Use of SIMS to Determine Pure and Oxidized Elements in a Solid Surface

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A quantitative analysis of oxidized elements in a solid surface which consists of pure and oxidized element has been studied using a SIMS equipped with a quadrupole mass filter. The apparatus is able to introduce gas into the specimen chamber in amounts as high as $1 \times 10^{-3}$ Torr without any problems for the primary beam system and the analyzer system by means of differential pumping techniques. The standard sample (Al, Si) composed of a pure and oxidized element is prepared by the method used for fabricating microelectronic devices. Ions such as Al$^+$ and Si$^+$ emitted from standard samples are represented by the linear superposition of ions emitted from the pure and oxidized element. The concentration of the oxidized element is determined by the ratio of the secondary ion intensity on exposure to oxygen to that on non-exposure to oxygen.

1. Introduction

Secondary ion mass spectrometry (SIMS) is a recently developed surface-analytical technique based on bombarding the sample with a primary beam of keV ions, and analyzing the secondary ions emitted. Since the instrument is capable of in-depth profiling down to the ppm level, SIMS has been quite widely used in surface analyses. However, there are few studies on surface chemical state by dynamic SIMS which uses primary ion with a high current density. Werner$^{2,3,4}$ showed that a specific cracking pattern in the mass spectrometer (the fingerprint spectra) reflects the chemical bonding in a sample; the concentration of metals (Cu, Cr, Ni) and their oxides can be calculated from the fingerprint spectra. His method needs standard samples in different oxidized states and identical conditions for the measurement of the secondary ion currents for each sample.

When oxygen is introduced into the specimen chamber with Ar$^+$ as the primary ion, there are many advantages in the field of analysis of solid surfaces and thin films: (a) the enhancement of the secondary ion yield,$^{5,6}$ (b) the reduction of relative sensitivity factors for elements,$^{6}$ (c) the elimination of the crystal orientation...
dependence on the secondary ion intensity,\(^7\)
(d) the decrease of the sputtering rate,\(^8\)
and (e) the improvement of the reproducibility of analytical values.\(^9\),\(^10\)

We used the oxygen introduction method for the determination of oxidized element in the solid surface, and examined the linear superposition of secondary ion intensity from the pure and oxidized element by using of the favorable standard samples which were prepared by techniques fabricating microelectronic devices.

2. Principle of quantitative analysis for an oxidized element

The secondary ion current \(I_A^+\) for an element A measured in a SIMS instrument is given as:

\[
I_A^+ = I_P \cdot Y_A \cdot \eta_A \cdot C_A
\]

where \(I_P\) is the primary ion current,
\(Y_A\) is the secondary ion yield for the element A, that is the number of emitted ions/primary ion,
\(\eta_A\) is the ion collection efficiency of the element A,
and \(C_A\) is the atomic concentration of the element A.

It is known that \(Y_A\) is dependent on the chemical bonding of an element and on the ambient oxygen pressure. Fig. 1 shows results for Al obtained in this study. The secondary ion intensity from a pure element increased with the increase of the oxygen partial pressure. When oxygen was sufficiently introduced into the specimen chamber, the secondary ion current was saturated at a constant value. We introduce a saturation pressure \(P_s\) defined as the pressure at which the secondary ion current levels off. The secondary ion current of \(Al^+\) from

Table 1. Nomenclature of yield of secondary ions of element A in different conditions. The suffixes E and OX represent the pure element and the oxidized element, respectively. The suffixes “on” and “off” represent the cases where oxygen was introduced and cut-off, respectively.

<table>
<thead>
<tr>
<th>Oxygen State</th>
<th>No introduction</th>
<th>Introduction at (P_s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure element</td>
<td>(Y_A (E, off))</td>
<td>(Y_A (E, on))</td>
</tr>
<tr>
<td>Oxidized element</td>
<td>(Y_A (OX, off))</td>
<td>(Y_A (OX, on))</td>
</tr>
</tbody>
</table>
the oxidized element was larger than that from a pure element and did not vary with the oxygen partial pressure. Since \( I_P \cdot \eta_A \cdot C_A \) in Eq. 1 was constant in the case of a surface composed of a single element or oxide \((C_A=1)\), the change of the secondary ion current corresponds to that of \( Y_A \). We define the various \( Y_A \)'s as shown in Table 1. Consider a sample X which is composed of a pure and oxidized element, and define these concentrations as \( C_A(E) \) and \( C_A(OX) \), respectively. Consequently, Eq. 2 holds

\[
C_A(E) + C_A(OX) = 1 \quad (2)
\]

