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Photoluminescence studies on thermal donors in boron- and aluminum-doped silicon

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Photoluminescence (PL) spectroscopy of excitons bound to thermal donors (TD's) has been applied to probe the generation kinetics of TD's in boron- and aluminum-doped Czochralski-grown silicon. The results were compared with magnetic-resonance data on the development of Si-NL8 and Si-NL10 TD-related EPR spectra. The results of the PL study provide evidence that TD centers are generated very similarly, with regard to the original acceptor doping of the material. At the same time the removal of acceptors from their substitutional positions is clearly different with the aluminum atoms being removed much faster. Taken together, the results of the study indicate that the different TD-growth development in Al- and B-doped Czochralski-grown silicon as evidenced by EPR measurements should be attributed to different behavior of the Fermi-level position in these two materials rather than to genuine differences in the generation of TD centers. It is argued that such a conclusion supports the identification of both TD-related Si-NL8 and Si-NL10 EPR spectra with different charge states of basically the same thermal-donor center.

I. INTRODUCTION

Thermal donors (TD's) in silicon are well known to be created after prolonged heat treatment (HT) of oxygen-rich (Czochralski-grown) silicon in the 300–500 °C region. Since their discovery in 1954,[1] many investigators have endeavored to unravel the microscopic structure and the growth mechanism for the defect. A wealth of data has been reported, both experimentally and theoretically—for a review see, e.g., Ref. 2. However, hitherto no generally accepted model exists, neither for the core structure of this evidently extended defect nor for the formation kinetics responsible for its multispecies character. As is nowadays established, the thermal donor is not a unique defect, but comprises a family of very similar shallow double donor centers. They can be directly accessed by infrared (ir) absorption spectroscopy, where two ionization series were identified containing at least nine species with very closely spaced ground-state energies.[3,4] The multispecies character of thermal donors was further elucidated from magnetic-resonance spectroscopy [electron paramagnetic resonance (EPR), electron-nuclear double resonance (ENDOR)] where two spectra labeled Si-NL8 and Si-NL10 were found to be TD related.[5] For one of these—the Si-NL8 spectrum—a direct identification with the singly ionized state of the infrared double donor could be made.[6] For the Si-NL10 spectrum, different models have been proposed.[7] One of these identifies the Si-NL10 center with an overcharged $(TD)^-$ state of the thermal donor. Direct oxygen involvement in the structure of thermal donors could be conclusively evidenced for the Si-NL10 spectrum following successful ^{17}O diffusion,[8] a result which was later also obtained for the Si-NL8 center.[9]

Photoluminescence spectroscopy (PL) has also been applied to the characterization of thermal donors. Tajima, Kanamori, and Iizuka reported TD-related spectral components with a no-phonon line at 1.143 eV, together with its transverse-acoustic (TA) and transverse-optic (TO) phonon replicas at 1.124 and 1.085 eV, respectively.[10] In addition to these $(TD)_q$ bands (where q denotes a momentum-conserving phonon involved in the emission), many sharp luminescence lines were subsequently observed in oxygen-rich silicon heat treated in the 450–500 °C range,[11,12] the origin of which has still not been clarified. Out of these, both the *P* line at 0.767 eV and the *H* line at 0.926 eV (Ref. 12) have ^{13}C- and ^{14}C-isotope shifts,[13] unambiguously demonstrating that carbon is part of the center involved. Hence, they cannot be correlated with the generation of thermal donors as has been attempted by Tajima, Stallhofer, and Huber.[14] More recently, Steele and Thewalt[15] and also Drakeford and Lightowlers[16] reported high-resolution PL spectra of the $(TD)_{NP}$ band at 1.143 eV, previously reported by Tajima, Kanamori, and Iizuka.[10] Instead of a featureless band, a well-resolved and reproducible structure was observed. This was attributed to recombination of excitons localized at different neutral TD species, thus providing further confirmation of the multiple nature of the TD centers.

