

Acceleration of Diffusional Jumps of Interstitial Fe with Increasing Ge Concentration in $\text{Si}_{1-x}\text{Ge}_x$ Alloys Observed by Mössbauer Spectroscopy

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Abstract. Radioactive ^{57}Mn isotopes have been implanted into $\text{Si}_{1-x}\text{Ge}_x$ crystals ($x \leq 0.1$) at elevated temperatures for Mössbauer studies of the diffusion of interstitial ^{57}Fe daughter atoms. The atomic jump frequency is found to increase upon Ge alloying. This is attributed to a lowering of the activation energy, i.e. the saddle point energy at hexagonal interstitial sites with Ge neighbour atoms.

Key Words: diffusion, Fe impurities, Mössbauer spectroscopy, SiGe.

1. Introduction

The diffusion of interstitial iron, Fe_i , in silicon is well investigated experimentally and diffusion coefficients determined, respectively, from long-range diffusion measurements by various techniques [1] and from atomic jump frequencies measured by Mössbauer spectroscopy [2] are in good agreement for both charge states of interstitial $\text{Fe}_i^{0/+}$. The diffusion of Fe_i^+ is faster by about an order of magnitude than that of Fe_i^0 at low temperatures. The diffusion mechanism is purely interstitial, i.e. atomic jumps between tetrahedral interstitial sites with the hexagonal site as the saddle point, which thus leads to an uncorrelated random walk. It is interesting to note that for the series of interstitial 3d elements in silicon theory predicts a change of the most stable site from a tetrahedral site for the early elements up to Fe_i to a hexagonal site for the late elements Co, Ni and Cu, the fastest diffusing elements in the series [3]. In this contribution we show that alloying of Ge increases the jump frequency of Fe_i in $\text{Si}_{1-x}\text{Ge}_x$, whereas the

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long-range diffusivity is apparently not affected [4] for $x < 0.1$. Semiconducting $\text{Si}_{1-x}\text{Ge}_x$, an almost ideal random alloy, may be of interest as a system of particular simplicity to study the alloying effect on interstitially diffusing impurities [4] and interstitial 3d elements and Fe in particular are important, mostly harmful impurities in silicon-based technologies.

2. Experimental

The experiments have been performed at the ISOLDE facility at CERN utilizing the isotopically clean and intense beams of radioactive $^{57}\text{Mn}^+$ ions ($T_{1/2} = 1.5$ min). These were implanted with 60 keV energy to fluences $< 10^{12}/\text{cm}^2$ into SiGe single crystals heated to temperatures < 1000 K by means of a halogen lamp. Mössbauer spectra for the 14 keV transition of the ^{57}Fe daughter atoms were recorded by resonance detectors (equipped with ^{57}Fe enriched electrodes) mounted on conventional drive systems outside the implantation chamber. All $\text{Si}_{1-x}\text{Ge}_x$ ($x \leq 0.1$) samples were n-type material (P or Sb concentrations $10^{16-17} \text{ cm}^{-3}$), epitaxially grown on silicon; a pure silicon n-type reference sample was also employed.

3. Results and discussion

The radiation damage due to the implantation is known to anneal during the lifetime of ^{57}Mn at temperatures > 500 K in silicon and leads to their substitutional incorporation [5]. This was also observed for the SiGe samples. An average recoil energy of 40 eV in the nuclear decay expels the majority of the ^{57}Fe daughter atoms into tetrahedral interstitial sites. Thus diffusional jumps of the interstitial $^{57}\text{Fe}_i$ during the lifetime of the Mössbauer state ($T_{1/2} = 100$ ns) can be detected by the resulting line broadening $\Delta\Gamma$, which is directly proportional to the jump frequency ν [6]. In velocity units this is $\Delta\Gamma = 2\hbar c\nu/E_0$ with E_0 the transition energy, \hbar Planck's constant and c the velocity of light. For a purely random walk the jump frequency is related to the diffusion coefficient D by $\nu = 6D/l^2$ with l the jump length.

