

Charge-State-Dependent Diffusion and Carrier-Emission-Limited Drift of Iron in Silicon

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(Received 7 October 1991)

The behavior of iron in silicon during low-temperature annealing was studied. The influence of electric fields on the underlying defect reactions is detailed. The depth profiles reveal Fe_i outdiffusion and no precipitation in the bulk up to 470 K. In the presence of electric fields, the kinetics differ considerably and can be understood in terms of carrier-emission-limited iron drift. Consequences of this mechanism are discussed. The outdiffusion and drift data indicate a charge-state-dependent diffusion mechanism, in contrast to the generally accepted lack of any charge-state effect.

PACS numbers: 61.70.Wp, 61.70.At, 66.30.Jt

Considerable motion of iron atoms in silicon can occur at moderate temperatures (below 500 K) when they are dissolved in the matrix at interstitial sites. The corresponding high diffusion coefficient enables various defect reactions, which have been the subject of many interesting works [1-3]. Nevertheless, not all the observed mechanisms involving interstitial iron (Fe_i) are fully understood today. In a recently published work [4], irreversible loss of Fe_i in *p*-type silicon after annealing at temperatures around 400 K has been observed by deep-level transient spectroscopy (DLTS). At these temperatures, the well-known iron-acceptor pairs are completely dissociated and do not contribute to the loss of Fe_i [1,2]. The role of the iron charge state (positive in *p*-type material and neutral in the depletion region) was studied, by measuring the precipitation kinetics in *p*-type silicon successively under zero voltage and under reverse bias. After annealing under zero bias, first-order kinetics were found, indicating a diffusion-limited precipitation of positively charged Fe_i on extended defects. A considerably faster loss of neutral Fe_i was observed during reverse bias annealing, following a law proportional to $\exp[-(t/\tau)^{3/2}]$. This behavior was tentatively ascribed to diffusion-limited precipitation of neutral Fe_i on growing nucleation centers according to the model of Ham [5].

In this work we report on the irreversible loss of Fe_i in *n*-type silicon, where it is neutral, during isothermal annealing. In order to further investigate the previously reported enhanced Fe_i loss in the depletion region, the influence of external electric fields on the Fe_i behavior is studied.

For our investigation we used Czochralski- and float-zone-grown *n*-type silicon, with a phosphorus concentration in the range of $(0.5-5) \times 10^{15} \text{ cm}^{-3}$. After chemical cleaning, the samples were scratched on both sides with an ultrapure (99.9999%) iron wire. They were then annealed in argon atmosphere at temperatures between 1200 and 1350 K for 30 to 120 min, and quenched in water, in order to yield a uniform interstitial iron depth distribution. A few tens of microns were removed by chemical etching and semitransparent gold dots were evaporated to form Schottky diodes for electrical characterization.

Fe_i is known to introduce a donor level at 0.39 eV from

the valence band, which can be easily detected by infrared-light-induced optical transitions [6]. The resulting photocapacitance signal is proportional to the Fe_i concentration. This technique can also be used in a differential mode in order to analyze the iron depth profile [7].

Isothermal annealing kinetics have been recorded at temperatures below 470 K, the sample being either zero or reverse biased (-10 V). In the latter case, photocapacitance measurements have been performed with a reverse bias lower than -10 V in order to analyze a region located in the depletion region during annealing.

The results obtained after annealing under zero bias have been described in detail in Ref. [7]. Briefly, the measured kinetics were different from the behavior observed in *p*-type silicon for both positively charged (under zero bias) and neutral Fe_i (under reverse bias). The loss of Fe_i was considerably slower following a "non-first-order" evolution. The results could, however, be successfully adjusted by considering the iron outdiffusion as the responsible mechanism. This was confirmed by the Fe_i depth distribution recorded after isothermal annealing, shown in Fig. 1. The solid lines are calculated error functions and are seen to fit the experimental results extremely well. The observations indicate that the stability of

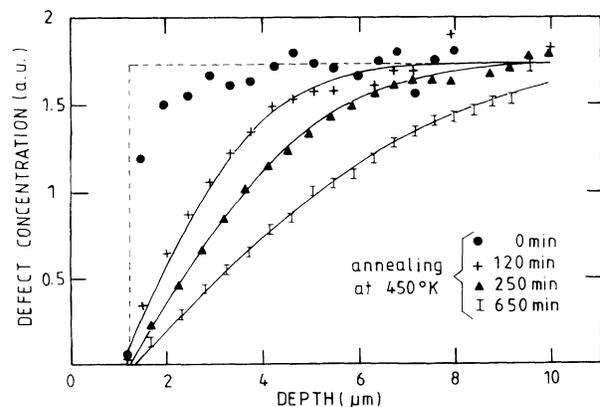


FIG. 1. Depth profiles of interstitial iron in *n*-type silicon after various annealing times. The dashed curve was taken as a boundary condition.

