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# Iron-related deep electron traps in epitaxial silicon resolved by Laplace-transform deep level transient spectroscopy

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## Abstract

The electronic properties and concentrations of iron-related deep-level defects in *n*-type epitaxial silicon have been studied by Laplace-transform deep level transient spectroscopy. Three electron traps with activation energies of 392, 455, and 472 meV have been revealed and compared with the known acceptor levels of iron-hydrogen complexes in *n*-type silicon obtained by using *ab initio* calculations. The detected electron traps are tentatively attributed to the acceptor levels of the  $(\text{Fe}_\text{s}\text{H})^{2/-}$ ,  $(\text{Fe}_\text{s}\text{H})^{0/-}$  and  $(\text{HFe}_\text{s}\text{H})^{0/-}$  complexes, respectively. The traps concentrations indicate that in as-grown epitaxial layers the  $(\text{HFe}_\text{s}\text{H})^{0/-}$  complexes are predominant defects which effectively decompose at room temperature by releasing one of the two hydrogen atoms. At the elevated temperatures, ranging from 80 to 240 °C, the decomposition rate of these complexes substantially increases. The dissociation of the  $(\text{Fe}_\text{s}\text{H})^{2/-}$ ,  $(\text{Fe}_\text{s}\text{H})^{0/-}$  complexes also takes place, however the rate of this process is lower than that for the  $(\text{HFe}_\text{s}\text{H})^{0/-}$  defects.

Keywords: epitaxial Si, deep levels, iron-hydrogen complexes, Laplace DLTS

## 1. Introduction

Iron is a common transition metal contaminant of silicon wafers introduced either during their fabrication or in technological processes used for manufacturing devices. Trace amounts of this element can be found in polycrystalline silicon used as a starting material for growing single crystals as well as in graphite and quartz components being a part of equipment applied to the wafers processing. In silicon epitaxial layers grown by chemical vapor deposition (CVD), the residual iron atoms may originate from substrate wafers, graphite heater, and gaseous chemicals, such as  $\text{H}_2$ ,  $\text{HCl}$  and  $\text{SiCl}_4$  [1]. It is well known that iron-related defect centers can cause either a substantial decrease in the minority charge carriers lifetime or an increase in the leakage current of silicon devices [2, 3]. Thus, the knowledge on the properties of iron-related point

defects and their monitoring in epitaxial silicon is of primary importance for the material quality assessment.

The iron covalent radius is 0.117 nm and it is slightly larger than that of silicon equal to 0.111 nm. The solubility of interstitial iron ( $\text{Fe}_\text{i}$ ) in silicon single crystals at 1100 °C is  $2 \times 10^{15} \text{ cm}^{-3}$  [3]. Iron, as a 3d transition metal, when located in an interstitial site can be in four different charge states: double positively charged (2+), singly positively charged (+), neutral (0) and, single negatively charged (-). The electron configurations corresponding to these charge states are  $3\text{d}^6 4\text{s}^0$ ,  $3\text{d}^6 4\text{s}^1$ ,  $3\text{d}^6 4\text{s}^2$  and  $3\text{d}^5 4\text{s}^1 4\text{p}^3$ , respectively [4, 5]. Isolated  $\text{Fe}_\text{i}$  is known to be located at the tetrahedral interstitial site and the donor level associated with the (+/0) change of the charge state is at  $E_\text{v} + 0.39 \text{ eV}$ . It should be added, however, there is a scatter of data and the value of  $E_\text{v} + 0.45 \text{ eV}$  for the activation energy of hole thermal emission from the  $\text{Fe}_\text{i}^+$  centre has also been reported [6,7]. It is interesting to note that the positively charged centre ( $\text{Fe}_\text{i}^+$ )

has an effective spin of  $S = 3/2$  and the spin of the neutral centre ( $\text{Fe}_i^0$ ), arising after the thermal emission of a hole, is 1 [4-7]. In  $n$  type material, when occupying the ideal substitutional site with  $T_d$  symmetry, the iron atom is negatively charged ( $\text{Fe}_s^-$ ) with a spin of  $1/2$  [4, 5]. The deep acceptor level associated with the  $(-/0)$  change of the charge state predicted by the calculations based on the first-principles theory is located at  $E_c - 0.41$  eV [4]. The position of this level in the bandgap, however, has not been verified experimentally so far and further studies would be useful for full understanding of the  $\text{Fe}_s$  electronic properties. It is worth adding that no donor level associated with  $\text{Fe}_s$  has been found by means of these calculations.

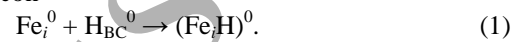
Interstitial iron is a fast diffusing impurity and can come deeply into the bulk of silicon wafers. At a temperature range of  $1100 - 1200$  °C, the  $\text{Fe}_i$  diffusion coefficient is  $\sim 5 \times 10^{-6}$  cm<sup>2</sup>/s [3]. It is worth adding that at room temperature (300 K), the  $\text{Fe}_i$  diffusion coefficient is  $\sim 1 \times 10^{-9}$  cm<sup>2</sup>/s and the diffusion length after 30 days can reach  $\sim 1$  mm [3]. Thus, during Si wafers processing, iron interstitials can penetrate the whole thickness of a typical silicon wafer.

