

Quantification of characteristic parameters for the dissociation kinetics of iron–boron pairs in Czochralski silicon

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We have developed a new process to quantify the dissociation kinetics of iron–boron (FeB) pairs in Czochralski silicon. It is based on determining the characteristic parameters for the association kinetics of FeB pairs by low-temperature thermal activation experiments. The dissociation rates can then be derived from the equilibrium concentration and association rates of FeB pairs at elevated temperatures. Our results show an activation energy of 1.20 eV and an attempt frequency of $9 \times 10^{12} \text{ s}^{-1}$ for FeB dissociation.

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Iron is one of the most harmful and ubiquitous metal impurities in silicon devices, such as solar cells and integrated circuits [1,2]. Generally, iron atoms mainly occupy interstitial lattice sites in silicon matrix [3]. However, in p-type crystalline silicon, the highly mobile interstitial iron is usually positively charged (Fe_i^+) and therefore tends to form Fe_iB_s pairs with negatively charged boron ion (B_s^-) at room temperature [2,4]. The equilibrium state of $[\text{Fe}_i\text{B}_s]/[\text{Fe}_i^+]$ depends on the temperature and the concentration of boron [5–7]. Since Fe_i^+ and Fe_iB_s have clearly different recombination activities [2], either the dissociation or the association of iron–boron (FeB) pairs in silicon will lead to a significant variation in carrier lifetime, which can be monitored by microwave photoconductivity decay (MW-PCD) technique [8,9]. It is now known that the formation of FeB pairs is a process limited to the diffusion of Fe_i^+ towards substitutional B in silicon [6,10]. The migration energy of Fe_i^+ , i.e. the activation energy of FeB pairs, has been reported to be in the range of 0.58–0.81 eV [2], while the diffusion constant (D_0) of Fe_i^+ is in the range of $0.6\text{--}1.8 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$. However, the characteristic parameters of dissociation kinetics of FeB pairs are seldom reported, except that a value of 1.17–1.2 eV has been reported by Istratov et al. [2] and Feichtinger and Mader

[11] with an attempt frequency of $1.8\text{--}5 \times 10^{10} \text{ s}^{-1}$. The reason is related to the fast dissociation rate of FeB pairs by thermal treatments, which cannot easily be practically controlled for the investigation of their temperature dependence [6,12]. It is thus of interest to find an alternative way to determine the characteristic parameters for the dissociation kinetics of FeB pairs in Czochralski (CZ) silicon.

This letter will demonstrate a new process to determine the characteristic parameters for the dissociation kinetics of FeB pairs, from which the dissociation rate is derived by building up equilibrium states between total dissociation and association. These results can help us understand the behaviors of FeB pairs in CZ silicon more deeply.

The samples are p-type $\langle 100 \rangle$ CZ silicon wafer with a boron concentration of $1 \times 10^{15} \text{ cm}^{-3}$. After the samples were dipped in a 0.1 mol l^{-1} ferric nitric acid (FeNO_3) solution, iron impurities were introduced into the samples by a $800^\circ\text{C}/3 \text{ h}$ anneal with in a protective argon atmosphere. The cooling process was performed by quenching in air after directly pulling the samples out of the furnace. Then a $50 \mu\text{m}$ surface layer was removed from both surfaces by chemical etching in a mixture of HNO_3 and HF ($\text{HNO}_3\text{:HF} = 3\text{:}1$ in volume) for 2 min. Subsequently, the samples were subjected to a Si_3N_4 double-surface passivation by plasma-enhanced chemical vapor deposition [9]. After dissociating all FeB pairs in the as-received samples by a $200^\circ\text{C}/$

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10 min anneal, the samples were kept in the dark at 50–140 °C to allow the generation of FeB pairs until a saturated concentration was reached. The evolution of the carrier lifetime in the samples with time was then inspected by MW-PCD equipment (Semilab WT2000) at room temperature, which detects the change in the reflectivity after laser pulse excitation using reflected microwaves. Note that in our measurements the level of excitation by a pulsed laser with a 904 nm wavelength and a 200 pulse duration was controlled at $4 \times 10^{16} \text{ cm}^{-3}$, which is not large enough to cause the dissociation of the FeB pairs.

