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Paramagnetic resonance of a new-oxygen-donor related center in silicon

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In Czochralski-grown silicon annealed in the temperature range between 650 and 800 °C, an anisotropic electron-spin resonance (ESR) spectrum was observed. Analysis of the angular dependence reveals monoclinic (C_s) symmetry of the representative g tensor, with one of the principal axes approximately oriented along a [113]-type direction. Investigations of the ESR signals in differently heat-treated crystals show that the center is only formed after a preannealing procedure at $T \sim 600$ °C followed by subsequent annealing. The center seems to be related to a microscopically crystalline oxygen precipitation phase.

New donors (ND) in oxygen-rich silicon are commonly known to occur after heat treatment in the temperature range 550–800 °C in contrast to so-called thermal donors being created by annealing near 450 °C. In spite of great efforts with a variety of different spectroscopic techniques resulting in a large amount of experimental data, little is known about the internal structure and symmetry of these defects.[1] There seems to be agreement that ND's are associated with large SiO_x precipitates. Some authors propose that ND's are caused by interface traps at internal Si-SiO_x interfaces.[2]

Magnetic resonance is usually a successful tool in providing detailed information on the chemical identity and the electronic structure of defects, but in that particular case of oxygen donors it is impeded by the absence of any hyperfine interaction. A recent electron-spin resonance (ESR) contribution on this subject yielded information about the g tensor and therefore the symmetry of a ND.[3] The authors deduced a nearly isotropic g value of 1.9984 and inferred a site symmetry close to T_d.

In this work we report on the investigation of an anisotropic ESR signal, whose angular dependence indicates monoclinic (C_s) symmetry, i.e., its g tensor has only one mirror plane in common with the crystal. One of the principal axes of the center is approximately aligned along a [113]-type direction. In order to create the center, a preheating procedure seems to be necessary.

Similarities of this low symmetry center with NL8,[4] an ESR center recently identified as a thermal donor,[5] will be discussed. We further show how our results are linked with deep-level transient spectroscopy (DLTS) measurements on ND's and transmission-electron-microscopy (TEM) investigations of oxygen-rich silicon performed recently. The measurements were done with a commercial Bruker ESR spectrometer operating at 9.7 GHz in the temperature range 4.2–25 K on Czochralski-grown silicon.

The samples had oxygen concentrations up to $\sim 10^{18}$ cm^{-3}, and carbon contents 5×10^{15}–10^{17} cm^{-3}. A few of them were additionally phosphorus doped with 1×10^{14} cm^{-3}. They were annealed at temperatures between 600 and 1000 °C. Preannealing was performed at 590 °C for 2 h. All treatments had been made by Dr. Zulehner of Wacker Chemitronic, who kindly provided the specimens. Depending on this pretreatment, either of two ESR defects were found in crystals annealed below 800 °C. One is characterized by a nearly isotropic broad line with $g = 1.9984$, as reported earlier by Suezawa, Sumino, and Iwaizumi.[3] However, as shown in Fig. 1(b), the angular