A powerful method enabling very low concentrations of iron atoms in silicon wafers to be detected is the deep level transient capacitance spectroscopy (DLTS) [2, 8]. Using this method, iron-related deep levels were observed mainly in  $p$ -type silicon [3, 8]. According to the reported results, the iron-related deep hole traps in this material are formed involving interstitial iron ( $\text{Fe}_i$ ) and their properties are strongly dependent on the heat treatment conditions [3, 8]. The iron-related deep levels in  $n$ -type silicon wafers prepared from an ingot obtained by the floating-zone method with a phosphorus concentration of  $1 \times 10^{14}$  cm<sup>-3</sup> were investigated by Sadoh *et al.* [9]. They used thermally stimulated capacitance (TSCAP) measurements combined with injection of minority charge carriers by illuminating the sample with a laser beam having a wavelength of 630 nm. The measurements revealed two hole traps with activation energies of 0.31 eV and 0.41 eV induced by the iron diffusion at 930 °C and subsequent etching with the acid mixture containing HF and HNO<sub>3</sub>. Based on the results of theoretical studies, the former was assigned to a complex involving interstitial iron and hydrogen ( $\text{Fe}_i\text{H}$ ) and the latter to an isolated interstitial iron ( $\text{Fe}_i$ ) [6, 9].

According to calculations performed on the grounds of first-principles theory, an interstitial iron in the silicon lattice occupies a tetrahedral ( $T_d$ ) site and is a donor centre ( $\text{Fe}_i^{+/0}$ ) with the energy level at  $E_v + 0.4$  eV which has been observed experimentally as a hole trap in  $n$ -type Si by Sadoh *et al.* [6, 9]. In the experiment this level was filled with the excess holes being minority charge carriers. In  $n$ -type material, the Fermi level is shifted towards the conduction band minimum and at room temperature interstitial iron donors are neutral

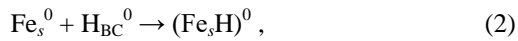
( $\text{Fe}_i^0$ ), as they are occupied by electrons. In  $p$ -type material, the  $\text{Fe}_i^{+/0}$  centre is observed in DLTS experiments through the thermal emission of holes being majority charge carriers [3, 8]. In  $p$ -type silicon, with the Fermi level located close to the valence band maximum, interstitial iron donors are mainly filled with holes and are positively charged ( $\text{Fe}_i^+$ ) at room temperature [4, 6, 7].

The experimentally detected hole trap at  $E_v + 0.31$  eV is in a very good agreement with the calculated donor level at  $E_v + 0.36$  eV attributed to the ( $\text{Fe}_i\text{H}$ ) pair. It is worth emphasizing that this trap has been observed as a minority-carrier trap in  $n$ -type silicon [9], as well as a majority-carrier trap in the  $p$ -type material [8]. This fact indicates that either in  $n$ -type or  $p$ -type silicon, iron can occupy interstitial positions and capture hydrogen atoms. Sadoh *et al.* [9] proposed the following reaction for the formation of neutral ( $\text{Fe}_i\text{H}$ )<sup>0</sup> pairs in  $n$ -type silicon



For the theoretical studies, it has been assumed that hydrogen predominantly diffuses as the neutral bond centred impurity  $\text{H}_{\text{BC}}^0$  and when it is bound, the iron atom moves from the tetrahedral interstitial position ( $T_d$ ) to hexagonal interstitial site ( $T_H$ ) [7]. The *ab initio* calculations gave the binding energy of 0.82 eV that is consistent with the low annihilation temperatures of 125 and 175 °C determined experimentally for the 0.31-eV hole trap in  $n$ -type and  $p$ -type silicon, respectively [7-9]. Recent results of density functional calculations reported by Santos *et al.* confirmed the low hydrogen binding energies for  $\text{Fe}_i\text{H}_n$  complexes, where  $n=1$  or 2 is the number of bound hydrogen atoms [5]. On the other hand, Santos *et al.* [5] concluded that the experimentally observed 0.31-eV hole trap is more likely attributed to the ( $\text{Fe}_i\text{H}_2$ )<sup>+/0</sup> donor centre, characterized by the energy level at  $E_v + 0.33$  eV, than to the ( $\text{Fe}_i\text{H}$ )<sup>+/0</sup> donor with the energy level at  $E_v + 0.36$  eV predicted by Gonzalez Szwacki *et al.* [7]. According to the calculations of Santos *et al.*, the energy level of the ( $\text{Fe}_i\text{H}$ )<sup>+/0</sup> donor lies deeper in the bandgap at  $E_v + 0.50$  eV [5].

