

# Determination of activation energy of the iron acceptor pair association and dissociation reaction

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**Abstract.** A method to measure the reaction rates of the iron acceptor pair association and dissociation is presented and applied. The activation energies of the dissociation and association reaction are determined for the acceptors boron, aluminum, gallium and indium. Additionally, the activation energies are reported for different illumination intensities. It is found that the activation energy of the association reaction varies for the investigated acceptors and that the activation energy of the dissociation reaction depends strongly on the illumination intensity. It is shown that neglecting of the dissociation reaction in the evaluation of relative interstitial iron content decrease causes a considerable overestimation of the activation energy of the iron acceptor association.

## Introduction

The observation of iron acceptor pair association in n-type silicon and under illumination with the electron quasi-Fermi level above the interstitial iron energy level [1] has led to the extension of the iron-acceptor-pairing model of Kimerling and Benton [2] by a dynamic approach [3]. The reason of the inaccuracy of the Kimerling and Benton model is that the quasi-Fermi levels can only be used to describe the carrier distribution in a non-equilibrium bandgap in limited cases [4]. Interstitial iron does not belong to these limited cases.

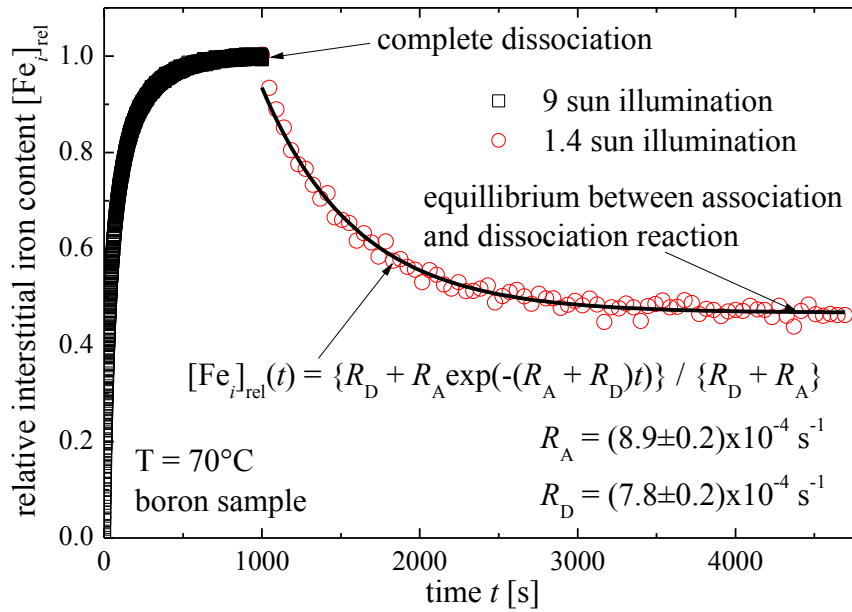
In this contribution the dynamic approach is used to measure the activation energies of the dissociation as well as association reaction of iron acceptor pairs. The iron acceptor pair reaction is monitored by time resolved charge carrier lifetime measurements. Samples doped with boron, aluminum, gallium and indium are investigated. The reaction rates of the dissociation as well as association reaction are obtained from the solution of rate equation assuming first order kinetics of equilibrium reactions. To obtain the activation energies the return of interstitial iron from the fully dissociated state to equilibrium is measured at varying temperature. Additionally, the activation energies are determined for different illumination intensities.

## Experimental

Four samples doped with different acceptors were investigated. The specific resistivity determined by 4-point-probe measurements, the crystal growing type and the measured lifetimes are given in Tab. 1. Details for the boron doped sample can be found in Ref. [5]. The aluminum doped sample was grown at Leibniz-institute for crystal growth (IKZ) by N. Abrosimov.

**Tab. 1:** Specific resistivity and lifetimes of the samples in the associated  $\tau_0$  and dissociated  $\tau_1$  state of the iron acceptor pairs at room temperature.

Sample	Type	$\rho$ [ $\Omega\text{cm}$ ]	$\tau_0$ [ $\mu\text{s}$ ]	$\tau_1$ [ $\mu\text{s}$ ]
Boron	CZ	11.7	3.2	4.5
Aluminum	CZ	3.5	24.4	25.3
Gallium	CZ	3.4	20.5	30.7
Indium	FZ	8.6	10.5	17.8



**Fig. 1:** Relative interstitial iron content as a function of time during iron acceptor pair reaction cycle.

The gallium and indium doped samples were grown at Wacker Siltronic AG by W. Zulehner. The acceptor type and density was verified by low-temperature photoluminescence spectroscopy [6] as well as by low-temperature FTIR spectroscopy [7].