Fe_i^0 is higher as compared to Fe_i^+ , the major sink for Fe_i being the sample surface. This is coherent with the absence of long-range Coulombic forces for Fe_i^0 . In Fig. 1, the iron concentration surprisingly vanishes at approximately $1 \mu\text{m}$ from the sample surface. A good fit could only be obtained when taking this limit as a boundary condition. The physical reason for this behavior will appear below.

The Fe_i behavior changes considerably when the samples are reverse biased during annealing. The corresponding isothermal annealing data are shown in Fig. 2. The concentration of Fe_i decreases faster than without applied voltage and follows an exponential law. The loss rate is found to increase strongly with the phosphorus concentration, as revealed by curves (2) and (4). Iron depth profiles measured after annealing at 400 K with an applied reverse bias (-10 V) for various durations clearly showed the Fe_i concentration to decrease uniformly over the entire depletion region [8].

The reaction responsible for the loss of Fe_i is irreversible, as subsequent annealing at zero bias does not yield a uniform increase of the Fe_i concentration, but rather a pure diffusion process which flattens the initially steep iron depth profile. This is clearly shown in Fig. 3, where the numerical solution of Fick's diffusion equation, with the open squares taken as the initial condition, fits the experimental data well. The Fe_i diffusion coefficient was adjusted to yield the best fit to the experimental results and will be discussed later.

The above results are rather surprising as Fe_i is known to be neutral in both the depletion and neutral regions of an n -type Schottky diode, according to the position of its associated deep level. To understand this unexpected behavior, one has to remember that in the depletion region the iron atoms are not constantly neutral. Indeed, from Shockley-Read-Hall statistics [9] we know that in a high-field region, where no carrier capture occurs, the charge state of a defect is completely determined by electron and hole emission processes. The average fraction

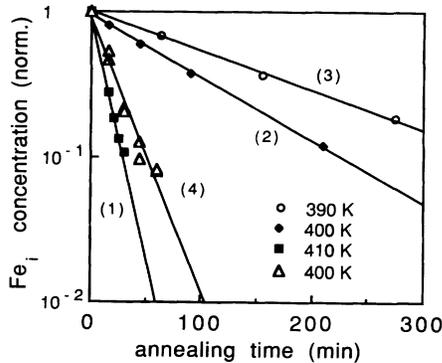


FIG. 2. Normalized Fe_i concentration after isothermal annealing with applied reverse bias. For curves (1)–(3) the phosphorus concentration was $5 \times 10^{14} \text{ cm}^{-3}$, while for curve (4) it was $2 \times 10^{15} \text{ cm}^{-3}$.

f^+ of positively charged Fe_i in a depletion region is given by

$$f^+ = e_n / (e_n + e_p), \tag{1}$$

where e_p and e_n are the hole and electron emission rates.

For the Fe_i donor level, which has a much higher electron (σ_n) than hole (σ_p) capture cross section [6,10], the ionized fraction at 400 K is about a few percent. This means that during annealing under high electric fields, a non-negligible amount of iron is charged and may drift out of the depletion region. For example, in the case of n -type silicon Fe_i would drift towards the sample surface.

Considering this mechanism in a depletion region of a Schottky diode, it is easily shown that the decrease of iron in this region follows an exponential law. As a matter of fact, the iron concentration is a solution of the diffusion equation

$$\frac{\partial [Fe_i]}{\partial t} = D \frac{\partial^2 [Fe_i]}{\partial x^2} - \mu_{\text{eff}} \frac{\partial [Fe_i] E(x)}{\partial x}, \tag{2}$$

where D is the Fe_i diffusion coefficient and $E(x)$ the electric field. The effective mobility μ_{eff} is defined by μf^+ , where μ is the iron mobility. It takes into account the electron emission step necessary for drift of Fe_i in the presence of an electric field. According to the temperature range investigated, any loss of iron in the bulk, due for example to precipitation, is neglected [7]. Looking at the first-order decrease of Fe_i , some simplifications can be made which lead to an analytical solution of Eq. (2). Namely, the Fe_i concentration is initially constant across the whole sample. Hence, at least at the beginning of the annealing, the Fe_i concentration gradient ($\partial [Fe_i] / \partial x$) in Eq. (2) is negligible, yielding

$$\frac{\partial [Fe_i]}{\partial t} = -\mu_{\text{eff}} [Fe_i] \frac{\partial E(x)}{\partial x}. \tag{3}$$