Substitutional iron can also form electrically active complexes with hydrogen and the calculated properties of the ( $\text{Fe}_s\text{H}$ ) pair in the zero-charge state are consistent with the results of the electron paramagnetic resonance (EPR) experiments [5-7]. The results of theoretical studies indicate that no donor level is created by the ( $\text{Fe}_s\text{H}$ ) pair and only an acceptor level at  $E_c - 0.62$  eV is formed in the bandgap which corresponds to the  $(-/0)$  charge state change [7]. In  $n$ -type silicon, this level could be experimentally observed by the thermal emission of electrons in the space charge layer. Based on the assumption that hydrogen interacts directly with  $\text{Fe}_s$  without breaking any of the four Fe-Si bonds, it has been proposed that the neutral ( $\text{Fe}_s\text{H}$ ) pairs with spin  $1/2$  observed by EPR technique are formed according to the reaction



with the binding energy of 1.39 eV [7]. The *ab initio* calculations have also shown that the  $(\text{Fe}_s\text{H})^-$  state with spin 1 is by 0.23 eV higher in energy than the  $(\text{Fe}_s\text{H})^0$  state [7]. This fact implies that the energy level corresponding to the (2/-) charge state change will be shifted by 0.23 eV towards the conduction band minimum [6, 7]. In other words, the acceptor energy level involved in the  $(\text{Fe}_s\text{H})^{2-/-}$  change is expected to be less deep and located at  $E_c - 0.39$  eV [6, 7]. Apart from the  $\text{Fe}_s\text{H}$  pairs, the calculations also predict the possibility of arising the electrically active  $\text{Fe}_s\text{H}_2$  complexes which are formed by trapping a bond centred hydrogen by a  $\text{Fe}_s\text{H}$  pair [7]. The binding energy of the hydrogen atom is calculated to be 1.75 eV and this result indicates that the complexes can decompose at elevated temperatures ( $> 200$  °C) [7]. The acceptor level corresponding to the  $(\text{Fe}_s\text{H}_2)^{-/0}$  charge state change has been found to be located at  $E_c - 0.71$  eV [7]. It is worth adding that there is an order in the acceptor levels positions related to the charge state and composition of  $\text{Fe}_s\text{H}_n$  complexes. The above mentioned data indicate that the lower defect charge and the higher defect complexity, the position of the acceptor level is deeper in the bandgap. It is easily seen that for the centres  $(\text{Fe}_s\text{H})^{2-/-}$ ,  $(\text{Fe}_s\text{H})^{-/0}$  and  $(\text{Fe}_s\text{H}_2)^{-/0}$  the acceptor levels are located at  $E_c - 0.39$  eV,  $E_c - 0.62$  eV and  $E_c - 0.71$  eV, respectively [7].

The first principles calculations made by Santos *et al.*, gave the acceptor level at  $E_c - 0.50$  eV for the  $(\text{Fe}_s\text{H})^{-/0}$ , however the  $(\text{Fe}_s\text{H})^{2-/-}$  level was not calculated [5]. On the other hand, interesting results on the  $\text{Fe}_s\text{H}_2$  centre electronic properties were received. It was found that this complex is a negative  $U$  defect characterized by two acceptor levels at  $E_c - 0.21$  eV and  $E_c - 0.30$  eV for the  $(\text{Fe}_s\text{H}_2)^{-/0}$  and  $(\text{Fe}_s\text{H}_2)^{2-/-}$ , respectively [5]. This fact means that in experiments, the two electron emission could be observed from the level at  $E_c - 0.26$  eV that is located half-way between the first and second acceptor levels and corresponds to the (2-/0) charge state change.

The results of experimental studies and *ab initio* calculations presented above indicate that two types of iron-hydrogen complexes are formed in  $n$ -type silicon. These are the complexes involving interstitial iron as well as the complexes involving substitutional iron. The complexes are characterized by deep levels, however, the former are donors and act as hole traps and the latter are acceptors acting as electron traps. The aim of this paper is to determine the properties and concentrations of electron traps in iron-contaminated  $n$ -type epitaxial silicon. The majority carrier traps are expected to be related to  $\text{Fe}_s\text{H}$  pairs and  $\text{Fe}_s\text{H}_2$  complexes, for the epitaxial growth takes place in the ambience of flowing hydrogen. The experimental studies described in the paper were performed by using the state-of-the-art Laplace-transform deep-level transient spectroscopy (LDLTS). Deep electron traps were produced in  $n$ -type

silicon epitaxial layers due to the iron diffusion occurring during the epitaxial growth from the back surface of substrates contaminated with iron atoms. The activation energies of detected traps were compared with the reported acceptor levels positions determined by *ab initio* calculations for the changes of the charge state of  $\text{Fe}_s\text{H}$  and  $\text{Fe}_s\text{H}_2$  defects. This comparison enabled a tentative identification of the detected traps to be made. It was found that isochronal annealing at temperatures above 80 °C significantly decreases the traps concentrations. This experimental fact is consistent with the result of *ab initio* calculations showing a low binding energy of hydrogen to substitutional iron.

## 2. Experiment

Iron-related deep traps were investigated in slightly phosphorus-doped  $n$ -type epitaxial layers with a thickness of 25  $\mu\text{m}$  and an electron concentration of  $\sim 4 \times 10^{12} \text{ cm}^{-3}$ . The layers were grown in  $\langle 111 \rangle$  direction on 380- $\mu\text{m}$  thick antimony-doped  $n^+$  substrates with an electron concentration of  $(2-3) \times 10^{18} \text{ cm}^{-3}$ . The substrate wafers of a 3-inch diameter were purposely contaminated with iron by scratching their back surface with an iron wire of 4N purity along the line perpendicular to the wafer flat and passing through the wafer centre. The epitaxial growth was carried out by chemical vapour deposition (CVD) in a GEMINI 1 reactor using hydrogen as a carrier gas and  $\text{SiCl}_4$  as a silicon source.

