

Photoluminescence of silicon thermal donors

B. J. Heijmink Liesert, T. Gregorkiewicz, and C. A. J. Ammerlaan

*Van der Waals-Zeeman Laboratorium, Universiteit van Amsterdam,
Valckenierstraat 65-67, NL-1018 XE Amsterdam, The Netherlands*

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All thermal-donor-related photoluminescence (PL) bands, i.e., bound-exciton recombination at neutral thermal donors (1.143 eV), the O_J (1.117 eV) and O'_J (1.052 eV) bands, and bound-exciton two-electron ($2e$) transitions at so-called N-O complexes, were studied in p -type Czochralski-grown silicon substrates doped with boron and aluminum. The influence of aluminum doping on the thermal-donor generation was found to be of secondary importance. For the O_J and O'_J bands an interpretation in terms of thermal-donor-related $2e$ transitions is proposed. For the N-O emission substantial evidence is presented which rules out the possibility of nitrogen involvement. Finally, for Al-doped material, four PL lines, labeled from PL-Si-NL2 to PL-Si-NL5, dominating the spectrum for extended heat-treatment times are reported.

I. INTRODUCTION

Thermal donors (TD's) are among the most studied centers in silicon. The widespread application of Czochralski-grown silicon substrates for device manufacturing and the high concentrations at which TD's may be generated stimulated research effort in the field. In spite of this, the issue of thermal donors remains remarkably confused as no consensus can be reached on the microscopic model of these centers.

Among the experimental techniques applied so far to the investigation of the structural and electronic properties of TD's, infrared (IR) absorption, and magnetic-resonance spectroscopy turned out to be particularly successful. On the basis of these studies basic features of TD's, e.g., the shallow double-donor character, multiplicity of species, symmetry, and participation of oxygen, could be established—see Ref. 1 and references therein. In addition to the above-mentioned techniques, TD's have also been investigated by other experimental methods commonly used in semiconductor research: resistivity and Hall effect, microscopy, and, more recently, photoluminescence (PL) spectroscopy.

PL spectroscopy has many important advantages, with high sensitivity and high resolution being among the most pronounced features. It has also been found to offer rather unique possibilities for direct correlation with other experimental methods, such as IR absorption and, to a certain extent, electron-nuclear double resonance (ENDOR). For the IR absorption data such a possibility is provided by the observation in the PL spectrum of so-called *two-electron* ($2e$) transitions. The correlation with ENDOR is based on some similarity between ligand ENDOR and donor-acceptor pair (DAP) recombination, as in both cases information about the spatial distribution of the electronic wave function may be obtained. Since ENDOR and IR absorption revealed many details of TD phenomena, the possibility of amending this knowledge provides a new impulse for the photoluminescence studies on TD's.

Several PL bands have been assigned to TD's.^{2,3} Some of them, such as the P line (767 meV), originally ascribed to thermal donors, were later found to be related to carbon-based defects. More recently the PL band originally reported by Tajima, Kanamori, and Iizuka² with a no-phonon (NP) line at ≈ 1143 meV, was further investigated in detail by PL Fourier spectroscopy⁴ and identified as bound-exciton (BE) recombination at thermal donors in the neutral charge state (TD⁰). The band was found to contain a series of sharp lines, directly confirming the multispecies character of TD's. In addition to the 1143-meV band, two more PL spectra, at 1117 meV (labeled O_J) and 1052 meV (labeled O'_J), are at the moment believed to be related to thermal-donor centers while different interpretations are given as to their precise origin.⁵⁻⁸

A puzzle in both the photoluminescence and IR absorption studies of TD's is represented by the so-called *nitrogen-oxygen* (NO) complexes. The set of effective-mass-like (EMT) (single-donor) states was observed originally by Suezawa *et al.*⁹ and identified with N-O complexes on the basis of production conditions. The actual ionization levels, as derived from those measurements, have turned out to be identical to those found before in nitrogen-lean Czochralski-grown silicon substrates and labeled as *shallow thermal donors* (STD's).¹ The photoluminescence of these centers of mysterious origin has been studied by Steele, Lenchyshyn, and Thewalt¹⁰ who could establish a direct correlation between the IR absorption and PL data by the observation of $2e$ transitions.

