

11.4 Thermal double donors in c-Si

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A INTRODUCTION

This Datareview discusses the generation and properties of thermal double donors in oxygen-containing silicon crystals. A wide variety of assessment techniques have been applied to identify their presence, structure and associated energy levels and these properties are discussed.

B BASIC OBSERVATIONS

Thermal double donors, TDDs, are generated in oxygen-rich silicon, such as Czochralski-grown silicon with oxygen concentration near 10^{18} cm^{-3} , by heat treatment in the temperature range 350 to 550°C [1]. Over the past 40 years their structure and properties have been investigated intensively by many experimental (Hall effect, optical electronic and vibrational absorption, deep level transient spectroscopy, magnetic resonance) and theoretical methods.

Confirming an early supposition [2], the double-donor character of TDDs was first observed by Hall effect measurements [3] with reported energies of 61 and 135 meV for the first (0/+) and second (+/++) ionisations, respectively. A decrease of the energies with extension of the heat treatment was observed, but the resolution of the analysis, even with the method of differential evaluation [4], was too low to reveal additional details.

Measuring the optical absorption related to the hydrogen-like electronic excitations of the TDDs, and benefiting from the high resolution of typically 1 cm^{-1} , it was discovered that the thermal double donors constitute a family of centres. Components, often called species, develop successively upon increase of the heat-treatment time from minutes to hours. Species were individually identified and labelled TDD_n with, at present, $n = 1$ to 16. Excited states of the donors follow very well the predictions of the effective-mass theory. Donors are distinguished by differences in their ground state energies (alternatively expressed as central-cell correction or chemical shift), which decrease in a stepwise manner from earlier to later species. It is thus understood that the TDD family consists of several very similar centres, but each member still with its own distinct atomic structure. Transition energies for the excitation from the 1s ground state to excited states with effective-mass labels $2p_0$, $2p_{\pm}$, etc., are given in TABLE 1 [5–11]. In one case a centre called the α trap is reported as the first TDD-species [12], but without giving data on the ionisation energies; no evidence for its presence was revealed in other research [13]. Likewise, a species TDD7' with donor binding energy 55.8 meV is mentioned only occasionally [14]. From TABLE 2 it appears that the transitions labelled $2p_{\pm}$ and $3p_{\pm}$ for (TDD_n)⁺ are split into two components. A similar splitting was reported for the spectra of (TDD4)⁰ to (TDD6)⁰, however without numerical data being given [8]. Such a doublet structure was also observed for other double donors, e.g. for Mg⁺ [15] and the chalcogen pairs S₂ and Se₂ [16], and is attributed to lifting of the degeneracy of the excited state by central-cell correction and valley-orbit interaction (chemical splitting) [17].

With an evident correspondence to the infrared absorption the TDDs were detected and species were identified by photothermal ionisation spectroscopy (PTIS) [18,19].

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TABLE 1 Positions of the infrared optical absorption lines, in cm^{-1} , due to the electronic transitions from 1s ground states to effective-mass excited states for the thermal donors TDD1-TDD16 in the neutral state. Binding energies E_i in meV, are calculated by adding 3.12 meV to the 1s to $3p_{\pm}$ transition energy if observed, otherwise 6.40 meV to the 1s to $2p_{\pm}$ energy. Energy conversion: $1 \text{ cm}^{-1} = 0.123985 \text{ meV}$. Data from [9] and [11]; details on TDD0 and TDD7' are given in [32,45] and [14], respectively.

TDDn	$2p_0$	$2p_{\pm}$	$3p_0$	$3p_{\pm}$	$4p_{\pm}$	$5p_{\pm}$	E_i
TDD1	461	507		533	541		69.2
TDD2	442	488	494	514	522	528	66.8
TDD3	423	470	475	496	503	509	64.6
TDD4	405	451	456	477	485		62.2
TDD5	388	434	441	460			60.1
TDD6	372	417	423	443			58.0
TDD7	357	404	412	429			56.5
TDD8	343	388	395				54.5
TDD9	330	376	383				53.0
TDD10	319	363					51.4
TDD11	307	351					49.9
TDD12	293	338	346	362	372	378	48.3
TDD13	282	324	331	349	358	363	46.6
TDD14	270	311	319	335	346	350	45.0
TDD15	259	298	305	323	332	339	43.4
TDD16	247	286	292	312	320	327	41.9

