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THE NL10 THERMAL DONOR IN SILICON

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ABSTRACT

The dominant thermal donor centre formed by prolonged annealing of oxygen-rich silicon gives rise to the Si-NL10 EPR spectrum. This centre has been investigated by electron nuclear double resonance techniques. The hyperfine interactions were measured with the oxygen and aluminium impurities as well as with atoms of the host silicon lattice. In addition the quadrupole interactions with the oxygen and aluminium nuclei were determined. On the basis of the results a microscopic model of the centre can be proposed.

INTRODUCTION

Heat treatment of oxygen-rich silicon in the 300-500 °C temperature region produces shallow double donors [1]. During the past three to four decades a tremendous amount of data was gathered. Oxygen involvement in the centres was suspected almost from the start. Early microscopic models therefore ascribed the donor activity to a cluster of four oxygen nuclei [2]. Only recently conclusive evidence was given for the oxygen incorporation in thermal donors [3,4].

In the past, important information concerning thermal donors has come from magnetic resonance experiments [5]. Several EPR (electron paramagnetic resonance) spectra could be related to the formation of thermal donors. The Si-NL8 and Si-NL10 spectrum were the only ones which reached concentrations comparable to thermal donors (as determined from the room-temperature resistivity measurements). In a systematic EPR investigation [6] practically no dependence on the acceptor type could be traced. Both centres have orthorhombic-I symmetry, crystallographic pointgroup 2mm.

This paper reports on an electron nuclear double resonance (ENDOR) study performed for the Si-NL10 centre. The measurements were done on a float zone, aluminium doped silicon sample diffused with oxygen. The oxygen was enriched with the ^{17}O isotope. The much higher resolving power of ENDOR in comparison to EPR made it possible to unravel the interactions with oxygen and aluminium nuclei in the Si-NL10 core as well as with surrounding host silicon atoms.

EXPERIMENTAL

In the 17-oxygen diffused (aluminium doped) silicon sample thermal donors were generated by annealing at 470 °C for 200 hours. After 200 hours the sample was on the brink of p to n-type conversion. The EPR spectrum showed a strong Si-NL10 signal with a concentration of ~5×10^{15} cm^{-3}.

The ENDOR measurements were performed with a superheterodyne K-band spectrometer operating at 23 GHz. We used a cylindrical TE_{011} resonance cavity. In the inner side wall of the cavity a spiral groove was cut, which was acting as an RF coil. ENDOR signals were recorded as changes in the intensity of the dispersion component of the EPR signal using double phase-sensitive detection. The sample was held at 4.2 K, the ENDOR measurements were performed under white light illumination. Light from a halogen source was transmitted to the sample by a quartz rod.

EXPERIMENTAL RESULTS

A. 17-OXYGEN ENDOR

The ENDOR spectra for the ^{17}O and ^{27}Al nuclei can be described by the spin-Hamiltonian:

$$\mathcal{H} = \mu_B \vec{B}\cdot\overleftrightarrow{g}\cdot\vec{S} - g_N\mu_N\vec{B}\cdot\vec{I} + \vec{S}\cdot\overleftrightarrow{A}\cdot\vec{I} + \vec{I}\cdot\overleftrightarrow{Q}\cdot\vec{I}, \qquad (1)$$

