Iron detection in the part per quadrillion range in silicon using surface photovoltage and photodissociation of iron-boron pairs

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The photodissociation of iron-boron pairs in p-type silicon produces lifetime killing interstitial iron and may be combined with noncontact surface photovoltage (SPV) measurement of the minority carrier diffusion length to achieve fast detection of iron. We found that, for iron concentrations ranging from 8×10^8 to 1×10^{13} atoms/cm^3, the pair dissociation using a white light (10 W/cm^2) was completed within 15 s. Surface recombination was a major rate limiting factor. Passivation of the surface enhanced the rate by as much as a factor of 20. The photodissociation rate increased with increasing temperature, however, the increase was smaller than that of the thermal dissociation rate. These characteristics are consistent with a previously proposed recombination enhanced dissociation mechanism. For practical iron detection, it is important that the detection limit of the approach is close to one part per quadrillion.

Recent interest in silicon with iron concentration limited to the part per quadrillion (ppq) range has been generated by growing evidence that, for thin gate oxides used in submicrometer technology, iron precipitates near the gate oxide interface can be a major cause of electrical breakdown.[1,2] In the integrated circuit fabrication environment, numerous tools, chemicals, and processing steps are frequent sources of uncontrolled Fe contamination.[1]

Since interstitial Fe in Si acts as an efficient recombination center, the process-induced Fe contamination may be detected by measurement of the bulk minority carrier lifetime. Surface photovoltage (SPV) measurement of the minority carrier diffusion length, L, in p-type Si has recently emerged as a sensitive method involving no wafer preparation other than a short anneal at temperatures below 250 °C.[3-5] Two key SPV features are[3] (1) the measurements are performed under very low excitation level where L is uniquely related to the concentration of different recombination centers, N_k, by $L^{-2} = D_n^{-1} \Sigma_k c_k N_k$ where D_n is the electron diffusion constant and c_k is the electron capture coefficient (a product of the capture cross section and the thermal velocity), and (2) Fe may be distinguished and separated from other recombination centers using low-temperature defect reactions which cycle Fe between the lifetime killing isolated interstitial, Fe_i, and the Fe-B pair which is about ten times less efficient in recombination.

In the 1–10 Ω cm p-type Si considered here, the Fe_i donor (0.39 eV above the valence band[3,6-8]) is ionized and its electron capture coefficient, $c_i = 5.5 \times 10^{-7}$ cm^3/s (at 300 K), is ten times larger than that of an electrically neutral Fe-B pair, c_p. An increase (decrease) of the interstitial concentration, ΔN_i, by dissociation (creation) of an equal amount of pairs, ΔN_p, causes a reduction (increase) of the diffusion length, $\Delta(1/L^2) = D_n^{-1} c_i \Delta N_i (1 - c_p/c_i)$.

Iron concentration is determined from two measurements:[3] when practically all of the Fe_i are paired and L is at its maximum, L_0 and when all pairs are dissociated and L is at its minimum, L_1. The pairing process and thermal pair dissociation have been quantitatively characterized.[3,9,10] The pairing time constant is $\tau_p = 557T/D_{Fe}N_B$ where D_{Fe} is the diffusivity of iron and N_B is the boron concentration.[3,9] For $N_B \geqslant 10^{15}$ cm^{-3}, τ_p is below 5 h at room temperature and 5 min at 80 °C. Therefore, the pairing is practically completed after storage of wafers for 24 h at room temperature or 20 min at 80 °C, recommended for L_0 measurement in Ref. 3. The thermal equilibrium fractions of iron remaining unpaired, evaluated from data in Refs. 2 and 9, are very small, namely, $\leqslant 10^{-3}$ at 300 °C and $\leqslant 5 \times 10^{-2}$ at 80 °C. The pair dissociation is realized by the "Fe activation step," i.e., a short anneal (5–10 min) at 200–250 °C and fast cooling (water quench)[3,9,10] to prevent pairing.

Other metal-boron pairs (e.g., Cr_iB_s) can also dissociate (or associate) during Fe activation.[4] This introduces ambiguity especially for low contamination levels. In this work, we discuss a modified approach based on the photodissociation of pairs[4,6-9] rather than thermal dissociation. At room temperature the photodissociation appears to be a distinctive feature of Fe-B pairs[4] contrasting it to Cr-B pairs.

The SPV measurements were performed using a fully automated linear constant photon flux apparatus described in detail elsewhere.[5] This system operates at a photon flux below 10^{14} photons/cm^2 s and wavelengths range from 0.8 to 1.02 μm. The photovoltage was acquired by a small semitransparent electrode positioned about 0.2 mm above the wafer surface. The wafer was held by vacuum on a variable temperature chuck which also served as a second electrode. A steady-state SPV signal was monitored with four digit accuracy. The diffusion length was determined from the dependence of the SPV on the light penetration depth, i.e., the inverse of the Si absorption coefficient, α. The values of α were recalculated for wafer temperatures ranging from 0 to 80 °C. This feature, combined with a short measuring time (about 2 s), made possible *in situ*

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measurement of pair association and photodissociation kinetics at different temperatures.

