

# Shallow thermal donors associated with H, Al and N in annealed Czochralski silicon distinguished by infrared spectroscopy

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**Abstract.** Electronic transitions of shallow thermal donors (STDs) in aluminium-doped Czochralski (CZ) Si annealed at 470 °C have different energies from those of STDs observed in annealed, hydrogenated boron-doped CZ Si. A third type of STD is observed in boron-doped Si pre-heated in nitrogen gas and annealed at 550 °C. Combinations of the three types of STDs can be observed in suitably treated samples. The incorporation of H and Al in STDs has been supported by electron–nuclear double-resonance measurements of the Si-NL10 electron paramagnetic resonance spectrum but the incorporation of nitrogen remains uncertain.

## 1. Introduction

Clustering of oxygen atoms in Czochralski (CZ) Si annealed in the temperature range  $350\text{ °C} < T < 500\text{ °C}$  leads to the formation of a family of double thermal donors [1, 2], TDN, that gives rise to an electron paramagnetic resonance (EPR) signal, labelled Si-NL8, when they are in their singly ionized charge state [3, 4]. The TDN series evolves with increasing anneal time and the binding energies of the electrons decrease as the index  $N$  increases from 1 (TD1) to 16 (TD16). Members of the series are easily resolved by infrared (IR) absorption measurements of the electronic transitions from either TDN or TDN<sup>+</sup>. Electron–nuclear double-resonance (ENDOR) measurements [5] of samples containing <sup>17</sup>O, with a nuclear spin  $I = 5/2$ , confirm the incorporation of oxygen atoms in the TD defects but ENDOR lines from other impurities, for example <sup>13</sup>C,  $I = 1/2$ , or <sup>14</sup>N,  $I = 1$ , have not been detected (see [6]).

Annealed CZ Si also gives rise to IR electronic absorption at energies below  $\sim 300\text{ cm}^{-1}$  from the so-called shallow thermal donors (STDNs) [6–15] and a second EPR spectrum labelled Si-NL10 [16]. The  $g$  tensor of this resonance has  $C_{2v}$  symmetry but is less

anisotropic than that of NL8, indicating that the unpaired electron is more delocalized. No hyperfine interactions are detected in the NL10 EPR spectrum but ENDOR transitions from <sup>17</sup>O demonstrate the presence of two or three oxygen atoms in the defect, a similar structure to that of the NL8 defect [16, 17]: additional undetected oxygen atoms could, however, be present. The strength of the NL10 EPR signal observed from aluminium-doped samples is greater than that observed from samples doped with boron, gallium or indium impurities. ENDOR transitions are observed from <sup>27</sup>Al ( $I = 5/2$ ), indicating that this atom forms part of the defect core structure in Al-doped material [16]. Corresponding ENDOR transitions from B, Ga or In are not detected from annealed crystals doped with these acceptor atoms, even though they may be expected to occupy the same sites as aluminium atoms. NL10 defects are still formed in such samples, however, and the recent measurement of ENDOR transitions from hydrogen (or deuterium) atoms indicates that hydrogen is present in this defect core structure [18]. Thus, we now know that there is an NL10(H) EPR spectrum as well as an NL10(Al) spectrum. These are characterized by a somewhat different anisotropy of the  $g$  tensors

but can be identified only via the associated ENDOR transitions.

IR measurements reveal a family of STDNs (cf the family of TDNs) in hydrogenated (or deuterated) boron-, indium- or phosphorus-doped CZ Si and it was shown that the electronic transitions occur at slightly lower energies ( $\sim 0.1 \text{ cm}^{-1}$ ) when H atoms are replaced by D atoms [6,19]. These observations demonstrate that at least one hydrogen atom is incorporated in the core of these STD defects and provide a link to the NL10(H) spectrum since there is also an indication that the relative strengths of the IR absorption and the EPR spectrum are correlated [6]. We now label this family of shallow single donors STDN(H).

Although there have been measurements of IR electronic absorption from annealed Al-doped CZ Si [20–22], we are unaware of reports of a family of well-resolved lines. We shall show that STD centres formed in lightly Al-doped Si annealed at  $470^\circ\text{C}$  have sharp electronic transitions but with slightly different energies from those of the STDN(H) family. We shall label this new spectrum STDN(Al).