During the association of the FeB pairs, the concentration of interstitial iron, $[\text{Fe}_i^+]$, remaining in the samples can be derived by the carrier lifetime as follows [9,13]:

$$[\text{Fe}_i^+] = C \left(\frac{1}{\tau_0} - \frac{1}{\tau(t)} \right) \quad (1)$$

where C is $3.4 \times 10^{13} \mu\text{s cm}^{-3}$, which is a standard constant at the usual excitation level of 10^{16} cm^{-3} for our system; τ_0 is the carrier lifetime at $t=0$ with all the FeB pairs being dissociated; and $\tau(t)$ is the carrier lifetime in the process of the FeB association. Figure 1(a) shows the variation of $[\text{Fe}_i^+]$ with time in the temperature range of 50–70 °C. It can be seen that $[\text{Fe}_i^+]$ decreases almost exponentially with increasing time at any temperature, due to the formation of FeB pairs. The slopes of the straight lines in Figure 1(a) actually reflect the rate of FeB generation, R_a . Thus, the concentration of interstitial iron, $[\text{Fe}_i^+]$, can be expressed as [14]

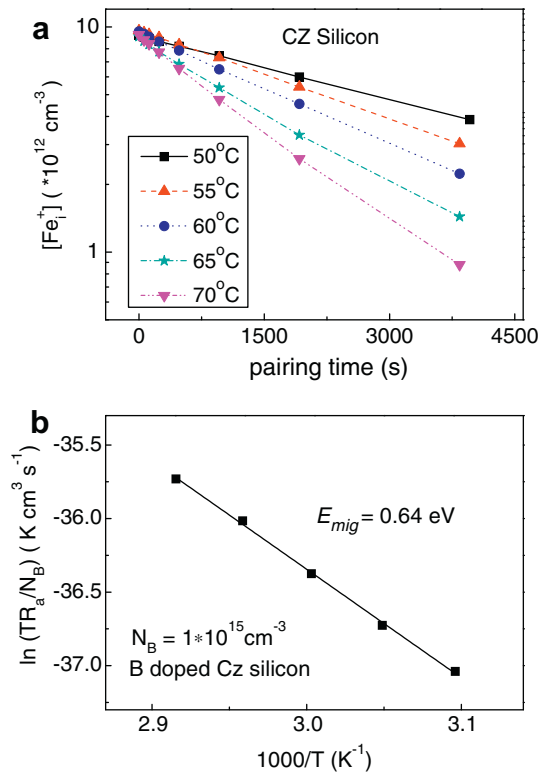


Figure 1. The pairing reaction of iron–boron pairs. (a) Time and temperature dependence of $[\text{Fe}_i^+]$. The straight lines represent exponential decays fitted to extract the association rate. (b) The active energy of E_{mig} was obtained by the fitting of Eq. (3). $E_{\text{mig}} = 0.64 \pm 0.01 \text{ eV}$.

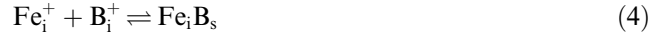
$$[\text{Fe}_i^+](t) = [\text{Fe}]_{\text{total}} \exp(-R_a t) \quad (2)$$

The total concentration of iron, $[\text{Fe}]_{\text{total}}$, is $9.3 \times 10^{12} \text{ cm}^{-3}$, as determined by the MW-PCD, which corresponds to the iron solubility at 800 °C $9.0 \times 10^{12} \text{ cm}^{-3}$ [2]. Note that the total concentrations of iron include the Fe_i^+ and FeB pairs at the experiment temperature, i.e. $[\text{Fe}]_{\text{total}} = \text{Fe}_i^+ + \text{FeB}$ [7]. This suggests that the R_a of FeB pairs increases with increasing temperature. Based on the diffusion-limited theory [15], the generation kinetics of FeB pairs can be described as the process of immobile acceptors trapping mobile donors [2]. The R_a of FeB pairs can thus be further expressed as [2,6]:

$$R_a = \frac{q^2}{\epsilon \epsilon_0 \kappa T} N_B D_0 \exp\left(-\frac{E_{\text{mig}}}{\kappa T}\right) \quad (3)$$

where ϵ is the dielectric constant of silicon, q is the unit charge, κ is the Boltzmann's constant, T is the absolute temperature, N_B is the concentration of boron, D_0 is the iron diffusion constant and E_{mig} is the activation energy of Fe_i^+ migration. Figure 1(b) shows the Arrhenius plot based on the data in Figure 1(a). An activation energy of $E_{\text{mig}} = 0.64 \pm 0.01 \text{ eV}$ can be obtained for the formation of FeB pairs, which is consistent with the values reported by Weber [10] and Macdonald et al. [16]. The diffusion constant obtained from Figure 1(b) is $3.8 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$, which is also quite close to the previously reported values [2,16].

The association and dissociation of FeB pairs in CZ silicon are in fact reversible, and can be represented by [6,12,17]



The corresponding generation rate can be expressed by the following equation [2,5]:

$$\frac{d[\text{FeB}]}{dt} = R_a \times ([\text{Fe}]_{\text{total}} - [\text{FeB}]) - R_d[\text{FeB}] \quad (5)$$

The boundary condition for resolving this equation is that at $t=0$, i.e. just after the FeB pairs are completely dissociated prior to their formation, the concentration of FeB is zero. So, the $[\text{FeB}]$ can be expressed as [2,5,18]:

$$[\text{FeB}] = \frac{R_a}{R_a + R_d} [\text{Fe}]_{\text{total}} (1 - \exp(-(R_a + R_d)t)) \quad (6)$$

where R_d is the dissociation rate of FeB pairs. From Eq. (6), it can be seen that when $t \rightarrow \infty$ the $[\text{FeB}]$ will reach to a saturated value, i.e. the reaction in Eq. (4) is kept in an equilibrium state. The R_d at a given temperature can thus be calculated directly from the corresponding saturated value of $[\text{FeB}]$ by the following equation:

$$R_d(T) = \left(\frac{[\text{Fe}]_{\text{total}}}{[\text{FeB}]} - 1 \right) R_a(T) \quad (7)$$

Note that the saturated $[\text{FeB}]$ is actually equal to $\frac{1}{\tau_0} - \frac{1}{\tau(t \rightarrow \infty)}$. Figure 2 shows the saturated $[\text{FeB}]$ s and the derived R_d at different temperatures. It can be seen that the saturated $[\text{FeB}]$ decreases with increasing temperature, while the R_d increases. This indicates that, at a relatively higher temperature, the dissociation process becomes more and more dominant. By definition, the dissociation kinetics of FeB pairs can be expressed as [2]:

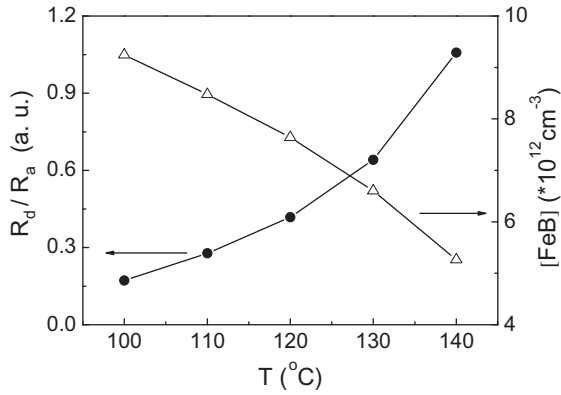


Figure 2. The saturated $[\text{FeB}]$ and the derived R_d at different temperatures. The samples were kept in the dark for enough time at a temperature ranging from 100 to 140 °C, and the concentration of FeB pairs is equal to the difference between $[\text{Fe}]_{\text{total}}$ and Fe_i^+ .

$$R_d = \nu \exp\left(-\frac{E_{\text{diss}}}{kT}\right) \quad (8)$$

where ν is the attempt frequency and E_{diss} is the activation energy of FeB dissociation. Figure 3 shows the Arrhenius plot of R_d as a function of $1/T$. Based on Eq. (8), an activation energy of 1.20 ± 0.02 eV has been deduced for the FeB dissociation in CZ silicon, which is in excellent agreement with the previous result [2]. Meanwhile, an attempt frequency of $9 \times 10^{12} \text{ s}^{-1}$ has been obtained for the FeB dissociation.

