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Citation: *AIP Advances* **3**, 082124 (2013); doi: 10.1063/1.4819481

View online: <http://dx.doi.org/10.1063/1.4819481>

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Iron-boron pair dissociation in silicon under strong illumination

Xiaodong Zhu, Deren Yang, Xuegong Yu,^a Jian He, Yichao Wu, Jan Vanhellemont,^b and Duanlin Que

State Key Laboratory of Silicon Materials and Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China

(Received 19 May 2013; accepted 6 August 2013; published online 22 August 2013)

The dissociation of iron-boron pairs (FeB) in Czochralski silicon under strong illumination was investigated. It is found that the dissociation process shows a double exponential dependence on time. The first fast process is suggested to be caused by a positive Fe in FeB capturing two electrons and diffusion triggered by the electron-phonon interactions, while the second slow one would involve the capturing of one electron followed by temperature dependent dissociation with an activation energy of (0.21 ± 0.03) eV. The results are important for understanding and controlling the behavior of FeB in concentrator solar cells. © 2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4819481>]

Iron is one of the most ubiquitous and unavoidable metal impurities in silicon solar cells.^{1,2} It is known that the positively charged interstitial iron atoms (Fe_i^+) tend to form iron-boron pairs (FeB) with negatively charged substitutional B atoms (B_s^-) at room temperature.²⁻⁴ It is well documented also that the pairs can be dissociated by thermal treatment,⁵ minority carrier injection,⁵ or illumination.⁴ Further more the formation and dissociation of FeB can be deliberately cycled. FeB is a strong recombination center with a donor level 0.1 eV above the valence band edge E_v , and a deep acceptor level (0.26 ± 0.03) eV below the conduction band edge E_c .^{2,6,7} The latter state is the dominant recombination center.^{8,9} Since Fe_i and FeB have different carrier recombination properties, either the dissociation or the association of FeB can be monitored by lifetime measurements.¹⁰⁻¹² The association energy E_a of FeB has been reported to be in the range of 0.65 to 0.69 eV, while the dissociation energy is in the range of 1.17 to 1.22 eV.^{13,14} However, the dissociation energy of FeB can be reduced to 0.09 eV with the help of minority carrier injection, due to a recombination-enhanced defect reaction (REDR)⁵ based on the following mechanism¹⁵⁻¹⁷: most of the energy released by multiphonon nonradiative (MPNR) capture or recombination of a carrier can be converted into vibrational energy which is initially localized in the vicinity of the defect. This vibrational energy, approximately equal to the carrier transition energy, E_{ct} ,¹⁵⁻¹⁷ is available to facilitate defect reactions such as diffusion,¹⁸ dissociation of impurity pairs,¹⁹ formation of complexes¹⁷ and motion of dislocations.²⁰ Due to this effect, the activation energy for FeB dissociation is reduced partly or completely leading to the observed athermal reaction and the increased reaction rate under illumination. Similarly, Nakashima *et al.*¹⁹ reported that the short-range motion of Fe_i atoms in FeB was athermal in silicon under 10 mA/cm² minority-carrier injection.

Concentrator photovoltaics (CPV) using high illumination intensities are characterized as high efficiency, low system cost, low-capital investment, which might become a major contributor to the future clean electricity.²¹ High concentration ratio (>100 suns) CPV cells are mainly based on III-V-based materials, while crystalline silicon (c-Si) based CPV cells mainly use a low to medium

^aCorresponding Author: yuxuegong@zju.edu.cn

^bOn leave from Department of Solid State Sciences, Ghent University, Krijgslaan 281 S1, B-9000 Ghent, Belgium.



