

Carbon-hydrogen-related complexes in Si

Vl. Kolkovsky^{a,*}, R. Stübner^b, K. Gwozdz^c, J. Weber^b

^a IPMS Fraunhofer, Maria-Reiche Str. 2, 01109 Dresden, Germany

^b Technische Universität Dresden, 01062 Dresden, Germany

^c Department of Quantum Technologies, Faculty of Fundamental Problems of Technology, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland



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ABSTRACT

Several deep level transient spectroscopy (DLTS) peaks (E42, E65, E75, E90, E262, and H180) are observed in *n*- and *p*-type Czochralski-grown Si samples subjected to hydrogenation by a dc H plasma treatment. The concentration of the defects is found to be proportional to the carbon and hydrogen content in our samples. The analysis of the depth profiles performed in Si samples hydrogenated by wet chemically etching shows that all these defects contain a single H atom. E65 and E75 appear only in samples with a high oxygen content which shows that oxygen is a constituent of these defects. The analysis of the enhancement of the emission rate of the defects with electric field shows that E65, E75, E90, and E262 are single acceptors whereas E42 is a double acceptor. The presence of a barrier for hole capture (about 53 meV) can explain the absence of the enhancement of the emission rate of H180, which can be attributed to a single acceptor state. From a comparison with theory, we assign E90 to CH_{1BC}, E42 (E262) to CH_{1AB}, and H180 to CH_{1Td}. The similarity of the electrical properties of E65 and E75 to those of E90 suggest that E65 and E75 may originate from the CH_{1BC} defect with an oxygen atom in its nearest neighborhood. Our results on the CH-related complexes give a conclusive explanation of some previously reported controversial experimental data.

1. Introduction

The performance of electronic devices can be greatly influenced by the presence of unintentionally introduced electrically active defects in silicon. Some impurities such as carbon or oxygen, which are electrically inactive in Si, can create electrically active complexes by interaction with other crystal imperfections and impurities. Nowadays the technological processing of devices often includes heat treatments of Si wafers in hydrogen (H) containing atmosphere in order to reduce the density of interface states or to passivate the electrical activity of the surface. As a result, hydrogen penetrates into the bulk of Si wafers where it leads to the appearance of a number of H-related defects in the active region of devices. Among those traps the electrical and structural properties of CH-related defects attract significant attention, since carbon is always present in both Czochralski (Cz) and float-zone (FZ) Si. Until now the experimental results concerning the CH-related defects are controversial. Generally, two CH-related deep level transient spectroscopy DLTS peaks, labeled E(0.16) and H1 in Refs. [1,2], can be observed in hydrogenated *n*-type and *p*-type Si with a low oxygen content [1,2]. E(0.16) and H1 were shown to be C- and H-related defects [1,2]. However, the charge state and exact origin of these defects are still under discussion [1–4]. Theory predicts the appearance of different

configurations of CH-related defects in Si [3]. We emphasize that Yoneta et al. [5] reported that in *n*-type Si samples with a high O content (around 10¹⁸ cm⁻³) E3 (E(0.16) in Ref. [1]) was not dominant in the DLTS spectrum. Besides E3 some other peaks labeled E1 and E2 appeared in hydrogenated *n*-type Si samples with a high O content. In Ref. [5] the authors suggested that these peaks could be correlated with COH-related defects since their concentration increased with the O and C content. However, the exact nature of these defects is still unknown. Some DLTS peaks were also recently reported in the lower part of the bandgap of Cz Si with a high oxygen content of about 13–17.5 ppma [6]. The authors attributed these peaks to the O₂-H defect. In the present study we review our recent findings [4,7–9], which shed light on the origin of carbon-hydrogen related complexes in *n*-type and *p*-type Si samples with different oxygen concentrations. Our results on the CH-related complexes give a first conclusive explanation of some previously reported controversial experimental data.

2. Experimental procedure

Samples were cut from different *n*-type and *p*-type Czochralski (Cz) and Float-Zone (FZ) Si wafers with a doping level of about

* Corresponding author.

E-mail address: uladzimir.kalkouski@ipms.fraunhofer.de (V. Kolkovsky).

