Hyperfine Interact
DOI 10.1007/s10751-011-0424-3

^{57}Fe charge states in MC-Si solar cells under light illumination after GeV-implantation of ^{57}Mn

Yutaka Yoshida · Kunifumi Suzuki · Yoshio Kobayashi · Takashi Nagatomo · Yuki Akiyama · Kenichi Yukihira · Kazuo Hayakawa · Hideki Ueno · Akihiro Yoshimi · Daisuke Nagae · Koichiro Asahi · Guido Langouche

Abstract Immediately after the GeV-implantation of ^{57}Mn nuclei produced by the RIKEN-RIBF facility, ^{57}Mn/^{57}Fe Mössbauer spectra in Si-solar cells are measured under light illumination. Comparing with the spectrum of p-type multi-crystalline-Si, the broad spectra of the solar cell under operation can be analyzed as a superposition of interstitial and substitutional Fe components with different charge states. The charge states of Fe impurities are created by the excess carrier injection followed by a directional carrier flow in the p-n junction. The present results provide us a possibility to clarify the carrier trapping process at the Fe impurities in Si-solar cells.

Keywords ^{57}Mn/^{57}Fe implantation Mössbauer spectroscopy · Si solar cell · Fe impurity · Carrier trapping · Energy conversion efficiency

1 Introduction

Iron impurities in Si have been intensively investigated for more than 50 years by different experimental techniques [1] including ^{57}Fe Mössbauer spectroscopy [2–9], because Fe impurities can be easily incorporated into the Si matrix during

---

Y. Yoshida (✉) · Y. Akiyama · K. Yukihira · K. Hayakawa
Shizuoka Institute of Science and Technology, Toyosawa 2200-2,
Fukuroi-city, Shizuoka 437-8555, Japan
e-mail: yoshida@ms.sist.ac.jp

Y. Kobayashi · T. Nagatomo · H. Ueno · A. Yoshimi
RIKEN Nishina Center, Wakō, Japan

K. Suzuki · D. Nagae · K. Asahi
Department of Physics, Tokyo Institute of Technology, Tokyo, Japan

G. Langouche
Institute for Nuclear and Radiation Physics, Physics Department, Leuven University,
Leuven, Belgium

the processes, and even an extremely low Fe concentration of $10^{11}/\mathrm{cm}^3$ can degrade seriously the electronic properties of silicon-based devices and solar cells. This is due to the deep levels formed in the Si band gap, producing strong trapping centres for the carriers in the devices. Interstitial $\mathrm{Fe_i}$ is well known to form an acceptor level at 0.39 eV from the valence band edge, while substitutional $\mathrm{Fe_s}$ is expected to form a donor level of 0.69 eV from the first principle calculation [10]. Although interstitial and substitutional Fe appeared as spectral components in ^{57}Fe Mössbauer experiments [2–9], the charge states could not be identified in terms of different isomer shifts of Mössbauer spectrum experimentally in comparison with the values calculated theoretically.

The present investigation is carried out to observe directly the charge states of Fe atoms in multi-crystalline Si solar cells under light illumination, which will shift the Fermi level by injecting excess carriers, and consequently the different charge states of interstitial and substitutional Fe are expected to appear in the spectrum. In order to study Fe impurities existing inside of a Si solar cell, however, we have to realize a well isolated ^{57}Fe probe with an extremely low concentration, and the probes must be introduced into a region where the carrier trapping processes are occurring during solar cell operation, i.e. light illumination. At the RI-beam facility in RIKEN we have been developing a novel technique of projectile fragmentation combined with ^{57}Mn/^{57}Fe implantation Mössbauer spectroscopy. The probes are deeply implanted into mc-Si solar cell, and Mössbauer spectra can be measured under operation immediately after each implantation of ^{57}Mn. This is possible because of the extremely high implantation energy of GeV, providing an implantation depth of 100 μm with a straggling of 50 μm.

In the present paper the first Mössbauer spectra of ^{57}Fe in mc-Si solar cell are reported in different conditions for excess carrier injection and subsequent carrier flow by light illumination. The results are compared with the spectrum measured in the same p-type mc-Si wafer.