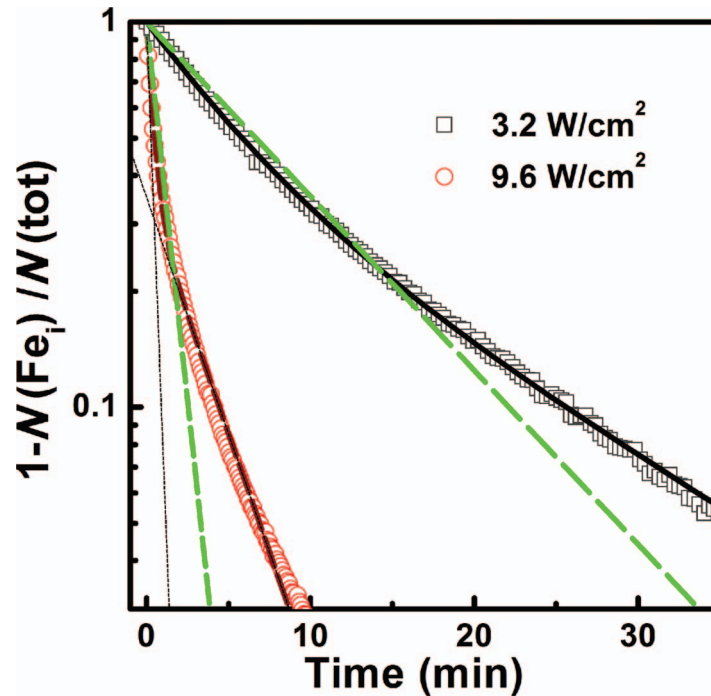


FIG. 1. The variation of the ratio of $1 - N(\text{Fe}_i)/N(\text{tot})$ with time at 22°C for illumination intensities of 3.2 (black squares) W/cm^2 and 9.6 W/cm^2 (red circles). $1 - N(\text{Fe}_i)/N(\text{tot})$ is equal to $N(\text{FeB})/N(\text{tot})$. The full lines show the results of a best fit according to Eq. (1), and the green dashed bold lines show the results of a single-exponential fit. The fine dashed lines show the individual components of the double exponential fit for the 9.6 W/cm^2 case.

concentration ratio (2 to 100 suns).²² The efficiency of modified c-Si CPV cells can reach up to 27% at a light concentration level of about 100 suns.²³ The association and dissociation kinetics of FeB during thermal treatment or minority carrier injection are well understood but the light-induced dissociation kinetics of FeB in such CPV cells under strong illumination has not been reported in detail so far.

In this letter, we have investigated the FeB dissociation behaviors induced by strong light illumination. Up to 104-sun light illumination, equivalent with 10.4 W/cm^2 , is used to dissociate FeB. The characteristic parameters of light-induced dissociation kinetics of FeB are quantified and a tentative model is presented to explain the observations. The results can be used to understand and predict the behaviors of FeB in concentrator photovoltaic cells.

The samples used in the present study are p-type (100) Czochralski (CZ) silicon wafers with a boron concentration (N_A) of 1.1×10^{16} cm^{-3} . The interstitial oxygen concentration is about 10^{18} cm^{-3} , as determined by Fourier transform infrared spectroscopy (FTIR) using the calibration factor of 3.14×10^{17} cm^{-2} . After dipping in a 0.1 mol/L ferric nitric acid ($\text{Fe}(\text{NO}_3)_3$) solution, the Fe impurities are introduced into the samples by annealing in argon ambient at 800°C for 100 min, followed by quenching in air. The concentration of iron introduced into the samples is about 10^{12} cm^{-3} , corresponding to the solubility of iron at 800°C .² Then, the samples are subjected to chemical polishing and surface-passivation by deposition of a SiN_x :H film. After storing the sample in the dark for one night to allow the formation of FeB, a 904 nm laser as a light source with variable power in the range of 2–11 W/cm^2 is used to illuminate the samples at temperatures between 25 and 45°C . The evolution of carrier lifetime with illumination time is measured by microwave photo-conductance decay (MW-PCD) technique.

Figure 1 shows the value of $1 - N(\text{Fe}_i)/N(\text{tot})$ at 22°C as a function of time for illumination intensities of 3.2 and 9.6 W/cm^2 . Note that the concentration of Fe_i is extracted from¹⁰ $N(\text{Fe}_i) = C(1/\tau_0 - 1/\tau_t)$, where $C = 3.4 \times 10^{13}$ $\mu\text{s} \cdot \text{cm}^{-3}$ is a prefactor determined from the recombination parameters of FeB and Fe_i , which is for the WT-2000 instrument, τ_0 is the carrier lifetime before

