Electrical studies of Fe-related defect complexes in silicon

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Abstract

Iron (Fe) is an important impurity in solar-grade silicon which contributes substantially in degrading the efficiency of solar cells. The degradation is mainly caused by the Fe atoms situating at an unperturbed tetrahedral interstitial sites (Fe\textsubscript{i}) in the silicon crystal, consequently acting as a recombination center. By altering the position and the neighboring environment at which the Fe atoms reside, there are opportunities in minimizing or neutralizing the electrical activity of Fe. Furthermore, utilizing the high mobility of Fe, one can increase the performance of a device by accumulating the Fe atoms from critical regions into regions where Fe can be tolerated. These approaches can help in realizing high efficient solar cells based on cheap and highly Fe-contaminated silicon. In this work, we have investigated the interaction between Fe and defects relevant to solar cells, using mainly electrical characterization methods such as capacitance-voltage measurement, deep level transient spectroscopy and admittance spectroscopy.

From the study of potential hydrogen passivation of Fe, hydrogen was introduced through wet chemical etching and further driven to a defined region. Using depth profiles, it is found that incorporation of hydrogen stimulates the dissociation of the iron-boron (Fe-B) pair, releasing and resulting in the unwanted Fe\textsubscript{i}. At the same time, no passivation of Fe by hydrogen has been observed.

On the investigation of the mechanism of phosphorus gettering of metal impurities, vacancies have been generated through proton-irradiation. The resulting irradiation-induced defects were examined for reactions with Fe after heat treatments. Based on the evolution of defect concentrations by isochronal annealings, it is found that Fe interacts with the divacancy and
the vacancy-oxygen complexes, forming deep levels of 0.28 eV and 0.34 eV above the valence band edge ($E_V$), respectively.

In the search for substitutional Fe to investigate its electrical activity and thermal stability, measurements were performed around the projected range of Fe-implantations after rapid thermal annealing. A shallow acceptor is uncovered with an energy level position of $E_V + 0.06$ eV and a defect concentration closely following the calculated concentration of the Fe-implantation dose. However, chemical analysis with secondary ion-mass spectrometry shows out-diffusion of Fe from the region around the projected range after annealing. This suggests that the formation of the shallow acceptor is only assisted/promoted by Fe without Fe being a part of the final complex.
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# Contents

List of Articles \hfill iv

1 Introduction \hfill 1

2 Basic semiconductor concepts and physics \hfill 5
  2.1 Schottky barrier contact \hfill 5
  2.2 Point defects and charge carrier emission \hfill 7
    2.2.1 Formation and stability of defects \hfill 7
    2.2.2 Electron and hole occupancy of a defect \hfill 9
    2.2.3 Capture and emission rate \hfill 10
    2.2.4 Poole-Frenkel effect \hfill 11

3 Methods \hfill 13
  3.1 Capacitance-voltage measurement (CV) \hfill 13
  3.2 Deep level transient spectroscopy (DLTS) \hfill 14
    3.2.1 Weighting functions \hfill 17
    3.2.2 Extraction of defect parameters \hfill 18
    3.2.3 Deep level depth profiling \hfill 19
  3.3 Admittance spectroscopy (ADSPEC) \hfill 20
  3.4 Simulation software (Synopsys TCAD) \hfill 22

4 Present work and suggestions for future work \hfill 25
  4.1 Material \hfill 25
  4.2 Preparation \hfill 26
List of Articles


Chapter 1

Introduction

Silicon has been the dominant semiconductor for more than half a century and intensively studied. This has given silicon an advantage as a material for solar cells where more than 80% of the market is based on crystalline silicon (1). Single crystalline and multicrystalline silicon are the main ones used and they differ generally by quality and cost. Multicrystalline silicon contains higher impurity concentration due to in-diffused metal during growth, and the impurities can easily form precipitates at grain boundaries (2, 3). These precipitates can degrade a solar cell by increasing the leakage current and increasing the probability of shunting. Moreover, the precipitates can also be dissolved during high temperature processing of a solar cell, producing point defects with strongly degrading effects, even at low concentrations (4, 5). Among the metal impurities, transition metals, such as iron (Fe), are particularly detrimental for the solar cell and integrated circuit performance. Solar cells based on single crystalline silicon will degrade similarly when contaminated with the metals.

The study of Fe in Si began already in 1956 (6) and is one of the most studied transition metals in silicon (7, 8). More than 30 Fe-related defects have been uncovered using electron paramagnetic resonance (EPR) and around 12 electrically active defects are firmly reported using electrical characterization methods. However, only 4 of the electrically active defects are relevant for boron-doped silicon which is mainly used for solar cells. Two of the defects are well-known for their degradation characteristics in commercial silicon-based solar cells, and they are the interstitial Fe (Fe$_i$) and the Fe-B pair (consisting of an interstitial Fe next to a substitutional boron (B)) (9). These
two defects are reversibly interchangeable and the dissociation of the Fe-B pair into the Fe$_i$ leads to a degradation of the solar cell. Such dissociation can be initiated by heat treatment, minority carrier injection or illumination\cite{10, 11}, where the latter one is the so-called light-induced degradation (LID). Interestingly, having $5 \times 10^{22}\text{cm}^{-3}$ of silicon atoms in a crystal, a significant degradation can already be observed with a concentration of Fe$_i$ of $1 \times 10^{12}\text{cm}^{-3}$\cite{12}. Large amount of research has been focused on reducing the concentration of electrically active Fe, by, for instance, accumulating Fe in a non-affecting region (gettering) or forming Fe-related complexes which are electrically in-active (passivation).

The principle of gettering is to create a spatial region capable of capturing a large amount of Fe by forming stable complexes. The gettering process can occur with, for instance, oxygen precipitates\cite{13}, structural damage\cite{14}, electrically charged regions\cite{15} or phosphorus in-diffusion\cite{16}. The latter method is essentially one of the steps in forming standard solar cells and, therefore, provide rinsing of the material “for free”. However, the phosphorus gettering process is not well understood in terms of the underlying defect reactions which sets limitations on the optimization of the gettering process. Thus, it is important to gain further understanding in the defects reactions with Fe.

Passivation of defects is commonly performed with hydrogen, as illustrated by the many reports showing its capability on vacancies\cite{17}, dangling bonds\cite{18}, grain boundaries\cite{19, 20} and dopants\cite{21}. For that reason, introduction of hydrogen is often an integrated process in the production of solar cells and efficiency improvements have been observed. However, reports have also shown that reactions between H and transition metals can form electrically active defects such as Au-H\cite{22}, Pt-H\cite{23} and Ag-H\cite{24}. In the case of Fe, experimental reports on the effect of H on Fe are scarce and contradicting\cite{25, 26, 27} which demands further examinations. Fortunately, theoretical estimates have been performed recently to predict the stability and the electrical activity of possible Fe-H complexes\cite{28, 29}, but the predictions still require experimental verifications.

In the work of this thesis, Fe has been introduced in silicon under various conditions and investigated for Fe-related complexes using electrical characterization techniques. The origin, formation and stability of Fe-related complexes are discussed.
This thesis is organized into four chapters. Chapter 2 introduces the basic semiconductor concepts and physics which assist in the understanding of the electrical characterization techniques used and the purposes of the experiments. Chapter 3 describes the electrical characterization techniques, and Chapter 4 summarizes the work in the manuscripts and published articles.
1. INTRODUCTION
Chapter 2

Basic semiconductor concepts and physics

This chapter introduces the basic concepts of semiconductor physics and will aid in the understanding of this thesis. Detailed concepts which are closely related to a subject, however, will only be briefly mentioned and references are given for those interested.

2.1 Schottky barrier contact

The Schottky barrier contact (SBC) is an important diode structure, formed between a semiconductor and an appropriate metal (30). A diode exhibits a non-linear current-voltage characteristics, and it can be understood by considering the energy potentials and the charge carrier distribution of the system, based on the Schottky-Mott limit (31). Figure 2.1a shows schematically a system consisting of a metal, for instance aluminium, and a semiconductor, for instance p-type silicon, in a non-interacting distance where energy potentials are situated relative to the vacuum level ($E_{\text{vac}}$). In the Si, electrons and holes (quasi-particle with opposite charge state of the electron) occupy energy levels in the conduction band and the valence band, respectively. These bands are separated by a band gap ($E_G$) which is intrinsically free of energy levels, and the gap distance is controlled by the conduction band edge ($E_C$) and the valence band edge ($E_V$). The amount of electrons and holes in the respective bands are expressed by the Fermi-level
2. BASIC SEMICONDUCTOR CONCEPTS AND PHYSICS

(E_F) and are exponentially dependent on the position of the E_F. In a semiconductor where the current is dominated by electrons, that is an n-type material, the Fermi-level is found close to the E_C, while the opposite is true for a p-type semiconductor.

Figure 2.1b shows a simplified schematic of the Al and the Si in direct contact. The Fermi-levels in Fig.2.1a is aligned due to diffusion of free charge carriers (holes, in this case) across the junction, leaving ionized dopants and giving rise to an electrical field which opposes the diffusion. This results in a region depleted of free charge carrier, called the depletion region (W), and the electrical field results in a built-in potential (V_{bi}). The V_{bi} multiplied by the elementary charge\(^1\), q, describes the energy barrier the free charge carriers must surmount in order to reach the metal from the semiconductor when no external voltage is applied. This energy barrier can be manipulated by simply applying a voltage (V_a) across the system. In a forward bias voltage, the energy barrier is decreased and the amount of charge carriers moving from the semiconductor to the metal increases exponentially, resulting in an exponential increase in the current density. While in a reverse bias voltage, the current density is affected by \Phi_F, which is determined by the choice of metal, and the amount of minority carriers (electrons, in the case of Fig.2.1b) in the semiconductor. Another direct consequence of applying a voltage over a diode is that the width of the depletion region changes, where W can

\(^1q \approx 1.602 \times 10^{-19} C\)
be expressed as

\[ W = \sqrt{\frac{2\varepsilon_0\varepsilon_r}{q} \left( \frac{1}{N_a} + \frac{1}{N_d} \right) (V_{bi} + V_a)}, \]

(2.1)

where \( \varepsilon_0 \) is the permittivity of free space\(^1\), \( \varepsilon_r \) is the relative permittivity of the semiconductor and \( N_a/N_d \) is the doping concentration of acceptors/donors.

Another important diode structure is the pn-junction where one material is doped p-type in one region and n-type in the neighbouring region, creating a difference in the Fermi-levels between the n-type and the p-type region (30). This difference results, again, in the diffusion of free charge carrier across the junction, producing the depletion region and the energy barrier. Although the general physics in the formation of the pn-junction is similar to a SBC, many phenomena and applicational differences exist which include the image force, minority carrier injection, switching speed and so on.

### 2.2 Point defects and charge carrier emission

Impurities and defects are important in order to provide a semiconductor with desirable electrical properties but may also be highly unwanted and detrimental to the device performance, as shown in the previous section with the dopants. This section will discuss properties of defects and their roles with charge carriers.

#### 2.2.1 Formation and stability of defects

In bulk materials, impurities and defects are introduced during growth and/or in the later processing steps. This can occur unintentionally by contamination from the environment or intentionally by various routes, such as ion-implantation and in-diffusion. Among the many lattice positions where a defect can be situated, Fig.2.2 shows a) an interstitial configuration and b) the substitutional configuration of a single impurity atom in a unit cell of silicon. Other defect configurations can, for instance, be bond-center, anti-bonding and hexagonal (32). More complicated configurations exist when combining multiple defects. This generates the possibility of higher dimensional defect, such as the one-dimension (1D) line defect, plane defect (2D) and clusters (3D) (34).

\(^1\varepsilon_0 \approx 8.854 \times 10^{-14} \text{ F/cm} \)
The stability of a defect configuration is determined upon the energy barrier required to interchange between defect configurations (35). The probability of surmounting an energy barrier increases exponentially with increasing temperature. For that reason, heat treatments (annealings) is commonly performed to investigate the evolution of and the interactions between defects present in a crystal. Furthermore, a heat treatment is terminated by cooling the crystal back to room temperature (RT) with a certain cooling rate. When a crystal is slowly cooled, a defect finds the most stable configuration. However, when the crystal is rapidly cooled (quenched), defects can be frozen into configurations differing from the most stable one. Quenching is, therefore, widely used in the study of Fe in silicon to freeze the in-diffused Fe to the interstitial lattice position which may otherwise form other Fe-related defect complexes at room temperature. (7).

A defect can also change its stability by altering the energy barrier for interchanging to other configurations. This can be performed by a change in the charge state of a defect(36). When a defect is introduced in the crystal, it can generate one or more energy levels within the band gap, which defines the charge state transitions. Thus, moving the Fermi-level will result in filling or emptying a defect for charge carriers, changing its charge state and, hence, its stability. As indicated in Sec.2.1 about SBC, the Fermi-level can easily be moved within the depletion region by applying a bias voltage in reverse. This enables a method of annealing in reverse bias voltage on a diode. The technique, not only allows a change in the defect annealing temperature, it also allows for defect reactions which would otherwise be hindered due to repulsion of same charge state (Coloumb repulsion).
2.2 Point defects and charge carrier emission

2.2.2 Electron and hole occupancy of a defect

As electrically active defects and impurities form energy level within the band gap, charge carriers can interact with the defects via the energy levels which results in filling or emptying of a defect of electrons and holes. Figure 2.3 shows the four possible charge carrier transitions between the energy bands and a defect, which changes the concentration of hole-filled ($p_T$) and electron-filled ($n_T$) defect from the total defect concentration ($N_T = p_T + n_T$). When a charge carrier is captured from and re-emitted to the same band, the transition is called trapping. While, if a charge carrier re-emittes to the other band, it is called recombination. Such transitions are associated with the rates of capture and emission of holes ($c_p p$ and $e_p$, respectively) and electrons ($c_n n$ and $e_n$, respectively), where the capture rates are dependent on the concentration of electrons in the conduction band ($n$) and holes in the valence band ($p$). For a given $n$ and $p$, electron occupancy of a defect can be deduced from the following partial differential equation

$$\frac{dn_T}{dt} = c_n n p_T + e_p p_T - c_p p n_T - e_n n_T = (c_n n + e_p)(N_T - n_T) - (e_p + c_n) n_T. \quad (2.2)$$

The equation can be solved for $n_T(t)$ to be

$$n_T(t) = n_T(0) e^{-t/\tau} + \frac{e_p + c_p n}{e_n + c_n n + e_p + c_p p} N_T (1 - e^{-t/\tau}), \quad (2.3)$$

![Figure 2.3: Schematics of capture and emission of charge carriers by a deep level, showing a) emission of an electron, b) capture of an electron, c) capture of a hole and d) emission of a hole.](image)
where \( n_T(0) \) is the electron occupancy of the defect at \( t = 0 \) and \( \tau = 1/(e_n + c_n n + e_p + c_p p) \). Similar equation for hole can be achieved by changing electron-related terms into hole-related terms.

Equation 2.3 can be reduced significantly when considering a defect in the depletion region which is initially filled with electrons (\( n_T = N_T \)) and in the process of being emptied. In such consideration, no free charge carriers are found in the bands (\( n = p = 0 \)) and the electron emission is dominating (\( e_n \gg e_p \)), which results in an important equation for various characterization techniques, such as deep level transient spectroscopy,

\[
n_T(t) \approx n_T(0)e^{-t/\tau} = N_T e^{-e_n t}.
\]

### 2.2.3 Capture and emission rate

The capture rate of electrons for a defect is defined as

\[
c_n = v_{th,n}\sigma_n n,
\]

where \( \sigma_n \) is the capture cross-section of the defect and \( v_{th,n} \) is the average thermal velocity of the electrons. The thermal velocity is defined as

\[
v_{th,n} = \sqrt{\frac{3kT}{m^*_n}},
\]

where \( k \) is the Boltzmann constant, \( T \) is the absolute temperature and \( m^*_n \) is the effective mass of electron. Similar equation can be deduced for holes by exchanging the electron-related indexes with \( p \).

The emission rate of electrons can be deduced by considering the principle of detail balance, which states that (Ref.(37) p.307) “under equilibrium conditions each fundamental process and its inverse must balance independent of any other process that may be occurring inside the material”. This means that electron capture and emission by a defect with the conduction band has to balance each other at equilibrium, leading to

\[
e_{n0}n_T = c_{n0}n_0(N_T - n_T),
\]

where the index 0 denotes equilibrium. Inserting for \( N_T \) and \( n_T \) using the Fermi-Dirac

\[
^1k = 1.381 \times 10^{-23} J/K
\]
\[
^2m^*_n = 1.08m_n
\]
distribution, the equilibrium emission rate becomes

\[ e_{n0} = c_{n0} N_C \frac{g_0}{g_1} \exp \left( -\frac{E_C - E_T}{kT} \right), \]  

(2.7)

where \( g_0 \) is the degeneracy of an unoccupied state, \( g_1 \) is the degeneracy of an occupied state and \( N_C \) is the effective density of states in the conduction band. Under the assumption that the emission and the capture rates change insignificantly under non-equilibrium conditions, the 0-index for \( e_{n0} \) and \( c_{n0} \) can be removed. Non-equilibrium conditions can, for instance, involve contributions from electric field, which can affect the emission rate.

### 2.2.4 Poole-Frenkel effect

The Poole-Frenkel effect is one of the effects which alter the energy barrier for emission of charge carriers by an electrical field (38), for instance in a depletion region. This effect exists only if an emitted charge carrier experiences a Coulomb attraction to the same defect. Figure 2.4 shows schematically an energy potential of a defect where the energy barrier is reduced by an applied electrical field. The reduction in the energy barrier can be expressed as

\[ \Delta E = 2q \sqrt{\frac{\xi q}{\varepsilon_0 \varepsilon_r}}, \]  

(2.8)

where \( \xi \) is the absolute value of the electrical field.

