Materials Science Forum Vol. 83-87 (1992) pp. 407-412

SILICON THERMAL DONORS: PHOTOLUMINESCENCE AND MAGNETIC RESONANCE STUDY OF BORON- AND ALUMINUM-DOPED SILICON

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

ABSTRACT

The generation of thermal donor centers (TD's) in boron- and aluminum-doped Czochralski-grown silicon as monitored by photoluminescence and magnetic resonance has been compared. In photoluminescence the TD-bound excitons were investigated; the results were examined against the magnetic resonance data on the development of Si-NL8 and Si-NL10 TD-related EPR spectra. The results of the photoluminescence study provide evidence that the generation of the TD centers is independent of the original (acceptor) doping of the material. At the same time the rate of the acceptor loss is clearly different with the aluminum atoms being much faster removed from their substitutional positions. Taken together, the results of the study indicate that the different TD generation kinetics in Al- and B-doped Czochralski silicon as evidenced by EPR measurements should be attributed to different behavior of the Fermi level position in these two materials rather than to real differences in the generation of TD centers.

1. Introduction

Silicon thermal donors (TD's) continue to be one of the most puzzling issues of the defect physics of silicon. In spite of concerted effort by both experimental and theoretical physics no consensus could be reached neither on the core structure of this evidently extended defect nor on the growth-development mechanism responsible for its multispecies character. Nevertheless a vast amount of evidence has been gathered and several aspects of TD centers and related phenomena could be clarified [1]. The fingerprints of TD centers were identified by most of the experimental techniques applied in semiconductor materials science. Among those the most direct information was provided by the infrared absorption spectroscopy where two TD-related ionization series were identified [2]. More information on the multispecies character of TD's was obtained from the EPR/ENDOR studies where two spectra namely Si-NL8 and Si-NL10 were found to be TD related [3]. More recently further confirmation of the multiple nature of the centers came from photoluminescence (PL) spectroscopy as the luminescence lines originating from TD-bound excitons (BE's) have been identified and studied [4].

In the present study the TD generation kinetics, as visualized by TD-bound exciton luminescence, has been followed for boron- and aluminum-doped Czochralski-grown silicon. The results were compared with data for the same material obtained from magnetic resonance studies. The objective of the study was to gain new insight into the TD issue by intercorrelation of the information provided by two independent techniques sensitive to different charge states of the same defect. In this case the magnetic resonance spectroscopy delivers information on paramagnetic states of thermal donors: the Si-NL8 spectrum on TD^+ [5] and, following a somewhat speculative identification, the Si-NL10 spectrum on the overcharged TD^- thermal donor state [6]. On the other hand the information obtained from optical measurements would come from the photoluminescence of excitons bound to the neutral TD^0 state of thermal donors.

2. Experimental

In the present study two kinds of samples were used with the following starting parameters:

1. boron-doped Czochralski-grown silicon: $[B_s] = 1.3 \times 10^{16}cm^{-3}$, $[O_i] = 1.3 \times 10^{18}cm^{-3}$, $[C] \leq 10^{15}cm^{-3}$
2. aluminum-doped Czochralski-grown silicon: $[Al_s] = 4 \times 10^{15}cm^{-3}$, $[O_i] = 1.3 \times 10^{18}cm^{-3}$, $[C] \leq 10^{15}cm^{-3}$

Prior to the experiment the samples were given the standard initial heat treatment of 1/2h, 1350°C in ambient gas atmosphere in order to disperse the oxygen and ensure the same, well-defined starting conditions. This heat treatment had no effect on the level of acceptor concentration. Following the initial heat treatment, thermal donor centers were subsequently generated in the samples by annealing them for various time intervals at a temperature of 470°C. After each annealing stage photoluminescence spectra have been measured.

The photoluminescence measurements were performed at 4.2 K. Luminescence was excited with a cw Ar^+-ion laser operating at 514.5 nm. 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 nitrogen-cooled Ge detector (North Coast EO-817). The detector output was amplified using conventional lock-in techniques. The signals were then digitized and fed into a computer for further data acquisition.