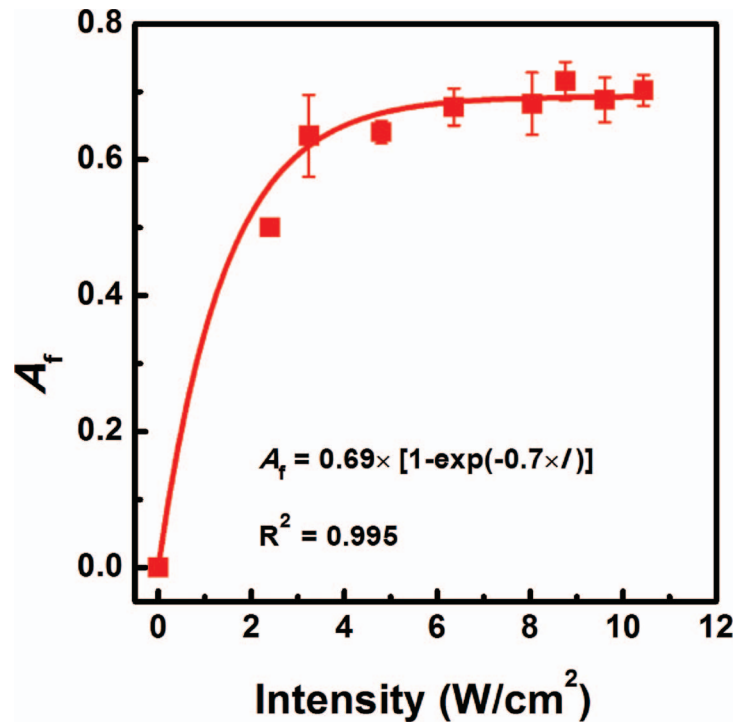


FIG. 2. Variation of A_f as a function of the illumination intensity at 22°C. The best fit yields $A_f = (0.69 \pm 0.01) \times [1 - e^{-(0.7 \pm 0.1)I}]$ with $R^2 = 0.995$.

illumination and τ_i is the carrier lifetime after illumination for a time t . In addition, the concentration of FeB, $N(\text{FeB})$, is determined by¹¹ $N(\text{tot}) - N(\text{Fe}_i)$, where $N(\text{tot})$ is the total Fe concentration. The value of $N(\text{tot})$ is $2 \times 10^{12} \text{ cm}^{-3}$ deduced from the lifetime measurement before and after illumination. Hence, the decrease of the ratio of $N(\text{FeB})/N(\text{tot})$ is given by $1 - N(\text{Fe}_i)/N(\text{tot})$. For a light intensity of 3.2 W/cm^2 , the decrease of the ratio $N(\text{FeB})/N(\text{tot})$ can be approximately fitted by a single-exponential function. With a light intensity of 9.6 W/cm^2 , however, it is obvious from Figure 1 that $N(\text{FeB})/N(\text{tot})$ no longer follows a single exponential behavior. It can be described well by a double exponential consisting of a fast and a slow components, which can be written as:

$$N(\text{FeB})/N(\text{tot}) = 1 - N(\text{Fe}_i)/N(\text{tot}) = A_f \exp(-R_f t) + (1 - A_f) \exp(-R_s t) \quad (1)$$

A_f is the fraction of $N(\text{FeB})$ dissociated by the fast process; R_f and R_s are the light-induced dissociation rates of FeB for the fast and slow processes, respectively. Such multiexponential process have been reported in the carrier lifetime and the cell performance degradation caused by boron-oxygen complexes.²⁴ For illumination with an intensity of 9.6 W/cm^2 , the best fit yields $A_f = (0.649 \pm 0.001)$ with a coefficient of determination R^2 of 0.997, compared with 0.891 for a single exponential fit. Using equation (1) to fit the data for the light intensity of 3.2 W/cm^2 , $A_f = (0.551 \pm 0.002)$ can be obtained, with R^2 of 0.999, compared with 0.987 for a single exponential fit. The double exponential dependency of Eq. (1) is therefore a good approximation to describe the results for the whole range of illumination intensities. Even though it was also attempted to fit the experimental data with the stretched exponential or Kohlrausch function $f_\beta(t) = e^{-t^\beta}$, the obtained values of R^2 were always smaller than Therefore, obtained with the double exponential fit whereby the obtained β values were smaller than 1, suggesting that the curve decays follow more than one (exponential) path.