IR electronic transitions from STDs have also been observed [9–15] in annealed CZ Si that was (a) grown from melts doped with silicon nitride, (b) grown in an  $\text{N}_2$  atmosphere or (c) given a post-growth heat treatment in nitrogen gas: an NL10-like spectrum has been reported for samples prepared by method (c) [13–15]. It has been generally inferred that nitrogen is incorporated in these STDs even though the presence of nitrogen in the crystals has only been demonstrated directly by IR vibrational absorption [23] for samples prepared by method (a). Even if nitrogen is present in the crystal, the evidence for its incorporation in the STD and NL10 centres is only circumstantial, since no ENDOR transitions from  $^{14}\text{N}$  ( $I = 1$ ) have been reported. An alternative proposal was that nitrogen acts as a catalytic agent [10, 11] for the formation of these STDs. We shall now show that two types of STD centres can be produced in Si pre-heated in  $\text{N}_2$  gas, namely STDN(H) and another species that we label STDN(X). ENDOR measurements for these samples are also outlined.

## 2. Experimental details

Details of the present CZ Si samples ( $[\text{O}_i] \sim 10^{18} \text{ cm}^{-3}$ ) and their treatments are given in table 1. Most samples (identified by the sample name in the first column) were given a thermal pre-treatment at  $1200\text{--}1300^\circ\text{C}$  in Ar,  $\text{H}_2$  or  $\text{N}_2$  gas at atmospheric pressure for 30–60 min, after which they were cooled rapidly, either by being dropped directly into silicone oil or by plunging the tube in which they were being heated into water at room temperature. Al3 was annealed at  $470^\circ\text{C}$  for periods of up to 8 h in a radio-frequency hydrogen plasma (13.56 MHz, 2 mbar, 40 W) but all the other samples were annealed in air. Sample Al2 and samples Al3, B1, B3 and B4 were given three and two sequential anneals respectively (table 1). All samples were wedged and polished and IR spectra at  $\sim 10 \text{ K}$  were obtained with a Bruker IFS 120 HR interferometer operated at a resolution of  $0.25 \text{ cm}^{-1}$ .

**Table 1.** Details of the CZ Si samples and their treatments.

Sample name	Dopant and concentration ( $\times 10^{15} \text{ cm}^{-3}$ )	Pre-treatment		Anneal	
		Gas	$T$ ( $^\circ\text{C}$ )	$T$ ( $^\circ\text{C}$ )	$t$ (h)
Al1	[Al] = 1.0 [C] < 2	NT <sup>a</sup>	—	470	14
Al2	[Al] = 1.0 [C] < 2	Ar	1200	470	13
				+ 550	16
				+ 650	16
Al3	[Al] = 1.0 [C] < 2	$\text{H}_2$	1200	470 <sup>b</sup>	8
B1	[B] = 0.5 [C] < 2	$\text{H}_2$	1200	470	22
				+ 550	16
B2	[B] = 0.5 [C] < 2	$\text{H}_2$	1200	470	16
B3	[B] = 0.5 [C] < 2	$\text{N}_2$	1270	470	24
				+ 550	16
B4	[B] = 0.5 [C] < 2	$\text{N}_2$	1270	550	24
				+ 650	16
C1	[C] = 20 [B] = 0.15	$\text{H}_2$	1300	470	16

<sup>a</sup> No treatment.

<sup>b</sup> Samples were annealed in air, apart from sample Al3 that was annealed in a hydrogen plasma.

## 3. Results and discussion

The absorption lines from the STDs in B1 (hydrogenated) (figure 1(a)), following the anneal at  $470^\circ\text{C}$ , relate to oxygen clusters with an incorporated hydrogen atom and were previously linked to the NL10(H) EPR spectrum [6]. An anneal of the as-grown sample in air at  $470^\circ\text{C}$  produced the same STD centres. It is concluded either that some hydrogen was present in this as-grown material or that hydrogen diffused in during the anneal. The absorption lines from the STDs generated in Al2 (figure 1(b)), following the anneal at  $470^\circ\text{C}$ , have different energies (table 2). It is inferred that there are two types of STDs and we label the second family of centres STDN(Al). The STDN(Al) spectrum was also observed in Al1. IR spectra from Al3 (hydrogenated) showed lines from both STDN(H) and STDN(Al) (figure 1(c)), demonstrating that the two STD defects can co-exist in samples annealed at  $470^\circ\text{C}$ . ENDOR measurements show that NL10(H) and NL10(Al) can also co-exist in such samples. Consequently, we relate the STDN(Al) IR spectrum to the NL10(Al) EPR spectrum, although quantitative correlations have not yet been established.

