ELECTRON PARAMAGNETIC RESONANCE STUDY OF HYDROGEN-IMPLANTED SILICON

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In hydrogen- and deuterium-implanted silicon several electron paramagnetic spectra have been observed. the two most prominent ones (which we labelled DK1 and DK3) have nearly-identical close-to-trigonal monoclinic-I g-tensors and first- and second-shell ^{29}Si hyperfine interaction. Also, their annealing behavior is similar. The differences between them are the observation of hydrogen hyperfine interaction for DK1, whereas DK3 shows no resolved H-HF structure, and a different measurement-temperature and microwave-power dependence. On basis of these results, we identify DK1 with VH, while for DK3 the underlying defect structure is yet to be determined. Also, the combined spectrum of DK1 and DK3 equals the long-known S1 (B2) and NL52 spectra.

1 Introduction

Hydrogen plays a major role in the fabrication of microelectronic devices. Its remarkably high diffusivity and strong power to passivate electrical active centres make it a device-controlling species [1]. In spite of its importance, not much is known about the microscopic nature of the hydrogen-containing defects. Electron paramagnetic resonance is one of the most powerful tools to study microscopic structures. In the past decade, some defects have been found and even identified, e.g., the famous bond-centered hydrogen, the basic hydrogen defect in silicon. Still, an extended study of hydrogen-related defects in silicon has not been performed yet. We report here on the observation of two of the defects we found in such a study.

2 Experimental techniques

For our studies we made use of a commercial EPR spectrometer (Bruker ES-P300e) which could be operated at X-band (9 GHz) or Q-band (34 GHz) in absorption mode. The magnetic field could be rotated in an (011) plane of the sample. To increase the resolution we made use of a technique in which the detection was done at the third harmonic, rather than the more usual first

harmonic. This reduced the linewidth substantially from 0.066 mT down to 0.044 mT in X-band.
The samples were prepared by implanting protons (or deuterons) into the (111) plane of a float-zoned silicon mono-crystal, of typical dimensions 15×5×0.5 mm^3 (the long axis being <011>). The implantation was done at ca. 20 K. Afterwards, the samples were brought back to room temperature and transported to the spectrometer. The measurement temperature ranged from 4 K to 300 K.

3 Results and Discussion

After implantation of deuterium a complex superposition of spectra arises. Figure 1 shows scans in the three main directions <100>, <111> and <011>. A careful study of the measurement-temperature and microwave-power dependence revealed that the most dominant lines belong to two different spectra, namely DK1 and DK3 (the other spectra encountered in this study will be presented elsewhere). At room temperature increasing the microwave power a factor 10 in X-band isolates DK3. Figure 2 shows the full angular dependence of the resonances of Figure 1. This reveals that both DK1 and DK3 have close-to-trigonal monoclinic-I symmetry. The use of the line-sharpening technique allowed for the unraveling of the spectra. To verify the involvement of hydrogen in the defect we made a new sample, prepared and measured under