In the present study, the TD generation kinetics, as visualized by TD-bound exciton luminescence, have been followed for boron- and aluminum-doped Czochralski-grown silicon. The results were compared with data obtained from magnetic-resonance studies on the same material. Not only is photoluminescence a very sensitive technique to study defects in semiconductors, but it also has the advantage of not being hampered by the actual position of the Fermi level in the sample. In contrast to this, both EPR and ir absorption results should be interpreted with care. One should bear in mind that the EPR measurement is sensitive to a particular charge state of the defect; in case of thermal donors, in total three different charge states are available: $(TD)^0$, $(TD)^+$, and

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$(TD)^{2+}$ [if the possibility of an overcharged $(TD)^-$ paramagnetic state is not considered]. Out of these only one, TD^+, is paramagnetic, and as such will be monitored by EPR *if* the Fermi level is sufficiently high. The same holds for ir-absorption spectroscopy, since the level at which the absorption is to be studied has to be populated. Should the Fermi level be influenced by other means than the creation of thermal donors upon annealing, this may be a source of severe deformation of the EPR- or ir-derived TD generation kinetics.

The aim of this study was to gain new insight into the TD issue by intercorrelating the information provided by two independent techniques sensitive to different charge states of the same defect. In this case, magnetic-resonance spectroscopy probes paramagnetic states of thermal donors: the Si-NL8 spectrum on the singly ionized $(TD)^+$ state[6] and, following a somewhat speculative identification, the Si-NL10 spectrum on the $(TD)^-$ acceptor state of the thermal donor.[17] On the other hand, the information obtained from photoluminescence spectroscopy would come from the radiative recombination of excitons bound to the neutral charge state $(TD)^0$.

II. EXPERIMENTAL DETAILS

A. Sample

Samples of size $2\times2\times10$ mm^3 were cut from commercially available material (Wacker Chemitronic, Germany), which is carbon lean, $[C]\leq10^{15}$ cm^{-3}. The starting parameters are as follows: (1) boron-doped Czochralski-grown silicon: $\rho\cong1.3$ Ω cm, $[B_s]\cong1.3\times10^{16}$ cm^{-3}, $[O_i]\cong1.3\times10^{18}$ cm^{-3}; (2) aluminum-doped Czochralski-grown silicon: $\rho=2.8-5.0$ Ω cm, $[Al_s]\cong4\times10^{15}$ cm^{-3}, $[O_i]\cong1.3\times10^{18}$ cm^{-3}.

Prior to the experiment, the samples were given the standard initial heat treatment of $\frac{1}{2}$ h, 1350 °C in argon gas atmosphere in order to disperse the oxygen and ensure the same, well-defined starting conditions. Resistivity measurements showed that this heat treatment had no effect on the acceptor concentration. Following the initial heat treatment, thermal donor centers were generated in the samples by annealing them for various time intervals (2–60 h) at a temperature of 470 °C. After each annealing stage, the samples were etched in a [HF]: [HNO_3] = 1:3 solution and cleaned with ethanol. Subsequently, photoluminescence spectra were measured.

B. Equipment

The photoluminescence (PL) measurements were performed at 4.2 K, using typically 100 mW of 514.5-nm Ar^+-ion laser light for optical excitation. To avoid spurious plasma lines, a 514.5-nm interference filter was used. The emerging luminescence was collected from the laser-irradiated side. It was dispersed by a high-resolution 1.5-m $f/12$ monochromator (Jobin-Yvon THR-1500) with a 600-grooves/mm grating blazed at 1.5 μm and detected by a liquid-nitrogen-cooled Ge detector (North Coast EO-817). The detector output was amplified using conventional lock-in techniques. The PL signal was digitized and fed into a computer for further data acquisition. To reduce voltage spikes at the detector output produced by the detection of cosmic muons, a sample-and-hold circuit was used as described in Ref. 18.

The sample resistivity was monitored at room temperature by a conventional four-point-probe technique. EPR measurements were performed with a superheterodyne spectrometer operating at 23 GHz (K band) and adjusted to detect the dispersion part of the signal. The magnetic field, modulated at a frequency of 83 Hz, could be rotated in the $(0\bar{1}1)$ plane of the silicon samples. The measurements were performed in the temperature region between 1.5 and 15 K. The experimental arrangement permitted *in situ* white-light illumination.

