

## Diffusion and Isomer Shift of Interstitial Iron in Silicon Observed via In-Beam Mössbauer Spectroscopy

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Diffusion of interstitial iron in silicon could be observed on an atomic scale for the first time: Coulomb-excited  $^{57}\text{Fe}$  nuclei were implanted into high-purity *n*-type silicon and Mössbauer spectra were recorded at temperatures between 300 and 850 K. The diffusional broadening of one spectral component identified as interstitial Fe could be observed. The isomer shift of interstitial Fe in Si was determined and the assumption that one single mechanism is governing the diffusion of Fe in Si between 300 and 1500 K is confirmed.

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Studies of iron in silicon are always hampered by the low solubility of the  $3d$  transition metal in this semiconducting host. At temperatures as high as 1200 K the solubility is extremely low, about  $10^{14} \text{ cm}^{-3}$ .<sup>1</sup> On the other hand, there is considerable interest in the behavior of Fe in Si both experimentally and theoretically as documented, e.g., in Refs. 1–3. Iron is present even in as-grown material and its importance can be seen from the fact that already very small contaminations ( $\approx 10^{14} \text{ cm}^{-3}$ ) can reduce the efficiency of solar cells drastically.<sup>2</sup> Since the work of Ludwig and Woodbury<sup>4</sup> it has been assumed that Fe dissolves mainly interstitially in Si. In extensive calculations of the electronic structure of interstitial iron<sup>2,3</sup> ( $\text{Fe}_i$ ) good agreement between the observed and the calculated level structure could be achieved.

Diffusion of Fe in Si has been studied in two temperature regions: above 1350 K with radiotracer techniques ( $D \geq 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ ) and around room temperature with various techniques recording the disappearance of an Fe interstitial signal (obtained after quenching) due to diffusion of the Fe atoms from the supersaturated solution to available sinks ( $5 \times 10^{-14} \leq D \leq 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ ). Weber<sup>1</sup> examined the existing experimental data and connected the high- and low-temperature data with a straight line bridging a gap of 6 orders of magnitude thereby postulating that the mechanism of diffusion should be the same over the entire temperature range.

There is, however, no direct microscopic evidence of an interstitial diffusion mechanism available since the techniques applied so far only measure the result of a macroscopic transport process. In this paper we apply a Mössbauer technique in combination with Coulomb excitation and implantation which yields a microscopic view of iron diffusion in the mentioned temperature gap. A further important result is the unique determination of the isomer shift  $\delta$  of interstitial Fe in Si. Since  $\delta$  measures the electron density at the nucleus, this result is of importance for calculations of the electronic structure of Fe in Si.<sup>2</sup> Several earlier attempts to identify  $\delta$  of  $\text{Fe}_i$  in

Si, discussed in Refs. 5–9, gave contradictory results.

By Mössbauer spectroscopy (MS) the diffusion of the probe atoms can be observed microscopically. If a jump of the Mössbauer atom occurs during the lifetime of the excited state, the resonance broadens.<sup>10–12</sup> From the 140-ns lifetime of the 14.4-keV level of  $^{57}\text{Fe}$  one therefore obtains sensitivity for diffusion in the range  $D \sim 10^{-8} - 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ .

With a special technique, the in-beam MS, we succeeded in studying isolated Fe atoms in Si between 300 and 850 K. We observed the diffusion of one species of implanted Fe and present the derived diffusion coefficients. Based on those we can identify interstitial Fe and obtain the isomer shift of  $\text{Fe}_i$  in Si.

The technique of in-beam MS was introduced several years ago.<sup>13</sup> Two new setups have recently been developed using ion beams from heavy-ion accelerators and strongly improved detection systems, one at Hahn Meitner Institut (HMI), Berlin,<sup>14–16</sup> and one at Gesellschaft für Schwerionenforschung, Darmstadt.<sup>7,8</sup> A beam of fast heavy projectiles (e.g., Ar with an energy of 89 MeV) is scattered at a  $^{57}\text{Fe}$  foil. Whereas the unscattered primary beam does not hit the sample, scattered  $^{57}\text{Fe}$  nuclei are ejected from the target and implanted into the sample material. A fraction of the scattered nuclei are Coulomb excited and the 14.4-keV Mössbauer level is populated via the decay of higher-lying states. The resonant level then decays with its lifetime of 140 ns and the radiation emitted from the Fe nuclei implanted into the sample is observed.