The Poole-Frenkel effect can be utilized to identify acceptors in p-type material or donors in n-type material by observing a dependence of emission properties as a function
2. BASIC SEMICONDUCTOR CONCEPTS AND PHYSICS

of electrical field. However, the lack of Poole-Frenkel in p-type (n-type) material does not necessarily prove the nature of donor (acceptor) (39).
Chapter 3

Methods

In this chapter, three of the most essential electrical characterization techniques and a simulation tool used in the thesis will be described. The Capacitance-voltage (CV) measurement is mainly used in determining the charge carrier concentration in order to control the doping concentration of a wafer and to investigate changes in samples after treatments. Both deep level transient spectroscopy (DLTS) and admittance spectroscopy (ADSPEC) are used to investigate defects including their energy level position and concentrations.

3.1 Capacitance-voltage measurement (CV)

One of the most important quantities in characterizing a diode is the capacitance, and defined as (40)

\[ C = \frac{\Delta q}{\Delta V} \]  

(3.1)

where \( \Delta q \) is the change in the charge and \( DeltaV \) is the change in the voltage. Normally, the capacitance is extracted by use of an AC voltage signal (for instance 1 MHz) with a small probing amplitude (typically between 30 to 100 mV) and measuring the current response. In a capacitance-voltage measurement, the AC-signal is superpositioned with a stepwise-changing DC-signal. For an ideal diode, the capacitance follows a voltage-
dependence given as

\[ C = A \sqrt{\frac{q\varepsilon_0 \varepsilon_r}{2}} \left( \frac{1}{N_a} + \frac{1}{N_d} \right)^{-1} \frac{1}{V_{bi} + V_a}, \]  

(3.2)

where \( A \) is the area of the junction. This equation can be simplified by introducing the depletion width (Eq.2.1) to

\[ C = \frac{\varepsilon_0 \varepsilon_r A}{W}, \]  

(3.3)

which is an important equation in providing the depth-information under investigation.

From a capacitance-voltage measurement, information about the effective charge carrier concentration as a function of depth can be extracted by, for instance, the following relation (40)

\[ N(W) = -\frac{2}{q\varepsilon_0 \varepsilon_r A^2} \left( \frac{\Delta C - 2}{\Delta V_a} \right)^{-1}. \]  

(3.4)

As an example, Fig.3.1 shows charge carrier concentration versus depth profiles for SBC before and after a heat treatment. It is known that formation of a SBC can unintentionally introduce hydrogen to the surface of the semiconductor (from, for instance, the metal), and that hydrogen passivates boron acceptors \( (32, 41, 42) \), forming the B-H complex, which reduces the charge carrier concentration. Thus, the amount of reduction in the charge carrier concentration can indirectly give information about the concentration of hydrogen. From Fig.3.1, it can also be seen that heat treatment can dissociate the B-H complex and distribute the hydrogen further into the semiconductor.

Equation 3.4 assumes a negligible or uniform concentration of deep-level defects. However, for a non-uniform concentration of deep acceptors (in n-type) in a sufficient amount to influence the overall carrier concentration, an artificial peak can occur (43).

### 3.2 Deep level transient spectroscopy (DLTS)

Deep level transient spectroscopy is a powerful electrical characterization technique capable of determining the capture cross-section, energy level position and concentration of defects(44). This technique utilizes the transient response of either capacitance,
3.2 Deep level transient spectroscopy (DLTS)

Figure 3.1: Charge carrier concentration versus depth profile before and after heat treatment on an aluminium SBC. It reveals the passivated region, which results from the formation of B-H, and can be related to the concentration of hydrogen.

Figure 3.2: Schematics showing the principle of DLTS through filling and emptying of a defect in a SBC by a voltage pulse.
type semiconductor. The occupancy of the deep levels can be reasoned by considering
the emission and capture rates of charge carriers described in Sec.2.2.2. For the deep
level close to the $E_C$, the emission rate of electrons dominates over the emission rate
of holes and the capture rate of electrons. Thus, this deep level remains emptied of
electrons (filled with holes). For the deep level close to the $E_V$, the emission rate
of holes dominates over the emission rate of electrons, but the emission rate of holes
competes with the capture rate of holes which varies spatially. At the depth $W_0 - \lambda$,
where $\lambda$ is the distance from the edge of the depletion region to the crossing depth
between the deep level and the Fermi-level, a transition in the dominance of capture
and emission rate of hole occurs. Thus, it is convenient to address the position of the
Fermi-level relative to defect levels to discuss the occupancy of defect levels.

In Fig.3.2b, the reverse bias voltage of the SBC is removed. As a consequence, the
depletion width is shorter than in Fig.3.2a and the Fermi-level moves below the region
depleted of holes of the deep level between $(W_0 - \lambda)$ and $(W_f - \lambda)$. This leads to a
capture process of holes, filling the defects.

When returning the SBC to its initial reverse bias voltage, shown in Fig.3.2c, the
instantaneous depletion width differs from $W_0$ due to the change in occupancy of the
defects within the depletion region. However, the defects in the region between $(W_0 - \lambda)$
and $(W_f - \lambda)$ are again under the Fermi-level which favours the emission of holes to
the valence band. The process of emission of holes creates a capacitive change as a
function of time, yielding a capacitance transient, as simulated in Fig.3.3a for different
temperatures. In a first approximation, the capacitance transient can be expressed as

$$\Delta C(t) = \frac{C_r N_T}{2N_a} e^{-\epsilon_p t}, \quad (3.5)$$

where $C_r$ is the capacitance under reverse bias voltage immediately before the voltage
pulse. From fitting of the measured capacitance transients to this equation, defect
properties, like defect concentration, energy level position and capture cross-section,
can be extracted. However, a more practical and visual method is available which
involves weighting functions.
3.2 Deep level transient spectroscopy (DLTS)

3.2.1 Weighting functions

A typical DLTS measurement is performed by repeatedly acquiring the capacitance transient after a filling pulse while heating or cooling of the sample. The capacitance transients are averaged within a temperature interval and the raw data of a DLTS measurement may appear, for example, as simulated in Fig. 3.3a. Such data representation are difficult to work with, especially in comparing between different DLTS measurements. Thus, mathematical treatments are used in order to convert the data into a spectrum with peaks as a function of temperature. Many weighting functions exist which differ by their capability of separating close-lying peaks and their tolerance of noise (45), for instance lock-in and GS4 weighting function, where a lock-in weighting function is widely used.

The lock-in weighting function provides a simple mathematical conversion with high tolerance of noise which is ideal for characterizing defects that are significantly different in charge carrier emission properties. This function converts the transient by simply subtracting the first half of the transient with the second half. Thus, the lock-in weighting function can be expressed as

\[
w_{\text{Lock-in}}(t_j) = \begin{cases} 
-1 & , \text{ for } 1 \leq j \leq 2^{i-1} \\
1 & , \text{ for } 2^{i-1} < j \leq 2^i 
\end{cases}
\]  

\[(3.6)\]

Figure 3.3: Principle of DLTS, simulated by Matlab, showing a) capacitance transients at different temperature, b) lock-in weighting function for the first three time-windows and c) DLTS spectra of the transients in a), extracted using lock-in weighting function in b).
where \( t_j \) is a discretized time (10 ms in Fig.3.3a) and \( i \) is the time-window (TW) which represents the length of time to be considered. Figure 3.3b shows the lock-in weighting function for the first three time-windows which involves the first 2, 4 and 8 data points of the transients. This leads to time-window dependent DLTS signals, \( S_i \), which is expressed as

\[
S_i = \frac{1}{2^i} \sum_{j=1}^{2^i} w_{\text{lock-in}}(t_j) \Delta C(t_j).
\] (3.7)

Figure 3.3c shows three DLTS spectra deduced from the transients in Fig.3.3a according to Eq.3.7 for the first three time-windows. A peak from each DLTS spectrum is visible due to a deep level and the peak position is shifted depending on the time-window. This shift is essential when extracting defect parameters.

In contrast to the lock-in weighting function, the GS4 weighting function has a lower tolerance to noise but higher capability (energy resolution) of separating peaks. The function which is given as (46)

\[
w_{\text{GS4}}(t_j) = \begin{cases} 
-1 & \text{for } 1 \leq j \leq 2^{i-2} \\
25 & \text{for } 2^{i-2} < j \leq 2^{i-1} \\
-48 & \text{for } 2^{i-1} < j \leq 3/2 \times 2^{i-1} \\
24 & \text{for } 3/2 \times 2^{i-1} < j \leq 2^i 
\end{cases}
\] (3.8)

requires four data points of a transient for the first time-window \((i = 2)\), and the DLTS signals are calculated with Eq.3.7 after replacing \( w_{\text{lock-in}} \) with \( w_{\text{GS4}} \). A detailed description of this weighting function can also be found in Ref.(47).

### 3.2.2 Extraction of defect parameters

Weighting functions have enabled the visualization of deep levels as peaks at given temperature depending on the parameters chosen for the time-windows. In addition, the temperature of a peak maximum represents an emission rate of a deep level at that temperature. Thus, using several time windows, a collection of emission rates at different temperatures are found. By rearranging Eq.2.7, a relation between the
3.2 Deep level transient spectroscopy (DLTS)

emission rate and temperature can be expressed as

\[
\ln \left( \frac{e_n}{T^2} \right) = \ln \left( \frac{8\pi^{3/2}m^*k^2}{h^3} \right) \frac{g_0}{g_1} \sigma_n - \left( \frac{E_C - E_T}{k} \right) \frac{1}{T},
\]

and visualized in an Arrhenius plot of \( \ln(e_n/T^2) \) versus \( 1/T \). Here, the slope of the Arrhenius plot uncovers the energy level position, while the extrapolated intersection to the ordinate gives the apparent capture cross-section. However, the above interpretations assume negligible change in the entropy when a charge carrier is emitted, which is explained more thoroughly in Appendix A.

The concentration of a deep level can be extracted by acquiring the \( \Delta C \) at \( t = 0 \) and using Eq.3.5. This concentration represents an average value over the investigated depth which is, in many cases, appropriate for uniformly distributed defects (44). However, in the case of a non-uniform defect distribution, a depth profile over the region of interest is necessary to quantify the defect concentration.

3.2.3 Deep level depth profiling

DLTS can reveal the depth distribution of a deep level. Various measurement procedures allow to acquire the necessary information for extracting the depth profile of a deep level. However, the essence remains in varying the filling pulse in order to fill and empty deep levels at defined depths.

One method involves gradually changing the filling pulse from a fixed reverse bias voltage at a fixed temperature. Thus, for every increment of the amplitude of the filling pulse, the investigated depth expands and gives the depth information needed. With this method, the deep level concentration can be expressed as (40)

\[
N_T(W_f - \lambda) = -\frac{qW_0^2}{\epsilon_0\epsilon_r} \left( \frac{W_f}{W_f - \lambda} \right) N_a^+(W_d)N_a^+(W_f) \frac{\delta(C_f/C_0)}{\delta V_f},
\]

where the conventions of the symbols are those in Fig.3.2. More specifically, \( C_0 \) is the capacitance at the fixed reverse bias voltage, \( C_f \) is the capacitance at the filling pulse voltage and

\[
\lambda = \sqrt{\frac{2\epsilon_0\epsilon_r}{qN_a^+}(E_F - E_T)}
\]

(3.11)
3. METHODS

which is similar to Eq. 2.1 on the depletion width.

As an example, from Paper II, Fig. 3.4 shows the depth profiling of the FeB pair and the Fe\textsubscript{i} before and after reverse bias annealing (RBA). This information is useful in determining the region where the FeB pair has dissociated to form Fe\textsubscript{i}. The measurements were acquired at 52 and 224K for the FeB pair and the Fe\textsubscript{i}, respectively, and the fixed reverse bias voltage was 8V.

3.3 Admittance spectroscopy (ADSPEC)

Admittance spectroscopy has the similar capability as DLTS in the sense that this is also an electrical characterization technique to extract information about the energy level position, capture cross-section and concentration of defects (and dopants). The difference between ADSPEC and DLTS lies in the detection limits. While DLTS has better detection limit of the defect concentration than ADSPEC, ADSPEC has the capability of investigating shallow levels, including dopants. Furthermore, ADSPEC can also be applied in cases where the defect concentrations is high (comparable) relative to the doping concentration, in contrast to that of DLTS.

Admittance spectroscopy can be performed by measuring the capacitance and/or conductance as a function of temperature in a diode structure (40, 48, 49). Since these quantities are measured by use of a small AC signal with a certain frequency,
energy levels are affected by the constantly changing Fermi-level which results in an alternatively filling and emptying process of the energy levels by charge carriers. At high temperatures, the emission of charge carriers is fast and the occupation of the energy levels respond to the AC frequency nearly instantaneously. On the other hand, at low temperatures, the emission rate of the charge carriers is low and they do not respond to the AC frequency. As a consequence, the capacitance will be reduced, while the conductance increases and reaches a peak value. Figure 3.5 shows ADSPEC data, where two peaks in the conductance spectra can be observed for each probing frequency. Each peak represent an energy level, which can be extracted using an Arrhenius plot with the following relation of

\[
\ln \left( \frac{2\pi f}{T^2} \right) \propto \frac{1}{T} \frac{E_T - E_V}{k}, \tag{3.12}
\]

where \( f \) is the probing frequency and \( T \) is the absolute temperature where the peak occurs.

The capacitance in an ADSPEC signal can be expressed as

\[
\Delta C = \frac{\epsilon_0 \epsilon_r N_T}{W N_D} \frac{1 - \frac{W - \lambda}{W + \lambda} \frac{N_T}{N_D}} {1 + \frac{W - \lambda}{W + \lambda} \frac{N_T}{N_D}}. \tag{3.13}
\]
3. METHODS

where $N_D$ is the doping concentration. From the Eq.3.13, it can be seen that the amplitude is significantly reduced when $(W - \lambda) \simeq W$. This condition occurs when the energy level of defects is close to that of the dopants.

3.4 Simulation software (Synopsys TCAD)

Synopsys TCAD is a package of simulation softwares which can be used to simulate electrical properties of devices, such as diodes and transistors (51). When a structure is created using a Sentaurus Structure Editor (SentaurusSE), various electrical quantities can be solved using Sentaurus Device (SentaurusD), such as capacitance and conductance. This is performed by achieving a self-consistent solution between the Poisson’s equation and the continuity equations for electrons and holes, respectively, expressed as:

$$\nabla \epsilon \nabla \phi = -q(p - n + N_d - N_a) - \rho$$

(3.14)

and

$$\nabla \cdot \vec{J}_n = q R_{net} + q \frac{\delta n}{\delta t}$$

$$- \nabla \cdot \vec{J}_p = q R_{net} + q \frac{\delta p}{\delta t}$$

(3.15)

where $\phi$ is the electrical potential, $\rho$ is the concentration of traps and fixed charges (dopants excluded), $J_{n(p)}$ is the electron (hole) current density, $R_{net}$ is the recombination rate and $t$ is the time. From these equations, the electrical field and the flow of charge carrier can be described for a diode junction (Sec.2.1).

SentarausD allows for simulation with an applied AC signal for the purpose of calculating capacitance and conductance. When such a calculation is performed on a diode structure at different temperature, ADSPEC spectrum can easily be simulated. Furthermore, transient signals are also possible to acquire. With the proper simulation of trap conditions, a DLTS spectrum can be simulated whether it is a standard DLTS measurement, depth profiling, optical DLTS, capture cross-section measurement or other. Examples of command files for simulating ADSPEC and standard DLTS can be found in Appendix B.

Figure 3.6 shows a program which has the purpose of organizing the many different programs in the Synopsys software package. The left part lists all the available projects where a project “ADSPEC_ALSi_FrontImp_5e15_60Hz.tmp” is opened and shown in the
Figure 3.6: A graphical user interface program (Sentaurus Workbench) which allows for easy control over the different programs in the Synopsys software package.

right part. Two simulations tools (SentaurusSE and SentaurusD) are loaded and 30 simulations are performed with the temperature being the variable. This project is for an ADSPEC simulation in the temperature range between 21 to 50K (steps of 1) with a reverse bias voltage between 0 to -10.5 (with 20 steps, not visible in the Fig.3.6). One acceptor defect of interest is implemented with energy level position, concentration and hole capture cross-section of $E_V + 0.057 \text{ eV}$ (not visible in Fig.3.6), $5 \times 10^{15} \text{ cm}^{-3}$ and $5 \times 10^{-14} \text{ cm}^2$, respectively.
3. METHODS
Chapter 4

Present work and suggestions for future work

This chapter gives an insight into the work reported in this thesis. The main results of each paper are highlighted and suggestions for future work are presented.

4.1 Material

The work in this thesis targets applications for solar cells with the main focus on Fe in silicon. Although multicrystalline silicon is the material which contains considerable amount of Fe, most of the studies are conducted using single crystalline silicon grown by Czochralski or float-zone method.

The single crystalline material is chosen in order to avoid contribution from other unintended impurities that are common in multi-cryostalline material. In addition to Fe impurities, the grain boundaries in multicrystalline silicon host many metal impurities such as copper, nickel and titanium (2). After high temperature treatments, these metals can dissolve into the grains, undergo various reactions and cause electrical signatures which can interfere with the signatures of Fe-related defects. This complicates the interpretation of data and provides a less reliable picture of the underlying reactions and mechanisms than in a material containing mainly Fe impurity. In as-grown single crystal silicon, the concentration of electrically active defects is typically below the
4. PRESENT WORK AND SUGGESTIONS FOR FUTURE WORK

detection limit of DLTS, and, thus, provides a suitable model system for investigating reactions of intentionally introduced defects and impurities, such as Fe.