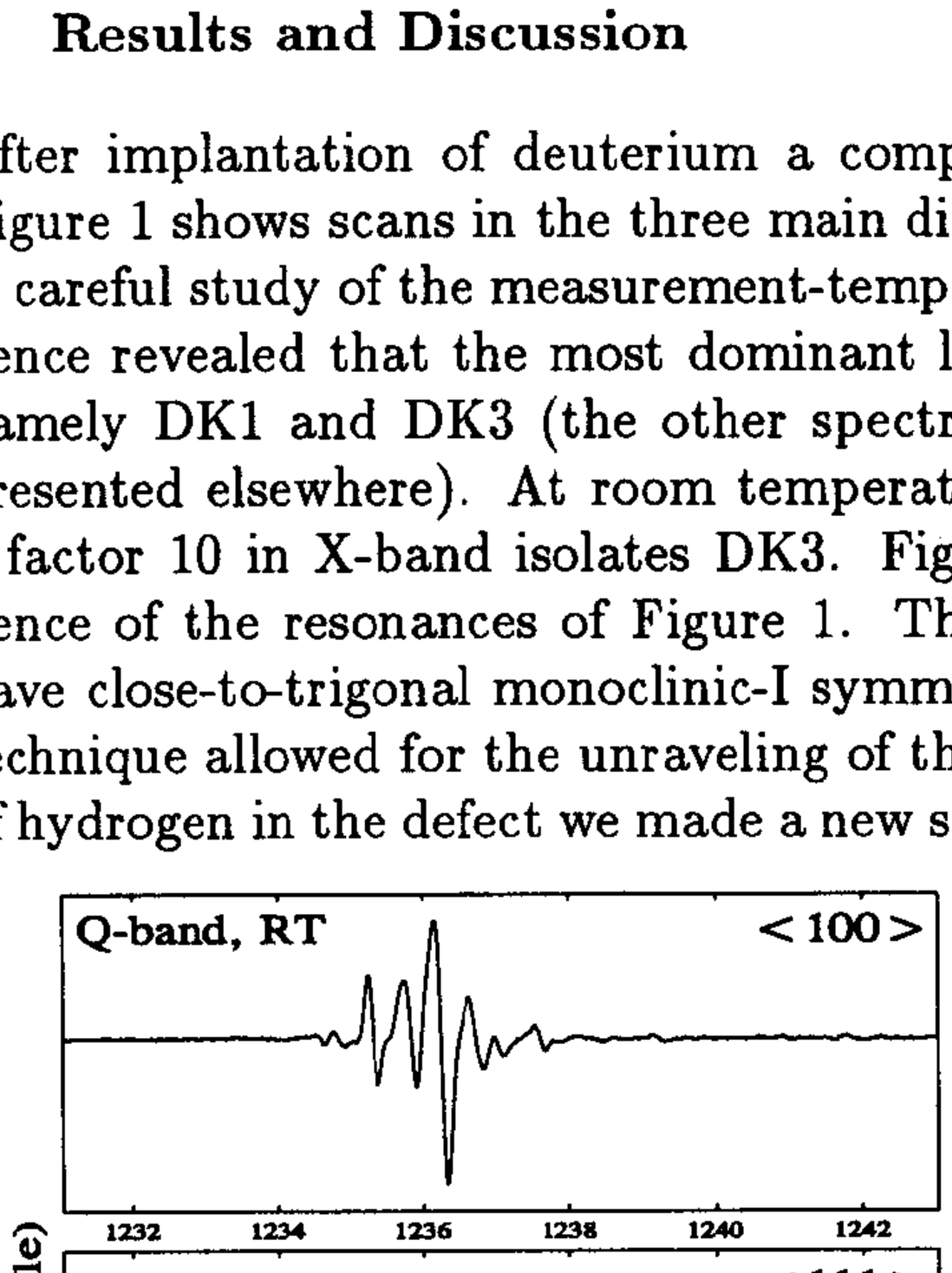

Figure 1. *Scans of Si:D with the field at the three main directions as acquired on the Q-band spectrometer at room temperature. The dominant lines belong to DK1 and DK3.*