An important aspect of the studies of thermal donors is the influence of the acceptor doping on the generation characteristics and properties of these centers. This follows the original notion by Fuller, Doleiden, and Wolfstirn,¹¹ that in Al-doped Czochralski-grown silicon substrates the generation of TD's, as monitored by resistivity measurements, was considerably enhanced. Also electron paramagnetic resonance (EPR) and ENDOR (Refs. 12 and 13) indicated a special role of aluminum in the generation of TD-related EPR spectra. Such observations

were further supported by IR-absorption studies,¹⁴ which revealed that in Al-doped silicon a special kind of thermal donor could be formed in addition to the "normal" ones. The idea of a special role of aluminum doping in the TD generation process has also been studied by photoluminescence.¹⁵ Aluminum doping was shown to have only a secondary influence on the generation of thermal-donor centers. The aim of the present paper is to follow the influence of different acceptor doping, with special emphasis on aluminum, on all TD-related photoluminescence bands. At the same time, the information obtained in this study also allows us to critically assess the microscopic assignment of these bands.

II. EXPERIMENTAL DETAILS

The material used in this study was commercial (Wacker Chemitronic), high-quality Czochralski-grown silicon substrates. Samples of $2 \times 2 \times 10 \text{ mm}^3$ size were cut from the same ingots. All samples were p type and carbon-lean, $[C] \leq 10^{15} \text{ cm}^{-3}$. They had the following starting parameters: (1) boron-doped Cz-Si: $\rho \approx 1.3 \text{ } \Omega \text{ cm}$, $[B_s] \approx 1.3 \times 10^{16} \text{ cm}^{-3}$, $[O_i] \approx 1.3 \times 10^{18} \text{ cm}^{-3}$; (2) aluminum-doped Cz-Si: $\rho = 3\text{--}5 \text{ } \Omega \text{ cm}$ $[Al_s] \approx 4.0 \times 10^{15} \text{ cm}^{-3}$, $[O_i] \approx 1.3 \times 10^{18} \text{ cm}^{-3}$.

For some reference measurements—see Sec. IV D— p -type Cz-Si doped with indium was used ($\rho = 7\text{--}11 \text{ } \Omega \text{ cm}$, $[In_s] \approx 4.5 \times 10^{14} \text{ cm}^{-3}$, $[O_i] \approx 1.3 \times 10^{18} \text{ cm}^{-3}$). Prior to the experiment all samples were given the standard initial heat treatment of $\frac{1}{2}$ h at 1350°C in an argon-gas atmosphere in order to disperse oxygen and ensure the same well-defined starting conditions. Following the initial heat treatment, thermal-donor centers were generated in the samples by annealing them for various time intervals (up to 600 h) at a temperature of 470°C . After each annealing stage the samples were etched in a $\text{HF:HNO}_3 = 1:3$ solution and cleaned with ethanol. Subsequently, photoluminescence spectra were measured.

The details of the PL experimental setup can be found elsewhere.¹⁵ Zeeman measurements were carried out in the Faraday configuration, with the sample mounted in the bore of a 6-T split-coil superconducting magnet (Oxford Instruments SM 4).

III. EXPERIMENTAL RESULTS

A. Excitons bound to neutral thermal donors

This part of the current research is an extension of our previously published data.¹⁵ In the present study the heat-treatment time has been extended up to 600 h and a wider variety of samples has been used. The results are depicted in Fig. 1. The immediate conclusion from the figure is that for both dopants the emission from TD⁰ bound excitons reaches a maximum after $\approx 20\text{--}30$ -h heat-treatment time. The somewhat larger spread in the data for aluminum-doped samples can most probably be attributed to the more inhomogeneous oxygen distribution resulting from a considerable chemical affinity between oxygen and aluminum. From Fig. 1 one can also note a trace of saturationlike behavior for annealing times larger than 100 h.

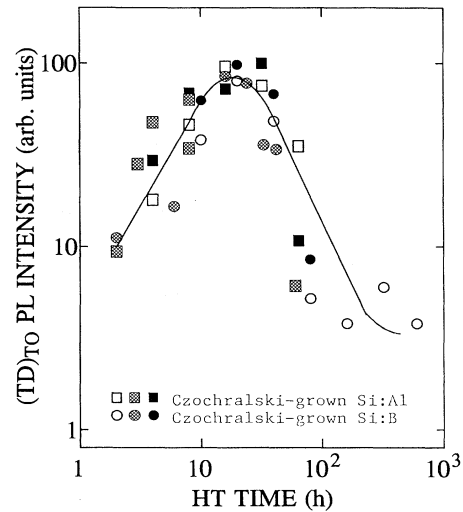


FIG. 1. Intensity of the TO replica of the TD⁰-bound-exciton line as a function of 470°C annealing time for Czochralski-grown silicon substrates doped with boron (\circ) and aluminum (\square). For both materials the results as obtained for three different samples of the same ingot are presented, as indicated by open, cross-hatched, and closed symbols. The line is drawn as a guide to the eye.