Furthermore, the non-uniformity of multicrystalline silicon can give rise to impurity distribution that varies laterally. Since DLTS, which can offer a high detection limit of four orders of magnitude below the doping concentration, does not enable easy mapping of a sample, spatial uniformity is preferable.

4.2 Preparation

With the underlining topic of Fe defects in silicon, a reliable and reproducible method to introduce a controllable amount of Fe is necessary. At the beginning, following the literature (27), an easy method for introduction of Fe was tested where FeCl₃ was dissolved and applied to the samples. Thereafter, the samples were heat treated in a sealed vacuumed quartz ampoule to avoid cross contamination. However, DLTS measurements of the samples did not show any resemblance of previously reported results. In addition, no reversible reaction from the detected defects, which could indicate the presence of Fe, were observed. The reasons may possibly be the purity of the chemical, the cleanliness of the ampoule and/or the preparation environment, since the samples had to be transferred out of the clean room for sealing of the ampoule.

The latter method was therefore abandoned at an early stage and replaced by ion-implantation. This method provides reproducible and controlled introduction of Fe in silicon and with negligible contamination from other elements. In addition, it also allows for placement of Fe in different depths of the samples which is crucial in Paper VI.

To minimize cross contaminations during heat treatments while distributing Fe uniformly in the sample, a dedicated tube furnace was mainly used. The quartz tube was cleaned thoroughly by immersing the whole tube, along with any quartz boats and quartz tools, into a chemical solution (aqua regia, 3:1, HCl:HNO₃) overnight. Then, the tube and the tools were rinsed in de-ionized water for several minutes. The cleanliness of the tube furnace was usually tested before heat treating the experiment samples by exposing cleaned as-received samples under the same experimental conditions. Thereafter, these control samples were measured with DLTS to check for electrically active defects introduced from the furnace. In some cases, the DLTS measurement on the
control samples detected Fe in a concentration on the order of $10^{10}\text{cm}^{-3}$. This concentration was a factor of around $10^{-4}$ of the doping concentration and considered as acceptable.

### 4.3 Detected defects in this work

This section provides an overview of the electrically active defects discussed in the appended papers, with the purpose of easing the literature search for reader, and they are listed in Table 4.1. The apparent capture cross-sections are mainly extracted from extrapolation of the Arrhenius plots which can give an uncertainty of 1-2 orders of magnitude. In addition, Arrhenius plot of the defect levels discussed in Paper IV and V are shown in Fig.4.1.

#### Table 4.1: Electrically active defects detected in the papers.

<table>
<thead>
<tr>
<th>Label</th>
<th>$E_V + XX$ [eV]</th>
<th>Apparent capture cross-section [cm$^2$]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-B</td>
<td>0.10</td>
<td>$4 \times 10^{-15}$</td>
<td>Paper II-V, (7)</td>
</tr>
<tr>
<td>Fe$_i$</td>
<td>0.40</td>
<td>$3 \times 10^{-16}$</td>
<td>Paper II-V, (7)</td>
</tr>
<tr>
<td>H(0.3)</td>
<td>0.27 ±0.03</td>
<td>$5 \times 10^{-15}$</td>
<td>Paper I</td>
</tr>
<tr>
<td>H(0.4)</td>
<td>0.38 ±0.03</td>
<td>$1 \times 10^{-15}$</td>
<td>Paper I</td>
</tr>
<tr>
<td>H(0.17)</td>
<td>0.17</td>
<td>$4 \times 10^{-16}$</td>
<td>Paper IV</td>
</tr>
<tr>
<td>H(0.28)</td>
<td>0.28</td>
<td>$6 \times 10^{-15}$</td>
<td>Paper IV</td>
</tr>
<tr>
<td>H(0.34)</td>
<td>0.34</td>
<td>$4 \times 10^{-14}$</td>
<td>Paper IV</td>
</tr>
<tr>
<td>H(0.25)</td>
<td>0.24</td>
<td>$1 \times 10^{-14}$</td>
<td>Paper V</td>
</tr>
<tr>
<td>H(0.29)</td>
<td>0.29</td>
<td>$9 \times 10^{-15}$</td>
<td>Paper V</td>
</tr>
<tr>
<td>H(0.34)</td>
<td>0.34</td>
<td>$2 \times 10^{-14}$</td>
<td>Paper V</td>
</tr>
<tr>
<td>$V_2$</td>
<td>0.18</td>
<td>$1 \times 10^{-16}$</td>
<td>Paper IV, V, (52, 53, 54)</td>
</tr>
<tr>
<td>C$_i$</td>
<td>0.30</td>
<td>$3 \times 10^{-14}$</td>
<td>Paper V, (55)</td>
</tr>
<tr>
<td>C$_i$O$_i$</td>
<td>0.35</td>
<td>$2 \times 10^{-15}$</td>
<td>Paper IV, V, (53, 55)</td>
</tr>
<tr>
<td>VOH</td>
<td>0.25</td>
<td>$3 \times 10^{-15}$</td>
<td>Paper IV, (53, 56)</td>
</tr>
<tr>
<td>Bi$_i$C$_s$</td>
<td>0.29</td>
<td>$2 \times 10^{-14}$</td>
<td>Paper V, (57)</td>
</tr>
<tr>
<td>$V_2$O</td>
<td>0.22</td>
<td>$1 \times 10^{-15}$</td>
<td>Paper V, (58, 59)</td>
</tr>
<tr>
<td>Not labelled</td>
<td>0.06 (fitted: 0.057)</td>
<td>$5 \times 10^{-14}$ (fitted)</td>
<td>Paper VI</td>
</tr>
</tbody>
</table>
4. PRESENT WORK AND SUGGESTIONS FOR FUTURE WORK

4.4 Paper I: Rapid thermal annealing-induced defects

In collaboration with the solar group at the Institutt for Energy Technology (IFE), multicrystalline silicon samples were rapid thermally annealed at 1000°C for 2 min. When the samples were investigated using DLTS, two significant electrically active deep levels were observed. The experiment was repeated using the same furnace with single crystalline wafers which had a lower doping concentration than the multicrystalline ones. By lowering the doping concentration, the detection limit for DLTS increases proportionally. In addition, the change in doping concentration might change the defect concentration which would suggest a defect involving the dopant (boron, in this case).

The two defects found in the multicrystalline sample appeared in the single crystalline ones as well, and various treatments and measurements were conducted to gather more information about their properties. It is found that the defects exhibit acceptor-like nature, are stable above 650°C and are most likely indiffused from the environment with high diffusivity. Comparing with the theoretical results, it is suggested that the deep levels arise from two defects involving Fe and vacancies/boron.

Figure 4.1: Arrhenius plots of the defect levels observed in Paper IV and V with corresponding defect properties shown in Table 4.1.
In a later stage, the same experiment were conducted on n-type samples to investigate the upper part of the midgap. However, difficulties were experienced in producing a reliable Schottky barrier contact with gold on heat treated samples where the gold contacts could easily be wiped off even with a clean room wiper. It was suspected that the surface could be the reason for the problem, but they remained even when the samples were etched by several microns.

A future work could be to try to investigate these defects using DLTS with optical excitation on p-type samples. This can be performed with illumination at the rearside with light above the band gap energy.

4.5 Paper II & III: Interaction between H and Fe

Hydrogen interaction with Fe has been a topic of great interest in solar cells, since hydrogen is easily introduced during the processing step and because hydrogen has a reputation of passivating defects, such as dangling bonds and vacancies (17, 60). From the literature, it has been suggested that hydrogen passivates Fe (25). However, it is also suggested that hydrogen dissociates the Fe-B pair (27, 61), forming Fe\(\text{I}\) which is a detrimental defect in solar cells. Furthermore, theory predicts a reaction of hydrogen with Fe\(\text{II}\) (neutral), but not with Fe\(\text{III}\) (positively charged), and that the resulting Fe-H pair has energy levels in the band gap (28). This led to the interest of a further investigation, where concentration versus depth profiles were carefully considered for both the Fe-B pair, Fe\(\text{I}\) and hydrogen, since both the Fe\(\text{II}\) and Fe\(\text{III}\) exists within a depletion region of a diode.

Thus, hydrogen was incorporated into Fe-contaminated boron-doped silicon samples and driven to regions of Fe\(\text{I}\) with different charge states. The hydrogen incorporation was attempted on the samples through boiling in water (62), heated HF (63) and wet chemical etching (WCE) (with HF:HNO\(_3\):CH\(_3\)COOH) (27, 64). The latter method was observed to be the most efficient one in terms of the amount of hydrogen introduced, as deduced from CV-measurements. However, the etching process occasionally produced rough surfaces and these samples were discarded.

After the etching, the samples were further cleaned and was Al deposited for SBC and stored for 1-2 weeks before commencing the measurements to allow the Fe\(\text{I}\),
which were dissociated from Fe-B during the etching, to reassociate with B. Thereafter, a continuous process of measurements and treatments were performed for the CV-measurements, DLTS spectra, reverse bias annealing (RBA) and depth profiles. During the RBA, the temperature and the capacitance were constantly monitored.

The main results are shown in Fig. 4.2 which shows the defect concentration versus depth profiles of the Fe-B pair and Fe\textsubscript{i} for the WCE and non-WCE samples, both before and after RBA. Firstly, it can be noticed that the Fe-B pair dissociates due to the RBA treatment and that the amount of released Fe\textsubscript{i} is larger for WCE samples than the ones without WCE. Secondly, the concentration of Fe\textsubscript{i} is significant only for the WCE samples in the region within the added vertical lines, which marks the depletion region containing Fe\textsuperscript{+}. This increase can not be explained by a diffusion of Fe\textsubscript{i} due to the similarity in the reduction and increase in defect concentrations, nor can it be explained by a dissociation of the Fe-B pair due to the lack of Coulombic attraction between Fe
and B. Hence, the observations strongly point towards a reaction between hydrogen and the Fe-B pair which results in formation of B-H, releasing Fe$_i^+$. Furthermore, from the DLTS spectra after RBA, which shows no new signals and from the depth profiles, it is concluded that passivation of Fe by H have not been observed.

For future work, although no formation of Fe-H complexes is observed electrically in this work with reactants as Fe-B or Fe$_i$, it may be interesting to investigate interaction between hydrogen and other complexes of Fe. In the work by Wünstel and Wagner (65), several electrically active Fe-related defects were observed by different cooling rates. Although unidentified, electrical neutralization by hydrogen of these defects can be of technological interest, for instance, in solar cells.

4.6 Paper IV & V: Irradiation-induced defects and Fe

A recent theoretical study made an extensive investigation into defect reactions between Fe and irradiation-induced defects in silicon (66). The calculations predicted several stable electrically active defects which were not firmly established or observed. This opened up for experimental investigations with the ambition that the results could be utilized in the optimization of gettering of Fe.

The sample preparation involved irradiation of an Fe-contaminated sample and, thereafter, performing DLTS measurements. The Fe-contaminated samples were shipped to Sweden for electron irradiation at 6 MeV. However, a failure in the accelerator arised and the irradiation was put on hold. Several months of waiting turned into about one year, and the final message was that the accelerator will never be put up to meet the specified parameters again. Fortunately, the electron irradiation was eventually performed when Vladimir Markevich travelled to Minsk, but the energy had to be reduced to 4 MeV. The samples were then measured with DLTS and defects were investigated after different isochronal annealings for 30 min.

However, as one may have noticed, the study involving irradiation-induced defects with Fe was first reported on proton-irradiated samples from this Ph.D. work and not electron-irradiated samples. While waiting for electron irradiation, proton irradiation was performed with the ion-implanter at MiNa-lab. The energy of the protons was set to the highest capability such that the projected range would be located a factor of 2-3 deeper than the region probed using DLTS. This was to minimize the contribution
of hydrogen on the investigated defects. Still, indications that hydrogen had been incorporated in the probing region was observed through the detection of a defect with the characteristics of the vacancy-oxygen-hydrogen (VOH) in the reference samples. This introduction of hydrogen, however, could also have occurred during the preparation of the samples, for instance from the deposited metal contact.

A number of different defects have been detected through the experiments with electron or proton irradiation on Fe-contaminated and boron-doped samples, as shown in Figs. 4.3 and 4.4. These defect levels are labelled according to their energy level position, where H(0.17) has an energy level position at $E_V + 0.17\,\text{eV}$. The investigation of the defects through isochronal annealing has aided in the understanding of the relation between the different defects. In proton-irradiated samples, the concentration of

![Figure 4.3: Spectra of DLTS measurements, with GS4 weighting function, on proton-irradiated Fe-contaminated and reference samples after different subsequent annealing temperature for 30 min. It shows three distinctive peaks (H(0.17), H(0.28) and H(0.34)) which are only found in the Fe-contaminated samples. These spectra are extracted from rate-window of $(320\,\text{ms})^{-1}$.](image-url)
H(0.34) is observed to follow the concentration of VOH in the reference samples. In addition, no signal indicating VOH in the Fe-contaminated samples are found. This indicates that H(0.34) and VOH are related either by a common precursor or that the VOH is a precursor for H(0.34) and, thus, indicating a reaction between Fe and VO.

**Figure 4.4:** Spectra of DLTS measurements, with GS4 weighting function, on electron-irradiated Fe-contaminated and reference samples at as-implanted state and annealed at 150, 200 and 250K for 30 min. It shows three distinctive peaks (H(0.25), H(0.29) and H(0.34)) which are only found in the Fe-contaminated samples. These spectra are extracted from rate-window of (640ms)$^{-1}$

Furthermore, the proton-irradiated Fe-contaminated samples contain a defect (H(0.28)) which evolves in its concentration towards the as-irradiated concentration of V$_2$, suggesting a relation between Fe and V$_2$. The same suggestion is made when Fe-contaminated samples are investigated after electron-irradiation. In these samples, the concentration of H(0.29) is observed to increase according the loss of V$_2$ for annealing temperatures below 225$^\circ$C when assuming that the DLTS signal of H(0.29) is overlapping with B$_i$C$_s$. For annealing at 225 and 250$^\circ$C, this relation deviates significantly, however, a peak
4. PRESENT WORK AND SUGGESTIONS FOR FUTURE WORK

(H(0.34)) is observed to emerge at those temperatures which compensate for the difference reasonably well. From these observations, it is further suggested that H(0.34) is another configuration of a complex between Fe and V₂.

Future work would be to repeat the experiments with epitaxially grown silicon that has a low content of oxygen and carbon. In addition, annealing at higher temperature should also be performed to investigate for further formation of Fe-related defects. Hydrogenation of electron-irradiated samples can be performed to investigate the H(0.34) defect in the proton-irradiated samples.

4.7 Paper VI: Fe-assisted formation of a shallow acceptor

Further motivated by the calculations performed in Ref.(66), a search for the substitutional Fe was initiated. The configuration, ⁰Fe⁰ (neutral and no spin), is predicted to be highly stable with a gain in energy of 2.92 eV when compared with isolated ¹Fe⁰ and the monovacancy, ⁰V⁰. This shows that Fe can react with the monovacancy and that this reaction can potentially be utilized for gettering and/or removal of the harmful effect of Fe⁺. However, the existence of substitutional Fe is only evidenced by Mössbauer spectroscopy(67) and β⁻ emission channeling measurements(68).

Based on the similar method of preparation of samples as in Ref.(68), p-type silicon was implanted with Fe and heat treated at different temperatures. Thereafter, the samples were characterized electrically using CV, DLTS and ADSPEC. The temperatures for heat treatment were first investigated at 400°C with the idea that the majority of the prominent irradiation-induced defects would be annealed out. However, charge carrier concentration versus depth profiles, deduced from CV measurements, showed compensation at the projected range and towards the surface which was too large to extract reliable data from DLTS. Still, DLTS and optical DLTS measurements were performed with the aim to detect distinctive differences between the Fe-implanted and Si-implanted samples. However, no significant difference could be drawn for that annealing temperature and up to 650°C. After annealing at 800°C, a full recovery of the doping profiling was achieved for the reference samples (silicon-implanted). It was then clear that an enhancement of the acceptor concentration at the projected range exists only in the Fe-implanted samples and not in the Si-implanted samples.
This peak was further investigated on samples with different implantation doses of Fe and Si, spanning from 5 to 625% of the doping concentration at the calculated implantation peak. Still, the peaks are only found in the Fe-implanted samples, and it is observed that the enhancement in the acceptor concentration has a close to one-to-one relation with the implanted dose. Different ADSPEC measurements were performed on the samples to reveal the electrical properties of the defect. Figure 4.5 shows the ADSPEC measurements on the samples with different implantation doses of Fe and the corresponding fitted curves from Sentaurus TCAD. The inset shows an enlarged picture of the marked area, where a signal can be observed to increase with increasing dose of the Fe implantation. Furthermore, a shift in the peak position towards low temperature occurs for increasing dose. The latter observation shows that the defect obeys the Poole-Frenkel effect and, thus, acts as an acceptor. This shows that the enhanced acceptor concentration observed with CV measurements is caused by this defect.

At that point, it was believed that the defect configuration could be substitutional Fe. However, chemical identification of the presence of Fe was necessary in order to
support the assignment. Thus, secondary ion-mass spectrometry (SIMS) was performed both using the SIMS in our lab and externally. Figure 4.6 shows the SIMS depth profiles of samples implanted with different doses of $^{54}\text{Fe}$. Unexpectingly, SIMS measurements show that Fe diffuses out of the projected range region during the heat treatment and that the final defect, thus, does not contain Fe. Hence, the presence of Fe only assists the formation of a shallow defect.

