Direct Observation of Carrier Trapping Processes on Fe impurities in mc-Si Solar Cells

Yutaka Yoshida, Yoshinori Tsukamoto, Masahiro Ichino and Kiyotaka Tanaka
Shizuoka Institute of Science and Technology,
Toyosawa 2200-2, Fukuroi city, Shizuoka 437-8555, Japan

yoshida@ms.sist.ac.jp

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Abstract. In-situ Mössbauer studies on $^{57}$Fe solute atoms in Si solar cells are performed: (1) GeV-$^{57}$Mn/$^{57}$Fe implantation into Si solar cells, (2) $^{57}$Fe diffused n-type Si under light illumination; (3) $^{57}$Fe diffused solar cells under applying external voltages. The carrier trapping cross sections for the interstitial components with different charge states, Fe$_{i}^{+}$ and Fe$_{i}^{2+}$, can be successfully obtained by evaluating the dynamical charge fluctuations within a time scale of 100ns between Fe$_{i}^{+}$ and Fe$_{i}^{2+}$ which appear in the Mössbauer spectra of $^{57}$Fe doped mc-Si solar cells. We further measure the distributions of substitutional Fe$_{s}^{+}$, interstitial Fe$_{i}^{0}$, and Fe$_{s}^{+}$ by a Mössbauer Microscope, which we have been developing specially for clarifying the carrier trapping process on an atomistic scale directly on the Fe impurities in Si-solar cells in comparison with the defect structures.

Introduction

Iron contamination in silicon solar cells is known to be one of the most serious obstacles to improve the energy conversion efficiency for silicon solar cells. The concentration of Fe impurities is found to be from $10^{11}$ to $10^{15}$ Fe/cm$^3$, and their distribution depends strongly on the defects such as vacancies, dislocations and grain boundaries in the silicon matrix. So far, the “interstitial” iron mapping has been considered to be possible by $\mu$-PCD and Photo-Luminescence (PL), and the analysis was based on a Zoth and Bergholz model [1], which took into account of the measurements of the carrier life time before and after breaking Fe-B pairs in B-doped p-type Si. However, a series of the experimental investigations using Mössbauer spectroscopy on Fe impurities in single crystal Si [2], in multi-crystal Si wafers, and even in mc-Si solar cells [3-6] have recently revealed that the Fe impurities in the Si matrix exist not only on the interstitial sites with Fe$_{i}^{0/+}$ and Fe$_{i}^{0}$-B$^-$ pair, but also on an interstitial site with a higher charge state of Fe$_{i}^{2+}$ as well as on the substitutional sites with Fe$_{s}^{0}$ and Fe$_{s}^{+}$ [6]. Furthermore, these components transform each other by changing external conditions. Therefore, the carrier trapping cross sections must be discussed for the different Fe states separately.

We have performed $^{57}$Fe Mössbauer experiments under different experimental conditions such as at high temperatures [2-4], under applying external stresses [5], under light illumination [6], and under applying external voltages as well. If a charge fluctuation between the different charge states of Fe atoms would occur within a life time of 100 ns due to the carrier trappings on the Fe impurities, the spectrum might show “a motional averaging” of the Fe components, which could provide a possibility to determine the carrier trapping cross sections corresponding to the Fe components. It should be noticed, however, that Mössbauer spectroscopy uses a recoil-free nuclear resonant absorption and emission of $\gamma$-rays, and therefore, the measurement itself will not produce an excited level on the Fe impurities. This must be completely different from other conventional evaluation techniques. Finally, we have developed a mapping technique in Mössbauer spectroscopy [7-9], which enables us to observe the Fe distributions of each component separately with a space resolution down to 50 $\mu$m.
On-line Mössbauer experiment on $^{57}\text{Mn}/^{57}\text{Fe}$ in mc-Si solar cell

In order to study Fe impurities inside a Si solar cell, we have to introduce, first of all, isolated $^{57}\text{Fe}$ probes 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 developed a novel technique of projectile fragmentation combined with $^{57}\text{Mn}^{57}\text{Fe}$ implantation Mössbauer spectroscopy. The nuclear probes are deeply implanted into the p-layer of mc-Si solar cell through the n-layer, and subsequently Mössbauer spectra can be measured under solar cell operation immediately after each implantation of $^{57}\text{Mn}$ within 2 min. This exotic measuring technique guarantees that all Mössbauer components in the spectrum are originated from the isolated $^{57}\text{Fe}$ probes, but not from Fe clusters and Fe precipitates. We have already reported [5] the spectra of $^{57}\text{Fe}$ both in p-type mc-Si and in the p-region of the p-n junction solar cell measured at 400 K with/without light illumination. The different charge states of interstitial $^{57}\text{Fe}$ atoms $\text{Fe}_{i}^{2+}$, $\text{Fe}_{i}^{1+}$, $\text{Fe}_{i}^{0}$, and substitutional $\text{Fe}_{s}^{0}$, and $\text{Fe}_{s}^{-1}$, could be clearly observed in the experiment.