This technique has several unique features. The deep implantation of the Fe ions (typically  $10 \text{ mg/cm}^2$ ) and a low total dose of  $10^{11}/\text{cm}^2$  leads to a small iron concentration in the range of  $10^{15}/\text{cm}^3$ . Thus, single, isolated Fe atoms are observed and since the decay of the excited nuclei is observed directly after implantation (within the lifetime of the nuclear level), there is no time for clustering or outdiffusion. Any material is accessible for the method, even if the solubility in the host is practically zero. On the other hand, it is not clear *a priori* what the

final lattice position of the implant will be and what influence one should expect from the damage cascade correlated with each implanted Fe atom.

The implanted samples were *n*-type, Czochralski-grown silicon, phosphorous doped, with a resistivity of 2 k $\Omega$  cm, and cut in the  $\langle 111 \rangle$  direction. Spectra were taken between 300 and 850 K at the VICKSI accelerator of HMI, Berlin. With the in-beam technique, implantation and measuring temperatures are identical. The Si samples were mounted in a halogen-lamp-heated oven, making temperatures up to 900 K accessible. The Mössbauer spectra have been taken with parallel-plate avalanche counters with one electrode made from stainless steel, enriched with  $^{57}\text{Fe}$ .

Our data have been analyzed with two single lines and one doublet. The selection of these components was mainly suggested by the development of the shape of the spectra with temperature, but also motivated by former work. The dominating doublet in our spectra appears also in former experiments where low-energy implantation at rather high dose was applied to dope Si with  $^{57}\text{Fe}$  or  $^{57}\text{Co}$ .<sup>17,18</sup> The authors assign the doublet to Fe atoms residing in a strongly damaged environment. The two additional single lines present in our work, which have also been seen by various other experimenters, could so far not conclusively be assigned to definite lattice sites in Si. A recent suggestive assignment by Langouche and de Potter<sup>6</sup> is in agreement with our lattice-position assignment discussed below. Before we discuss our data, it should be mentioned that Fe in Si has also been investigated with the in-beam technique by Latshaw, Russel, and Hanna.<sup>19</sup> Their data are, in general, in agreement with ours; however, they have less statistical accuracy and were not analyzed with a diffusion *Ansatz*.

All of our Mössbauer spectra have the overall shape of asymmetric doublets which change continuously in shape from 300 to 850 K (see Fig. 1). Some additional data taken below 300 K down to 20 K show only minor variations of the spectral shape and will not be discussed here (see Refs. 7 and 20). However, at temperatures above 300 K the changes are remarkable. Up to 570 K the spectra can be fitted with two components, one single line (SL I) and a superimposed symmetric doublet. Raising the temperature further, the linewidth of SL I increases. At 650 K the asymmetry of the whole spectrum is reversed and a second single line (SL II) has taken over an appreciable portion of the spectrum. At 750 K, SL I has disappeared and SL II dominates at 850 K. Whereas all isomer shifts as a function of temperature can be described by the second-order Doppler shift (SOD), the quadrupole splitting and linewidth of the doublet do not show a systematic trend with temperature.

Most important is the increase of the linewidth of SL I as a manifestation of a diffusion process. The connection between line broadening  $\Delta\Gamma$  in a Mössbauer spectrum and the diffusion coefficient was first given by Singwi and

