11]. This suggests that at least the local arrangements of Fe atoms in the NL19 and TU6 related defects are different. Other structures for the FeP pair could also be proposed; however, without further experimental evidence their consideration seems unjustified.

#### 4. Conclusions

The first clear evidence of the existence of an Fe–P complex in Si was obtained from ESR measurements of the TU6 signal from electron-irradiated Si samples pre-doped with P and Fe. The complex contains single Fe and P atoms and possesses monoclinic-I symmetry. Determination of the exact microstructure, properties and formation mechanism of the defect responsible for the TU6 ESR spectra may help to resolve many problems related to the Fe impurity in Si. Besides that, other transition metals may form similar pairs with donors by a similar mechanism. Therefore, results related to the complex may have special importance for the gettering problem for n-type Si material. Further investigation of the defect is a matter of considerable interest for fundamental and applied Si research.

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