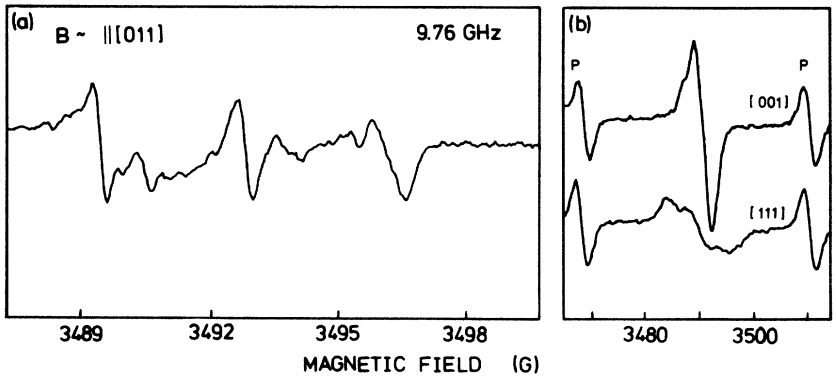

FIG. 1. ESR spectra in heat-treated Czochralski-grown silicon. Measurements were performed at 16 K and 9.7 GHz. (a) Anisotropic centers after preannealing at 590 °C for 2 h followed by annealing at 770 °C for 20 h: The three resonances occurring with strongest intensity were found to originate from the same center. (b) "Isotropic" center after 65 h at 650 °C, no preannealing: The ESR signal is identical to that reported by Suezawa *et al.* (Ref. 3). Analysis of the spectrum reveals a "breathing" behavior in the linewidth and intensity, shown here for the [001] and [111] orientations of the magnetic field.

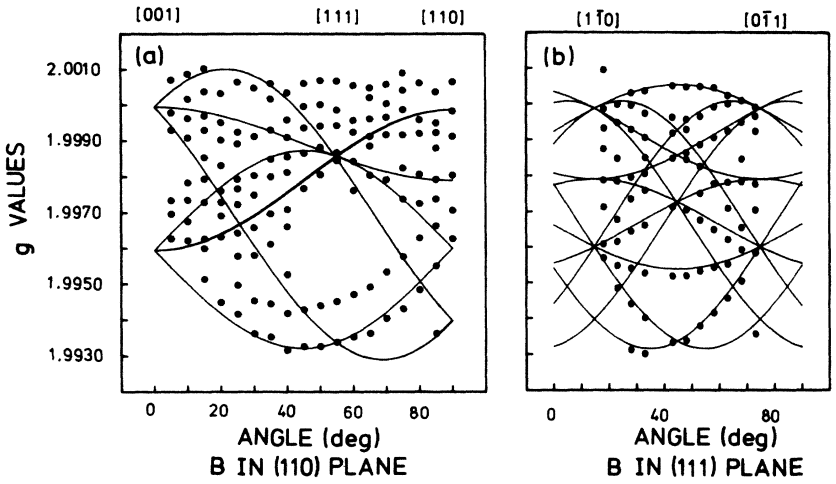

FIG. 2. (a) Angular dependence of the ESR spectrum for rotation of the magnetic field in a (110) plane. Experimental data are denoted by circles. Solid lines indicate a simulation using the parameters given in the text. (b) Angular dependence in the (111) plane of rotation. Agreement between experimental data and the lines based on the model described in the text is seen.

variation of this resonance reveals a "breathing" behavior, indicating that both the linewidth and intensity are angular dependent. The other center is described in further detail below. It was observed only in crystals which had been preannealed. Low carbon contents of the crystals tended to favor its formation. In samples heated above 800 °C the concentration of both types of centers had decreased below the detection limit.

The newly found center shows a variety of sharp ESR lines [Fig. 1(a)] characterized by a pronounced angular variation. The line positions were recorded for rotations of the magnetic field **B** in (011), (111), and (100) planes, respectively; results for the former two cases are shown in Figs. 2(a) and 2(b). Figure 3 indicates the corresponding behavior for a (100) rotation. Although the information contained in one such rotation, e.g., around [110], in principle, is sufficient to fix the parameters describing the underlying center, in the present case varying linewidths and intensities in several cases prevented the identification of expected line positions. It is not known presently what causes this unusual behavior. It is seen, however, that the line positions for all three rotations, containing redundant information, can be reproduced by the same g-tensor model.

In fitting the angular dependences it is assumed that the resonances can be described by the Hamiltonian $\mathcal{H}=\mathbf{S}\cdot\tilde{g}\cdot\mathbf{B}$, with $S=\frac{1}{2}$. Best agreement was obtained with

$$g_1=1.9929(1)\ ,$$
$$g_2=1.9979(1)\ ,$$
$$g_3=2.0010(1)\ ,$$
$$\tau=33\pm1^\circ\ .$$

The orientations of the principal axes and the definition of the fitting angle τ are given in Fig. 4. It is seen that the g tensor shares only a (110)-type miror plane with the crystal; the magnetic symmetry of the center is thus monoclinic (C_s).