The saturated FeB concentration at a given temperature can also be represented by the following relation [16]:

$$\frac{[\text{FeB}]}{[\text{Fe}_i^+]} = \frac{Z}{N_i} N_B \exp\left(\frac{E_{\text{bind}}}{kT}\right) \quad (9)$$

where Z is the number of pair configurations about one set (4 for the tetrahedral interstitial site), N_i is the lattice site density in silicon ($5 \times 10^{22} \text{ cm}^{-3}$), N_B is the boron concentration and E_{bind} is the binding energy of FeB pairs. Based on Eq. (9), the value of E_{bind} can be derived from the equilibrium concentrations of FeB pairs at different temperatures, which is 0.62 ± 0.02 eV.

Figure 4 shows the energy diagram for the formation and dissociation reaction of FeB pairs in CZ silicon,

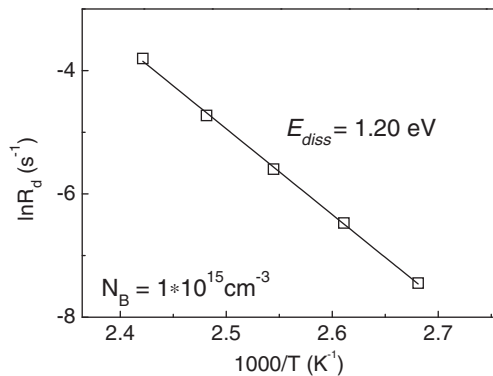


Figure 3. The Arrhenius plot of the pair-dissociation rate for CZ silicon, giving an activation energy of pairing dissociation of E_{diss} of 1.20 ± 0.02 eV.

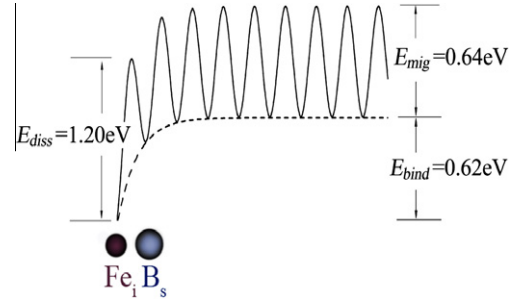


Figure 4. An energy diagram of the FeB interaction in silicon. E_{mig} is the formation energy, E_{diss} is the dissociation energy of the pairs and E_{bind} is the binding energy.

which are present by three characteristic energies, i.e. the migration energy of Fe_i^+ , E_{mig} ; the dissociation energy, E_{diss} ; and the binding energy, E_{bind} . E_{mig} corresponds to the energy that Fe_i^+ needs to overcome the scattering of crystal field, which is about 0.64 eV. The second characteristic energy, E_{diss} , corresponds to the activation energy of the defect annihilation process, which is about 1.20 eV. The third characteristic energy, E_{bind} , corresponds to the binding energy between Fe_i^+ and B_s^- in FeB pairs, which is about 0.62 eV. It should be noted that $E_{\text{diss}} < E_{\text{bind}} + E_{\text{mig}}$, which is a result of Coulomb attraction between Fe_i^+ and B_s^- .

We have developed a new process to quantify the characteristic parameters for the dissociation kinetics of FeB in CZ silicon. First, the characteristic parameters of FeB pairing were obtained by thermal activation at low temperatures. Then, an equilibrium situation between the dissociation and association of FeB pairs was built up at elevated temperatures. From the association rate and the saturated concentration of FeB pairs, the dissociation rate of FeB pairs can be derived. The activation energy of 1.20 eV was obtained for the dissociation process of FeB pairs in CZ silicon and the corresponding attempt frequency is $9 \times 10^{12} \text{ s}^{-1}$. These values are in good agreement with the results previously reported by Feichtinger and Mader [11].

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