The typical accuracy for a single diffusion length measurement was 1% or better. For the highest purity silicon with $L \approx 1000$ μm, 3-mm-thick samples were used. With data averaging and 16 repetitions, the standard deviation for $L \approx 1000$ μm was ± 2 μm.

The wafers, obtained from commercial suppliers, were measured as-received, or after a buffered HF dip which increases positive surface charge and enhances the SPV signal.[5] Czochralski-grown silicon, intentionally doped by adding Fe to the melt, and unintentionally contaminated wafers were used with iron concentrations ranging from 8×10^8 to 1×10^{13} cm^{-3}. Iron at concentrations exceeding 5×10^{10} cm^{-3} was confirmed by deep level transient spectroscopy (DLTS) measurement. Lower concentrations were determined by SPV using the Fe-B association kinetics as the Fe fingerprint.[3]

In the photodissociation study, the wafers were illuminated with pulses of halogen bulb light of variable duration (2–60 s) and intensity (1–20 W/cm^2). Prolonged high-intensity illumination in air may decrease the SPV signal for some wafers due to photodehydration of the surface. The positive surface charge recovers within minutes in air or immediately after wafer exposure to water vapor.

The experiment started with Fe-B pairing complete and the diffusion length value, L_0. Then L was measured after consecutive light pulses until the low limit, L_1, was reached. The light intensity was always high enough to assure a photodissociation rate, R_D^I, much larger than the thermal dissociation and association rates, R_D^T and R_A^T, respectively. Under these conditions, the change of pair concentration is $dN_p/dt = -R_D^I - R_D^T + R_A^T \approx -R_D^I = -N_p/\tau_d$, where τ_d is the photodissociation time constant.

The key characteristics are (1) the photodissociation can be accelerated (τ_d reduced) by increasing the illumination intensity; (2) the cycle of photodissociation followed by thermal association is very reproducible as demonstrated by identical results obtained over 20 cycles; (3) L_1 is 5%–10% lower than that after thermal Fe activation (this difference is due to partial pairing during cooling); and (4) using broadband optical filters, we have found that the threshold photon energy for the photodissociation of Fe-B pairs coincides with the Si energy gap.

In Fig. 1, the concentration of Fe-B pairs, determined from diffusion length decay data (using $D_n \approx 33$ cm^2/s), is shown as a function of the total exposure time. The upper figure corresponds to 5 W/cm^2 incident light with the wafers kept in air. The pair concentration decay is an exponential process characterized by $\tau_d \approx 13$ s, which is similar for both wafers in spite of the very large differences in the diffusion lengths and the Fe concentrations.

A striking reduction of τ_d (or an enhancement of the photodissociation rate) was observed upon surface passivation reducing the surface recombination[11] such as immersion in diluted HF or SiO$_2$ coating. As shown in the lower portion of Fig. 1, for the wafers immersed in 5% HF+95% H$_2$O, the τ_d was about three times shorter in the
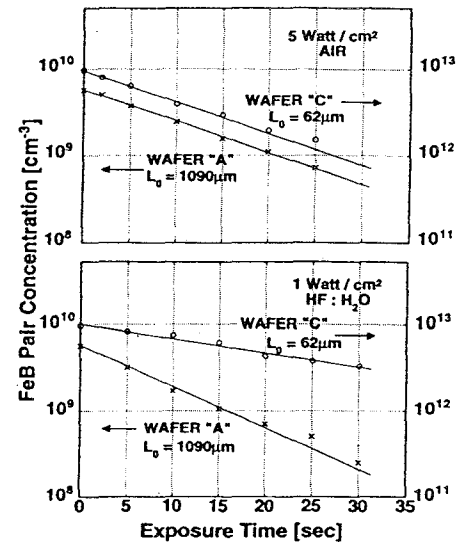

FIG. 1. An Fe-B pair concentration decay vs exposure time to white light. The "x" corresponds to Wafer (A) with $N_B = 1.8 \times 10^{15}$ cm^{-3}, $L_0 = 1090$ μm, and $L_1 = 848$ μm while the "O" corresponds to Wafer (C) with $N_B = 1.38 \times 10^{16}$ cm^{-3}, $L_0 = 62$ μm, and $L_1 = 29$ μm. The upper figure corresponds to illumination in air while the lower figure corresponds to illumination in diluted HF.

long diffusion length wafer [Wafer (A)] as compared to that in the short diffusion length wafer [Wafer (C)]. In HF+H$_2$O, the pair photodissociation was so fast that the light intensity had to be reduced to 1 W/cm^2 to measure the decay. A quantitative comparison of the photodissociation rate for different surface conditions affecting the surface recombination velocity is given in Table I. In this experiment, the pairs were dissociated at 22 °C using a 5 s, 1 W/cm^2 light pulse. Prior to illumination, a 20 min anneal at 80 °C was always used to restore the initial conditions. The results in Table I show a 20 times enhancement of the pair dissociation rate under conditions corresponding to low surface recombination.