Following a second anneal at  $550^\circ\text{C}$  of samples Al3 and B1 (both hydrogenated, table 1), the IR absorption lines from the STDN(H) centres were barely visible (absorption from TD centres was absent) but the absorption from the STDN(Al) centres in Al3 increased in strength by a factor of  $\sim 10$ , showing the much higher stability of these defects compared with STDN(H). Following a further anneal of Al3 at  $650^\circ\text{C}$  for 16 h, the strength of the STDN(Al) lines fell somewhat, implying some degree of dissociation.

In the nitrated sample B3 (table 1) annealed at  $470^\circ\text{C}$ , IR absorption lines relating to STDN(H) dominated the spectrum, although other weaker lines were also present in the same spectral region. After a second anneal at  $550^\circ\text{C}$ ,

**Table 2.** The frequencies ( $\text{cm}^{-1}$ ) of the IR transitions of STDN(H), STDN(Al) and STDN(X) shallow donors and comparisons with published work.

STDN(H)		STDN (Al)	STDN(X)			
H <sub>2</sub> (Q)	[16]		N <sub>2</sub> (Q) <sup>a</sup>	[11] <sup>b</sup>	PTIS	[9] <sup>c</sup>
		—	184.6			
187.4		187.0	187.8		188.0	
190.7		189.7	190.9	191.1	190.9	190.8
195.4		195.0	194.7	194.8	194.9	195.0
198.2	198.1 <sup>d</sup>	198.3	197.6	197.7	197.6	197.7
					198.9	
204.2	204.2 <sup>d</sup>	204.1		200.3		200.2
					203.8	
208.7		206.4	207.3	207.5	207.3	207.4
226.1		225.5				—
230.6		229.3	230.7		230.9	—
233.7		232.3	233.8	233.8	233.8	233.7
238.4	238.2	237.4	237.8	237.8	237.9	237.9
241.1	241.1 <sup>d</sup>	—	240.4	240.4	240.4	240.5
—				242.5	242.4	242.4
246.8	246.7 <sup>d</sup>		247.1		246.8	
—	249.7 <sup>d</sup>	248.6	249.8	249.9	249.6	249.9
253.6						—
	264.5		259.9	260.2	260.3	—
					264.2	
			266.6	266.7	266.5	266.7
267.1	267.2	267.3		268.9	268.7	268.8
273.0	273.3			274.1	273.9	
278.5	276.1	275.1	276.2	276.2	275.9	

<sup>a</sup> IR measurements on quenched nitrated sample B3 (annealed at 550 °C).

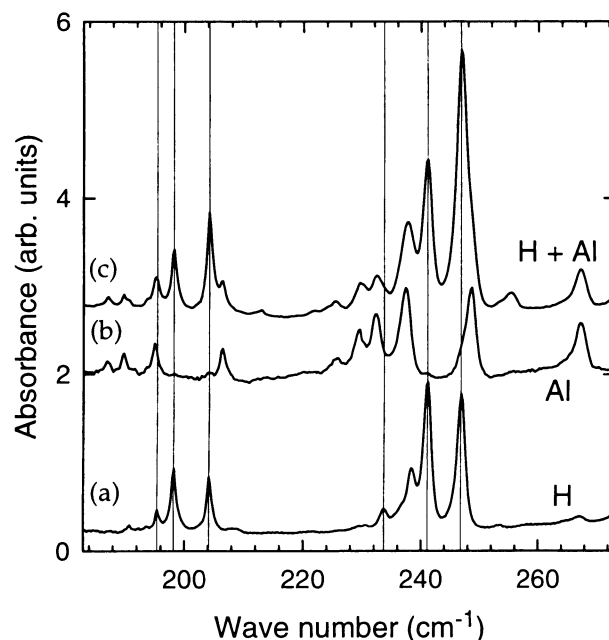
<sup>b</sup> Our IR data for a sample (MPI, Stuttgart) previously measured by photothermal ionization spectroscopy (PTIS) [11].