III. RESULTS

A. EPR and resistivity measurements

The EPR spectra labeled Si-NL8 and Si-NL10 were shown to be related to thermal donors.[5] Following this result, the generation kinetics of these centers have been investigated in different materials.[5,19] Figure 1(a) shows

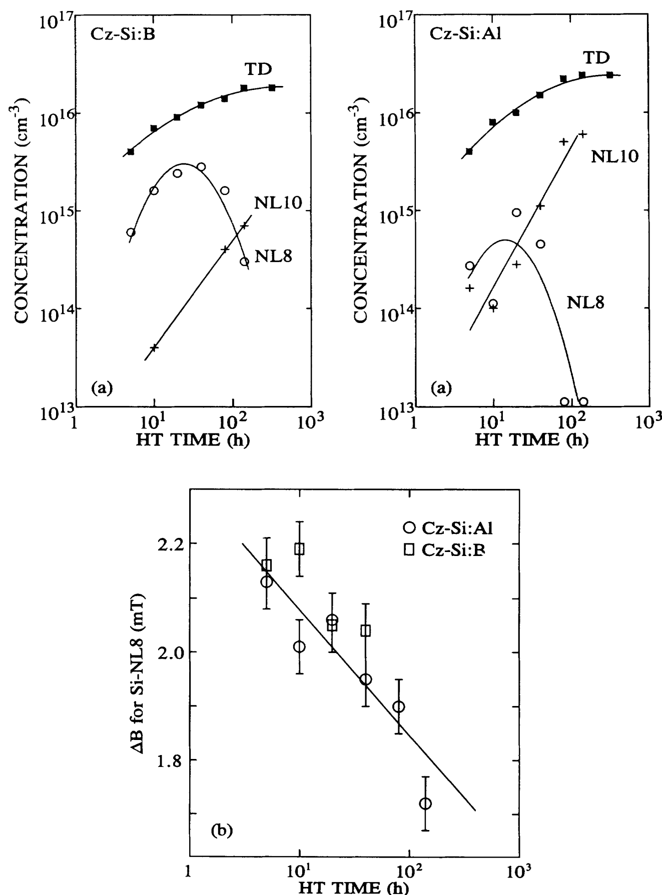

FIG. 1. (a) Generation kinetics of thermal donors (TD's, ■) (on the basis of resistivity measurements) and TD-related Si-NL8 (○) and Si-NL10 (+) EPR centers, and (b) the annealing time dependence of g-value shifting for the Si-NL8 $[(TD)^+]$ EPR spectrum as observed under (white-light) illumination in Czochralski-grown silicon.

the concentration of HT centers Si-NL8 and Si-NL10 in the p-type material used in the current study as obtained from EPR measurements. Although the absolute values in the figure are only accurate within an order of magnitude, the relative changes are far more reliable, since data were obtained for the same material. Also included in Fig. 1(a) is the generated TD concentration as calculated from room-temperature resistivity measurements, assuming that every TD supplied one electron to the conduction band. The curves through the points serve as a guide for the eye.

In addition to the information on TD generation kinetics, the EPR studies also revealed a shifting of the g value of the Si-NL8 spectrum upon heat-treatment time, while preserving the $2mm$ symmetry of Si-NL8 centers. This effect is most pronounced for the off-diagonal element g_{yz} of the Cartesian g tensor. The decrease of separation in magnetic field $\Delta B(\propto g_{yz})$ of the two Si-NL8 EPR resonances with $\mathbf{B}\|[111]$ as a function of heat-treatment time is depicted in Fig. 1(b). It reflects the gradual decrease of anisotropy of the Si-NL8 spectrum. A similar effect has been observed also for the Si-NL10 center.

B. Photoluminescence results

Exemplary photoluminescence spectra from boron- and aluminum-doped crystals after a 33- and 8-h HT at 470 °C are shown in Fig. 2. The spectra consist of the