Except for the orientation of axes the g tensor of the present center is quite similar to that of NL8,[4] recently identified as the predominant thermal donor in Czochralski-grown silicon.[5] Its principal values are

$$g_1=1.9932 \text{ along } [110]\ ,$$
$$g_2=1.9999 \text{ along } [\bar{1}10]\ ,$$
$$g_3=2.0009 \text{ along } [001]\ .$$

It is likely that the similarity of the g tensors reflects com-

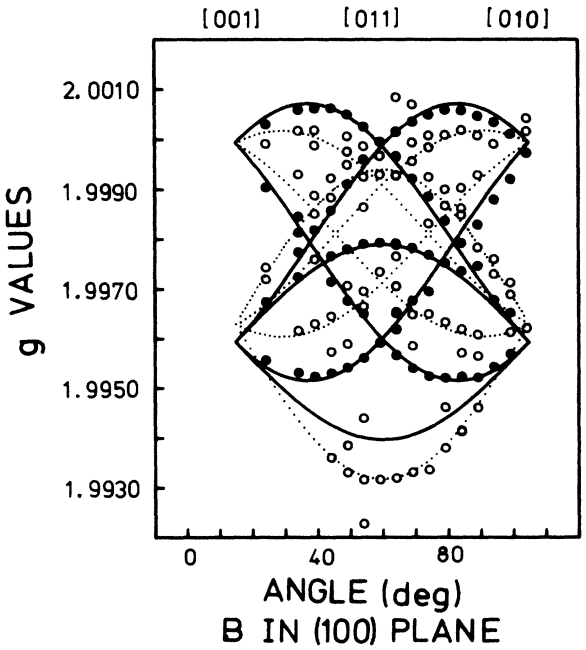

FIG. 3. Angular dependence in the (100) plane of rotation. Open circles represent weak resonances; full circles strong ones. Continuous lines indicate the simulation of the predominant strong resonances; dotted lines represent a tentative model to simulate the majority of the remaining weak resonances. (Parameters of both models are listed in the text.)

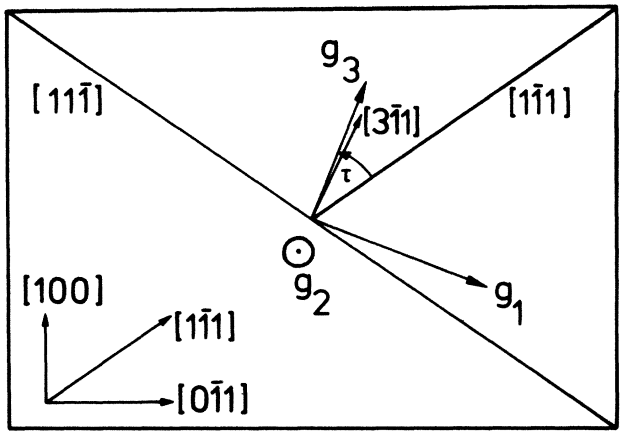

FIG. 4. Geometrical model of the g tensor showing the orientations of the principal axes. It is seen that one of the axes coincides with a [113]-type direction.

parable microscopic structures.

The features not connected by fitting lines (Fig. 2) belong to different centers: These signals have lower intensities, which, furthermore, vary from sample to sample with respect to those of the dominant ESR lines. In addition, these stronger lines, fitted by the above model, change their intensities in a different way than the rest of the resonances, when the crystals are illuminated *in situ* with near band-gap light. In Fig. 3 a tentative model is also presented (dotted lines), which fits the majority of the weaker resonances not accounted for so far. The simulation is based on the following g tensor:

$$g_1 = 1.9929(1),\ g_2 = 1.9994(1),\ g_3 = 2.0002(1)\ ,$$
$$\tau = 66 \pm 1^\circ\ .$$

The geometry is analogous to that given in Fig. 4. Again it is seen that these g-tensor components are close to those of NL8.

