

Temperature dependence of the iron donor level in silicon at device processing temperatures

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Iron depth profiles in a p -type silicon epitaxial layer on a p^+ -type silicon substrate have been examined by deep-level transient spectroscopy and computer simulations. By comparing the experimental results with the simulations, we revealed the position of the iron deep donor level to be 0.42 ± 0.04 eV from the valence-band edge at 412–580 °C, which is in a device processing temperature range. The iron donor level was nearly temperature independent within error. Knowing the temperature dependence of the iron donor level at the device processing temperatures, we can design iron gettering in silicon more precisely. © 2000 American Institute of Physics.

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The p/p^+ structure was initially introduced to decrease the density of crystal defects in the near-surface region, and to prevent latch-up effects. Additionally, it was found that the p^+ substrate provides an efficient segregation gettering sink for ionized impurities. This gettering mechanism may be very efficient even at relatively low temperatures due to the small distance which the impurities have to diffuse to get to the substrate. Detailed studies of the segregation effect of iron, which is a model impurity in silicon, indicated that the segregation is very weak at high temperatures, while at room temperature the segregation coefficient, $S = \text{Fe}_{\text{total}}(p)/\text{Fe}_{\text{total}}(p^+)$, which determines the ratio of iron concentrations in the p epilayer and in the p^+ substrate in the equilibrium after infinitely long anneal, was estimated to be as significant as 10^{-3} – 10^{-6} (see our recent review¹ and the references therein). Hence, intermediate temperatures, where iron can diffuse quickly, and where the segregation coefficient is sufficient for efficient gettering, are most important for gettering. Unfortunately, no experimental data for the segregation coefficient of iron at temperatures below 700 °C are available.^{2–4} The efficiency of the p/p^+ gettering is determined by both the solubility and effective diffusivity of iron in silicon, which are determined by the position of the iron donor level in the silicon band gap. Therefore, for better control of the p/p^+ segregation gettering, the determination of the temperature dependence of the iron donor level in silicon is essential. In this study, we attempted to determine the iron donor level at temperatures from 412 to 580 °C.

First, we describe the mechanism of enhancement of iron solubility in p^+ and the basic equations which enable one to calculate the segregation coefficient. The total dissolved iron concentration is given by a sum of concentrations of three separate species, neutral interstitial iron Fe_i^0 , interstitial ionized iron Fe_i^+ , and iron paired with an acceptor such as boron, FeB . As shown by Weber,⁵ the concentration

of Fe_i^0 is determined by the reaction of dissolution of iron silicide, FeSi_2 , and depends only on temperature. On the contrary, the concentration of the ionized interstitial iron and FeB pairs is determined by the Fermi-level position in the sample, i.e., by its doping level. If a part of the neutral interstitial iron becomes ionized, the concentration of neutral iron is replenished by dissolution of additional iron from the surface silicide or by diffusion of iron from the p epilayer. The balance of reactions between FeSi_2 , Fe_i^0 , Fe_i^+ , and FeB (in the case of boron-doped silicon) can be easily calculated by using the expressions for the solubility of iron, dependence of the ionized fraction of iron on the position of iron defect level relative to the Fermi-level position in the band gap, and the mass-action law for the equilibrium fraction of FeB pairs.⁶ A simple transformation enables one to obtain the following expression for the total iron concentration:⁶

$$\begin{aligned} N(\text{Fe}_{\text{total}}) &= N(\text{Fe}_i^0) + N(\text{Fe}_i^+) + N(\text{FeB}) \\ &= 8.4 \times 10^{25} \times \exp(-2.86 \text{ eV}/k_B T) \\ &\quad \times \left\{ 1 + \frac{1}{2} \exp\left(\frac{E_T - E_F}{k_B T}\right) \right. \\ &\quad \times \left. \left[1 + \frac{4 \times N(B)}{5 \times 10^{22}} \exp\left(\frac{E_B}{k_B T}\right) \right] \right\}, \end{aligned} \quad (1)$$

where E_B is the binding energy of the FeB pairs (0.65 eV according to Kimerling and Benton⁷ and 0.58 eV according to Wijaranakula⁸), $N(B)$ is the concentration of boron acceptors in the sample, E_T is the position of the iron energy level in the band gap, and E_F is the position of the Fermi level. Equation (1) can be used to predict the segregation coefficient of iron in the p^+ substrate, provided the temperature dependence of the iron trap level E_T and the pairing constants of iron with boron E_B are known with sufficient accuracy.

