Defect profiles in ion-irradiated metal samples by slow positron beams in comparison with simulation profiles

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Abstract. Metal (Fe and Ni) samples ion-irradiated at 100 – 773 K were characterized by Doppler broadening measurements with slow positron beams to investigate depth profiles of irradiation-induced defects. Obtained results were compared with defect profiles calculated by Monte-Carlo simulation. Defects profiles obtained by positron measurements were always deeper than those by the simulation. The difference between measured and simulated profiles was observed even in the case of the Fe sample irradiated at 100 K where vacancies are immobile. The origin of such differences was discussed with respect to vacancy diffusion, depth calculation, surface contamination and ion channeling.

1. Introduction
Ion irradiation causes radiation damage that considerably affects properties of materials. Defects induced by ion irradiation diffuse and react with each other, leading to recombination or evolution to secondary defects. It is important to know the distribution and the motion of defects in ion-irradiation studies. Positron annihilation spectroscopy using energy-variable slow-positron beams has been extensively used as a depth-dependent characterization technique for defects (vacancies) in ion-irradiated layers [1,2]. Some of the previous studies on ion irradiation to Si [3,4] or steel [5] reported that defect profiles given by positron measurements are deeper than calculated defect profiles. It should be noted that implanted positrons diffuse and spread in samples before annihilation and thus defect profiles must be deduced by taking account of positron diffusion. Even after the diffusion calculations, obtained defect profiles were deeper than the calculated profiles in these studies. Moreover, defects were detected after irradiated layers were precisely etched off [3]. The origin of the deep defect profiles is not well understood but they were ascribed to diffusion of defects or channeling of ions [6]. In this study, we investigate pure metal samples (Fe and Ni) to compare defect profiles by positron measurements with defect profiles by numerical simulation.

2. Experimental procedure
Pure Fe (99.994%) and Ni (99.994%) were cut into a size of 1.5 cm × 1.5 cm and mechanically mirror-polished. To remove mechanical damage, the samples were annealed in quartz tube furnaces at 973 K for 0.5 h in flowing H₂ atmosphere (Fe) or at 1173 K for 1 h in vacuum (Ni). Radiation
damage was introduced by 150 keV Ar\textsuperscript{+} irradiation at room temperature (RT), 573 K and 773 K or 200 keV C\textsuperscript{+} irradiation at 100 K. These ion species were chosen owing to the limitation of available ions of the equipments. We believe that the chemical effects of Ar or C ions do not affect the results because the Ar (C) concentrations are sufficiently low at the depths of interest (e.g., >200 nm in the case of Ar). The ion beam was defocused and adjusted to the samples to achieve uniform and continuous irradiation. Incident angles of Ar\textsuperscript{+} and C\textsuperscript{+} beams were 0\degree and 30\degree from the normal to the sample surface, respectively. Doppler broadening of annihilation radiation was used as a slow-positron measurement technique at energies below 30 keV. Obtained S-E curves were analyzed by the VEPFIT code \[7\]. Depth profiles of vacancies were calculated by the TRIM (SRIM) code based on a Monte-Carlo method \[8\].

3. Results and discussion

Figure 1 shows the Doppler broadening S parameter as a function of positron energy for the Fe samples irradiated with 150 keV Ar\textsuperscript{+} to a dose of 5×10\textsuperscript{15} cm\textsuperscript{-2} at 573 and 773 K, together with S parameters for the unirradiated Fe sample. Solid lines are fits to S parameters of the three samples. At positron energies above 5 keV, S parameters of the irradiated samples were higher than those of the unirradiated samples owing to defects induced by ion irradiation. Low S parameters below 5 keV were presumably caused by oxygen atoms recoiled from oxide layers on the Fe samples.

The S-E curves were imported in the VEPFIT code and the depth dependence of S parameters was calculated as shown in figure 2. Firstly, we determined the S parameter and diffusion length of bulk from the unirradiated sample and fixed them in the analysis. Then, initial parameters for other layers (S parameter, diffusion length and layer thickness) were approximately determined. Starting from the initial parameters, a fitting process for each single layer was performed layer by layer from the surface layer to deep layers to obtain optimum fitting results.

A 3-layer model was applied to describe the sample structure for the irradiated samples in figure 1, where the top and middle layers correspond to the irradiation-induced defects and the 3rd layer corresponds to bulk Fe. The increase in S parameters (i.e., damage layers) extends to 400 or 450 nm. Similar experiments were performed for Fe at RT and Ni as summarized in table 1 \[9\]. The calculated depth was always deeper than the projected ranges and the simulated profiles.

![Figure 1](image1.png)

**Figure 1.** Doppler-broadening S parameter as a function of positron energy for Fe samples irradiated with 150 keV Ar\textsuperscript{+} to a dose of 5×10\textsuperscript{15} cm\textsuperscript{-2} at 573 and 773 K.

![Figure 2](image2.png)

**Figure 2.** Depth dependence of the S parameter corresponding to the S-E curves in figure 1. A simulated vacancy profile (closed circles) and a projected range (Rp) are shown for comparison.

