

# Relative Yields of Secondary Ions Sputtered from Fe, FeO, Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> by Cs<sup>+</sup> and O<sub>2</sub><sup>+</sup>

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The relative yields of secondary ions sputtered from metallic iron and three iron oxides, FeO, Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>, by Cs<sup>+</sup> and O<sub>2</sub><sup>+</sup> have been examined. In mass spectra of the negative ions by Cs<sup>+</sup>, Fe ion counts from oxides are found to be higher than that from pure iron by a factor of about thirty, while differences of secondary ion yields between Fe and FeO are small in mass spectra of positive ions by O<sub>2</sub><sup>+</sup>.

## 1. Introduction

Quantification in secondary ion mass spectrometry (SIMS) is mainly limited by the matrix effect; occurrence of secondary ions sputtered from a sample is strongly influenced by the characteristic feature of the matrix species [1]. For example, a sputter profile measured in an iron sample covered by an oxide layer does not usually give a real depth profile, since yields of secondary ions sputtered from an oxide layer are much higher than those for a metallic matrix. Therefore, in order to improve quantification in SIMS analysis, especially depth profile, relative yields of sputtered ions from different matrixes or samples should be investigated systematically. Thus, the objective of the present work is to provide information on the relative yields of secondary ions sputtered from metallic iron and three iron oxides, FeO, Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>, by Cs<sup>+</sup> and O<sub>2</sub><sup>+</sup>.

## 2. Experimental

Samples used were an iron sheet of 4N purity, referred to as sample Fe, and three iron oxide samples, FeO, Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>. The oxide samples were prepared by oxidizing the iron sheet at 1400 K, to form these oxide layers of which the total thickness was about 1 mm. The surface of each oxide layer was revealed by mechanical polishing. They were identified using Fourier-Transform infrared

spectroscopy, as exemplified in Fig.1.

SIMS measurements were performed using CAMECA IMS-3f. After the sputter profile of a sample reached a steady state, several negative ions bombarded by Cs<sup>+</sup> or positive ions by O<sub>2</sub><sup>+</sup> were counted under given conditions.

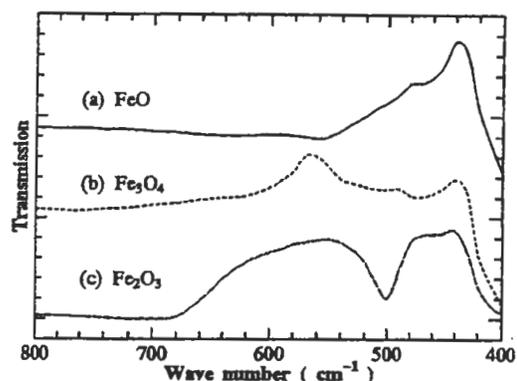


Figure 1. Infrared spectra from layered structure of three iron oxide, FeO, Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> by FT-IR microscopy.

## 3. Results and Discussion

### 3.1 Secondary ion mass spectra

Figures 2 (a), (b), (c) and (d) show mass spectra of secondary negative ions by Cs<sup>+</sup> for Fe, FeO, Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub> in the mass range between 70 and 140, respectively. Ion peaks of FeO, FeO<sub>2</sub> and Fe<sub>2</sub> are observed in mass spectra of sample Fe. On the other hand, in the iron oxide samples, additional peaks of Fe<sub>2</sub>O and FeO<sub>3</sub> are detected. It should be