We assume that ions are independently emitted from a surface composed of various states. The ions are the sum of the individual ions of the constituents. That is, ions emitted from the surface are represented by the linear superposition (additive property). When oxygen gas is not introduced into the specimen chamber, the secondary ion current \( I_A(X, \text{off}) \) from the sample X is given by

\[
I_A(X, \text{off}) = I_P \cdot \eta_A \left[ Y_A(E, \text{off}) \cdot C_A(E) + Y_A(OX, \text{off}) \cdot C_A(OX) \right] \quad (3)
\]

Substitution of Eq. 2 into Eq. 3 leads to Eq. 4

\[
I_A(X, \text{off}) = I_P \cdot \eta_A \left[ Y_A(E, \text{off}) + (Y_A(OX, \text{off}) - Y_A(E, \text{off})) \cdot C_A(OX) \right] \quad (4)
\]

Eq. 4 yields a straight line when \( I_A(X, \text{off}) \) is plotted against \( C_A(OX) \).

3. Experimental

3.1. Instrumentation

Fig. 2 shows the SIMS apparatus developed and used in this study. The apparatus

![Diagram](image-url)
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has been described in more detail\(^{10}\). The primary ion beam \(\text{Ar}^+\) was created from a PIG ion source. Ions formed were extracted and focused onto a specimen by an einzel and an electrostatic quadrupole lens with a beam diameter of 0.1\(\text{–}4\) mm. Secondary ions from the sample were extracted by applying 200 volts to the drawing-out electrode. The resulting ion energy was 200eV. It is necessary to decelerate the extracted secondary ions to the appropriate energy range of about 10\(\text{–}20\) eV for a quadrupole mass analyzer. The decelerator also works as a high energy pass filter. A four stage electrostatic lens system was designed for this purpose. The secondary ions were filtered out by a parallel plate deflector. This deflector works as an energy analyzer. The energy filtered ions were mass separate with the quadrupole mass analyzer and then were detected by an electron multiplier. Oxygen gas can be introduced into the specimen chamber through the gas inlet valve, which controls oxygen partial pressure up to about \(10^{-3}\) Torr. The pressure in the entire system, except the specimen chamber, is maintained through the aid of a differential pumping system, even if the pressure in the specimen chamber reaches \(10^{-3}\) Torr.

Experimental conditions in this study are as follows; the primary ion species was Ar, the primary ion accelerating voltage was 12 kV, and the primary current density was 0.5 mA/cm\(^2\). The angle of incidence was 45°. The primary beam was scanned to 1mm\(^2\) by deflection plates. The oxygen gas pressure around the specimen was measured using a Bayard-Alpert gauge. No correction of oxygen was performed.

3.2. Preparation of standard samples

Standard samples used in this study were prepared by methods used for fabricating microelectronic devices. Fig. 3 shows examples of standard samples in the case of Si. These samples were composed of a repeating pattern of the pure element and the oxidized element. These pattern size were of the order of a few micrometer. The ratio of the area of pure element to that of the oxidized element was varied by pattern size as shown in Fig. 3. The silicon dioxide pattern was grown to a thickness of 1000Å by thermal oxidation in a Si wafer in dry \(\text{O}_2\) at 1200°C. The \(\text{Al}_2\text{O}_3\)-Al pattern sample were prepared in a similar way. Aluminum was deposited.
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by an electron beam on a Si wafer to a thickness of about 1 μm. Aluminum oxide was produced by an anodic oxidation to a thickness of 700 Å.

3.3. Measurement of the normalized secondary ion current

The secondary ion current from a standard sample X changes when bombarded with primary ions, as shown in Fig. 4. The initial rise (region A) is due to surface contamination. Secondary ion intensity becomes constant (region B). This intensity is represented by Eq. 3. In region C, the oxidized element has sputtered out and secondary ions are emitted from only the pure element. Therefore, ion intensity decreases and becomes \( I_A(E,\text{off}) \). When oxygen gas is introduced into the specimen chamber at the pressure \( P_s \), secondary ion intensity rapidly increases and levels off at a constant value, \( I_A(E,\text{on}) \). Then, \( I_A(E,\text{on}) \)

should be equal for every standard sample. However, this value varied when sample was changed. This reason may be that the sample position or the incident angle of the primary beam was changed in each measurement. Normalizing the measured secondary ion current of standard sample \( I_A(X, \text{off}) \) to that of the pure element \( I_A(E,\text{on}) \) eliminates the untraceable effects of changes in position etc., during a series of measurements. Therefore, we evaluated \( I_A(X, \text{off}) \) divided by \( I_A(E,\text{on}) \) instead of the absolute intensity \( I_A(X, \text{off}) \) obtained from standard samples.