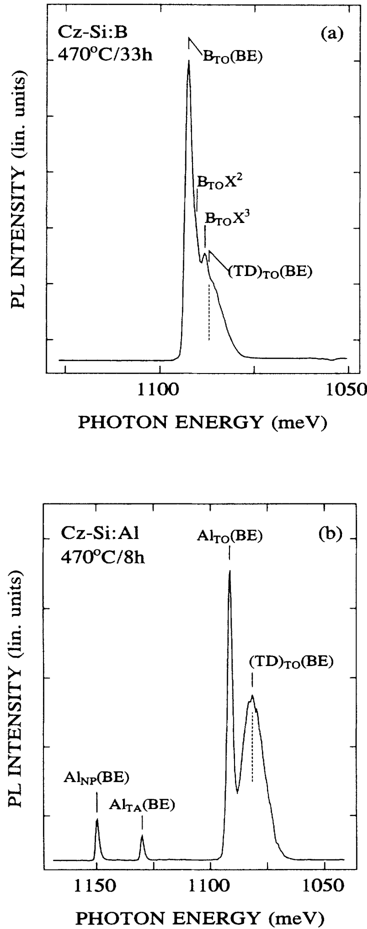

FIG. 2. Photoluminescence spectra of Czochralski-grown silicon doped with (a) boron, and (b) aluminum after heat treatment at 470 °C. Spectra were recorded at 4.2 K, using 514.5-nm Ar^+-laser excitation. The bound-exciton (BE) recombinations at neutral acceptors (B,Al) and TD's are indicated, together with transitions attributed to boron-related bound multiexciton complexes ($B_{TO}X^m$, $m=2,3$).

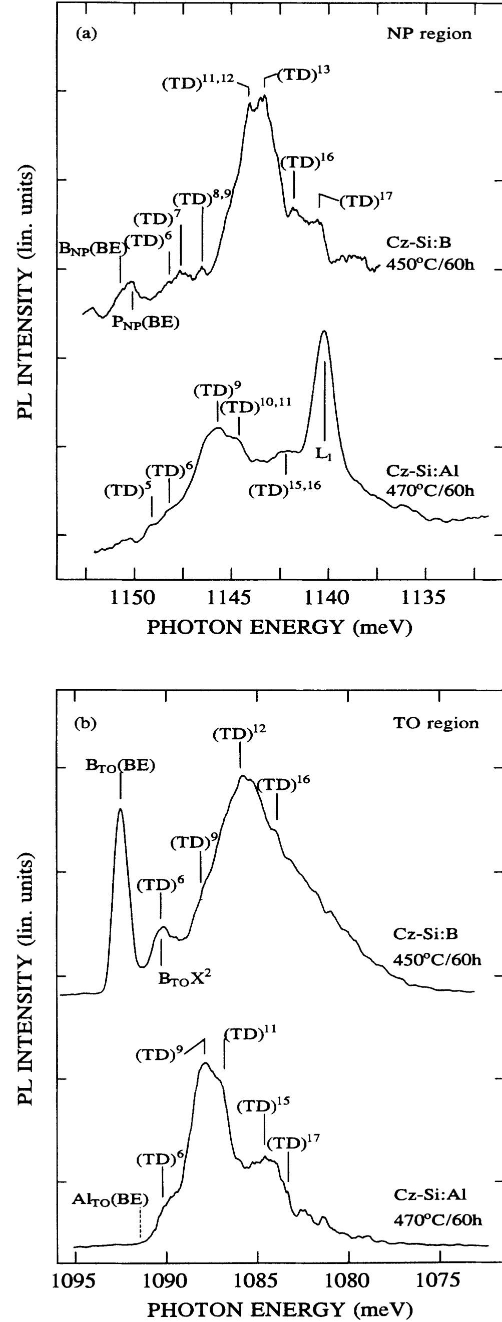

FIG. 3. Detailed TD-bound-exciton (BE) photoluminescence spectra of Czochralski-grown (Cz) silicon doped with boron and aluminum: (a) NP range, and (b) TO-phonon-assisted range. Individual lines related to BE recombination at different TD species are marked at the energies identified earlier by Steele and Thewalt (Ref. 15).

no-phonon (NP) lines of the radiative decay of bound excitons (BE's) at neutral acceptors, with their transverse-acoustic (TA) and transverse-optic (TO) phonon replicas—B_q(BE) and Al_q(BE), respectively, with q = NP, TA, or TO. The luminescence from boron-related bound multiexciton complexes (BMEC's) is also observed, labeled $B_{TO}X^m$, with the superscript indicating the number of excitons in the complex. For both materials, the TO replica of BE recombination at thermal donors—$(TD)_{TO}$(BE)— may clearly be recognized. We note that, most probably due to the high acceptor concentrations in our samples, free-exciton transitions are not observed.

A more detailed spectrum of the NP region for both p-type samples is presented in Fig. 3(a). Apart from the luminescence from boron-related BE's, separate lines could be resolved and are related to bound-exciton recombination at different TD's, which are marked in the figure. The labeling $(TD)^j$ ($j=1,2,\dots$) as used in this study is resembling earlier identified lines,[15] and should not be confused with the numbering of species as deduced from ir-absorption spectroscopy.[3,4] Figure 3(b) shows detailed TO-phonon-assisted spectra as recorded for B- and Al-doped silicon. For both samples, some of the TD species as identified in the NP region may be resolved.