3. Results and discussion

As has already been mentioned in the introduction the magnetic resonance investigations revealed two TD-related EPR spectra labelled Si-NL8 and Si-NL10. Following this conclusion the generation kinetics of these centers has been investigated in different materials [3, 7]. The studies have shown that both centers could be generated in (originally) p-type material regardless of the actual type of acceptor while in n-type only Si-NL10 centers could be observed. The most important 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. Since at the same time the actual microscopic identification of the Si-NL10 center is a matter of considerable controversy this particular finding promoted the idea of relating this center to some form of aluminum-based thermal (single?) donor or Al-TD complex. Such idea was further supported by the fact that the hyperfine interactions with the ^{27}Al nuclei have indeed been observed for, at least some, Si-NL10 centers [8, 9]. Simultaneously the possibility that in the aluminum-doped material some distinctly different from *normal* TD's form of thermal donor centers is generated has also been investigated by infrared absorption [10].

In addition to the above mentioned information on the generation kinetics of TD centers the EPR studies revealed also that, while the individual TD species could not be directly resolved, the multispecies character of thermal donors manifested itself in nonhomogeneous character of both spectra and the so called *g-shifting effect* as the relative concentration of the individual species varied. The g-shifting effect is experimentally observed as the lowering of anisotropy of both spectra for longer annealing times and can be conveniently expressed as a change of the splitting of two resonance lines as observed in the [111] crystallographic direction. Fig.1 summarizes briefly the EPR results; Fig.1(a) compares the generation kinetics of Si-NL8 and Si-NL10 centers in two types of material used in the current study; in Fig.1(b) the gradual decrease of the anisotropy of the Si-NL8 (TD^+) spectrum for these materials is depicted.

The generation kinetics as deduced from EPR measurements has to be treated with certain 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 TD^{++} (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. Therefore the EPR-based TD kinetics not only reflects the generation process of thermal donors but also the change of the Fermi level position. Since the process of the loss of acceptors has been found to occur in parallel to TD generation [11], the actual position of the Fermi level for a given heat-treatment time will be influenced by two different processes: creation of donors and annihilation of acceptors. The EPR experiment is not capable of separating the two contributions.

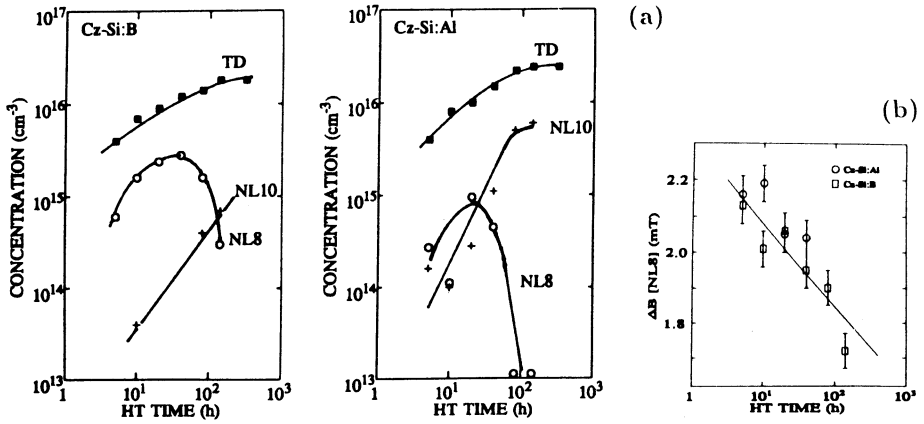

Figure 1:(a) *Generation kinetics of TD's (on the basis of resistivity measurements) and TD-related EPR centers, and* (b) *the annealing time dependence of g-shifting for the Si-NL8 EPR spectrum in Czochralski-grown silicon.*