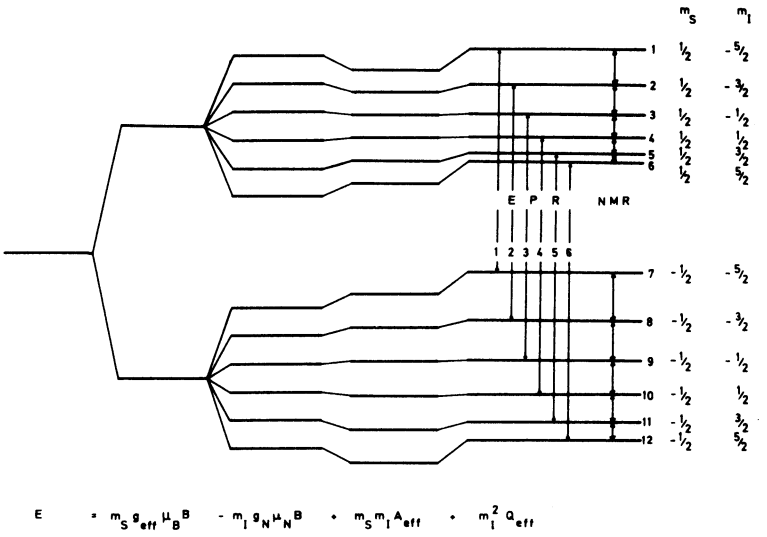

Figure 1. Schematic representation of the energy level scheme for the S=1/2 and I=5/2 system. This scheme is applicable to both ^{17}O and ^{27}Al nuclei in the centre.

where S=1/2 and I=5/2. The corresponding level diagram is shown in figure 1. In the measurement data up to eight oxygen shells could be distinguished. All of them were of the same symmetry type, mirror plane point group m. In the experiment it was possible to discriminate between the two mirrorplanes of a 2mm defect. It was found that all the oxygen atoms are lying in one plane.

The localization of the defect electron on the oxygen nuclei was low. All the oxygen interactions looked alike, as can be seen in figure 2 for the two

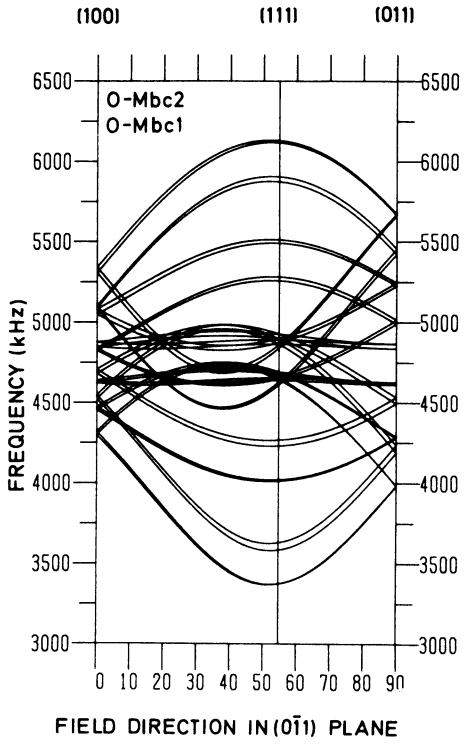

Figure 2. Computer simulation of the angular ENDOR pattern corresponding to one EPR orientation for two oxygen mirror-class tensors.

shells Mbc1 and Mbc2. This is caused by an almost identical quadrupole interaction, and an isotropic hyperfine interaction for all the oxygen shells. Analysis of this quadrupole interaction gives information about the bonding of the oxygen atoms. It is concluded that the oxygen atoms occupy their usual interstitial puckered bond-centered position.

B. 27-ALUMINIUM ENDOR

The sample used for the ENDOR experiments was doped with aluminium. Although the spectrum Si-NL10 is not solely correlated to the aluminium doped material [6], we discovered ENDOR originating from 27-aluminium nuclei. Analysis of the ENDOR spectra shows that the aluminium nucleus is on the 2-fold axis of the defect. Although not essential for the formation of the Si-NL10 defect aluminium takes when present active part in the formation. The quadrupole interaction could not give an answer to the bonding mechanism of the aluminium atom to the defect.

C. 29-SILICON ENDOR

ENDOR interactions were also measured with the host silicon atoms. (4.7% of the silicon atoms possess a nuclear spin of I=1/2). The biggest silicon hyperfine tensor observed in the experiment had an interaction of only 2.5 MHz. This is an indication of a very shallow defect character (probably more shallow than Si-NL8). The tensor had the 2mm point group symmetry type, and was <100>

axial. Other silicon tensors found in the experiment also showed an approximate <100> axiality. If the biggest hyperfine interaction originates from an atom on the twofold axis this means that none of the two mirror planes is symmetry forbidden. The ground state of the Si-NL10 defect centre therefore has A_1-symmetry, just like the ground states of the TD^+ and the TD^0 [7]. Wave functions of the other allowed types A_2, B_1, and B_2 are zero on one or two of the mirror planes by symmetry.