B. O_j and O'_j bands

The annealing-time dependence of the O_j and O'_j bands is depicted in Fig. 2 for several samples of aluminum and boron doping. As can be seen, within the experimental accuracy the results are practically independent

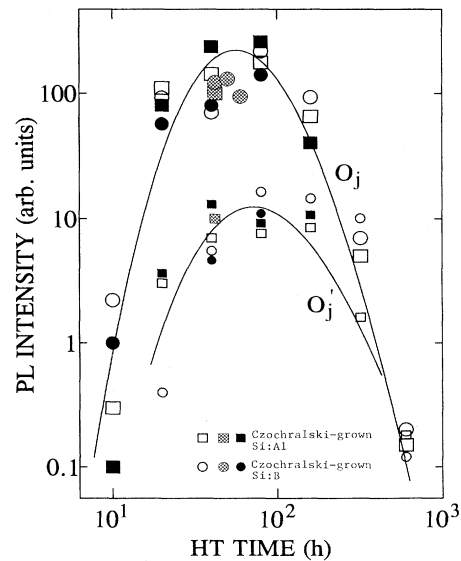


FIG. 2. Development kinetics for the O_j and O'_j bands for Czochralski-grown silicon substrates doped with boron (\circ) and aluminum (\square). For every dopant the results as obtained for three different samples are presented. The curves through the points serve as a guide to the eye.

of the dopant, indicating the same generation process of O_j and O'_j bands in both kinds of investigated material. Furthermore, the maxima of the O_j and O'_j bands coincide for annealing times of ≈ 70 –80 h while the (total) PL intensity of O_j is always one order of magnitude higher than that of O'_j . More similarities are revealed by Fig. 3, where the O_j spectra, as recorded by B- and Al-doped samples, are compared.

C. Acceptor-bound-exciton photoluminescence

It is by now rather well established that the formation of TD's is accompanied by the generation of silicon self-interstitials which can subsequently replace dopant atoms. This *kick-out* mechanism is especially effective for aluminum. In the present study the annealing-time dependence of the concentration of substitutional acceptors was followed by monitoring the TO phonon-assisted BE recombination at neutral acceptors—see Fig. 4. It can be seen that the removal mechanism is also valid for boron acceptors in which case considerably longer annealing times have to be employed when compared to aluminum-doped material.

D. Nitrogen-oxygen complexes

A rather unexpected result of the present study is the observation of PL lines attributed previously to N-O complexes.¹⁰ Figure 5 shows a PL spectrum recorded in the TO-replica region for an Al-doped sample after a 13-h—

Fig. 5(a)—and 17-h—Fig. 5(b)—heat treatment. The spectra show a clear growth of N-O identified bands accompanied by the already mentioned decrease of aluminum-related BE emission. The N-O bands consist of BE recombination at 1092.8 meV and $2e$ transitions around 1065 meV. It should be noted that, since the resolution in our experiment is lower than in the original study,¹⁰ the lines related to $2e$ transitions in Fig. 5 are not homogeneous and represent superpositions of corresponding transitions for several N-O complexes. A further discussion on the identification of these lines will be given in Sec. IV C.

E. Other photoluminescence lines

In addition to the PL bands already known to be TD related, the current study has revealed more lines whose appearance coincides with the generation of thermal donors. In particular, a set of four strong and sharp emission lines has been observed in Al-doped material and is labeled here PL-Si-NL2–PL-Si-NL5. It should be noted that, while these lines were clearly visible in Al-doped material, their generation in B-doped silicon cannot be excluded at this stage. In some measurements, performed on B-implanted material, weak PL features similar to the Si-NL j lines ($j=2, 3, 4, \text{ or } 5$) could be seen. However, these particular results require further confirmation and do not form part of this study. In Fig. 6 a typical PL spectrum, as recorded for a Cz-Si:Al sample following a heat treatment for 17 h at 470°C, is shown; the lines are observable with high signal-to-noise ratio. Table I gives the precise positions and linewidths of the NL j lines.

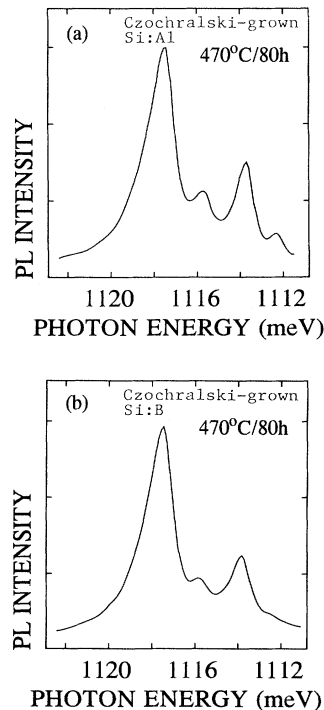


FIG. 3. O_j photoluminescence spectra as recorded for (a) Cz-Si:Al and (b) Cz-Si:B, both thermally treated for 80 h at 470°C.