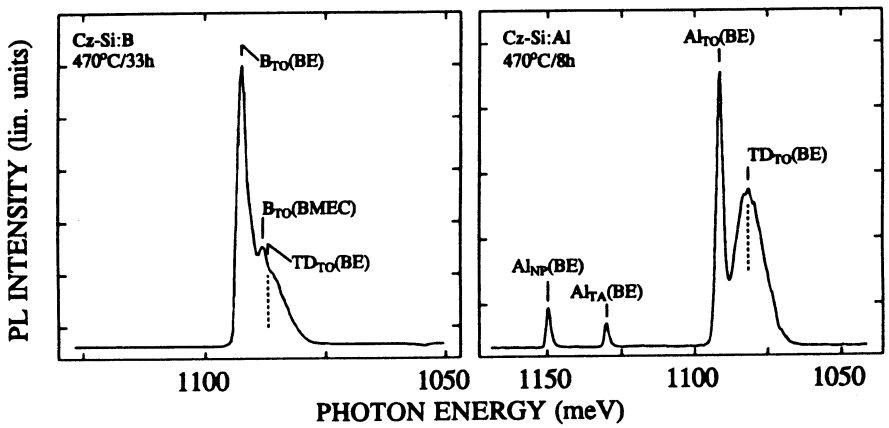

Figure 2: *Photoluminescence spectra of boron- and aluminum-doped Czochralski silicon under Ar^+-excitation.*

A very similar kind of argument can also be made for the TD generation kinetics as derived from infrared absorption studies [2]. Also in this case the level at which the absorption is to be studied has to be populated, i.e., the Fermi level has to be sufficiently high. In case of p-type material this effect may be a source of severe deformation of the results.

The photoluminescence experiment, performed under nonequilibrium conditions of laser excitation, is free from the above outlined limitation. One can therefore expect that TD generation kinetics derived from PL measurements should be far more reliable than those based on resistivity, EPR or IR absorption data.

Fig.2 presents the PL spectra as recorded for boron- and aluminum-doped material. The acceptor and TD-related luminescence lines are marked. In both cases the TO replica of the TD-bound exciton line may clearly be recognized in the vicinity of the strong acceptor lines. The spectra are in full analogy with earlier data on TD luminescence [4, 11] which were able to separate the contribution from the individual thermal donor species. A similar goal has also been attempted here and is illustrated in Fig.3. Fig.3(a) presents details of the no-phonon (NP) TD-bound exciton luminescence for boron-doped silicon. As can be seen in the present experiment some of the earlier identified lines [4] could be resolved and are marked in the figure. For the sake of completeness also the positions of boron-related exciton lines are depicted.

