Oxygen Incorporation in Thermal-Donor Centers in Silicon

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The paper presents for the first time microscopic evidence for the presence of oxygen in thermal-donor centers in silicon. The evidence as obtained by electron nuclear double resonance on the magnetic isotope ¹⁷O is conclusive.

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Upon heat treatment at temperatures close to 450 °C shallow donor states are formed in oxygen-rich silicon.¹ The defects giving rise to those states are generally termed thermal-donor centers and have been thoroughly studied over the past thirty years. As a result of this research effort, a lot of experimental data have been gathered. However, these are not well correlated and frequently contradicting.² Nevertheless, it is generally accepted that centers of donor character are formed as a result of oxygen clustering during annealing at 450 °C. No consensus has been reached on the structure of those centers, although many models have been developed. The models range from the first simple one of Kaiser. Frisch, and Riess,¹ who proposed a cluster of four oxygens to constitute the thermal donor, to the most recent model of Ourmazd, Schröter, and Bourret.³ The latter model, based on kinetics derived from infrared-absorption measurements,⁴ postulates several similar donor species incorporating a silicon interstitial and a varying number of oxygen atoms.

Although practically all the existing models assumed direct oxygen incorporation in the structure of these defects (with the notable exception of a recent paper by Newman⁵), the evidence sustaining this notion is only circumstantial. The following experimental results are indicative for oxygen involvement in thermal-donor centers: (1) They 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 thermal-donor centers is accompanied by a decrease of interstitial oxygen concentration.

The most important structural information on heattreatment donor centers gathered thus far has been obtained by Muller *et al.*,⁶ who discovered a number of EPR-active centers in heat-treated oxygen-rich silicon. These were predominantly of 2mm point-group symmetry and could be correlated with thermal-donor centers (as found from the conductivity measurements) on the basis of the production conditions. One of these centers, Si-NL8, has recently been identified by Lee, Trombetta, and Watkins⁷ as a thermal donor, although their results appear remarkably consistent with just one of nine shallow double-donor states TD1-TD9 observed for thermal donors in infrared absorption.⁸ The role of acceptors in the formation of those centers has recently been studied⁹ and it was found that the same centers were formed irrespective of the acceptor doping. A particularly striking result of these studies was the enhanced formation of the Si-NL10-family spectrum accompanied by a similar enhancement in formation of donor centers (as measured by conductivity changes) for oxygen-doped float-zone (FZ) Si:Al material. The concentrations reached could be correlated with the Si-NL10 spectrum for all the samples studied as shown in Fig. 1. From these results it was concluded that Si-NL10 constituted the predominant thermal-donor center in the final stage of the heat treatment. In the comparison of the concentrations derived from resistivity and magnetic resonance, it should



FIG. 1. Concentrations of centers giving rise to Si-NL8 (open circles), Si-NL9 (triangles), and Si-NL10 (plusses) spectra and thermal-donor concentration (filled circles) vs annealing time ($T_{ann} = 470$ °C) for FZ oxygen-doped silicon and Czochralski silicon doped with boron and aluminum.

be realized that EPR intensities do not allow an accurate determination of the concentration of the paramagnetic species. Relative values, such as the variation with heat-treatment time, are more reliable than absolute numbers.

By now it is well established that the Si-NL8 EPR spectrum corresponds to one⁷ or several⁸ thermal-donor centers. Our conclusion that also Si-NL10 is related to thermal-donor centers⁹ is based on the following experimental evidence: (1) NL10 centers are produced by thermal annealing of oxygen-rich silicon at T = 450 °C: (2) both the concentration and the production kinetics of NL10 centers correlate well with the observed changes of the electrical conductivity; (3) symmetry of the NL10 centers is orthorhombic I, point group 2mm, identical to that of NL8 and to the symmetry found for thermaldonor states TD1-TD9 from ir absorption under stress¹⁰; (4) g factors of NL10 are typical for shallow donors¹¹ in the classification of Lee and Corbett¹²; (5) similarly to NL8, NL10 also constitutes a family of defects with time-dependent g factors.

The EPR studies could not establish the presence of oxygen in centers related either to spectrum Si-NL8 or Si-NL10, in spite of the high concentration (46%) of the magnetic isotope ¹⁷O $(I = \frac{5}{2})$ present in the samples.

