Si-NL10: Paramagnetic Acceptor State of the Silicon Thermal Donor

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Electron paramagnetic resonance studies on several donor- and acceptor-doped, oxygen-rich, silicon samples have been performed. The intensity of the spectrum Si-NL10 has been investigated as a function of heat-treatment time, temperature, and illumination. The results provide evidence for an acceptor character of the Si-NL10 center strongly supporting the recently proposed idea of relating it to the silicon thermal donor level TD^-.

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Si-NL8 and Si-NL10 heat-treatment centers[1] are related to silicon thermal donors[2,3] (TD's) and as such have been thoroughly studied by both electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR).[1,4-6] The centers appear to be very similar in almost every aspect. Here is short summary of their most characteristic features:

(a) Both centers are observed in oxygen-rich, *p*-type silicon, regardless of the dopant (B, Al, Ga, In) present, by thermal annealing at a temperature of $\cong 450\,^{\circ}C$, thus concurrent with the generation of TD's.[5] Also, the decomposition of the centers by higher-temperature heat treatment coincides with the removal of TD's. Additionally, Si-NL10 can also be created in *n*-type oxygen-rich silicon for which the Si-NL8 spectrum is not observed.[7]

(b) Both centers have a very similar EPR spectrum of orthorhombic symmetry (point-group *2mm*), the difference being the smaller anisotropy of the Si-NL10 spectrum in comparison to Si-NL8.[1]

(c) The centers undergo transformation with heat-treatment time, which is evidenced by a gradual change of the observed *g* values, the effect first observed for the Si-NL8 spectrum by Muller, Sieverts, and Ammerlaan.[4] Recent studies of the Si-NL10 center in aluminum-doped silicon[6] revealed that different species of this center develop gradually upon heat treatment. Each species is characterized by a slightly different EPR spectrum. As not only the total but also the relative concentrations of various species are changing with heat-treatment time, a characteristic quasicontinuous *g*-value-shifting-effect is produced. The symmetry of later species of the Si-NL10 center was found to be lowered to monoclinic, although the splitting due to the lower symmetry is very small and cannot be resolved by EPR. Such detailed studies for the Si-NL8 center are not yet available, but it is most likely that in that case the *g* shifting is also caused by the existence of different species.

It can be concluded on the basis of the above summary that both centers present ideal candidates to be the EPR image of TD's in paramagnetic charge states. Moreover, the concentration of the Si-NL10 centers is usually in close correlation with the concentration of TD's as determined from room-temperature resistivity changes. Recently Lee, Trombetta, and Watkins[8] experimentally identified the Si-NL8 spectrum with the singly ionized state TD^+. This identification stimulated further detailed studies of both centers. Especially the nature of the Si-NL10 center, for which the oxygen involvement has been proven in the meantime,[9] appeared rather mysterious.

In the detailed ENDOR study that followed,[6] the microscopic structure of the Si-NL10 center has been unraveled. The center has been found to incorporate a growing number of oxygen atoms, whose clustering creates most probably interstitial silicon or aluminum (in the case of aluminum-doped material). The smallest possible species contained two oxygen atoms; the growth occurred by subsequent addition of a single oxygen atom along an $\{0\bar{1}1\}$ crystallographic direction. All the oxygen atoms incorporated in the center were in the usual puckered bond-centered interstitial position, in one $\{011\}$ plane. From the available data it was speculated that in the core of the defect a vacancy was present. In the interpretation of the experimental data two possible identifications of the Si-NL10 center were proposed. According to one of them the Si-NL10 is an (acceptor-based) oxygen aggregate which grows and transforms upon annealing, in parallel to the simultaneous development of silicon TD's. In that case the center should produce a single, shallow, effective-mass-like donor level in the energy gap. The second, more spectacular possibility, identifies Si-NL10 as the acceptor state TD^-. Such an identification indeed followed naturally from the microscopic structural model which involved a vacancy. In that case the TD^0, TD^+, and TD^{++} states would correspond to structures similar to V^0, V^+, and V^{++}, respectively. For the isolated vacancy, which has a deep-defect character, the energy levels are compressed by Jahn-Teller effects to fit within the silicon band gap. It was then argued that in the case of the Si-NL10 center the presence of a growing oxygen cluster around the vacancy core would certainly influence the energy-level scheme. The situation here would be to some extent similar to