Now, \( I_A(E,\text{on}) \) holds the following equation, since \( C_A(E) = 1 \) in region D.

\[
I_A(E,\text{on}) = I_P \cdot Y_A \cdot Y_A(E,\text{on})
\]

(6)

Since the primary beam was scanned, the bombarded area of the sample was very large compared to the pattern size. Therefore, the concentration of the oxidized element in the bombarded area was equal to the calculated value in Fig. 3.

4. Results and Discussion

As described in Section 2, if the secondary ion current from the mixture of the pure and the oxidized element has additive properties, Eq. 4 holds. Dividing Eq. 4 by \( I_A(E,\text{on}) \), we obtain

\[
\frac{I_A(X, \text{off})}{I_A(E,\text{on})} = \left( \frac{Y_A(OX, \text{off}) - Y_A(E, \text{off})}{Y_A(E,\text{on})} \right) \times \frac{C_A(OX)}{Y_A(E,\text{on})} + \frac{Y_A(E,\text{off})}{Y_A(E,\text{on})}
\]

(7)

Eq. 7 gives a straight line.

The experimental data \( I_{AI}(X, \text{off}) / I_{AI}(E, \text{on}) \) was plotted as the ordinate and the concentration of oxidized Al as the ordinate.
abscissa in the case of Al. The result is shown in Fig. 5.

![Al Ion Intensity Graph](image)

Fig. 5. The Al$^+$ ion intensity for sample X normalized by Al$^+$ ion intensity from oxygen saturated Al as a function of the concentration of Al$_2$O$_3$.

All experimental data are approximately on a straight line. Similar results were obtained in the case of Si (Fig. 6). From these results, it may be concluded that the ion emitted from the surface had an additive property. Therefore, the use of Fig. 5 and Fig. 6 makes it possible to determine the quantity of the oxidized element.

$I_A(E, on)$ which was used for the purpose of normalizing in Fig. 4 is absent in actual analytical samples. We tried the following method, on the basis of the assumption that a linear superposition is applicable to the case of oxygen exposure. When oxygen is introduced into the specimen chamber at pressure $P_s$ for sample X, the secondary ion intensity $I_A(X, on)$ is given by

$$I_A(X, on) = I_p \cdot Y_A \{(Y_A(OX, on) - Y_A(E, on))C_A(OX) + Y_A(E, on)\}$$

Division of Eq. 4 by Eq. 8 leads to the following equation:

$$\frac{I_A(X, off)}{I_A(X, on)} = \frac{(i - j)C_A(OX) + j}{(k - 1)C_A(OX) + i}$$

where $i = \frac{Y_A(OX, off)}{Y_A(E, on)}$, $j = \frac{Y_A(E, off)}{Y_A(E, on)} \times k = \frac{Y_A(OX, on)}{Y_A(E, on)}$

The coefficients $i$, $j$, and $k$ are constant and are obtained from experiments in advance. Eq. 9 represents a hyperbola. The curve passes through $j$ at $C_A(OX) = 0$ and $i/k$ at $C_A(OX) = 1$.

Table 2 shows the experimental value of $i$, $j$ and $k$ in the case of Si and Al. Substituting the value in Table 2 in Eq. 9, we obtain the graph as shown in Fig. 7. A solid curve shows the calculated curve expressed by Eq. 9. The open circle in Fig. 7 is the experimental value obtained from
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Table 2. Experimental values of $i$, $j$ and $k$ which are the intensity ratios of the measuring secondary ions emitted from the oxide and the pure elements of Si and Al

<table>
<thead>
<tr>
<th>Standard sample</th>
<th>Coefficient Coefficient Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$i = Y_A(\text{OX,off}) / Y_A(\text{E,on})$</td>
</tr>
<tr>
<td>Si</td>
<td>0.92</td>
</tr>
<tr>
<td>Al</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Fig. 7. The ratio of Si secondary ion intensity with oxygen introduced to that without oxygen as a function of the concentration of SiO₂.
The solid curve was calculated from Eq. 9. The open circles indicate the experimental values.