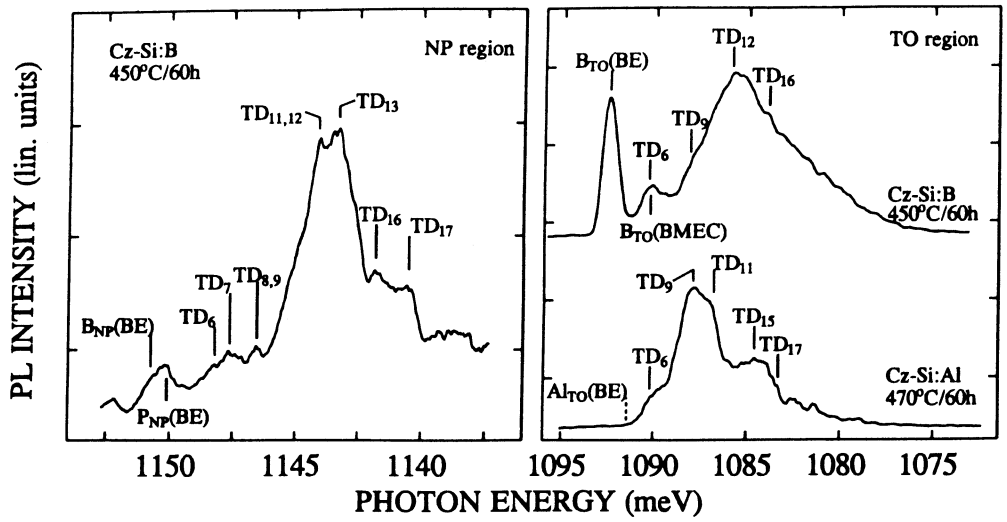

Figure 3: *TD-bound exciton photoluminescence spectra of Czochralski (Cz) silicon:* (a) *NP range, Cz-Si:B,* (b) *TO replica range, Cz-Si:B and Cz-Si:Al. Individual TD species at the energies identified earlier by Steele and Thewalt [4] are marked.*

Fig.3(b) shows detailed spectra as recorded for B- and Al-doped silicon in the TO replica region of the TD-bound exciton luminescence. For the B-doped sample the same TD species (as in the NP region) can be accounted for, thus supporting the identification. Additionally, a strong signal of boron-bound excitons, reflecting the concentration of substitutional boron acceptors, is present. Also for the Al-doped material, some of the TD species identified earlier may be resolved. At the same time the aluminum-bound exciton line is no longer visible.

Upon annealing the relative concentration of individual TD species changes as does the total number of thermal donor centers. In the less detailed luminescence spectra this process may be visualized by the shift of the TD-related emission band towards higher photon energies and by a change of its total intensity. Both effects are illustrated in Fig.4. Fig.4(a) presents the shift of the center of the TO replica of the TD-related luminescence for two kinds of samples used in the experiment. As can be seen both materials behave in a similar manner and the shift of the luminescence towards higher energies resembles very much the shift of g-values of the Si-NL8 and Si-NL10 spectra towards lower anisotropy. In Fig.4(b) the annealing time dependence of the intensity of the TD band is compared for two kinds of acceptor dopants. It coincides well with the behavior as expected for TD centers on the basis of IR absorption studies. It should be noted that the kinetics appears to be a little slower in the aluminum-doped material. However, the effect is small and as such can probably be attributed to a somewhat lower oxygen contents (TD formation rate is known to depend on the fourth power of the initial oxygen concentration).

The results of the current study as depicted in Figs.2,3, and 4 indicate that the generation of thermal donors is not dependent on the actual acceptor dopant. In more detail the study shows that the aluminum doping has no accelerating effect for TD kinetics which is (predominantly) governed by the initial oxygen concentration. For both boron and aluminum doping the generation kinetics of TD's as monitored by luminescence proceeds in a very similar manner. This conclusion is illustrated in Fig.3. As shown in this figure, identical TD species are formed in both materials, thus indicating identical TD generating processes. It should be mentioned here, that such conclusion does not rule out the possibility that in aluminum-doped silicon in addition to *normal TD's* also some other aluminum-based form of TD-like centers is formed. This however seems to be rather unlikely in view of very similar generation kinetics of *normal*

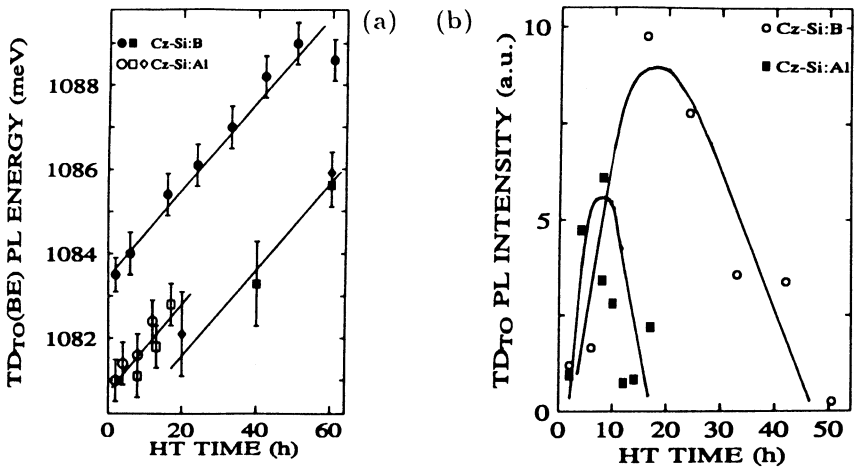

Figure 4: *The annealing time dependence of the TD-bound exciton emission band in the TO region:* (a) *the shift of its center, and* (b) *the change of its total intensity.*

