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OXYGEN ENDOR OF THERMAL DONORS IN SILICON

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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 on samples that had been enriched to 46% in the ^{17}O magnetic isotope. Measurements of the nuclear g-value on several of the double resonance lines unambiguously revealed hyperfine interactions with this oxygen isotope. This provides for the first time conclusive evidence for the incorporation of oxygen in a thermal donor.

1. INTRODUCTION

Heat-treatment (ht) of oxygen-rich silicon in the 450 °C temperature region produces shallow double donor states. The defects giving rise to these states are termed thermal donors (TD's). Over the past 30 years an intensive research has been carried out to reveal the mechanisms of this donor formation and the detailed atomic and electronic structure of TD's. Several atomic models have been developed starting with the original one by Kaiser, Frisch and Reiss (KFR model) who proposed a cluster of four oxygens to constitute the TD [1]. In the following years numerous more advanced models were proposed in order to account for the gradually growing evidence [2].

Although practically consensus has been reached as to oxygen incorporation in the structure of TD's (with the noteable exception of a recent letter by Newman [3]), the evidence sustaining this notion is only circumstantial. Oxygen involvement in TD's is assumed on the basis of the experimental observations that: (1) TD's can be created only in oxygen-rich silicon, (2) the kinetics can be described by power dependences on the interstitial oxygen concentration and (3) the formation of TD's is accompanied by a decrease of interstitial oxygen concentration.

In the past magnetic resonance studies have contributed significantly to the characterization of TD's. Several EPR (Electron Paramagnetic Resonance) spectra related to the ht centres were reported [4,5]. These could be correlated to TD's on the basis of the production conditions. Following the EPR results

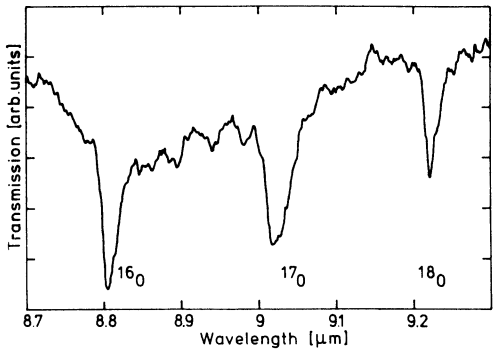

Figure 1. Infrared transmission spectrum at 9 μm of the sample used in the experiment (T = 4.2 K).

orthorhombic-I symmetry, crystallographic pointgroup 2mm, has been postulated for TD's. The present paper reports a continuation of these studies. The aim of the project was to give direct evidence of oxygen incorporation in the structure of TD's. In view of the fact that earlier EPR studies [6] failed to reveal any hyperfine structure in the observed spectra of ht centres (in spite of a high concentration of the ^{17}O magnetic isotope) it was necessary to apply the much higher resolving power of Electron Nuclear DOuble Resonance (ENDOR).

2. EXPERIMENT

In the experiment high-grade, low carbon concentration, float-zone silicon was used. Selected samples were doped with oxygen in a carefully controlled, ultra-clean diffusion process. Oxygen was diffused from gas enriched with ^{17}O isotope for 10 days at a temperature of 1380 °C using an infrared elliptical mirror oven. Details of this process may be found in [6]. Results of the oxygen diffusion were verified by measuring the oxygen-related optical absorption in the infrared near 9μm. A transmission spectrum at 4.2 K of the sample used in further ENDOR studies is shown in figure 1. The total oxygen concentration of the sample calculated from the infrared absorption with the 1980 ASTM calibration standard was 7×10^{17} cm^{-3}, the isotope composition being: ^{16}O : 39%, ^{17}O : 46%, ^{18}O : 15%.