<sup>c</sup> Lines at 171.3, 181.0, 211.5 and 222.0  $\text{cm}^{-1}$  [9] are due to electronic transitions of phosphorus from the excited T<sub>2</sub> level of the split ground state.

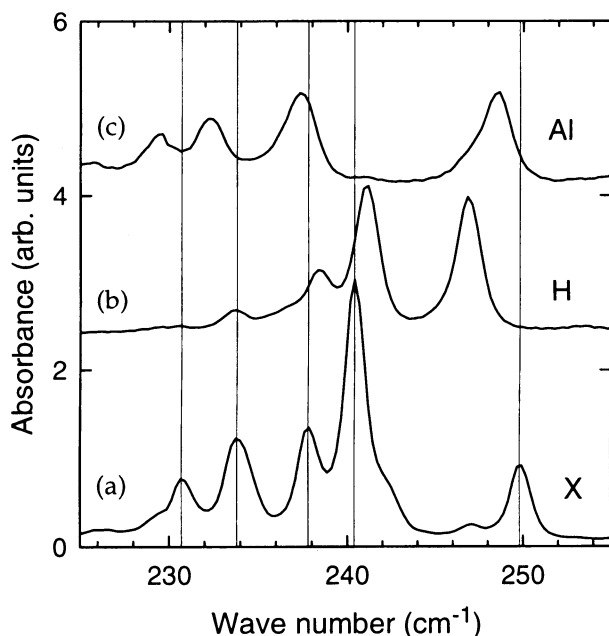
<sup>d</sup> Lines also reported in [24] for irradiated, hydrogenated silicon.

the latter transitions increased in strength by a factor of  $\sim 5$  (figure 2(a)) and absorption from the STDN(H) and TDN defects was greatly reduced. We label the STD transitions in this annealed sample STDN(X), since their energies (table 2) are different from those of either STDN(H) (figure 2(b)) or STDN(Al) (figure 2(c)): X is an unknown component of the donor. For the nitrated sample B4 annealed at 650 °C, all absorption from STDN(X) was lost, showing that these centres are unstable at this temperature for extended anneals although it has been reported that they survive shorter heat treatments of  $\sim 30$  min [9].

The present IR absorption spectra demonstrate that at least three different types of STDs can form in annealed CZ Si. The presence of hydrogen and aluminium in the cores of STDN(H) and STDN(Al) respectively is consistent with ENDOR measurements. ENDOR measurements made on a sample (similar to B3) pre-heated in nitrogen gas at 1270 °C and then annealed at 550 °C do not reveal the presence of <sup>14</sup>N, although there are differences in the anisotropy of the <sup>29</sup>Si ENDOR transitions compared with those related to the NL10(Al) spectrum. These differences are currently under



**Figure 1.** IR electronic absorption lines ( $1s \rightarrow 2p_0$  near 200  $\text{cm}^{-1}$  and  $1s \rightarrow 2p_{\pm}$  near 240  $\text{cm}^{-1}$ ) from STDN centres produced by anneals at 470 °C of (a) hydrogenated boron-doped Si (B1), showing the STDN(H) spectrum, (b) Al-doped Si pre-heated in Ar (Al2), showing the STDN(Al) spectrum, and (c) hydrogenated, Al-doped Si (Al3), showing the superposition of the STDN(H) and STDN(Al) spectra. The vertical lines are included as a guide for the eye.



**Figure 2.** IR electronic absorption lines ( $1s \rightarrow 2p_{\pm}$ ) from STDN centres produced in (a) Si pre-heated in nitrogen gas (B3) and annealed at 550 °C showing the STDN(X) spectrum, (b) hydrogenated Si annealed at 470 °C (B1) showing the STDN(H) spectrum and (c) Al-doped Si pre-heated in Ar gas and annealed at 470 °C (Al2), showing the STDN(Al) spectrum. The vertical lines are included as a guide for the eye.

investigation. In addition, no IR vibrational absorption from N–N pairs [23] was observed in unannealed (no

550 °C treatment), nitrided float zone (and CZ) samples, indicating that the concentration of in-diffused nitrogen is less than  $\sim 10^{15} \text{ cm}^{-3}$ .