Spectra measured at different temperatures and for two Ge concentrations are compared to those for pure silicon in Figure 1 and the analysis in terms of three spectral components is indicated: two single lines for substitutional Fe_S and interstitial Fe_i^0 on tetrahedral sites, respectively, and a quadrupole-split, broadened line attributed to the formation of $\text{Fe}_i\text{-V}$ pairs with the vacancy created in the recoil event at high temperatures [7]. As the intensity of the latter line is rather low at the temperatures of interest here, the quadrupole splitting and its $T^{3/2}$ temperature dependence were fixed in the simultaneous analysis of all data for a given sample to the values established for silicon at higher temperatures [7]. Both the line width and the spectral area of all components were free parameters, whereas the isomer shifts (IS) were constrained to follow the second order Doppler shift (SOD). (To ease the comparison of the spectra, in

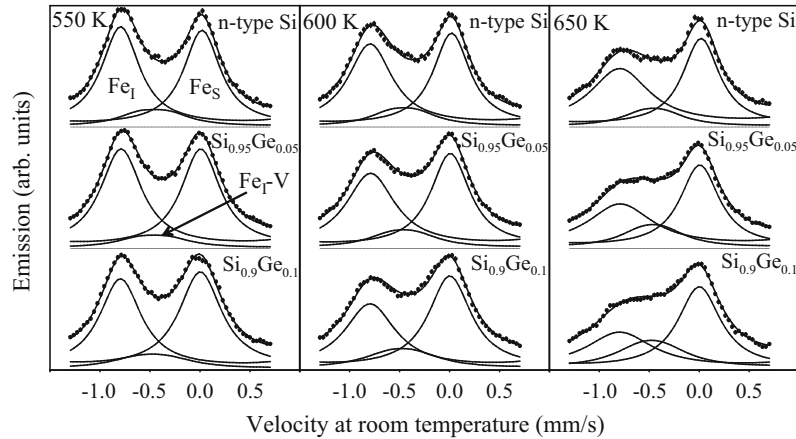


Figure 1. ^{57}Fe Mössbauer spectra obtained after implantation of ^{57}Mn into the Si and SiGe samples held at the temperatures indicated. The *solid lines* show individual fitting components and their sum.

Figure 1 the SOD has been corrected for thus that the velocity scale refers to room temperature and the sextet spectra resulting from the magnetic splitting in the detector have been transformed into a single emission feature). This analysis then gave IS values at room temperature for the Fe_i^0 and $\text{Fe}_i\text{-V}$ components, which deviated no more than within the error margins from those for pure silicon [7] or germanium [8], which are also very similar for these components. The isomer shift for substitutional Fe_S increased slightly with increasing Ge concentration as would be expected from the difference in the values for pure germanium and silicon; the uncertainties on these values and the restricted Ge concentrations do not allow to deduce a functional dependence. These fits to the data, although not perfect yet as can be seen in Figure 1 by small, apparently systematic deviations, are nevertheless sufficient to extract the line broadening of the interstitial line at high temperatures. In fact, it appears visible directly in the spectra at 600 and 650 K that the broadening increases with increasing Ge concentration for a given temperature. The line broadening extracted from the analysis is plotted as a function of temperature in Figure 2(A) for the samples in this study. Obviously, the broadening is generally more pronounced for the SiGe samples than for pure silicon at a given temperature, however, relatively large error bars and the restricted temperature range, 550–650 K, where significant broadening is detectable and the intensity of the $\text{Fe}_i\text{-V}$ line is sufficiently small not to affect the results, make difficult the deduction of a functional dependence of the broadening on both temperature and Ge concentration. For a given sample, the jump frequency is assumed to obey the usual diffusion coefficient equation resulting in a temperature dependence of the broadening given by $\Delta\Gamma = \alpha \exp(-E_a / kT)$, where α is a proportionality constant, E_a the (constant) diffusion activation energy and k Boltzmann's constant. As discussed in detail in [2] due to the limitations given above, it is not