Before the epitaxial growth, the substrates were heated up to 1175 °C in 15 minutes and then etched at this temperature in gaseous HCl for 6 minutes. Next, in 4 minutes, the temperature was lowered to 1120 °C and the substrates were kept at this temperature for 30 minutes in order to deposit  $n$ -type silicon layers using  $\text{PH}_3$  as a phosphorus source. Finally, the  $\text{PH}_3$  flow was switched off and the  $\text{B}_2\text{H}_6$  flow was switched on for 1 minute to make a thin  $p^+$  layer on the top of the  $n$ -type layer. The wafers with the epitaxial  $p^+/n$  junction were in 5 minutes cooled down to 600 °C and in the last step were cooled down to room temperature in 20 minutes. Next, the Ohmic contacts were made by evaporating Al layers of  $\sim 500$  nm thick on the both sides of wafers with the  $p^+/n/n^+$  structures and then the wafers were cut into chips of  $2.5 \times 2.5 \text{ mm}^2$  in area. For investigations of iron-related defects properties, the chips with the scratch made with the iron wire were selected. To confirm that detected defect centres are formed due to the iron diffusion during the epitaxial growth, the control epitaxial  $p^+/n/n^+$  structures on the substrate wafers not contaminated with iron were made and the chips with this structures were also used for LDLTS measurements.

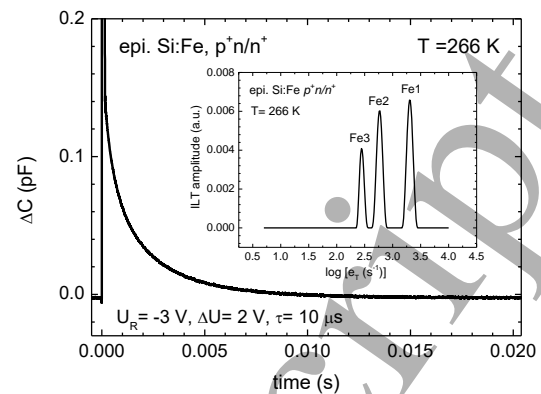
The capacitance transients were measured by using the state-of-the-art experimental system built of a Boonton 7200 capacitance meter, a home-made compensator of the steady state capacitance, a Janis nitrogen cryostat, and a LakeShore

340 temperature controller. The system also contains a GPIB card to control the capacitance and temperature measurement settings as well as a 16-bit NI PCIe-6251 card with the BNC 2120 attachment enabling the analog-to-digital conversion and data acquisition to be made with a sampling rate of 1.25 MS/s. The measurements are controlled by means of a dedicated computer program operating in the LabVIEW integrated environment. The application fully controls both the DLTS measurements as well as taking the steady-state capacitance-voltage characteristics. The measurements of capacitance relaxation waveforms were performed at a temperature range of 80 – 320 K with a temperature increment of 3 K. During the measurements, the reverse bias  $V_R = -3$  V and the filling pulse amplitude  $V_F = 2$  V were used. The filling pulse width was 10  $\mu$ s and the filling pulse repetition period was 75 ms. To extract the traps parameters, the capacitance relaxation waveforms recorded at various temperatures were transformed into spectra by means of the correlation procedure as well as by the numerical procedure based on the inverse Laplace transformation algorithm (ILT) implemented in the CONTIN program [10]. Using the same iron-contaminated  $p^+/n/n^+$  structures, the DLTS measurements were carried out two times: the first time directly (within 7 days) after the epitaxial growth and the second time after around 8500 days from the day of the deposition. For this time, the samples have been stored at room temperature ( $\sim 24$  °C) in the clean room environment. After the long-term storage at room temperature, the samples were further used for the measurements of electron traps properties and concentrations before and after isochronal annealing at temperatures of 80, 160 and 240 °C.