$2 \times 10^{15} \text{ cm}^{-3}$ and different concentrations of carbon and oxygen. Hydrogen was introduced by wet chemical etching at room temperature for 2 min in an acid consisting of $\text{HNO}_3:\text{HF}:\text{CH}_3\text{COOH}$ with a volume ratio of 5:3:3 or by a dc H plasma treatment performed at 320 K or 370 K. Schottky diodes were produced by resistive evaporation of Au (*n*-type Si) or Al (*p*-type Si) in vacuum onto the polished side of the samples at room temperature. Ohmic contacts were prepared by rubbing the backside of the samples with an eutectic InGa alloy. The quality of the Schottky and Ohmic contacts was characterized by current-voltage (*I*-*V*) measurements in the range of 50–300 K. Capacitance-voltage (*C*-*V*) measurements were performed at 1 MHz. Laplace DLTS [10] with two filling pulses was employed to investigate the electronic properties (activation enthalpy, capture cross section, charge state) of deep levels and their depth profiles. The labeling of the DLTS peaks in this work corresponds to the temperatures at which the peaks were observed in the DLTS spectra for an emission rate of 48 s^{-1} . Deep level concentration profiles were measured at a fixed reverse bias while varying the two pulse biases. The electrical field was calculated from the *C*-*V* profile as described in Ref. [11]. The field effect has been investigated at fixed pulse biases while varying the reverse bias.

3. Results

Fig. 1 shows DLTS spectra recorded in *n*-type Cz Si ($[\text{O}_i] \sim 1 \times 10^{18} \text{ cm}^{-3}$, $[\text{C}_s] = 5 \times 10^{15} \text{ cm}^{-3}$) after hydrogenation by a dc H plasma treatment. Several DLTS peaks (E42, E65, E75, E90, E120, and E262) were observed after hydrogenation. In contrast, no DLTS peaks were detected in this sample before hydrogenation. One should also emphasize that all these defects except E120 were observed in Si samples after wet chemical etching [4,7–9] and, therefore, we rule out that they were generated by the damage of the crystal lattice during the dc H plasma treatment. In order to investigate the electrical and annealing properties of E42, E65, E75, E90, and E262 the high-resolution Laplace DLTS technique was employed. All DLTS peaks consisted of single Laplace DLTS lines and no fine structure was observed. Information about the charge state of a defect can be obtained from the analysis of the shift of the emission rate of a defect under different reverse biases [12]. The emission rates of E42, E65, E75, E90, and E262 were indeed enhanced with the electric field. However, this enhancement was significantly weaker compared to that expected from the three-dimensional Poole-Frenkel model [12]. A model of a square-well potential, which is characteristic for neutral defects, describes well the enhancement of the emission rates of E65,

Table 1

The electrical properties of the defects observed in Figs. 1 and 3. Their assignment from this study is also presented.

Defect	Activation enthalpy (meV)	Apparent capture cross section (cm^{-2})	Charge state	Assignment
E42	60	2×10^{-17}	(-/-)	$\text{CH}_{1\text{AB}}$
E65	110	1.4×10^{-16}	(-/0)	$\text{CH}_{1\text{BC}} + \text{O}_i$
E75	130	8.6×10^{-16}	(-/0)	$\text{CH}_{1\text{BC}} + \text{O}_i$
E90	160	2.2×10^{-16}	(-/0)	$\text{CH}_{1\text{BC}}$
E90'	140	2.8×10^{-16}	(0/+)	CH_n ($n > 1$)
E262	510	2×10^{-15}	(-/0)	$\text{CH}_{1\text{AB}}$
H180	330	5×10^{-16} (barrier 53 meV)	(-/0)	$\text{CH}_{1\text{TD}}$

E75, E90, and E262 [12]. Details on these experimental results are given in Refs. [4] (E90), [7] (E65, E75), and [8] (E262). Based on these experimental findings we conclude that these defects are single acceptors in *n*-type Si. In contrast, the enhancement of E42 is characteristic for a double-acceptor in *n*-type Si and it is modelled by an inverted Morse potential [8,13]. The assignment of E65, E75, E90, and E262 to single acceptors and E42 to the double acceptor state is also consistent with the order of magnitude of the apparent capture cross section of the defects (see Table 1) since the capture cross section of E42 is significantly smaller compared to other defects from Fig. 1.