Suggestions for future works are extensive, due to the interesting and challenging behaviour observed for the first time. Firstly, experiments should be performed to investigate the chemical composition of the defect by, for instance, varying the concentration of dopant, oxygen and carbon. Furthermore, the type of dopant can also be varied. Secondly, the assisted formation of this shallow defect can be investigated through implantation of elements with similar chemical behaviour as Fe. Thirdly, diffusion and stability of this shallow acceptor can be investigated through isochronal and isothermal annealings.
Appendix A

Emission rate and capture cross-section

The emission rate of electron can be deduced from Eq. 2.7, written as

\[ e_n = v_{th,n} \sigma_n N_C \frac{g_0}{g_1} \exp \left( \frac{-E_C - E_T}{kT} \right). \]  

(A.1)

This equation is often used to extract the \( E_T \) and the capture cross-section, \( \sigma \), of defect levels in the band gap. The capture cross-section is commonly deduced through the intercept of the ordinate in a \( \ln(e_n/T^2) \) versus \( 1/T \) plot. However, this practice can give errors by a factor of 10-100, as shall be discussed.

Thermodynamically, the emission of electron is a change in the Gibbs energy, \( \Delta G \), given as

\[ \Delta G = E_C - E_T = \Delta H - T \Delta S, \]  

(A.2)

where \( H \) is the enthalpy and \( S \) is the entropy of the defect. Inserted in Eq. A.1, the emission rate of electron can be expressed as

\[ e_n = v_{th,n} \sigma_n N_C \frac{g_0}{g_1} \exp \left( \frac{\Delta S}{k} \right) \exp \left( -\frac{\Delta H}{kT} \right). \]  

(A.3)

Thus, comparing with Eq. A.1, the extraction of the capture cross-section from an Arrhenius plot has an additional factor of \( \exp(\Delta S/k) \), which can produce an error of a few orders of magnitude when assuming that \( \Delta S \) is negligible (37).

One method to determine the capture cross-section more accurately is by an alternative method of DLTS. In contrast to the standard DLTS measurement, the voltage pulse duration is varied at a constant temperature at the occurrence of a DLTS peak. With a short pulse duration, the filling of the defect level is close to 0, while with a long pulse width, the defect level becomes saturated. The transition can be fitted, for
capture of electrons, with (69)

\[ n_T(t_p) = n_T(\infty)(1 - \exp(-c_n n t_p)), \quad (A.4) \]

where \( t_p \) is the voltage pulse duration. It should be noted that the saturation time of the defect is exponentially dependent on the doping concentration. For silicon with doping concentration of \( 10^{16}\text{cm}^{-3} \) and a defect level with capture cross-section of \( 10^{-14}\text{cm}^2 \), the saturation time is in the order of 10 ns. This puts a high requirement on the performance of the instruments. To avoid this problem, the doping concentration of the material can be reduced to meet the capability of instruments.
Appendix B

Software command files

Command files for SentaurusSE and SentaurusD are shown for an example of ADSPEC and DLTS simulation.

B.1 ADSPEC simulation

In this simulation, the important output files which contain the information about the voltages, conductances and capacitances are the “ADSPEC.00e3.n<node>.acs.dles.plt”, where <node> is a number assigned for the different simulations. From Fig. 3.6, the <node> is any real number between 7 to 38.

Variables need to be specified in Sentaurus Workbench are: PDoping for the doping concentration, A1c for a defect concentration, A1hXsection for capture cross-section of the defect, Voltage for the different simulation voltages (20 steps from 0V to Voltage) and Temp for the temperature. These inputs are also shown in Fig. 3.6.

Structure file (for SentaurusSE)

```lisp
(sdegeo:set-default-boolean "ABA")
(define width 50)
(define height 25)
(define Pdoping @PDoping@)

;;;; Structure
(sdegeo:create-rectangle (position 0 0 0) (position width height 0) "Silicon" "region1")
(sdegeo:create-rectangle (position 0 0.8 0) (position width 2.2 0) "Silicon" "ProjRange")

;;;; Doping
(sdedr:define-constant-profile "Const.P1" "BoronActiveConcentration" Pdoping)
(sdedr:define-constant-profile-region "PlaceC.P1" "Const.P1" "region1")
(sdedr:define-constant-profile "Const.P2" "BoronActiveConcentration" Pdoping)
```
B. SOFTWARE COMMAND FILES

```lisp
(sdedr:define-constant-profile-region "PlaceC.P2" "Const.P2" "ProjRange")

;;; Contact

(sdegeo:define-contact-set "SchottkyC" 4 (color:rgb 0 0 1) "##")
(sdegeo:define-2d-contact (find-edge-id (position (/ width 2) 0 0)) "SchottkyC")

(sdegeo:define-contact-set "OhmicC" 4 (color:rgb 0 1 0) "##")
(sdegeo:define-2d-contact (find-edge-id (position (/ width 2) height 0)) "OhmicC")

(render:rebuild)

;;; Refinement

(sdedr:define-refinement-window "RefWinContact1" "Rectangle" (position 0 0 0)
(position width 3 0))
(sdedr:define-refinement-window "RefWinRest" "Rectangle" (position 0 0 0)
(position width height 0))

(sdedr:define-refinement-window "RefWinBoundary" "Rectangle" (position 0.75 0 0)
(position 3 height 0))

(sdedr:define-refinement-size "RefDefContact1" width (/ 1 100) width (/ 1 150))
(sdedr:define-refinement-placement "PlaceRFContact1" "RefDefContact1" "RefWinContact1")

(sdedr:define-refinement-size "RefDefRest" width (/ 1 1) width (/ 1 25))
(sdedr:define-refinement-placement "PlaceRFRest" "RefDefRest" "RefWinRest")

(sdedr:define-multibox-size "MB.Channel" (/ 1 1) (/ 1 500) 100 100 1 1.35)
(sdedr:define-multibox-placement "PlaceMB.Channel" "MB.Channel" "RefWinBoundary")

;; save and build

(sdeo:save-tdr-bnd (get-body-list) "@tdrboundary/o@")
(sdedr:write-cmd-file "@commands/o@")
(system:command "mesh -f tdr n@node@_msh")
```

Calculation file (for SentaurusD)

```
Device A1SiSchottkyA {
    File {
        Grid = "@tdr"
        Param = "@parameter@"
        Current = "@plot@"
        Plot = "@tdrdat@"
    }

    Electrode {
        Name="SchottkyC" Voltage=0 Material="Aluminum" Schottky
        Name="OhmicC" Voltage=0
    }

    Physics {
        Mobility (DopingDep HighFieldsat Enormal)
        EffectiveIntrinsicDensity( OldSlotboom )
        Temperature=@Temp@
    }

    Physics (Material = "Silicon") {
    }
}
```

Calculation file (for SentaurusD)
B.1 ADSPEC simulation

( 
  (Acceptor Level EnergyMid=0.044 from ValBand
  Conc=2e15 hXsection=7e-14 eXsection=2000e-13
  Add2TotalDoping PooleFrenkel)
)
}

Physics (Region = "ProjRange") {
  Traps(
    (Acceptor Level EnergyMid=0.057 from ValBand
     SpatialShape=Gaussian SpaceMid=(25 1.5 0) SpaceSig=(100 0.2 0)
     Conc=@A1c@ hXsection=@A1hXsection@ eXsection=1e-1
     Add2TotalDoping PooleFrenkel)
    (Acceptor Level EnergyMid=0.044 from ValBand
     Conc=2e15 hXsection=7e-14 eXsection=1e-20
     Add2TotalDoping PooleFrenkel)
  )
}

################################ End device A ################################

File{
  Output = "@log@"
  ACExtract = "@acplot@"
}

Plot {
  eDensity hDensity eCurrent hCurrent
  eQuasiFermi hQuasiFermi eVelocity hVelocity
  eMobility hMobility eLifeTime hLifeTime
  eTrappedCharge hTrappedCharge
  eGapStatesRecombination hGapStatesRecombination
  "hRelativeEffectiveMass" "eRelativeEffectiveMass"
  "hEffectiveStateDensity" "eEffectiveStateDensity"
  hGradQuasiFermi eGradQuasiFermie Eparallel hEparallel

  Potential SpaceCharge ElectricField
  Doping DonorConcentration AcceptorConcentration
  BandGapNarrowing EffectiveBandGap

  AugerRecombination SRHRecombination TotalRecombination
  Band2Band "BuiltinPotential" TotalTrapConcentration

  EffectiveBandGap EffectiveIntrinsicDensity
  ConductionBandEnergy ValenceBandEnergy
  Bandgap RefractiveIndex ElectronAffinit
  Temperature Band2Band EquilibriumPotential
}

Math {
  Extrapolate
  RelErrControl
  Digits=8
  Error=1e-10
  NotDamped=30
  Iterations=5

  ErrRef(Electron)=1.0e10
  ErrRef(Hole)=1.0e10
  ExtendedPrecision
}
B. SOFTWARE COMMAND FILES

System {
    AlSiSchottkyA diode1 (SchottkyC=s OhmicC=b)
    Vsource_pset vs (s 0) {dc=0}
    Vsource_pset vb (b 0) {dc=0}
}

Solve {
    Coupled (iterations=500) {Poisson}
    Coupled (iterations=100) {Poisson hole}
    Coupled (iterations=100) {Poisson hole electron}

    NewCurrentPrefix="ADSPEC_60e3_"
    Quasistationary {
        InitialStep=1e-5 MaxStep=1 MinStep=1.e-20
        Goal { Parameter=vb.dc Voltage=@Voltage@ }{ ACCoupled (StartFrequency=60e3 EndFrequency=60e3 NumberOfPoints=1
        Decade Node(b s) ACCompute (Time = (Range = (0 1) Intervals = 20))} {Poisson hole electron}
    }

    System("rm ADSPEC*diode*.plt")
}

B.2 DLTS simulation

In this simulation, the important output files which contain the information about the capacitance in a transient are the “Cap<point>,<node>_ac.des.plt”, where <point> is a number for the different simulated point in a transient. Only two points from a capacitance transient are simulated in the program file for SentaurusD, which allows for simulating the first time-window of a lock-in weighting function. However, more transient points can easily be added and simulated with the cost of an increase in the computation time.

Three parameters are needed in the Sentaurus Workbench: PDoping for acceptor doping concentration, Voltage for the reverse bias voltage (the pulse voltage is 0 V) and Temp for the different temperatures.

Structure file (for SentaurusSE)

(define width 100)
(define height -500)
(define Pdoping @PDoping@)

;---------Structure-------------
(sdegeo:create-rectangle (position 0 0 0) (position width height 0) "Silicon" "base")
(sdegeo:create-rectangle (position 0 (+ height 0.8) 0) (position width
(+ height 1.3) 0) "Silicon" "defect")

;---------Doping-------------
(sdedr:define-constant-profile "Const.P1" "BoronActiveConcentration" Pdoping)
(sdedr:define-constant-profile-region "PlaceC.P1" "Const.P1" "base")
(sdedr:define-constant-profile-region "PlaceC.P2" "Const.P1" "defect")

;---------Contact-------------
(sdegeo:define-contact-set "BC" 4 (color:rgb 0 0 1) "##")
(sdegeo:define-2d-contact (find-edge-id (position (/ width 2) 0 0)) "BC")
(sdegeo:define-contact-set "FC" 4 (color:rgb 0 1 0) "##")
(sdegeo:define-2d-contact (find-edge-id (position (/ width 2) height 0)) "FC")
(render:rebuild)

;--------Refinement----------
(sdedr:define-refinement-window "RefWinJC" "Rectangle" (position 0 height 0)
 (position width (+ 3.0 height) 0))
(sdedr:define-refinement-window "RefWinRest" "Rectangle" (position 0
 (+ height 3.5) 0) (position width 0 0))
(sdedr:define-refinement-size "RefDefJC" (/ width 1) (/ 1 200) (/ width 1)
 (/ 1 250))
(sdedr:define-refinement-placement "PlaceRFJC" "RefDefJC" "RefWinJC")
(sdedr:define-refinement-size "RefDefRest" (/ width 1) (/ 1 1.1) (/ width 1)
 (/ 1 10))
(sdedr:define-refinement-placement "PlaceRFRest" "RefDefRest" "RefWinRest")

;---------save and build---------
(sdeio:save-tdr-bnd (get-body-list) "@tdrboundary/o@")
(sdedr:write-cmd-file "@commands/o@")
(system:command "mesh -f tdr n@node@_msh")

Calculation file (for SentaurusD)

Device AlSiSchottky {  
  File {
    Grid = "@tdr@
    Param = "@parameter@
    Current = "@plot@
    Plot = "@tdrdat@
  }

  ####### Define contact type #######
  Electrode {
    {Name="FC" Voltage=0 Workfunction=4.0 Schottky}
    {Name="BC" Voltage=0}
  }
  ####### End define contact type #######

  ###### Physics ######

  Mobility (DopingDep HighFieldsat Enormal)
  EffectiveIntrinsicDensity( OldSlotboom )
  Temperature=@Temp@
}
B. SOFTWARE COMMAND FILES

Physics (Region = "defect") {
    Traps(
        (Donor Level EnergyMid=0.25 fromCondBand
         Conc=1e13 hXsection=1e-15 eXsection=1e-15
         ElectricField Add2TotalDoping )
        (Acceptor Level EnergyMid=0.4 fromValBand
         Conc=2e13 hXsection=1e-15 eXsection=1e-15
         ElectricField Add2TotalDoping )
    )
}

End physics

File{
    Output = "@log@"
    ACExtract = "@acplot@"
}

Plot {
    eDensity hDensity eCurrent hCurrent
    eQuasiFermi hQuasiFermi eVelocity hVelocity
    eMobility hMobility eLifeTime hLifeTime
    eTrappedCharge hTrappedCharge
    eGapStatesRecombination hGapStatesRecombination
    "hRelativeEffectiveMass" "eRelativeEffectiveMass"
    "hEffectiveStateDensity" "eEffectiveStateDensity"
    hGradQuasiFermi eGradQuasiFermi
    eParallel hParallel eDirectTunneling hDirectTunneling
    eBarrierTunneling hBarrierTunneling
    Potential SpaceCharge ElectricField
    Doping DonorConcentration AcceptorConcentration
    BandGapNarrowing EffectiveBandGap
    AugerRecombination SRHRecombination TotalRecombination
    Band2Band "BuiltinPotential" TotalTrapConcentration
    EffectiveBandGap EffectiveIntrinsicDensity
    ConductionBandEnergy ValenceBandEnergy
    Bandgap ElectronAffinity
    RefractiveIndex EquilibriumPotential
}

Math {
    #Extrapolate
    RelErrControl
    Rhsmin=1e-10
    Digits=8
    Error=1e-10
    NotDamped=100
    Iterations=80
    Method=ParDiSo #(NonsymmetricPermutation IterativeRefinement=15)
    Transient=BE
    Number_of_Threads=2
    WallClock
    ExtendedPrecision
}

System {
    AlSiSchottky diode1 (FC=b BC=s)
B.2 DLTS simulation

Vsource_pset vs (s 0) \{dc=0\}
Vsource_pset vb (b 0) \{dc=0\}

}\n
Solve {
Poisson
Coupled (Iterations=100){Poisson Electron}
Coupled (Iterations=100){Poisson Hole}
Coupled (Iterations=100){Poisson Electron}
Coupled (Iterations=100 Method=Blocked LineSearchDamping=0.1
NotDamped=3) {Poisson Electron Hole}

set(TrapFilling=Frozen)
Save(FilePrefix="InitSave00")

#### Ramp to reverse bias ####
Quasistationary (InitialStep=1e-1 MaxStep=1 MinStep=1.e-15
Goal { Parameter=vs.dc Voltage=@Voltage@ }
){ACCoupled (StartFrequency=1e6 EndFrequency=1e6
NumberOfPoints=1 Decade Iterations=10 Node(s b)
ACCompute (Time = (Range = (0 1) Intervals = 2))
){ Poisson Electron Hole }

Save(FilePrefix="InitSave0")

#### Calculate the capacitance at \@Voltage\ ####
NewCurrentPrefix="CapInit_"
Quasistationary (InitialStep=1e-1 MaxStep=1 MinStep=1.e-6
Goal { Parameter=vs.dc Voltage=@Voltage@ }
){ACCoupled (StartFrequency=1e6 EndFrequency=1e6
NumberOfPoints=1 Decade Node(s b)
ACCompute (Time = (Range = (0 1) Intervals = 2))
){ Poisson Electron Hole }

Save(FilePrefix="InitSave")

#### Release the traps and start the transient sim. ####
Unset(TrapFilling)
Transient (
  InitialTime = 0 # [s]
  FinalTime = 0.015 # [s]
  # ----- Control the time step size ----- InitialStep = 1e-4
  MinStep = 1e-15
  MaxStep = 5.e-1
) \{Coupled(Iterations=10){ Poisson Electron Hole \}

Set(TrapFilling=Frozen)
Save(FilePrefix="Save_1:\")

############ Transient point 1 ###############
NewCurrentPrefix="Cap1_"
Quasistationary (InitialStep=1e-2 MaxStep=0.3 MinStep=1.e-6
Goal { Parameter=vs.dc Voltage=@Voltage@ }
){ ACCoupled (StartFrequency=1e6 EndFrequency=1e6
B. SOFTWARE COMMAND FILES

```plaintext
NumberOfPoints=1 Decade Node(s b)
ACompute (Time = (Range = (0 1) Intervals = 4))
) { Poisson Electron Hole }

Unset(TrapFilling)
Transient {
  InitialTime = 0 # [s]
  FinalTime = 0.01 # [s]
  InitialStep = 1e-4
  MinStep = 1e-10
  MaxStep = 5.e-1
} {Coupled(Iterations=25) { Poisson Electron Hole }

Set(TrapFilling=Frozen)
Save(FilePrefix="Save2_.")

############ Transient point 2 #############

NewCurrentPrefix="Cap2_."
Quasistationary {
  InitialStep=1e-2 MaxStep=0.3 MinStep=1.e-6
  Goal { Parameter=vs.dc Voltage=@Voltage@ }
} {ACCoupled (StartFrequency=1e6 EndFrequency=1e6
  NumberOfPoints=1 Decade Node(s b)
  ACCompute (Time = (Range = (0 1) Intervals = 4))
} { Poisson Electron Hole }

System("rm Save_*")
System("rm Cap7_.diode1*")
```

46
References


REFERENCES


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REFERENCES


REFERENCES


Paper I

Electrically active centers introduced in p-type Si by rapid thermal processing.