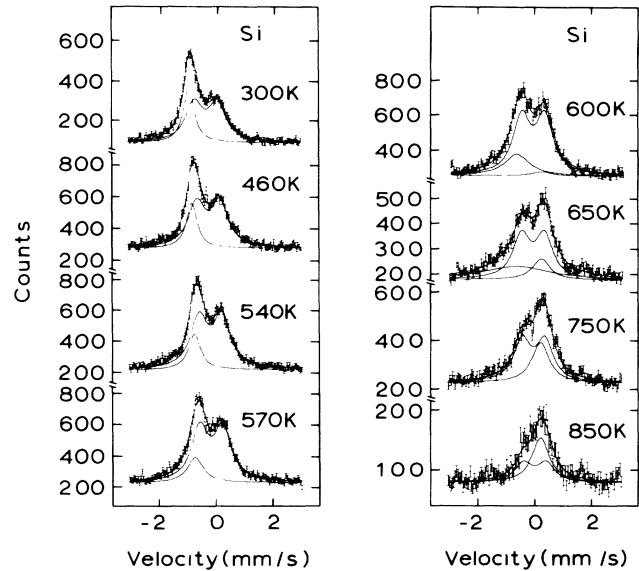


FIG. 1. Mössbauer spectra of Fe implanted into Si between 300 and 850 K. Solid lines result from a simultaneous fit. Linewidth  $\Gamma$ , isomer shift  $\delta$ , quadrupole splitting  $E_Q$  (all in mm/s) at 300 K: SL I,  $\delta = +0.84(1)$ ,  $\Gamma = 0.48(1)$ ; doublet,  $E_Q = 0.83(1)$ ,  $\delta = +0.23(1)$ ,  $\Gamma = 0.74(2)$ . SL II at 750 K:  $\delta = -0.27(1)$ ,  $\Gamma = 0.80(1)$ . Isomer shifts are given relative to  $\alpha$ -Fe.

Sjölander.<sup>10</sup> Assuming that diffusion consists of thermally activated consecutive jumps of an atom from one lattice position to an equivalent one, they calculated the increase of the linewidth for a polycrystalline sample to be

$$\Delta\Gamma = 12\hbar D l^{-2}, \quad (1)$$

where  $l$  is the elementary jump length and  $D$  is the diffusion coefficient which normally follows an Arrhenius law  $D = D_0 \exp(-E_a/kT)$  with activation energy  $E_a$  and Boltzmann's constant  $k$ . Equation (1) gives  $\Delta\Gamma$  for the simplest diffusion mechanism where the atom performs a random walk through the lattice without correlation between successive jumps. Diffusion by a purely interstitial mechanism, where the atom jumps from one interstitial site to one of the nearest-neighbor interstitial sites, should fulfill this condition. The diffusional width  $\Delta\Gamma$  observed from a single-crystal sample depends on the angle of emission of the  $\gamma$  ray relative to the jump vector and is not exactly of Lorentzian shape.<sup>11</sup> However, integration over the solid angle covered by our detectors and folding with emission and absorption Lorentzians shows that the expected deviations from the isotropic approximation and the Lorentzian shape are negligible in our case. Thus, Eq. (1) should be appropriate to describe the increase in linewidth.

In Fig. 2 the solid diamonds denote the linewidth of SL I as it results from individual fits to each spectrum discussed so far and the solid line represents Weber's<sup>1</sup> interpolation. To calculate  $\Delta\Gamma$  from his diffusion constants we have used a jump length of  $l = 2.35 \text{ \AA}$ , which in

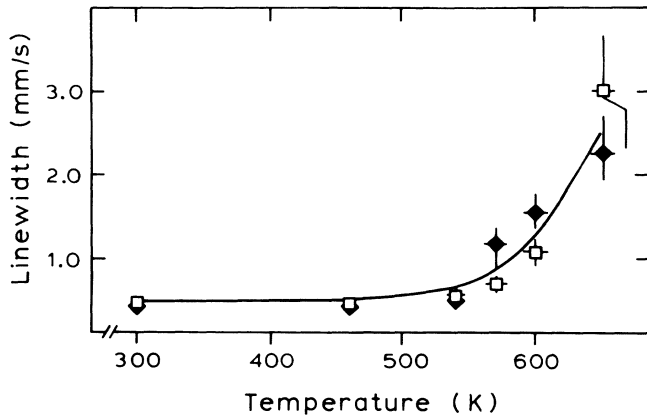


FIG. 2. Linewidth of single line I.  $\blacklozenge$ , from individual fits;  $\square$ , from simultaneous fit; solid line, Weber's interpolation.

the Si lattice is the distance between tetrahedral interstitial positions.