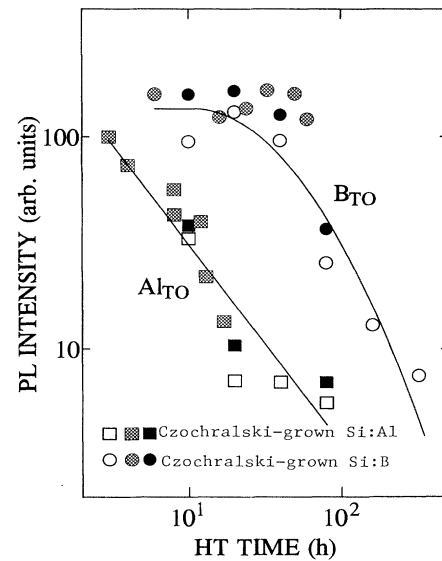


FIG. 4. Annealing-time dependence of the TO replica intensity of acceptor-bound-exciton recombination for material doped with boron (\circ) and aluminum (\square). For both kinds of materials the results for three different samples—open, cross-hatched, and closed symbols—are given. The curves through the points guide the eye.

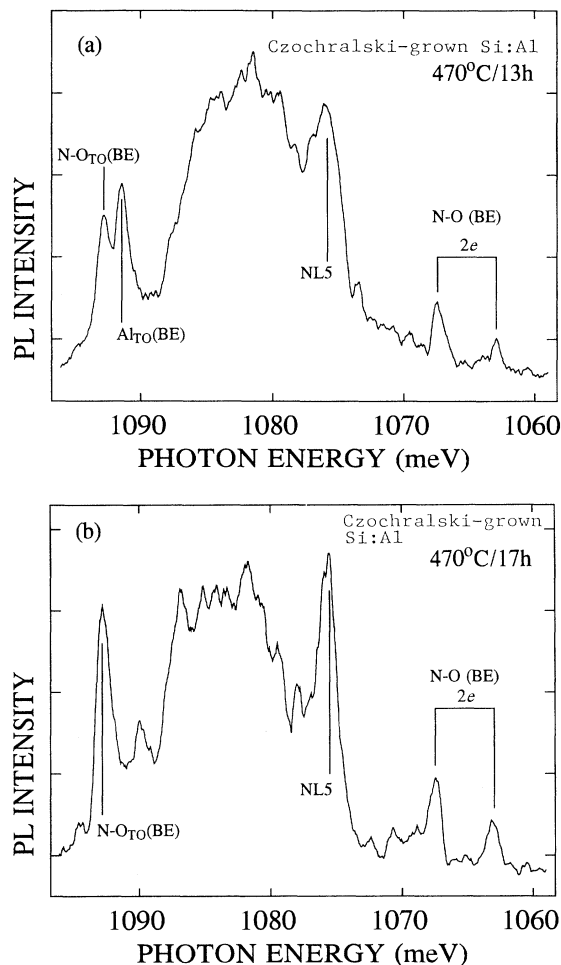


FIG. 5. Photoluminescence from N-O complexes: the PL spectrum as recorded for a Cz-Si:Al sample following a heat treatment at 470°C for (a) 13 h and (b) 17 h. The TO replica as well as two-electron ($2e$) transitions are indicated.

Following their observation, the generation kinetics of the NL_j lines during heat treatment at 470°C have been studied. The results suggest the mutual correlation of all four lines; from Fig. 7 a clear coincidence may be concluded of the actual development of the two more energetic lines, PL-Si-NL2 and PL-Si-NL3. In addition to the PL spectra in zero magnetic field, Zeeman measurements have been performed on the NL_j lines. For magnetic field values up to 5 T and with the emission being monitored along the field direction, no splitting of any of the NL_j lines could be observed. One should note here that the Zeeman splitting of an electron with spin $S = \frac{1}{2}$ and $g_e = 2$ at 5 T (0.6 meV) would be easily observable under the available experimental conditions.