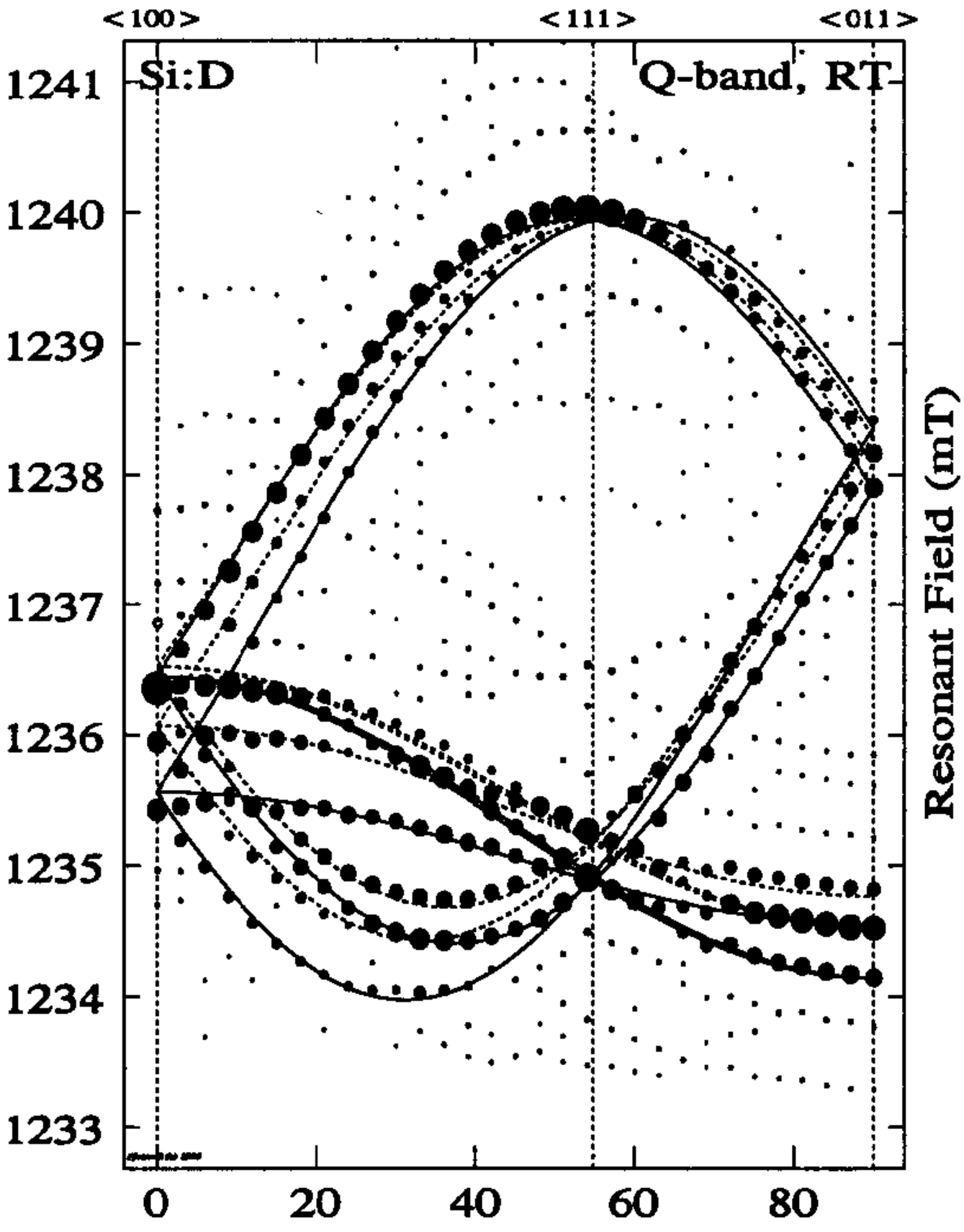

Figure 2. *Angular dependence of the resonances of Figure 1, measured at room temperature and at Q-band. A monoclinic-I g-tensor is fitted to the datapoints and the result is shown for DK1 (solid lines) and DK3 (dashed lines). The size of a dot is relative to the intensity of the resonance (unassigned points are scaled down a factor 2 for clarity). The typical linewidth is 0.07 mT (0.044 for X-band).*

similar conditions only with hydrogen instead of deuterium as implantation species. Figure 3 shows that such a switch incurred an extra two-fold splitting of the lines belonging to DK1. This clearly establishes the involvement of a single hydrogen atom in the defect. Although the splitting is rather small (corresponding in an LCAO analysis to a density of 0.2% of an s-electron on the hydrogen atom) the hydrogen is expected to be inside the very core of the defect. Small densities are expected and are common for bond-off hydrogen [3]. The g-values (derived by fitting a spin Hamiltonian to the datapoints of Fig. 2) are typical for unpaired electron(s) on a dangling bond or parallel broken bonds [4]. Also, the high electron density on a single silicon atom (determined from the ^{29}Si-HF lines) are normal for vacancy-type defects. Together with the (close) presence of a hydrogen atom this leads to a model of VH as the underlying defect structure for DK1. For DK3 no H-HF was resolved. Still, we cannot exclude the possibility of any (more distant) hydrogen present in the defect. The fact that DK3 has nearly the same parameters as DK1 hints at a similar underlying defect structure. And, because it still has to be paramagnetic a hydrogen or equivalent atom needs to be present.

