^{57}Fe diffusion in n-type Si after GeV implantation of ^{57}Mn

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Abstract

At the RI-beam facility of the RIKEN, $^{57}\text{Mn}/^{57}\text{Fe}$ isotopes are separated and implanted into n-type FZ-Si ($6 \times 10^{16} \text{ As/cm}^3$), and subsequently the atomic jump processes of ^{57}Fe in the Si matrix are observed by Mössbauer spectroscopy on a time scale of 100 ns between 330 and 1200 K. The spectra consist of two components due to “interstitial Fe” and “substitutional Fe”, both of which yield the same isomer shifts as those reported in p-type Si, showing long-range diffusion with increasing temperature. The spectra are compared with those simulated from a theoretical model.

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1. Introduction

Dilute systems of iron in silicon crystals have been intensively investigated for more than 50 years by different experimental techniques [1–3], including ^{57}Fe Mössbauer spectroscopy [4–7]. However, there remains many unsolved problems [3], such as lattice sites and charge states, and therefore, the basic research on “iron in silicon” appears to be still one of the most important issues in solid-state physics and its related applications. Generally iron atoms are thought to occupy only interstitial sites in silicon leading to a fast diffusion. Substitutional iron atoms were not found experimentally by standard evaluation techniques, although Mössbauer spectroscopy often found a “substitutional Fe component” after implantation [4–6] and also after diffusion annealing [7]. Usually, iron atoms were introduced into Si matrix by diffusion annealing and quenching processes from high temperatures. The nature of Fe impurities were then evaluated at low temperature in such samples, which must contain differently distributed and/or clustered iron atoms.

Accordingly, in order to clarify the problems on the charge states of Fe and their diffusion processes, we inevitably need a new experimental method, which provides isolated Fe atoms in Si even up to high temperatures. Recently, we have developed such an in situ experimental method, by which we could measure $^{57}\text{Mn}/^{57}\text{Fe}$ Mössbauer spectra in p-type Si between 300 and 800 K [8]: The spectra consist of two singlets below 700 K, changing to one singlet between 700 and 800 K. The isomer shifts of the singlets at 300 K are 0.809(13) and $-0.042(38) \text{ mm/s}$, which refer to the value of $\alpha\text{-Fe}$ at room temperature. These components can be assigned to interstitial and substitutional Fe, respectively. Above 600 K, the interstitial component disappears, and simultaneously the center shifts show relaxation effects. These dynamical behaviors could be interpreted to be due to the jumping process of interstitial Fe atoms into vacancies.

The present investigation is specially designed to introduce isolated Fe atoms in Si matrix and immediately to observe the diffusion process of Fe atoms by Mössbauer spectroscopy at the temperatures between 300 and 1200 K. Accordingly, the diffusion processes of the iron atoms can be directly observed at high temperatures on an atomistic scale, in order to clarify the impurity diffusion of Fe atoms

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and the formation processes of “substitutional Fe atoms” in Si at high temperatures.

2. Experimental procedure

^{57}Mn nuclei were produced by a nuclear projectile fragmentation of a $^{58}\text{Fe}^{21+}$ primary beam ($E = 63 \text{ MeV/nucleon}$) with a Be target, and separated by an on-line isotope separator, RIPS [9]. Subsequently, ^{57}Mn were implanted into a Si sample, and Mössbauer spectra of ^{57}Fe were measured immediately after the β -decay of the radioactive isotope of ^{57}Mn ($\tau_{1/2} = 1.45 \text{ m}$). The total fluence of ^{57}Mn was $2 \times 10^{12} \text{ }^{57}\text{Mn/cm}^2$ typically for one spectrum. ^{57}Mn nuclei were implanted into sample through a Ta collimator with a diameter of 20 mm.