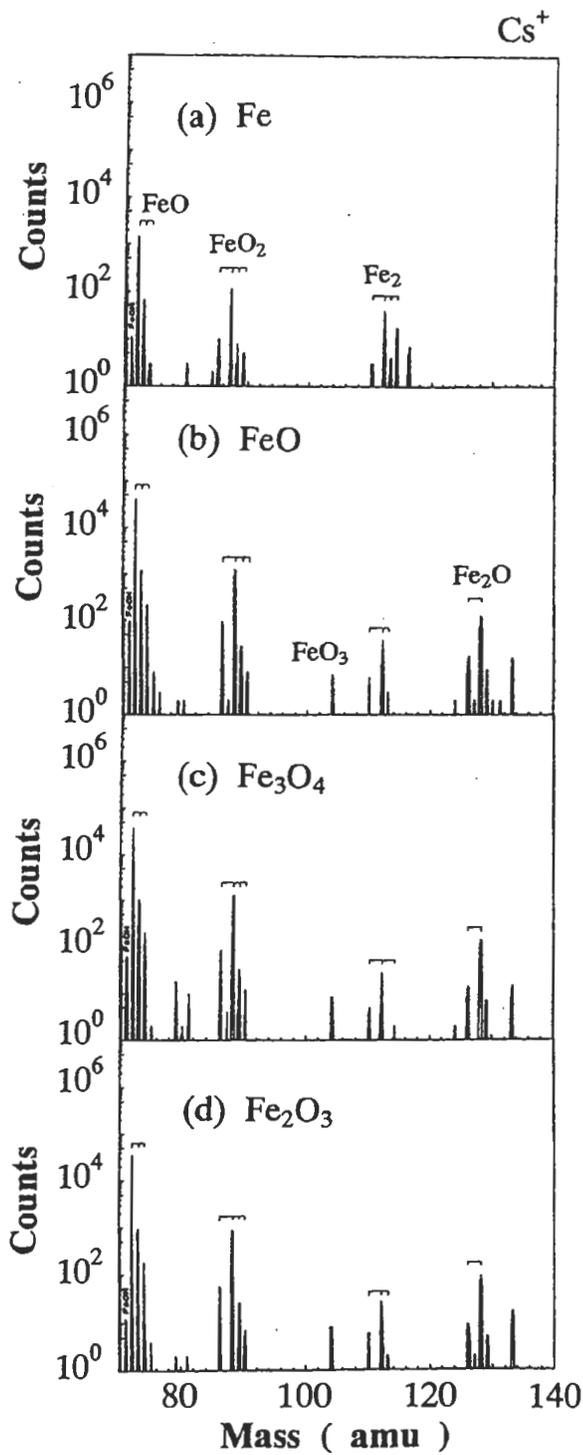


Figure 2. Secondary negative ion mass spectra from (a)Fe, (b)FeO, (c) Fe<sub>3</sub>O<sub>4</sub> and (d) Fe<sub>2</sub>O<sub>3</sub> by Cs<sup>+</sup>.