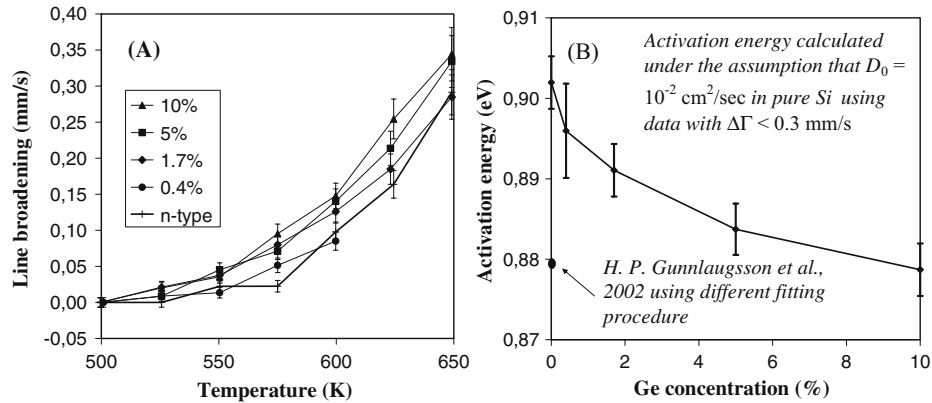


Figure 2. (A) Line broadening of the Fe_i line for the different SiGe samples in this study versus temperature. (B) Activation energy versus Ge concentration obtained from the analysis of the data in (A), assuming a constant pre-exponential factor corresponding to $D_0 = 10^{-2} \text{ cm}^2/\text{s}$.

possible to determine both α and E_a from a fit to the data with meaningful accuracy. Therefore, in fits the pre-exponential factor was kept constant and equal to that for Fe_i^0 in silicon [7] in order to reveal a possible Ge concentration dependent trend for E_a . As discussed below, thus determined E_a values should be considered as upper limits with unknown deviations from the true values; these deviations should, however, increase with increasing Ge concentration. Figure 2(B) shows the results from this analysis: a clear trend for a decrease of the activation energy with increasing Ge concentration. Note, as indicated in Figure 2(B), that results for Fe_i^0 in silicon from a different analysis model [2] give slightly different absolute values for E_a , however, the trend is robust. Thus the lowering of the activation energy contributes substantially to the increase of the jump frequency with increasing Ge concentration.

As this increase of the jump frequency is much smaller than the difference in jump frequencies for Fe_i^+ and Fe_i^0 , we first consider the possibility of a mixture in charge states. The Fe_i donor level is known to approach the valence band with increasing Ge concentration and the band gap shrinks [4]. In view of the illumination of the samples, the band gap shrinkage and the almost constant doping levels of the samples it is therefore likely that a mixture in charge states would tend to more neutral Fe_i with increasing Ge concentration. However, this would result in an effect on the jump frequency opposite to that observed. For positively charged Fe_i^+ no change in the diffusion coefficient has been measured up to $x \sim 0.1$ [4], however, the relative increase detected here for Fe_i^0 if transferred to Fe_i^+ would be within the error margins of those measurements. We thus consider a change in the diffusion mechanism. In the tetrahedral interstitial site in silicon the Fe_i atoms are surrounded by 10 atoms forming four puckered, six-membered rings with the hexagonal site in the center. Depending on its nearest or next-nearest location to a tetrahedral site, a Ge impurity atoms among the 10 atoms would be member of three or two of these rings. A decrease of the

Fe_i energy in such a hexagonal saddle point configuration then corresponds to a decrease of the activation energy and would explain an increase in the jump frequency for such a direction. As a further consequence, the Fe_i atoms can no longer be considered to perform a truly random walk. After an elementary jump via a hexagonal site with one Ge neighbour atom, this same site is available again and thus a return jump more probable than jumps in other directions, giving rise to a (pre-exponential) correlation factor $f < 1$ and such jumps do not contribute to the long-range diffusion for sufficiently small Ge concentrations. Also entropy changes due to alloying tend to decrease the pre-exponential factor. A more detailed discussion of the atomic jumps in such a model will be postponed to a forthcoming publication, however, evidently it offers an attractive, qualitative explanation for the measured effect, which should also show up in the macroscopic diffusion at higher Ge concentrations. In the measurements the recoiling Fe atoms may be assumed to be randomly distributed on tetrahedral sites with a statistical probability of having randomly distributed Ge atoms among the mentioned 10 atoms. As an ensemble average is measured to determine the line broadening, the concluded lowering of the activation energy on an atomic level should be more substantial than is apparent from Figure 2(B).

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