The absence of any hyperfine structure in the EPR spectra can lead to two alternative conclusions: (1) There is no oxygen in the studied thermal-donor centers, or (2) oxygen is incorporated in those centers, but the hyperfine interaction of the unpaired spin density with the ¹⁷O nucleus is small, because of substantial spin delocalization or for symmetry reasons. It is also possible that the hyperfine structure is not observed because of severe line broadening caused by strongly varying hyperfine interactions.

In view of the above, it was necessary to apply the much higher resolving power of electron nuclear double resonance (ENDOR). On the basis of previously gained EPR experience, an aluminum-doped sample was selected for these measurements. The sample, originally lowcarbon-content FZ silicon, was diffused with oxygen enriched in the magnetic isotope ¹⁷O in a commercial ir elliptical-mirror oven.⁹ The infrared transmission spectrum at 9 μ m for the sample cooled to 4.2 K is depicted in Fig. 2. The total oxygen concentration of the sample calculated from the infrared absorption with the 1980 American Society for Testing and Materials calibration standard was 7×10^{17} atoms cm⁻³ in the following isotope ratio:

 $^{16}\text{O}:$ $^{17}\text{O}:$ $^{18}\text{O} = 0.39:0.46:0.15.$

The sample then received prolonged (200 h) heat treatment at 470 °C in ambient argon-gas atmosphere. As a result, an intense Si-NL10-family spectrum was produced in the sample. An EPR measurement, as shown in Fig. 3, revealed that this was the only spectrum present.

The ENDOR experiment was conducted in a K-band spectrometer with the sample at a 4.2-K temperature and revealed numerous resonance lines. They have been unambiguously established as associated with the Si-NL10 spectrum by the use of the "ENDOR-induced EPR"¹³ (also known as the "field-stepped ENDOR") technique. The majority of the ENDOR resonances was found to be grouped into two regions roughly symmetrical around v=4.75 MHz, which is the nuclear Zeeman frequency of the ¹⁷O nucleus for the magnetic field values close to 0.8 T employed in the K band. Since the ENDOR lines found thus far were located in the narrow range from 4.5 to 5.0 MHz, it is to be expected that the hyperfine structure is not resolved in EPR as was discussed in Refs. 6 and 9.

In view of the clean diffusion technique used and concentration of the Si-NL10 spectrum reached, the likely candidates for the observation in ENDOR include the



FIG. 2. Infrared transmission spectrum in the 9- μ m band of the sample used in the experiment. T = 4.2 K.



FIG. 3. EPR spectrum of the sample used for the ENDOR study.

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FIG. 4. Part of the ENDOR spectrum including line labeled a for frequencies below the nuclear Zeeman frequency of the ¹⁷O nucleus measured for two values of the magnetic field *B*.

following magnetic nuclei:

²⁹Si, $g_N = -1.10954$, $I = \frac{1}{2}$, abundance 4.7%; ²⁷Al, $g_N = 1.4554$, $I = \frac{5}{2}$, abundance 100%; ¹⁷O, $g_N = -0.7572$, $I = \frac{5}{2}$, abundance 46%; ¹³C, $g_N = 0.3511$, $I = \frac{1}{2}$, abundance 1.1%. The magnetic system can be described by the following spin Hamiltonian:

$$\mathcal{H} = \mu_{\mathbf{B}} \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} - g_{N} \mu_{N} \mathbf{B} \cdot \mathbf{I} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} + \mathbf{I} \cdot \mathbf{Q} \cdot \mathbf{I}.$$

The first-order solution to this spin Hamiltonian is

$$E_{|m_s,m_l\rangle} = g\mu_B Bm_S - g_N \mu_N Bm_l + A_{\text{eff}} m_S m_l + Q_{\text{eff}} m_l^2,$$

with $m_S = \pm \frac{1}{2}$ and $m_I = \pm \frac{1}{2}$ for $I = \frac{1}{2}$ nuclei and $m_I = \pm \frac{1}{2}, \pm \frac{3}{2}, \pm \frac{5}{2}$ for $I = \frac{5}{2}$ nuclei.