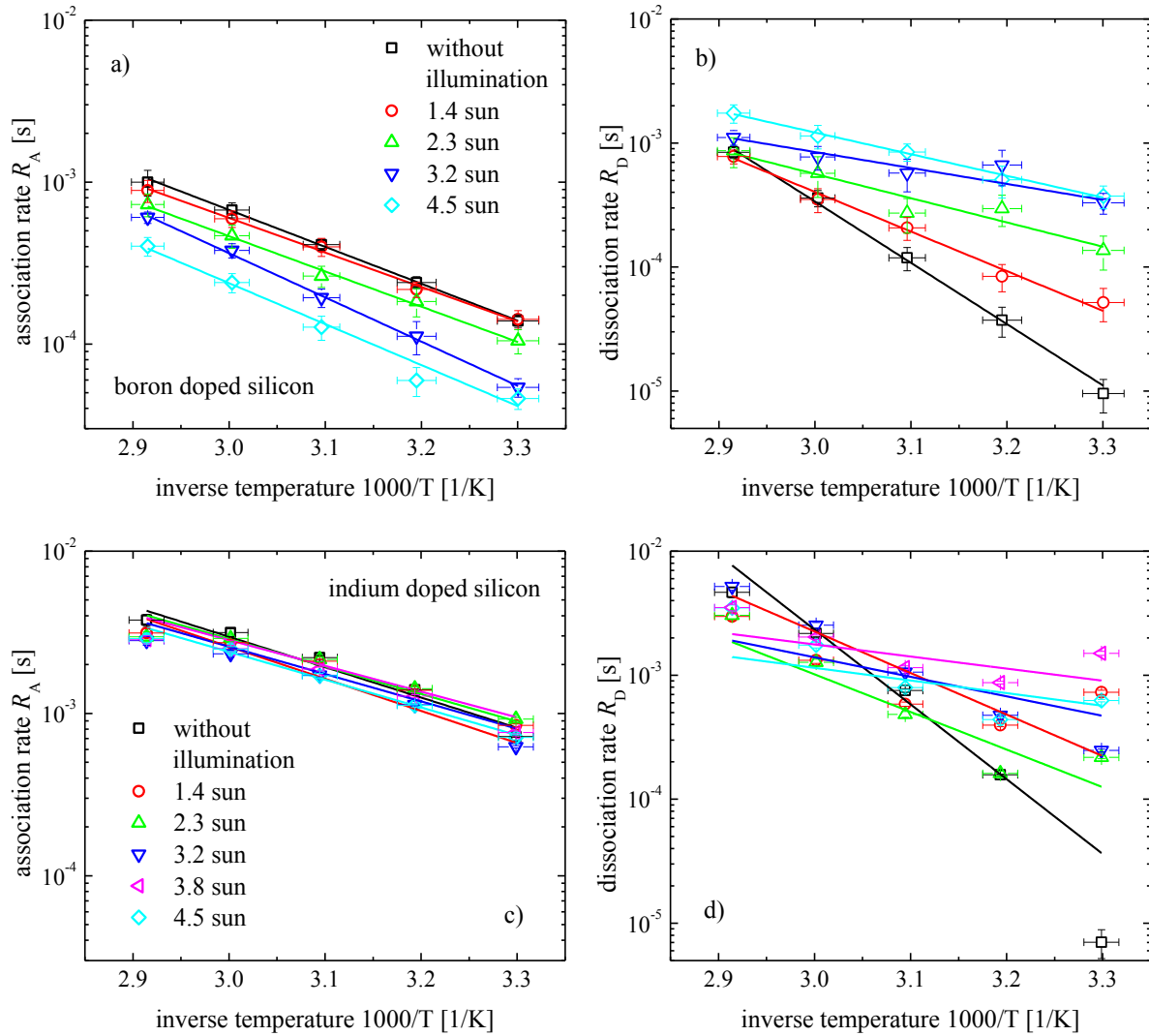
The samples were contaminated with iron as described in Refs. [1,5]. Before the lifetime measurements, all samples were KOH etched, RCA cleaned and surface passivated by a PECVD nitride layer [8]. To exclude the light-induced degradation defect during illumination dependent lifetime measurements, all samples were illuminated for 48 hours with a halogen lamp (~1 sun) at room temperature.

