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ELECTRONIC STATES OF THERMAL DONORS IN SEMICONDUCTORS

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ABSTRACT

In the paper the most recent information on thermal donor (TD) centers as obtained by magnetic resonance, infrared absorption and photoluminescence spectroscopy is reviewed. Special attention is given to the results and problems for which no satisfactory explanation can be given at the moment. It is shown that a wealth of new information can be revealed by mutual correlation of the results obtained by different experimental techniques. To this end a study of bistability of thermal donors in silicon and germanium, and multiplicity of electronic states of TD's is discussed in more detail. Finally, novel possibilities as offered for the TD studies by double excitation spectroscopy and observation of 2-electron transitions are mentioned.

1 Introduction

Thermal donors are among the most confused subjects of materials science of semiconductors in general and in silicon in particular. Already at an early stage of solid state technology development it has been recognized that when oxygen-rich silicon (or germanium) is exposed to isothermal annealing in temperature range 300-500°C electrically active centers of shallow donor character are generated. The centers, termed "thermal donors" (TD's), attain a considerably high concentration and can therefore strongly influence the electrical properties of the material. This renders them of practical importance in device manufacturing and stimulated research effort in the field. Naturally, although some work has been done in germanium, most of the available information concerns TD centers in silicon. Unfortunately, in spite of concerted effort by both experiment and theory, the TD issue remains open as, so far, no TD model capable of accounting for all the observed data could be proposed. This

follows from the fact that TD centers are rather unique in the complexity of their structure and, due to extended character, are difficult to access by experiment. Nevertheless, extensive evidence has been amassed and several particular aspects could be clarified. In the past, while almost all the experimental techniques have been applied, the most valuable contributions have been delivered by magnetic resonance, infrared absorption and photoluminescence spectroscopy. In what follows the major results as obtained by these methods will be briefly reviewed. Special emphasis will be given to these findings which, at this stage, lack satisfactory explanation.

2 Magnetic Resonance

Magnetic resonance spectroscopy is capable of providing structural information on microscopic scale. In the past several successful models of defect centers could be developed on the basis of data obtained by electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR). The EPR studies on heat-treated silicon revealed two TD-related paramagnetic centers - Si-NL8 and Si-NL10 [1]. The most important conclusion of this finding was an orthorhombic-I symmetry which could then be assigned to TD centers. Another significant observation was the g-shifting effect; the g values as determined for both centers were found to change in a semicontinuous manner upon prolonged heat treatment. This effect could later be related to the multispecies character of TD's, i.e. to the situation when there existed at the same time a family of several, very similar, TD species whose concentration varied considerably with duration of annealing. The angular dependence of g values for both centers is depicted in Fig.1; also the characteristic transformation of the spectra upon annealing time is indicated.

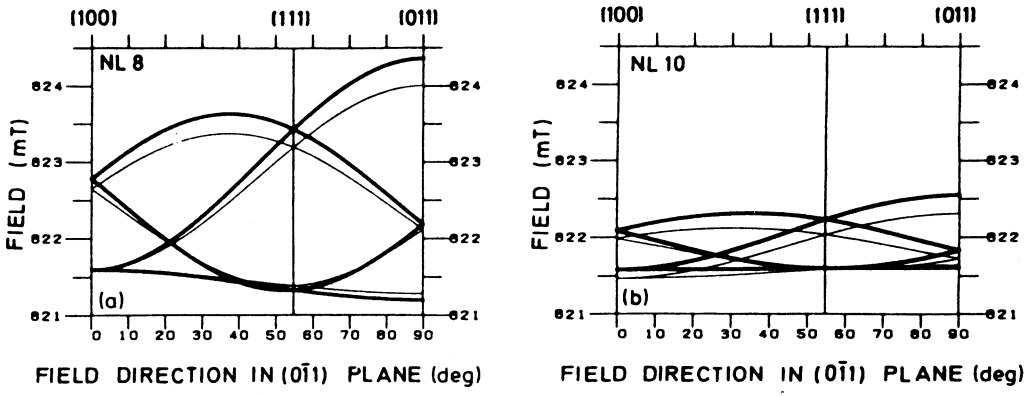

Figure 1: Angular dependence for the Si-NL8 (a) and Si-NL10 (b) EPR spectra, ν = 23 GHz. Thick and thin lines correspond to heat-treatment times of 10 and 100 hours, respectively.