To check the data evaluation for systematic errors we used a second type of fitting procedure in a way that a simultaneous fit to all data was performed with temperature-independent parameters for the quadrupole splitting and for the linewidths of the doublet and SL II. Isomer shifts of all three components were allowed to develop with temperature according to SOS. The linewidth of SL I was permitted to vary with temperature according to an Arrhenius behavior with  $E_a$  and  $D_0$  as fit parameters. The results of this procedure agree with the evaluation of the individual spectra. Figure 1 shows the data and the components as found with the simultaneous fit. In Fig. 2 the open squares denote the resulting line broadening. The broadenings according to the individual fits and the common fit agree within errors, although there seems to be a systematic trend in the deviations. These differences could be due to a correlation of the linewidth with a shift in line position slightly stronger with temperature than that according to SOD. This additional shift, indicated by the results from the individual fits, would correspond to an increase in the electron density  $|\Psi(0)|^2$ , e.g., caused by an increasing delocalization of iron  $3d$  electrons with temperature; see below. More details are discussed in Ref. 21.

In Fig. 3 we show an Arrhenius plot with the data compiled by Weber, his interpolation, and our results from both fitting procedures. The resulting diffusion coefficients agree very well with Weber's picture. Thus, it can be stated from our results that the diffusion mechanism of Fe in Si is the same over the entire temperature range; otherwise it would be very unlikely to find an agreement between the measured and interpolated diffusion coefficients.

Since it is widely accepted that the diffusion mechanism of Fe in Si is interstitial, we can conclude that SL I represents atoms on interstitial sites. As no quadrupole splitting is observable, our result is compatible with the generally accepted assignment of  $Fe_i$  to the tetrahedral

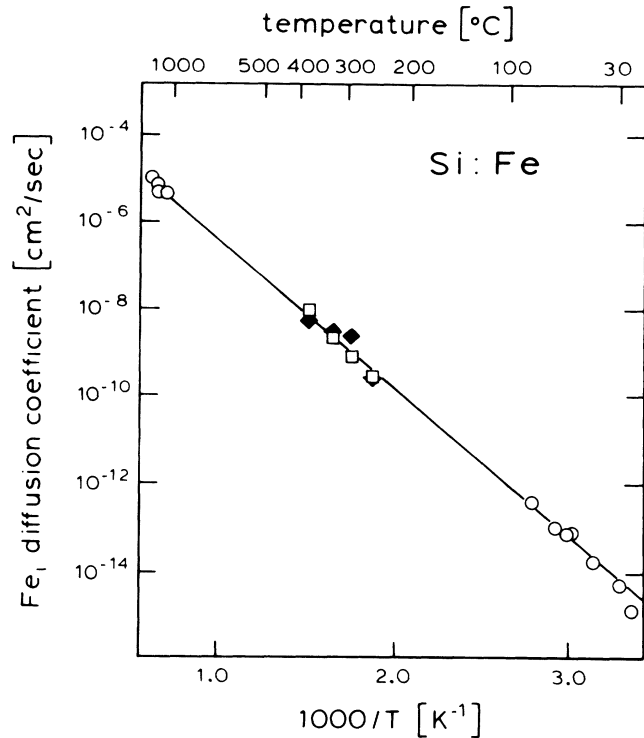


FIG. 3. Diffusion coefficients of Fe in Si.  $\circ$ , as cited in Ref. 1;  $\blacklozenge$ , from individual fits;  $\square$ , from simultaneous fit.

interstitial site. A small symmetry distortion, however, cannot be ruled out by our data, since the experimental linewidth at low temperatures is 50% larger than expected for an unsplit line of natural width. Based on this conclusion we can definitely assign the isomer shift of this component,  $\delta(\text{SL I, 300 K}) = +0.84(2)$  mm/s, to  $Fe_i$ .