TABLE 2 Positions of the infrared optical absorption lines, in cm^{-1} , due to the electronic transitions from 1s ground states to effective-mass excited states for the thermal donors TDD1-TDD9 in the positive charge state, $(\text{TDDn})^+$. Binding energies E_i in meV, are calculated by adding 12.48 meV to the average 1s to $3p_{\pm}$ transition energy if observed, otherwise 25.60 meV to the average $2p_{\pm}$ excitation energy. Energy conversion: $1 \text{ cm}^{-1} = 0.123985 \text{ meV}$. Data from [8] and [9].

TDDn	$2p_0$	$2p_{\pm}$		$3p_{\pm}$		$4p_{\pm}$	$4f_{\pm}$	$5p_{\pm}$	$6p_{\pm}$	E_i
TDD1	854.4	1044.3	1048.6	1155.3	1156.6	1187.4	1197.3	1211.1	1223.2	156.3
TDD2	806.3	991.7	998.2	1105.2	1107.2	1138.0	1147.0	1160.8	1173.6	149.7
TDD3	762.8	945.0	952.3	1057.7	1060.0	1090.1	1199.3	1113.2		143.8
TDD4	713.8	889.0	904.6	1011.8	1014.6	1044				138.2
TDD5	679.1	847	862	972.1	978					133.0
TDD6	645	791.1	825.2							128.3
TDD7	613	769	791							123.6
TDD8	585	729	756							119.3
TDD9	559	700	729							116.0

Infrared absorptions of vibrational character at 975 and 988 cm^{-1} were assigned to thermal donor species TDD1 and TDD2. A band at 1000 cm^{-1} correlates well with TDD3, while a band at 1006 cm^{-1} can be related to species TDD4 to TDD9 [20].

Also, the method of deep level transient spectroscopy (DLTS) has been applied to successfully detect the ionisation levels of the TDDs [21–23]. As an example of specific further studies, the passivation of TDDs by hydrogen and their reactivation by thermal anneal was investigated using DLTS, yielding hydrogen dissociation energies of 1.90 eV for TDD1 and 1.67 eV for TDD2 [24]. As for the Hall effect, the resolution of standard DLTS is too low to separate the individual TDD species, but in both techniques a decrease of the energies with extension of the heat-treatment time is observed; this

reflects the more prominent presence of shallower components in the integral signal for longer times [3,9]. In a new version of the DLTS, named Laplace-transform DLTS, an improvement of resolution by more than one order of magnitude has been realised and structure was observed in the emissions of both ionisation levels of some TDDs [25].

TDDS in their singly charged states, having an odd number of electrons, are paramagnetic centres with electron spin $S = 1/2$. They were detected by electron spin resonance (ESR) and the spectrum labelled Si-NL8 [26] was associated with thermally generated donors. The assignment of Si-NL8 to the optically characterized TDDs was strongly corroborated by experiments monitoring reorientations of the centres induced by uniaxial stress [27,28]. In the early work, ESR was unable to resolve individual species and the spectral lines corresponded to broader sums over all individual species. Only a shift of g values with heat-treatment time was observed with g tensors becoming more isotropic [29]. This reflects the fact that later, shallower, species have more extended wave functions and experience smaller anisotropic core effects. Orthorhombic symmetry was observed in the angular rotation patterns, with principal directions in $[1,0,0]$, $[0,1,1]$ and $[0,1,-1]$, indicating two perpendicular planes of reflection symmetry of the TDD structures. Principal components of the g tensor for short and long heat-treatment times are given in TABLE 3. Only in recent high-frequency ESR were individual species resolved [30].