In Fig.1, the spectra of a mc-Si solar cell measured at 300 K are presented: (a) before, (b) under and (c) after Xe-lamp illumination. Additionally, the differences between (a) and (b), (b) and (c), and (a) and (c) are plotted to show the changes of the spectra. For the eye guide, the dotted line are also plotted at the isomer shift corresponding to $\text{Fe}_{i}^{2+}$ state. Please notice, that the Doppler velocity scale, i.e. the energy scale of the spectrum is converted in this source experiment in contrast to other absorber experiments in Laboratory described in the following chapters. No considerable change can be seen in the difference between (a) and (c), indicating no defect accumulations around the $^{57}\text{Mn}^{57}\text{Fe}$ probes during the measurements, although the implantation energy reaches up to GeV. Under light illumination, the interstitial $\text{Fe}_{i}^{2+}$ and $\text{Fe}_{i}^{1+}$ partly disappear, accompanied by the increases of other components, manifesting themselves in the excess carrier trapings on the interstitial Fe atoms. When the light is switched off, the spectrum appears as before.

The interstitial $\text{Fe}_{i}^{2+}$ can be observed by this highly energetic implantation technique only in a sample such as mc-Si wafer, which must contain a considerable amount of lattice defects. Accordingly, this higher charged state must be related with Fe interstitials adjacent to the defects in the solar cell already existing before the measurements. 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.
$^{57}$Fe diffusion into n-type Si wafers

N-type Si wafers with a thickness of 540 μm contained $6 \times 10^{18}$ Sb cm$^{-3}$ and also $1 \times 10^{12}$ P cm$^{-3}$, respectively. The wafers were cut into square plates of 20×20mm$^2$. After removing a surface oxide layer by a 20% HF solution, $^{57}$Fe stable isotopes were deposited onto the Si wafers with a thickness of 3.3nm, and finally, the wafers were annealed at 1000°C for one week. This heat treatment would provide a Gaussian distribution of $^{57}$Fe substitutional from the surface down to about 1 μm, and in addition, a homogenous distribution of $^{57}$Fe interstitial at least down to 10 μm in the Si wafer, which was measured in our former experiment using SIMS. We used a set-up enabling us to measure an in-situ Mössbauer spectrum under light illumination at room temperature. Si sample was fixed in an acryl-holder with an angle of 45°against the 14.4 keV $\gamma$-ray direction. Accordingly, the sample was kept to be electrically isolated from the ground during UV illumination. The UV light source was a Xenon lump (MAX-302) produced by Asahi Spectra Co., Ltd., and a mirror module was used to select an UV energy range between 3.5 and 5.5eV. We measured each Mössbauer spectrum for one week with a 1.85GBq $^{57}$Co-in-Rh source, yielding a $\gamma$-intensity of orders of $10^8$s$^{-1}$ on the sample, which was 10 orders of magnitude lower than the light photon intensity, i.e., $10^{18}$s$^{-1}$. This means that the influence on the carrier production in the sample from the 14.4 keV and other higher energetic $\gamma$-rays emitted from the Mössbauer source are considered to be negligible.

Mössbauer spectra of $^{57}$Fe in n-type Si (Sb: $6 \times 10^{18}$/cm$^3$) are shown in Fig.2 (a). The most upper spectrum was measured in the dark before UV illumination, the middle spectrum under UV illumination, and the lowest spectrum in the dark after UV illumination. The spectrum before illumination consists of two singlets, A and B, which can be assigned to substitutional Fe$_s^0$ and interstitial Fe$_i^0$, respectively, on the basis of a theoretical calculation of the isomer shifts as well as a series of our works. The spectrum under UV irradiation, however, changes from the spectrum in the dark: a broad singlet, C, appears, while the areal fraction of A and B decrease. Finally, the spectrum after illumination returns back to the initial spectrum in the dark, consisting only of A and B, i.e., substitutional and interstitial Fe components. The singlet C appears to correspond to interstitial Fe$_i^+$. There is no trace for Fe-silicide or oxide components in the spectra.