Following the EPR results also ENDOR spectroscopy could be applied to TD studies. The experiments as conducted on both Si-NL10 [2] and Si-NL8 [3] revealed detailed information on the electronic structure of TD's. The most spectacular findings were the direct confirmation of the participation of oxygen and experimental evidence of the multispecies form. The ENDOR results have also shown

that while the overall symmetry of the TD center may appear as orthorhombic, small deviations from it toward monoclinic type are permitted.

In spite of the detailed information provided by magnetic resonance experiments it was not possible to propose a convincing structural TD model on their basis. This was a direct consequence of a very delocalized character of the center; in both cases only a few percent of the paramagnetic electron could be accounted for. At the same time EPR and ENDOR findings present us with several difficult problems which have to be answered before further progress in the understanding of the TD issue can be achieved. Here, while quite a few of these, such as aluminum or nitrogen participation, concern the interpretation of ENDOR data and distinction between hyperfine interaction with constituents of the extended defect and with ligand atoms, the most difficult question concerns EPR measurements and relates to the existence of two different TD-related paramagnetic centers. One of them, Si-NL8, has been conclusively identified with the singly ionized TD^+ state [4]; the particular assignment of the other one, Si-NL10, remains unclear. A seemingly similar situation exists also in the EPR results of TD centers in germanium. However, in this case the second EPR spectrum could be identified as light-induced triplet state of the neutral charge state TD^0. Such an identification is not available for Si-NL10 since the ENDOR measurements conclusively assign S=1/2 spin value for this center. Once this possibility has been eliminated other identifications can be considered [5] and then the negatively charged TD^- state appears as the most reasonable candidate [6]. However, as a direct proof for the formation of such a state has not been obtained, it is fair to note that the identification of the Si-NL10 spectrum with the TD^- state remains, for the time being, speculative.

3 Infrared Absorption

So far the most detailed information on TD's has been delivered by infrared (IR) absorption spectroscopy [7] which was able to identify the excitation series of electrons bound to TD centers. On the basis of these measurements TD's were identified as shallow double donors whose excitation spectra could well be described within the effective mass approximation. Further, the IR spectroscopy was the first one to unravel the multispecies character of TD centers as the excitation series of up to 11 distinctly different types of donors could be identified. Their ionization energies were found to be within 69.2 and 49.9 meV, and 156.3 and 116 meV for the first and the second ionization levels, respectively. By comparing the spectra of samples exposed to different annealing, the generation kinetics of individual TD species could be followed and it was concluded that they were developing subsequently with "later", more shallow, species being most probably formed from the "earlier", deeper, ones. A more detailed investigation has disclosed that the first two thermal donors, TD1 and TD2, were exhibiting bistable behavior and, in samples with a certain position of Fermi level, could only be detected if upon cooling down from room temperature continuous band-to-band excitation was provided. Also some information on the TD ground state could be obtained; IR measurements performed under uniaxial stress revealed that the ground state wave function was constructed from a single pair of conduction band valleys only [8].

However, in addition to the above summarized wealth of information, the infrared spectroscopy of heat-treated Czochralski silicon presents us also with data which are more difficult to interpret. Besides the two already mentioned, yet one more shallow donor excitation series, termed *shallow thermal donors* (STD), has been identified. The STD series was first observed in photo-thermal ionization spectroscopy [9] and provisionally assigned to a family of oxygen-related shallow single-donor centers with the ionization energies of $\approx$ 35 meV. The importance of this finding was at first clearly underestimated due to the fact that STD's were detected with very low concentrations only. Later studies revealed, however, that STD's could be formed in concentrations comparable to those of TD's. In Fig.2 an IR absorption spectrum of an aluminum-doped Czochralski silicon sample is shown;