Fig. 8. The ratio of Al⁺ secondary ion intensity with oxygen introduction to that without oxygen as a function of the concentration of Al₂O₃.
The solid curve was calculated from Eq. 9. The open circles indicate the experimental values.

standard samples. Similarly, Fig. 8 shows the case of Al. The experimental values agree well with the calculated results. Therefore, we can estimate the quantity of the oxidized element by means of a ratio of the secondary ion intensity from a sample at ultimate pressure to the secondary ion intensity at pressure $P_s$.

Wittmaack¹¹ showed that in the case of Si the top-most layer was nearly identical to the oxidized element when oxygen was introduced into the specimen chamber sufficiently to saturate the secondary ion of the element. He deduced this from the close agreement in yield of the various silicon ions emitted from oxygen saturated silicon and silicon dioxide. We obtained the same conclusion from analysis of the secondary ion intensity as a function of oxygen pressure.¹¹

The fact that $i$ is nearly equal to 1 in Table 4 can be explained in terms of the

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above-mentioned phenomenon. When a constant \( i \) is not obtained, we can use the following method as a convenient approximation. The constant \( i \) was equal to \( k \) as shown in Table 2. This relation shows that the oxidized surface was not affected by the presence of oxygen. It seems that oxygen was not absorbed on the oxidized surface or that the absorption of oxygen on the oxidized surface did not change the ion yield. Thus, we believe that this relation \((i = k)\) holds true for most elements.

Substitution of \( k = i \) into Eq. 9 leads to Eq. 10.

\[
y = \frac{I_a(X, \text{off})}{I_a(X, \text{on})} = \frac{(k-j)C_a(OX) + j}{1+(k-1)C_a(OX)} (10)
\]

Eq. 10 represents a hyperbola. Fig. 9 shows the hyperbola calculated from Eq. 10 for various choices of parameter \( k \) from 0.6 to 1. This graph represents \( j = 0 \). This relation holds for most metals. The equation where \( j = 0.16 \) in the case of Al is rather exceptional.

When the value of \( k \) was not obtained, we used a \( k = 1 \) as a first approximation. The working curve makes an approximation of a straight line which passes through \( Y = 0 \) at \( C_a(OX) = 0 \) and \( Y = 1 \) at \( C_a(OX) = 1 \). Even if \( k = 0.6 \) in the worst case, relative error is within 25%. The value of \( k \) changed under experimental conditions, such as when the secondary ion energy measured in SIMS was changed. Further details will be published.\(^{12} \) We can choose a condition where \( k(-i) \) is nearly equal to 1. Then the working curve \((k = 1)\) in Fig. 9 makes a good approximation.

The oxygen introduction method mentioned above is used to compare secondary ion intensity under the introduction of saturated oxygen to secondary ion intensity without oxygen introduction. The same argument can be used in a comparison under the condition of saturated oxygen pressure and the condition of arbitrary oxygen pressure below \( P_s \). The accuracy is high when the secondary ion intensity change under the oxygen introduction is great.

The oxidation number of the oxide cannot be determined with this method. In this case, the fingerprint spectra method developed by Werner is excellent. However, the absolute secondary ion intensity must be measured accurately. The oxygen introduction method used in this study will be used in combination with the fingerprint spectra method, to determine the oxidation number. The oxidized state can easily be measured because the measurement of the absolute secondary ion intensity is not necessary when both methods are used together.
5. Conclusion

(1) The concentration of the oxidized element was determined by the ratio of secondary ion intensity on exposure to oxygen to that on non-exposure, as shown in Fig. 7 and Fig. 8. With this method it is not necessary to measure the absolute secondary ion intensity measured in SIMS. Therefore, it is easy to determine the concentration of the oxidized element. This analytical method offers a new advantage for the oxygen introduction method in SIMS.

(2) IC microelectronic fabricating techniques could be a convenient means of preparing homogeneous standard samples for quantitative analysis of oxidized elements.

(3) A linear superposition of ions emitted from the pure and the oxidized element was ascertained in the case of Si and Al. This assumption may also hold true for other elements.

(4) When an oxidized sample cannot be obtained, the simple approximate calibration curve is obtained by the Eq. 9 where \( i = k = 1 \).

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References

12) K. Kusao, Y. Yoshioka and F. Konishi, (to be published).