The isomer shift by itself gives a strong clue to identify Fe atoms on interstitial positions. It is by far more positive than commonly encountered for Fe in elemental hosts<sup>22</sup> or in Fe/Co-Si alloys and corresponds to an unusually low electron density  $|\Psi(0)|^2$ . Such a low  $|\Psi(0)|^2$  can actually be expected for  $Fe_i$  in Si since in Ref. 4 an electron configuration  $3d^8$  was assigned to  $Fe_i^0$  in Si, supported later experimentally; see, e.g., Ref. 23 and theoretically Ref. 2. Because of the absence of  $4s$  electrons and strong shielding of  $3s$  electrons from the core, a  $3d^8$  configuration results in a low  $|\Psi(0)|^2$  and consequently a large positive  $\delta$ , which can be estimated as  $\delta > 2$  mm/s.<sup>24</sup> This is much larger than our experimental value, but delocalization of  $3d$  electrons can reduce the  $3s$  shielding and  $\delta$  as well. The calculations of Ref. 2 resulted in such a delocalization of  $\sim 30\%$ , in order to reproduce the experimental value of the magnetic hyperfine field. These rather qualitative arguments support our interpretation of SL I as due to  $Fe_i$ .<sup>25</sup> In Ref. 2, calculated differences of  $\delta$  between interstitial Fe in  $n$ -type and  $p$ -type Si were compared with experimental results of studies in which the assignment of the com-

ponents was quite uncertain due to the occurrence of Co complexes in the samples. The present study is free of such ambiguities.

Some more results can be obtained from the data.

*Site population.*—SL I represents  $\sim 30\%$  of the total resonance area in our spectra. Neglecting slight effects due to different recoil-free fractions, we can conclude that we implant roughly 30% of the Fe atoms into interstitial sites. Correlated defects, produced in the slowing down process of the Fe atom, do not influence the diffusion properties of these atoms within the accuracy of our data. Thus, we conclude that the large majority of interstitially implanted Fe atoms do not encounter a lattice defect within up to  $\sim 15$  jumps at highest temperatures.

*Doublet and SL II.*—The doublet represents about 70% of the area of the spectra below 600 K. At 600 and 650 K the sum of SL II and the doublet remain at this proportion. Whether below 600 K SL II is populated or not cannot be decided from the spectra. From 600 to 850 K, the area of SL II increases relative to that of the doublet, suggesting that the latter relaxes into SL II or that SL II is preferentially populated. To test the relaxation hypothesis we tried a simultaneous fitting procedure to all the spectra, assuming that the doublet represents a metastable state, decaying into the ground-state SL II, and that SL II is not primarily populated. Theoretical line shapes for relaxation spectra were used.<sup>26,27</sup> Assuming a thermally activated process, the reciprocal lifetime of the excited state was allowed to vary according to an Arrhenius behavior:  $\tau^{-1} = \tau_0^{-1} \times \exp(-E_a/kT)$ . This model describes the data equally well. The result for SL I remained the same within errors; in particular, the line broadenings agreed with the former analysis. For the decay of the doublet into the single line SL II we found  $E_a = 0.47(7)$  eV and  $\tau_0 = 7 \pm 2 \times 10^{-11}$  s.

As mentioned above, the quadrupole-split doublet represents Fe atoms in a strongly perturbed environment. An annealing process with an activation energy of 0.47 eV might transform these atoms from the perturbed into an unperturbed position; SL II might belong to a substitutional lattice position. A similar activation energy has, for example, been assigned to the migration energy of a neutral vacancy  $V^0$  [0.45(4) eV (Ref. 28)]; however, assigning a definite annealing process to our data remains speculative.

With time-differential MS it is, in principle, possible to distinguish dynamic annealing from a change in the implantation conditions. The technique is discussed in Refs. 7, 9, and 27. All the spectra shown have been taken time differentially, but the statistical quality of the data is not sufficient to distinguish between the two cases. This investigation will be a subject of further research.

