

Dynamics of iron-acceptor-pair formation in co-doped silicon

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The pairing dynamics of interstitial iron and dopants in silicon co-doped with phosphorous and several acceptor types are presented. The classical picture of iron-acceptor pairing dynamics is expanded to include the thermalization of iron between different dopants. The thermalization is quantitatively described using Boltzmann statistics and different iron-acceptor binding energies. The proper understanding of the pairing dynamics of iron in co-doped silicon will provide additional information on the electronic properties of iron-acceptor pairs and may become an analytical method to quantify and differentiate acceptors in co-doped silicon. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4830227>]

Interstitial iron (Fe_i) and the complexes it forms with acceptors (FeAcc) in silicon (Si) are thoroughly studied and well documented: in p-type Si at room temperature and in darkness, the positively charged Fe_i is known to diffuse through the Si lattice to form coulombic pairs with negatively ionized acceptors. The pairs can be broken by intense illumination and/or annealing above 200 °C which allows the Fe_i to diffuse freely through the lattice, as reviewed in Ref. 1. Since Fe_i has very different defect parameters depending on its pairing status, measurement of the minority carrier lifetime (lifetime) coupled with Shockley-Read-Hall (SRH) defect modeling represents a simple method of monitoring the state of the Fe_i . It allows the extraction of the Fe_i concentration (N_{Fe_i}) and—through observation of pair-association dynamics—the total concentration of acceptors (N_{Acc}).^{2–5} Although such measurements on compensated Si have been published before,⁶ no report known to the authors studies the particularities of Fe_i pairing dynamics in Si containing several types of acceptors—a situation which is encountered in solar grade feedstock containing multiple native dopants such as boron and aluminum. Often gallium is also added to the feedstock of multicrystalline ingots to achieve tighter resistivity control.⁷

In this paper, the association dynamics of iron-dopant pairs in co-doped material is presented. The classical picture of FeAcc pairing dynamics is expanded to include a redistribution of iron between different dopants. Lifetime changes after full dissociation of Fe_i -dopant pairs are found to follow a distinct and fully reversible pattern depending on the dopant types contained in the material. Fig. 1 illustrates the different cases observed.

In Si doped with one acceptor only, the classical dynamics of FeAcc formation is observed: after re-pairing of all Fe_i , the lifetime remains stable (Fig. 1(a)). When phosphorous is added, the lifetime is sometimes found to increase after the first decay. If this increase is not properly fitted, N_{Fe_i} and N_{Acc} determination may be erroneous (Fig. 1(b)). The origin of this increase could not be unequivocally identified;

however, it appeared only for material compensated with P (other n-type dopants were not tested).

When a second acceptor is added to the material, the lifetime initially behaves as described in the cases above. Additionally, a very long time component (several days) is observed. Since this component only appears when several acceptor types are present, it is interpreted as a redistribution of Fe_i to the acceptor that offers the highest binding energy. As FeAcc1 and FeAcc2 usually have different recombination parameters,^{8,9} this thermalization can be traced by measuring the lifetime.

To quantify the lifetime, $\tau(t)$ measured t seconds after the dissociation of Fe_i -dopant pairs is fitted with a sum of three exponentials

$$\tau(t) = A_\infty + A_1 e^{-t/a_1} + A_2 e^{-t/a_2} + A_3 e^{-t/a_3}, \quad (1)$$

where A_j , a_j ($j = 1, 2, 3$) is the amplitude and time constant of the j^{th} exponential component and A_∞ is an offset which corresponds to the lifetime of the system in thermal equilibrium. Using this fitting procedure, the lifetime can readily be extracted at any point of the curve, and the different components can be separated. In general $a_1 < a_2 \ll a_3$ was found indicating that the three processes are sequential and can be considered independently. Note that for a quantification of defects involved, $1/\tau$ must be used since it is proportional to the defect density. However, first, a qualitative interpretation of the components is given.

The first exponential decay is observed in all samples studied. It is related to the well known pairing of Fe_i with the first acceptor it encounters. It can be used to determine total acceptor densities and Fe_i concentrations if the SRH parameters of all Fe_i states involved are known.^{2–5} Note that in co-doped material the acceptor concentration ratios also need to be known.