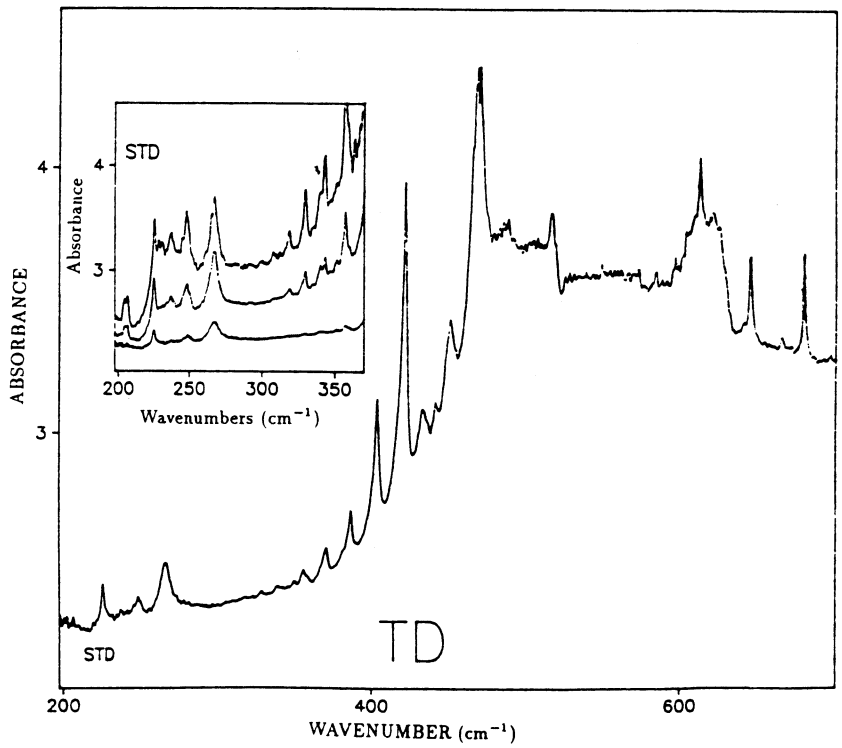

Figure 2: Absorption spectrum of Cz-Si:Al sample annealed for 14 h at 470°C. Individual absorption lines belonging to TD^0 and STD series are marked - after Ref.14.

absorption lines due to STD's as well as the first ionization level of TD's can be seen. The microscopic assignment of the STD series is at the moment puzzling. The seemingly plausible suggestion to correlate it with some (structural) modification of the TD center has to be disregarded as the possible involvement of such candidates as shallow acceptors (to account for a single-donor character) and nitrogen (to explain enhanced generation kinetics) has been contradicted by an experiment. In this context it has to be mentioned that a possible relation of STD's to TD's is further complicated by their opposite development trends: with increasing of the heat-treatment time TD centers become

more shallow while the STD's become deeper.

4 Photoluminescence

Photoluminescence (PL) spectroscopy was applied to TD studies only more recently. This was caused by the fact that, in spite of high sensitivity, it penetrates only a relatively small part of the crystal close to its surface. At the same time the concentration of oxygen (and TD's) is there considerably lowered by outdiffusion during heat treatment. Nevertheless several TD-related PL bands have been reported and one of these could be identified with excitons bound to the neutral charge state of the thermal donor TD^0 BE [10].

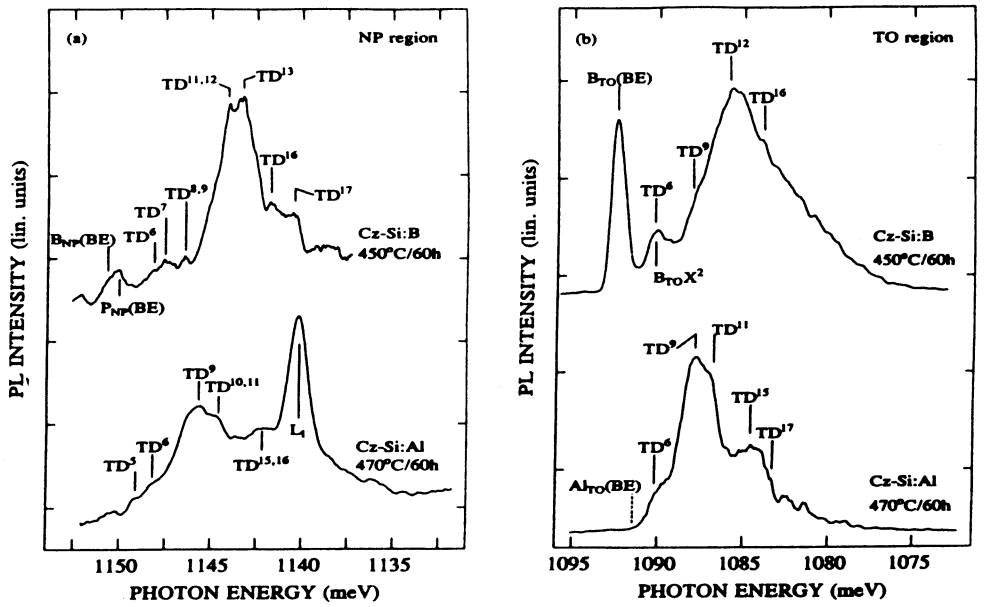

Figure 3: TD-bound exciton photoluminescence spectra of boron- and aluminum-doped Czochralski silicon: (a) NP range, (b) TO replica range. Individual TD species at the positions identified in Ref.10 are marked.