IV. DISCUSSION

A. Role of acceptor doping

In the current study all the TD-related photoluminescence bands have been studied. Special attention has

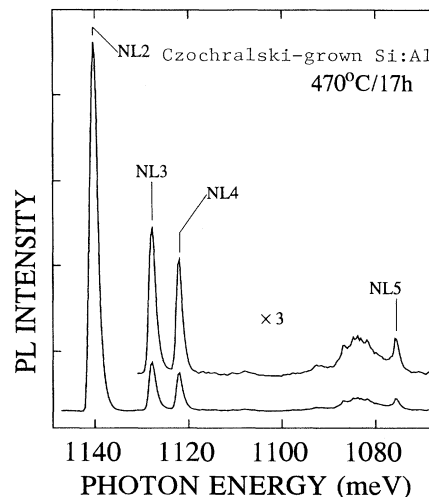


FIG. 6. Photoluminescence spectrum of a Cz-Si:Al sample after an anneal for 17 h at 470°C. The PL-Si- NL_j lines ($j = 2, 3, 4,$ or 5) are indicated.

been paid to any influence which a different acceptor doping might have on the occurrence of PL lines. As in our previous study,¹⁵ it can be concluded from Fig. 1 that the difference of TD^0 (BE) luminescence between aluminum- and boron-doped material is minor and can at most be seen in the generation kinetics. No influence can be observed on the energy positions of individual PL components of the band.

The effect of acceptor doping seems to be even smaller for the two other prominently TD-related PL bands, O_j and O'_j . As evidenced by Figs. 2 and 3, they are, both spectroscopically as well as in their overall generation kinetics, identical regardless of a dopant. This suggests that these emission bands are related to defects formed without participation of an acceptor atom. Such a notion is important in view of the fact that the O_j and O'_j bands appear for somewhat longer annealing times than the TD^0 (BE) lines, and could therefore be linked to the removal of acceptors and, as such, considered to be a side effect of the TD generation.

In contrast to the TD^0 (BE), O_j and O'_j PL described above, differences between acceptor doping can be seen in the formation kinetics of the new photoluminescence (PL-Si- NL_j) lines, and of PL from N-O complexes and acceptor BE's. While the presence of the NL_j lines in boron-doped silicon cannot be absolutely excluded at this stage, their kinetics—see Fig. 7—could only be studied in Al-doped samples. The situation is more complicated for the N-O complexes which could be observed here only in Al-doped material, whereas they are not aluminum related. The enhanced intensity of N-O PL could in this case be due to a different behavior of the Fermi level in both materials: for Al doping not only are the acceptors removed faster from their isolated substitutional sites—see Fig. 4—but also interstitial aluminum itself is a (double) donor with its $+/+ +$ level located within the forbidden gap of silicon.¹⁶ This will push the Fermi level still higher and could therefore seriously alter the (steady)

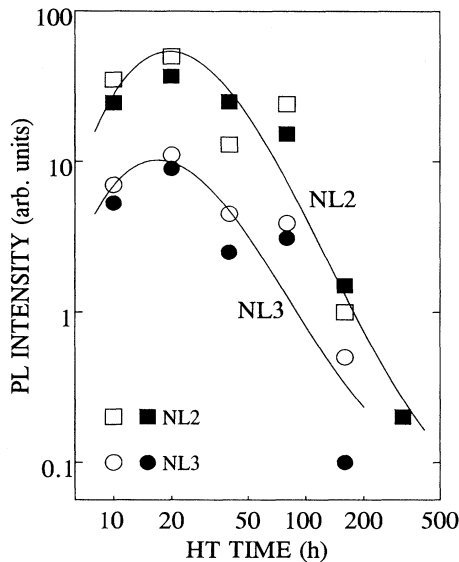


FIG. 7. Generation kinetics during heat treatment at 470 °C of the PL-Si:NL2 (\square) and PL-Si-NL3 (\circ) lines. The measurements were performed on two samples—open and closed symbols, taken from the same ingot of aluminum-doped Czochralski-grown silicon. The curves through the points serve as a guide to the eye.

charge states of defects in comparison to the situation for B-doped material. It is possible that the same effect is also responsible for the observation of the NL $_j$ lines in Al-doped samples only.

B. Origin of the O_J and O'_J bands

The idea that the O_J and O'_J bands are (directly or indirectly) related to thermal donors is generally accepted. Nevertheless, three different interpretations exist at the moment as to their detailed origin—see Refs. 5, 6, 7 and 8. Weber and Queisser⁵ identified the O_J band as free-to-bound (FB) transitions between the bound electrons of particular first thermal-donor ionization levels and free valence-band holes. The O'_J band, observed as a single line, was ascribed by them to a zone-center optical phonon (O^I) replica of the strongest O_J line. However, more detailed studies^{6–8} strongly criticized the FB interpretation pointing out that in silicon this transition type is improbable. Furthermore, the O'_J band contained components which could not be visualized as O_J replicas. In the present study we note that if the individual O_J lines were to be directly identified with separate TD species, its line structure should transform upon heat treatment. As can be seen from Fig. 3, the O_J band looks very similar in two different samples; it is unlikely that such a situation could be accidental. Second, the half-width of the O_J and O'_J lines (≈ 1.0 meV) is smaller than expected for FB transitions.