The second exponential term is tentatively ascribed to the dissolution of Fe_i -donor pairs created during strong illumination.⁶ Note that in general $A_2 < 0$, which indicates that the involved complex is less recombinative than the involved

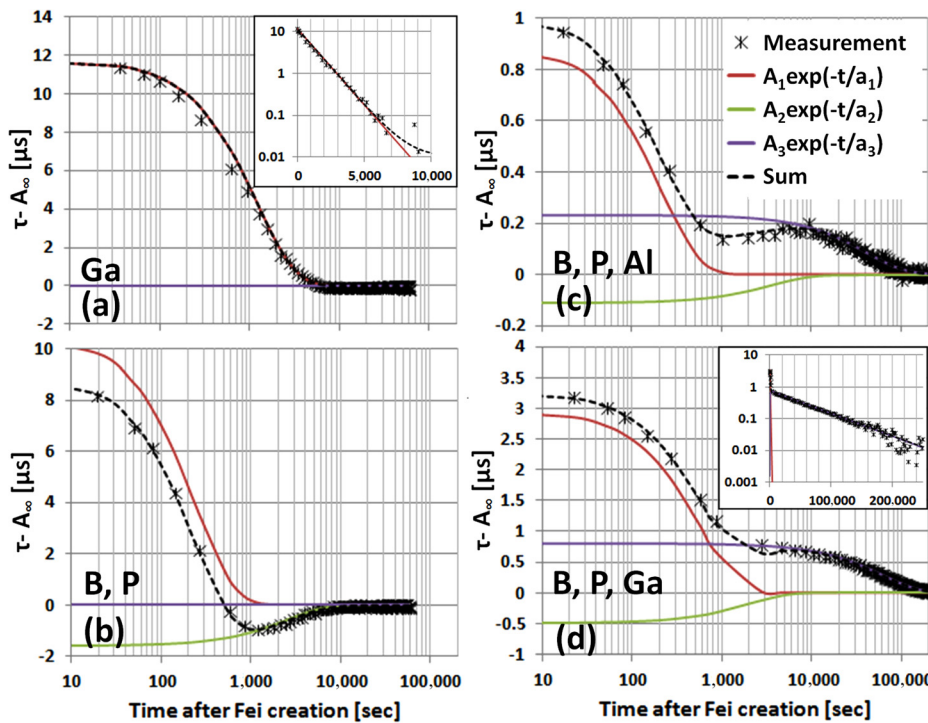


FIG. 1. Exemplary lifetime measurements at 300 K after intense illumination (nearly all Fe_i dissociated) for p-type Si doped with (a) Ga only, (b) B, P, (c) B, P, Al, (d) B, P, Ga. The insets show the more familiar logarithmic decays confirming exponential decays over several orders of magnitude. The time scale is greater than 2 days.

FeAcc pairs (Fig. 1(b)). In the following, this component is included for fitting without further analysis.

The third exponential term appears exclusively when a second acceptor is present (tested here with B and Ga and B and Al, Figs. 1(c) and 1(d)). It is ascribed to the migration of Fe_i from one acceptor type to another in the process of reaching a thermodynamical equilibrium.

The rest of this paper will focus on this redistribution process since it is expected to relate to the defect properties of FeAcc1 and FeAcc2 and their respective concentrations. An in-depth study of these processes opens the possibility for direct control of earlier theoretical calculations on the binding energies of FeAcc pairs¹⁰ and may provide a sensitive probe to detect and differentiate several types of acceptors in co-doped Si. In the following, the hypothesis that it indeed represents the redistribution of Fe_i from one type of acceptor to another type is discussed.

By the end of the first exponential decay, all Fe_i with initial concentration N_{Fe_i} have re-paired with an acceptor. Since the pairing is driven by long-distance Coulomb interaction, no preference for any type of acceptor is expected.¹¹ Since $a_1 \ll a_3$, redistribution is still negligible, and the concentration of Fe_i paired with Acc1 (N_{FeAcc1}) or Acc2 (N_{FeAcc2}) is expected to relate to the acceptor concentrations N_{acc1} and N_{acc2} according to

$$N_{\text{FeAcc1}}/N_{\text{FeAcc2}} = N_{\text{acc1}}/N_{\text{acc2}}, \quad (2)$$

while satisfying

$$N_{\text{FeAcc1}} + N_{\text{FeAcc2}} = N_{\text{Fe}_i}. \quad (3)$$

If only Coulomb interaction is considered, the two acceptor types have the same binding energy E , and the Fe_i population has reached its thermal equilibrium by the end of the first exponential decay as in Fig. 1(a). However, simulations have shown that elastic terms may induce a binding energy

difference ΔE for dopant atoms of different size.^{1,10} As a consequence, the Fe_i population is expected to thermalize into a new distribution. Because different FeAcc pairs have different SRH parameters, this redistribution entails the lifetime changes observed in Figs. 1(c) and 1(d).