![Mössbauer spectra of $^{57}$Fe in n-type Si](image)

Fig.2 Mössbauer spectra of $^{57}$Fe in (a) n-type Si (Sb: $6 \times 10^{18}$/cm$^3$), and (b) n-type Si (P: $10^{12}$).
In Fig. 2(b), Mössbauer spectra of $^{57}$Fe in n-type Si (P:10$^{12}$; in the dark (before), under UV illumination, and in the dark (after), respectively. Both the spectra before and under UV illumination consist of two singlet A, B. In the case of the spectrum after illumination, on the other hand, the spectrum consists of the components, A, B, and C and D in addition. In the case of the Sb-highly doped Si, the new component of C appears under illumination, but in the case of P doped Si the spectrum does not change, but the line-width of singlet B gets slightly narrower. However, the spectrum changes considerably after illumination: two singlets, C and D, are immersing at the expense of the area fractions of the singlets, A and B. The singlet D is tentatively assigned to substitutional Fe$_{i^+}$, i.e., the accepter state of substitutional Fe, the existence of which was predicted in the first principle calculation [10]. The position of each component (the isomer shift) depends on the electron density at the $^{57}$Fe nucleus. The isomer shift of the most left hand side corresponds to the highest density in comparison with those of the other singlets, which appears to be consistent with the accepter state of Fe$_{i^+}$.

We have measured the spectra of $^{57}$Fe doped n-type Si samples before, under and after UV illumination with a photon intensity of 10$^{18}$s$^{-1}$. The substitutional Fe atoms, which distribute with a Gaussian diffusion profile down to about 1 μm from the surface, are supposed to be illuminated directly from UV light. The interstitial Fe atoms are, however, expected to distribute homogeneously, which turns out only a small part of the interstitial Fe atoms are directly illuminated. The UV illumination may cause a transformation either from the substitutional Fe atom to the interstitial Fe atom or from the neutral substitutional Fe and the interstitial Fe to their charged states. Under illumination: In the low P-doped sample, the excess carriers react with the charged states of the substitutional and the interstitial Fe atoms effectively, so that only the neutral states can be seen, while in the highly Sb-doped sample, the transformation from the charged state to the neutral state of the interstitial Fe atoms seems to be partly suppressed due to the majority carriers and the Sb dopants. This results in the singlet of Fe$_{i^+}$. After illumination: In the case of low P-doped sample with a very low electron concentration, the excess carriers are supposed to diffuse and subsequently to react with neutral substitutional and interstitial Fe atoms, leading to the Fe$_{i^+}$ and Fe$_{i^-}$ components which immerse in the dark after UV illumination, on one hand. In the case of highly Sb-doped sample, on the other hand, the excess carriers are compensated and therefore, the same spectrum is obtained as before illumination.

**$^{57}$Fe deposited on n-region of mc-Si solar cells under external voltages**

Typical Mössbauer spectra of $^{57}$Fe diffused n-region of mc-Si solar cell are shown in Fig.3. The spectra were measured as functions of the external voltages between -0.9 and +0.9 V in dark before visible light illumination, and also under visible light illumination. All the spectra measured under dark and also light illumination look similar at first glance, and can be fitted using three sets of singlet, which can be assigned to substitutional Fe$_{i^0}$, interstitial Fe$_{i^0}$, and interstitial Fe$_{i^+}$, respectively (from left to right in Fig.3). However, the line width of the interstitial Fe$_{i^+}$ component varies at different voltages. In addition, the spectrum, (b), under light illumination changes slightly from those of the dark measurements (a): The line width of interstitial Fe$_{i^+}$ component becomes slightly broader, indicating a higher rate of the charge fluctuation between Fe$_{i^+}$ and Fe$_{i^{-2+}}$ due to excess carrier trappings induced by the light illumination.
In order to deduce the carrier trapping cross section for Fe_{1/2}^{+}, we have to analyse these broad components by taking into account of the charge fluctuation, which was developed by S. Dattagupta [11]: If we have two singlets having the isomer shifts of \(\omega_1\) and \(\omega_2\) with the area intensities \(p_1\) and \(p_2\), the whole spectrum is known to depend on the fluctuation rate \(\omega_R\) and the spectral function can be expressed by the following equation (1):

\[
\phi(\omega) = \frac{\text{const}}{1 + i(\omega - \omega_1 - \alpha \Delta \omega - \Delta \omega) + (\omega - \omega_1 - \alpha \Delta \omega + \Delta \omega)^2} + \frac{\omega^2}{(\omega - \omega_2 + \Delta \omega + \alpha \Delta \omega)^2}
\]

(1)

\[
\omega = \frac{1}{\omega_1 + \omega_2}
\]