Electrically active centers introduced in p-type Si by rapid thermal processing

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Electrically active defects introduced in boron-doped silicon by rapid thermal annealing were studied using deep level transient spectroscopy. Thermal treatment at 1000 °C for 2 minutes induced two hole traps with energy levels at 0.3 eV and 0.4 eV above the valence band edge and concentration between $5 \times 10^{12}$ and $5 \times 10^{13}$ cm$^{-3}$. Both defects exhibit Poole-Frenkel effect and show thermal stability up to 650°C. Depth profiling reveals that these defects extend more than 3 μm into the bulk and decrease in concentration towards the surface. The origin and formation kinetics of these centers will be discussed and compared with theoretical predictions in the literature.

1 Introduction Rapid thermal processing (RTP) has received a considerable attention recently due to increasing control of dopant diffusion for the emitter formation in solar cells. Activation of dopants from ion implantation using RTP can minimize the diffusion time and enable ultra shallow emitters which will put a less stringent criteria for surface passivation in solar cells [1]. However, electrically active defects and impurities may be introduced or activated by RTP due to the high temperatures of the treatment followed by rapid cooling. In fact, impurities can be quenched with concentrations well above the solubility level and in particular, transition metals, which can reduce the minority carrier lifetime considerably, may dissolve from grain boundaries in multicrystalline silicon (mc-Si) [2]. Although the concentrations of metals in single crystalline silicon are much lower in comparison with mc-Si, defects with characteristics of transition metals have been observed after a RTP treatment and proposed as residuals [3].

Recently, several first principle calculations on transition metals in Si have been reported (see for instance [4–6]). In this study, we elucidate the properties of RTP induced electrically active defects and compare with theoretical predictions.

2 Experiment Samples were cut from multicrystalline Si and Czochralski Si (Cz-Si) with boron doping concentration of $\sim 1 \times 10^{16}$ cm$^{-3}$ and $\sim 2 \times 10^{15}$ cm$^{-3}$, respectively, and heat treated using rapid thermal annealing (RTA) at 1000°C for 2 min. The rapid thermal annealing was performed using the RTP system ‘AS-Micro’ from AnnealSys, where the samples were contained in a SiC-coated graphite susceptor. Heating was provided by infrared tubular halogen lamps and the cooling rate was about 30 K/s. Characterization of electrically active defects was performed using deep level transient spectroscopy (DLTS) in the temperature range from 77 to 300 K employing Schottky barrier (SB) contacts. The SB contacts were prepared by thermal evaporation of aluminum through a metal mask, and Ohmic contacts were realized through scratching silver-paste at the backside of the samples. The DLTS signal was extracted using lock-in
weighting function, and six rate-windows ranging from \((20 \text{ ms})^{-1}\) to \((640 \text{ ms})^{-1}\) were used. For investigation of the thermal stability of the induced defects, cycles of DLTS measurement and heat treatment were performed on the Cz-Si samples. The heat treatments were realized at 650, 750, 850 and 900 °C for 30 min in air after removal of the silver-paste and aluminum contacts using aceton and HF, respectively.

### 3 Results and discussion

Figure 1 shows two DLTS measurements on Cz-Si samples taken with reverse bias at -5 and -20 V before any additional heat treatment after RTP and one DLTS measurement on Cz-Si as-grown sample (no RTP). Two peaks are observed on RTP samples and labelled H(0.3) and H(0.4), whereas no peaks are observed in the as-grown sample. The energy level position, defect concentration and apparent capture cross-section extracted from the Arrhenius plot for H(0.3) are found to be 0.27 ± 0.03 eV above the valence band edge \((E_V)\), \(6 \times 10^{12} \text{ cm}^{-3}\) and \(5 \times 10^{-15} \text{ cm}^2\), respectively. The H(0.4) peak has energy position of 0.38 ± 0.03 eV above \(E_V\), defect concentration between 3.8-4.5 \(\times 10^{13} \text{ cm}^{-3}\) and an apparent capture cross-section of \(1 \times 10^{-15} \text{ cm}^2\). No other peaks are revealed for Cz-Si in the temperature range of 77 to 300 K. The temperature-axis in Fig. 1 is shortened in order to emphasize the shift of DLTS signal towards lower temperature when larger reverse bias is applied. Each peak in the DLTS spectra can be related to a specific emission rate, given a rate-window and a weighting function, which is characteristic to a trap. When the peak position shifts to a lower temperature, the emission rate of the trap has increased, indicating that the energy barrier for charge carrier emission \((E_T - \Delta E_T\), where \(E_T\) is the energy level of the trap) is lowered. Under an external electric field, this can occur through a Poole-Frenkel effect when Coulomb interaction exists between the emitted charge carrier and the trap [7]. According to the fundamental description in Ref. [7], the change in the energy barrier, \(\Delta E\), is proportional to the square root of the electric field times a constant of \(3.9 \times 10^{-4} \text{ eV V}^{-1/2} \text{cm}^{1/2}\) for Si. Figure 2 shows the Arrhenius plot for H(0.3) and H(0.4) with different averaged electric field in the depletion zone; in addition to a shift, it can be seen that the gradient (which is proportional to the energy barrier) decreases slightly with increasing electric field. The proportionality constant for the field-dependence was estimated to be \(4 \times 10^{-4} \text{ eV V}^{-1/2} \text{cm}^{1/2}\), in close agreement with that predicted from Ref. [7]. Hence, both H(0.3) and H(0.4) are considered to be traps of acceptor nature.

DLTS measurement taken after subsequent heat treatments at 650, 750, 850 and 900 °C for 30 min are depicted in Fig. 3. A decrease in the DLTS signal can be observed for both peaks after heating above 650 °C. However, in contrast to H(0.4), the decrease in H(0.3) ceases between 750 and 850 °C before continuing above 850 °C.
This could suggest H(0.3) has a complex mechanism for the annealing process.

Concentration-versus-depth profiling was performed after each heat treatment, by varying the amplitude of the pulse bias and keeping the reverse bias constant at $-10 \text{ V}$. Figure 4 shows the depth profile for H(0.4) before and after different heat treatment steps, and the defect concentrations decrease toward the sample surface indicating that the surface acts as a sink. Although the signal to noise ratio was lower for H(0.3) than for H(0.4), similar depth profiles were observed after and before heat treatment at 650 °C (not shown).

To further investigate the defect profiles deeper into the bulk, one Cz-Si sample was wet chemical etched using a solution containing HNO$_3$, HF and CH$_3$COOH (7:5:4, respectively) for 3 min, where approximately 60 μm of the front side was etched off. This sample exhibited no detectable defect level in the specified temperature range (not shown), which indicates that the defect concentration into the sample reaches a maximum before falling below the detection limit. This suggests an indiffused impurity from a limited source rather than residuals and from the extension of the depth profile, the impurity could be a fast diffuser such as Fe, Co, Ni or Cu. First principle calculations have predicted that both substitutional Cu and Ni have acceptor levels close to $E_V$ [6]. However, substitutional Cu and Ni are also predicted to have donor-like energy levels close to $E_V$, which will in this case appear in the DLTS spectra with equal amplitude as H(0.4). Such levels are not observed in our samples, as discussed below.

From experiments related to nickel, several deep levels in the lower half of the band gap have been reported in the literature [8,9]. In agreement with the theoretical work in Ref. [6], Kitagawa et al. ascribed a donor level to substitutional Ni at $E_V + 0.18 \text{ eV}$, which is not found in this study.

Similar to Ni, Cu has been observed experimentally with several deep levels in the lower half of the band gap [10]. The earliest reported energy levels were the ones at $E_V + 0.24 \text{ eV}$ and $E_V + 0.49 \text{ eV}$ and regarded as originating from substitutional Cu [11]. From Hall effect measurements on intentionally Cu-contaminated p- and n-type Si samples which showed an amphoteric behavior of Cu, Collins et al. concluded that the former and the latter energy level were of donor- and acceptor-type, respectively. Similar results were obtained by Brotherton et al. using DLTS in a later study [12]. In addition, they found a clear correlation between the two levels in terms of concentration and concluded that the levels arose from one defect with different charge states. Consequently, if H(0.3) and H(0.4) were due to substitutional Cu, a field-dependent emission should be minimal for H(0.3) and the concentrations of H(0.3) and H(0.4) should be equal.

On the other hand, substitutional metal impurities may form complexes with intrinsic defects and/or dopants. Using first principle calculations, Estreicher et al. have pre-
dicted several possible configurations of Fe with vacancy, carbon, oxygen or boron [4]. For vacancy-related complexes, vacancies were assumed to be present due to, for in-
stance, irradiation. The energy level positions were mainly estimated using the marker method, where the perfect crys-
tal was chosen as the reference point. Predictions were made for Fe, {Fe,V}, {Fe,V\textsubscript{2}}, {Fe,\textsubscript{Si}}, {Fe,C\textsubscript{i}}, Fe\textsubscript{i}, \{V\textsubscript{Fe}V\}, \{Fe,O\textsubscript{i}\}, \{Fe,\textsubscript{B\textsubscript{s}}\} and \{Fe,B\textsubscript{s}\} centers. Four centers were found to possess an acceptor level in the lower half of the band gap, but two of these (\{Fe,V\} and \{Fe,V\textsubscript{2}\}) were also predicted to have donor levels above \(E_V + 0.25\) eV (which would be readily detected in our measurements). The two other complexes, \{Fe,B\textsubscript{s}\} and \{VFeV\}, exhibit only one acceptor level in the lower half of the band gap where each corresponds well to H(0.3) and H(0.4), respectively.

Furthermore, multicrystalline samples with a higher boron concentration than the Cz samples used have also been studied and they reveal comparable DLTS signals for the H(0.3) and H(0.4) peaks with concentrations between 1-2\(\times 10^{13}\) cm\(^{-3}\) (see Fig. 5). This supports a relation of H(0.3) to boron, and a tentative assignment to the \{Fe,B\textsubscript{s}\} center.

**Figure 5** Normalized DLTS signal versus temperature for an mc-Si sample. The doping concentration and applied reverse bias were \(1 \times 10^{16}\) cm\(^{-3}\) and -5 V, respectively. The corresponding Arrhenius plot for H(0.3) and H(0.4) are shown in Fig. 2.

**4 Conclusion** As-grown mono- and multi-crystalline boron-doped silicon were treated by RTP and electrically characterized using DLTS. Two defect levels of acceptor-type were observed with energy position of \(E_V + 0.3\) eV and \(E_V + 0.4\) eV. Both levels were thermally stable up to 650 °C and arise possibly from interaction between Fe impurities diffusing from the surface and vacancies/boron in the bulk.

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**References**

Hydrogen-induced dissociation of the Fe-B pair in boron-doped p-type silicon.

C.K. Tang, L. Vines, B.G. Svensson and E.V. Monakhov

Hydrogen-induced dissociation of the Fe-B pair in boron-doped p-type silicon

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Keywords: Iron, Iron-boron pair, hydrogen, silicon, DLTS

Abstract. The interaction between hydrogen and the iron-boron pair (Fe-B) has been investigated in iron-contaminated boron-doped Cz-Si using capacitance-voltage measurements (CV) and deep level transient spectroscopy (DLTS). Introduction of hydrogen was performed by wet chemical etching and subsequent reverse bias annealing of Al Schottky diodes. The treatment led to the appearance of the defect level characteristic to interstitial iron (Fe\textsubscript{i}) with a corresponding decrease in the concentration of the Fe-B pair. Concentration versus depth profiles of the defects show that dissociation of Fe-B occurs in the depletion region and capacitance-voltage measurements unveil a decrease in the charge carrier concentration due to passivation of B. These quantitative observations imply strongly that H promotes dissociation of Fe-B releasing Fe\textsubscript{i} whereas no detectable passivation of Fe-B or Fe\textsubscript{i} by H occurs.

Introduction

Transition metal impurities, like iron, in silicon have received considerable attention due to their detrimental effects in integrated circuits and solar cells[1]. For solar cells, iron contamination results in a reduction in minority carrier lifetime with considerable adverse device performance even at low iron concentration. Gettering and passivation of the electrically active iron-related defects, with the aim of suppressing the lifetime degradation, have frequently been studied [2, 3, 4, 5]. In the case of passivation, especially hydrogen has been investigated. However, experimental reports on the effects of hydrogen on the iron behavior have shown conflicting results. On one hand, report based on lifetime measurements concluded that hydrogen passivate iron [4]. On the other hand, an increase in the concentration of the lifetime killing interstitial Fe (Fe\textsubscript{i}) center was observed with deep level transient spectroscopy (DLTS), tentatively attributed to hydrogen-stimulated dissociation of the Fe-B pair [6, 7]. The increase of Fe\textsubscript{i} was found to coincide with the region where B-H was formed after the introduction of hydrogen via wet chemical etching. Annealing under reverse bias led to an increase in the Fe\textsubscript{i} signal in the depletion region and an indication of a small peak at the depletion edge where a concentration maximum of B-H was located. Two mechanisms for release of Fe\textsubscript{i} were proposed in Refs.[6] and [7]. The first one, which does not involve hydrogen, is based on the Fermi-level position and the accompanied change in the charge state of Fe\textsubscript{i}. By obtaining a neutral Fe\textsubscript{i}, the binding energy between Fe and B\textsuperscript{-} reduces and formation of Fe-B quenches [8]. The second one involves hydrogen in a reaction with Fe-B forming Fe\textsubscript{i} and B-H. However, no decrease in Fe-B equivalent to the increase of Fe\textsubscript{i} as a function of depth has been verified yet.

\textit{Ab-initio} calculations using VASP and SIESTA have recently been performed to investigate the interaction of hydrogen with Fe\textsubscript{i} and Fe-B [9]. Various \textit{a priori} configurations were estimated for their stability in different charge and spin states. In the case of Fe-B and H, it was predicted that the most stable configuration consists of an isolated \textsuperscript{3/2}Fe\textsuperscript{+} and \textsuperscript{0}B-H\textsuperscript{0} with 3/2 and 0 spin state, respectively. The gain in energy was 0.25 eV compared to \textsuperscript{3/2}Fe-B\textsuperscript{0} and \textsuperscript{0}H\textsubscript{BC}\textsuperscript{+} (H in bond centered configuration). In addition, a stable configuration was also predicted between Fe\textsubscript{i} and H, in the case of \textsuperscript{1}Fe\textsubscript{i}. The gain in energy varied with the H reactant in \textsuperscript{1/2}H\textsubscript{BC}\textsuperscript{0} and \textsuperscript{0}H\textsubscript{BC}\textsuperscript{+} states and was found be 0.82
and 0.40 eV, respectively. The resulting Fe-H pair exhibits a deep donor level at 0.36 eV (SIESTA: 0.42 eV) above the valence band edge ($E_V$) and a deep acceptor level at 0.26 eV (SIESTA: 0.30 eV) below the conduction band edge ($E_C$). However, an additional H could release the Fe from Fe-H by forming $\text{Fe}_i$ and $\text{H}_2$.

The interchange of $\text{Fe}^{+}_i$ to $\text{Fe}^0_i$ can readily be achieved in a diode structure by an external bias. Additionally, it also provides the possibility of controlling the depth at which the transition of charge state occurs. This gives the opportunity to examine possible reaction between $\text{Fe}^0_i$ with $\text{H}^+$ which should appear in a defined region controlled by the external bias and give rise to the predicted energy levels if theory holds.

In this study, hydrogen has been introduced into iron-contaminated p-type boron-doped silicon via wet chemical etching to investigate its interaction with iron. The absolute concentration versus depth profiles of the defects were monitored. A strong indication of hydrogen-induced dissociation of Fe-B was found, where the decrease in the concentration of Fe-B was accompanied by a corresponding increase in the concentration of $\text{Fe}^0_i$. Moveover, no passivation of $\text{Fe}^0_i$ and Fe-B by hydrogen was detected.

**Experiment**

Samples were cut from as-grown Czochralski Si wafers with a boron doping concentration of $3 \times 10^{14}$ cm$^{-3}$. Iron was introduced by ion implantation on the back-side of the samples with energy and dose of 700keV and $1 \times 10^{12}$ cm$^{-2}$, respectively. Heat treatment was thereafter performed at 900°C for 1h in a belt furnace to distribute the Fe uniformly in the sample. At the end of the heat treatment, the samples were transferred into an air-cooled area in the furnace.

