Analysis of Insulator Samples with AES

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Introduction

Auger Electron Spectroscopy (AES) makes it possible to analyze a sample at an extremely shallow region such as about 6 nm from the top surface of the sample, enabling you to analyze elements present in a minute area such as 10^2 nm^2 on the surface if you use the focused electron beam as a probe. However, this attractive feature is limited only to the analysis of conductor and semiconductor samples; on the other hand, for the analysis of insulator samples, it becomes difficult even to observe the electron image of the sample due to charging phenomenon.

However, it does not necessarily mean that you cannot perform the Auger analysis for the insulator sample. Actually, if you have some knowledge and experience, you can perform the Auger analysis even on the insulator sample while suppressing charging by using the sample tilt method; and you can also perform the Auger analysis by taking the advantage of high spatial resolution of 1 μm diameter or less depending on the state of the insulator sample. In particular, after introducing the "Ar neutralizer gun" that can irradiate low speed Ar ions about 10 to 30 eV to suppress charging, the charge on the sample surface can be controlled relatively easily, making it possible to analyze a sample at an extremely shallow region such as about 6 nm from the sample surface.

This section describes the charging phenomenon when the electron beam enters into the sample. Fig. 3 shows an optical and a secondary electron image of a general printed circuit board on which Au electrodes are wired. In the secondary electron image, the glass epoxy resin portion exhibits a typical secondary electron image of a charged material, revealing that the contrast is unstable and the secondary electron

Basic Principle for Analyzing the Insulator Sample

Kinetic energy of Auger electron and surface potential

Because the kinetic energy (K) of an Auger electron can be uniquely determined by the type of an element and its transition process, the element can be identified from the energy (Fig. 1). The kinetic energy becomes the value reflecting the difference between the binding energies of the electron shells involved in the Auger transition, so in the case of the KL1L2,3 transition process shown in Fig. 1, the kinetic energy can be expressed as in Eq. (1).

\[ K_{KL1L2,3} = (E_K - E_{L1}) - E_{L2,3} + \phi \]  

where, \(E_K\) is the binding energy of an electron shell and \(\phi\) is the work function.

This Eq. (1) is used to obtain the kinetic energy of the Auger electron and it is presupposed that the sample surface is kept at the earth electric potential. However, in the case of the insulator sample, because the surface is not kept at the earth electric potential but in an electrostatically isolated state, the electrostatic energy of the actually measured electron is detected at the value with the surface potential \(V_S\) added to the kinetic energy of the Auger electron. Therefore, when you obtain the electrostatic energy \(U\) of the electron by taking the surface potential into consideration, it becomes as Eq. (2).

\[ U = K - V_{S(x,y)} \]  

where, \(U\) is the electrostatic energy of the observed electron, \(K\) is the kinetic energy of the Auger electron, and \(V_{S(x,y)}\) is the surface potential, which is the function of the position \((x, y)\) of the sample surface and the time \(t\), and has a negative sign because the electron has the negative charge.

The energy of the electron measured using the Auger Electron Spectroscopy represents this electrostatic energy \(U\). In the case of the conductor sample, because the surface potential becomes always \(V_S = 0\) regardless of the sample position, the equality \(U = K\) holds, the measured electrostatic energy corresponds directly to the kinetic energy of the Auger electron. On the other hand, in the case of the insulator sample, because the sample surface is in an electrically isolated state, even if the analysis position is fixed in place, because the magnitude of the surface potential changes depending on the amount of the incident electrons and the diffusion speed of the charged electrons, the electrostatic energy of the observed electron does not become stable. This is a fatal problem in the Auger analysis. If the shift of the peak position changes by the fluctuation of the surface potential \(V_S\) due to the effect of charging in a sufficiently short time compared with the measurement time of the spectrum, it disturbs the accurate spectrum measurement. For example, the peaks become broader as in the superimposed spectrum shown in the right figure in Fig. 2 or a ghost peak appears. In order to perform Auger analysis with high accuracy, you need to search a condition to become \(V_S = (constant)\) regardless of the measurement time even if the surface potential \(V_S\) does not become zero.

