Hyperfine Interact
DOI 10.1007/s10751-013-0949-8

Time-resolved Mössbauer spectra obtained after ^{57}Mn implantation in Si

Y. Kobayashi · M. Mihara · T. Nagatomo · Y. Yamada · M. K. Kubo · J. Miyazaki · W. Sato · S. Sato · A. Kitagawa

Abstract A new detector system for the coincidence technique between Mössbauer γ-rays and energetic β-rays originating from ^{57}Mn has been developed for in-beam Mössbauer spectroscopy using ^{57}Mn implantation. This system enables time-resolved Mössbauer measurements of ^{57}Fe at various elapsed times after β^--decay of ^{57}Mn with sufficient quality. We applied this system to the time-dependent measurement of the site distributions of dilute

Proceedings of the 32nd International Conference on the Applications of the Mössbauer Effect (ICAME 2013) held in Opatija, Croatia, 1–6 September 2013.

Y. Kobayashi (✉)
Graduate School of Engineering Science, University of Electro-Communications, Chofu, Tokyo 182-8585, Japan
e-mail: kyoshio@pc.uec.ac.jp

Y. Kobayashi · T. Nagatomo
Nishina Center for Accelerator-Based Science, RIKEN, Wako, Saitama 351-0198, Japan

M. Mihara
Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

T. Nagatomo
J-PARC Center, KEK, Tokai, Ibaraki 319-1195, Japan

Y. Yamada
Department of Chemistry, Tokyo University of Science, Shinjuku, Tokyo 162-8602, Japan

M. K. Kubo
Division of Arts and Science, International Christian University, Mitaka, Tokyo 181-8585, Japan

J. Miyazaki
College of Industrial Technology, Nihon University, Narashino, Chiba 275-8576, Japan

W. Sato
Depertment of Chemistry, Kanazawa University, Kanazawa, Ishikawa 920-1192, Japan

S. Sato · A. Kitagawa
National Institute of Radiological Science (NIRS), Inage, Chiba 263-8555, Japan

Published online: 01 November 2013

Fe atoms in n-type Si. It was suggested that Fe atoms were already located at substitutional and interstitial positions in Si within a time of about 100 ns after the β^--decay of ^{57}Mn, and that the occupancy ratio between these positions was hardly dependent on the elapsed time after the β^--decay.

Keywords In-beam Mössbauer spectroscopy · Ion implantation · Radioactive ^{57}Mn beam · $\beta - \gamma$ coincidence method · Time-resolved Mössbauer spectroscopy

1 Introduction

In-beam Mössbauer spectroscopy using implantation of the short-lived Mössbauer probe, ^{57}Mn ($T_{1/2} = 87.2$ s), is one of the useful tools for *in situ* characterization of the lattice position, electron configurations, and diffusion process of dilute Fe atoms at the atomic scale in various materials. Recently, we have developed a detection system using the anticoincidence method between Mössbauer γ-rays and energetic β-rays originating from ^{57}Mn nuclei, in order to improve the quality of the ^{57}Fe Mössbauer spectra obtained with extremely low implantation fluence of ^{57}Mn [1]. We succeeded in obtaining ^{57}Fe Mössbauer spectra using ^{57}Mn implantation into Al [1], MgO, α-Al_2O_3 [2], and LiH [3] with sufficient quality by applying the $\beta - \gamma$ anticoincidence detection system. The obtained results suggest that it is further required to develop a highly-efficient and unprecedented detection system for on-line measurements of ^{57}Fe Mössbauer spectra using the short-lived ^{57}Mn beam.

The emission measurement is a traditional technique extensively used in ^{57}Fe Mössbauer spectroscopy. Mössbauer emission spectroscopy using the nuclide ^{57}Co has been applied widely to study site occupation, lattice defects, diffusion, surface and interfaces, and aliovalent charge/spin states induced by the aftereffect, in a large number of solids [4]. Furthermore, time-differential Mössbauer emission spectroscopy yields unique information on the relaxation process following the electron capture of ^{57}Co, which takes place on a time scale comparable to the lifetime of the excited level of 140 ns. The elapsed time between the nuclear decay and the Mössbauer quantum is measured for each registered event [5]. However, there is an experimental disadvantage in that the time-differential emission technique usually requires a relative long measurement time, ranging over a period of some days, to obtain a spectrum.