Wet chemical etching (WCE) was performed for 30 seconds (7:5:2, HNO$_3$:HF:CH$_3$COOH) on a set of samples in order to introduce hydrogen at the surface while reference samples were cleaned in HF only. Schottky barrier (SB) contacts were realized by thermal evaporation of Al through a metal mask onto the front side. Ohmic contact was achieved by applying silver-paste on the back-side. Reverse bias annealing (RBA) was performed at 350K for 20 minutes with reverse bias voltage ($V_{rb}$) of 4V.

DLTS measurements were performed with a $V_{rb}$ of 6V, pulse bias of -6V and pulse width of 50ms in the temperature range of 40 to 300K. The DLTS signal was extracted by applying a lock-in weighting function, and six rate-windows ranging from $(5\text{ ms})^{-1}$ to $(160\text{ ms})^{-1}$ were used. The first DLTS measurements on SB contacts were taken after two weeks of storage at room temperature (RT). Depth profiles of the defects were performed by progressively changing the pulse bias from 0 to -6V while maintaining a $V_{rb}$ of 6V at a fixed temperature.

**Results and discussion**

Figure 1 shows the charge carrier concentration versus depth profile, measured by capacitance-voltage measurement, before and after RBA for samples with and without WCE. For WCE samples, a decrease in charge carrier concentration towards the surface can be observed while the profiles in the reference samples remain constant. The charge carrier concentration difference arises from the introduction of H where passivation of B occurs by the formation of the B-H pair[11]. After RBA, the H has diffused further into the WCE samples while the reference samples remain unaffected. The depth of H penetration during RBA was found to depend on the applied reverse bias, as expected due to the electric field within the depletion region forcing H$^+$ to the edge of the region.

Figure 2 shows the DLTS spectra for the corresponding samples in Fig.1. Before RBA, one dominant peak occured at $\sim$55K in all samples, with a concentration of $5 \times 10^{12}$ cm$^{-3}$. Extracted from the different rate-windows, the energy level position and the capture cross-section were found to be $E_V$+0.10 eV and $4 \times 10^{-15}$ cm$^2$, respectively. These values are in good agreement with the identification of the Fe-B pair [1]. After RBA, a new peak emerged at $\sim$242K with energy level position of
Fig. 1: Charge carrier concentration versus depth profiles before and after RBA for samples with and without WCE.

Fig. 2: DLTS spectra before and after RBA on samples with and without WCE. One dominant peak at \(\sim 55\text{K}\) can be observed before RBA and a second peak (\(\sim 242\text{K}\)) appears after RBA with an amplitude depending on the pretreatment. The DLTS spectrum for the WCE sample is displaced in the y-direction for clarity. The curves are extracted from rate-window (20ms)\(^{-1}\).

\(E_V + 0.40\text{eV}\) and capture cross-section of \(3 \times 10^{-16}\text{cm}^2\), in good agreement with the previous identification of Fe\(_i\) [1]. During storage at RT, the concentration of this peak decreased in all samples while the concentration of the Fe-B pair increased correspondingly. The evolution of the peaks is due to the (re)association of Fe\(_i\) with B forming the Fe-B pair. This behaviour is a well known characteristic of Fe in boron-doped silicon, where the stable Fe-B pair can dissociate in a reversible reaction into Fe\(_i\) by thermal treatment, illumination or minority carrier injection[10]. Although all samples experienced the RBA, the samples treated in WCE showed a larger increase in the DLTS signal of Fe\(_i\) by a factor of 3 than the samples without WCE. Indeed, the DLTS signal is altered by the reduction in the charge carrier concentration for WCE samples, shown in Fig.1. However, if the altered DLTS signal is solely caused by the reduction of charge carrier concentration, the average carrier concentration in
the measured region must also be reduced by a factor of 3, which is not the case. Thus, the presence of H affects the dissociation of the Fe-B pair.

Figure 3 shows the concentration versus depth profiles of FeB and Fe\textsubscript{i} for WCE samples. The appearance of Fe\textsubscript{i} and the correlated loss in Fe-B, observed in Fig. 2, originates from a distinct layer, defined by RBA, within the DLTS profiling region.

As mentioned previously, one possibility for the release of Fe\textsubscript{i} is a change in the charge state of Fe\textsubscript{i} from positive to neutral which has been shown, by Kimerling et. al.\cite{8}, to extinguish the pairing of Fe\textsubscript{i} and B\textsuperscript{−}. Since the applied reverse bias during RBA raises the Fermi-level above the level of Fe\textsubscript{i} (transferring it to the neutral state), the resulting defect profiles may be caused by the Fermi-level effect within the depletion region. It should be emphasized that the region where Fe changes the charge state is not located at the depletion edge but a distance closer to the surface, due to the so-called lambda-effect\cite{12}. Thus, release of Fe\textsubscript{i} should not occur at the depletion edge (W) but at W-\(\lambda\).

The vertical lines in Fig. 3 at 5.2\(\mu\)m and 4.5\(\mu\)m highlight the depletion edge and the region where Fe\textsubscript{i} changes its charge state from + to 0, respectively. If the release of Fe\textsubscript{i} is caused solely by the Fermi-level effect, it is expected that no release of Fe\textsubscript{i} exists deeper than 4.5\(\mu\)m. However, a considerable amount of Fe\textsubscript{i} can still be observed demonstrating the significance of direct dissociation of the Fe-B pair promoted by H: Fe-B + H \rightarrow B-H + Fe\textsubscript{i}.

It may be argued that Fe\textsubscript{i} released close to the surface has in-diffused to such an extent that it could account for the measured defect profiles. However, the gain in [Fe\textsubscript{i}] as a function of depth agrees closely with the loss of [Fe-B], implying that no significant net diffusion has occured in the measured region (brackets denote concentration values).

As mentioned in the introduction, an interaction of H with Fe\textsuperscript{0} \cite{9} may be expected in the depletion region. However, based on our quantitative observations, any formation of Fe-H complexes cannot be confirmed under the present experimental conditions; indeed, if hydrogen is to passivate Fe\textsubscript{i} or Fe-B, a dissimilar concentration change between the two defects should occur. In addition, no new level in the vicinity of 0.3-0.4 eV above \(E_V\) is observed, as predicted for a donor state of the Fe-H pair. Thus, no evidence for passivation of Fe\textsubscript{i} or Fe-B by H is obtained.
Conclusion

The effect of hydrogen on the Fe-B pair has been investigated in iron-contaminated boron-doped Cz-Si samples subjected to WCE. Interaction between hydrogen and Fe-B has been observed through monitoring of the concentration versus depth profiles of Fe-B and Fe_i before and after RBA. Strong indication of hydrogen-induced dissociation of Fe-B into Fe_i and B-H was found confirming recent theoretical predictions and previous tentative experimental findings. Moreover, passivation of Fe_i by hydrogen has not been detected.

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Interaction between hydrogen and the Fe-B pair in boron-doped p-type silicon.

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Interaction between hydrogen and the Fe-B pair in boron-doped p-type silicon

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The effect of hydrogen incorporation into iron-contaminated boron-doped Cz-Si has been investigated using deep level transient spectroscopy. In-diffusion of hydrogen by wet chemical etching followed by reverse bias annealing of Al, Schottky diodes result in the appearance of the defect level characteristic to interstitial iron (Fe$_i$), and the concentration of iron-boron pairs (Fe-B) decreases correspondingly. Quantitative observations from various defect concentration versus depth profiles imply strongly that H promotes dissociation of Fe-B releasing Fe, whereas no detectable passivation of Fe-B or Fe$_i$ by H occurs. © 2011 American Institute of Physics. [doi:10.1063/1.3619848]

Iron in silicon is well known for its effect in degrading the performance of devices, such as in integrated circuits and solar cells. Significant reduction in minority carrier lifetime, even at low iron concentration, is one of the main issues in solar cells based on p-type multicrystalline silicon. The efficiency of lifetime recovery by reducing the concentration of electrically active iron-related defects through gettering or passivation has frequently been investigated. For the passivation, especially hydrogen has been studied. However, experimental reports on the effects of hydrogen on the iron behavior have shown various results. On one hand, passivation of iron by hydrogen was concluded through lifetime measurement. On the other hand, deep level transient spectroscopy (DLTS) studies have observed an increase in the lifetime killing interstitial Fe (Fe$_i$) as possibly due to stimulated dissociation of the Fe-B pair by hydrogen. In the latter reports, wet chemical etching (WCE) was performed to introduce H at the surface which resulted in an increase of Fe$_i$ in the region where B-H was formed. Annealing under reverse bias led to an increase in the Fe$_i$ signal in the depletion region and an indication of a small peak at the depletion edge where B-H reached its maximum concentration. Two mechanisms for release of Fe$_i$ were discussed in Refs. 6 and 7. The first one involves a change in the Fermi-level position and changing the charge state of Fe$_i$ from positive to neutral, which reduces the binding energy between Fe and B$^-$ and quenches the formation of Fe-B. The second one involves hydrogen in a reaction with Fe-B forming Fe$_i$ and B-H but no decrease in Fe-B equivalent to the increase of Fe$_i$ as a function of depth has been verified yet.

The interaction between Fe$_i$, Fe-B, and H has recently been predicted through ab-initio calculations using Vienna Ab-initio Simulation Package (VASP) and Spanish Initiative for Electronic Simulations with Thousands of Atoms (SIESTA) by Sanati et al. The stability of various a priori configurations was estimated in different charge and spin states. In the case of Fe-B and H, it was predicted that the most stable configuration consists of an isolated $^{3/2}$Fe$^+$ and $^0$B-H$^+$ with 3/2 and 0 spin state, respectively. The gain in energy was 0.25 eV compared to $^{3/2}$Fe-B$^0$ and $^0$H$_{BC}^+$ (H in bond centered configuration). In addition, a stable configuration was also predicted between Fe$_i$ and H, in the case of $^0$Fe$_i^0$. The gain in energy varied with the H reactant in $^{3/2}$H$_{BC}^+$ and $^0$H$_{BC}^+$ to be 0.82 and 0.40 eV, respectively. The resulting Fe-H pair exhibits a deep donor level at 0.36 eV (SIESTA: 0.42 eV) above the valence band edge (E$_V$) and a deep acceptor level at 0.26 eV (SIESTA: 0.30 eV) below the conduction band (E$_C$). However, an additional H could release the Fe from Fe-H by forming Fe$_i$ and H$_2$.

The charge state of Fe$_i$ can easily be modified in a diode structure by applying an external bias which moves the Fermi-level and interchange Fe$_i^+$ to Fe$_i^0$. Such an experiment provides the opportunity for examining possible reaction between Fe$_i^0$ with H$^+$ which should appear in a specific region and give rise to new energy level positions, as predicted theoretically.

In this study, we have incorporated hydrogen in iron-contaminated p-type silicon through wet chemical etching and investigated its effects on iron. The results of different defect concentration versus depth profiles strongly favour dissociation of Fe-B in the presence of H, where the absolute loss in the concentration of Fe-B is accompanied by a corresponding gain in the concentration of Fe$_i$. In addition, our results show no detectable passivation of Fe$_i$ and Fe-B by H.

Samples were cut from as-grown Czochralski Si wafers of p-type with a boron doping concentration of ~1.3 × 10$^{14}$ cm$^{-3}$. Iron was introduced by ion implantation on the back-side of the samples with energy and dose of 700 keV and 7 × 10$^{11}$ cm$^{-2}$, respectively. Heat treatment was thereafter performed at 900 °C under nitrogen flow for 1 h in a tube furnace to distribute the Fe homogeneously in the samples. After the heat treatment, the samples were quenched rapidly in water to room temperature (RT).

WCE was performed for 30 s (7:5:2, HNO$_3$:HF:CH$_3$ COOH) on one set of samples in order to introduce hydrogen at the surface. Reference samples, which did not undergo WCE, were dipped in HF. All samples were, thereafter, further cleaned in RCA3 (H$_2$O, HCl, H$_2$O$_2$, 5:1:1, at 80 °C). Schottky barrier (SB) contacts were realized by thermal evaporation of Al through a metal mask on the front-surface.

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and Ohmic contacts were achieved by applying silver-paste on the back-side. Since the sample processing steps may introduce unintentional hydrogen at the surface, one set of the reference samples were heat treated (HT) at 180 °C for 30 min to distribute any accumulated hydrogen into the sample. Reverse bias annealing (RBA) was performed at 350 K for 30 min with a reverse bias voltage (V_{rb}) of 4 V.

DLTS measurements were performed with a V_{rb} of 8 V, pulse bias of −8 V, and pulse width of 50 ms in the temperature range of 40 to 300 K. The DLTS signal was extracted using a lock-in weighting function, and six rate-windows ranging from (5 ms)^{-1} to (160 ms)^{-1}. The first DLTS measurements were performed after two weeks of storage at room temperature after the sample preparation.

Figure 1 shows DLTS spectra before and after RBA on samples with and without WCE treatment. Before RBA, one dominant peak can be observed at 55 K in all samples, with samples with and without WCE treatment. Reverse bias annealing (RBA) was performed at 350 K for 30 min with a reverse bias voltage (V_{rb}) of 4 V.

FIG. 1. (Color online) DLTS spectra before and after RBA on iron-contaminated samples with/without WCE treatment. The curves are taken with a rate window of (40 ms)^{-1}. An offset in ΔC/C_{rb} has been applied to the data for samples without WCE for clarity.

FIG. 2. (Color online) Charge carrier concentration vs depth profile before and after RBA on samples with/without WCE treatment. It reveals the passivated region, which results from the formation of B-H, and can be related to the concentration of hydrogen.

The depletion edge and the significance of the lambda-length occur at the depletion edge.15 Thus, release of Fe\textsubscript{i} by thermal treatment, illumination or minority carrier injection.10 Although all samples experienced the RBA, the samples treated in WCE showed a higher DLTS signal of Fe\textsubscript{i} than the samples without WCE. In particular, it can be noticed that the HT sample exhibits a weak Fe\textsubscript{i} signal. However, from the Fig. 1, it can be misleading to conclude on a direct interaction between hydrogen and Fe, since changes in the charge carrier concentration (from RBA) can affect the DLTS signal.

The depletion edge and the significance of the lambda-length are highlighted in Fig. 3 with added lines. The depth of the depletion region is determined from the capacitance that
was recorded continuously during the RBA at 350 K. Due to the H re-distribution, a change in the capacitance takes place during RBA; it amounts, however, to only 0.3%, i.e., /C24 20 nm in the depletion edge depth and can be neglected.

The characteristics of a release of Fe by the Fermi-level effect are fulfilled in the HT samples where the influence of H is small. The depth profile in Fig. 3(b) shows that the increase of Fe occurs close to the charge state transition region (as highlighted by the vertical lines). However, in the WCE samples, a significant release of Fe can be observed not only in the region with Fe0 but also in the part of the depletion region where Fe+ exists. Moreover, the concentration of released Fe in the depletion region is higher by a factor of 1.5-2 in the WCE sample as compared to the HT sample. This demonstrates the significance of the mechanism, where Fe is released due to a direct dissociation of Fe-B promoted by H: Fe-B + H → B-H + Fe.

It may be argued that Fe released close to the surface has in-diffused to such an extent that it could account for the measured defect profiles. However, the gain in concentration of Fe as a function of depth agrees closely with the loss of in concentration of Fe-B, implying that no significant net diffusion has occurred in the measured region.

As mentioned in the introduction, an interaction of H with Fe0,9 may be expected in the depletion region. However, based on our quantitative observations, we can not confirm formation of Fe-H complexes under the present experimental conditions; indeed, if hydrogen is to passivate Fe or Fe-B, a dissimilar concentration change between the two defects should occur. In addition, no new level in the vicinity of 0.3–0.4 eV above Ev predicted for a donor state of the Fe-H pair, is observed. Thus, no evidence for passivation of Fe or Fe-B by H is obtained.

In conclusion, hydrogen has been incorporated into iron-contaminated boron-doped Cz-Si and demonstrated to interact with the Fe-B pair. By monitoring the absolute concentration of Fe-B and Fe versus depth before and after RBA, strong evidence of hydrogen-induced dissociation of the Fe-B pair into Fe and B-H are found confirming previous tentative experimental findings and recent theoretical predictions. In addition, no detectable passivation of Fe by hydrogen is observed.

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FIG. 3. (Color online) Defect concentration vs depth profile for Fe-B and Fe measured on (a) samples with WCE and (b) HT samples without WCE.

References:

Deep level transient spectroscopy on proton-irradiated Fe-contaminated p-type silicon.

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Deep level transient spectroscopy on proton-irradiated Fe-contaminated p-type silicon

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Proton-irradiation has been realized on Fe-contaminated p-type Czochralski silicon and investigated for interaction between Fe and irradiation-induced defects using deep level transient spectroscopy. From isochronal thermal annealings, three distinctive Fe-related defects are observed with energy level position of 0.17, 0.28 and 0.34 eV above the valence band edge. From the evolution of the defect concentration at different annealing temperature, it is suggested that Fe has reacted with prominent irradiation-induced defects, such as the vacancy-oxygen complex and the divacancy center.

1 Introduction 
Iron is an important impurity in silicon due to its known harmful effects on the performance of both integrated circuits and solar cells [1]. In p-type silicon, improvement of solar cells by reducing the concentration of Fe can be achieved by performing a phosphorus in-diffusion step (gettering), which is essentially a part of the formation of the emitter layer. However, the mechanism of phosphorus gettering is not well understood. In addition, even with the standard phosphorus in-diffusion, complete silicon-based solar cell may still exhibit light-induced degradation of 3-4 relative percentages with degradation characteristics of Fe contamination [2].