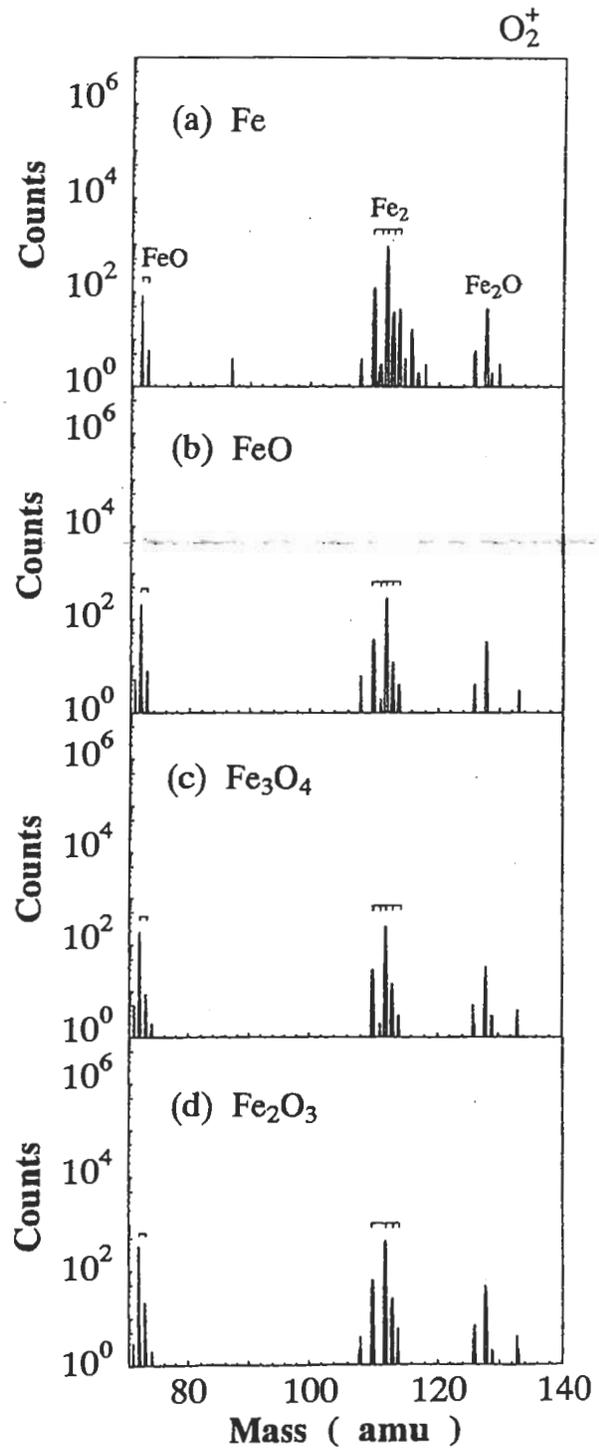


Figure 3. Secondary positive ion mass spectra from (a)Fe, (b)FeO, (c) Fe<sub>3</sub>O<sub>4</sub> and (d) Fe<sub>2</sub>O<sub>3</sub> by O<sub>2</sub><sup>+</sup>.

noted that a Cs (133 amu) peak from the oxide samples is clearer than that from Fe, although the mechanism is unclear.

Similarly, mass spectra of secondary positive ions by  $O_2^+$  are as shown in Fig.3. Peaks of  $Fe_2O$  are observed in all samples. Since the amount of oxygen in sample Fe is very small, these  $Fe_2O$  peaks may originate mainly from the reaction of the samples with the primary ions. On the other hand, signals of  $FeO_2$  which were observed in negative ion spectra, as shown in Fig.2, seem to be insignificant in these samples, although small amounts of ions from sample Fe were detected.

### 3.2 Relative yields of secondary ions

In order to compare relative yields of the secondary ions, ion counts were accumulated during prolonged time. Fig.4 summarizes the relative counts of secondary ions Fe (56 amu), FeO (72 amu),  $FeO_2$  (88 amu) and  $Fe_2O$  (128 amu) which were obtained under given conditions. Iron-oxygen cluster ions from sample Fe may be due to the background. The intensities of negative secondary iron ions from oxides are about thirty times as high as those from the iron matrix. The iron-oxygen cluster ions from the oxides sputtered by  $Cs^+$  are considered to have originated mainly from the matrix, since their intensities are much higher than those of the background ions. However, the difference between these three oxides seems insignificant.

The relative yields of positive ions sputtered by  $O_2$  are summarized as shown in Fig.5. The iron-oxygen cluster ions from metallic iron sputtered by  $O_2$  may be formed by the reaction of iron with primary ions. Although the oxygen concentration of the oxides is high, the intensities of the iron-oxygen clusters are only three times as high as those from pure iron. This indicates that the formation of these cluster ions is dominated by primary oxygen ions, irrespective of the matrix. It is interesting to note that the intensities of secondary iron ions from the oxides are enhanced by a factor

of about three, which is much smaller than the factor in negative ions. This may result from the strong influence of the primary oxygen ions. Consequently, the difference of intensities of every kind of ion between metallic iron and three iron oxides seems to be small, compared to the case of negative ions sputtered by  $Cs^+$ .

The above results imply that these three oxide species are hardly distinguished by SIMS analysis. Nevertheless, the factors for correction between metallic iron and the iron oxides have been obtained in this work. Using these factors, semi-quantitative discussion in depth profiles may be possible.