D. FIELD-STEPPED ENDOR

Field-stepped ENDOR experiments showed that the Si-NL10 spectrum is a composition of several similar spectra. This is illustrated in figure 3 for the

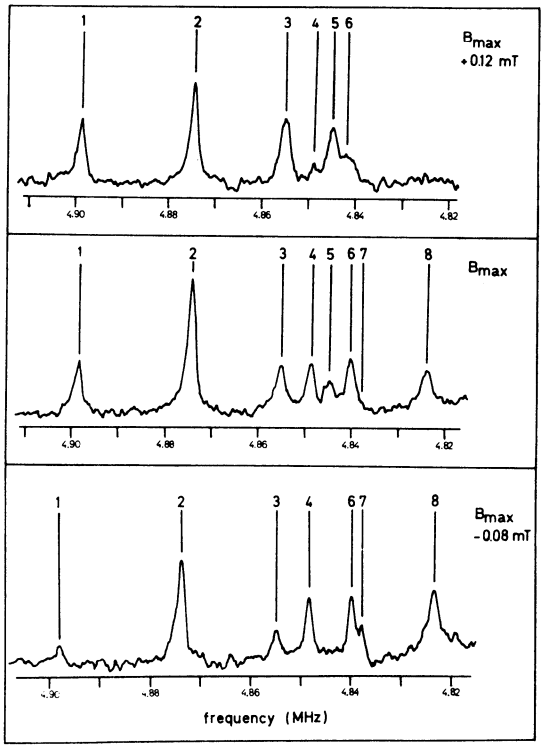

Figure 3. The illustration of the field-stepped ENDOR effect for eight oxygen tensors. The magnetic field is in the [011] direction and B_{max} corresponds to the magnetic field position in the centre of the EPR line.

oxygen field-stepped ENDOR; oxygen ENDOR arising from the transition 3↔4 yields maximum intensity of the ENDOR line for different magnetic fields. It is concluded that prolonged annealing gives a varying concentration of different species of very similar centres, which then results in a semi-continuous g-shifting process [6].

The field-stepped ENDOR technique allowed to correlate the oxygen and the aluminium ENDOR shells. It was concluded that the smallest species of the NL10 centre consists of two oxygen and one aluminium atom. The centre grows by addition of oxygen atoms along the $[0\bar{1}1]$ direction one at a time, thereby lowering its symmetry to m.

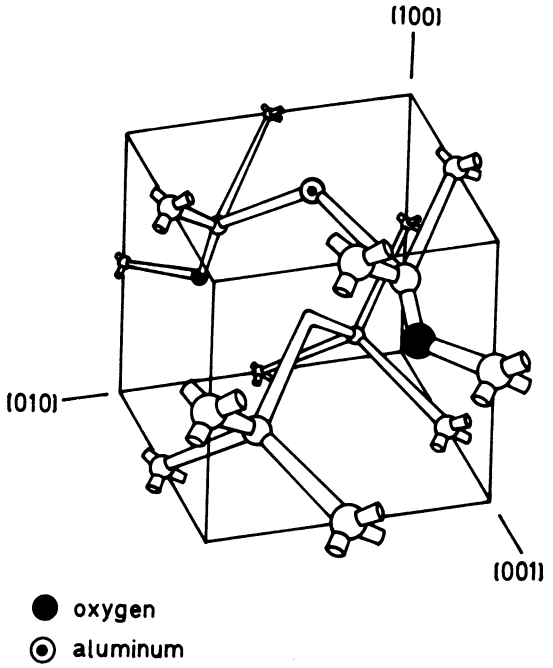

Figure 4. Structural model for the Si-NL10 centre.

A structural model as depicted in figure 4 is proposed. On the basis of the measurements no conclusion could be reached about the position of the aluminium on the twofold axis, and about its possible bonding to the lattice.

ACKNOWLEDGMENT

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