In the present experiment, an n-type float-zone Si wafer ($6 \times 10^{18} \text{ As/cm}^3$) with a thickness of $600 \mu\text{m}$ was used and cut into a square plate of $40 \times 40 \text{ mm}^2$. The Si sample was fixed in a Ta holder, and was set 45° against the beam direction. The holder was covered by cylindrical Ta heat shields with two Zr thin foil, and the vacuum chamber has a Be window on a conflat flange for the detection of γ -radiation. The maximum temperature was 1200 K achieved by a PBN heater plate of $45 \times 45 \text{ mm}^2$ attached to the Ta holder. The measurement of Mössbauer spectrum was started at 600 K, and was subsequently performed at 800, 1000, 1100, and 1200 K. The specimen temperature was then decreased, and the spectra were measured at 900, 700, 650, 500, 400, and finally 330 K. The vacuum in the chamber was kept better than that of 10^{-5} Pa . Using a ^{57}Fe -enriched stainless-steel absorber, 14.4 keV γ -rays were detected through a 200- μm -thick Be window by a parallel-plate avalanche counter. The detector was mounted on a Mössbauer driver.

3. Results and discussion

Typical Mössbauer spectra of ^{57}Fe in n-type FZ-Si in the temperature region between 330 and 1200 K are shown in Fig. 1. The spectra from 300 to 700 K can be fitted by two singlets of Lorentzians, while the spectra from 800 up to 1200 K can be analyzed only by a broad singlet. The two singlets at 330 K at the left- and the right-hand site have been assigned to ^{57}Fe atoms on interstitial and substitutional sites in Si matrix, respectively. This assignment is based on a theoretical calculation of the isomer shifts [10], which relate with the charge density at ^{57}Fe nucleus. The spectra and their fitting parameters are changing anomalously with elevating temperature. These behaviors are, at the first glance, in good agreement with the former experiments on p-type FZ-Si wafers up to 800 K [8]. The resonance area of the interstitial ^{57}Fe component at the left-hand side decreases strongly above 500 K.

A “peak position of a component” in the Doppler velocity scale provides us information both on the different lattice sites of ^{57}Fe atoms and their charge states. This shift is called “center shift”, depending on the isomer shift and

Fig. 1. Mössbauer spectra of ^{57}Fe in n-type FZ-Si measured between 330 and 1200 K. Notice that the vertical scale for the region above 900 K is blown up with a factor of 2, in order to show the small and broad resonance effects more clearly.

the second-order Doppler (SOD) shift. As a reference, the broken line in Fig. 1 shows the usual temperature dependence of a spectrum component due to the SOD shift. Both the interstitial and the substitutional components, however, do not simply follow the SOD shift. The center shift of the interstitial component deviates from the SOD shift, moving continuously to the substitutional position with increasing temperature. This anomaly is accompanied with the strong decrease of the resonance area. Furthermore, the center shifts of the substitutional singlet between 800 and 1000 K are different from the extrapolation of the center shift, but above 1100 K the shift goes back to the position of the substitutional again. This is an essential observation to interpret the whole dynamical phenomena, which will be discussed later.

In Fig. 2 the total resonance area is plotted as a function of temperature. The total area decreases up to 800 K with increasing temperature, as usually expected from a Debye model with a Debye temperature of 260 K. The total area, however, suddenly decreases at 900 and 1000 K, but increases again at 1100 and 1200 K. This means that more than 50% of the total number of ^{57}Fe atoms is missing in the spectra at 900 and 1000 K. This sudden decrease of the

Fig. 2. Total resonance area as a function of temperature. The line corresponds to a Debye model with $\Theta_D = 260$ K.

area can be clearly seen in the spectra in Fig. 1. In addition, the line width of the singlet increases with increasing temperature. These observations indicate clearly that the ^{57}Fe atoms are jumping within the lifetime of the 14.4 keV nuclear excited state, i.e., 100 ns, leading to a line width which is too broad to be seen as a Lorentz emission line. Furthermore, the area recovery above 1100 K suggests that the jump frequency of the ^{57}Fe atoms is suppressed due to a certain recombination reaction, such as the interstitial ^{57}Fe atoms jumping into vacancies.

