

SHALLOW THERMAL DONORS IN ANNEALED CZ SILICON AND LINKS TO THE NL10 EPR SPECTRUM: THE RELEVANCE OF H, Al AND N IMPURITIES

R. C. Newman¹, M. J. Ashwin¹, R. E. Pritchard¹, J. H. Tucker¹, E. C. Lightowlers², T. Gregorkiewicz³, I. S. Zevenbergen³, C. A. J. Ammerlaan³, R. Falster⁴, and M. J. Binns⁴

¹ IRC for Semiconductor Materials, The Blackett Laboratory, Imperial College, London SW7 2BZ, UK

² Department of Physics, King's College London, Strand, London WC2R 2LS, UK

³ Van der Waals-Zeeman Laboratorium, Universiteit van Amsterdam, Valckenierstraat 65-67, NL-1018 XE, Amsterdam, The Netherlands

⁴ MEMC Electronic Materials Inc., 501, Pearl Drive (City of O'Fallon) P.O. Box 8, St. Peters, Missouri 62276, USA

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Abstract. Heat treatment of Czochralski Si at $\sim 470^\circ\text{C}$ leads to the formation of shallow thermal donors (STDs) with ionisation energies of $\sim 36\text{ meV}$ that are detected by infrared (IR) absorption. The STDs produced in hydrogenated samples (B, P or In-doped) are shown to incorporate H atoms and give rise to a distinct set of electronic transitions. A different family of lines is detected in Al-doped samples. Such samples also give rise to NL10 electron paramagnetic resonance (EPR) spectra and ENDOR measurements reveal the presence of H(D) or Al atoms in the defect cores. STDN(H) and STDN(Al) are produced simultaneously in hydrogenated Al-doped samples. Samples pre-heated in nitrogen gas at high temperatures show yet a third set of IR electronic transitions but ^{14}N is not detected by ENDOR. There is a suggestion that these centres incorporate a lattice vacancy. We demonstrate that there are at least three types of shallow thermal donors that have not always been distinguished by IR measurements in previous work.

Introduction.

Clustering of oxygen atoms in Czochralski (CZ) silicon annealed in the range $350 < T < 500^\circ\text{C}$ leads to the formation of a family of double thermal donors, TDN [1,2] with $N = 1$ to 16. Individual members of this family are resolved by infrared (IR) measurements of the electronic transitions from either TDN^0 or TDN^+ . In their singly ionised charge state, the donors also give rise to the NL8 electron paramagnetic resonance (EPR) spectrum [3,4] and electron nuclear double resonance (ENDOR) measurements of ^{17}O -doped samples demonstrate the presence of O atoms in the TD cores [5]. ENDOR signals from other impurities (^{13}C , ^{14}N) are not detected (see, for example, Ref. 6). In spite of the wealth of information, there is still uncertainty about the detailed structure of these defects.

Another family of defects that gives rise to the less anisotropic EPR NL10 spectrum [7] is also generated in annealed CZ Si. NL10 is always stronger in samples doped with Al and ENDOR measurements confirm the presence of both oxygen and ^{27}Al in the defect cores [7,8]. However, the presence of ^{27}Al is not essential for the detection of NL10 and in other samples, an ENDOR signal from hydrogen has been observed [6,9]. In hydrogenated Al-doped material both ENDOR signals can be detected indicating that these defects can be of the type NL10(Al) or NL10(H). Again the detailed structure of these defects is not known but it resembles the TD structure with the addition of an Al atom, a H atom or possibly some other impurity or a defect.

Electronic IR absorption lines are detected at energies below $\sim 300 \text{ cm}^{-1}$ and recently their strengths have been linked with the strength of NL10(H) [6]. These IR absorption lines have been studied by many workers and correspond to a second family of donors that are known as shallow thermal donors, STDN [6, 10-15]. However, these absorption lines have not been differentiated into separate families of STDNs and so it is not clear whether or not the same donor defects have been examined in each study. For example, it has been shown that the STD defects responsible for the IR absorption lines reported in Ref. 6, must incorporate at least one H atom since the transitions shifted slightly to lower energies when H atoms were replaced by D atoms. Other workers have measured IR absorption in annealed Al-doped CZ Si below 300 cm^{-1} [15], but a well-resolved family of lines was not reported. There have also been many reports of STD transitions detected in nitrogen treated samples [11-14] and some workers have proposed that nitrogen is incorporated in these STD defect cores [11,14].

The aim of the present work is to clarify the situation by examining a range of annealed CZ samples: namely, hydrogenated material, Al-doped material and nitridated material. We will show that after suitable annealing treatments, these three types of samples can produce three different families of STDN absorption lines and three different types of ENDOR signal from their NL10 spectra. We link STDN(H) to NL10(H) and STDN(Al) to NL10(Al) but the third family of lines produced in nitridated material, STDN(X), does not link to an ENDOR signal from ^{14}N . The presence of nitrogen is not ruled out but, alternatively, a different defect/impurity may be incorporated in this donor core.