Sensitivity to surface recombination proves the recombination-enhanced mechanism[9] in which $1/\tau_d$ (or the dissociation rate) is determined by the concentration of excess electrons, Δn. Under steady state, $\Delta n \sim I/(S + D_a/L_a)$, where I is the incident photon flux, S is the surface recombination velocity and D_a and L_a are the ambipolar diffusion constant and diffusion length, respectively. For $S \gg D_a/L_a$, Δn is low and virtually insensitive to L_a, how-

TABLE I. Effects of surface condition on pair photodissociation (5 s exposure to white light of 1 W/cm^2 intensity).

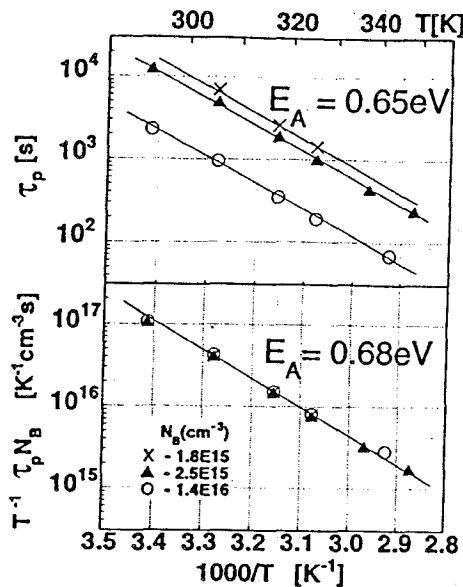| Surface condition	Concentration of dissociated pairs (cm^{-3})	Fraction of dissociated pairs (%)	Surface recombination
SiO$_2$ present immersed in H$_2$O	11.0×10^{10}	36	Low
SiO$_2$ removed immersed in HF:H$_2$O	4.5×10^{10}	15	Low
SiO$_2$ removed immersed in H$_2$O	6.0×10^9	2	High

FIG. 2. The pair association time, τ_p, after photodissociation as a function of temperature. The lower figure presents an activation plot which is the signature of Fe.

ever, when $S < D_a/L_a$, Δn increases and becomes sensitive to L consistent with Fig. 1 and Table I.

Photodissociation is temperature dependent and decreasing the temperature slows down the process. For the wafer immersed in liquid nitrogen, no change of L could be detected, even after 20 W/cm^2 illumination for several minutes. Increasing the temperature accelerates the photodissociation. Around room temperature, τ_d decreases approximately twice per 20 °C temperature increase. This temperature dependence is pronounced, but, at the same time, much weaker than that of the thermal dissociation.[9,12]

The Fe-B pairing after photodissociation was found to be identical to that after thermal dissociation. The process was exponential with annealing time. The temperature dependence of the association time constant, τ_p, is shown in Fig. 2. It is also seen that τ_p decreases linearly with increasing boron concentration. Our pair association results are in excellent agreement with previous measurements and with the pair association treatment based on the Coulomb interaction model[9] (note that the results in Fig. 2 refute the recently proposed diffusion limited model[12] projecting $N_B^{-2/3}$ dependence of τ_p). From the association time constant, $\tau_p = 557T/D_{Fe}N_B$, one can define the quantity $T^{-1}\tau_p N_b$ which is dependent only on the Fe$_i$ diffusivity. In the lower portion of Fig. 2, the thermal activation plot of the quantity $T^{-1}\tau_p N_b$ (equal to $557/D_{Fe}$) is given. The

plot is the same for all wafers and gives an activation energy, $E_A = 0.68$ eV, in excellent agreement with the Fe diffusivity data compiled in Ref. 8. This plot, determined only by the metal diffusivity, can be considered an identification factor of the metal pairing analogous to the commonly used emission rate plot of DLTS.

To estimate the detection limit of the approach, we have used an ultraclean 3-mm-thick Si slab with $N_b = 5 \times 10^{15}$ cm^{-3}. The diffusion length was measured in a 16 measurement averaging cycle mode. The L_0 value, after completion of Fe-B pairing (20 min at 80 °C), was 1126 μm with a standard deviation, $\sigma = 2.1$ μm. The photodissociation, by 10 s, 20 W/cm^2 light pulse, reduced the diffusion length to $L_1 = 918$ μm with $\sigma = 1.8$ μm. This corresponds to a total Fe concentration 2.8×10^9 cm^{-3}. The wafer was annealed at 80 °C for 20 min and the measurements were repeated, however, in small photodissociation steps using short duration, lower intensity light pulses. The smallest clearly detectable step was a change of L from 1126 ± 2.1 μm to 1119 ± 2.0 μm. This corresponds to ΔN_i of about 7×10^7 cm^{-3} which is close to 1 ppq. We take this value as an estimate of the detection limit of the approach.

In summary, we have shown that using photodissociation of Fe-B pairs and the SPV technique, Fe can be detected in p-type Si at very low concentrations. During both the photodissociation and SPV measurement, only light is used as the medium contacting the wafer. We also show that photodissociation is consistent with a recombination enhanced mechanism.

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