A problem of charging when the electron beam enters the sample surface

This section describes the charging phenomenon when the electron beam enters into the sample. Fig. 3 shows an optical and a secondary electron image of a general printed circuit board on which Au electrodes are wired. In the secondary electron image, the glass epoxy resin portion exhibits a typical secondary electron image of charged material, revealing that the contrast is unstable and the secondary electron
intensity fluctuates wildly. In order to analyze this phenomenon, the three situations are considered using the model as shown in Fig. 4.

When the electron beam enters the insulator sample surface, after the incident electrons generate secondary electrons including Auger electrons, they escape from the sample as backscattered electrons or remain inside the sample as they are. Let the charge remained on the sample surface be \( Q_s \) as shown in Fig. 4, the following equation holds.

\[
Q_s = Q_I - (Q_E + Q_D) \quad \cdots \cdots \cdot (3)
\]

where, \( Q_I \) is the charge entered into the sample as the incident electrons, \( Q_E \) is the charge escaped from the sample surface as the secondary and backscattered electrons, and \( Q_D \) is the charge leaked out of the sample due to the diffusion of the electrons. On this occasion, if the potential \( V_S \) on the insulator sample surface is assumed to form a capacitor between the insulator sample surface and the sample holder in the reverse side, it is expressed by the following equation.

\[
V_S = \frac{Q_s}{C_s} = \frac{1}{C_s} (Q_I - (Q_E + Q_D)) \quad \cdots \cdots \cdot (4)
\]

From Eq. (4), it is found that the surface potential \( V_S \) is proportional to \( Q_s \), and that the sign becomes either positive or negative depending on the charge difference between \( |Q_I| \) and \( |Q_E + Q_D| \). Next, the difference of each parameter according to the difference of \( Q_S \) is qualitatively shown in Fig. 5 based on the present model.

Fig. 5 shows three cases: (i) when the surface potential is positive, (ii) when the condition becomes negative, and (iii) when the charge becomes too large for the electron beam to enter into the sample surface because the surface potential becomes nearly equal to the accelerating voltage of the electron beam. The reason why the contrast of the secondary electron image becomes unstable or the electron intensity fluctuates wildly to result in obtaining an image that is entirely unmatched with the actual surface shape is mainly because the phenomenon of (iii) occurs. In the case of (ii), the Auger analysis is not possible because the electrons cannot enter into the sample surface. In the second case (ii), however, you can observe a secondary electron image and measure an Auger spectrum at the beginning because the charge is small compared with the case (iii); Usually, this situation is not stable. As long as the incident charge meets the condition \( |Q_I| > |Q_E + Q_D| \), the surface charge increases and eventually results in the state (iii), making it impossible to perform the stable analysis.

As a conclusion, only if the surface potential satisfies \( V_S > 0 \) as in the case of (i), where the condition \( |Q_I| < |Q_E + Q_D| \) is satisfied, the electron beam can always enter the sample surface, making it possible to constantly perform the Auger analysis. If you observe an insulator sample itself or even a conductor sample when it is electrically isolated, you cannot perform a highly reliable measurement unless you create the state in which the surface potential becomes positive as in the case (i) using some method and then perform the Auger analysis. Specifically, to increase the escaped charge \( (Q_E) \) due to the secondary and backscattered electrons, you use the "Sample tilt method", and to increase the leaked charge \( (Q_D) \) due to the diffusion, you only apply the "Charge suppression method using the neutralizer gun." The details of these methods will be explained in the later sections.

### A problem of charging when detecting the Auger electrons

The previous section has described a problem that the electron beam cannot enter into the sample surface, but this section describes a problem that becomes unable to detect Auger electrons after generating them due to the effect of charging.