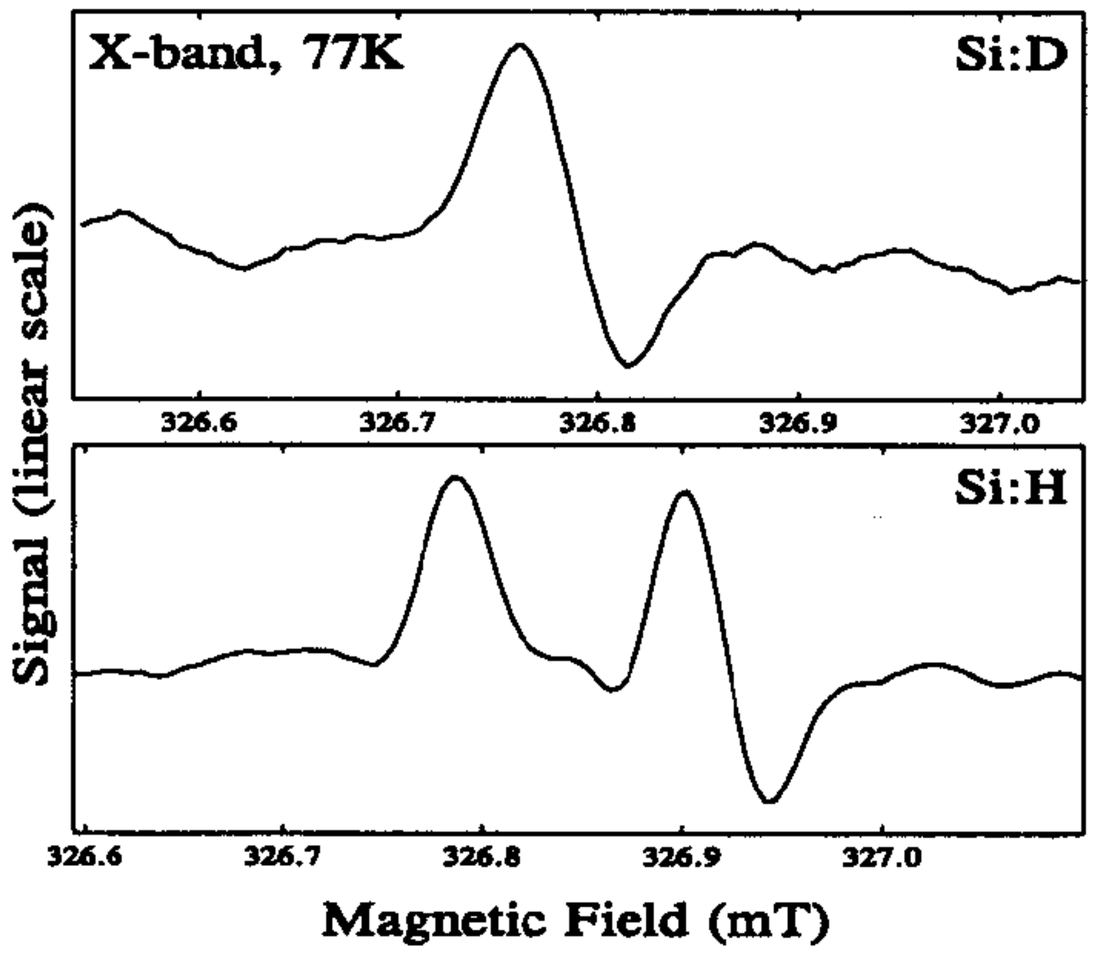

Figure 3. *Scans of Si:D (top) and Si:H (bottom) taken at the <111> field direction in X-band at 77K. This proves the involvement of hydrogen (deuterium) in the defect for DK1. The unresolved triplet splitting for deuterium (I=1, g_N=0.86) is changed into a resolved doublet splitting for hydrogen (I=1/2, g_N=5.6).*

Finally, we want to point out that these two spectra combine into the well-known S1[5,6] (formerly B2) and NL52[7] spectra, although we never observed any of the anomalous hyperfine-line-intensity effects of NL52[7]. This was probably due to the fact that we cannot go low enough in temperature to observe such effects.

As shown above, with enhanced EPR techniques we were able to decompose it into two different spectra and determine the true (monoclinic-I) symmetry and the small hydrogen hyperfine interaction for one of them. On basis of this, we were able to supply a microscopic picture of the defect, thus resolving a puzzle concerning this omnipresent defect in hydrogen-implanted silicon.

This work was sponsored by ACAP (Aarhus Center for Advanced Physics).

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