Enhancement of Excited Secondary Fe Atoms under Oxygen Ion Bombardment

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Resonance enhanced multiphoton ionization (REMPI) spectra of sputtered Fe atoms for three kinds of sample matrices have been measured to confirm the matrix effects for SNMS using Ar⁺ and O₂⁺ beams. It is shown that the intensity of Fe-56 atoms sputtered in higher energy state, that is the ground state multiplets and the first excited state, increases with increasing surface oxygen concentration in the spectra. Depth profile measurements of Fe-54 implanted in SIMOX have been also performed for three kinds of (1+1) schemes by REMPI-SNMS. The depth profile for Fe-54 sputtered in the ground state has corresponded to the SRIM2003 calculation result. On the other hand, the intensity of Fe-54 sputtered in the first excited state has been enhanced in the SiO₂ layer. By a comparison with the result of the REMPI spectrum measurement, this enhancement may be influenced by not only the surface oxygen concentration but also matrix elements in samples. [DOI: 10.1380/ejssnt.2009.191]

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I. INTRODUCTION

Secondary ion mass spectrometry (SIMS) is employed for wide variety of analytical application. The characteristics of SIMS, such as high sensitivity, are also useful for a material analysis in steel-making field, but it is difficult to measure these materials by SIMS because the secondary ion yield is dependent on atomic composition, chemical state, and so on of the target sample. To avoid the dependence called the matrix effect, secondary neutral mass spectrometry (SNMS) has been energetically studied in 1990’s. The secondary neutrals are ionized by postionization technique, for example a resonance enhanced multiphoton ionization (REMPI) method, and then the ionized neutrals are detected by the same manner as SIMS.

In the REMPI method, photon energy is matched with a specific energy gap between an initial state and an intermediate state of atoms, clusters or molecules on each transition. This means that characteristics of SNMS combined with REMPI are not only an elemental selectivity but also an electronic state selectivity for the secondary neutral detection [1, 2]. Here, it is important to know a population distribution of secondary neutrals, which may influence the REMPI yield. To understand the population distribution of sputtered particles, some mechanisms of the sputtered-particle excitation process have been considered.

For single-element metal samples, the population distribution of sputtered atoms is related to its velocity distribution and the electronic band structure in the bulk [3, 4]. In addition, a fraction of cluster formation in sputtered particles increased with increasing oxygen density at the surface, which is followed by a production of atoms with excited state as the result of a dissociation of the neutral cluster [5, 6]. Then, the velocity distribution and the fraction of the cluster formation depend on the condition of a primary ion beam such as incident energy, incident angle, ion species, and so on. We have also reported that the lowest lying excited state increased on oxygen ion beam irradiation [7, 8].

However, it is difficult to expand these understandings into an analysis for alloy metal samples because the phenomena may be more complicated due to nonlinear process, namely dynamic mixing and preferential sputtering. Unfortunately, experimental approach has been still not enough for practical use though there are a few reports for alloy sample analysis [2, 9].

In the present study, we propose the partial population distributions of sputtered Fe-56 atoms from a SS304 sample by Ar⁺ and O₂⁺ beam irradiations and from a Fe and a FeO samples by Ar⁺ beam irradiation to confirm the yield change of Fe-56 atoms sputtered in higher energy states under various conditions of oxygen density at the surface.

Depth profiles of implanted Fe-54 in SIMOX are also measured to know the matrix effect using three kinds of (1+1) REMPI schemes by REMPI-SNMS with Ar⁺ beam. In addition, the Fe-54 depth profile obtained by REMPI-SNMS is compared with that obtained by SIMS.