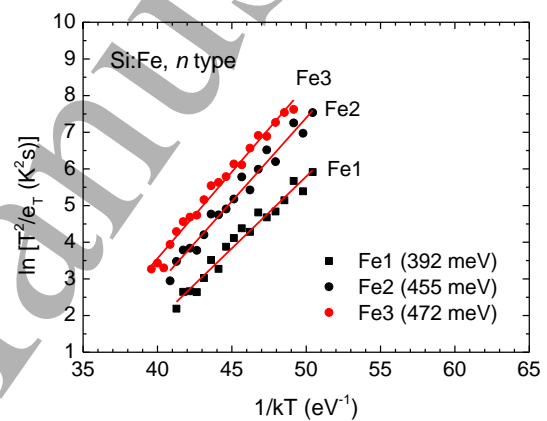
### 3. Results and discussion

The capacitance relaxation waveform measured at 266 K and multiplied by -1 for a Fe-contaminated  $p^+/n/n^+$  epitaxial Si structure subjected to the long term storage at room temperature after the epitaxial deposition is shown in Fig. 1. The inset demonstrates the 1D Laplace spectrum derived from this waveform with three sharp peaks indicating the thermal emission of electrons from the Fe1, Fe2, and Fe3 traps induced by the iron diffusion from the substrate. The Arrhenius plots received from the 2D Laplace spectra for the detected iron-related deep electron traps are presented in Fig. 2. The spectra were created by assembling a number of one-dimensional Laplace spectra  $S_{Lj}(e_T)$ , received for various values of the thermal emission rate  $e_T$  as a result of the ILT transformation of capacitance relaxation waveforms recorded at  $J$  temperatures ranging from 200 to 320 K. The plots in Fig. 2 illustrate the dependences of  $\ln(T^2/e_T)$  versus  $1/kT$ , where  $T$  and  $k$  denote the absolute temperature and the Boltzmann constant, respectively. The values of electron emission activation energy  $E_a$  and pre-exponential factor  $A$  in the Arrhenius

equation, calculated from the slope and intercept of each line, respectively, are listed in Table 1.



**Figure 1.** Inverted capacitance relaxation waveform recorded at 266 K for an iron-contaminated epitaxial Si  $p^+/n/n^+$  sample. The inset shows one-dimensional Laplace spectrum with three sharp peaks associated with the Fe1, Fe2, and Fe3 iron-related electron traps.



**Figure 2.** Arrhenius plots for thermal electron emission from iron-related traps detected in  $n$ -type epitaxial silicon. The straight lines are fitted by linear regression to the experimental data taken from the 2D Laplace spectra.

**Table 1.** Parameters and concentrations of deep electron traps detected in iron-contaminated epitaxial silicon.

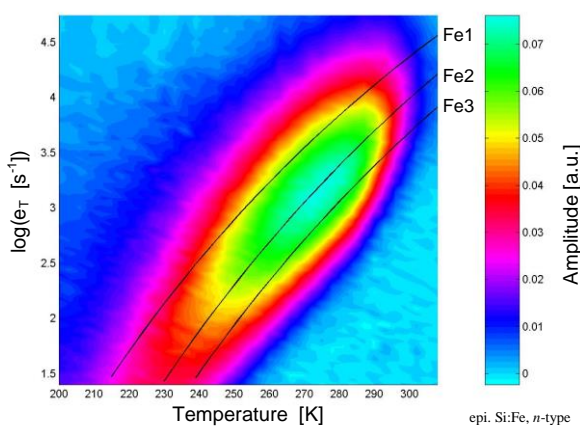
Trap	$E_a$ (meV)	$A$ ( $K^{-2}s^{-1}$ )	$\sigma_n$ ( $cm^2$ )	$N_T$ ( $cm^{-3}$ )	Defect
Fe1	$392 \pm 10$	$9.94 \times 10^5$	$1.4 \times 10^{-16}$	$1.9 \times 10^{10}$	$(Fe_sH)^{2-/-}$
Fe2	$455 \pm 10$	$4.76 \times 10^6$	$6.6 \times 10^{-16}$	$1.8 \times 10^{10}$	$(Fe_sH)^{-/0}$
Fe3	$472 \pm 10$	$4.54 \times 10^6$	$6.3 \times 10^{-16}$	$1.1 \times 10^{10}$	$(HFe_sH)^{-/0}$

The values of electron capture cross-section as well as the traps concentrations and proposed identifications are also given in this table. The electron capture cross-sections for the Fe1, Fe2, and Fe3 traps were determined as  $\sigma_n = A/\gamma_n$ , where  $\gamma_n$  is the effective mass-dependent material constant that for  $n$ -type Si is equal to  $7.17 \times 10^{21} cm^{-2}s^{-1}K^{-2}$ . The traps concentrations were obtained from the amplitudes of the capacitance relaxation waveforms in the manner typical of DLTS technique [11]. It should be noted that the Fe1, Fe2 and Fe3 traps concentrations given in Table 1 are in the

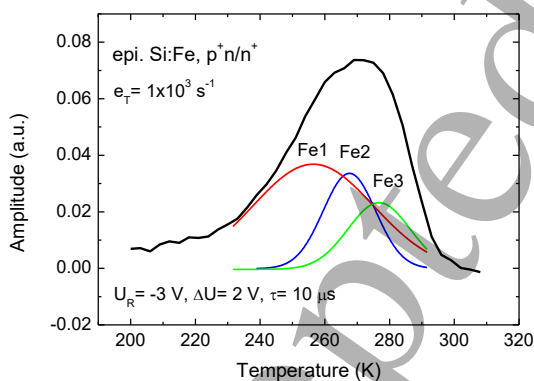


samples that have been stored for the long time at room temperature. Directly after the epitaxial growth, only the Fe1 and Fe3 traps were found and their concentrations were  $8.0 \times 10^{11}$  and  $2.4 \times 10^{12} \text{ cm}^{-3}$ , respectively. The Fe2 trap was not detected, for its concentration was probably below  $10^{11} \text{ cm}^{-3}$ .