As mentioned in the introduction, E65, E75, and E90 have been already observed in previous studies [4,5]. There was shown that they contained carbon and hydrogen (E65, E75, E90), as well as oxygen (E65, E75). However, the number of H atoms in E65 and E75 is still unknown.

In order to shed light on the nature of these defects we employed the approach that was suggested in Ref. [14]. In this study, Feklisova and Yarykin demonstrated that after wet chemical etching (WCE) the reduction of the concentration of H-related defects with depth should be identical if they contained identical numbers of H atoms. One should emphasize that this method is also valid even if the concentration of the H-related defects is not the same.

Following this idea, depth profiles of E65 and E75 recorded after WCE for 5 min at room temperature are compared in Fig. 2. The concentration depth profile of the phosphorous-hydrogen (PH) complex is also presented in this figure. The PH concentration was calculated by subtracting the concentration of the net free carrier concentration in as-grown samples from the concentration observed after WCE. The introduction of H lead to the passivation of phosphor-

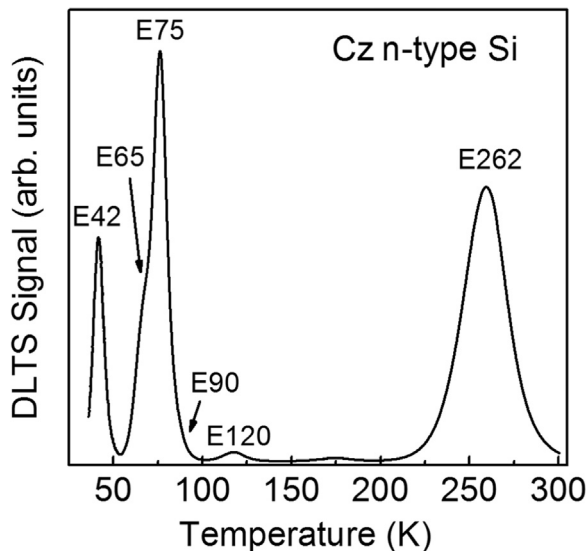


Fig. 1. DLTS spectrum recorded in *n*-type Cz Si subjected to hydrogenation by a dc H-plasma treatment.

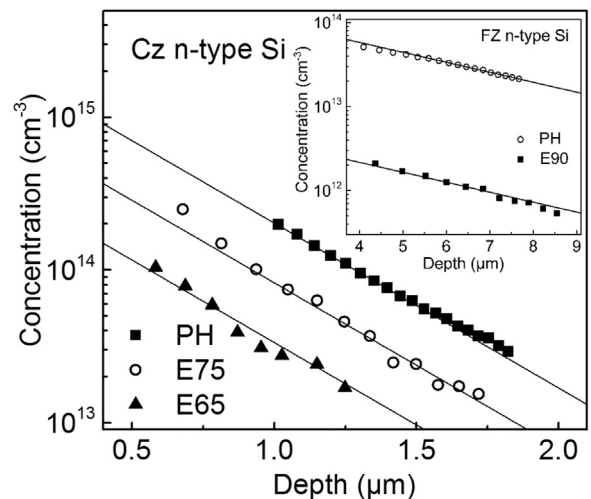


Fig. 2. The depth profiles of E65, PH, and E75 recorded in a Cz Si sample after WCE for 5 min at room temperature. The solid lines show an identical slope for the concentration of the defects. The inset shows the depth profiles of E90 and PH in a FZ Si sample after WCE at room temperature.

ous and to the formation of PH complexes close to the surface of the sample [15]. The slope of the reduction of the concentration of E65 and E75 was found to be the identical to that of the phosphorous-hydrogen (PH) complex. The results presented in Fig. 2 confirms that E65 and E75 contain only one H atom.