^{57}Mn predominantly decays to the first excited state of ^{57}Fe accompanied by emission of energetic β-rays. It is not difficult to consider that the emission of β-rays from ^{57}Mn in a sample triggers the time measurement, and the following Mössbauer γ-transition of 14.4 keV stops the time measurement. β-decay is relatively free from the aftereffect induced by the Auger process, as occurs in the electron capture process of ^{57}Co. ^{57}Mn can be a useful probe for time-dependent studies of atomic and solid state physics, materials science, and chemistry, such as for example lattice positions and dynamic behavior of dilute Fe probes in semiconductors and the exotic oxidation states and coordination environment around the probes after β-decay, as a counterpart to Mössbauer absorption and emission spectroscopy. The use of ^{57}Mn as a probe is expected to provide unique information on local atomic and electronic configurations at various elapsed times after nuclear transformation during the lifetime of the excited Mössbauer state.

In this work, we developed a new time-dependent detection system for the $\beta - \gamma$ coincidence method that establishes various elapsed times after β-decay of ^{57}Mn combined with the anticoincidence method, with the aim to improve the quality of spectra obtained, by

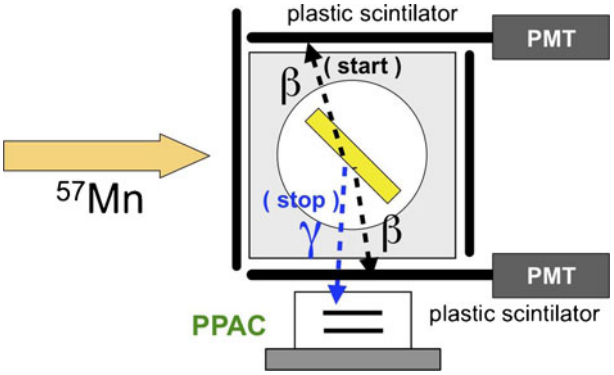

Fig. 1 Experimental layout of the $\beta - \gamma$ coincidence measurement of in-beam Mössbauer spectra of ^{57}Fe using ^{57}Mn implantation

using a parallel-plate avalanche counter (PPAC) for counting the Mössbauer γ-rays and a plastic scintillation counter for β-rays. This new detection system was first applied to the time-dependent Mössbauer study of site distributions of dilute Fe atoms in n-type Si.

2 Experimental

(a) Production and implantation of ^{57}Mn into n-type Si

The experiments were performed at the Heavy-Ion Medical Accelerator in Chiba (HIMAC) at the National Institute of Radiological Sciences (NIRS). ^{57}Mn ions were produced through the nuclear projectile fragmentation reaction of ^{58}Fe ions with the energy of 500 MeV/nucleon and a production target of ^{9}Be with a thickness of 27 mm. The ^{57}Mn nuclei were separated by an in-flight RI beam separator installed in the secondary beam hall at HIMAC. The primary beam was provided as a 0.25-sec-pulsed beam every 3.3 s in HIMAC, so that the ^{57}Mn beam had the same beam structure.

After passing through the separator, the purity of ^{57}Mn was typically about 90 % of the secondary beam. The typical intensity and energy of the ^{57}Mn beam before passing through the energy degraders in front of the Si sample were about 1.2×10^6 particles per pulsed-beam and 256 MeV/nucleon, respectively. The energy degraders consist of a 4-mm-thick Pb Plate, a 4-mm-thick Al plate, and two wedge-shaped acrylic plates, and were used to stop all of the ^{57}Mn nuclei at an adequate depth in the Si.

In this experiment, an n-type Si wafer with a thickness of 600 μm was used. The size of the Si wafer was 40 mm $\times$ 40 mm and in the form of a square plate. The Si sample was fixed on the cold head of a He gas-flow type cryostat, and was set 45$^{\underline{o}}$ against the ^{57}Mn beam direction.

(b) $\beta - \gamma$ coincidence detection system

Figure 1 illustrates the experimental layout of the $\beta - \gamma$ coincidence detection system. The Mössbauer γ-rays arising from ^{57}Mn were detected by the PPAC during the beam-off period after 0.25-sec irradiation of ^{57}Mn. The PPAC was mounted on the Mössbauer transducer (Wissel, MVT-1000). Velocity calibration of the Mössbauer spectra was carried out using a ^{57}Co/Fe source at room temperature.