The image of the broad spectral fringe obtained by the correlation procedure with the superimposed lines illustrating the temperature dependences of the electron emission rate determined for detected traps by means of the ILT procedure is shown in Fig. 3. The fringe presents the projection of the fold visible in the 3D space on the plane defined by the axes for the temperature ( $T$ ) and emission rate ( $e_T$ ). The cross-section of this fold for the emission rate  $e_T = 1000 \text{ s}^{-1}$  is shown in Fig. 4.



**Figure 3.** Spectral fringe obtained by the projection of the correlation spectral surface on the plane defined by the temperature ( $T$ ) and thermal emission rate ( $e_T$ ) axes. The superimposed solid lines illustrate the temperature dependences of the electron emission rate derived from the 2D Laplace spectra for the Fe1, Fe2, and Fe3 deep electron traps.



**Figure 4.** One-dimensional correlation spectrum for an electron emission rate of  $1000 \text{ s}^{-1}$  with the peaks corresponding to the Fe1, Fe2, and Fe3 traps resolved by Gaussian fitting.

The presented results are similar to those reported for  $\text{Au}_s(-/0)$  and  $\text{Au}_s\text{H}$  pairs resolved by the Laplace DLTS technique in phosphorus-doped  $n$ -type Czochralski silicon wafers containing gold atoms introduced by diffusion and

hydrogen atoms injected by etching using a CP4 etch [12]. In this material two deep electron traps with activation energies of 542 meV and 558 meV have been revealed. They were assigned to the G4 centre identified with the gold-hydrogen complex  $\text{Au}_s\text{H} (-/0)$  and to the Au-acceptor centre  $\text{Au}_s (-/0)$ , respectively. It has been also suggested that apart from the G4 centre, the  $\text{Au}_s\text{H}$  complexes in other charge states may also occur in  $n$ -type Si [12]. The results of recent studies have shown, however, that the G4 centre is more likely attributed the  $\text{Au}_s\text{H}_2 (-/0)$  than to  $\text{Au}_s\text{H} (-/0)$  [13]. Thus, the electronic properties gold-hydrogen complexes have not been fully understood yet and more experiments are needed to verify calculated positions of acceptor levels related to these complexes.

The formation  $\text{Fe}_s\text{H}_n$  ( $n=1$  or  $2$ ) complexes is determined by the  $\text{Fe}_s$  properties in the Si lattice as well as by the properties of hydrogen atoms. At temperatures around  $1100^\circ\text{C}$ , there are high concentrations of both charge carriers (electrons and holes) and ionized hydrogen atoms  $\text{H}^+$  and  $\text{H}^-$  [3]. At temperatures below  $800^\circ\text{C}$ , the majority of hydrogen in silicon is molecular [3]. The results of calculations based on the first-principles spin-density-functional theory indicate that the iron atom may be located at the ideal substitutional site with  $T_d$  symmetry and its  $(-/0)$  charge change may occur [4]. In other words, in  $n$ -type Si, a substitutional iron atom may be either neutral ( $\text{Fe}_s^0$ ), with the spin of 0, or negatively charged ( $\text{Fe}_s^-$ ), with its nucleus spin of  $1/2$  [4]. The electron configuration of the negatively charged iron atom in silicon lattice is  $[\text{Ar}]3d^5 4s^1 4p^3$  with the  $s$  and  $p$  orbitals used for making the  $sp^3$  bond with the four adjacent silicon atoms. Thus we can assume that the changes in the  $\text{Fe}_s$  charge state are related to the variations of the number of electrons in the  $d$  orbital. For the neutral iron  $\text{Fe}_s^0$  the electron configuration is  $[\text{Ar}]3d^4 4s^1 4p^3$ . It is worth adding that the maximal number of electrons in  $d$  orbital is 10 and depending on the position of the Fermi energy, a substitutional iron atom in  $n$ -type Si can also capture two electrons, becoming a doubly ionized acceptor  $\text{Fe}_s^{2-}$  with the electron configuration  $[\text{Ar}]3d^6 4s^1 4p^3$ , or even three electrons, becoming a triply ionized acceptor  $\text{Fe}_s^{3-}$  with the electron configuration  $[\text{Ar}]3d^7 4s^1 4p^3$ . The  $(\text{Fe}_s\text{H})$  pairs are likely to be formed during cooling the layers down to room temperature after the epitaxial growth when  $\text{H}^+$  diffuses toward  $\text{Fe}_s^-$ . At elevated temperatures ( $500^\circ\text{C}$ ), hydrogen is in the positive charge state ( $\text{H}^+$ ) and behaves like a proton heading to the region of high electronic charge density. The sufficiently high charge density occurs in the vicinity of the  $\text{Fe}_s^-$  acceptor and the neutral  $\text{Fe}_s\text{H}^+$  pair arises. At a lower temperature of  $\sim 200^\circ\text{C}$ , the pair can capture an additional electron causing the increase in the number of electrons in the iron  $d$  orbital from 5 to 6 and the formation of the negatively ionized  $\text{Fe}_s^{2-}\text{H}^+$  pair.