Dörnen and Hangleiter⁶ suggested to identify the O_J and O'_J bands as donor-acceptor pair recombinations (DAP's) between, respectively, the first and second TD ionization levels and a (substitutional) acceptor. The agreement of the energy values of the emissions could be obtained by taking donor-acceptor Coulomb interaction into account. The present study provides direct evidence that the DAP identification cannot be correct, since the O_J (and O'_J) bands are found to be identical for materials doped with different acceptors—see Fig. 3. A difference, roughly equal to the difference between the ionization energies of boron and aluminum (≈ 11 meV), would be expected for DAP recombination. Furthermore, in case of aluminum doping, the O_J (and hence also the O'_J) band should decay much faster upon annealing since, as shown in Fig. 4, the concentration of substitutional acceptors is diminishing in this case at a higher rate. Contrary to this, the O_J and O'_J generation kinetics are identical in both kinds of materials—see Fig. 2.

Finally, recent studies^{7,8} identify the O_J and O'_J bands as bound-exciton and bound-multiexciton-complex recombination at two (different) kinds of isoelectronic binding centers formed as a result of the thermal-donor transformation process. In this interpretation the relation of both bands to TD's would only be indirect: the O_J and O'_J bands were observed for annealing times when TD's have been transformed into electrically neutral clusters capable of binding (multiple) excitons, with the O'_J band appearing as a followup of the O_J . Data obtained in the current study also contradict this interpretation. From Fig. 2 it can be concluded that, regardless of the dopant, both PL bands are coincident. Further evidence is provided by Fig. 8 where the combined PL data are plotted together with results of the TD generation kinetics (based on resistivity measurements). As can be seen, the O_J and O'_J bands indeed appear somewhat later than the TD⁰(BE) lines, but are not anticoincident with TD's themselves. This notion is supported by results obtained by Weber and Queisser.⁵ Taken together, there seems to be enough evidence in favor of relating the O_J and O'_J bands to the TD's themselves, and not to neutral centers into which TD's could be transformed upon prolonged heat treatment.

Summarizing, one is bound to conclude that none of the so-far proposed interpretations of the O_J and O'_J bands appears to be correct. A microscopic identification of the defects responsible for these lines is needed. It should be able to account for the following features of the O_J and O'_J bands.

- (1) The small linewidth of the O_J and O'_J bands of ≈ 1.0 meV is typical for PL lines of excitonic origin.
- (2) The O_J and O'_J bands cannot be attributed to DAP recombination, since their line position is independent of the actual acceptor dopant in the sample.
- (3) The O_J and O'_J bands are linked to TD's, and not to TD aftermath.
- (4) Since the O_J and O'_J bands consist of a few components only, these cannot be *directly* related to TD species. Also, the annealing-time development of these

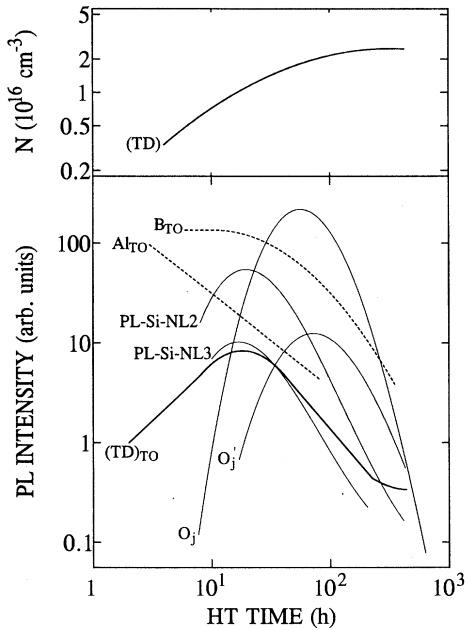


FIG. 8. Combined dependence of all TD-related PL bands investigated in this study on the annealing time (lower part). The intensities of individual PL bands have been scaled to equal laser power. In addition, the TD development kinetics are given as determined on the basis of resistivity measurements on the material used in this study (upper part).

components does not resemble that of TD species as observed by IR absorption.