To generate TD's the samples were subjected to ht at 470 °C for times up to 1000 hrs. The formation of ht centres was monitored by EPR and compared with the formation of TD's as measured by resistivity changes under the assumption that each TD supplies one electron to the conduction band. The results for samples with boron and aluminium doping are shown in figure 2. Similar data for crucible-grown material, standard for TD studies, are also presented. As can be seen, in particular for longer ht times, spectrum Si-NL10 represents the dominant form of TD. The ENDOR experiment was conducted in a K-band spectrometer tuned to dispersion, at an incident microwave power of 2 μW, with the sample at 4.2 K temperature.

3. RESULTS

Numerous ENDOR resonance lines were observed for the NL10 EPR spectrum. Figure 3 presents a typical ENDOR spectrum as observed for one of the orientations of NL10. For the conditions of the experiment - microwave frequency $\nu \simeq 23$ GHz, electronic g-value $g_e \simeq 2$, resonance magnetic field B ≃ 820 mT - the

nuclear Zeeman frequency $f_z = g_N\mu_N/h$ of the ^{17}O nucleus, for which $g_N = 5.772$ MHz/T, is near 4.75 MHz. A resonance spectrum roughly symmetrical around this frequency suggests the presence of oxygen hyperfine interaction. To analyse the spectrum in a more conclusive manner the following spin Hamiltonian is probably adequate:

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

where a quadrupole interaction is included in view of the high nuclear spin $I = 5/2$ of the ^{17}O oxygen isotope. To first order the energy eigenvalues of the Hamiltonian are given by:

$$E_{|m_S,m_I\rangle} = g_e\mu_B B m_S - g_N\mu_N B m_I + A_{eff} m_S m_I + Q_{eff} m_I^2. \quad (2)$$

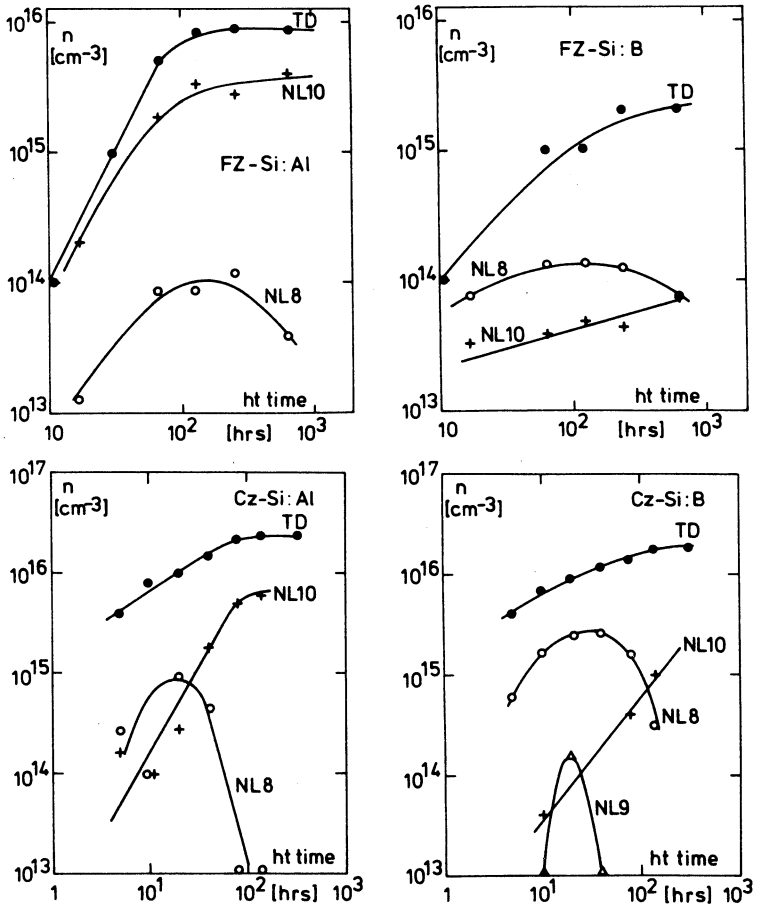

Figure 2. Concentrations of centres giving rise to Si-NL8 (o), Si-NL9 (Δ) and Si-NL10 (+) spectra and thermal donor concentration (•) versus annealing time ($T_{ann} = 470$ °C) for float-zone, oxygen-doped and Czochralski silicon doped with boron and aluminium.