As in the NP region, the TD photoluminescence in the B-doped material is partly obscured by bound (multiple) exciton recombination at boron acceptors. In the Si:Al sample, however, the emission due to Al-related BE recombination is no longer visible. In the PL spectrum from Si:B, traces may be seen, labeled P_{NP}(BE), due to BE recombination at neutral phosphorus donors. The observation of P-related emission is, however, different from sample to sample.

The generation of thermal donors upon heat treatment has been monitored in the TO region, where PL signals are significantly stronger. In Fig. 4, eight TO spectra are shown for boron-doped silicon obtained after stepwise annealing at 470 °C of the same sample for the times indicated. The broad underlying band at the low-energy side

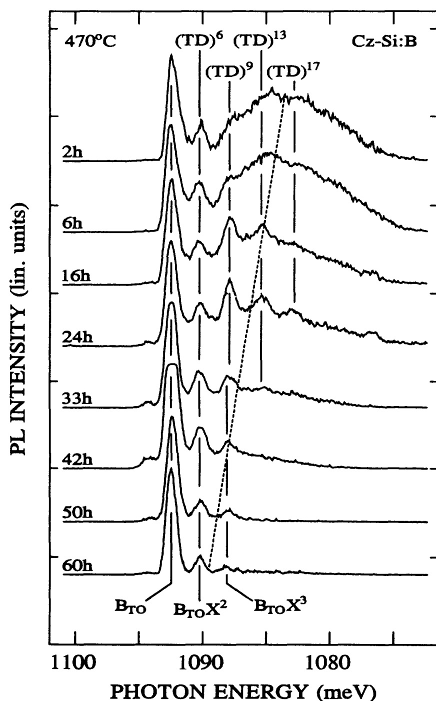

FIG. 4. Evolution of TD-related bound-exciton recombination in the TO region for Czochralski-grown Si:B upon 470 °C HT. The spectra have been normalized to equal B_{TO} height. The dashed line indicates the shift of the $(TD)_{TO}$ band toward higher photon energies upon annealing. Separate lines [labeled $(TD)^j$] can be resolved due to radiative recombination of excitons localized at different TD species. This structure, however, is partly obscured by luminescence from boron-related multiply bound excitons (labeled $B_{TO}X^m$).

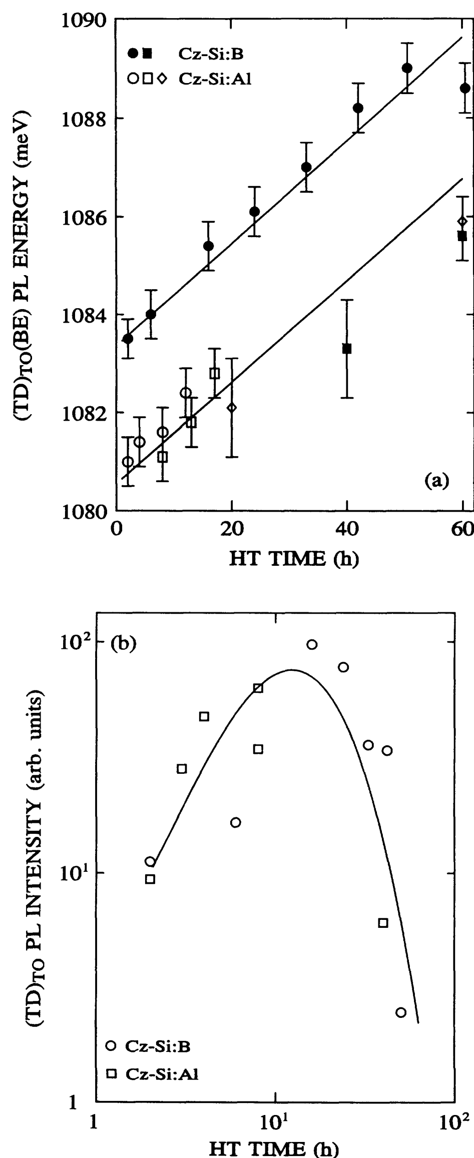

FIG. 5. The annealing-time dependence of the TD-bound-exciton emission band in the TO region for various boron- and aluminum-doped silicon crystals: (a) the shift of its center, and (b) the change of its total intensity.