that of the A center for which the presence of an oxygen atom creates an acceptor level at ~ 170 meV below the conduction band.[10] Following the analogy with the vacancy and the A center somewhat further, for the thermal donors also an acceptorlike TD^- state, similar to V^-, should be expected. In that case the Si-NL10 presents itself indeed as an attractive candidate. Apart from the already mentioned experimental indications which relate the Si-NL10 to the thermal donors, there was yet one more characteristic feature: in p-type material the Si-NL10 spectrum could be observed almost exclusively under illumination, while for n-type material, illumination showed almost no effect on the intensity of the EPR signal.

It was the aim of this project to investigate whether the Si-NL10 spectrum could indeed be attributed to the center of acceptor character.

Following the aim of the study, three kinds of samples were used:

(1) float zoned FZ-SI:Al, doped with oxygen; $[O_i] \cong 5\times10^{17}$ cm^{-3}, $[Al] = 9\times10^{15}$ cm^{-3}, $[C] \leqq 10^{15}$ cm^{-3}.

(2) Czochralski grown Cz-Si:P; $[O_i] \cong 1.5\times10^{18}$ cm^{-3}, $[P] = 5\times10^{13}$ cm^{-3}.

(3) Cz-Si:P; $[O_i] \cong 1.1\times10^{18}$ cm^{-3}, $[P] = 3\times10^{15}$ cm^{-3}.

The samples were oriented in such a way that the angular dependence of the EPR spectrum in the $\{0\bar{1}1\}$ plane could be measured. All the samples were given an initial heat treatment of $\frac{1}{2}$ hour at $\cong 1380$ °C and then quenched to room temperature in order to disperse the oxygen. This was followed by annealing at 450 °C for various time durations. After each annealing step both the EPR spectrum and the room-temperature resistivity were recorded.

The EPR spectra were measured with a K-band ($\cong 23$ GHz) superheterodyne spectrometer tuned to dispersion. The measurements were performed in a temperature range between 4.2 and $\cong 10$ K. The experimental arrangement allowed for white-light illumination of the sample in the microwave cavity. In the case when the absolute intensity of the EPR signal was to be determined, a standard Si:Sb sample was simultaneously inserted into the cavity; no (white light) illumination was used in that case.