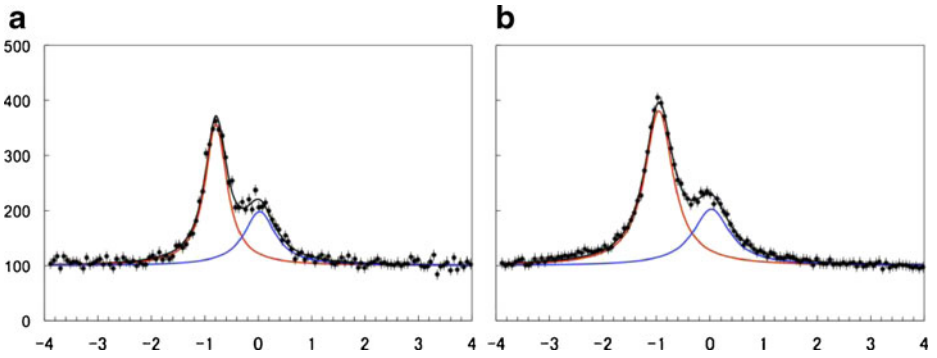

Fig. 2 ^{57}Fe Mössbauer spectra of ^{57}Mn implanted into n-type Si without the $\beta - \gamma$ coincidence method at **a** 295 K and **b** 15 K. The left- and right-hand components were assigned to Fe atoms on interstitial and substitutional sites, respectively. The isomer shift is given relative to Fe metal at room temperature

Four plastic scintillators were placed around the sample to detect the β-rays emitted from ^{57}Mn, as shown in Fig. 1. The size of each plastic scintillator was 80 mm × 80 mm × 0.5 mm (BC-400, Bicron), large enough to cover the PPAC and the Mylar windows of the cryostat. The β-ray detection efficiencies were as large as 98 % by connecting adiabatic light guides with good photon-transmission efficiency to photomultiplier tubes (R329-02, Hamamatsu). The β event was identified by a coincidence measurement between the plastic scintillation detectors and the PPAC. On the other hand, Mössbauer γ-rays do not interact with any material in the system except the ^{57}Fe-enriched cathode plate of the PPAC. It is possible to distinguish between the β- and γ-rays emitted from ^{57}Mn in these detectors by the anticoincidence method. The time-dependent Mössbauer spectra at the elapsed time (every 100 ns in the present study) after β^--decay of ^{57}Mn were measured by the coincidence method that collected the β events detected by any of the four plastic scintillation counters beginning at the *START* clock signal, that is $t = 0$, and the Mössbauer γ-rays by the PPAC as the *STOP* signal. Timing signals of the $\beta - \gamma$ coincidence events were accumulated by a multistop time-to-digital converter (TDC) and recorded by the KODAQ program developed by K. Omata at KEK, Japan [6].

In addition, a plastic scintillator placed in front of the PPAC was also used for the $\beta - \gamma$ anticoincidence measurement to reduce the background in the Mössbauer spectrum [1].

3 Results and discussion

The stopping range and longitudinal straggling width of ^{57}Mn were calculated to be 250 μm from the surface of Si and 200 μm, respectively, by considering the energy spread and energy loss in the degraders and the Si sample. The implantation fluence was estimated to be 3×10^6 particles/(cm^2 h), and ^{57}Fe arising from ^{57}Mn was considered to be completely isolated in the Si.

The in-beam Mössbauer spectra obtained after ^{57}Mn implantation in Si were measured at 15 K for 18.5 h and at 295 K for 23.5 h. The typical Mössbauer count rates of the PPAC were 2 cps/1024ch after reduction of noise levels by the $\beta - \gamma$ anticoincidence method. The in-beam Mössbauer spectra were obtained without the $\beta - \gamma$ coincidence method, as shown in Fig. 2. Both spectra could be fitted with two components of singlets, in which one is assigned to ^{57}Fe atoms on an interstitial site ($I.S. = -0.79(1)$ mm/s at 295 K and