In order to improve the gettering efficiency of Fe, it is important to understand the underlying mechanism and the defects which are formed during the gettering process. In a recent report regarding phosphorus gettering, it has been shown that phosphorus atoms do not directly contribute to the gettering mechanism [3]. The authors propose a mechanism which involves reaction with injected vacancies and oxygen. Such interactions can also be investigated through generation of vacancies by irradiation of an Fe-contaminated sample and using an electrical characterization technique, such as deep level transient spectroscopy (DLTS), with the aid of theoretical predictions [4].

In this study, Fe-contaminated and Fe-lean float-zone (Fz) silicon samples have been irradiated by protons and investigated for possible reactions of Fe with radiation-induced defects after subsequent isochronal annealings. Several defects are observed distinctively in the Fe-contaminated samples after annealing above 150 °C. Two of the Fe-related defects are possibly formed with divacancy and vacancy-oxygen complexes.

2 Experiment 
Samples were cut from Fz boron-doped silicon with doping concentration of $2 \times 10^{14}$ cm$^{-3}$, as confirmed by capacitance-voltage (CV) measurements. Cleaning of the samples was performed with an HF-dip before the introduction of Fe by ion-implantation at the back-side of the samples. The implantation energy and dose were 700 keV and $2 \times 10^{12}$ cm$^{-2}$, respectively. After implantation, the samples were heat treated in a tube furnace at 1000 °C for 1 h under nitrogen flow to distribute Fe uniformly in the sample [5]. Thereafter, the samples were further cleaned using the standard RCA-steps.

Aluminium contacts were deposited onto the front-side to form Schottky barrier contacts for CV-measurements and DLTS. Ohmic contacts were formed at the back-side by scratching on silver-paste. For DLTS, six rate-windows
were used ranging from (20 ms)$^{-1}$ to (640 ms)$^{-1}$ and the signals were extracted by the GS4 weighting function [6]. The reverse and pulse bias voltages were 15 and -15 V, respectively.

After DLTS measurements, which confirmed that the Fe-contaminated samples only contained the Fe-B pair and/or interstitial Fe ($Fe_{i}$) deep levels, proton-irradiation was performed with an energy of 1.8 MeV and a dose of $3 \times 10^{11}$ cm$^{-2}$. The reference samples, which were not intentionally contaminated with Fe, received the same proton-irradiation. As estimated by SRIM [7], the projected range of H$^+$ is $\sim 40 \mu$m which is a factor of $\sim 3$ deeper than the region investigated with CV and DLTS. The proton-irradiated samples were stored for more than two weeks at room temperature before commencing the measurements and the isochronal annealing (30 min).

3 Results and discussion Figure 1 shows the DLTS spectra for Fe-contaminated (Fig. 1a) and reference (Fig. 1b) samples at as-implanted state and after subsequent isochronal annealings up to 200 $^\circ$C. The well-known irradiation-induced defects can be observed in the as-implanted samples, such as the divacancy ($V_{2}$) [8–10] and the interstitial carbon-interstitial oxygen pair ($C_{i}O_{i}$) [9,11] with the respective energy level positions of 0.18 eV and 0.36 eV above the valence band edge ($E_{v}$). A minor peak caused by the irradiation at 213 K can also be seen with energy level of $E_{v}+0.48$ eV, labelled as H(0.48). However, the origin of this defect is still under investigation.

In addition to the irradiation defects, the Fe-contaminated samples contain a peak at 48 K with energy level of $E_{v}+0.10$ eV and defect concentration of $3 \times 10^{13}$ cm$^{-3}$. This defect arises from the Fe-B pair and it can be dissociated in a reversible reaction by illumination, minority carrier injection or heat treatment into Fe, and B [5,12]. The energy level position of Fe$_{i}$ is $E_{v}+0.40$ eV and it is clearly visible in Fig. 1 at 221 K after annealing at 125 $^\circ$C for 30 min. It can also be noted that the sum of the concentration of the Fe-B pair and Fe$_{i}$ is decreasing by subsequent annealing. Several reasons can explain the decrease. Interstitial Fe is highly mobile and can diffuse to the surface. It can also undergo reactions with other defects such as the irradiation-induced defects, forming electrically active or inactive defects.

Figure 2 shows the evolution of the concentration of defects by subsequent isochronal annealings. Focusing on the reference samples, both $V_{2}$ and $C_{i}O_{i}$ are observed to anneal out at an earlier stage than normally reported [13]. In addition, a peak appears after annealing at 125 $^\circ$C with energy level of $E_{v}+0.25$ eV and capture cross-section of $3 \times 10^{-15}$ cm$^{2}$. This peak has previously been identified as vacancy-oxygen-hydrogen complex (VOH) [9,14], which indicates that hydrogen has diffused either from the surface or from the implantation region to the DLTS probing region. Within this assumption, the early annealing of $V_{2}$ and $C_{i}O_{i}$ can thereby be explained by passivation by hydrogen. Passivation of the $C_{i}O_{i}$ center by H have both been experi-
For the Fe-contaminated samples, the same trend for the annealing behaviour for \( V_2 \) and \( C_{iO_i} \) is not observed. On the contrary, the concentrations increase after annealing at 125 °C. For \( V_2 \), further annealing leads to a reduction in the concentration which is a similar trend as the reference samples. Whereas for \( C_{iO_i} \), the concentration evolution differs from that observed for the reference samples throughout the annealing series; for example, even an increase in the concentration is observed after 200 °C annealing. From the above observations, it is shown that a different and more complex annealing behavior of irradiation-induced defects exist in the presence of Fe. The interaction with Fe will be discussed later.

Apart from the intrinsic irradiation-induced defects and the prominent Fe defects discussed previously (the Fe, and the Fe-B pair), three peaks are distinctive to Fe-contaminated samples, and observed at 101, 139 and 150 K. Figure 3 shows the Arrenius plots of these defects and the extracted energy level positions are 0.17, 0.28 and 0.34 eV above \( E_V \) with capture cross-sections of \( 4 \times 10^{-16} \), \( 6 \times 10^{-17} \) and \( 4 \times 10^{-14} \) cm\(^2\), respectively. The defects are correspondingly labelled as \( H(0.17) \), \( H(0.28) \) and \( H(0.34) \).

The generation of \( H(0.34) \) is similar to the generation of VOH in the reference sample (see Fig. 2). In addition, it should be noted that the VOH complex has not been detected in the Fe-contaminated sample. These observations indicate that \( H(0.34) \) and the VOH complex have a common precursor, the vacancy-oxygen pair (VO or A-center), or, that the VOH complex is the precursor of \( H(0.34) \) resulting in a defect configuration of VOH-Fe.

Interestingly, the VO-Fe defect has previously been reported by You et al. [18] in n-type Si with energy level position of 0.36 eV below the conduction band edge (\( E_C \)). The formation of VO-Fe was found to occur after annealing between 100 and 150 °C which agrees with the appearance of \( H(0.34) \) in this study. Furthermore, an Fe-related defect with energy level position of \( E_V +0.33 \) eV has been reported by Wünstel and Wagner after slowly cooling of heat treated Fe-indiffused Si-samples [19]. From the comparison between Czochralski and Fz Si-samples, it was found that the defect concentration was reduced in the Fz samples. Hence, the authors suggested that the defect is a complex of Fe and oxygen. Thus, previous literature data support the finding in this study that the \( H(0.34) \) center can involve a vacancy, Fe and oxygen, and it may possess multiple levels in the band gap.

The hole trap \( H(0.28) \) appears after annealing at 150 °C for 30 min and increases steadily for higher temperature until it reaches a maximum at 250 °C. This converged concentration is similar to the initial concentration of \( V_2 \) which puts a question of whether \( C_{iO_i} \) has reacted with \( V_2 \). The evolution of the concentrations of \( H(0.28) \) and \( V_2 \) during the annealing series do not show an unambiguous correlation; however, several other reactions may have occurred simultaneously giving rise to passivation of defects and/or creation of overlapping signals.

According to calculations by Estreicher et al. [4], Fe\(_i\) can form several stable configurations with \( V_2 \) where one configuration possess one donor and one acceptor state with their respective energy level position of \( E_V +0.25 \) eV and \( E_V +0.36 \) eV (\( E_C -0.75 \) eV). Thus, if the donor state is identified as \( H(0.28) \), a second signal with similar amplitude is expected in the DLTS-measurement. An additional peak with the suggested energy level position is not observed. However, one may speculate that the peak is overlapping with \( C_{iO_i} \) which is located closely to \( E_V +0.36 \) eV. Interestingly, the amplitude of \( C_{iO_i} \) in DLTS shows an increase during the annealing, in contrast to that of the reference sample. Hence, it may be speculated that the second level of the predicted Fe\(_i\)-\( V_2 \) is overlapping with \( C_{iO_i} \).

\( H(0.17) \) exists only in a narrow temperature interval of \( \sim 50^\circ \). Its relation to other irradiation-induced defects are not unambiguous and the literature on Fe-related defect with such energy level position is scarce. However, the defect is associated with Fe but shows no relation to \( H(0.28) \) and \( H(0.34) \) which presumably indicates an independent defect and, thus, unlikely to involve \( V_2 \) or VO.

**4 Conclusion** Boron-doped Fe-contaminated Fz silicon has been proton-irradiated and investigated for Fe-related defects using DLTS after subsequent isochronal annealings. Three distinctive Fe-related deep levels have been observed after different annealing temperatures. The Fe-
related defects $H(0.28)$ and $H(0.34)$ are likely complexes formed with $V_2$ and VO, respectively.

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References

Paper V

Divacancy-iron complexes in silicon.

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In manuscript
Divacancy-iron complexes in silicon

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Iron and irradiation-induced defects have been investigated in p-type float-zone silicon after MeV electron-irradiation using deep level transient spectroscopy. Isochronal annealing (30 min) was performed up to 250°C, and three distinctive energy levels are observed in the Fe-contaminated samples with positions of 0.25, 0.29 and 0.34 eV above the valence band edge, respectively. The two latter ones are found to accompany the change in concentration of the divacancy center (V$_2$) during the isochronal annealing which suggests an interaction between Fe and V$_2$.

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I. INTRODUCTION

Iron is well-known for its detrimental effects on the performance of silicon solar cells and integrated circuits. Solar cells based on p-type silicon can be significantly improved by gettering during a phosphorus in-diffusion step which accumulates Fe close to the surface and reducing its concentration in the bulk. Although this process is commonly employed, the underlying mechanism of the gettering of Fe is not fully understood. Furthermore, solar cells receiving the phosphorus gettering may still exhibit light-induced degradation with degradation characteristics of Fe contamination.

To further improve the gettering efficiency of Fe, it is important to understand the underlying mechanism and the defects formed during the gettering. Recently, it is shown that the major contribution of Fe gettering does not occur by the formation of a phosphorus-iron complex, where intentionally introduced Fe is gettered with a similar concentration versus depth profile regardless of the phosphorus depth profile. In Ref.3, propose a mechanism involving oxygen and vacancies, injected during the phosphorus in-diffusion, was proposed.

Indeed, a reaction between the vacancy-oxygen complex and Fe have been reported in n-type silicon by You, using deep level transient spectroscopy (DLTS), and the defect was shown to be stable up to 300°C. The disappearance of the DLTS signal was suggested to be caused by the formation of a more stable complex, presumably substitutional Fe and interstitial oxygen. Furthermore, although not discussed in Ref.[4], the divacancy center ($V_2$) decreases in concentration after annealing at 80°C for 2.5h, suggesting a reaction between $V_2$ and Fe. This is also addressed by Komarov, who investigated reactions between irradiation-induced defects with residual impurities in n-type silicon. Komarov observed the appearance of a hole trap at 0.184 eV above the valence band edge ($E_V$) after annealing at 150°C which
remained stable at 400°C. Tentatively, this defect was assigned to FeV₂, with the basic
argumentation that Fe was present in the samples.

Theoretical calculations have recently been reported on the interaction between irradiation-
induced defect and Fe. The calculations predict two stable complexes between V₂ and Fe,
The one with the lowest total energy is labelled as VFeV, where the Fe is situated half way
between two vacancies. This configuration has a single acceptor level at Eᵥ+0.38 eV (Eᵥ-
0.73 eV, where Eᵥ is the conduction band edge) and a double acceptor level at Eᵥ-0.55 eV.
The other configuration is FeV₂ which has one donor level at Eᵥ+0.25 eV and one acceptor
level at Eᵥ+0.36 eV (Eᵥ-0.75 eV).

Recently, we have investigated the interaction between Fe and proton-irradiation-induced
defects in p-type silicon using DLTS after isochronal annealing. Several Fe-related defects
were observed, and one appeared after 150°C with an energy level position of Eᵥ+0.28 eV,
labelled as H(0.28). Based on the evolution of the concentrations of H(0.28) and V₂, H(0.28)
was tentatively assigned as a divacancy-Fe complex, although, the involvement of hydrogen
(arising from proton-implantation) could not be ruled out.

In this study, Fe-contaminated and Fe-lean float-zone (Fz) p-type silicon samples have
been irradiated by electrons and investigated for possible reactions of Fe with irradiation-
induced defects. Several deep level defects are observed exclusively in the Fe-contaminated
samples after annealing above 125°C, and two of these involve possibly V₂.

II. EXPERIMENT

Samples were cut from Fz boron-doped silicon with doping concentration of 2×10¹⁴ cm⁻³,
as confirmed by capacitance-voltage (CV) measurements. Dry oxidation was performed
at 1000°C for 8h after an HF-dip, and circular holes of 2 mm in diameter were opened at
the frontside using photolithography for the preparation of a pn-junction. Phosphorus was implanted at the frontside with an energy and dose of 36 keV and $1 \times 10^{14} \text{cm}^{-2}$, respectively. Thereafter, Fe was implanted at the rear side with energy and dose of 700 keV and $1 \times 10^{14} \text{cm}^{-2}$, respectively. After the implantation, the samples were heat treated at 875°C for 1h to activate the n$^+$-layer and to diffuse Fe to the frontside of the sample.\textsuperscript{8}

Aluminium contacts of 1 mm in diameter were deposited onto the n$^+$-layer of the pn-junction, and Ohmic contacts were formed at the rear side by applying silver-paste. The samples were electrically characterized using CV-measurement and DLTS. For DLTS, six rate-windows were used ranging from $(20 \text{ms})^{-1}$ to $(640 \text{ms})^{-1}$ and the signals were typically extracted by the GS4 weighting function\textsuperscript{9}. The reverse and pulse bias voltages were 4.5 and -4.5V, respectively.

After initial DLTS measurements, which confirmed that only the Fe-contaminated samples (and not the control ones) contained the Fe-B pair and/or interstitial Fe (Fe\textsubscript{i}) while other centers were below the detection limit, electron-irradiation was performed with an energy of 4 MeV and a dose of $2 \times 10^{14} \text{cm}^{-2}$. The reference samples, which were based on Al Schottky barrier contact and not intentionally contaminated with Fe, received the same electron-irradiation. The electron-irradiated samples were stored for three weeks at room temperature before commencing characterization and isochronal annealing (30 min) from 125 to 250°C with an interval of 25°C.

**III. RESULTS AND DISCUSSION**

Figure 1 shows the DLTS spectra of Fe-contaminated (Fig.1a) and reference (Fig.1b) samples in the as-implanted state and after annealing at 150, 200 and 250°C. The ordinate in the temperature interval of 90 to 160K has been enhanced by a factor 8 for clarity. Fo-
FIG. 1. Spectra of DLTS measurements, with GS4 weighting function, on electron-irradiated Fe-contaminated and reference samples before and after annealing at 150, 200 and 250°C for 30 min. Three distinctive peaks, H(0.25), H(0.29) and H(0.34), are only found in the Fe-contaminated samples. These spectra are extracted from rate-window of (640ms)$^{-1}$.

Focusing on the as-implanted samples, prominent irradiation-induced defects can be observed both in the reference and the Fe-contaminated samples, such as the $V_{2}^{10-12}$ and the interstitial carbon-interstitial oxygen pair ($C_{i}O_{i}$)$^{11,13}$ with the respective energy level positions of 0.18 eV and 0.35 eV above $E_V$. Small amount of interstitial carbon ($C_{i}$)$^{13}$ can also be observed at 139K ($\sim E_V+0.30$ eV), but it becomes negligible after annealing above room temperature.

In the Fe-contaminated samples (Fig.1a), the Fe-B pair is observed at 47K ($\sim E_V+0.10$ eV) and concentration of $1.7\times10^{13}$ cm$^{-3}$. Fe-B can dissociate into Fe$_i$ in a reversible reaction by heat treatment, illumination or by minority carrier injection.$^8,14$ Fe$_i$ occurs at $E_V+0.40$ eV
FIG. 2. Evolution of the defect concentrations in Fe-contaminated (open symbol) and reference samples (filled symbol) to subsequent annealings of 30 min. Data from as-irradiated samples are plotted at annealing temperature of 25°C. "V2+H(0.29)+H(0.34)-BiCs" is a result from adding the concentration of V2, H(0.29) and H(0.34) in the Fe-contaminated samples and subtracting BiCs from the reference samples.

and can be readily observed in Fig.1 at 218K after annealing at 150°C. It should be mentioned that the sum of the concentration of the Fe-B pair and the Fei decreases by subsequent annealing. Fei is highly mobile and the decrease may be explained by migration to the surface, or reactions with other defects such as the irradiation-induced ones.