The signal-to-noise ratio for E90 in Cz Si hydrogenated by WCE was relatively small and therefore we were not able to obtain a reliable depth profile of E90 in this sample. For comparison, a FZ sample with a reduced oxygen concentration and a carbon concentration of about $5 \times 10^{15} \text{ cm}^{-3}$ was hydrogenated by WCE. In this sample, E90 was dominant and no traces of E65 and E75 were observed. The inset in Fig. 2 shows the depth profiles of E90 and PH in this FZ Si after WCE. The concentration of PH was obtained in a similar way to that from Fig. 2. The slope of the concentration of E90 was identical to that of PH and therefore E90 also contains one H atom. Another defect, labeled E90', which has very similar electrical properties as E90 can be resolved by the Laplace DLTS technique after reverse bias annealing in FZ Si. E90' was only observed in regions with high hydrogen concentrations. The analysis of the enhancement of the emission rate of the defect with electric field shows that E90' is a single donor. The slope of the depth profile of E90' was significantly steeper compared to that of PH and therefore this defect could contain more than one H atom. A detailed analysis concerning the electrical properties of E90' is presented in Ref. [4]. One should emphasize that the concentration of E65, E75, E90, and E90' increases with increasing the C and H content in the samples. Due to a small signal-to-noise ratio we were not able to obtain reliable depth profiles of E120 and therefore we will not discuss the origin of this peak.

The defects corresponding to E42 and E262 anneal out at similar temperatures and their concentration reduces by a factor of two at about 375 K [8]. Moreover, their depth profiles were also identical and therefore we conclude that they belong to different charge states of the same defect. In samples subjected to hydrogenation by WCE with a doping level $> 5 \times 10^{14} \text{ cm}^{-3}$ the concentration of this defect was below the detection limit of our DLTS setup. However, E42 and E262 were detected in samples hydrogenated by WCE with a low doping level of about $1 \times 10^{14} \text{ cm}^{-3}$ [8]. By comparing the depth profiles of E42 and E262 with that of PH or E90 a similar slope of the concentration of these defects was found. This dependence indicates that the defect that gives rise to E42 and E262 also contains a single H atom. We did not observe any dependence of the concentration of E42 and E262 on oxygen or shallow dopants. However, the concentration of E42 and E262 increases with the C content in the samples [8]. Table 1 combines the electrical properties (activation enthalpy, charge state, and the capture cross section) of the defects observed in Fig. 1.

Fig. 3 shows the DLTS spectrum recorded in *p*-type Cz Si subjected to hydrogenation by a dc H-plasma treatment. One DLTS peak H180 was dominant in this spectrum. Laplace DLTS measurements show that this peak consists of one component (see the inset in Fig. 3). The concentration of H180 increases in samples with higher C and H concentrations. The activation enthalpy and the apparent capture cross section obtained from the Arrhenius plot for H180 are also shown in Table 1. We did not observe a shift of the emission rate of this defect with electric field. However, measurements of the direct capture cross section performed at different temperatures showed the presence of a capture barrier for holes of around 53 meV. The depth profile of H180 was analyzed in Ref. [9] and it was shown that the slope of the concentration of H180 is identical to that of BH. Therefore, this defect consist of a single H atom.

4. Discussion

A number of DLTS peaks E42, E65, E75, E90, H180, and E262 were observed in *n*- and *p*-type Si hydrogenated by WCE or a dc H plasma treatment. Some of the peaks (E65 and E75) appear only in samples with a high O content whereas other peaks could be observed

