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Individual Thermal Donor Species Studied with High-Field Magnetic Resonance

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Thermal donors generated in p-type boron-doped Czochralski-grown silicon by a 450 °C heat treatment have been studied by high-field magnetic resonance spectroscopy. The experiments were conducted at a microwave frequency of 140 GHz and in a magnetic field of approximately 5 T. The symmetry of the g-tensor of four individually resolved Si-NL8 species was determined. It turned out that only one of the early species shows a true orthorhombic symmetry. Upon prolonged heat treatment times the relative concentration of the most anisotropic (early) species showed a clear decrease, while that of the later species increased.

Introduction. When oxygen-rich silicon is subjected to a heat treatment at temperatures around 450 °C a family of very similar, yet distinct, shallow double donors is formed. These so called thermal donors (TDs) constitute a long-standing puzzle in the materials science of silicon because at this moment, some 40 years after their discovery, still no microscopic model accounting for their structure and all available experimental data is firmly established. The shallow electrical character and wide-spread abundance make TDs relevant for device development, performance and stability. Among the numerous methods that have been applied in the research of TDs infrared absorption and magnetic resonance showed to be among the most informative. Infrared absorption spectroscopy was the first to reveal the major problem which hinders the progress in the structure determination of these defects, the multispecies character. Upon prolonged heat treatment a series of thermal donors develops with each species having its own generation and decay kinetics. In a recent absorption study 16 different species were reported [1]. In electron paramagnetic resonance (EPR) two spectra were assigned to thermal donors [2, 3]: Si-NL8 and Si-NL10. The Si-NL8 spectrum has been identified as a singly ionized charge state TD^+. EPR showed the overall symmetry of TD centers to be orthorhombic I (C_{2v}) although ENDOR and FSE experiments on the Si-NL10 center [4] showed for several species a small monoclinic distortion. The multispecies character of TDs has manifested itself in EPR research by shifting of the g-tensor values with increasing heat treatment time.

Experience shows that the g-tensor, which describes the Zeeman interaction between spin S of the center and the magnetic field, in practice identifies the defect and forms its unique fingerprint. The multispecies character should then be observed as a series of similar EPR spectra. In practice the g-tensors are very similar and in conventional EPR only broadened superimposed lines are detected. In our previous study we have shown that by application of high frequency (140 GHz) four individual thermal donor species could be resolved [5]. In this paper the complete angular dependence of Si-NL8 in a 24 h treated sample measured with high-field EPR is presented. Based on these measurements the symmetry of the four species is postulated. Further, a comparison is made between 24 and 40 h heat-treated samples evidencing growth kinetics of individual TDs.

The experiments were performed with the high-frequency D-band spectrometer operating at 140 GHz, which is described into more detail in [5]. Measurements were performed at 2 to 3 K (cooled in darkness) while tuned to dispersion. Samples were cut from 1.3 Ω cm Cz-Si:B (Wacker Chemitronic) having 1.3×10^{18} cm^{-3} oxygen concentration. After an initial oxygen dispersing annealing at 1250 °C for 1 h one sample was heat treated for 24 h at 450 °C while the other was treated for 40 h. The samples were mounted as to rotate in the magnetic field around a ⟨011⟩ crystallographic direction.

Experimental Results. As already mentioned, high-field EPR is capable of resolving individual TD species. The complete angular dependence pattern of Si-NL8 taken at 140 GHz is presented in Fig. 1. The asterisks denote experimental points while the solid line represents a simulation based on the orthorhombic g-tensor values for Si-NL8$_2$ as reported in [5].

The superimposed TD spectrum as observed in EPR at standard frequencies (up to 35 GHz) exhibits the orthorhombic I symmetry although, for the Si-NL10 spectrum, ENDOR and FSE (Field Scanned ENDOR) revealed the existence of monoclinic components.