of the boron-related B_{TO} line is the $(TD)_{TO}$ band. All spectra have been normalized to equal B_{TO} intensity. As may be seen in Fig. 4, the $(TD)_{TO}$ band shifts upon annealing, with a simultaneous change of its total intensity. These effects are illustrated in Fig. 5 for both kinds of materials used in the experiment. Figure 5(a) presents the shift of the maximum of the TO replica of TD-related bound-exciton luminescence, whereas in Fig. 5(b) the intensity of this band is plotted against annealing time. The solid curves are only drawn to guide the eye. The intensity of the $(TD)_{TO}$ band for a particular HT time has been obtained by integrating the corresponding TO spectrum after subtracting the 60-h HT spectrum, since at this annealing time the TD-related emission has dropped to zero—see Fig. 4. The implicit assumption, that B-related BE luminescence does not change upon heat treatment, is justified later.

IV. DISCUSSION

A. PL contra EPR results

The PL spectra shown in Figs. 2 and 3 are in full analogy with earlier data on TD luminescence,[15,16] which were able to separate the contribution from the individual thermal-donor species. For both acceptor-doped silicon crystals employed here, the same TD species can be accounted for in both NP and TO spectral regions, thus supporting the identification. In the more intense TO region, the resolution is diminished due to phonon broadening. Since the concentration of a given impurity is reflected by the PL intensity, one expects the relative intensities from excitons bound to different TD species to change with HT time. Separate lines are observed on the $(TD)_{TO}$ band (see Fig. 4), the relative intensities of which change upon annealing, in full analogy to the rise and fall of TD species. However, not too much information can be deduced from this observation, since emission due to B-associated BMEC's overlaps this structure.

The broad underlying band in Fig. 4 is due to unresolved BE recombination at thermal-donor species, and as such reflects the TD concentration in the sample. It shifts toward higher photon energies and reaches a maximum in overall intensity near 20-h HT for Si:B. As can be seen in Fig. 5, the behavior in Al-doped silicon is quite similar to that in B-doped crystals. The slight differences between the kinetics in both materials are easily explained by small variations of the oxygen contents, since the TD formation rate is known to depend on the fourth power of the initial oxygen concentration.[20] The latter could also explain the somewhat slower kinetics in the material as used by Steele and Thewalt,[15] when compared to our samples. These authors observe a maximum of TD-related BE emission in a somewhat later annealing stage, between 32 and 64 h, which then may well be due to a smaller initial oxygen concentration in their crystals. The shift of the $(TD)_{TO}$ luminescence toward higher energies is very much reminiscent of the g-value shifting of the Si-NL8 and Si-NL10 spectra toward lower anisotropy. In EPR, one measures the superimposed resonances of all TD species. The later species, being the shallower ones as is known from ir-absorption studies, have a more isotropic character as is also shown by the gradual evolution of TD centers toward lower anisotropy—see Fig. 1(b). Since shallower TD species are generated upon annealing, the exciton localization energy becomes consequently smaller by virtue of Haynes's rule.[21] The resulting increase of the BE recombination energy shifts the TD-related emission band toward higher energy—see Fig. 5(a).

The results of the current study as depicted in Figs. 2, 3, and 5 indicate that the generation kinetics of TD's as monitored by photoluminescence proceed very similarly, independent of the actual acceptor dopant. Aluminum doping has no accelerating effect for TD kinetics, which are (predominantly) governed by the initial oxygen concentration. As shown in Fig. 3, identical TD species are formed in both materials, thus indicating identical TD generation processes. It should be mentioned here that such a conclusion does not rule out the possibility that in aluminum-doped silicon, in addition to *normal* TD's, some other aluminum-based form of TD-like centers is also formed. In such a case, however, their concentration could not be significant in view of the very similar generation kinetics of *normal* TD's for both materials.

The above conclusion appears in contradiction to the results of ir-absorption studies,[22] as well as to the resistivity and magnetic-resonance findings as summarized in Fig. 1. EPR investigations of HT centers in both n-type and p-type silicon showed that both Si-NL8 and Si-NL10 centers could be generated in (originally) p-type material regardless of the actual type of acceptor,[5] while in n type only Si-NL10 centers could be observed.[19] Another conclusion was that in aluminum-doped material the generation of Si-NL10 centers was considerably enhanced in comparison to more commonly used boron-doped silicon.