The kinetics of p/p^+ gettering is determined by the diffusion coefficient of iron in the epilayer and in the substrate, which is determined by the effects of trapping of iron by the

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ionized boron.⁹ The effective diffusivity of iron in boron-doped materials was calculated from the following formula:

$$D^{\text{eff}} = f \times D^{\text{eff}}(\text{Fe}^+) + (1-f) \times D(\text{Fe}^0), \quad (2)$$

where f is the fraction of ionized iron. Using the same approach as was used in our recent study of the effective diffusivity of ionized copper in silicon,¹⁰ the effect of trapping of Fe_i^+ by boron on the effective diffusivity of iron is calculated as

$$D^{\text{eff}}(\text{Fe}_i^+) = \frac{D^{\text{int}}(\text{Fe}_i^+)}{1 + \tau_{\text{diss}} \times D^{\text{int}}(\text{Fe}_i^+) q^2 / \epsilon \epsilon_0 k_B T}, \quad (3)$$

where τ_{diss} is the dissociation time constant, q is the elementary charge, and ϵ and ϵ_0 are the dielectric constant of silicon and dielectric permittivity of vacuum, respectively. There have been various contradictory reports of values for $D(\text{Fe}^0)$ and $D^{\text{int}}(\text{Fe}^+)$. Istratov, Heislmaier, and Weber¹¹ showed that a single line could be fit through the literature data for both data points tentatively associated with diffusion of ionized iron, and associated with diffusion of neutral iron,

$$D = (1 \times 10^{-3}) \times \exp\left(\frac{-0.67 \text{ eV}}{kT}\right). \quad (4)$$

This can be considered as an indication that the difference in diffusivity of neutral and ionized iron, if it exists, is rather small (see Ref. 11 for a detailed discussion). In lieu of accurate expressions for the diffusivities of Fe_i^0 and Fe_i^+ , we used Eq. (4) for both $D_{\text{Fe}^+}^{\text{int}}$ and D_{Fe^0} in this study. According to the recent study of Heislmar *et al.*,⁶ the dissociation time constant is expressed as

$$\tau_{\text{diss}} = (9.35 \times 10^{-16}) \times \exp\left(\frac{1.40 \text{ eV}}{kT}\right). \quad (5)$$

While the physics of segregation gettering is well understood as mentioned above, its accurate modeling is hardly possible since the position of the iron donor level in the band gap below 1000 K is unknown.

While the segregation coefficient is defined as a simple ratio of iron concentrations in two adjacent layers, it is difficult to determine it experimentally since: (i) electrical measurement methods such as deep-level transient spectroscopy (DLTS) or surface photovoltage (SPV) cannot be used to determine iron concentrations in p^+ substrates; (ii) the kinetics of gettering, which is to a significant extent determined by the effective diffusion coefficient of iron in the p^+ , is not known, i.e., it is difficult to say how long one should wait for the equilibrium distribution of iron to be established; (iii) long anneals at intermediate temperatures may result in precipitation of supersaturated iron at oxygen precipitates in the p^+ substrate; the final distribution of iron will be determined by both segregation and relaxation effects; and (iv) we have to consider a possible effect of out-diffusion of iron to the surface of the epilayer rather than to the bulk, which may affect the results of the electrical measurements of iron concentrations in the epilayer. To avoid these effects, we measured the evolution of profiles of iron distribution in thick epilayers with the annealing time, which was kept reasonably short to avoid the relaxation gettering effect, and fitted the profiles using the gettering simulator.^{6,12} The narrowing of

the silicon band gap is significant at high temperatures and was taken into account in this study. Standard equations were used to determine the Fermi levels in the p and p^+ materials. The computer simulation was run for each of the five annealing temperatures (412, 460, 498, 540, and 580 °C) and the iron donor level was adjusted until a good match between the simulations and the experimental results was obtained.

The boron doping levels in the p layer and p^+ substrate were determined by spreading resistance measurements to be 9.0×10^{14} and $2.5 \times 10^{18} \text{ cm}^{-3}$, respectively. The thickness of the epilayer measured by spreading resistance analysis combined with bevel polishing of the wafer was $32 \pm 1 \text{ }\mu\text{m}$. Preliminary studies showed strong out-diffusion of iron to the surface of the wafer, unless the wafer was oxidized prior to anneals. Therefore, a 100 nm oxide was grown on the samples before iron diffusion to prevent out-diffusion of iron to the surface. The oxide was removed from the backside of the p^+ substrate using a plasma etch and iron was scratched on the bare backside. The samples were then annealed at a high temperature (1005 °C), where the segregation between the p and p^+ material is minimal, followed by a quench in silicone oil. Quench of the samples enabled us to “freeze in” the distribution of iron, whereby the concentrations of iron in the epilayer and in the substrate were equal to the equilibrium iron solubility at the diffusion temperature. These samples were then annealed at low temperatures of 412–580 °C, where segregation is significant for various times. The concentrations of iron in the epilayer were measured using deep-level transient spectroscopy. In order to obtain the depth profiles of iron, the samples were chemically etched several times and DLTS measurements were performed after each etching. In addition, the DLTS measurements were done with several choices of the reverse-bias voltages to obtain more minute depth profiles. Iron concentrations were determined carefully taking into account both the high trap concentration effect, which causes a nonexponential transient,¹³ and the lambda-point effect.¹⁴