The tentative identification of the Fe1(392 meV), Fe2 (455 meV) and Fe3(472 meV) electron traps given in Table 1

was made on the grounds of the reported results obtained by *ab initio* calculations [4-7]. The results of theoretical studies are thoroughly described in the introduction to this paper and strongly confirm the possibility of the  $\text{Fe}_3\text{H}$  pairs and  $\text{Fe}_3\text{H}_2$  complexes formation in Fe-contaminated *n*-type silicon exposed to environment containing hydrogen. These defects can be in various charge states depending on their formation conditions and the Fermi level position in the material. The comparison of the Fe1, Fe2 and Fe3 traps activation energies with the calculated acceptor levels positions for the charge state changes of  $\text{Fe}_3\text{H}_n$  ( $n=1$  or  $2$ ) defects indicates that there is an excellent agreement between the Fe1 trap activation energy of 392 meV and the acceptor level at  $E_c - 0.39$  eV for the  $(\text{Fe}_3\text{H})^{2-/}$  [7]. A very good agreement there is also between the Fe2 trap activation energy of 455 meV and the acceptor level at  $E_c - 0.50$  eV reported by Santos *et al.* for the  $(\text{Fe}_3\text{H})^{-0}$  [5]. On the other hand, the acceptor level for this defect calculated by Gonzalez Szwacki *et al.* was found to be located deeper in the bandgap at  $E_c - 0.62$  eV [7]. The Fe3 trap with the activation energy of 472 meV has been attributed to the  $(\text{Fe}_3\text{H}_2)^{-0}$ , although the acceptor level for this defect was found to be located at  $E_c - 0.71$  eV [7]. However, we took into account the results of recently reported studies implying that the formation of complexes involving a transition metal atom in the substitutional position and two hydrogen atoms is highly probable [3, 7, 13]. Besides, there is a discrepancy between the results of *ab initio* calculations. According to the results obtained by Santos *et al.*, the  $\text{Fe}_3\text{H}_2$  is a negative  $U$  centre with the effective acceptor level for two-electron ( $0/2-$ ) emission at  $E_c - 0.26$  eV [5].

The parameters of the Fe1 and Fe2 electron traps (Table 1) are in good agreement with those of the B and C traps whose deep energy levels were found to be located at  $E_c - 0.41$  and  $E_c - 0.48$  eV, respectively, detected in phosphorus-doped *n*-type epitaxial silicon purposely contaminated with iron [14]. The net donor concentration in the 10- $\mu\text{m}$ -thick epitaxial layers was  $\sim 1.7 \times 10^{14} \text{ cm}^{-3}$ . The iron was introduced by diffusion, performed at 1050 °C for 2 h from the epitaxial layer surface covered with iron atoms with a concentration of  $1 \times 10^{13} \text{ atoms/cm}^2$ . On the other hand, in the case of iron-contaminated *n*-type silicon wafers produced from a phosphorus-doped single-crystal with a net donor concentration of  $\sim 5 \times 10^{14} \text{ cm}^{-3}$  grown by Czochralski-method, the DLTS measurements revealed three Fe-related deep levels at  $E_c - 0.29$  eV (E1),  $E_c - 0.36$  eV (E2), and  $E_c - 0.48$  eV (E3) [15]. These results indicate that the only defect center present either in the hydrogen-lean bulk silicon or in the hydrogen-rich epitaxial silicon layers is the Fe-related deep electron trap with the activation energy of around 480 meV. The fact that it is observed in various investigations independently of the hydrogen concentration in the Fe-contaminated material implies that it may be

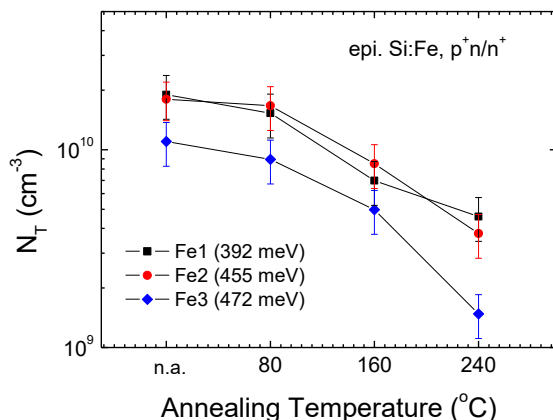
identified with the iron acceptor  $\text{Fe}_3^-$ . It is worth emphasizing that the presence of neutral and negatively charged substitutional iron species in *n*-type silicon has been proved by results of Mössbauer spectroscopy measurements [16]. At an excess of vacancies (V) produced by diffusion or electron irradiation, the substitutional iron atoms can be formed according to the reaction  $\text{Fe}_i + \text{V} \rightarrow \text{Fe}_3^-$  [2,16].