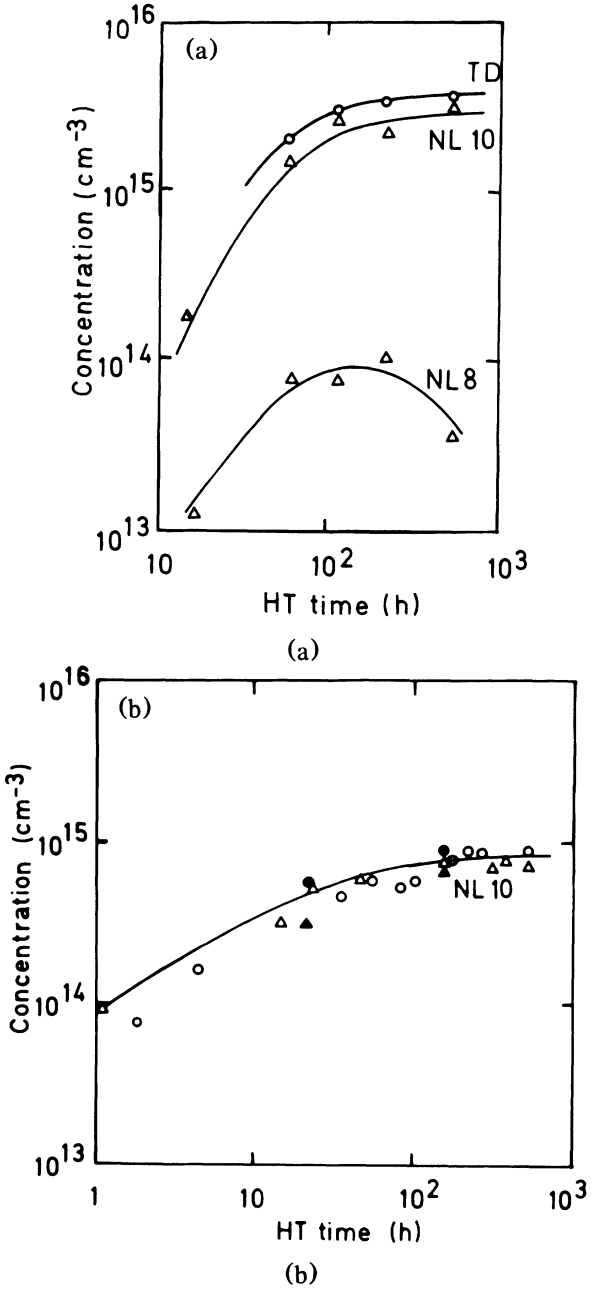

FIG. 1. Concentration of EPR-active heat-treatment centers with illumination of the sample (triangles) and electrically active thermal donors (circles) as a function of annealing time for a sample of (a) FZ-Si:Al, p type, oxygen doped, type (1), $[O_i] \cong 5\times10^{17}$ cm^{-3}, $[Al] = 9\times10^{15}$ cm^{-3}; and (b) Cz-Si:P, n type, type (2) $[O_i] \cong 1.5\times10^{18}$ cm^{-3}, $[P] = 5\times10^{13}$ cm^{-3} (open symbols) and type (3) $[O_i] \simeq 1.1\times10^{18}$ cm^{-3}, $[P] = 3\times10^{15}$ cm^{-3} (filled symbols).

In Fig. 1 the concentration of heat treatment centers Si-NL8 and Si-NL10 as obtained from the EPR measurements is compared with the thermal-donor concentration. The latter was calculated from the room-temperature resistivity changes under the assumption that each thermal donor contributes two electrons to the conduction band. The results for the three different groups of samples are presented. The solid curves are drawn to guide the eye only. The measurements were performed with white-light illumination of the sample. As can be noted, in each case the concentration of the Si-NL10 centers follows closely the calculated concentration of thermal donors. Especially in the case of n-type material the agreement is very good; for p-type silicon the observation of the Si-NL10 center was preceded by the occurrence of the Si-NL8 spec-

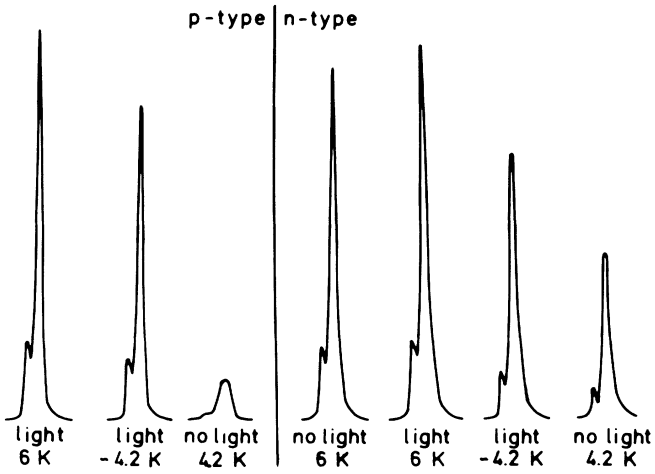

FIG. 2. The influence of temperature and (white light) illumination on the intensity of the Si-NL10 EPR spectrum for *p*- and *n*-type [sample (3)] oxygen-rich silicon.

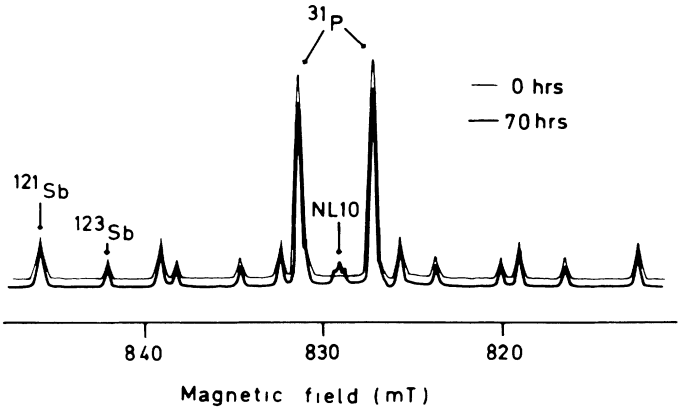

FIG. 3. EPR spectrum of the type-(3) sample before annealing (0 h) and after 70 h heat treatment. The EPR spectrum of the standard antimony-doped silicon sample placed simultaneously in the cavity is also shown.

trum.