By its enhanced resolution, high-field EPR is expected to be more capable of determining the symmetry of individual Si-NL8 species. However, from the pattern in Fig. 1 the symmetry of the individual species cannot be determined unambiguously which is

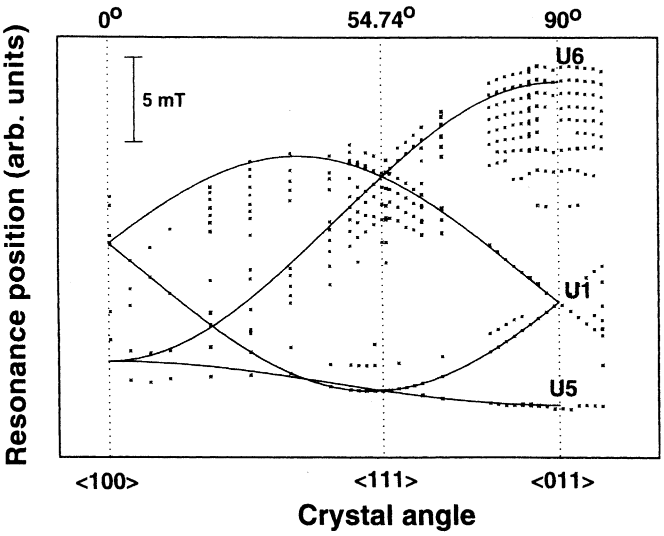

Fig. 1. Angular dependence of the Si-NL8 center measured at 140 GHz. The sample is rotated around a ⟨011⟩ axis, which is perpendicular to the magnetic field. Asterisks denote experimental points. To guide the eye a simulation using orthorhombic g-tensor values for Si-NL8$_2$ is plotted (solid line)

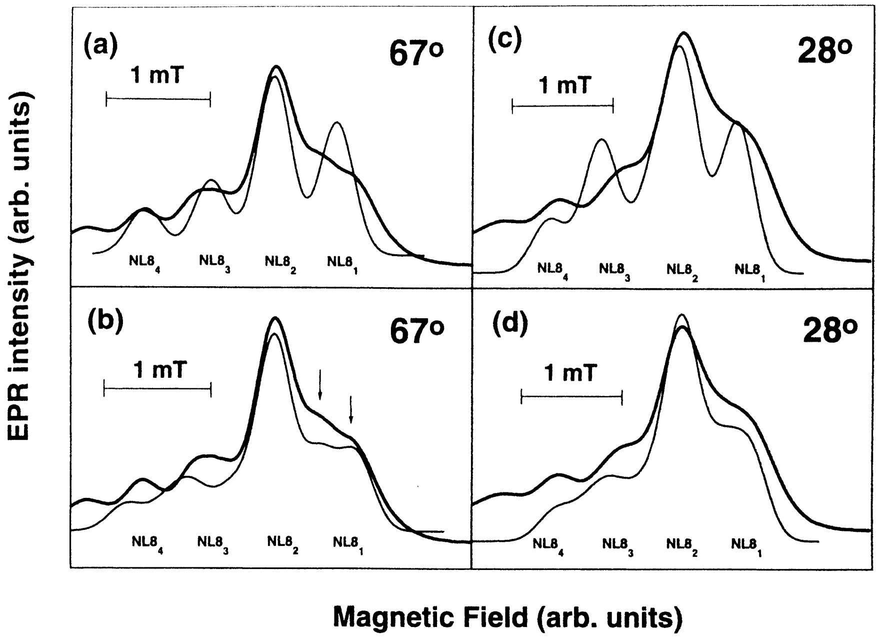

Fig. 2. Comparison between the high-field part of the measured (thick trace) and the simulated (thin trace) spectrum at 67° and 28° away from ⟨100⟩. Simulations are based on the g-tensor values reported in [5]. In the upper panels orthorhombic symmetry for all species is assumed while in the lower panels Si-NL8_1, Si-NL8_3 and Si-NL8_4 were assumed monoclinic. The arrows in b) indicate the splitting of Si-NL8_1 into two nearly resolved peaks, caused by a small monoclinic distortion of the g-tensor

caused by the relatively small spacing of the lines compared to their linewidths. This is demonstrated by the thick trace in Fig. 2b which represents the spectrum measured at 67° (with respect to ⟨100⟩). The line belonging to Si-NL8_1, which is clearly resolved at ⟨011⟩ (see Fig. 3, thick trace), has evolved into a broad shoulder consisting of two hardly distinguishable peaks which are indicated by arrows in the plot. A similar broadening and consequent decrease of peak amplitude applies to the lines belonging to Si-NL8_3 and Si-NL8_4.