The aforementioned contradiction may be understood in view of the remarks presented in the Introduction. In contrast to the luminescence of thermal-donor-bound excitons, all the above-mentioned techniques are sensitive not only to the generation of TD centers upon annealing, but also to the actual position of the Fermi level. Different results obtained from these techniques could then be explained, if, in the aluminum-doped material, the Fermi-level position would be influenced by yet another mechanism, independent from the generation of TD's. Such a mechanism could be provided by a gradual removal of acceptors from the substitutional positions, and has indeed been found to take place in parallel to the generation of TD's.[16] In the present study, the existence of this mechanism is further confirmed, as can be seen in Fig. 6, where the intensity of acceptor-related photoluminescence is depicted as a function of HT time. It can clearly be seen that, while the concentration of boron remains almost constant all through the annealing procedure, the concentration of aluminum is quite soon diminished below the detection limit. In this situation, the behavior of the Fermi level is very much different in both materials (especially since interstitial aluminum has donor character), and thus could provide a very natural explanation for the seemingly catalytic role of aluminum in the TD generation process.

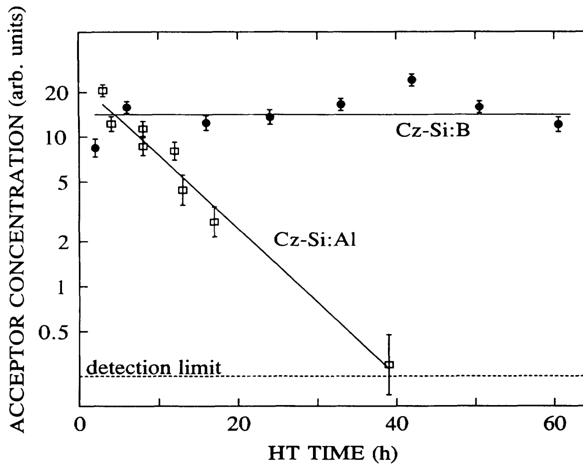

FIG. 6. Decay of acceptor-bound exciton luminescence during the annealing process of Czochralski-grown silicon doped with boron and aluminum.

B. On the microscopic identification of Si-NL10 centers

While the identification of the Si-NL8 center with the singly ionized thermal-donor state $(TD)^+$ (Ref. 6) has generally been accepted, the particular microscopic assignment of the Si-NL10 spectrum is a matter of considerable controversy and confusion.[7] This mainly stems from the fact that, while there is much evidence supporting the idea that both EPR spectra in question should be related to different (charge or spin) states of structurally the same thermal-donor center, at the same time there also seems to exist some form of correlation between the generation of the Si-NL10 center and the presence of aluminum. Not only aluminum doping increases the concentration of the observed Si-NL10 centers, but also hyperfine interactions with ^{27}Al nuclei have been observed in an ENDOR experiment performed on the Si-NL10 center in aluminum-doped silicon.[23] At the same time, no corresponding interactions with the acceptor could be found by ENDOR in boron-doped material.[24] These particular experimental findings promote the idea of relating the Si-NL10 spectrum to some kind of aluminum-oxygen complex,[7] and not to a different state of the TD center. On the other hand, this complex would have to be in many aspects very similar to "standard" thermal donors, with the involvement of oxygen, multispecies character, and generation conditions being the most important similarities. Taken together, the abovementioned considerations would indicate some kind of aluminum–thermal-donor pairing. In line with this, Drakeford and Lightowlers[16] tentatively attributed sharp features in their PL spectra of Si:Al samples to bound-exciton decay at isoelectronic Al-TD complexes. However, upon closer examination, this seemingly plausible idea has also to be rejected. Formation of a *substitutional-aluminum–thermal-donor* pair in the temperature region of $\approx 450\,^{\circ}\mathrm{C}$ is impossible in view of the negligible diffusion of both components, while formation of an *interstitial-aluminum–thermal-donor* complex is also unlikely in spite of the relatively high diffusion coefficient expected for interstitial aluminum. A substitutional aluminum atom of acceptor character becomes a (double) donor when moved into an interstitial position. The second donor level (Al_i^+, Al_i^{2+}) is at $E_V+0.17$ eV,[25] while the position of the first donor level (Al_i^0, Al_i^+) is not precisely known, but is believed to be degenerate with the conduction band. Thus, depending on the Fermi-level position, interstitial aluminum will exist in the singly or doubly ionized charge state (Al_i^+ or Al_i^{2+}). Therefore, it cannot experience any Coulomb attraction to another (double) donor center, whether in the neutral $[(TD)^0]$ or in the ionized $[(TD)^+$ or $(TD)^{2+}]$ charge state.