The iron acceptor pair kinetics was monitored by lifetime measurements with a Semilab WT-2000 microwave-detected photoconductance decay (MWPCD) device. The lifetime of the excess minority charge carriers was calculated from the MWPCD signal at an excess charge carrier density of  $\Delta n = 5 \cdot 10^{14} \text{ cm}^{-3}$ , calibrated by comparison with a quasi-steady-state photoconductance decay (QSSPC) [9] measurement [10]. Additionally, this calibration was verified on few samples using the fixed position of the cross over point [11]. It has to be noted that the measurement of the relative iron content only requires a fixed excess carrier density at which the lifetime is obtained.

The excitation laser (200 ns pulse, wavelength 904 nm, average intensity 9 sun) of the MWPCD device dissociates the iron acceptor pairs during the continuous lifetime measurement and no additional illumination is needed (see black squares in Fig. 1). The MWPCD halogen bias light was used to illuminate the samples during association of the iron acceptor pairs. The illumination intensity of the MWPCD bias light, at the used measurement distance of 0.8 mm from the sample surface, was determined with a calibrated reference cell. During the lifetime measurement, the bias light was switched off to measure the effective lifetime instead of the differential lifetime [12]. To observe the iron acceptor pair kinetics at different temperatures a temperature controlled hot plate was placed below the measurement head.

The change in the relative interstitial iron content  $[\text{Fe}_i]_{\text{rel}}$  was calculated from the MWPCD lifetime values before  $\tau_0 = \tau(t=0)$  and during/after illumination  $\tau(t)$  of the sample [13,14] as follows:

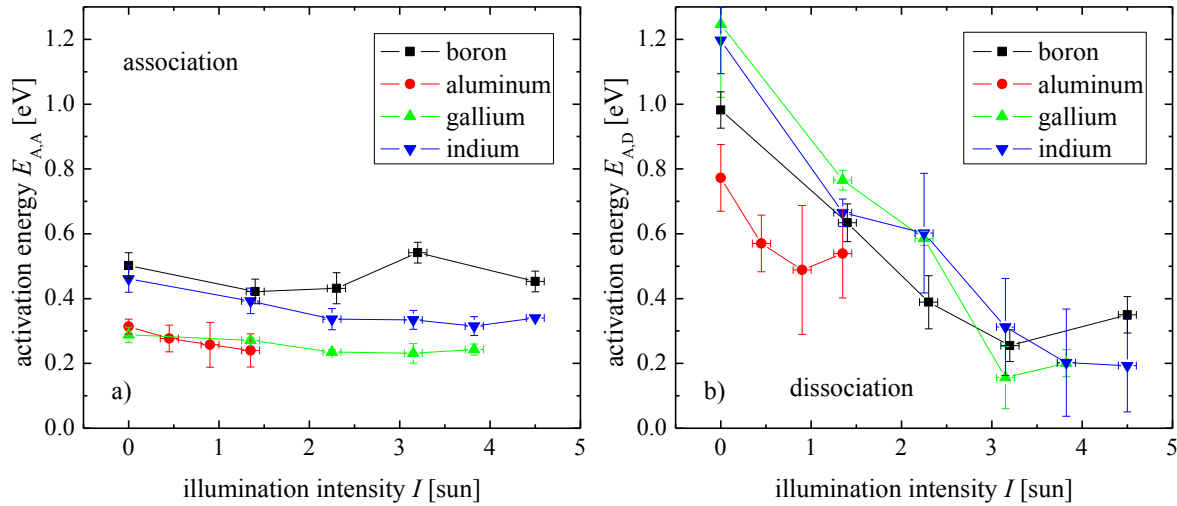
$$[\text{Fe}_i]_{\text{rel}} = \frac{[\text{Fe}_i](t)}{[\text{Fe}_i]} = \frac{\tau_0^{-1} - \tau(t)^{-1}}{\tau_0^{-1} - \tau_1^{-1}}. \quad (1)$$



**Fig. 2:** Association and dissociation rates of the boron (a,b) and indium (c,d) doped samples as a function of temperature for different illumination intensities.

$[Fe_i]$  is the total interstitial iron content and  $\tau_1$  is the lifetime measured after complete dissociation of the iron acceptor pairs. A measurement example of the relative interstitial iron content as a function of time during an iron acceptor pair reaction cycle is depicted in Fig. 1. Complete association of iron acceptor pairs at  $t = 0$  was achieved by storing the samples for about 12 h in darkness at room temperature. Dissociation of iron acceptor pairs during heating up the sample for measurements at elevated temperatures was neglected. The time constants for the thermal dissociation is too large to generate a significant amount of dissociated iron acceptor pairs during putting the sample on the hot plate and measuring the first lifetime value ( $t = 0$ ), which takes only several seconds. The lifetimes of the investigated samples in the associated and dissociated state is given in Tab. 1.