As this part of the spectrum is induced by a single orientation, the line broadening can only originate from the lowering of symmetry; any possible misalignment of the sample will not result in the observed splitting of the spectrum of orthorhombic symmetry. This suggests that only Si-NL8_2 exhibits orthorhombic symmetry whereas the other species have lower symmetry. In order to clarify this issue the observed spectrum is compared to a simulation based on the orthorhombic g-tensor values which were reported previously [5] and to a simulation where a small monoclinic distortion on these g-tensors, the off-diagonal element g_{xz} is taken to be 7.5×10^{-5}, is applied. The results for the high-field part of the spectrum at 28° and 67° are shown in Fig. 2. In all panels the thick trace represents the measurement while the thin trace represents the simulated spectrum. The relative intensities of the individual components of the calculated spectrum were determined from the measured spectrum in the ⟨011⟩ direction. In the upper panels (Figs. 2a and c) the experimentally observed spectrum

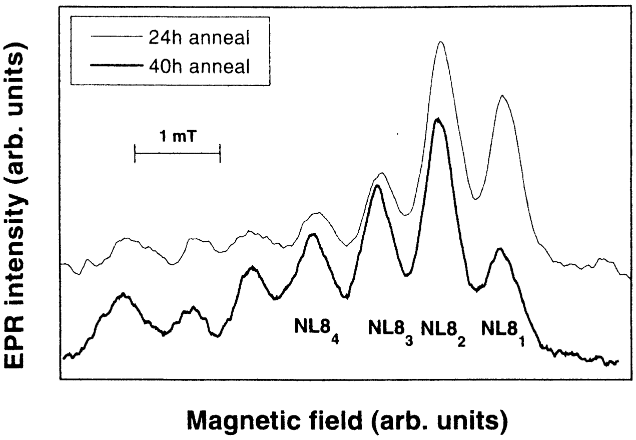

Fig. 3. Individual Si-NL8 species resolved in the U6 point for a 24 h (thin trace) and a 40 h (thick trace) heat treated sample. Both spectra are scaled to have equal intensity for the Si-NL8$_2$ species. The relative intensity of the early Si-NL8$_1$ species decreases while the later species, Si-NL8$_3$ and Si-NL8$_4$, increase for the longer annealing time

is compared to the simulation assuming four orthorhombic species while in the lower panels (Figs. 2b and d) only for Si-NL8$_2$ true orthorhombic symmetry is assumed and monoclinic symmetry for the other species. Although none of the simulations shows a perfect match, the assumption Si-NL8$_2$ being orthorhombic and the others being monoclinic gives the best agreement. Consequently, we propose that only Si-NL8$_2$ is characterized by a true orthorhombic symmetry while the other ones show monoclinic distortion.

Finally, the growth of the defect was investigated by comparing EPR spectra of samples annealed for 24 and 40 h. In Fig. 3 both spectra recorded near the ⟨011⟩ crystallographic direction are presented. Only part of the spectrum belonging to the U6 point, where individual species can be resolved, is shown. Both traces are scaled such that the line belonging to Si-NL8$_2$ has equal intensity for both the 24 h (thin trace) and the 40 h annealed sample (thick trace). It is clearly seen from the figure that the relative intensity of the most anisotropic species Si-NL8$_1$ lowers by almost a factor two for prolonged annealing. Furthermore, the more isotropic species Si-NL8$_3$ and Si-NL8$_4$ grow significantly. The depicted result represents the first direct EPR observation of the growth and decay of individual thermal donor species and conclusively explains the previously mentioned g-value shifting seen in EPR measurements of TDs. Our results confirm the idea that a series of species contribute to the EPR spectrum and that with increased heat treatment time later (less anisotropic) species are formed while the intensity of earlier species decreases causing the g-tensor of the superimposed EPR spectrum shift toward more isotropic values. At the low field side of Si-NL8$_4$ the spectrum of the 40 h sample shows additional peaks, presumably originating from other, later, species.

The observed kinetics of the TD formation is in good agreement with the result of relevant IR absorption studies [6]. These show that the TD species with the larger ionization energy are generated first and then decay as the more shallow ones, which are expected to have also a more isotropic wave function, come up.

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