The experimental results and computer simulations for annealing temperatures at 412 °C (685 K) and 580 °C (853 K) are shown in Figs. 1 and 2, respectively. The fits for the intermediate temperatures, 460, 498, and 540 °C, were similar. We found that the iron level position is almost temperature independent within uncertainties, and lies at $0.42 \pm 0.04 \text{ eV}$ from the valence-band edge. The uncertainty of 0.04 eV takes into account not only the uncertainties of our measurements and procedures, but also the possible effect of the inaccurate knowledge of the equilibrium binding energy of FeB pairs, E_B , and their dissociation energy E_D . To determine the possible effect of these two parameters on the calculated position of the iron donor level, we fitted our experimental profiles for the value of E_B varied from 0.65 eV (Ref. 7) to 0.58 eV,⁸ and for the value of E_D varied from 1.17 eV (Ref. 15) to 1.40 eV.⁶ The position of the iron donor level in the silicon band gap determined from the fits is presented in Fig. 3. The other reported values of the iron donor level are also plotted. The iron level does not keep increasing at lower temperatures, as one can extrapolate from the data of McHugo and co-workers^{2,3} and Gilles, Schröter, and Bergholz,⁴ rather it reaches a constant value. Although this

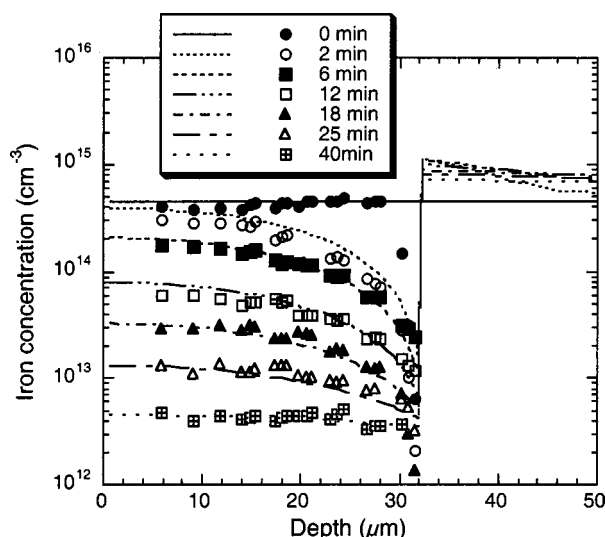


FIG. 1. Experimental data (symbols) and computer simulations (lines) of the iron concentration profiles in a p -type silicon epitaxial layer on a p^+ silicon substrate annealed at 412 °C.

value appears to be slightly higher than the low-temperature position of the iron level, $E_v + 0.38$ eV, the accuracy of our fits is not sufficient to conclude whether the iron level position remains constant with respect to the valence band edge at $T < 1000$ K, or if it slightly goes upwards to reach a maximum at 800 K. The determined position of the iron donor level corresponds to its segregation coefficient of 0.005 at 412 °C and 0.08 at 580 °C in p/p^+ structures with the substrate doping level, similar to that used in this study. These values were calculated using Eq. (1) and are consistent with the segregation coefficient obtained by simulations of quasi-infinitely long time anneals.

In conclusion, we have determined the temperature dependence of the iron donor level in crystalline silicon at

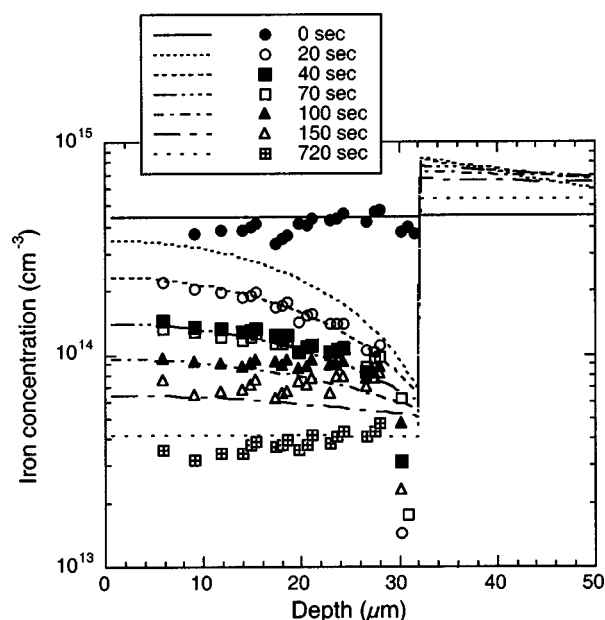


FIG. 2. Experimental data (symbols) and computer simulations (lines) of the iron concentration profiles in samples annealed at 580 °C.