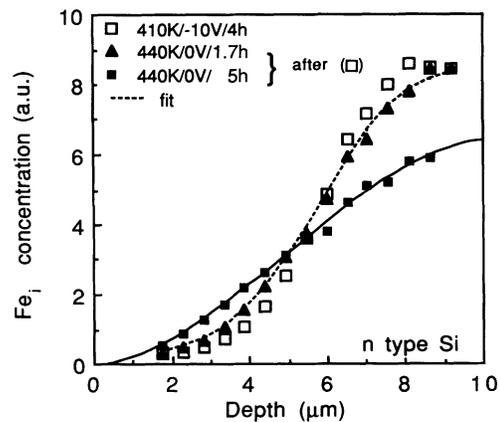


FIG. 3. Fe_i depth profiles in n -type silicon. The dotted line is a numerical solution of the diffusion equation with $D = 1.25 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$. The data shown as open squares were taken as the initial condition.

Using the expression of the electric-field gradient in a depletion region for uniform doping N_d , Eq. (3) can be rewritten as

$$\frac{\partial[Fe_i]}{\partial t} = -\mu_{eff}[Fe_i] \frac{qN_d}{\epsilon} \tag{4}$$

where ϵ is the dielectric constant of silicon. Using expression (1) for μ_{eff} , Eq. (4) leads to an exponential decrease of the Fe_i concentration with the rate

$$\tau^{-1} = \frac{q^2 N_d D e_n}{\epsilon k T (e_n + e_p)} \tag{5}$$

Finally as the rate is independent of depth, the Fe_i distribution will remain flat and Eq. (4) is valid even for larger times, provided the Fe_i concentration is evaluated far enough from the edge of the depletion region. Equations (4) and (5) explain in a simple way all of the experimental findings: the first-order kinetics, the doping-level dependence of the loss rate, and the irreversibility of the defect reaction.

In Eq. (2) we did not make explicit a possible charge-state-dependent Fe_i diffusion coefficient. However, as only the drift term was shown to be significant in our experiment, the diffusion coefficient in expression (5) corresponds to the positively charged iron. In other words, the drift of iron in the depletion region is limited by a carrier emission step, necessary to render iron positively charged. Using $\sigma_p = 5.6 \times 10^{-16} \exp[-(0.048 \text{ eV})/kT] \text{ cm}^2$ for hole capture and $\sigma_n = 10^{-10} \times T^{-3/2} \text{ cm}^2$ for electron capture, as published respectively by Brotherton, Bradley, and Gill [10] and Lemke [6], we can get Fe_i^+ diffusion data as a function of temperature. The results are plotted in Fig. 4 and will be discussed below.

A better understanding of the annealing results in both n -type and p -type silicon is possible when taking into account carrier-emission-limited drift of Fe_i . In n -type silicon, the boundary condition at $1 \mu\text{m}$ below the surface in Fig. 1 corresponds to the depletion region width under

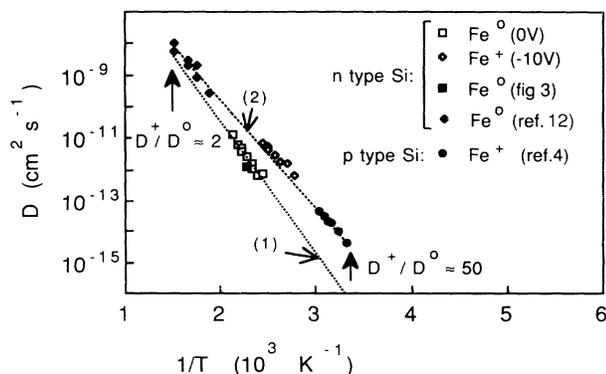


FIG. 4. Summary of our Fe_i diffusion coefficient data and comparison with literature. Curves (1) and (2) are described respectively by $D(Fe_i^0) = 10^{-2} \exp[-(0.84 \text{ eV})/kT]$ and $D(Fe_i^+) = 1.4 \times 10^{-3} \exp[-(0.69 \text{ eV})/kT]$.

zero bias of the Schottky barrier. The electric field extends the effective sink for Fe_i to a $1\text{-}\mu\text{m}$ -thick layer. In the absence of a Schottky barrier, it is the energy band bending close to the sample surface which determines the effective sink width.

In p -type silicon, outdiffusion of Fe_i has not been observed [4]. It appears that the presence of the electric field in the zero-bias depletion region is responsible for this behavior. Indeed, according to the direction of the electric field in this material, Fe_i drifts towards the bulk, hindering outdiffusion. The double-DLTS depth profile measurements shown in Fig. 5 reveal that the same mechanism is responsible for the annealing kinetics observed under reverse bias and reported in Ref. [4]. The data shown as open circles correspond to the initial depth distribution of iron-acceptor pairs in the samples of Ref. [4]. Because of room temperature storage, this is identical to the distribution of total iron dissolved in the matrix, as each interstitial iron atom is linked to an acceptor atom. The measured Fe_i distribution after annealing at 390 K under -8 V for 80 min is shown by the solid circles and can be qualitatively understood in the following way. During annealing, iron-acceptor pairs dissociate and free iron atoms are submitted to carrier-emission-limited drift towards the bulk, leading to the observed Fe_i accumulation around $2 \mu\text{m}$. The decrease in Fe_i concentration in the neutral region is due to iron-acceptor pairing during cooldown.