Experimental Details.

Most CZ Si samples ($O_i \sim 10^{18} \text{ cm}^{-3}$) were given a thermal pre-treatment at $1200 - 1300^\circ\text{C}$ in Ar, H_2 (hydrogenation) or N_2 gas (nitridation) at atmospheric pressure for 30 - 60 min. The samples were then cooled rapidly by either dropping them directly into silicone oil, or the tube in which they were heated was plunged into water. The material was either aluminium doped ($[\text{Al}] = 1 \times 10^{15} \text{ cm}^{-3}$) or lightly boron-doped ($[\text{B}] = 5 \times 10^{14} \text{ cm}^{-3}$), both with carbon concentrations less than $2 \times 10^{15} \text{ cm}^{-3}$. The samples were then annealed in air or in a radio-frequency hydrogen plasma (13.56 MHz, 2 mbar, 40 W) in the range $470 - 650^\circ\text{C}$ for periods of up to 24 h. It was found that the various STD defects have different dissociation temperatures, allowing selective formation of a particular family of STDs by the choice of an appropriate anneal temperature. 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 cm^{-1} .

Results and Discussion.

Figure 1a shows the IR electronic absorption lines from the STDs in a hydrogenated boron-doped sample following an anneal at 470°C for 22h. These lines (Table 1, column 1) relate to oxygen clusters that incorporate a hydrogen atom and were previously linked to the NL10 (H) EPR spectrum [6]. Annealing this material in air at $470^\circ\text{C}/16\text{h}$ without a pre-hydrogenation treatment produced the same STD centres at a lower concentration, indicating that hydrogen is present in the as-grown material. The absorption lines from the STDs generated in annealed Al-doped material (Fig. 1b) have different energies (Table 1, column 3) and so it is inferred that there are two types of STD centres, STDN(H) and STDN(Al). IR spectra from hydrogenated Al-doped material (Fig. 1c) show lines from both STDN(H) and STDN(Al) demonstrating that the two types of STD defect can co-exist in samples annealed at 470°C . ENDOR measurements demonstrate that NL10(H) and NL10(Al) can also co-exist in such samples and so a new result from the present work is

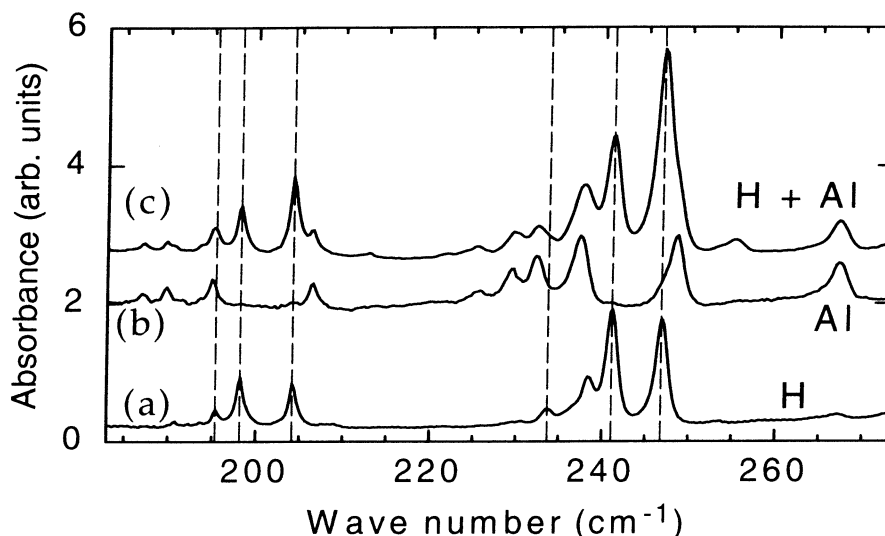


Fig. 1 IR absorption lines ($1s \rightarrow 2p_0$ near 200 cm^{-1} and $1s \rightarrow 2p_{\pm}$ near 240 cm^{-1}) detected in samples annealed at 470°C . (a) Hydrogenated boron-doped Si showing the STDN(H) spectrum, (b) Al-doped Si pre-heated in Ar showing the STDN(Al) spectrum, and (c) hydrogenated Al-doped Si showing the superposition of the STDN(H) and STDN(Al) spectra. The vertical lines are guides for the eye.

that we can relate a family of absorption lines, STDN(Al), to the NL10(Al) spectrum. Both Al-doped and boron-doped material also showed strong absorption from TD centres following an anneal at 470°C .