For the extraction of the association as well as the dissociation rate  $R_A$  and  $R_D$  the dynamic model as described in Ref. [3] is used. By assuming the simultaneous presence of the association and dissociation reaction during return from complete dissociation to equilibrium, the rates  $R_A$  and  $R_D$  can be obtained from the measured relative interstitial iron content as shown in Fig. 1. The latter assumption has to be done since the occupancy probability of the interstitial iron level is in between zero and one and additionally changes for the investigated range of illumination intensities and temperatures [4].



**Fig. 3:** Activation energy of the iron acceptor pair a) association and b) dissociation reaction as a function of illumination intensity for different acceptors.

## Results and discussion

The association and dissociation rates of the iron acceptor pairs as a function of temperature and illumination intensity in case of boron and indium are depicted in Fig. 2. The energies are obtained from a linear fit to the natural logarithm of the association and dissociation rate as a function of the inverse temperature. These activation energies are plotted as a function of the illumination intensity in Fig. 3. The error bars of the activation energy represent the error of the linear fit to the data points. The average activation energy of the iron acceptor association reaction of all illumination intensities is summarized and compared to literature data in Tab. 2.

The interpretation of the obtained activation energies in frame of the iron acceptor pair kinetics is a complex problem since two physical mechanisms are overlapping. These are the diffusion of interstitial iron and the interaction of electrons with interstitial iron [3]. The latter is discussed in frame of the occupancy probability of the interstitial iron level [4]. The diffusion of interstitial iron depends on the occupancy probability and on the temperature [15] and the occupancy probability itself depends on the temperature as well as on the excess carrier density. Furthermore, generation and recombination of electron hole pairs may have an impact on the iron acceptor pair kinetics. Those processes are known as recombination enhanced defect reaction (REDR) [16]. Hence, an identification of the activation energy of the iron acceptor pair association with the migration energy of the positively charged interstitial iron is too simple. The impact of other processes e.g. the temperature dependence of the occupancy probability must be considered as well.

**Tab. 2:** Comparison of the activation energy of the iron acceptor pair association reaction with literature data.

Acceptor	$E_{A,A}$ [eV] this work	$E_{A,A+D}$ [eV] $I = 0$ sun, this work	$E_{A,A+D}$ [eV] literature	Refs.
Boron	$0.47 \pm 0.08$	$0.55 \pm 0.01$	0.45 - 0.68	2,17-23
Aluminum	$0.27 \pm 0.03$	$0.62 \pm 0.05$	0.7	19
Gallium	$0.25 \pm 0.03$	$0.53 \pm 0.01$	0.47, $0.25 \pm 0.05$	19,24
Indium	$0.38 \pm 0.07$	$0.55 \pm 0.02$	/	/

We found that neglecting the dissociation reaction in the evaluation of the decay of the relative iron content (see Fig. 1) leads to an overestimation of the activation energy (see Tab. 2). The activation energy obtained in case of neglecting the dissociation reaction is denoted by  $E_{A,A+D}$ .

The activation energy of the association reaction shows a difference between the acceptors (see Tab. 2). This indicates that the binding energy of the iron acceptor pairs has a component related to the type of acceptor. This is in good agreement with the observation of a thermalization between different types of acceptors in silicon co-doped with several types of acceptors [25].

The activation energy of the dissociation reaction depends strongly on the illumination intensity (see Fig. 3). With increasing illumination intensity and hence increasing excess carrier density the activation energy of the iron acceptor pair dissociation reaction decreases. The dissociation of iron acceptor pairs needs additional supply of energy to surmount the energy barrier for migration of neutral iron [26,3]. Two ways were proposed [26]. A further electron capture of neutral interstitial iron would cause a coulombic repulsion and second an energy supply by a REDR process. Both processes seem to be feasible to explain the observed decrease in the activation energy of the dissociation reaction.

## Summary

In consequence of the approach of the dynamic model to describe iron acceptor pair kinetics the iron acceptor pair association and dissociation reaction occurs simultaneously. In this contribution a method to measure the reaction rates of the iron acceptor pair association and dissociation is presented and applied. Reaction rates are measured for the acceptors boron, aluminum, gallium and indium, for different illumination intensities as well as for varying temperature. The activation energies of the dissociation and association reaction were determined for these acceptors and for different illumination intensities. It was found that the activation energy of the association reaction varies for the investigated acceptors, which is a hint that the binding energy of the iron acceptor pairs has a component related to the type of acceptor. The activation energy of the dissociation reaction depends strongly on the illumination intensity. We found that neglecting the dissociation reaction in the evaluation of relative interstitial iron content decrease leads to a considerable overestimation of the activation energy of the iron acceptor association.

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