Figure 2 summarises the concentration of the observed defects levels after subsequent annealings (30 min). The data for CiOi have been subtracted with $2 \times 10^{12}$ and $5 \times 10^{12}$ cm$^{-3}$ for the Fe-contaminated and the reference samples, respectively, to increase the clarity of the figure. In the reference samples, the concentration of CiOi is stable above 250°C, in accordance with the dissociation energy of $\sim 2.0$ eV of the complex.$^{15}$ For the V2, a slight decrease takes place after 250°C, which can be associated with the formation of V2O$^{16}$; indeed, a peak appears at 116K in Fig.1, with a position of $E_V+0.22$ eV and an apparent capture cross-section of $1 \times 10^{-15}$ cm$^2$, in accordance with previous observations.$^{16,17}$ For the
Fe-contaminated samples, however, a different trend occurs for V_2 and C_iO_i. Both defects exhibit a reduction in concentration already after 150^\circ\text{C}, with the exception of a sudden increase of C_iO_i at 225^\circ\text{C}. Hence, a different and more complex annealing behavior of the irradiation-induced defects is unveiled due to the presence of Fe as will be discussed in more detail later.

Three distinctive peaks are exclusively observed in the Fe-contaminated samples at 130, 136 and 153K with the corresponding labels of H(0.25), H(0.29) and H(0.34). The Arrhenius plots of these levels are shown in Fig.3, and the extracted energy level positions are 0.25, 0.29 and 0.34 eV above E_V with apparent capture cross-sections of 1\times10^{-14}, 9\times10^{-15} and 2\times10^{-14}\text{cm}^2, respectively. The data points for H(0.25) and H(0.29) are extracted after simulating the DLTS spectra, as displayed in Fig.4 (only two rate windows are displayed for clarity.)
FIG. 4. Simulated (Sim.) DLTS spectra for the H(0.25) and H(0.29) peaks between 120 to 150K for rate window 1 (RW1) of (640ms)$^{-1}$ and rate window 2 (RW2) of (320ms)$^{-1}$.

Figure 3 contains two additional set of data; one set is extracted from the peak at 135K in the reference samples after annealing above 150°C. The Arrhenius plot for the reference sample reveals an energy level position and an apparent capture cross-section of $E_V + 0.29$ eV and $2 \times 10^{14}$ cm$^2$, respectively, and the level is identified as the interstitial boron-substitutional carbon (B$_i$C$_s$).\textsuperscript{18} Based on the similar properties of B$_i$C$_s$ and H(0.29), it may be tempting to attribute H(0.29) solely as B$_i$C$_s$. However, in addition to the larger concentration in the Fe-contaminated samples than in the reference samples (Fig.2), the concentration versus depth profiles differ significantly, as shown in Fig.5. B$_i$C$_s$ remains close to constant as a function of depth in the reference sample, as expected in MeV electron-irradiated samples, while H(0.29) exhibits a significant increase in concentration towards the bulk. This implies that H(0.29) is not primarily due to B$_i$C$_s$, but forms when an impuritydiffuses from the back towards the surface. Since Fe is highly mobile at elevated temperatures, it is one main candidate to be involved in H(0.29). The second set added in Fig.3 is taken from Ref.[7] and is the data for the tentatively assigned divacancy-Fe complex, H(0.28). A close agreement is found between the H(0.29) and H(0.28) data sets.
FIG. 5. Concentration versus depth profiles of H(0.29) in the Fe-contaminated samples and the B_Cs in the reference samples.

If H(0.29) is assumed to be the donor state of FeV₂, as predicted in Ref.[6], a second signal at E_V+0.36 eV with similar amplitude is expected in the DLTS-measurement. However, a peak with the suggested energy level position has a strong overlap with the dominating C_iO_i and can not be readily resolved.

H(0.34) in this work has a position close to that calculated for the single acceptor of VFeV, in Ref.[6]. Furthermore, H(0.34) is formed after annealing at 225°C and increases further at 250°C which indicates a rather stable defect, consistent with that predicted VFeV.

If H(0.34) and H(0.29) are due to Fe-related complexes invoking V₂, a correlation in the defect concentration versus annealing temperature is a necessary condition. Assuming that B_Cs in the Fe-contaminated samples has the same concentration as in the reference samples, the sum of V₂, H(0.29) and H(0.34) (Fe-contaminated samples) minus B_Cs (reference samples) is depicted in Fig.2 (labelled as “V2+H(0.29)+H(0.34)-BiCs”). This curve follows closely the concentration of V₂ in the reference samples below 250°C. Above 250°C, other reactions start to dominate the annealing of V₂, like formation of V₂O._16,17 From these considerations, it is suggested that H(0.29) and H(0.34) are caused by complexes formed
through reactions between mobile Fe and V$_2$.

H(0.25) appears at 125°C and remains essentially stable at temperatures above 175°C (Fig. 2). Although its concentration correlates with the loss of C$_i$O$_i$ below 175°C, suggesting a relation to C$_i$O$_i$, the pattern is not unambiguous above 175°C. One may speculate that a further (higher order) reaction between Fe and C$_i$O$_i$ passivates the H(0.25) complex which will account for the decrease in the concentration of C$_i$O$_i$ and possibly also the saturation of H(0.25). However, the literature on interaction between Fe and C$_i$O$_i$ is scarce and further investigations should be pursued; for instance with isothermal annealing including reverse biasing.

IV. CONCLUSION

Boron-doped and Fe-contaminated Fz silicon samples have been electron-irradiated and investigated for Fe-related defects using DLTS after isochronal annealings up to 250°C. Three distinct deep levels are exclusively revealed in the Fe-contaminated samples after annealing. The concentration of two ones, H(0.29) and H(0.34), accompany the loss in concentration of V$_2$, suggesting an interaction between mobile Fe and V$_2$, in full accordance with previous theoretical predictions in the literature.

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Iron-assisted formation of a shallow acceptor in p-type silicon.

C.K. Tang, L. Vines, B.G. Svensson and E.V. Monakhov
Iron-assisted formation of a shallow acceptor in p-type silicon

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Electrically active defects located around the projected range of Fe- and Si-implanted p-type silicon samples have been investigated after rapid thermal annealing at 800°C. Charge carrier concentration versus depth profiles reveal an enhancement of the acceptor concentration in the Fe-implanted samples, proportional to the implantation dose. No deep levels are detected with sufficient concentrations to account for the enhancement whilst admittance spectroscopy reveals a corresponding shallow acceptor state at 0.06 eV above the valence band edge. Secondary ion-mass spectrometry shows that majority of the Fe diffuses out of the implanted region after annealing and the final configuration of the shallow acceptor center involves neither iron nor boron.

1 Introduction
Iron in silicon is of crucial importance in various technological applications. Research on iron-related defects has been pursued for more than half a century [1], and many Fe-complexes have been established using electron paramagnetic resonance and electrical characterization techniques. The electrically active iron-related defects cause mainly deep levels and some complexes possess multiple energy levels within the band gap, causing Fe to become an active recombination center. In combination with its high mobility, Fe is highly detrimental for integrated devices/circuits and silicon-based solar cells.

Electrical studies of Fe involve often the well established and well understood interstitial Fe (FeI), which is obtained by in-diffusion at high temperatures followed by quenching (see for instance, Refs.[2] and [3]). On the other hand, the understanding of substitutional Fe (FeS) is limited and the energy level position of FeS is under debate. A theoretical study by Beeler et al.[4] employing spin-unrestricted calculation has suggested that substitutional Fe does not possess any energy level in the band gap. Whereas, Estreicher et al.[5] have calculated a deep acceptor of 0.41 eV and 0.29 eV below the conduction band edge (Ec) using the VASP and SIESTA codes, respectively. From experimental point of view, Kaminski et al.[6] have tentatively assigned a deep acceptor, 380 meV below Ec, to FeS by use of high-resolution photo-induced transient spectroscopy on irradiated and Fe-contaminated high-resistive p-type samples. The assignment is also linked with indications of acceptor levels of FeS, unveiled by Mössbauer spectroscopy[7], in the upper half of the band gap and, furthermore, an unassigned Fe-related complex at Ec-0.4 eV has been observed by Tanaka and Kitagawa[8] using deep level transient spectroscopy (DLTS). However, the Ec-0.4 eV level is of donor-type and shows instability even at room temperature, contradicting an identification as FeS.

In fact, the existence of FeS has only been evident by Mössbauer spectroscopy (see for instance, Refs.[7] and [9]) and β− emission channeling measurements[10]. In Ref.[10], silicon crystals were implanted at room temperature with the radioactive isotope 59Mn which decays to 59Fe with a recoil energy around 200 eV. This recoil energy implies that the Fe atoms are reimplanted and hence their final lattice position is not related to the last site of 59Mn. The samples were then rapidly heated up to high temperatures and annealed for 10 min. Investigating the region around the projected range of the 59Mn ions, it was found that the majority of the Fe atoms occupied a displaced substitutional site, a displaced tetrahedral interstitial site and an ideal substitutional site. The largest fraction of Fe at the
ideal substitutional site was found when the samples were annealed between 800-900°C.

In this study, we have made an attempt to confirm the findings from the Mössbauer and channeling measurements, and investigate electronic properties of Fe$_X$. Fe was introduced by ion-implantation and rapid thermal annealing (RTA) was performed at 800°C for 2 to 8 seconds. The results reveal formation of a shallow acceptor level at the projected range of Fe implantation. This level, however, cannot be identified as Fe$_X$ since the majority of the implanted Fe atoms is found to diffuse from the implanted region after RTA.

2 Experiment

The investigated samples were cut from a Czochralski as-grown p-type Si wafer with boron doping concentration of $2.3 \times 10^{15}$cm$^{-3}$, confirmed by capacitance-voltage (CV) measurements. After cleaning by an HF-dip, the front side of the samples were subjected to implantation of 1.9 MeV $^{56}$Fe ions. This energy corresponds to a projected range of 1.5\,µm according to SRIM calculation[11]. Seven ion doses (0.63, 1.3, 2.5, 5.1, 13, 32 and 80\,×\,10$^{10}$cm$^{-2}$) were used such that the peak concentration of Fe corresponds to 5, 10, 20, 40, 100, 250 and 625\% of the doping concentration (as estimated from the SRIM calculation), and these samples are labelled correspondingly as Fe5, Fe10, Fe20, Fe40, Fe100, Fe250 and Fe625. Samples with implantation of $^{54}$Fe ions were also prepared for secondary ion-mass spectrometry (SIMS) analysis to increase the detection limit and the doses used correspond to those of the Fe40, Fe100 and Fe250 samples. Reference samples were made for the first six samples by Si-implantation to distinguish between Fe-induced and recoil-induced defects. The Si implantation energy (1.6 MeV) and the doses (1.3, 2.5, 5.0, 10.2, 26 and 65\,×\,10$^{10}$cm$^{-2}$) were selected in correspondence with the projected range and the peak vacancy generation of the Fe-implants, respectively, as estimated by SRIM calculations. In analogy with the Fe-implanted samples, the Si-implanted samples are labelled as Si5, Si10, Si20, Si40, Si100 and Si250.

After implantation, the samples were cleaned using standard RCA steps before RTA at 800°C for 2, 4 and 8s with a heating temperature ramp rate of 50K/s. Thereafter, Schottky barrier contacts were formed on the front side by depositing Al via thermal evaporation through a metal mask. Ohmic contacts were formed using silver-paste at the backside.

For electrical characterization, capacitance-voltage measurement, DLTS and admittance spectroscopy (ADSPEC), were performed. For the DLTS measurements, the reverse and pulse bias voltages were selected to ensure investigation of majority carrier traps with the full coverage of the implantation peak. Studies of minority carrier traps were performed with so-called optical DLTS (ODLTS) which utilized optical pulses from the rearside with an energy above the band gap for charge carrier filling. The DLTS signals were extracted with a lock-in type weighting function, and using eight rate-windows ranging from (5\,ms)$^{-1}$ to (640\,ms)$^{-1}$. For the ADSPEC measurements, the probing frequencies of the capacitance and conductance were 1, 4, 16, 60, 250 and 1000 kHz with a test level signal of 100\,mV. Several different reverse bias voltages were applied during the ADSPEC measurements.

Secondary-ion-mass spectrometry was performed before and after the RTA treatment to investigate the concentration of $^{54}$Fe versus depth, using a Cameca IMS7f micro-analyzer. A primary beam of 10 keV $^{16}$O$_2$ ions was rastered over a 130\,×\,130\,µm$^2$ surface area and secondary ions were collected from the central region of the sputtered crater. Crater depths were measured using a Veeco Dektak 8 stylus profilometer, and a constant erosion rate was assumed for converting the sputtering time into sample depth. Implanted reference samples were used to convert the SIMS signal of $^{54}$Fe into concentration values.

3 Results and discussion

Figure 1 shows the charge carrier concentration as a function of depth for Si20, Fe5, Fe10 and Fe20 samples heat treated at 800°C for 2, 4 and 8s. Sample Fe20 will be used as a reference for later comparison. For the Si-implanted samples, all profiles are similar regardless of RTA duration or implantation dose; thus, for clarity, only the results for the Si20 sample with RTA for 2s are included in Fig.1. For all the samples, a minor decrease in the charge carrier concentration occurs towards the surface. This decrease is due to passivation of boron acceptors by hydrogen during the Schottky contact preparation[12].

In the case of the Fe-implanted and annealed samples, an enhancement of the hole concentration occurs around 1.5\,µm, i.e., close to the calculated projected range of the
Fe ions. In addition, the enhancement of the hole concentration increases linearly with the implantation dose and a close one-to-one relationship with the calculated peak concentration of Fe holds, as shown in Fig.2. This strongly suggests that the defect is formed under the influence of Fe. Furthermore, the enhancement exists already after RTA for 2s and it remains stable for longer annealing durations. The above considerations imply that Fe is directly involved in the formation of a shallow acceptor center.

Figure 3 shows ADSPEC spectra for the Fe20 and Si20 samples with 4s of RTA at different reverse bias voltage of 1.0, 2.5, 3.0 and 7.0V. For the Fe20 samples, the corresponding depth of the depletion region at room temperature can be seen in Fig.1 by the vertical lines, which shows that the probing regions are located approximately before, at, and after the Fe-induced acceptor peak. Thus, the signal corresponding to the acceptor can be associated with the peak at ~41K which appears and disappears by variation of voltage, as shown in the inset of Fig.3a. The energy level position is found to be $E_V + 0.066eV$. The height of the peak in the ADSPEC spectra is expected to be relatively small, as described in Ref.[13]. In short, the ADSPEC signal amplitude is governed by a product of $(1 - x_t/w)$, where $w$ is the depletion width and $x_t$ is the depth to the crossing of the Fermi-level to the energy level. In the case of shallow levels, the $x_t$ is close to $w$, reducing the ADSPEC signal significantly, as confirmed by simulations shown below.

For the Si20 sample (Fig.3b), the boron-signal at 26K is clearly visible, as in the Fe20 samples. However, no signal around ~41K is detected regardless of the applied reverse bias. This corroborates the association of the 41K peak with the defect causing the enhanced acceptor concentration since it occurs only in the Fe-implanted samples.

Figure 4 shows the ADSPEC data for Fe20, Fe40, Fe100, Fe250 and Fe625, including simulations using Sentaurus TCAD[14], where the marked area is magnified in the inset. The reverse bias voltages applied correspond to the depth at which the Fe-induced acceptor peak position occurs and the inset unveils that the peak increases with increasing dose. Furthermore, a small shift in the peak position takes place as a consequence of the variation in the electrical field, which is the characteristic of acceptors in p-type material due to the Poole-Frenkel effect[15] and it is also evident in the simulated curves.

In the simulations, the acceptor profile is constructed as a Gaussian profile with the peak concentration equal to the calculated peak concentration of Fe from SRIM, and the energy level position and the capture cross-section of the acceptor are set to $E_V + 0.057eV$ and $4 \times 10^{-14}$ cm$^2$, respectively. The extracted curves are taken from a reverse bias voltage with a depth close to the peak concentration of the acceptor peak. At last, the simulated curves are normalized to the experimental boron-signal amplitude.

Deep level transient spectroscopy combined with optical excitation on the Fe20 and Si20 samples resolves no levels above midgap, while conventional DLTS unveils a few levels below midgap in the Fe20 samples (not shown).
The implanted Fe may act as a trap for mobile interstitial boron, causing an enhancement in the concentration of substitutional or possibly perturbed substitutional boron after annealing. Boron depth profiles have been investigated using SIMS on the samples Fe625 and Si250 before and after RTA. For all the samples, the boron concentration is observed to be constant as a function of depth with an average value around $2 \times 10^{15} \text{cm}^{-3}$ and a standard deviation of $3 \times 10^{14} \text{cm}^{-3}$. Thus, within the experimental accuracy no re-distribution of boron has occurred and the induced shallow acceptor does not seem to involve boron.

It may be speculated that a defect complex is stabilized by Fe, allowing further reactions with other defects which eventually detach Fe. Since the concentration of the defect can reach above $10^{15} \text{cm}^{-3}$, it is unlikely that residual metal impurities are involved. Carbon and oxygen are common impurities with concentrations above $10^{16} \text{cm}^{-3}$ and can potentially contribute to the formation of the observed acceptor. On the other hand, oxygen clusters are typically associated with the formation of shallow thermal donors (see, for instance, Ref.[16]) and not shallow acceptors. Intrinsic defects, such as vacancy and self-interstitial, are formed during the implantation and are commonly of acceptor type. These defects may temporarily form stable complexes with Fe which further builds up to more stable intrinsic complexes with the absence of Fe. However, further investigations need to be pursued in order to reveal the structural and chemical nature of the shallow acceptor defect, which persists up to $\sim 1000^\circ C$.

In conclusion, rapid thermal annealing has been performed on Fe-implanted p-type silicon samples and formation of an Fe-assisted shallow acceptor center, located around in the projected range, is shown. No deep levels with similar concentration have been detected, which suggests that the defect has only one shallow level. The chemical composition of the defect is unknown but it involves neither Fe nor B.

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References