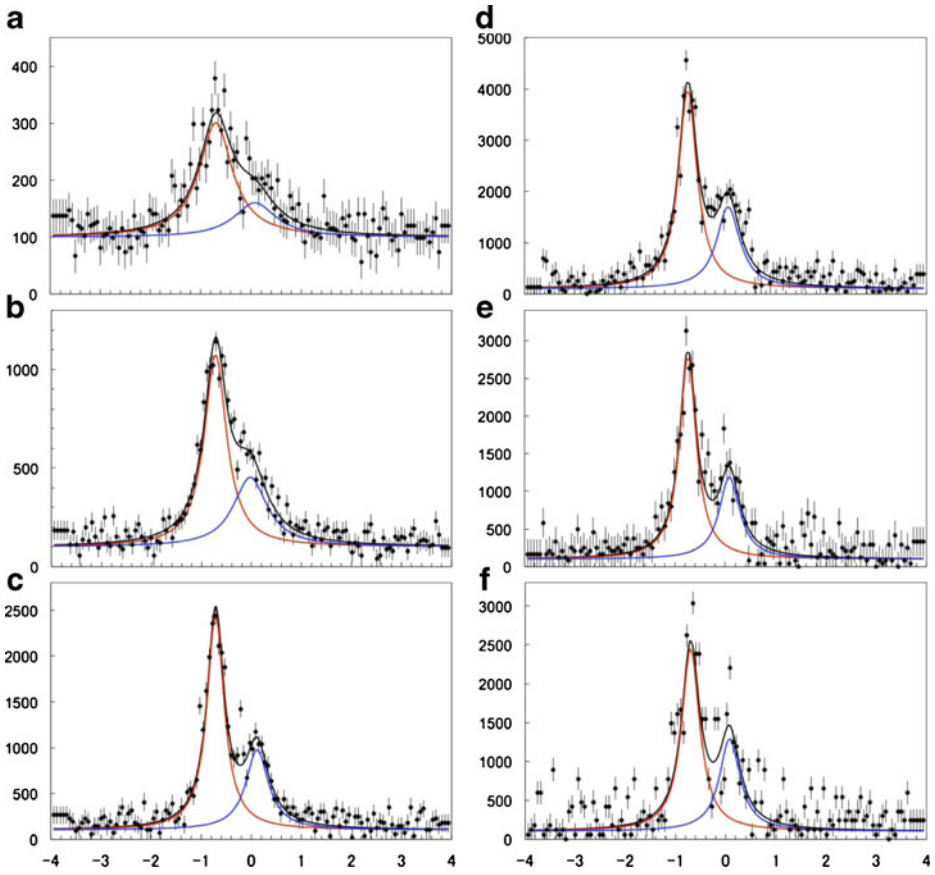

Fig. 3 Time-resolved ^{57}Fe Mössbauer spectra of ^{57}Mn implanted into n-type Si with the $\beta - \gamma$ coincidence method at the elapsed time τ ($0 \leq \tau \leq 600$ ns) after β-decay of ^{57}Mn in Si at 295 K. The left- and right-hand components were assigned to Fe atoms on interstitial and substitutional sites, respectively. The isomer shift is given relative to Fe metal at room temperature. **a** $10 \leq \tau \leq 100$ ns. **b** $100 \leq \tau \leq 200$ ns. **c** $200 \leq \tau \leq 300$ ns. **d** $300 \leq \tau \leq 400$ ns. **e** $400 \leq \tau \leq 500$ ns. **f** $500 \leq \tau \leq 600$ ns

$I.S. = -0.95(5)$ mm/s at 15 K), and another is a substitutional site ($I.S. = 0.03(2)$ mm/s at 295 K and $I.S. = 0.05(2)$ mm/s at 15 K) in Si. The site determination was based on previous results by Yoshida et al. [7, 8]. The area intensity ratios between the interstitial and substitutional sites at 15 K and 295 K were also consistent with the previous ones. However, the peak-to-background ratios were drastically increased by the $\beta - \gamma$ anticoincidence method, from 8 % to 400 %, despite the lower ^{57}Mn implantation fluence. It became obvious that the anticoincidence method plays an important role in the experimental condition of the lower concentration of emission probes.

The typical time-resolved Mössbauer spectra at 295 K extracted at a different elapsed time τ ($0 \leq \tau \leq 600$ ns) after β-decay of ^{57}Mn in Si are shown in Fig. 3. These spectra could be analyzed by two singlets in the same manner. The present results obtained at the elapsed time longer than 200 ns after β-decay of ^{57}Mn were almost similar in principle to the results obtained without the $\beta - \gamma$ coincidence analysis shown in Fig. 2. At the elapsed time less than 100 ns after β-decay, the linewidths of the two components of the interstitial