2 Experimental procedure

Radioactive isotopes of ^{57}Mn ($\tau_{1/2} = 1.45$ m) were produced by the nuclear projectile fragmentation of $^{58}\mathrm{Fe}^{21+}$ primary beam (E = 63 MeV/nucleon) with a Be target, and were subsequently separated as a secondary beam by an on-line isotope separator, RIPS at the RIKEN RI-beam facility. Mössbauer spectra of ^{57}Mn/^{57}Fe in p-type multi-crystalline-Si as well as in Si-solar cells were measured at 300 K and 400 K under Xe lamp illumination immediately after the implantation of ^{57}Mn with energy of GeV. The implantation was performed through an aluminum foil degrader with a thickness of 200 μm, so that the ^{57}Mn probes stopped at approximately 100 μm from the surface of the sample. The total fluence of ^{57}Mn was 2×10^{12} $^{57}\mathrm{Mn/cm^2}$ typically for one spectrum, requiring a measurement time for 4 h per spectrum.

3 Results and discussions

The mc-Si solar cell is covered with Ag electrode lines and a Si-N layer on the top, and Ag electrode layer at the bottom. The ^{57}Mn implantation was performed through

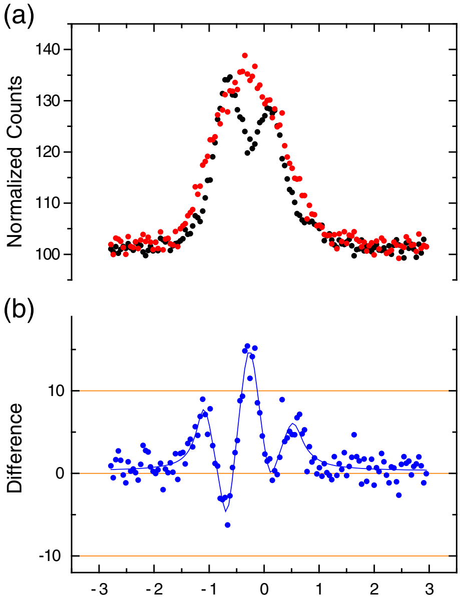


Fig. 1 (**a**) Mössbauer spectra of ^{57}Mn/^{57}Fe in p-type multi-crystalline-Si (*black points*) as well as in Si-solar cells (*red points*) were measured at 400 K under Xe lamp illumination. The difference of the two spectra is shown with blue points in Fig. 1 (b)

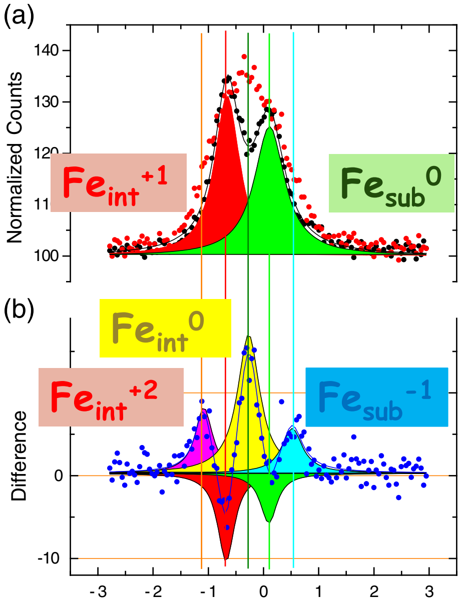
this top surface. During a Mössbauer spectral measurement under dark condition, an I–V characteristic of the p-n junction was measured after every hour. The value of the highest current at a forward voltage of 0.7 V increases substantially after 1 h in comparison with that obtained before the spectral measurement, but does not further increase at later times during the measurements. Accordingly, we may ignore the defect accumulation due to ^{57}Mn implantation, because the I–V characteristic does not further change with increasing implantation dose.

The spectra of ^{57}Fe in p-type multi-crystalline (mc)-Si and in the p-region of the p-n junction Solar cell are measured at 400 K under light illumination. The spectra are shown in Fig. 1(a) with red and black points, respectively. The "black spectrum" consists of two components, as is shown in Fig. 2(a), which can be assigned to interstitial and substitutional Fe in Si matrix with the isomer shifts of 0.8 and -0.06 mms^{-1}, respectively. On the other hand, the "red spectrum" of the solar cell appears to be very broad, and therefore, to be difficult to analyze by a superposition of singlets. To understand such broad spectrum, we subtract the "black spectrum" from the "red spectrum", obtaining the difference, which is shown in Fig. 1(b). The difference spectrum can be fitted by three appearing components (pink, yellow, and light blue) and two disappearing ones (red and green), as are shown in Fig. 2(b).