II. EXPERIMENTAL

An experimental setup is shown in Fig. 1. The experimental apparatus has been previously described in detail [8]. Brieﬂy, the SNMS system is based on a SIMS instrument with a quadrupole mass spectrometer (SIMS6650, ULVAC-PHI, Inc.). Duoplasmatron ion source produces primary ion beams such as Ar⁺ and O₂⁺ with the incident energy range from 8 keV to 250 eV. Another ion source also produces the Cs ion beam with the incident energy range from 10 keV to 250 eV. Each incident angle is 60˚ with respect to a normal direction of a sample surface. Both ion sources can be operated in either a continuous or a pulsed beam mode. A sample surface is scanned with the focused beam about 10 µm in diameter at a raster-scanning mode. The primary beam current is typically tuned to be 200 nA on the continuous beam mode in the squared area of 300×600 μm at the sample surface. Secondary ions and ionized secondary neutrals are extracted by a potential of -200 V, and are introduced to the 90°
sector of the energy analyzer followed by the quadrupole mass spectrometer. A positive bias of 27V is applied on the target to improve a transmission efficiency of the ionized secondary neutrals into the detector. Ion signals are recorded using the multi-channel scalar (MCS) synchronized to the laser pulse to obtain a good signal to noise ratio. The main chamber is evacuated to a base pressure of 5×10^{-8} Pa.

Laser light passes through a height of 1 mm above the sample surface to create the ionized secondary neutrals at a third harmonic output of Nd:YAG laser light, generates a length tunable laser system, sample surface to create the ionized secondary neutrals at one of the target to improve a transmission efficiency of the ion-spectrometer. Laser light, pulsed ion beam and Multi channel scalar system are newly introduced.

A. Iron REMPI spectra measurements

Iron REMPI spectra around 300 nm for the SS304 sample have been measured during 3 keV-Ar^+ and -O_2^+ irradiations. Typical Fe-REMPI spectra are shown in Fig. 2. Each spectrum intensity was normalized with the intensity of 298.36 nm line, a^3D_4→y^3D_3→ auto ionization (A.I.).

Each spectra was normalized in a SIMS measurement. The pulsed beam mode was done for sputtering. The charge compensation was performed with 3 keV electron beam irradiation. Relative peak intensities are also measured, as is shown in Fig. 2.

FIG. 2: Typical Fe-REMPI spectra under 3 keV-Ar^+ and -O_2^+ irradiations to the SS304 sample. Each spectra was normalized with the intensity of 298.36 nm line, a^3D_4→y^3D_3→ auto ionization (A.I.).

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the FeO sample. De-excitation from the $a^2F_J$ state to the $a^2D_J$ state has very low transition probability of the order of $10^{-3}$/s which correspond to the lifetime of a few hundred second. Assuming the sputtered atom velocity of about 5000 m/s [10], we can estimate that sputtered atoms spend a time of the order of 100 ns from the sample surface to the laser ionization region in our setup. Thus we ascribe that the $a^2F_J$-excited atoms may survive with reflecting the surface electronic structure. Although almost all sputtered atoms are distributed at the ground state, the intensity of sputtered atoms with higher energy state somewhat varies.

B. Depth profile of Fe-54 in SIMOX

First, the Fe-54 depth profiling of REMPI-SNMS is compared with that of SIMS, which is shown in Fig. 4. The 5 keV-Ar$^+$ beam with the current of 200 nA has been used in both experiments. The Fe-54 is ionized by (1+1) REMPI scheme using laser light whose wavelength is 298.36 nm for $a^2D_4 \rightarrow y^2D^3_3 \rightarrow A.I.$ In case of SIMS, the signal intensity of Fe-54 from the SiO$_2$ layer is three orders of magnitude higher than the signal intensity from the Si layer. In contrast, the Fe-54 depth profile by REMPI-SNMS is in agreement with the calculation result from the SRIM 2003 code. It is confirmed that REMPI-SNMS is more quantitative than SIMS.