![Fig. 2 O KLL (SiO₂) spectrum and its superimposed spectrum when the surface potential \( V_S \) is changed (+5, 0, -5, -20 V).](image)

![Fig. 3 An optical and a secondary electron image of a printed circuit board masked with an aluminum foil.](image)

![Fig. 4 Charging model when the electron beam is entered on the surface of the insulator sample.](image)
charge accumulated on the glass epoxy resin surrounding the electrode. Fig. 7 shows schematic diagrams illustrating the two possible cases: (i) when the glass epoxy resin around the electrode is negatively charged and (ii) when it is positively charged.

The diagram of the case (i) illustrates the circumstance in which the electron beam is irradiated on the glass epoxy resin surrounding the sample in order to confirm the analysis points on the sample and measure the secondary electron image, accumulating the electrons to negatively charge the glass epoxy resin. In this case, the negative electric field generated by the charging on the glass epoxy resin deflects the trajectory of the low energy electrons, causing a phenomenon that they do not enter the detector. For this reason, although the Au peaks at the high energy side as shown in Fig. 6 are not affected by the charging on the glass epoxy resin, it is obtained an abnormal spectrum in which the low energy electrons are not detected.

On the other hand, the case of (ii) is often encountered when Ar ions in stead of electrons accumulate on the glass epoxy resin surrounding the sample to positively charge the glass epoxy resin because you increase the Ar ion current to irradiate the sample using the neutralizer too much. In this case, similarly, the positive electric field generated by the charging on the glass epoxy resin deflects the trajectory of the low energy electrons, causing a phenomenon that they do not enter the detector. Also in this case, although the Au peaks at the high energy side as shown in Fig. 6 are not affected by the charging on the glass epoxy resin, it gives an abnormal spectrum in which the low energy electrons are not detected.

### Method for Suppressing Charging in the Auger Analysis

#### Sample tilt method

Up to the previous section, it is shown that keeping the surface potential constant is necessary to measure the Auger electrons and that controlling the surrounding charging state is also necessary when detecting the Auger electrons. This section describes the sample tilt method that increases $Q_S$ as a method for creating the state of the surface potential $V_S > 0$, so that the low energy electrons are detected.

#### Example of the Monte Carlo simulation

<table>
<thead>
<tr>
<th>Sample tilt angle θ (degree)</th>
<th>Remaining rate of the incident electrons (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
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<tr>
<td>10</td>
<td>90</td>
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<tr>
<td>20</td>
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<td>80</td>
<td>20</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
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</tbody>
</table>

Accelerating voltage: 10 kV  Number of the incident electrons: 32000  Sample: SiO₂

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as in the case (i) in Fig. 5.

If you tilt the sample in the Auger analysis, the emission yield of secondary electrons increases because the incident angle of the electron beam becomes shallower and the region to excite the secondary electrons comes closer to the sample surface. Fig. 8 shows the relation between the sample tilt angle $\theta$ and the incident angle of the electron beam.

When the incident direction of the electron beam is tilted by $\theta$ from the vertical direction of the sample, suppose that secondary electrons are generated along the length $L$ as shown in Fig. 8. Supposing that the secondary electrons generated at each point along the length $L$ are absorbed until they escape from the sample surface, the number of the secondary electrons generated from the sample surface is expressed as in Eq. (5). From this equation, it is found that the amount of the generated secondary electrons increases roughly in proportion to $1/\cos \theta$ as you increase the sample tilt angle $[1]$. Therefore, if you simply tilt the sample, the secondary electrons are generated in larger numbers, enabling you to make the surface potential positive as a result.

$$N = \int_{0}^{L} n e^{-kx} dx = \int_{0}^{L} n e^{-kL \cos \theta} dx = \frac{n}{\cos \theta} \cdot \left[ e^{-kL \cos \theta} - e^{-k0} \right]$$

$N$ : The number of secondary electrons generated from the sample surface

$n$ : The number of secondary electrons generated per unit length

$k$ : Attenuation coefficient

$x$ : Distance from the emission point of secondary electrons to the surface ($x = L \cos \theta$)

When you tilt the sample, not only the secondary electrons are generated in larger numbers, but also you can reduce the charge. Figure 9 shows the remaining rate of the incident electrons inside the sample obtained from the Monte Carlo simulation.