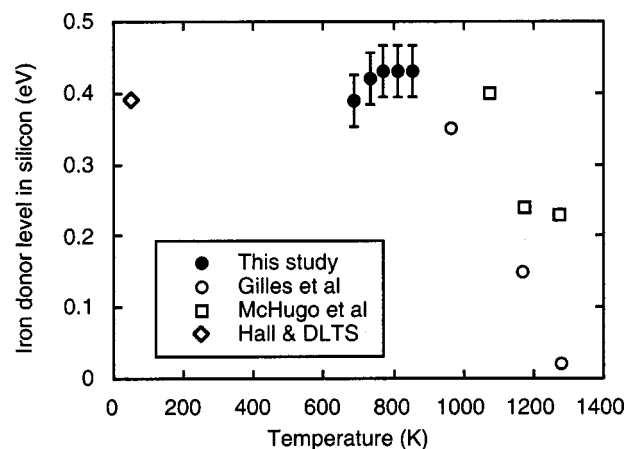


FIG. 3. Temperature dependence of the iron donor level in silicon (closed circles). The values reported by other authors are also plotted (open symbols).

412–580 °C (685–853 K) by fitting the iron concentration profiles in a p -type epitaxial layer on a p^+ -type substrate with the simulated profiles. The iron donor level was almost constant within error and was 0.42 ± 0.04 eV from the valence-band edge in the temperature range. With this temperature dependence of the iron donor level, the effective diffusivity and segregation behavior of iron in silicon can be simulated. Such simulations are useful in optimizing the semiconductor process to maximize gettering of iron.

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- ¹A. A. Istratov, H. Hieslmair, and E. R. Weber, Appl. Phys. A: Mater. Sci. Process. **70** (in press).
- ²S. A. Mchugo, R. J. McDonald, W. R. Smith, D. L. Hurley, and E. R. Weber, Appl. Phys. Lett. **73**, 1424 (1998).
- ³S. A. Mchugo, R. J. McDonald, W. R. Smith, D. L. Hurley, A. A. Istratov, H. Hieslmair, and E. R. Weber, in *Defect and Impurity Engineered Semiconductors and Devices II*, edited by S. Ashok, J. Chevallier, K. Sumino, B. L. Sopori, and W. Gots (Materials Research Society, Warrendale, PA, 1998), p. 361.
- ⁴D. Gilles, W. Schröter, and W. Bergholz, Phys. Rev. B **41**, 5770 (1990).
- ⁵E. R. Weber, Appl. Phys. A: Solids Surf. **30**, 1 (1983).
- ⁶H. Hieslmair, A. A. Istratov, C. Flink, S. A. Mchugo, and E. R. Weber, Physica B **273-274**, 441 (1999).
- ⁷L. C. Kimerling and J. L. Benton, Physica B & C **116**, 297 (1983).
- ⁸W. Wijaranakula, J. Electrochem. Soc. **140**, 275 (1993).
- ⁹H. Reiss, C. S. Fuller, and F. J. Morin, Bell Syst. Tech. J. **35**, 535 (1956).
- ¹⁰A. A. Istratov, C. Flink, H. Hieslmair, and E. R. Weber, Phys. Rev. Lett. **81**, 1243 (1998).
- ¹¹A. A. Istratov, H. Hieslmair, and E. R. Weber, Appl. Phys. A: Mater. Sci. Process. **69A**, 13 (1999).
- ¹²H. Hieslmair, Ph.D. thesis at University of California, Berkeley (1998).
- ¹³D. Stievenard, M. Lannoo, and J. C. Bourgoin, Solid-State Electron. **28**, 485 (1985).
- ¹⁴P. Blood and J. W. Orton, in *The Electrical Characterization of Semiconductors: Majority Carriers and Electron States*, edited by N. H. March (Academic, London, 1992), p. 358.
- ¹⁵F. Feichtinger, Acta Phys. Austriaca **51**, 161 (1979).