The line widths of the interstitial and substitutional components increase with increasing temperature, as can be seen in Fig. 1. Provided that these broadenings are only due to ^{57}Fe jumps on the different lattice sites in the Si matrix at least above 500 K, we could estimate the “Mössbauer diffusivities” for both components using the line broadenings, $\Delta\Gamma$, ranging between 0.5 and 1.2 mms $^{-1}$. Assuming the elementary jump length of $R = 0.235$ nm, we deduce the “Mössbauer diffusivities” for each component by the following formula [11]:

$$D = \frac{R^2}{12\hbar} \Delta\Gamma.$$

Fig. 3. “Mössbauer diffusivities” for interstitial and substitutional components. These were obtained from the line broadenings of spectral components separated by a simple Lorentz fitting.

Fig. 3 presents the Arrhenius plot of the “Mössbauer diffusivities” for the interstitial and the substitutional ^{57}Fe atoms in comparison with the “macroscopic diffusivity” which was evaluated by Weber and his colleagues [3] using numerous experimental results. The singlets between 800 and 1000 K are thought to be due to substitutional ^{57}Fe , although their center shifts do not fit to that of the substitutional component, as can be seen in Fig. 1. Below 500 K, however, there are small broadenings of about 0.1 mms $^{-1}$ in both components. These broadenings appear to be originated from other reasons such as influences from defects and/or charge fluctuation. At around 600 K the interstitial diffusivities have the values comparable with the “macroscopic diffusivity”, while the substitutional diffusivities above 800 K are two orders of magnitude lower than that of the “macroscopic diffusivity”.

In the former report [8], the relaxation behaviors observed in the present experiment can be interpreted in terms of a diffusion-reaction process of interstitial Fe atoms with vacancies within the time scale of 100 ns, leading to the formation of substitutional Fe atoms in the Si matrix. Instead of the above simple fitting analysis, we are now trying to reproduce the whole changes observed in

Fig. 4. Mössbauer spectra simulated by a theoretical model (see text) assuming a dynamical relaxation due to a diffusion reaction between interstitial Fe with vacancies, which form substitutional Fe atoms.

the spectra up to 1200 K by taking into account of a relaxation rate, ω_R between the interstitial and the substitutional ^{57}Fe which arises from the above-mentioned “diffusion reaction [8]”. There is one theoretical model proposed by Dattagupta [11] for a system with a charge fluctuation.

In addition, we have to incorporate the effect from the diffusion broadening to the spectra, $\Phi(\omega)$:

$$\Phi(\omega) = \frac{\text{const}}{\left[\Gamma + \Delta\Gamma_S + i(\omega - \bar{\omega} - \alpha \cdot \Delta\omega) + \frac{(\Delta\omega)^2(1-\alpha^2)}{\Gamma + \Delta\Gamma_I + i(\omega - \bar{\omega} + \alpha \cdot \Delta\omega) + \omega_R} \right]}$$

Here $\alpha = p_s - p_i$ where p_s and p_i are the substitutional and the interstitial fractions, respectively. $\bar{\omega} = 1/2(\delta_s - \delta_i)$ and $\Delta\omega = 1/2(\delta_s + \delta_i)$ where δ_s and δ_i are the isomer shifts for the substitutional and the interstitial components, respectively. $\Delta\Gamma_S$ and $\Delta\Gamma_I$ are the line broadenings due to diffusion. The values of p_s and p_i are deduced from the numerical solutions which are obtained from the kinetic equations for the diffusion reaction mainly due to the interstitial jumps within 100 ns [8]: In this model an interstitial Fe atom jumps with an activation enthalpy of 0.67 eV within the lifetime of ^{57}Fe , 100 ns, and subsequently finds a vacancy, which results in the formation of

the substitutional Fe atoms. The number of vacancies related with one interstitial Fe is a parameter. An example of the simulation using the model is shown in Fig. 4. The general tendency of the temperature dependence of the Mössbauer spectra, which is shown in Fig. 1, appears to be reproducible by the simulation. There remain, however, further details to be improved in the simulation.

4. Summary

The isolated Fe atoms can be experimentally obtained in n-type Si wafer from 330 and 1200 K by a newly developed Mössbauer experimental set-up using a RIKEN on-line nuclear fragment separator, RIPS. Combining this facility with a high-energy implantation technique provides us a unique experimental condition which enables us to follow a dynamical behavior of nuclear probes such as $^{57}\text{Mn}/^{57}\text{Fe}$ in any materials even in a system where no practical solubility has been reported.

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