TABLE 3 Principal g values of the Si-NL8 spectrum observed after short and long heat-treatment (h-t) times at 450°C. Data from [29].

h-t time (h)	Principal g value		
	$\parallel [1,0,0]$	$\parallel [0,1,1]$	$\parallel [0,1,-1]$
1.5	1.9999	2.0013	1.9926
270	1.9999	2.0008	1.9937

C BISTABILITY

A special feature of the species TDD0, TDD1 and TDD2 (labels alternatively used are bistable thermal donor BTD- α , BTD- β and BTD- γ) is a large electron-lattice interaction. As a result, different charge states of the centre have different atomic configurations. Also, due to the accompanying negative U , the ordering of the electronic energy levels is turned over; the level $++/+$ lies above the $+/0$ level. In this case the charge carrier statistics are controlled by the occupancy level, which lies halfway between the $++/+$ and $+/0$ levels, i.e. $E(++/0) = [E(++/+) + E(+/0)]/2$. For the Fermi level E_F above the occupancy level the charge state is the neutral one and the centre will be in an atomic configuration A. For E_F below $E(++/0)$ the centre is doubly positively charged and is in atomic configuration B. The single positive charge state is never stable. The centre is structurally bistable. Configurations A and B are separated by a potential barrier, which allows freezing of the centres in each of these configurations. For instance, configuration B, state B^{++} , is reached when cooling in the condition $E_F < E(++/0)$. This is the configuration with the double donor character of the TDDs, in which the charge states $B^+ = TDD^+$ and $B^0 = TDD^0$ can be created by appropriate change of the Fermi level. When cooling from the neutral state, and avoiding the presence of free carriers, the TDDs are not formed. Configuration A, in which electrons are tightly bound, exhibits no electrical activity and is hence difficult to observe directly. More tentatively a local vibrational mode at 1020 cm^{-1} has been attributed to this centre [31]. Experiments demonstrating the bistability were performed using the Hall effect [12,32–34], DLTS [23,35], infrared electronic absorption [9,34,36] and infrared vibrational absorption [37]. TABLE 4 specifies the energies characterising the negative- U properties. Later species, $n > 2$, are stabilized in the TDD configuration uniquely by their peripheral structure.

TABLE 4 Energies, in eV, characterizing the negative-U properties of thermal donor species $n = 0, 1$ and 2. Data from [45].

Species/trap	$E_c - E(+++)$	$E_c - E(0/+)$	$E_c - E(++/0)$	U
TDD0/ α	≈ 0.16	≈ 0.75	≈ 0.45	≈ -0.6
TDD1/ β	0.16	0.48	0.32	-0.32
TDD2/ γ	0.155	0.29	0.22	-0.14

D SYMMETRY

A final detailed model for the atomic and electronic structure of thermal donors has not yet been established. It is, however, generally assumed that the centres consist of an electrically active core, surrounded by a peripheral defect region which grows with heat treatment and which distinguishes the species [38–40]. The presence of oxygen in the centres as a crucial component was accepted from the earliest days based on conditions of growth [1], and was unambiguously confirmed by electron-nuclear double resonance (ENDOR) [41] on the Si-NL8 EPR spectrum in samples enriched in the ^{17}O isotope. The Si-NL8 spectrum reveals orthorhombic, 2mm (C_{2v}), symmetry of the thermal donors, with two perpendicular mirror symmetry planes [42]. Oxygen atoms are all located on one of these planes. To maintain the orthorhombic symmetry it is practically necessary to add oxygen atoms in pairs in the growth process. It can, however, not be excluded that oxygen atoms are added one by one, resulting in orthorhombic or monoclinic symmetry of the TDDs. The effect on the nearly isotropic g tensor could easily be too small for observation. Some support for an alternating symmetry can be derived from the splitting of $2p_{\pm}$ and $3p_{\pm}$ energy levels which shows a zig-zag effect for n is even and odd species. In the lower symmetry of the TDDs the ground state in the effective-mass description will be composed of Bloch functions from the two minima along the [100] axis of the orthorhombic centre. This conclusion was confirmed by observed splitting of optical transitions [43] and deep level transient spectroscopy [22,44] under externally applied uniaxial stress.

E CONCLUSION

Thermal double donors are formed in oxygen-rich silicon crystals on heating at 350–550°C. Hall effect, optical absorption, photothermal ionisation spectroscopy, deep level transient spectroscopy, electron spin resonance and electron-nuclear double resonance have all been used to determine the presence, structure (symmetry) and energy levels of the various species of donors, and the data are tabulated.

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