The difference between the measured and simulated profiles could be explained as a result of vacancy diffusion. Vacancy diffusion is a temperature dependent process. Diffusion of monovacancies in pure Fe occurs at room temperature because of its relatively low activation energy.
(<0.6 eV). On the other hand, monovacancy diffusion in Ni is negligible at room temperature as calculated in our rate-equation analysis assuming an activation energy of 1.0 eV. However, there was no clear temperature dependence in both Fe and Ni cases in the temperature range of RT to 773 K.

### Table 1. Calculated depth of damage layers in Fe and Ni after 150 keV Ar\(^+\) irradiation. The projected ranges of Ar\(^+\) were 68 and 61 nm in Fe and Ni, respectively.

| Substrate | Temperature (K) | Fe | Ni |
|-----------|----------------|----|----|
|           |                 | RT | 573| 773| RT | 573| 773|
| Dose (cm\(^{-2}\)) | 1×10\(^{15}\) | 5×10\(^{15}\) | 5×10\(^{15}\) | 1×10\(^{15}\) | 5×10\(^{15}\) | 5×10\(^{15}\) |
| Depth (nm) | 5.2×10\(^{2}\) | 4.5×10\(^{2}\) | 4.0×10\(^{2}\) | 6.0×10\(^{2}\) | 4.7×10\(^{2}\) | 5.5×10\(^{2}\) |

To further investigate the temperature dependence, the Fe sample was irradiated at 100 K where Fe monovacancies are immobile [10]. By using an in-situ positron measurement system at the University of Tokyo [11], an Fe sample was irradiated with 200 keV C\(^+\) to a dose of 5×10\(^{14}\) cm\(^{-2}\) at 100 K, followed by the Doppler broadening measurement at 100 K in the same vacuum chamber. Since the 150 keV Ar\(^+\) beam was not available with the system, the 200 keV C\(^+\) beam was used.

Figure 3 shows the result of the Doppler-broadening measurements for the Fe sample irradiated at 100 K. The S-E curve for the unirradiated condition (open circles) was obtained at 100 K from the same sample before the irradiation. The S parameters increased after the irradiation in all the energies except for the near-surface region below 1 keV. The S-E curves in figure 3 were analyzed and the depth dependence of S parameters was calculated as shown in figure 4. A 4-layer model was applied to describe the sample structure, where the 4th layer corresponds to bulk (undamaged) Fe in this case. The diffusion length and the S parameter of the bulk Fe at 100 K were obtained from the S-E curve of the sample before irradiation. The increase in the S parameters shows that the damage layer extends to 570 nm. The depth of the damage layer was, again, deeper than the projected range of Ar\(^+\) (199 nm) in Fe and the simulated defect profile. These results suggest that the vacancy diffusion cannot account for the difference between the measured and simulated profiles.

Positron implantation profiles in this study were calculated by a Makhovian function [2] with the empirical parameters reported by Vehanen et al. [12]. It is known that the Makhovian parameters are slightly material- and energy-dependent [2]. However, we estimated that the errors originating from such dependences were less than 18% in the energy range of 5 – 30 keV. It is unlikely that the differences between the measured and simulated profile are attributed to the errors of the Makhovian function.

**Figure 3.** Doppler-broadening S parameter as a function of positron energy for an Fe sample irradiated with 200 keV C\(^+\) to a dose of 5×10\(^{14}\) cm\(^{-2}\) at 100 K.

**Figure 4.** Depth dependence of the S parameter corresponding to the S-E curve in figure 3. A simulated vacancy profile (closed circles) and a projected range (Rp) are shown for comparison.
It is necessary to take account of the influence of the recoil atoms from surface contaminations such as native oxide and hydrocarbon originating from vacuum systems. Maximum recoil energies of H, C and O atoms by 150 keV Ar$^+$ can be calculated as 14.6, 107 and 123 keV, respectively. The projected ranges of such recoils were calculated to be 137 nm (C in Fe) at most. This depth is close to the simulated defect profiles for Ar$^+$ and much shallower than the measured defect profiles. Thus the influence of the contamination atoms is negligible.

As the samples used in this study are in the form of polycrystalline with grain sizes of the order of 10 µm, it is necessary to consider channeling effects of ion beams. When incident ions are aligned to crystalline axes of each grain, ion ranges can be extended to several times the projected ranges in amorphous samples [13]. Indeed, the influence of channeling on Doppler broadening measurements was clearly demonstrated in the case of As$^+$ implantation in Si [14]. The observed difference between the measured and simulated defect profiles can be attributed to the channeling effect but further investigations are required to confirm it.

4. Summary
Defect profiles in Fe and Ni samples ion-irradiated at 100 K – 773 K were characterized by Doppler-broadening measurements and compared with defect profiles calculated by a Monte-Carlo simulation. Measured defect profiles were always deeper than simulated defect profiles. The difference was observed in the case of irradiation to Fe at 100 K where vacancies are immobile. The origin of such differences cannot be explained by vacancy diffusion, errors of positron implantation depths and recoils from the surface impurities. The effect of channeling to polycrystalline grains was suggested as a possible explanation.

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