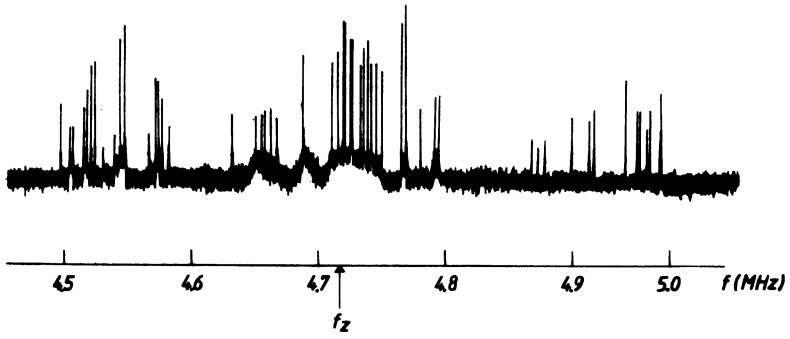

Figure 3. Typical ENDOR scan for one of the orientations of the Si-NL10 EPR spectrum.

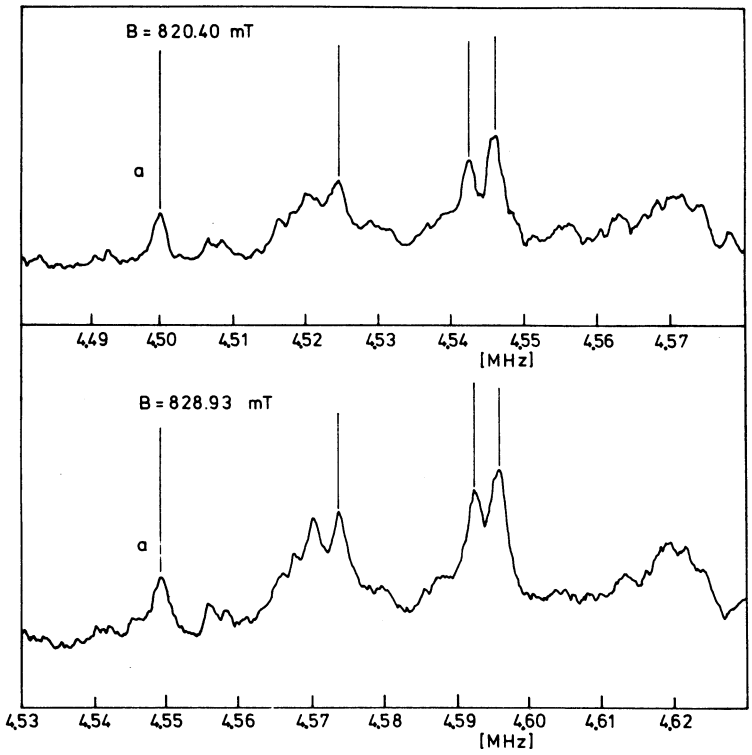

Figure 4. Part of the ENDOR spectrum for frequencies close to the nuclear Zeeman frequency of the ^{17}O nucleus measured for two values of the magnetic field B.