Since the SRH parameters of FeB and FeGa pairs are fairly well defined,^{8,9} a quantitative interpretation is exemplarily performed on samples co-doped with B and Ga. After pairing of all Fe_i , the lifetime in Fig. 1(d) (ignoring the offset A_∞) can be described according to

$$\frac{1}{\tau} = \frac{1}{\tau_{\text{FeB}}} + \frac{1}{\tau_{\text{FeGa}}} + \frac{1}{\tau_{\text{other}}}, \quad (4)$$

where $\tau_{\text{FeB}} \sim 1/N_{\text{FeB}}$ and $\tau_{\text{FeGa}} \sim 1/N_{\text{FeGa}}$ are the minority carrier lifetimes calculated for the FeB and FeGa defect complexes using the SRH formalism. N_{FeB} and N_{FeGa} are the respective concentration of these defects. τ_{other} is the lifetime if no Fe_i were present. When the acceptor concentrations in the material are known, Eqs. (2)–(4) allow the determination of N_{Fe_i} and τ_{other} from the first exponential decay.

In the next step, the condition given in Eq. (2) is relaxed, and the lifetime in the third exponential is simulated by transferring iron from one acceptor type to the next until the measured lifetime is reached.

For instance, the pairing state of Fe_i extracted from the τ -t-curve shown in Fig. 1(d) changes as follows: After ~ 2000 s, all Fe_i ($N_{\text{Fe}_i} = 5.5 \times 10^{10} \text{ cm}^{-3}$ in this case) have paired with either B or Ga according to their acceptor concentration ratio (0.43 boron, 0.57 gallium). For $t > 10\,000$ s, a redistribution from FeB to FeGa is observed. The redistribution saturates at 0.25 FeB and 0.75 FeGa , which means that the Fe_i has migrated from B to Ga to reach its thermodynamical equilibrium.

Two parameters of the redistribution are of interest: (1) its amplitude, i.e., the amount of Fe_i moving from one

acceptor to another type and (2) its decay time. Both are expected to relate to the respective concentrations of the two acceptor types.

In thermal equilibrium, the Fe_i distribution between two acceptors exemplified by B and Ga is expected to follow Boltzmann statistics. The binding energy, or rather the binding energy difference between the Fe_i bound to B or Ga given by $\Delta E = E_{\text{FeB}} - E_{\text{FeGa}}$, will determine the occupation of the two states according to

$$N_{\text{FeB}} = \frac{N_{\text{Fei}}}{Z} * N_{\text{B}} * e^{-\Delta E/kT} \quad \text{and} \quad N_{\text{FeGa}} = \frac{N_{\text{Fei}}}{Z} * N_{\text{Ga}}, \quad (5)$$

where kT is the thermal energy. The partition function is given by $Z = N_{\text{B}} e^{-\Delta E/kT} + N_{\text{Ga}}$, where the degeneracy of the respective FeAcc state has been approximated by the acceptor concentration.

The amplitude of the redistribution allows the extraction of different parameters depending on the information available beforehand. Two cases are differentiated.

Case 1: dopant concentrations and defect parameters are known. Equations (4) and (5) can be solved to extract the binding energy difference ΔE . For example presented above, $\Delta E = 0.029$ eV is found at 300 K. This means that the redistribution to FeGa complex is due to a higher binding energy of FeGa pairs than FeB pairs. This is contrary to the expectation that the large ionic radius of Ga would leave little space for Fe_i in its vicinity as computed by Zhao *et al.*¹⁰ A vacancy-Ga- Fe_i complex as proposed for the similarly sized germanium¹² as well as boron¹³ may offer an explanation for this phenomenon.

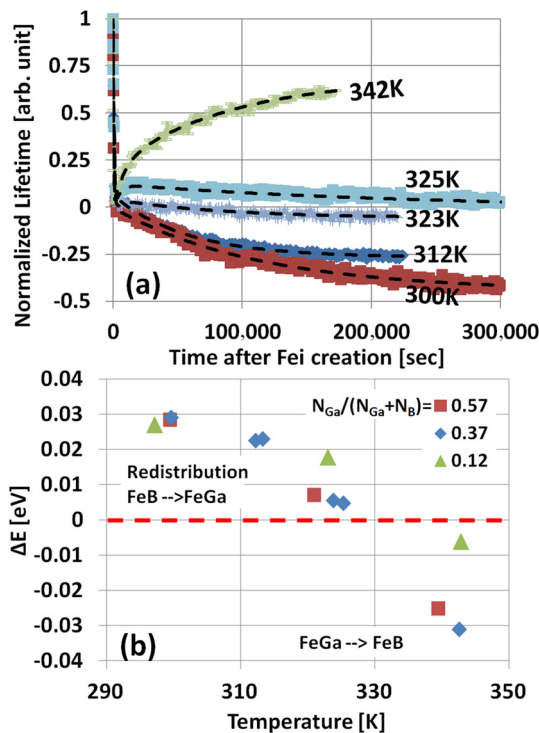


FIG. 2. (a) A temperature series on a sample containing B, P, and Ga ($N_{\text{Ga}}/(N_{\text{B}} + N_{\text{Ga}}) = 0.37$). (b) The binding energy difference ΔE for additional samples. $\Delta E > 0$ indicates higher binding energy of FeGa .