In Fig.3 the no-phonon (a) and optical-phonon-replica (b) BE PL spectra as obtained for boron- and aluminum-doped Czochralski-grown silicon are depicted. As can be concluded PL measurements present a direct experimental confirmation of the multispecies character of the TD centers with excitation lines of several species being clearly distinguishable. From the wavelength of the observed PL spectrum a very shallow exciton binding energy, of the value comparable to that of other shallow dopants as boron, aluminum and phosphorus, may be concluded. At the same time the results shown in Fig.3 argue against any participation of a dopant in the TD structure as identical positions of excitons bound to individual TD species are observed regardless of an impurity.

Besides the above discussed TD BE lines at least two more PL bands, termed O_J and $O_{J'}$, have

been positively identified as TD related. Their precise assignment, however, is not clear as three different interpretations exist at the moment. These comprise a donor-acceptor pair recombination involving TD, free-to-bound transition from the first and the second TD ionization level for the O_J and $O_{J'}$ band, respectively, and, finally, BE recombinations at isoelectronic centers created from TD's by extended annealing. Since none of these interpretations is convincing and can in some way be contradicted by experimental evidence [11], further interpretation effort is clearly required for the currently available PL spectroscopy data on TD's.

5 Correlation of Results Obtained by Different Techniques

As evident from the results briefly reviewed in preceding sections the information on TD's, although extensive, lacks sufficient understanding. One can expect that this situation could be considerably improved if results obtained by different techniques could be mutually correlated. Such an approach is usually difficult since in different experiments seldom the same state of the center is being probed. Nevertheless, correlations in the field of TD's have been successfully followed in the past.

One of the most successful results of this kind concerns the bistable behavior of TD centers in germanium. Following the identification of germanium TD's by IR absorption spectroscopy it has been noticed that the excitation lines due to the earliest species could only be observed if the investigated samples were cooled upon above-gap illumination. Subsequently the effect of bistability was investigated also by EPR: this resulted in a one-to-one correlation between germanium TD species as observed in EPR and IR absorption [12]. Since, as mentioned earlier, IR spectroscopy revealed bistability also for (the first two species of) silicon TD's, a similar correlation with Si-NL8 and Si-NL10 EPR spectra has been attempted. Here unfortunately, until the present time, no signs of bistable behavior could be detected in a magnetic resonance experiment. In a somewhat analogous experiment a direct correlation between the influence of illumination on the EPR and ENDOR spectra of the Si-NL10 center has been investigated. Also in this case, in view of the many uncertainties, the actual significance of the obtained results is not clear [13].

Also correlation of the evidence concerning the multispecies character of TD's has been studied. Here the mutual identification of the individual TD species as revealed by IR absorption and ENDOR has been attempted. The experiments, in which the development kinetics were followed, turned out to be very difficult and, consequently, a precise correspondence could not be established [13]. In contrast to that, in a recent study, a mutual correlation of the Si-NL10 centers and STD's has been obtained by comparison of their production kinetics [14]. The IR- and EPR-determined generation curves allowed for their mutual identification and the significance of this finding for the TD issue is presently considered. It should nevertheless be mentioned here that, in this particular case, only the correspondence with the overall EPR signal has been found and not with individual species of the Si–NL10 center. In addition to the NL10-STD correlation, in the same study the evidence of the bistable behavior of the deepest STD species has been obtained.

6 Further Correlations: Directions for Future Research

As illustrated by the examples given in the preceding section, in the situation in which the possibilities of direct application of various experimental techniques to TD studies seem to be exhausted, the search for mutual correlations between the existing experimental data proves especially informative. This trend should be continued and, in what follows, two further possibilities for the application of such studies in the field of TD's will be briefly discussed. In both cases early results are already available and appear to be very promising.