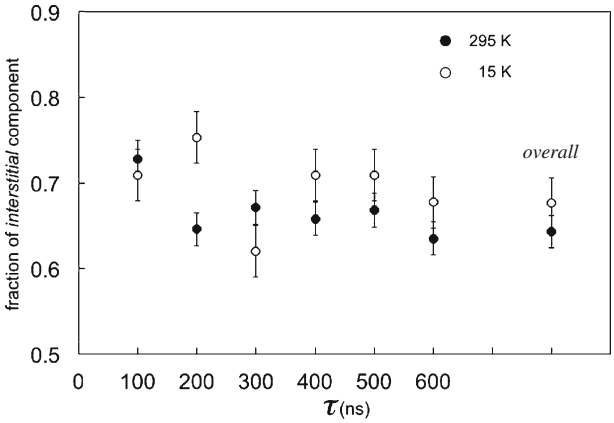

Fig. 4 Fractions of interstitial Fe components as a function of the elapsed time τ ($0 \leq \tau \leq 600$ ns) after β-decay of ^{57}Mn in Si at 295 K. The *overall* data obtained without the $\beta - \gamma$ coincidence technique (Fig. 2) are added for comparison

and the substitutional sites were broadened to about 0.9 mm/s, and the resonance areas decreased due to the uncertainty principle. It was suggested that Fe atoms were located in both interstitial and substitutional positions with the lattice distribution ratio of almost 7: 3 in Si, on a time scale of less than ∼100 ns after the β^--decay of ^{57}Mn below room temperature, as shown in Fig. 4. This means that the local environment around the isolated ^{57}Fe atoms in Si was not seriously damaged in the time range of the present study after β-decay of ^{57}Mn. It was reported that Fe atoms jump on different lattice sites in Si above 500 K, from the result that the linewidths of the interstitial and substitutional components increase with increasing temperature [7]. We plan to introduce this newly developed system to the diffusion and atomic jump process of Fe atoms in Si and other semiconductors in the near future.

4 Conclusion

A new detection system with the coincidence method between Mössbauer γ-rays and energetic β-rays emitted from ^{57}Mn has been developed. The $\beta-\gamma$ coincidence ^{57}Fe Mössbauer spectra of ^{57}Mn implantation into n-type Si were measured for the first time. The time-dependent spectra at different elapsed times after β^--decay at 15 K and 295 K could be analyzed by two components of singlets, which were assigned to interstitial and substitutional positions in Si, respectively. The derived isomer shifts and the ratio of resonance area intensity of the interstitial site against the substitutional one varied little with the elapsed time after β^--decay of ^{57}Mn in Si. It can be expected that this new Mössbauer detection system using the coincidence method provides unique information on local atomic and electronic configurations of dilute Fe atoms within the lifetime of the 14.4-keV nuclear excited state at various elapsed times after nuclear transformation, especially on the recoil-atom chemistry.

Acknowledgments We are thankful to Dr. S. Kamiguchi of the Chemical Analysis Team in RIKEN for synthesis of ^{58}Fe-enriched ferrocene as an ion source of the primary beam, and the operating staff at HIMAC in NIRS. This work was partially supported by a Grant-in-Aid for Scientific Research (C) (Research Project Number 25410062) of the0020Japan Society for the Promotion of Science (JSPS).

References

1. Nagatomo, T., Kobayashi, Y., Kubo, M.K., Yamada, Y., Mihara, M., Sato, W., Miyazaki, J., Sato, S., Kitagawa, A.: Nucl. Instr. Meth. B. **269**, 455–459 (2011)
2. Kobayashi, Y., Nagatomo, T., Yamada, Y., Mihara, M., Sato, W., Miyazaki, J., Sato, S., Kitagawa, A., Kubo, M.K.: Hyp. Int. **198**, 173–178 (2011)
3. Nagatomo, T., Kobayashi, Y., Kubo, M.K., Yamada, Y., Mihara, M., Sato, W., Miyazaki, J., Mae, K., Sato, S., Kitagawa, A.: Hyp. Int. **204**, 125–128 (2012)
4. Nagy, D.L.: Hyp. Int. **83**, 3–19 (1994)
5. Alflen, M., Hennen, C., Tuczek, F., Spiering, H., Gütlich, P., Kajcsos, Zs.: Hyp. Int. **47**, 115–126 (1989)
6. see in web page of http://www-ps.kek.jp/kodaq/
7. Yoshida, Y., Kobayashi, Y., Yukihira, K., Hayakawa, K., Suzuki, K., Yoshida, A., Ueno, H., Yoshimi, A., Shimada, K., Nagae, D., Asahi, K., Langouche, G.: Physica B. **401–402**, 101–104 (2007)
8. Yoshida, Y., Suzuki, K., Kobayashi, Y., Nagatomo, T., Akiyama, Y., Yukihira, K., Hayakawa, K., Ueno, H., Yoshimi, A., Nagae, D., Asahi, K., Langouche, G.: Hyp. Int. **204**, 133– (2012)