It was desirable to link our ESR results to the DLTS information on ND's recently obtained by Hölzlein, Pensl, and Schulz.[2] Therefore, we investigated two samples which had been characterized by such DLTS measurements. These were kindly made available to us by Dr. G. Pensl (University of Erlangen). Both samples had been cut from the same starting material (⟨111⟩ silicon; $[O_i] = 1.7\times10^{18}$ cm^{-3}; $[C_s] = 3\times10^{16}$ cm^{-3}; $[P] = 1.9\times10^{14}$ cm^{-3}) and were annealed at 650 °C for 65 h. One sample was additionally preannealed at 500 °C for 26 h. Again, in the sample not preannealed, we detected only the nearly isotropic ESR signal with $g = 1.9984$.[3] In this specimen Hölzlein *et al.*[2] had observed via DLTS a continuous trap energy distribution ranging from 0.07 to 0.3 eV below the conduction-band edge. According to their SiO_x interface model[2] these traps were assigned to so-called "interface states." The ESR signal at 1.9984 thus can be assumed to be correlated to these interface states. The additionally preannealed crystal produced no analyzable DLTS results due to a high density of states of a variety of shallow ND levels with concentration higher than the P background doping.[6] Since the angular-dependent ND centers, reported in the present paper, were observed in that preannealed sample, we tend to correlate it to such shallow traps. Hölzlein *et al.* invoke "Coulomblike" states near the Si-SiO_x interface, caused by fixed positive charges, as a model for these shallow traps, which they generally find to have rather high concentrations in the preannealed samples.

It should be emphasized that the distinct angular dependence of the present anisotropic ND center reflects a crystalline microscopic structure of the defect. Two types of oxygen precipitates are known to coexist in the annealing temperature range 600–700 °C: an amorphous phase and a crystalline silica, coesite, structure.[7,8] Because of its anisotropy, the present center can only be related to the latter type of precipitates or their precursors. Such coesite structures have been identified with high-resolution electron microscopy[7,8] to be ribbonlike defects elongated along [110] on (100) or (311) planes. The fact that one of the g-tensor principal axes is aligned nearly along a [311] direction lends further support to a connection between anisotropic center and such coesite precipitates. This is supported by the fact that the pre- and post-annealing procedures used here tend to stabilize the [311]-type structures.[8] On the other hand, it is tempting to associate the more structureless isotropic line at $g = 1.9984$ to a superposition of centers in an amorphous environment near amorphous SiO_x precipitates.

Discussions with W. Bergholz, G. Pensl, and W. Zulehner are gratefully acknowledged. We thank the latter two colleagues for kindly furnishing the specimens used in this study.

[1]For a review, see, for example, A. Bourret, in *Proceedings of the Thirteenth International Conference on Defects in Semiconductors,* edited by L. C. Kimerling and J. M. Parsey, Jr. (The Metallurgical Society of The American Institute of Mining, Metallurgical and Petroleum Engineers, New York, 1985), p. 129; see also, P. Wagner, C. Holm, E. Sirtl, R. Oeder, and W. Zulehner, in *Festkörperprobleme,* edited by P. Grosse, Advances in Solid State Physics, Vol. XXIV (Vieweg, Braunschweig, 1984), p. 191.

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[8]W. Bergholz, J. L. Hutchinson, and P. Pirouz, J. Appl. Phys. **58**, 3419 (1985); W. Bergholz, J. L. Hutchinson, and G. R. Booker, in *Semiconductor Silicon 1986,* edited by H. R. Huff, T. Abe, and B. Kolbesen (Electrochemical Society, Pennington, NJ, 1986), p. 874.