### 3.3 Sputtering rate

Since the sputtering rate influences the yields of measured secondary ion, the value should be compared between different matrices. A surface profiler was used for measuring the depth of the sputtering craters, and they were calculated as summarized in Fig.6. The results show that the sputtering rate of samples Fe and FeO appears to be lower than the value for samples  $Fe_3O_4$  and  $Fe_2O_3$ , but the difference is not so large, compared to counts of secondary ions.

### 4. Concluding remarks

- (1) In mass spectra of the negative ions by  $Cs^+$ , Fe ion counts from oxides are higher than that from pure iron by a factor of about thirty.
- (2) In mass spectra of positive ions by  $O_2^+$ , differences of secondary ion yields between Fe and FeO are small. Ions of FeO,  $FeO_2$  and  $Fe_2O$  may be formed by reaction with primary oxygen ions.
- (3) Using SIMS by  $Cs^+$  and  $O_2^+$ , FeO,  $Fe_3O_4$  and  $Fe_2O_3$  seem to be hardly distinguished.

### 5. References

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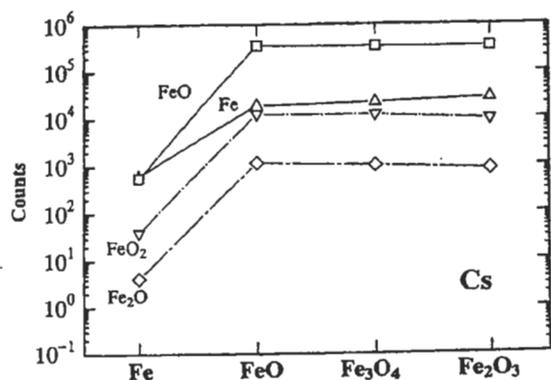


Figure 4. Relative counts of secondary ions Fe(56 amu), FeO(72 amu), FeO<sub>2</sub>(88 amu) and Fe<sub>2</sub>O(128 amu) sputtered by Cs<sup>+</sup>.

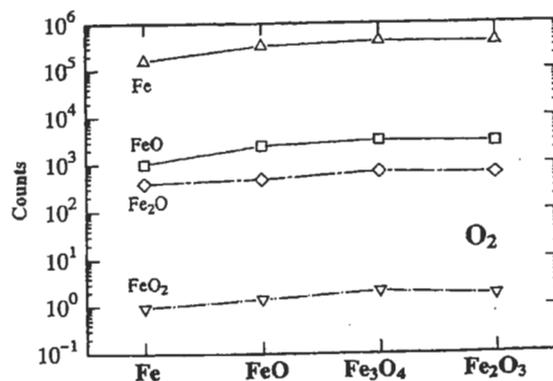


Figure 5. Relative counts of secondary ions Fe(56 amu), FeO(72 amu), FeO<sub>2</sub>(88 amu) and Fe<sub>2</sub>O(128 amu) sputtered by O<sub>2</sub><sup>+</sup>.

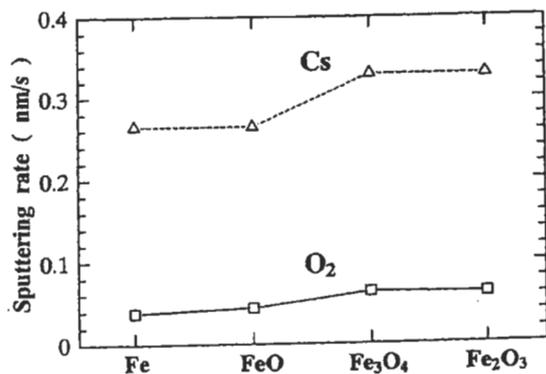


Figure 6. Sputtering rates of samples Fe, FeO, FeO<sub>2</sub> and Fe<sub>2</sub>O sputtered by Cs<sup>+</sup> and O<sub>2</sub><sup>+</sup>.