Another difference between the *n*- and *p*-type material, as far as the Si-NL10 studies are concerned, is the influence of light and temperature on the intensity of the EPR signal. This is depicted in Fig. 2 for the samples of type (1) and (3). For the *p*-type material the intensity of the Si-NL10 spectrum depends strongly on (white light) illumination; in our experiment the observed Si-NL10 signal was increased by a factor of almost 5 by shining light on the sample. That effect was clearly caused by the illumination and not by an increase of the temperature of the sample which is inevitably connected with the illumination. For high-resistivity *n*-type silicon with relatively low phosphorus concentration a similar, however, much smaller in magnitude, effect has been observed. In the case of heavily doped samples of type (3), a small increase of the signal upon illumination (at 4.2 K) turns out to be only seemingly related to the light. As can be seen in Fig. 2, in that case the intensity of the Si-NL10 spectrum depends clearly on temperature and exhibits a maximum at a few degrees above liquid helium ($\cong$6 K). The temperature behavior of the Si-NL10 signal seems to be stronger than in *p*-type material.

The important experimental observation that in *p*-type material the intensity of the Si-NL10 can strongly be enhaced by illumination, while such effect is much weaker for high-resistivity *n*-type material [samples of type (2)] and practically none for higher phosphorus doping level [samples of type (3)], poses the question whether in *n*-type material the phosphorus donors already provide the electrons to populate the pertinent Si-NL10 level. As in this material the phosphorus EPR spectrum is present at the same time, its intensity can be monitored simultaneously with the Si-NL10 signal. In the series of measurements it was found that the ratio of the intensities for the two EPR signals, Si-NL10 to phosphorus, increased indeed with the annealing time. However, it could not be decided whether this was entirely due to an increase of the Si-NL10 signal or that a simultaneous decrease of the phosphorus donor signal took place. In that situation an independent measurement was necessary to determine the absolute intensity of the phosphorus EPR signal. For this purpose the EPR spectrum for the sample of type (3) was measured prior to thermal annealing and after annealing at 450 °C for 70 h. To provide an absolute standard for the intensity, and thus concentration, determination, a separate small sample of antimony-doped silicon was simultaneously introduced into the cavity. The experiment was performed *without* (white light) illumination. The result is shown in Fig. 3. As can be seen from the figure the decrease of the phosphorus-donor signal intensity upon annealing is unambiguous. The measurement of the temperature-dependent intensity established the relative decrease of the phosphorus signal of $\cong$10% which is in reasonable agreement with the concentration of the Si-NL10 centers and thermal donors.

The results illustrated by Fig. 3 have to be regarded in connection with the already mentioned earlier observations that (i) in *p*-type silicon the Si-NL10 spectrum intensity depends strongly upon illumination while almost no such effect can be observed in heavily doped *n*-type material, and (ii) in *n*-type silicon the agreement between the concentration of thermal donors and the Si-NL10 centers is especially good. Together this experimental evidence provides, in our opinion, strong indication of the acceptor character of the Si-NL10 center. The position of the corresponding energy level would have to be very close to that of the phosphorus donor making it a very deep acceptor level. In *n*-type silicon the Si-NL10 level could be populated at the expense of the nearby phosphorus-donor level thus leading to the

observed decrease of its EPR signal. In p-type oxygen-rich silicon subjected to heat treatment, the Fermi level is locked to the thermal-donor level; in that case the Si-NL10 center can only be generated by illumination.

If we take into consideration all the available experimental evidence which relates the Si-NL10 center to thermal donors, the results of the present study provide major support to an identification of the Si-NL10 as the TD^- acceptor state of the silicon thermal donor.

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