(5) Most probably the O_j and O'_j bands anticoincide with the $TD^0(\text{BE})$ lines; one should note here that the $TD^0(\text{BE})$ lines vanish sooner with annealing time than the actual decay of TD^0 's.

A possible interpretation could be looked for within the framework of TD-related two-electron ($2e$) transitions. Transitions of this type will be more probable for systems with considerable overlap between the wave functions of the exciton and electron, both localized at the same center. Shallow EMT donors with considerable delocalization easily fall into this category and indeed $2e$ transitions have in such cases been observed. Here, three further remarks should be made in view of the delocalized character of the TD electron. First, one may expect a significant interaction between this electron and the electron of the bound exciton. As a result, the ground-state energy of the thermal-donor electron can be significantly shifted. Second, it is possible that the TD electron has sufficient momentum so that phonon participation may no longer be required for momentum conservation. In this case, $2e$ transitions could become more intense. Finally, one expects the $2e$ transition probability to depend on the effective lifetime of TD-bound electrons. Upon prolonged heat treatment, the Fermi level rises due to the increase of the TD^0/TD^+ population ratio. This will lead to an increase of the effective lifetime of electrons localized at shallow TD^0 centers. In this way one could un-

derstand why the O_j and O'_j bands appear for only somewhat longer heat-treatment times and grow in intensity with a simultaneous decay of the $TD^0(\text{BE})$ band which would, in our interpretation, correspond to the principal bound-exciton transition leaving the TD^0 center in its ground state.

C. Nitrogen-oxygen (N-O) complexes

The observation in this study of PL bands related to the so-called N-O complexes was surprising. The N-O BE luminescence was reported by Steele, Lenchyshyn, and Thewalt,¹⁰ its identification as $2e$ transitions related to N-O complexes was possible on the basis of earlier published IR absorption data.⁹ While the mutual correlation of the above-mentioned PL and IR absorption data certainly appears correct, the identification of the center involved as consisting of oxygen and nitrogen was based on production conditions only. The possibility of direct involvement of nitrogen in these complexes has been investigated and criticized by Griffin *et al.*¹⁷ The current study undermines such possibility further, since the investigated samples were neither intentionally doped with nitrogen, nor exposed to the high-temperature preannealing in nitrogen atmosphere. In view of the apparent confusion of this issue, the problem of the role of nitrogen and also the actual identification of the N-O complexes is at the moment investigated in a combined PL, IR absorption, and magnetic-resonance study. Here we will constrain ourselves to the observation that, while the existence of N-O-related PL in boron-doped material cannot be excluded, the centers could really be observed and studied only in aluminum-doped samples. In addition to the two lines visible in Fig. 5 at 1067.4 and 1063.0 meV, yet one more band, at 1058.1 meV, could be found for longer annealed material. The observed bands can be identified as a superposition of $1s \rightarrow 2s$ and $1s \rightarrow 2p^0$, $1s \rightarrow 2p^\pm$, and $1s \rightarrow 3p^\pm$, respectively, corresponding to the G , F , and C STD species.

D. Identification of Si-NL j photoluminescence lines

The four PL lines (Si-NL2 to Si-NL5), as listed in Table I, were observed only in aluminum-doped material, although we have some indications that the most prominent line, PL-Si-NL2, can be also generated upon boron implantation of Czochralski-grown silicon substrates.

The Si-NL2 line has an energy very close to indium-related BE recombination whose no-phonon (NP) transition occurs at 1140.76 meV.¹⁸ Although an accidental contamination of our high-quality starting material with indium was not very likely, this possibility was investigated. Figure 9 presents direct experimental comparison of the NL2 and $In_{NP}(\text{BE})$ lines, with the difference in line position clearly exceeding the instrumental resolution. At the same time, as can be seen from Fig. 6 and Table I, the NL j lines have small linewidths and symmetric line shapes. In view of this, they most probably originate from either excitonic or internal transitions. The absence of splitting or broadening of the NL j lines for magnetic-field values up to 5 T further contradicts a possible inter-

TABLE I. Spectroscopic parameters of the four photoluminescence lines labeled PL-Si-NLj ($j=2, 3, 4, \text{ or } 5$).

Line	Line position		Half-width ^a (meV)	Sample
	(meV)	(μm)		
PL-Si-NL2	1140.43 ^b	1.08719 ^c	0.3	Cz-Si:Al, Cz-Si:B(?)
PL-Si-NL3	1127.7 ^d	1.0995 ^e	1.2	Cz-Si:Al
PL-Si-NL4	1121.8 ^d	1.1052 ^e	1.1	Cz-Si:Al
PL-Si-NL5	1075.5 ^d	1.1528 ^e	1.3	Cz-Si:Al

^aFull width at half-height.