Hydrogenated samples of the boron- and Al-doped material, given a second anneal at 550°C for 16h, showed no absorption from TDN centres and absorption from STDN(H) centres was barely visible. However, the same treatment given to the Al-doped sample, led to absorption from STDN(Al) that increased in strength by a factor of ~ 10 demonstrating that these centres are more stable than STDN(H). Following a further anneal of this sample at $650^\circ\text{C}/16\text{h}$, the strengths of the STDN(Al) lines decreased by factors of 2-5, implying some degree of dissociation at this higher temperature.

In a nitridated boron-doped sample annealed at $470^\circ\text{C}/24\text{h}$, 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 $550^\circ\text{C}/16\text{h}$, the latter lines increased in strength by a factor of ~ 5 (Fig. 2a) while absorption from STDN(H) and TDN centres was greatly reduced. The STD transitions in this material (Table 1, column 4) are different from both the STDN(H) (Fig. 2b) and STDN(Al) (Fig. 2c) transitions and are labelled STDN(X) where X is an unknown component of the donor. For a nitridated boron-doped sample annealed at $650^\circ\text{C}/16\text{h}$, all absorption from STDN(X) was lost showing that all these centres had dissociated after this long period of annealing.

The present IR absorption spectra demonstrate that at least 3 different types of shallow thermal donors can form in annealed CZ silicon. ENDOR measurements of the NL10 spectrum generated in a nitridated sample annealed at 550°C did not reveal the presence of ^{14}N in the STDN(X) core. However, ^{29}Si ENDOR measurements revealed the presence of hyperfine interactions larger than those measured for the NL10(Al) spectrum. These differences are currently under investigation but there is a possibility that there is a third NL10 spectrum, labelled NL10(X), which we could relate to the STDN(X) transitions. X is an unknown constituent of the defect but the ENDOR measurements suggest that it is not

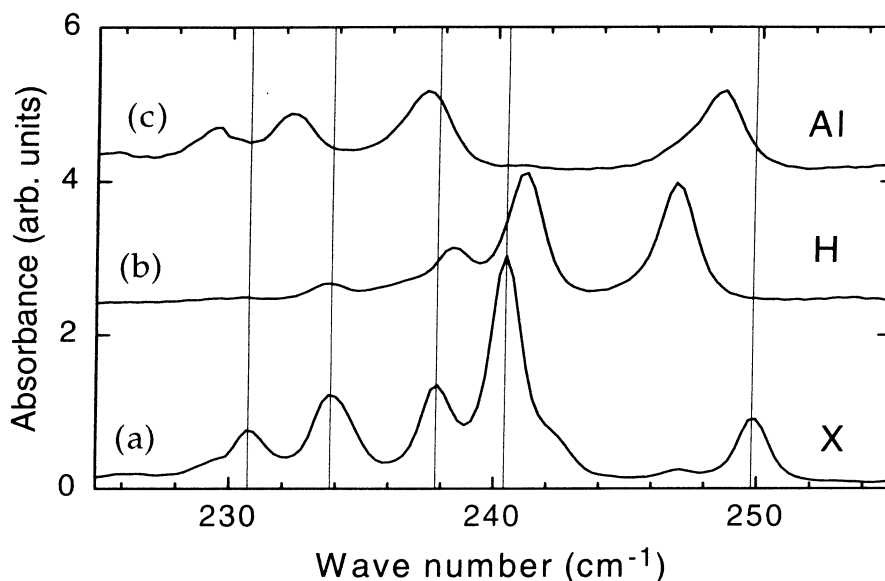


Fig. 2 IR absorption lines ($1s \rightarrow 2p\pm$) of (a) the STDN(X) spectrum produced in Si pre-heated in nitrogen gas and annealed at 550°C, (b) the STDN(H) spectrum, and (c) the STDN(Al) spectrum.

necessarily a nitrogen atom even though the material was annealed in N_2 gas. This conclusion is supported by IR absorption measurements of unannealed samples (float zone and CZ) nitridated at 1270 °C for 1 h. Localised vibrational modes from N-N pairs were not detected, indicating that the concentration of such pairs introduced by our procedure must be less than 10^{15} cm^{-3} . An alternative possibility is that vacancies are incorporated in the STDN(X) centres instead of nitrogen. It is well known from diffusion measurements of buried impurity marker layers that rapidly diffusing vacancies are produced at the surface of silicon samples heat treated at high temperatures in nitrogen gas [16]. This would include samples grown in a N_2 atmosphere, irrespective of whether or not the melts contained Si_3N_4 . For crystals doped with Si_3N_4 , the growth atmosphere has not always been specified but nitrogen atmospheres have been used.