Under the illumination density smaller than 3 W/cm^2 , A_f decreases rapidly, depending exponentially on the light intensity (see Fig. 2). The dissociation of FeB is well described by the classical single-exponential function. A best fit is obtained for $A_f = (0.69 \pm 0.01) \times [1 - e^{-(0.7 \pm 0.1)I}]$ with $R^2 = 0.995$. The FeB dissociation by the fast process thus increases exponentially with the

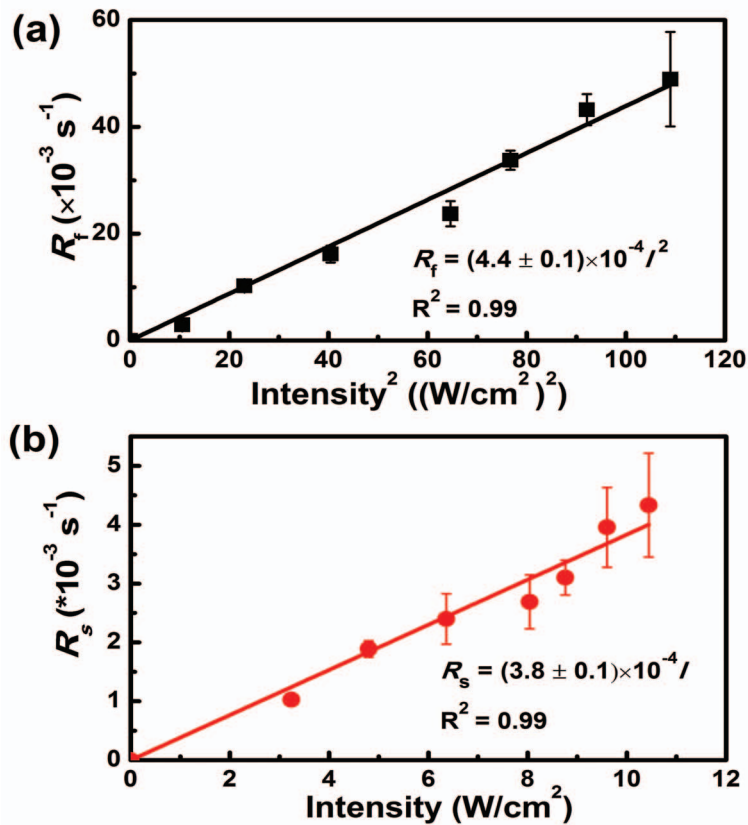


FIG. 3. (a) R_f as a function of the square of the illumination intensity at 22 °C. The best fit yields $R_f = (4.4 \pm 0.1) \times 10^{-4} I^2$ with $R^2 = 0.994$; (b) R_s as a function of the illumination intensity. A linear fit yields $R_s = (3.8 \pm 0.1) \times 10^{-4} I$ with $R^2 = 0.992$.

light intensity. At the same time, R_f is much larger than R_s for high light intensities, as shown in Fig. 3. Hence, under the illumination density larger than $3 \text{ W}/\text{cm}^2$, the dissociation of FeB should be described by the double exponential function in Eq. (1), which is applicable to CPV optical systems, where the illumination level is usually greater than several tens of suns.

Figure 3(a) shows R_f as a function of the square of the laser intensity (I) at 22 °C. The best fit yields $R_f = (4.4 \pm 0.1) \times 10^{-4} I^2$, with a R^2 of 0.994. A quadratic dependence on light intensity implies that two electron capture events are involved in FeB dissociation. One possible mechanism is that the capture of two electrons to form Fe_i^- will lead to Coulomb repulsion in between the FeB.²⁵ Another possible mechanism⁵ is that the capture of the first electron forms Fe_i^0 eliminating the Coulomb attraction between Fe_i and B_s , and then the capture of the second electron triggers the electron-phonon interactions leading to REDR and causing the observed athermal diffusion of Fe_i^0 away from B_s^- .

Contrary to R_f , R_s increases linearly with light intensity as shown in Fig. 3(b). By fitting the data, it can yield $R_s = (3.8 \pm 0.1) \times 10^{-4} I$, with R^2 of 0.992. This means that during the slow process, only one electron is captured, leading to the linear dependence on light intensity. This result is obviously contrary to the quadratic dependence for the fast dissociation process. Two possible mechanisms are suggested here. The first mechanism is that the Fe_i^+ in FeB captures one electron to cause the iron atom neutral, thus breaking the Coulomb binding of FeB. Some additional thermal energy is then still needed for the full dissociation, compared with the fast process where all energy needed is supplied by Coulomb repulsion and/or electron-phonon interactions. The second possible mechanism is that the dissociation of FeB happens by REDR, i. e. the MPNR capture or recombination of a free carrier releases the excess vibrational energy to facilitate the dissociation. A similar mechanism was