The ENDOR transitions are defined by $\Delta m_S = 0$ and $\Delta m_I = \pm 1$, therefore yielding the following expressions for the ENDOR frequencies: For $I = \frac{1}{2}$,

$$hv = \Delta E = |g_N \mu_N B \pm 1/2A_{\text{eff}}|;$$

for
$$I = \frac{5}{2}$$
.

$$hv = \Delta E = |g_N \mu_N B \pm 1/2A_{\text{eff}}|,$$

$$hv = \Delta E = |g_N \mu_N B \pm 1/2A_{\text{eff}} \pm 2Q_{\text{eff}}|,$$

$$hv = \Delta E = |g_N \mu_N B \pm 1/2A_{\text{eff}} \pm 4Q_{\text{eff}}|.$$

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

$$v_n - v_0 = (g_N \mu_N / h) (B_n - B_0),$$

where v_n and B_n are the results of the *n*th measurement compared with a reference measurement at magnetic field B_0 yielding a resonance at v_0 . Thus a linear dependence of $v_n - v_0$ on $B_n - B_0$ results for which the slope is determined by g_N , the nuclear g value of the nucleus involved. Experimentally this shift with magnetic field B could be accomplished by insertion of a quartz rod into



FIG. 5. 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.

the microwave cavity, shifting its resonance frequency. The Si-NL10 resonances are then observed at magnetic fields that are shifted up to 1.5%.

Figure 4 presents one group of the observed ENDOR lines as measured for two different values of magnetic field, $B_1 = 828.93$ mT and $B_2 = 820.40$ mT. It can be seen that the spectrum is clearly reproduced, being shifted by approximately 50 kHz. This therefore allows an unambiguous chemical identification of any arbitrarily chosen single resonance line in the ENDOR spectra obtained for different magnetic field values, through the determination of the nuclear g value g_N . In Fig. 5 we have collected the shifts of the resonance frequencies as a function of the magnetic field of resonance line a, taken from the lower-frequency part of the ENDOR spectra (shown in Fig. 4), and similarly of a line b belonging to the group of ENDOR lines above the nuclear Zeeman frequency. As evidenced by Fig. 5, the experimental data for those two resonances clearly fall on the line characteristic for the ¹⁷O nucleus. The presence of oxygen in thermal donors is therefore conclusively confirmed.

In the similar way as the one described above, some of the ENDOR resonances observed for higher frequencies were identified as arising from the interaction with ²⁷Al and ²⁹Si nuclei. However, especially for aluminum, this identification is more tentative because of increased linewidth (about 5 times bigger than for oxygen) as well as a worse signal-to-noise ratio and requires further confirmation by revealing the full angular dependence of hyperfine interactions.

Further experiments, currently under way, will finally unravel the structure of the thermal donors by establishing the symmetry of the hyperfine interactions with oxygen and other nuclei involved in the center.

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¹W. Kaiser, H. L. Frisch, and H. Reiss, Phys. Rev. 112, 1546 (1958).

²A. Bourret, in *Proceedings of the Thirteenth International* Conference on Defects in Semiconductors, Coronado, California, 1984, edited by L. C. Kimerling and J. M. Parsey, Jr. (The Metallurgical Society of the AIME, Warrendale, Pennsylvania, 1985), p. 129.

³A. Ourmazd, W. Schröter, and A. Bourret, J. Appl. Phys. 56, 1670 (1984).

⁴R. Öder and P. Wagner, in *Defects in Semiconductors II*, edited by S. Mahajan and J. W. Corbett (North-Holland, New York, 1983), p. 171.

⁵R. C. Newman, J. Phys. C 18, L967 (1985).

⁶S. H. Muller, M. Sprenger, E. G. Sieverts, and C. A. J. Ammerlaan, Solid State Commun. **25**, 987 (1978).

⁷Keon M. Lee, J. M. Trombetta, and G. D. Watkins, *Microscopic Identification of Electronic Defects in Semiconductors*, edited by N. M. Johnson, S. G. Bishop, and G. D. Watkins, MRS Symposium Proceedings **46** (Materials Research Society, Pittsburgh, Pennsylvania, 1985), p. 263.

⁸Recently J. Michel *et al.*, Phys. Rev. Lett. **57**, 611 (1986), correlated up to five thermal-donor species, all being part of the same NL8 EPR spectrum, to TD1-TD9 states observed in ir absorption.

⁹T. Gregorkiewicz, D. A. van Wezep, H. H. P. Th. Bekman, and C. A. J. Ammerlaan, Phys. Rev. B **35**, 3810 (1987).

¹⁰M. Stavola, K. M. Lee, J. C. Nabity, P. E. Freeland, and L. C. Kimerling, Phys. Rev. Lett. **54**, 2639 (1985).

¹¹E. G. Sieverts and S. M. Muller, Phys. Status Solidi (b) **110**, K89 (1982).

¹²Y. H. Lee and J. W. Corbett, Phys. Rev. B 8, 2810 (1973).

¹³J. R. Niklas and J. M. Spaeth, Phys. Status Solidi (b) 101, 221 (1980).