(2)

\[
\Delta \omega = \frac{1}{2}(\omega_1 - \omega_2)
\]

(3)

\[
\alpha = p_1 - p_2
\]

(4)

Assuming that the fluctuation occurs only between Fe_{1/2}^{+} and Fe_{1/2}^{2+}, we applied these formula for the fitting analysis of the interstitial component of Fe_{1/2}^{+} and Fe_{1/2}^{2+}, and obtained \(\omega_R\) and \(\alpha = p_1 - p_2\), both of which can be used to evaluate the relaxation times \(\tau_1\) and \(\tau_2\):

\[
\tau_1 = \frac{\pi(\alpha + 1)}{2\omega_R} \quad (\text{Fe}_{1/2}^{+} + h^+ \rightarrow \text{Fe}_{1/2}^{2+})
\]

(5)

\[
\tau_2 = \frac{\pi(1 - \alpha)}{2\omega_R} \quad (\text{Fe}_{1/2}^{2+} + e^- \rightarrow \text{Fe}_{1/2}^{+})
\]

(6)

corresponding to the the carrier trapping processes with (5) hole and (6) electrons, respectively. Since the carrier trapping cross section can be expressed by

\[
\sigma = \frac{1}{N \psi_{ih} \tau}
\]

(7)

where the carrier concentrations of electrons and holes are \(N_e = 1 \times 10^{10}\) and \(N_h = 1 \times 10^{16}/\text{cm}^3\), respectively, and the carrier velocity, \(v_{th} = 1.1\text{cm/s}\), in the vicinity of the interstitial Fe_{1/2}^{+} and Fe_{1/2}^{2+}, we can evaluate the cross sections using the fitting parameters of \(\omega_R\) and \(\alpha\) as follows:

\[
\sigma_e (\text{Fe}_{1/2}^{2+}) = 10^{-11} \sim 10^{-12} \text{ cm}^2
\]

\[
\sigma_h (\text{Fe}_{1/2}^{+}) = 10^{-18} \sim 10^{-19} \text{ cm}^2
\]

57Fe mapping by a Mössbauer Microscope

We have developed a Mössbauer spectroscopic microscope [6-8] which measures conversion and Auger electrons emitted after “Mössbauer effect”, i.e., recoil-free nuclear resonance absorption of focused 14.4keV \(\gamma\)-rays. This microscope is, therefore, sensitive only for 57Fe, and the resolution reaches down to 50 \(\mu\text{m}\) so far. In the mc-Si matrix, the distribution of Fe impurities must be strongly correlated with the defects such as vacancies, dislocations and grain boundaries. The mapping intensity of the MS image depends not only on the numbers of 57Fe, but also on the Mössbauer spectral components. Accordingly, by adjusting the Mössbauer resonance condition to each spectral component, we are able to measure separately the mapping images for different components. We have applied this new technique to study a mc-Si solar cell without SiN layer, in which 57Fe impurities were intentionally deposited with a thickness of 1.7nm, and subsequently, were diffused into the n-region with electrodes at room temperature.

Figure 4 shows the Fe mapping images of the 57Fe-diffused mc-Si wafer corresponding to (a) substitutional Fe_{0}, (b) interstitial Fe_{0}, (c) interstitial Fe_{1}, and (d) the CCD picture of measured region of the mc-Si solar cell, and (e) the Mössbauer spectrum, respectively. In the picture (d) two electrodes
Fig. 4 Mössbauer Mapping images: (a) substitutional Fe$^0_s$, (b) interstitial Fe$^0_i$, (c) interstitial Fe$^+_i$, (d) measured region of mc-Si solar cell with electrodes, and (e) the transmission Mössbauer spectrum. The color scale for the Mappings of (a), (b) and (c) is the total electron counts at each mapping point.

can be seen. Roughly speaking, the mapping intensities of (a), (b) and (c) are proportional to the area intensities corresponding to Fe$^0_s$, Fe$^0_i$ and Fe$^+_i$, respectively. It should be noted that the Fe impurities distribute not only along the grain boundaries, but also in the grain matrix.

**Conclusion**

We investigated Fe impurities in mc-Si solar cells which were introduced either by highly energetic implantation, or by diffusion process. The different Fe charge states on different lattice sites could be detected directly during implantation and/or light illumination. Clearly observed in the on-line and the conventional experiments is that the interstitial components of Fe$^0_i$, Fe$^+_i$ and Fe$^{2+}_i$ change their charge states under light illumination through the carrier trappings. The Fe mapping images show that the Fe impurities distribute differently in different grains.

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