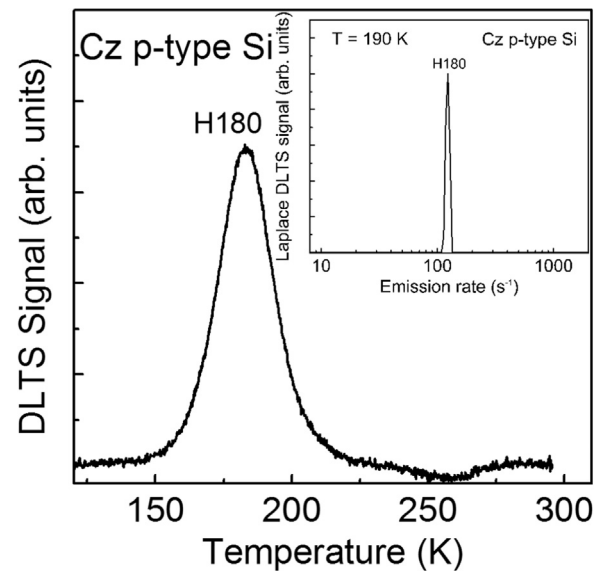


Fig. 3. DLTS spectrum recorded in *p*-type Cz Si subjected to hydrogenation by a dc H-plasma treatment. The inset shows the Laplace DLTS spectrum recorded at 190 K in the same sample.

in both Cz and FZ samples after hydrogenation by a dc H plasma treatment or WCE. The higher concentration of the defects corresponding to the peaks E42, E65, E75, E90, H180, and E262 in samples with higher C or H content allows us to correlate them with CH-related defects. The analysis of the depth profiles of the defects shows that all of them contain one hydrogen atom. To the best of our knowledge no studies which show a preferential location of a carbon atom near another carbon atom exist in the literature. The low concentration of carbon in our samples ($< 10^{17} \text{ cm}^{-3}$) makes it unlikely that E42, E65, E75, E90, H180, and E262 contain more than one C atom. The identical annealing behavior and the similar depth profiles of E42 and E262 show that these peaks belong to different charge states of the same defect. From the analysis of the enhancement of the emission rate of these defects these charge states are determined as the double acceptor state (E42) and the single acceptor state (E262). E90 and H180 cannot be assigned to the same defect since their annealing behavior under illumination is different [2] and they were not always observed together in combined DLTS and minority carrier transient spectroscopy (MCTS) measurements, as discussed in Ref. [9]. Therefore, we assign E42 (E262), E90, and H180 to different configurations of the CH complex.

The electrical properties of E90 are similar with those reported for E3' in Ref. [3] and therefore we attribute these peaks to the same defect. In Ref. [3] Andersen et al. demonstrated the trigonal symmetry of this defect by combining Laplace DLTS with uniaxial stress measurements. In good agreement with these results, E90 is assigned to the single acceptor state of the $\text{CH}_{1\text{BC}}$ configuration. The appearance of the E90' defect, which is shown to be a single donor and which can be only resolved by the Laplace DLTS technique after the reverse bias annealing experiments, can explain the difference between the experimental results reported previously in Refs. [1,3]. By comparing with theory H180 and E262 are tentatively attributed to single acceptor states of $\text{CH}_{1\text{Td}}$ and $\text{CH}_{1\text{AB}}$, respectively. In this case E42 is the double acceptor state of $\text{CH}_{1\text{AB}}$.

E65 and E75 are shown to contain C, O, and H, they are single acceptors, and the electrical properties of these defects are similar to that of E90. Therefore, we suggest that E65 and E75 belong to the $\text{CH}_{1\text{BC}}$ configuration of the CH complex with one oxygen atom in its nearest neighborhood. The presence of two levels E65 and E75 can be explained by two non-equivalent orientations of oxygen in respect to the $\text{CH}_{1\text{BC}}$ bonding in the crystal lattice of Si. However, theoretical

calculations are necessary in order to shed light on the exact origin of these defects.

5. Conclusions

In the present study we showed that a number of DLTS peaks (E42, E65, E75, E90, E262, and H180) could be observed in *n*- and *p*-type Cz Si hydrogenated by a dc H plasma treatment. From the analysis of the enhancement of the emission rate of the defects with electric field we concluded that E65, E75, E90, E262, and H180 were single acceptors while E42 is a double acceptor. The depth profiles of the defects showed that E42 (E262), E90, and H180 belonged to different configurations of the CH defect. E65 and E75 were attributed to COH-related defects with a single H atom. Comparing with theory we assigned E90 to CH_{1BC}, E42 (E262) to CH_{1AB}, and H180 to CH_{1TD}. The similarity of the electrical properties of E90 and those of E65 and E75 demonstrated that E65 and E75 could originate from CH_{1BC} with an oxygen atom in its nearest neighborhood.

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