For the bound-exciton recombination at an isoelectronic center it may be possible that part of the recombination energy will be transferred to an electron already localized at the binding center. In such case, besides the principal BE line, also so-called *two-electron replicas* (2-e) are observed on the low-energy side at distances determined by the excitation energies of the electron localized on the center itself. Since those energies are usually determined in an absorption experiment, then, with parity requirements kept in mind, observation of 2-e transitions provides an elegant link between PL and IR absorption data. Fig.4 presents a successful observation of such transitions. The excitation lines

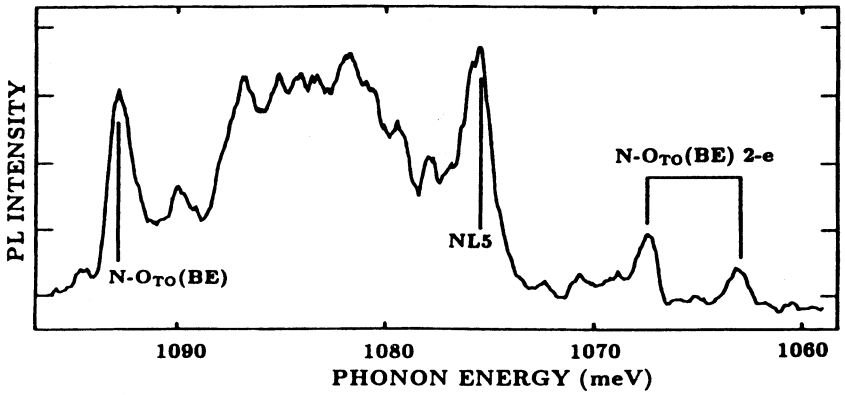

Figure 4: Two-electron transitions of so-called N-O complexes as observed in aluminum-doped Czochralski silicon.

have originally been identified with oxygen-nitrogen complexes [15] but, at this moment, their relation to TD centers seems to be firmly established [11] with the excitation energies fully coinciding with the earlier mentioned IR-detected STD series. Further, the research currently on the way, indicates that also the O_J and $O_{J'}$ PL series can be identified within the 2-e scheme involving excitation of TD-bound electrons.

Another very recent example of a successful cross-disciplinary study in the field of TD's are the results obtained by *Impact Ionization Spectroscopy* (IIPL). In this kind of experiment microwave heating of optically excited free carriers is applied in parallel to PL-generating laser excitation. In this sense IIPL constitutes a special case of double-excitation spectroscopy. Upon increasing the microwave power above a certain threshold the shallow states may be ionized. This can result in blocking of particular recombination mechanisms while enhancing deeper ones. When applied to the

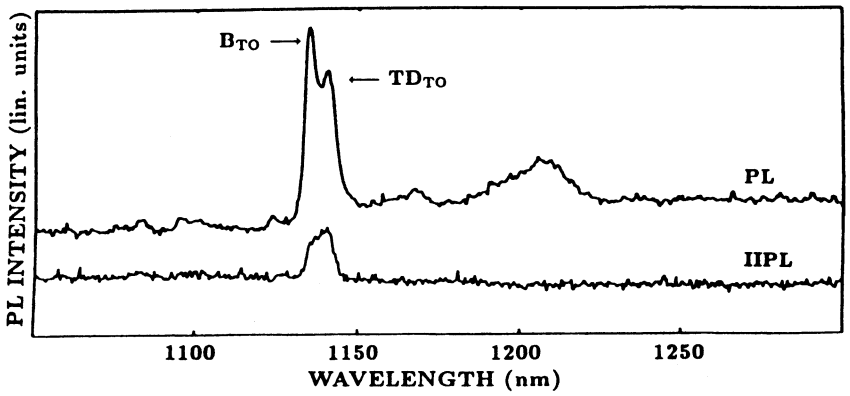

Figure 5: Photoluminescence (PL) and impact ionization photoluminescence (IIPL) spectra of Cz-Si:B, annealed for 60 h at 470°C.

TD BE system one can expect that, in view of its relatively low exciton binding energy, a decrease of the relevant intensity of the relevant PL band should be observable already for a rather low power level. Fig.5 presents the result of such an experiment; in the figure the microwave-induced changes of luminescence as observed for a boron-doped, heat-treated Czochralski silicon sample are compared with the PL spectrum. As can be concluded from the figure, application of microwave field leads to a clear few-percent increase of TD BE luminescence. Such a result is counter intuitive and indicates an existence of an efficient nonradiative recombination mechanism involving traps of very shallow character. While, as mentioned before, the result presented in Fig.5 is only preliminary and clearly requires detailed studies, it could, if further confirmed, provide a major support for the idea that a negative charge state of the TD center exists within the bandgap of silicon.

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