To our knowledge, this is the first observation of a carrier-emission-limited impurity drift and we would like to emphasize that this mechanism can lead to some important practical consequences. In operating power devices, for example, strong electric fields and moderate temperatures are easily achieved, exposing these devices to similar defect motion and perhaps to related instabilities. For instance, interstitial iron should accumulate in the p -type region of a p^+n junction, according to the direction of the electric field in the depletion region. Thus even for an initially low uniform iron contamination, the iron concentration in the p -type region can rise

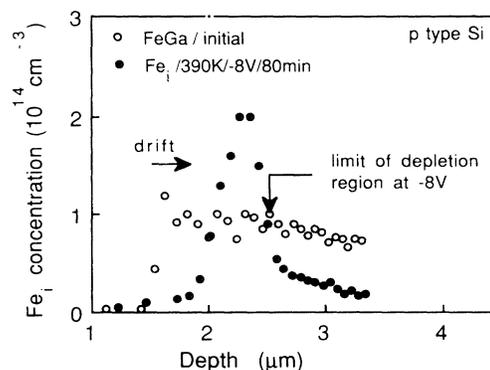


FIG. 5. $FeGa$ and Fe_i depth profiles in p -type silicon measured by double DLTS.

above a critical value for these devices.

Let us now discuss the diffusion coefficient data obtained by the above measurements and summarized in Fig. 4. The data determined from reverse-bias annealing experiments describe the iron diffusion in its positive charge state. Iron-acceptor pairing kinetics at temperatures between 300 and 350 K has been used by several authors [4,11] to measure the iron diffusion coefficient. They found that $D(\text{Fe}_i^+) = 1.4 \times 10^{-3} \exp[-(0.69 \text{ eV})/kT]$ which, evaluated between 400 and 470 K, fits well with our data. The slight deviation towards higher values may be due to the capture cross sections used to calculate the diffusion coefficient. Indeed, they have been extrapolated from measurements performed at a much lower temperature range than our annealing experiments. Nevertheless, the agreement between both sets of data confirms the carrier-emission-limited drift to be responsible for the reverse-bias annealing results.

Annealing under zero bias led to the diffusion data for neutral iron [7] and is best fitted by the expression $D(\text{Fe}_i^0) = 10^{-2} \exp[-(0.84 \text{ eV})/kT]$ [see curve (1) in Fig. 4], which is considerably different from the diffusion coefficient of positively charged iron. Furthermore, the $D(\text{Fe}_i^0)$ value obtained from the results in Fig. 3 nearly coincides with curve (1) and strengthens the assertion of a charge-state-dependent diffusion coefficient discussed in Ref. [7]. The nearly one order of magnitude variation of D with the iron charge state is indeed well above experimental error, especially as both data sets have been obtained in the same sample, changing only the applied bias. This is the first evidence for a charge-state-dependent Fe_i diffusion mechanism. The reason that it was not previously detected may be due to the fact that the diffusion coefficient difference is low at higher temperatures. The data published by Schwalbach *et al.* [12], also shown in Fig. 4, correspond to neutral Fe_i diffusion. However, in the investigated temperature range, the charge-state effect is small and difficult to detect. On the other side, the effect increases towards low temperatures. The ratio $D(\text{Fe}_i^+)/D(\text{Fe}_i^0)$ is about 50 at 300 K, affecting considerably the behavior of iron in diffusion-limited reactions.

In conclusion, the kinetic analysis with or without applied voltage allowed us to observe iron drift limited by a carrier emission step. The large discrepancy between electron and hole capture cross sections of the iron donor level is responsible for the unexpected magnitude of this mechanism in our experiment. In general, when studying defect reactions involving neutral species under strong electric fields, carrier-emission-limited drift should be considered.

Finally, the kinetic analysis led to diffusion data of iron in both charge states and revealed a charge-state-dependent diffusion mechanism of iron in silicon.

The authors would like to thank Dr. W. Zulehner from Wacker Chemitronic company for providing the silicon samples used in this work. They are also indebted to N. Amroun for the double-DLTS measurements. This work has been supported by the GCIS foundation (Groupeement des Circuits Intégrés sur Silicium). Laboratoire PHASE is UPR du CNRS No. 292.

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