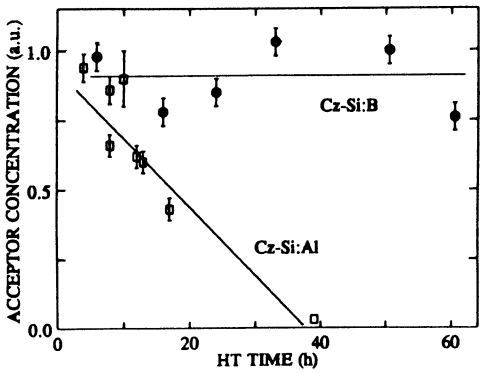

Figure 5: *Decay of acceptor-bound exciton luminescence for the Czochralski silicon as used in this study.*

TD's for both materials.

The above conclusion appears in contradiction to the results of IR absorption studies [10] as well as to the resistivity and magnetic resonance findings as summarized by Fig.1. This apparent contradiction may be understood in view of the remarks presented at the beginning of this section. In contrast to the luminescence of bound excitons, all the above mentioned techniques are sensitive not only to the generation of TD centers 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 also by yet another mechanism, independent from the generation of TD's. Such mechanism could be provided by gradual removal of acceptors from the substitutional positions and has indeed been concluded to take place in parallel to the generation of TD's [11]. In the present study it is further confirmed as can be concluded from Fig.5, where the intensity of acceptor-related luminescence is depicted as a function of the annealing 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 of the seemingly catalytic role of aluminum in the TD generation process.

Taken together the results of the current study argue very much against the idea that in aluminum-doped silicon a different kind of TD centers is being created.

Acknowledgment

This project has been partially sponsored by the Netherlands Foundation for Fundamental Research on Matter (Stichting voor Fundamenteel Onderzoek der Materie, FOM).

References

[1] A. Bourret, in *Proceedings of the Thirteenth International Conference on Defects in Semiconductors,* edited by L. C. Kimerling and J. M. Parsey, Jr. (TMS-AIME, New York, 1985), p.129.

[2] P. Wagner and J. Hage, Appl. Phys. A **49**, 123 (1989).

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

[4] A. G. Steele and M. L. W. Thewalt, Can. J. Phys. **67**, 268 (1989).

[5] K. M. Lee, J. M. Trombetta, and G. D. Watkins, in *Proceedings of the International Conference on Microscopic Identification of Electronic Defects in Semiconductors, San Francisco, 1985,* edited by N. M. Johnson, S. G. Bishop, and G. D. Watkins (MRS, Pittsburgh, 1985), p.263.

[6] H. H. P. Th. Bekman, T. Gregorkiewicz, and C. A. J. Ammerlaan, Phys. Rev. Lett. **61**, 227 (1988).

[7] H. H. P. Th. Bekman, T. Gregorkiewicz, D.A. van Wezep, and C. A. J. Ammerlaan, J. Appl. Phys. **62**, 4404 (1987)

[8] T. Gregorkiewicz, H. H. P. Th. Bekman, and C. A. J. Ammerlaan, Phys. Rev. B **38**, 3998 (1988).

[9] J. Michel, N. Meilwes, J. R. Niklas, and J.-M. Spaeth, in *Shallow Impurities in Semiconductors 1988*, (Institute of Physics, Bristol, 1989), p.201.

[10] M. Claybourn and R. C. Newman, Mater. Sci. Forum **38-41**, 613 (1989).

[11] A. C. T. Drakeford and E. C. Lightowlers, Mat. Res. Soc. Symp. Proc. **104**, 209 (1988).