The present study adds some interesting experimental information to this highly confusing issue. While for boron doping the Fermi level mainly shifts upon annealing due to the generation of (thermal) donors, in aluminum-doped samples this effect is strongly enhanced by the simultaneous occurrence of yet two more processes: the decrease of the substitutional acceptor concentration, and creation of extra donor centers due to the (double) donor character of interstitial aluminum. Since, as mentioned before, the increased generation of the Si-NL10 center in aluminum-doped silicon was one of the two major arguments against its identification with a different state of the same thermal donors which in their singly ionized form give rise to the Si-NL8 spectrum, the results of the present study in fact support such identification. As discussed at length in Ref. 7, the negative charge state $(TD)^-$ was the most likely candidate to be linked to the Si-NL10 spectrum. Also on this issue, the current results provide some extra arguments. The fast increase of the Fermi level due to interstitial aluminum donors in Al-doped material would explain both the much faster decay of the Si-NL8 spectrum [transformation of $(TD)^+$ in $(TD)^0$ as acceptors are being annihilated], as well as the enhanced production of Si-NL10 centers as the simultaneous generation of interstitial aluminum donors raises the Fermi level high enough to populate the $(TD)^-$ state.

Additionally, one should note that in this situation ionized donors Al_i^+ (or Al_i^{2+}) and negatively charged pseudoacceptors $(TD)^-$ would be present in the sample. In view of a relatively high diffusivity of interstitial aluminum, the Coulomb attraction between these centers could lead to some kind of pairing, in a way similar to Al_i^{2+}-Al_s^- pair (Si-G19) centers.[26] Due to the evidently (very) extended character of the spin wave function of the Si-NL10 center,[23] such a pairing procedure would not necessarily lead to generation of a totally different EPR spectrum, but could merely result in a rather subtle shift of the g-tensor values (just as the addition of oxygen atoms during the TD transformation process leads only to very small changes in g-tensor values in spite of the symmetry lowering of TD's upon growth). By EPR, indeed small differences between the g values of the Si-NL10 spectrum as determined in boron- and aluminum-doped materials have been concluded.[5] On the other hand, the hyperfine interaction with the aluminum nuclei should in this case be observable by ligand ENDOR, which is indeed the case.

V. CONCLUSIONS

From the PL study, substantial evidence is provided to show that the growth development of TD's in B- and Al-doped oxygen-rich Czochralski-grown silicon is independent of the (original) acceptor doping of the material. Detailed PL spectra show that the same TD species are generated upon annealing in Si:B and Si:Al. The rise and fall of the TD-related bound-exciton luminescence in the course of the annealing process is the same in both crystals. Also, the shift of this emission toward higher photon energies, as expected since shallower TD species are generated upon heat treatment, is similar. Slight differences between the kinetics in the two materials are likely to be due to small differences between the oxygen concentration in the starting material.

In parallel with TD generation, acceptors are removed from their substitutional sites. In Al-doped silicon, this loss of substitutional acceptors is much faster compared to B-doped silicon. Thus, the actual position of the Fermi level for a given heat-treatment time is not only influenced by creation of thermal donors but also by annihilation of acceptors. Since the EPR experiment is incapable of separating the two contributions, the seemingly catalytic role of aluminum in the TD generation, as concluded from EPR studies, can probably be explained by a different behavior of the Fermi level in Si:Al and Si:B. In aluminum-doped material, not only generation of thermal donors occurs, but also removal of Al acceptors from their substitutional sites and creation of extra interstitial Al-donor centers. Both processes result in an extra increase of the Fermi level in case of aluminum doping when compared with boron doping. If one assumes identification of the Si-NL10 center with the overcharged $(TD)^-$ state, this extra increase of the Fermi-level position may then very well explain the increased generation of these Si-NL10 centers in aluminum-doped silicon.

Taken together, the results of the present PL studies give additional information on the role of aluminum in the TD generation process and in this way provide powerful evidence for the identification of both Si-NL8 and Si-NL10 TD-related EPR spectra with different charge states of structurally the same thermal-donor center.

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