The iron diffusion through substrate to the epitaxial layer is predominantly controlled by the interstitial mechanism [3]. We have performed simulations indicating that the concentration of interstitial iron atoms in the epitaxial layers is around  $2 \times 10^{14} \text{ cm}^{-3}$ . However, the concentration of substitutional iron is significantly lower, of the order of  $10^{12} \text{ cm}^{-3}$ , for it is limited by the vacancy concentration [2,4]. Directly after the epitaxial growth, the Fe1 and Fe3 traps concentrations were found to be  $8.0 \times 10^{11}$  and  $2.4 \times 10^{12} \text{ cm}^{-3}$ , respectively, and the Fe2 trap was not detected, for its concentration was probably below  $10^{11} \text{ cm}^{-3}$ . In other words, directly after the epitaxial growth only two electron traps were present in the Fe-contaminated layers: the predominant Fe3 trap, and the Fe1 trap, whose concentration was several times lower.

The experiment aimed at determination of the low temperature annealing effect on the traps properties and concentrations was performed in two stages: the long term room temperature (RT) annealing and isochronal annealing for 30 min at elevated temperatures (80, 160 and 240 °C). In the first stage, the Fe-contaminated epitaxial  $p^+n/n^+$  samples were annealed at a temperature  $\sim 24^\circ\text{C}$  when they have been stored for around 8500 days in the clean room conditions. After the long-term storage, the LDLS measurements were carried out again and the three electron traps: Fe1, Fe2 and Fe3 were found. The properties and concentrations of these traps are listed in Table 1. We observe a substantial decrease in the Fe1 and Fe3 traps concentrations in time to the values of  $1.9 \times 10^{10}$  and  $1.1 \times 10^{10} \text{ cm}^{-3}$ , respectively, which indicates that the long-term RT annealing of these traps occurs and as a result of this annealing the Fe2 trap is observed at a concentration of  $1.8 \times 10^{10} \text{ cm}^{-3}$ . The concentrations of B(0.41 eV) and C(0.48 eV) electron traps reported in [14] were also found to decrease in time when stored at room temperature. The initial concentrations of these traps were  $2.2 \times 10^{10}$  and  $2.5 \times 10^{10} \text{ cm}^{-3}$ , respectively and after 200-day storage at RT, these traps concentrations dropped to  $1.3 \times 10^{10}$  and  $2.3 \times 10^{10} \text{ cm}^{-3}$ , respectively.

In the second stage, the Fe-contaminated epitaxial  $p^+n/n^+$  diodes that had been previously annealed at RT were subjected to isochronal annealing for 30 min at temperatures of 80, 160 and 240 °C. The effect of the annealing temperature on the Fe1, Fe2 and Fe3 traps concentrations is demonstrated in Fig. 5. It is easily seen that the Fe1 and Fe2 traps concentrations decrease approximately with the same

rate with increasing the temperature and this rate is lower than that of the Fe3 trap concentration.



**Figure 5.** Changes in the concentrations of the Fe1, Fe2 and Fe3 electron traps detected in Fe-contaminated *n*-type epitaxial silicon induced by annealing at elevated temperatures (n. a. stands for non-annealed sample).

The dependences shown in Fig. 5 support the proposed identification of the Fe1 and Fe 2 electron traps as the defect centres attributed to the  $\text{Fe}_3\text{H}$  pair in various charge states. The results are also in favour of attributing the Fe3 electron trap to the  $\text{Fe}_3\text{H}_2$  complex. As it is expected, the both types of complexes decompose at elevated temperature, and the rate of decomposition in the case of the latter is higher than that of the former. As it shown above, the decomposition of the  $\text{Fe}_3\text{H}_2$  complex takes also place at room temperature, however, with much smaller rate.

#### 4. Conclusions

The state-of-the-art Laplace DLTS technique has been implemented to determine the properties and concentrations of deep electron traps in Fe-contaminated *n*-type silicon epitaxial layers deposited by the CVD method using hydrogen as a carrier gas. Three iron-related electron traps located at  $E_c - 392$ ,  $E_c - 455$  and  $E_c - 472$  meV have been resolved and tentatively attributed to the acceptor energy levels of  $(\text{Fe}_3\text{H})^{2-/-}$ ,  $(\text{Fe}_3\text{H})^{-0}$  and  $(\text{HFe}_3\text{H})^{-0}$  complexes, respectively. In order to determine how the low temperature annealing affects the traps properties and concentrations, first the long term room temperature annealing and then the isochronal annealing for 30 min at temperatures of 80, 160 and 240 °C were made. Directly after the epitaxial growth, only the 0.455-meV and 0.472-meV traps were observed. As a result of the annealing at room temperature for around 8500 days, the concentration of the former dropped from  $8.0 \times 10^{11}$  to  $1.9 \times 10^{10} \text{ cm}^{-3}$  and that of the latter decreased from  $2.4 \times 10^{12}$  to  $1.1 \times 10^{10} \text{ cm}^{-3}$ . This result implies that in as-grown epitaxial layers the  $(\text{HFe}_3\text{H})^{-0}$  complexes are predominant defects which effectively decompose at room temperature by releasing one of the two hydrogen atoms. At the elevated temperatures, ranging from 80 to 240 °C, the

decomposition rate of these complexes substantially increases. The dissociation of the  $(\text{Fe}_3\text{H})^{2-/-}$ ,  $(\text{Fe}_3\text{H})^{-0}$  complexes also takes place, however the rate of this process is lower than that for the  $(\text{HFe}_3\text{H})^{-0}$  defects.

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