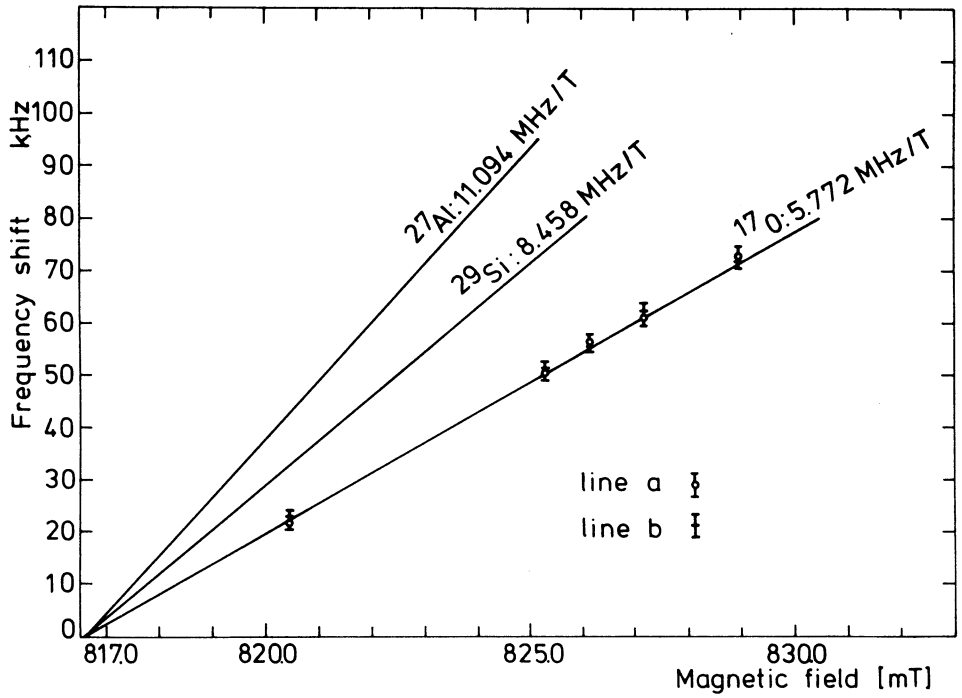

Figure 5. The frequency shift of the ENDOR lines a and b as a function of magnetic field B. Solid lines are plotted with slopes determined by nuclear g-values corresponding to ^{17}O, ^{27}Al and ^{29}Si nuclei.

ENDOR transitions between the states $|m_S,m_I\rangle$ and $|m_S,m_{I-1}\rangle$ will be found at frequencies f given by:

$$hf = g_N\mu_N B - A_{eff}m_S - Q_{eff}(2m_I-1). \quad (3)$$

If the ENDOR resonances are measured for several magnetic fields B_n their positions f_n will shift as given by the following expression:

$$f_n - f_o = \frac{g_N\mu_N}{h} \cdot (B_n - B_o), \quad (4)$$

where f_n, B_n are the results of the n-th measurement with respect to a reference measurement at magnetic field B_o yielding a resonance at f_o. The shift of frequencies f with magnetic field B is proportional to g_N. The application of this principle for the determination of g_N is illustrated in figure 4. The same ENDOR spectrum was measured for two values of the magnetic field differing by approximately 8 mT. As a result a shift of ENDOR frequencies by about 50 kHz is observed (note that the ENDOR linewidth is of the order of a few kHz only). As can be seen an identical shift is found for the several lines composing the spectrum. Complete data on the magnetic field dependence for two arbitrarily chosen resonance lines a and b is represented in figure 5. The slope of the straight line gives $g_N\mu_N/h$ = 5.77 MHz/T, thus uniquely identifying the nucleus involved as ^{17}O. Other candidates for hyperfine interactions have their g_N

values well outside experimental error margins, which can also be clearly concluded from figure 5. The presence of oxygen in TD's associated with the Si-NL10 EPR spectrum is therefore conclusively established by direct experimental evidence [7].

In a similar way as described above some of the ENDOR resonance lines observed for other frequency ranges were identified as arising from hyperfine interactions with ^{29}Si and (tentatively) ^{27}Al nuclei.

Full angular dependent patterns, to determine the site symmetry of the oxygen atom(s), have not yet been measured, the experiments being currently underway. Tentatively, a pattern with mirrorplane class symmetry has been found, implying that the TD associated with Si-NL10 contains at least two oxygen atoms on one of the mirrorplanes of the defect.

ACKNOWLEDGEMENTS

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