Mössbauer spectroscopic microscope

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Abstract. A “Mössbauer spectroscopic microscope” has been developed using a Multi-Capillary-X-ray (MCX) lens, operating in a laboratory combined with a scanning electron microscope (SEM). This microscope yields a two-dimensional mapping image of $^{57}$Fe probes with a space resolution of about 50$\mu$m in comparison with the microstructure observed by SEM.

1. Introduction
In materials science different measuring techniques are usually combined to characterize the microstructure of materials. Mössbauer spectroscopy provides atomistic information at a nuclear probe in a matrix through the hyperfine interactions, while the microstructure is studied, for instance, by scanning electron microscope and/or X-ray diffraction. The information obtained by Mössbauer spectroscopy is limited to a few nearest neighbors from the probe. In the case of state-of-art materials for electronic and magnetic devices, however, there seems to be strong demands to clarify the atomistic nature of the nuclear probes and the microstructure down to submicron meter scale simultaneously.

Recently, X-ray optical devices for focusing X-rays down to several 10 nm have been widely developed for X-ray microanalysis at synchrotron facilities as well as at laboratories. We use one of such technique, i.e., a Multi-Capillary-X-ray (MCX) lens [1], which makes us possible to focus the $\gamma$-rays of 14.4keV emitted from a standard $^{57}$Co-in-Rh source in order to build a Mössbauer spectroscopic microscope. This MCX lens consists of thousands of small capillaries with a diameter of about 2$\mu$m. The $\gamma$-rays are introduced and totally reflected inside of the capillaries, changing the propagation directions, so that the $\gamma$-rays can be focused down to a diameter of 250$\mu$m. In this communication, we will describe the Mössbauer microscope and will show its typical applications to a contamination problem of multi-crystalline silicon wafers for solar cells. A preliminary result was already reported in the last international conference of the applications of the Mössbauer effect (ICAME2007) at Kanpur [2].

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2. Mössbauer Microscope

A new MCX lens is specially designed for 14.4keV $\gamma$-rays, which provides a spot size of 256 $\mu$m in diameter at a focal distance of 58 mm from the outlet of lens for $\gamma$-rays. The 35% fluence of the parallel incoming $\gamma$-rays is transmitted through the MCX lens. The sample is fixed on a X-Y stage in a vacuum chamber. The conversion electrons are measured as a function of the position of the $\gamma$-ray spot on the sample using a three-stage micro channel plate (MCP) assembly, which is produced by Hamamatsu photonics Japan. The number of the mapping positions is typically $40 \times 40 = 1600$. The position is varied with a step size between 25$\mu$m and 250 $\mu$m.

The mapping image is produced from a contour plot based on the counts of conversion electrons detected in the whole area, for instance, $1 \times 1$ and $10 \times 10$mm$^2$. One complete mapping will take 10 hours typically. Both the step size and the spot size of the focused $\gamma$-ray determine the space resolution of the mapping images. Furthermore, we have installed a field-emission type scanning electron microscope (Mini-EOC, APCO Ltd.) to our system (figure 1) with a space resolution of 20 nm in order to observe a microstructure of a sample which can be compared with the Fe mapping image measured by the Mössbauer spectroscopic microscope.

Figure 1. Mössbauer spectroscopic microscope combined with SEM.

Figure 2. Pulse height spectra of MCP corresponding to the $\gamma$-rays’ spot positions of (a) $^{57}$Fe enriched Fe-Ni alloy, (b) $^{57}$Fe deposited multi-crystalline Si, (c) Al-sample holder.

Figure 3. Mapping image of conversion electrons emitted from $^{57}$Fe in mc-Si, FeNi alloy and Al holder for an area of $10 \times 10$mm$^2$ by setting the PHA-window between 200 and 1000 channel.
The electrons emitted from each focused position of the $\gamma$-rays are detected by the MCP which is sensitive not only to the conversion electrons, but also to the photo electrons and other radiation like X-rays and $\gamma$-rays. It is shown in figure 2 and 3 that these electrons can be well distinguished by setting a proper measuring window for the output signals from the MCP, because the pulse heights of the signals from the $^{57}$Fe containing samples (figure 2 (a) and (b)) are much higher than those from the aluminum sample holder (figure 2 (c)). The measuring window of the MCA output was set between 200 and 1000 channels of the PHA spectrum in figure 2. Figure 3 shows a mapping image from an area of 10×10 mm$^2$ measured by a vibrating $^{57}$Co source within a Doppler velocity range of ±8 mms$^{-1}$. Two different samples of $^{57}$Fe in mc-Si and $^{57}$Fe-Ni alloy are fixed by an Al sample holder. The black lines drawn in Fig.3 show the boundaries between the Al holder and the samples. Inhomogeneous distributions of $^{57}$Fe atoms can be seen in both samples. Note that the highest counts zone is between 984 and 1036 in figure 3, while the lowest zone is close to zero, indicating an extremely high signal to noise ratio of about 20 for detecting $^{57}$Fe atoms in a sample.

3. A mapping image of $^{57}$Fe deposited multi-crystal Si

Silicon materials in solar cells are known to be contaminated by Fe impurities through the cell production process, which degrade the photovoltaic efficiency of the cell. We have installed a FE-SEM into our Mössbauer microscope, in order to observe an area using both microscopes. A SEM-picture of two crystal grains of multi-crystalline Si is shown in figure 4. The $^{57}$Fe deposited sample with a thickness of 3 nm was annealed at 1000 °C for one week. We performed to map roughly the same area of the sample as is shown in figure 4, and the mapping intensity, which is presented in figure 5, changes considerably from one grain (left) to another (right). This appears to be due to either different concentrations of $^{57}$Fe in the grains, or to different depth distributions of $^{57}$Fe from the surface to 100nm, i.e., a measuring depth possible for the conversion electrons. Furthermore, the intensity depends on the local concentration of $^{57}$Fe as well as on the resonance conditions corresponding to the chemical states and the lattice sites of $^{57}$Fe atoms in the sample. The latter conditions provide us a possibility to get a mapping image of a certain spectral component selectively. A result obtained from a solar cell of multi-crystalline Si, which is not shown in this report because of

![Figure 4. SEM picture of $^{57}$Fe deposited multi-crystalline Si, showing two different grains.](image)

![Figure 5. Mapping image of $^{57}$Fe deposited multi-crystalline Si for an area of $1 \times 1$mm$^2$.](image)
the lack of the space, suggests that substitutional and interstitial Fe atoms distribute differently in different grains. This result may be due to an inhomogeneous distribution of vacancies in different grains, which was produced during the solidification process of the sample. In Si crystal, on the other hand, Fe impurities are thought to diffuse dominantly via interstitial mechanism. Substitutional Fe may be formed by a defect reaction between an interstitial Fe and a vacancy during the annealing. Accordingly, such reaction is considered to be one of the reasons for the inhomogeneous distribution of substitutional and interstitial impurities. The details will be published elsewhere.

4. Summary
A new instrument “Mössbauer spectroscopic microscope” is presented in this paper. This microscope is sensitive only to $^{57}$Fe atoms, because we detect the conversion electrons emitted from a $^{57}$Fe containing sample after recoil-free absorptions of γ-rays, i.e., Mössbauer effect. Subsequently, we map the electron counts as a function of the sample position, where the γ-rays are focused by a multi-capillary X-ray lens (MCX) [1]. The microscope can be applied for materials research on Fe containing electronic and magnetic devices to investigate the microstructure and the electronic and magnetic states simultaneously.

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