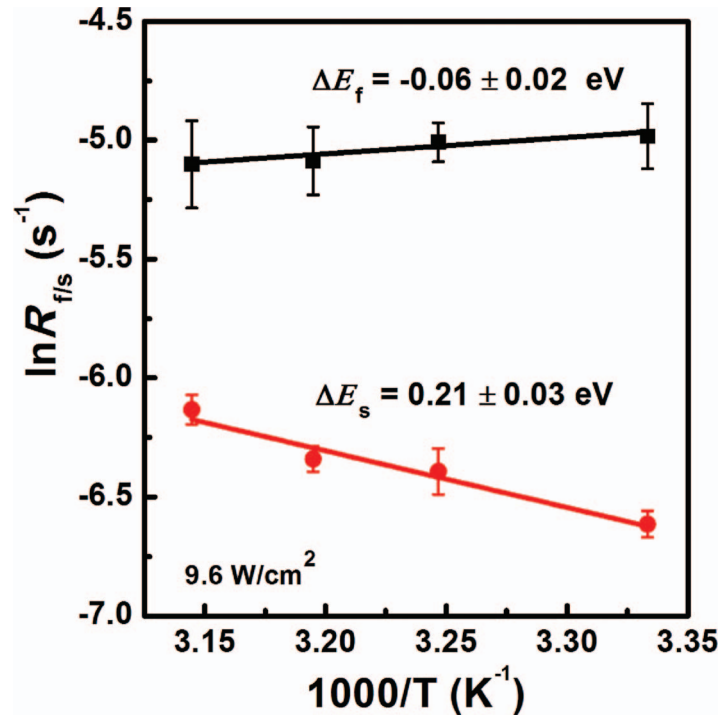


FIG. 4. Arrhenius plots between 27 and 45 °C of R_f and R_s for illumination with an intensity of 9.6 W/cm². Activation energies of (-0.06 ± 0.02) eV and (0.21 ± 0.03) eV are obtained for the fast and slow processes, respectively. This shows that the fast dissociation process is athermal.

already proposed to explain the migration of Fe_i^+ in iron-aluminum pairs (FeAl) from the 1st to 2nd neighbors of Al under illumination.¹⁸

Figure 4 shows the Arrhenius plot of R_f and R_s as a function of $1/T$. Note that the light-induced dissociation of FeB is the dominant process during all experiments. For the fast dissociation process, R_f is not dependent on temperature. The Coulomb repulsion energy between Fe_i^- and B_s^- is about 0.52 eV², which is somewhat smaller than the reported diffusion barrier energy (0.67 eV) for Fe_i^+ in silicon.^{2,6} However, the migration barrier from the 1st to 2nd neighbors of B is (0.9–1.0) eV and (0.78–0.90) eV for Fe_i^0 and Fe_i^+ , respectively.^{18,26} Even though there is no data available about the migration energy for Fe_i^- , it should be larger than that of Fe_i^0 , due to its larger radius.²⁶ The Coulomb repulsion energy is thus not large enough to completely dissociate FeB. For the second mechanism, while, the athermal diffusion of Fe_i^0 away from B_s^- might be caused by REDR, leading to the observed athermal dissociation with an activation energy of (-0.06 ± 0.02) eV, which is very close to the recombination-enhanced dissociation energy of 0.09 eV reported by Kimerling *et al.*⁵ As shown in Fig. 4, the activation energy, ΔE_s , is (0.21 ± 0.03) eV for the slow dissociation process. If one electron is absorbed by the FeB to make the electrically neutral Fe atom, the energy of about (0.9–1.0) eV is still needed to fulfill full dissociation, which is larger than the observed (0.21 ± 0.03) eV thermal energy. Consequently, the slow dissociation process is triggered by the MPNR capture or recombination of a free carrier under illumination to obtain the dissociation energy from the carrier transition energy, E_{ct} and the thermal activation energy, ΔE_s for the separation of FeB and the diffusion of Fe_i^+ .

In summary, the FeB dissociation in CZ silicon under strong illumination with up to 104 suns has been studied. The FeB dissociation shows a double exponential dependence on time which corresponds with two different dissociation processes. The fast athermal dissociation is controlled by Coulomb repulsion and electron-phonon interactions, and the slow dissociation is temperature dependent with a thermal activation energy of (0.21 ± 0.03) eV. The results are important to understand and control behaviors of FeB in silicon under strong light illumination, particularly for concentrator photovoltaic cells.

This work is supported by National Natural Science Foundation of China (No. 61274057), National Key Technology R&D Program (2011BAE03B13), and Innovation Team Project of Zhejiang Province (2009R50005). Jan Vanhellemont is indebted to FWO (project VS.040.11N).

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