To confirm binding energy difference, the measurement was repeated in the temperature range between 300 K and 342 K on several samples with varying $N_{\text{Ga}}/(N_{\text{B}} + N_{\text{Ga}})$ ratio. Fig. 2(a) shows representative measurements on a highly co-doped, compensated sample with $\text{B} = 4.5 \times 10^{16} \text{ cm}^{-3}$ and $\text{Ga} = 2.6 \times 10^{16} \text{ cm}^{-3}$ ($\text{P} = 5.9 \times 10^{16} \text{ cm}^{-3}$). At 300 K, thermalization again reduces the lifetime indicating a redistribution towards the more recombinative FeGa complex. Indeed Ga offers a higher binding energy for Fe_i in all samples studied below 325 K (Fig. 2(b)).

As the temperature is increased, ΔE is reduced and even becomes negative above ~ 325 K (Fe_i now redistributes to B). The data set presented here is insufficient for a final explanation, but vacancy related Fe_i states close to Ga could become deactivated at higher temperatures (however, a single deactivation energy for this state could not be extracted). Another explanation could be that the thermalized population remains the same for all temperatures but that the SRH parameters of an involved defect (e.g. FeGa) are strongly temperature dependent. This option has been excluded by bringing the system out of thermal equilibrium by increasing the temperature from 300 K to 342 K. Relaxation times are of the order of days as expected for a redistribution of Fe_i (not shown here).

Case 2: defect parameters and binding energy difference ΔE are known. The determination of the concentrations of Fe_i , Acc1, and Acc2 now becomes possible. A proper understanding of the processes involved may make this method a simple and sensitive probe to detect and quantify acceptor co-doping in p-type Si when sufficient iron is present in the sample.

The time constant of the third exponential decay (a_3) is interpreted as a measure for the migration time of Fe_i moving from one acceptor type to the next. The probability of encountering a preferred acceptor type is expected to scale with the respective concentration of the two acceptors. If this redistribution is thermally activated, temperature dependent measurements should yield an activation energy. The measurements showed a general trend of lower a_3 for increasing temperatures, but a single activation energy could not be extracted. The Quasi Steady State PhotoConductance (QSSPC) measurement itself injects charge carriers which may be the primary enabler for the redistribution process. Further studies are needed to clarify this point. Once the time constant of the third exponential decay is well understood, it may also allow the determination of acceptor concentrations in co-doped p-type Si.

In this paper a process of redistribution of Fe_i from one acceptor type to the next has been postulated. Even if this redistribution is not entirely unexpected, confirmation by direct measurement of respective pair populations is needed. If Fe_i indeed moves from B to Ga, existing models of the FeAcc pair binding energy may need to be reevaluated. The present analysis is also hampered by the incomplete understanding of the P related dynamics (second exponential term).

The measurements presented were obtained as follows: Multicrystalline bricks co-doped with Ga and Al were made from electronic grade and solar grade Si. The dopant concentrations in the feedstock are known, and the concentrations at the position of measurement were back-calculated using

Scheil equations.¹⁴ Measurements were performed using a QSSPC blocktester by Sinton Consulting (BCT-300 with software version 4.4.1) on as-cut or polished bricks. The bulk lifetime was estimated at an injection density of $1 \times 10^{15} \text{ cm}^{-3}$ and corrected for traps using the software bias light method.¹⁵ The same setup was used to dissociate Fe_i by flashing 200 times or until lifetime saturation was reached. The temperature was controlled using a hotplate loaded with 60 kg of Si for added thermal mass. The temperature was monitored using a Pt1000 resistor and was stable to $\pm 0.5^\circ\text{C}$.

Summarizing, the iron-dopant pairing and subsequent redistribution dynamics in co-doped material is presented. The classical picture of FeAcc pairing dynamics is expanded to include the redistribution of iron between different dopants. This redistribution is monitored by lifetime measurements and may take up to several days at room temperature. Using Boltzmann statistics, the difference in Fe_i binding energy between Ga and B is calculated. At room temperature, Ga has a $\sim 0.028 \pm 0.02 \text{ eV}$ higher binding energy than B, and Fe_i is found to distribute towards Ga. This trend is inversed above 325 K. The proper understanding of the complex dynamics of iron in compensated Si will provide additional information on the electronic properties of iron-acceptor pairs and may provide an analytical method to quantify and differentiate acceptors in co-doped Si.

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