These singlets can be assigned to different charge states of ^{57}Fe atoms on interstitial Fe$_i$ sites and substitutional Fe$_\mathrm{s}$ sites: $\mathrm{Fe}_\mathrm{i}^{2+}$, $\mathrm{Fe}_\mathrm{i}^{1+}$, $\mathrm{Fe}_\mathrm{i}^{0}$, $\mathrm{Fe}_\mathrm{s}^{0}$, and $\mathrm{Fe}_\mathrm{s}^{-1}$ and are colored by pink, red, yellow, green and light blue, respectively in Fig. 2(b). The isomer shift values are in good agreement with those of previous absorber experiments obtained in ^{57}Fe deposited mc-Si [8]. Notice that the ^{57}Mn probes were implanted into the p-type region of mc-Si solar cell, which is the same material as the p-type mc-Si wafer.

The present results indicate that the light illumination changes not only the Fermi level (quasi-Fermi level) by the excess carrier injection, but also the carrier trapping

Fig. 2 (**a**) and (**b**) The difference spectrum can be analyzed by the appearing three singlets (pink, yellow, and light blue components in Fig. 2 (b)) and the two disappearing singlets (red and green components in Fig. 2 (b)). The colored lines are eye guides, showing the positions of the singlets which correspond to different charge and lattice states of Fe in Si



processes. The latter must be due to the directional excess carrier flow through the p-n junction, which affects the carrier trapping kinetics with electrons and holes at the Fe impurities, leading to the different charge states on both Fe substitutional and interstitial sites in the p-region in mc-Si solar cell. This is, in fact, the first in-situ observation of the carrier trapping processes at Fe impurities in mc-Si solar cell, which degrades the energy conversion efficiency.

4 Summary

For more than half a century the carrier trapping process at Fe impurities in Si has been one of the central problems in defect solid state physics and also in semiconductor industry, because Fe impurities are thought to degrade strongly LSI devices and Si solar cell performance. Fe gettering techniques have been successfully developed for LSI devices to remove Fe impurities from the device active zone, while for multi-crystalline Si-solar cells, i.e., the dominant production of the solar cell market, the complicated defect distributions have prohibited one from achieving Fe gettering. The present Mössbauer study clearly shows for the first time the Fe interstitial and substitutional impurities with different charge states in mc-Si solar cell, which are created through the carrier trapping process during the solar cell operation.

Acknowledgements Drs. M.Yamatani, K. Niira, and K. Shirasawa, KYOCERA Corporation, are greatly acknowledged for providing us the Si solar cells specially made for the present investigation. The RIBF facility members at RIKEN have intensively supported to provide us the excellent stable and highly intensive beam of ^{58}Fe for the projectile fragmentations. Dr. Atsushi Yoshida is appreciated for his kind supports and valuable advices for the RIPS operations since more than 10 years.

References

1. Istratov, A.A., Hieslmair, H., Weber, E.R.: Appl. Phys. **A69**, 13 (1999)
2. Schwalbach, P., Laubach, S., Hartick, M., Kankeleit, E., Keck, B., Menningen, M., Sielemann, R.: Phys. Rev. Lett. **64**, 1274 (1990)
3. Gunnlaugsson, H.P., Weyer, G., et al.: Appl. Phys. Lett. **80**, 2657 (2002)
4. Yoshida, Y.: In: ALTECH 2003 analytical and diagonistic techniques for semiconductor materials, devices, and processes, vol. 479 (2003)
5. Kobayashi, Y., Yoshida, Y., et al.: Hyperfine Interact. **126**, 417 (2000)
6. Yoshida, Y., Kobayashi, K., et al.: Defect Diffus. Forum **194–199**, 611 (2001)
7. Yoshida, Y., Kobayashi, Y., Hayakawa, K., Yukihira, K., Yoshida, A., Ueno, H., Shimura, F., Ambe, F.: Physica B **376–377**, 69 (2006)
8. Yoshida, Y., Ogawa, S., Arikawa, K.: Physica B **340–342**, 605 (2003)
9. Yoshida, Y., Horie, S., Niira, K., Fukui, K., Shirasawa, K.: Physica B **376–377**, 227 (2006)
10. Estreicher, S.K., Sanati, M., Gonzalez Szwacki, N.: Phys. Rev. B **77**, 125214 (2008)