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- <sup>1</sup>E. R. Weber, *Appl. Phys. A* **30**, 1 (1983).
- <sup>2</sup>H. Katayama-Yoshida and A. Zunger, *Phys. Rev. B* **31**, 7877 (1985).
- <sup>3</sup>F. Beeler, O. K. Andersen, and M. Scheffler, *Phys. Rev. Lett.* **55**, 1498 (1985).
- <sup>4</sup>G. W. Ludwig and H. H. Woodbury, *Solid State Phys.* **13**, 223 (1962).
- <sup>5</sup>A. R. Regel and P. P. Seregin, *Fiz. Tekh. Poluprovodn.* **18**, 1153 (1984) [*Sov. Phys. Semicond.* **18**, 723 (1984)].
- <sup>6</sup>G. Langouche and M. de Potter, *Nucl. Instrum. Methods Phys. Res., Sect. B* **19/20**, 322 (1987).
- <sup>7</sup>S. Laubach, P. Schwalbach, M. Hartick, E. Kankleit, G. Klingelhöfer, and R. Sielemann, *Z. Phys. B* **75**, 173 (1989).
- <sup>8</sup>P. Schwalbach, in *Proceedings of the Twenty-Fourth Zakopane School on Physics, 1989*, edited by J. Stanek and A. T. Pedziwiatr (World Scientific, Singapore, 1990), Vol. 2.
- <sup>9</sup>S. Laubach, P. Schwalbach, M. Hartick, E. Kankleit, B. Keck, and R. Sielemann, *Hyperfine Interact.* (to be published).
- <sup>10</sup>K. S. Singwi and A. Sjölander, *Phys. Rev.* **120**, 1093 (1960).
- <sup>11</sup>P. A. Flinn, in *Applications of Mössbauer Spectroscopy*, edited by R. L. Cohen (Academic, New York, 1980), Vol. 2.
- <sup>12</sup>W. Petry and G. Vogl, *Mat. Sci. Forum* **15-18**, 323 (1987).
- <sup>13</sup>G. D. Sprouse, G. M. Kalvius, and F. E. Obenshain, in *Mössbauer Effect Methodology*, edited by I. J. Gruverman (Plenum, New York, 1968), Vol. 4.
- <sup>14</sup>M. Menningen, R. Sielemann, G. Vogl, Y. Yoshida, K. Bonde-Nielsen, and G. Weyer, *Europhys. Lett.* **3**, 927 (1987).
- <sup>15</sup>Y. Yoshida, M. Menningen, R. Sielemann, G. Vogl, G. Weyer, and K. Schröder, *Phys. Rev. Lett.* **61**, 195 (1988).
- <sup>16</sup>Y. Yoshida, *Hyperfine Interact.* **47**, 95 (1989).
- <sup>17</sup>G. Langouche, I. Dézsi, M. van Rossum, J. de Bruyn, and R. Coussement, *Phys. Status Solidi (b)* **89**, K17 (1978).
- <sup>18</sup>B. D. Sawicka and J. A. Sawicki, *Phys. Lett.* **64A**, 311 (1977).
- <sup>19</sup>G. L. Latshaw, P. B. Russel, and S. S. Hanna, *Hyperfine Interact.* **8**, 105 (1980).
- <sup>20</sup>P. Schwalbach, M. Hartick, U. Imkeller, E. Kankleit, S. Laubach, M. Menningen, and R. Sielemann, *Hyperfine Interact.* **47**, 573 (1989).
- <sup>21</sup>P. Schwalbach, Ph.D. thesis, Technische Hochschule Darmstadt (unpublished).
- <sup>22</sup>I. Dézsi, U. Gonser, and G. Langouche, *Phys. Rev. Lett.* **62**, 1659 (1989).
- <sup>23</sup>S. Greulich-Weber, J. R. Niklas, E. R. Weber, and J. M. Spaeth, *Phys. Rev. B* **30**, 6292 (1984).
- <sup>24</sup>M. Van der Heyden, H. Micklitz, S. Bukshpan, and G. Langouche, *Phys. Rev. B* **36**, 38 (1987).
- <sup>25</sup>Note added: Results of  $|\Psi(0)|^2$  calculations for Fe in Si agree with this interpretation; J. Kübler (private communication).
- <sup>26</sup>E. Kankleit, *Z. Phys. A* **275**, 119 (1975).
- <sup>27</sup>S. Laubach, Ph.D. thesis, Technische Hochschule Darmstadt, 1989 (unpublished).
- <sup>28</sup>G. Watkins, in *Deep Centers in Semiconductors*, edited by S. T. Pantelides (Gordon and Breach, New York, 1986).