It is found in Fig. 9 that the amount of electrons escaping from the sample as the backscattered electrons among the incident electrons increases and the amount of electrons remained inside the sample decreases as the sample tilt angle increases. In the case of the insulator sample, the large remaining rate of the incident electrons shows that the sample is strongly charged, and the larger you make the sample tilt angle, the smaller the remaining rate of the incident electrons and the smaller the charge on the sample surface.

As described above, if you tilt the sample, the generated secondary electrons increase and the amount of the incident electrons remaining inside the sample decreases; so if you tilt the sample more than a certain angle, the emission amount of the secondary electrons exceeds the remaining amount of the incident electrons, resulting the sample surface charged positively. This is the method for suppressing charging by the sample tilt method.

Figure 10 shows the secondary electron images of the kapton surface at three sample tilt angles, and Figure 11 shows the Auger spectra of the sample surfaces. It is found that although unstable contrast and intensity variation characteristic of charging appear up to the tilt angle $60^\circ$, at the tilt angle $75^\circ$, a relatively stable secondary electron image and the normal Auger spectrum can be obtained.
act Ar ions for the circumference around the analysis position to suppress the surrounding non-uniform charging [2].

In addition, the Ar ions have a role to absorb and diffuse the electrons, which are hard to diffuse and disappear inside the sample, on the sample surface by appropriately distributing on the charged sample surface. In other words, this low-speed Ar ion irradiation method corresponds to a method for increasing the amount of Qs to create the state of the surface potential Vc > 0, as in the case (i) in Fig. 5, and has a large role to alleviate the charging phenomenon as shown in Fig. 13.

Confirming the charging state using the Auger spectrum

Although the charging on the sample is suppressed using two methods: "Sample tilt method" and "Charging suppression method using the neutralizer gun," you can judge whether the charge suppression is sufficient or insufficient from the Auger spectrum. Fig. 14 shows the Auger spectrum of the ungrounded electrode surface, and Fig. 15 shows the Auger spectrum of the grounded electrode surface. Looking at Fig. 14, it is found that all Au peaks in the spectrum of the ungrounded electrode surface are shifted forward higher energy and do not appear at their original positions. This is because the gold electrode is negatively charged by the electron beam, causing a negative surface potential and all the secondary electrons generated there are measured at higher energy by the surface potential according to Eq. (2).

As described above, if you continue to enter the electron beam on the condition where the surface potential is negative, the surface potential gradually decreases in the negative side and does not also remain stable so that you cannot measure a reproducible spectrum. In this way, if a negative surface potential is formed on the sample surface, you need to adjust the measurement condition by applying the sample tilt method, decreasing the accelerating voltage, and performing other methods so that the Au peaks of the measurement target surely become the shifted states (positive surface potentials) to the low energy side than the original energy values.

On the other hand, as shown in Fig. 15, for the Auger spectrum of the grounded electrode surface, all Au peaks are measured at normal positions irrespective of the condition where the neutralizer gun is on or off, revealing that the gold electrode surface is the earth potential. In addition, turning on the neutralizer gun, the charging on the glass epoxy resin surrounding the Au electrode disappears and the normal Auger spectrum is obtained. When you measure an Au electrode like this occasion, you can judge whether the Au electrode is grounded or not from the information that whether all the Au peaks are detected at the original peak positions or not.

Concluding Remarks

In the Auger analysis, from the feature of conducting the element analysis at a few nm from the sample surface, you cannot use the charge prevention processing by the surface conductor coating that is generally employed in the SEM and EPMA. In addition, in the Auger analysis, because the incident probe is electrons and the detection signal is also electrons, if the sample is charged even a little, the spectrum deforms, making it difficult to analyze the sample. It is shown, however, that if you understand what happens on the sample surface and properly deal with the problem, you can perform the Auger analysis. For example, the problem that you cannot analyze an electrode on a printed circuit board is often caused by the fact that the Au electrode of the measurement target is not grounded even while you have placed too much trust in the charging suppression method using the neutralizer gun. We hope you find the methods presented in this article informative.

References