We now compare the present IR measurements with published STD electronic energies (Table 1). The energies of the STDN(X) lines measured in our nitridated samples ($N_2(Q)$) coincide with those quoted in Ref. 11 for nitrogen-doped samples and those given in Ref. 12 for nitridated samples. The latter data were obtained by photo-thermal ionisation spectroscopy (PTIS) and agree with our IR absorption measurements for the same sample (column(a)). On the other hand, transitions measured for samples heated in N_2 gas and then annealed at 480°C [14] coincide with the STDN(H) transitions. At this lower anneal temperature, STDN(X) defects may also have been present but the transitions may have been obscured by stronger STDN(H) lines, as found in the present work. Finally, STDs have been reported in hydrogenated, electron-irradiated material [17] and may correspond to STDN(H) transitions. It was speculated that these centres incorporated both a lattice vacancy and hydrogen but the presence of hydrogen was not demonstrated.

We have suggested previously that STDN(H) and NL10(H) centres are TDN defects passivated by a single H atom [6,9]. However, our measurements show that STDN(H) is stable up to 500°C in contrast to deep-level transient spectroscopy (DLTS) measurements which show that passivated TDs (predominately TD1 and TD2) dissociate at $\sim 200^\circ\text{C}$ [18]. Since the H atoms in these defects are most likely bonded to either O or Si, the DLTS

STDN(H)		STDN(Al)	STDN(X)			
H ₂ (Q)	(Ref. 14)		N ₂ (Q)	(a)	PTIS [12]	(Ref. 11)
		-	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 ^b	198.3	197.6	197.7	197.6	197.7
					198.9	
204.2	204.2 ^b	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 ^b	-	240.4	240.4	240.4	240.5
-				242.5	242.4	242.4
246.8	246.7 ^b		247.1		246.8	
-	249.7 ^b	248.6	249.8	249.9	249.6	249.9
253.6						-
				256.9	257.0	-
	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	

TABLE 1. The frequencies (cm^{-1}) of the IR transitions of STDN(H), STDN(Al) and STDN(X) shallow thermal donors and comparisons with published work. (a) Our IR data for a sample (MPI, Stuttgart) previously measured by PTIS (Ref. 12). (b) Lines also reported in Ref. 17 for irradiated, hydrogenated silicon. Q indicates quenched samples.

measurements are consistent with the expectation that H-O and H-Si bonds would dissociate at $T \ll 500^\circ\text{C}$. We considered the possibility that STDN(H) defects are formed by H passivation of TDs as the samples cool to room temperature. To test this idea, a hydrogenated boron-doped sample was cut into two pieces that were annealed together at $470^\circ\text{C}/16\text{h}$. One piece was cooled rapidly by dropping it into liquid nitrogen while the other piece was cooled slowly over a period of 16 h. There was no difference in the strength of the resulting STDN(H) spectra suggesting that these defects are not formed during the cooling period. We conclude that STDN(H) centres have slightly different structures to hydrogen passivated TD centres.

Another possibility is that STDN(H) centres incorporate a carbon atom in the defect core. In this case, a stronger H-C bond would form which could be stable up to $\sim 500^\circ\text{C}$. This was investigated by annealing a hydrogenated, carbon contaminated sample ($[\text{C}] = 2 \times 10^{16} \text{ cm}^{-3}$) at a temperature of 470°C for 16h. However, this sample showed no IR absorption from STDN(H) centres and only very weak absorption from TDN centres and so we find no evidence to support this proposal. Evidently the hydrogen passivation of extended defects is more complex than the passivation of simple point defects.

Conclusions.

We have demonstrated that three types of STD defect relating to the clustering of oxygen atoms can exist in annealed CZ Si. Each defect gives rise to a characteristic family of IR electronic absorption lines and therefore can be distinguished by IR absorption spectroscopy. One type of STD defect is formed exclusively in Al-doped material and we relate STDN(Al) to NL10(Al). The second type of STD centre incorporates hydrogen and can be formed in *all* annealed CZ Si since H is always present at low concentrations in as-grown material. These defects also give rise to the NL10(H) spectrum. The third type of shallow thermal donor, STDN(X), is detected in nitridated material and incorporates a defect or impurity that we label X. The consensus view, based on circumstantial evidence, is still that X corresponds to a nitrogen atom since the absence of a ^{14}N ENDOR signal in the NL10(X) spectrum could be explained by a small overlap of the electron wavefunction with the nitrogen nucleus. Alternatively, we suggest that nitridation may act as a catalytic process for the formation of STDN(X), allowing X to be identified with a lattice vacancy. Finally, we note that the thermal stability of STDN(Al) centres is greater than that of STDN(X) centres that are, in turn, more stable than STDN(H) centres. The relative stability of the STDN(Al) defects is expected since the formation energy of Al_2O_3 (300 kcal/mol) is some 50 % greater than that of SiO_2 . However, the high thermal stability of STDN(H) defects suggests that bonds other than H-Si and H-O are formed in these centres.

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