Second, the Fe-54 depth profiles are measured using three kinds of (1+1) REMPI schemes, i.e. $a^2D_4 \rightarrow y^2D^3_3 \rightarrow A.I.$ (scheme $\#1$), $a^2D_4 \rightarrow y^2F^5_5 \rightarrow A.I.$ (scheme $\#2$) for the ground state, and $a^2F_4 \rightarrow x^2F^5_5 \rightarrow A.I.$ (scheme $\#3$) for the first excited state, which is shown in Fig. 5. Each depth profile has been normalized with the maximum intensity in their profile. Both depth profiles using scheme $\#1$ and $\#2$ are in fairly good agreement with the SRIM2003 result though the implanted Fe-54 atoms may be diffused into a deep region by ion beam irradiations. So, the intermediate state of the Fe atoms is not influenced by the surface oxygen concentration and the matrix elements of the sample in the REMPI process.

On the other hand, the depth profile using scheme $\#3$ is strongly enhanced in the SiO$_2$ layer. The Fe-54 atoms sputtered in the first excited state increases under oxygen existence, as is described in subsection 3.2. The peak Fe-54 intensity is higher by 11 than the results obtained by scheme $\#1$ and $\#2$ in the SiO$_2$ layer. This difference corresponds to the ratio between the Fe-56 intensities for the SS304 sample under the O$_2^+$ beam irradiation and for the Fe sample under Ar$^+$ beam irradiation, that is 10.7 calculated using the values listed in table 1. Thus, the Fe-54 atoms sputtered in the excited state are related not only surface oxygen concentration but also matrix elements in the sample qualitatively, however it is difficult to estimate the matrix effect for REMPI-SNMS quantitatively.

http://www.sssj.org/ejsnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejsnt/)
TABLE I: Relative peak intensities of $a^5D_j \rightarrow y^5D_{j-1}$ → auto ionization (A.I.) and partial $a^5F_j \rightarrow x^5F_{j-1}$ → A.I. transitions in the REMPI spectra shown in Fig. 2 and 3. Each intensity was normalized with the sum of intensity for all the measured transitions in each spectrum.

| Transition                  | Resonance wavelength (nm) | Intensity (a.u.) |
|-----------------------------|---------------------------|------------------|
| $a^5D_4 \rightarrow y^5D_3$ → A. I. | 298.36                    | 0.439            |
| $a^5D_3 \rightarrow y^5D_2$ → A. I. | 299.44                    | 0.251            |
| $a^5D_2 \rightarrow y^5D_1$ → A. I. | 300.09                    | 0.114            |
| $a^5D_1 \rightarrow y^5D_0$ → A. I. | 300.81                    | 0.034            |
| $a^5F_5 \rightarrow x^5F_4$ → A. I. | 299.95                    | 0.107            |
| $a^5F_4 \rightarrow x^5F_3$ → A. I. | 300.96                    | 0.056            |

IV. CONCLUSIONS

We have measured the Fe-56 REMPI spectra under the Ar$^+$ beam irradiation to the Fe, SS304, and FeO on Fe sheet samples and under the O$_2^+$ beam irradiation to the SS304 sample to confirm the yield change of Fe-56 atoms sputtered in higher energy states under various conditions of oxygen density at the surface. Iron atoms sputtered in excited states are the most intense under the O$_2^+$ beam irradiation to the SS304 sample. Thus the excited Fe atoms may increase with increasing surface oxygen concentration.

The depth profiles of Fe-54 implanted in SIMOX have been measured to understand the matrix effect of REMPI-SNMS using three kinds of (1+1) REMPI schemes, i.e., two schemes from the ground state through different intermediate states and one scheme from the first excited state. Depth profiles by REMPI from the ground state have been in fairly agreement with the SRIM2003 result, while the depth profile by REMPI from the first excited state has been enhanced in the SiO$_2$ layer. It is found that this enhancement may be influenced by not only surface oxygen concentration but also matrix elements in the sample. Therefore, it is better to utilize the REMPI from the ground state for Fe quantitative analysis because the Fe atom sputtered in the excited state is relatively sensitive for surface condition.

We have not mentioned the depth resolution in the profile because we could not use an electronic gating to avoid the crater edge effect. Further study should be needed to improve the depth resolution by the electronic gating synchronized to both ion beam scanning and laser pulse with the ion detection system.

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