An alternative possibility is that vacancies are incorporated in the STDN(X) centres instead of nitrogen atoms. It is well known from diffusion measurements of buried impurity marker layers that rapidly diffusing vacancies are produced at the surface of Si samples heat treated at high temperatures in nitrogen gas [25]. These observations are supported by recent deep-level transient spectroscopy (DLTS) measurements on nitrided samples following in-diffusion of platinum impurities [26]. The injection of vacancies should also occur for samples grown in an  $\text{N}_2$  atmosphere, irrespective of whether or not the melts contained  $\text{Si}_3\text{N}_4$ . For crystals doped with  $\text{Si}_3\text{N}_4$ , the growth atmosphere has not always been specified but nitrogen atmospheres have been used [27].

We now compare the present IR measurements with published energies of STD electronic transitions (table 2). Our IR measurements of a nitrogen-doped sample (growth atmosphere not specified) provided by MPI, Stuttgart, agree with those measured previously by PTIS [11]. These energies, together with those quoted in [9] also for nitrogen-doped material, coincide with the STDN(X) transitions obtained from our nitrided material. On the other hand, measured energies reported for samples heated in nitrogen gas and then annealed at 480 °C [15] coincide with the energies that we find for STDN(H). It is apparent that the latter samples must have contained hydrogen so that formation of the STDN(H) centres predominated, as found for our sample annealed at 470 °C. The STDN(H) centres were also reported for samples that had been first hydrogenated and then irradiated with high-energy electrons prior to low-temperature anneals [24]. It is inferred that the intentional introduction of lattice vacancies does not affect the type of STD centre formed during anneals at  $T < 470 \text{ °C}$ .

Previously, we suggested that the STDN(H) and NL10(H) centres are TDN defects passivated by a single hydrogen atom [6, 18, 19]. However, our measurements indicate that STDN(H) and NL10(H) [18] are stable up to 500 °C, in contrast to DLTS measurements which show that passivated TDN centres (primarily TD1 and TD2) dissociate at  $\sim 200 \text{ °C}$  (20 min anneal) [28]. The latter observation is consistent with the expectation that H–O and H–Si bonds would dissociate at temperatures significantly lower than 500 °C. We therefore considered the possibility that the STDN(H) centres are formed by the H passivation of TD centres as the samples are cooled to room temperature. To test this possibility, sample B2 (hydrogenated) was cut into two pieces that were annealed together at 470 °C. One piece was cooled rapidly by dropping it into liquid nitrogen and the other piece was cooled slowly over a period of 16 h. There was no difference in the strengths of the absorption from either the STDN(H) or the TDN centres. It appears, therefore, that the STDN(H) centres are not formed during the cooling period. The present study does not resolve the different thermal stabilities of STDN(H)/NL10(H) centres and passivated TDs and so we can only conclude that

they are slightly different defects. For example, the DLTS measurements relate to passivation of bistable TD1 and TD2 defects when they are in their lowest energy states, whereas the STDN defects may correspond to TD centres with  $N > 2$  that have captured a hydrogen atom. We investigated the possibility that a carbon atom is incorporated in the STD core so that a stronger H–C bond forms [29]. However, a hydrogenated, carbon-contaminated sample (C1) annealed at 470 °C showed no IR absorption from STDN(H) and only very weak absorption from TDN centres [30]. We therefore find no evidence to support this proposal. Evidently the hydrogen passivation of extended defects is more complex than the passivation of simple point defects.

#### 4. Conclusions

We have demonstrated that three types of STD defects relating to the clustering of oxygen atoms can exist in annealed CZ Si. Each type of defect gives rise to a characteristic family of IR electronic absorption lines that can be distinguished by high-resolution absorption spectroscopy. It is clear from the data presented in table 2 that great care is required in making assignments. One family of shallow donors, STDN(Al), formed exclusively in Al-doped material, has greater thermal stability than the STDN(X) family that is, in turn, more stable than the STDN(H) family. The relative stability of the STDN(Al) centres is expected since the formation energy of  $\text{Al}_2\text{O}_3$  (300 kcal mol<sup>-1</sup>) is some 50% greater than that of  $\text{SiO}_2$  [31]. Circumstantial evidence has been reported for the incorporation of nitrogen in the STDN(X) centres and the absence of an ENDOR signal from <sup>14</sup>N has been attributed to a small overlap of the electron wave function with this nucleus [28]. Alternatively, the STDN(X) and NL10(X) spectra may arise from oxygen clusters that incorporate a lattice vacancy.

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