^b ± 0.05 meV.

^c ± 0.00005 μm .

^d ± 0.1 meV.

^e 0.0001 μm .

pretation of the NLj lines in terms of donor-acceptor recombination or free-to-bound emission.

The most likely candidate which could be responsible for the internal transitions is interstitial aluminum which is generated by the annealing process—see Sec. IV A. When considering the identification of the new lines with BE recombinations one has to conclude, on the basis of the development kinetics of the most prominent PL-Si-NL2 and PL-Si-NL3 lines—see Fig. 7—that the possible candidates for the center binding the exciton should be searched for within the TD family. Moreover, since the PL lines can be (exclusively) observed in aluminum-doped material, the exciton trap is either aluminum related, or its appearance is caused by a high position of the Fermi level, which is characteristic for Al-doped samples. In view of the above, two plausible identifications of the PL-Si-NLj lines may be mentioned:

(1) Exciton bound to a neutral $\text{Al}^+\text{-TD}^-$ complex. The possibility that such complexes are formed in the material used in this study is quite realistic. The existence of a negative state of the TD center¹⁹ should certainly be influenced by the Fermi-level position, which is, in this case, controlled by interstitial aluminum-donor formation. The diffusion constant for an interstitial impurity could be sufficiently high to form donor-acceptor pairs as a result of the long-range Coulomb interaction. If this identification is assumed, the NLj lines would only be observed in aluminum-containing material; the investigations currently in progress should give a definitive answer.

(2) TD^- bound exciton. Such an identification appears rather improbable since the m_h/m_e ratio of effective hole and electron mass is, for silicon, close to unity. Bound-exciton recombination at ionized donors or acceptors is expected to occur if this ratio is much larger than unity, in analogy with the H_2^+ molecule. However, BE transitions at a negative TD state could perhaps still be probable due to charge unbalance.

The Zeeman measurements provide evidence that the PL-Si-NL2 line involves spinless states. In view of this, the binding of an exciton should in both cases be such as to quench the orbital momentum of the valence-band-like hole in order to form an excited singlet ($J=0$) state. This would most probably require a model of an exciton

with a deeply bound hole. Further, the electron-hole exchange coupling parameter would have to be negative, in order to place the excited singlet state below the excited triplet.

Finally, it may be mentioned that it is also possible to interpret NL5 as a O^Γ phonon replica of the most prominent NL2 line. Yet another possibility would be to identify NL5 as a TO phonon replica of a $2e$ N-O transition, while NL3 and NL4 could correspond to no-phonon N-O-related $2e$ lines (with their TO replicas at 1067.4 and 1063.0 meV). Further studies are required to provide definitive identifications.

V. CONCLUSIONS

The generation kinetics of TD-related PL bands in boron- and aluminum-doped silicon samples have been studied over a large range of heat-treatment times up to 600 h. The $\text{TD}^0(\text{BE})$, O_j , and O'_j bands, bound-exciton $2e$

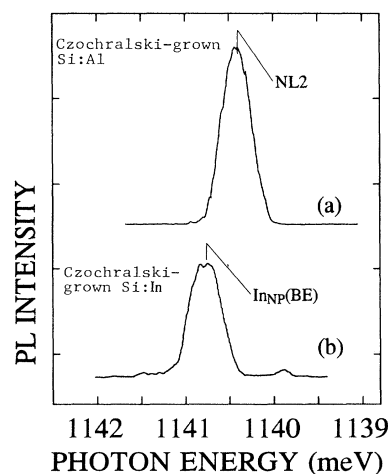


FIG. 9. Comparison of the PL-Si-NL2 line with indium-bound exciton emission, $\text{In}_{\text{NP}}(\text{BE})$; PL spectra were recorded for (a) aluminum-doped Czochralski-grown silicon substrates annealed for 17 h at 470°C , and (b) indium-doped Czochralski-grown silicon substrates.

replicas of N-O-related PL, as well as acceptor-bound-exciton emission have been investigated. In view of the results of the study, the influence of aluminum doping on the generation of thermal donors was found to be of secondary importance manifesting itself, most probably, only via a faster rise of the Fermi level upon annealing. On the basis of new experimental results an interpretation of the O_j (and O'_j) bands in terms of TD-related two-electron transitions has been proposed. The observation in aluminum-doped samples of the PL bands previously ascribed to $2e$ transitions at nitrogen-oxygen complexes clearly requires further investigations. Also, for

aluminum-doped material more TD-related PL bands have been observed. A possible origin of this emission has been proposed.

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