Auger Analyses Using Low Angle Incident Electrons

Kenichi Tsutsumi, Yuji Nagasawa and Toyohiko Tazawa
Electron Optics Division, JEOL Ltd.

Introduction

Auger Electron Spectroscopy (AES) is widely used, as well as X-ray Photoelectron Spectroscopy (XPS), for surface analyses such as foreign particle analysis and structure analysis, because it can analyze a shallow surface, for example, about a 6 nm deep region from the top surface of a sample. In recent years, many high-technology materials, including not only high-density storage media such as hard disks and DVDs but also functional materials with a special treatment processed in the 1 to 2 nm region from the surface, have been developed, ever increasing the requirement for analyzing a shallow surface of less than the 6 nm deep region. When analyzing such a sample, most researchers generally analyze it by applying a special XPS method such as Angular Resolved X-ray Photoelectron Spectroscopy (ARXPS) or Total Reflection X-ray Photoelectron Spectroscopy. When actually applying these methods, however, it is presupposed that the sample must have an extremely flat and homogeneous surface with a broad area of a few square millimeters. For this reason, if the sample does not have a homogeneous surface lacking in uniformity or the sample has a surface area too small to analyze, it is very difficult to measure and evaluate the sample. Consequently, there is great hope to establish a method for analyzing the thin film surface of a 1 to 2 nm deep region using an AES with a high special resolution. However, since the AES detects Auger electrons, unlike the XPS, by exciting the sample with electrons, it originally has a low PB ratio, and moreover, if one wants to analyze the sample using a shallow detection angle like the ARXPS, it becomes difficult to detect a peak itself because the sensitivity goes down. As a result, it was not possible to analyze the 1 to 2 nm deep thin film using the method of lowering the detection angle. Therefore, in the present article, we propose and introduce the low angle incident electron Auger analysis method, which enables one to analyze the surface of the 1 to 2 nm deep region by irradiating it with the low angle incident electrons, even though scattering the spatial resolution a little.

Here, we observe the variation of the Auger spectra for the sample of tilted angles, by citing the sample of hard disk as an example; and then, we consider the principle and the depth resolution of the low angle incident electron Auger analysis.

Sample Angle Dependence for The Auger Spectra in a Hard Disk

Escape depth of Auger electron and the thin film structure of a hard disk

To start with, we describe the escape depth of an Auger electron. Figure 1 shows a graph (left) representing the relationship between the kinetic energy of an electron and the mean free path ($\lambda_0$). Figure 1 also shows another graph (right) representing the relationship between the escape depth of the Auger electron and the total detection amount by taking into account the fact that the energy of the Auger electron attenuates by being scattered inside the sample.

The mean free path represents the average distance that an electron having a definite energy in a substance can move without causing any energy loss by its interaction with other electrons, and its value does not greatly depend on the kind of the substance, but generally depends on the kinetic energy of the electron. Since the Auger electron is hardly distinguishable from other secondary electrons except for the fact, in particular, that it has a characteristic kinetic energy, it must escape from the surface of the substance without causing any energy loss after it is generated on the surface; so there is a close relationship between the escape depth and the mean free path of the Auger electron.

In addition, it is known that the number of the electrons, which can escape from the inside of the sample, decreases exponentially according to the depths of the generated electrons, because they are scattered inside the substance. Figure 1 (right) shows the phenomenon described above. If one calculates the amount of escaped electrons by integrating them for the escape depth up to 3 times of the mean free path ($\lambda_0$) by letting the total amount of escapable Auger electrons to 1, it occupies 95% of the total amount; so the escape depth of the Auger electron corresponds to about 3 times of the mean free path.

More specifically, since the Auger analysis employs the electrons having energies from 0 to 2000 eV, the mean free path becomes about 2 nm at maximum according to Fig. 1 (left); so the maximum escape depth of the Auger electron is considered to be about 6 nm.

As described above, since the escape depth of Auger electron becomes constant depending on the kinetic energy of the electron, one can selectively detect the element present near the surface more by decreasing the detection angle for the surface of the sample. To study it, we conducted the experiment of the sample tilt angle dependence in the AES using a sample of a hard disk whose structure is known.

Figure 2 illustrates the layer structure of the hard disk employed in the present experiment. Inside the hard disk, there exists a 15 to 25 nm thick magnetic layer containing Co for recording data, on the other, there exists a 3 to 5 nm thick diamond-like carbon (DLC) layer for protecting the magnetic layer, and on the top surface, a lubricant agent containing F is applied for a 1 to 2 nm thickness so that the slider for reading the magnetic information can move smoothly. The thickness of each layer introduced here is only applicable for hard disks produced a few years ago. The thickness of each layer in recently produced hard disks is made much thinner than this.

Looking at the layer structure of this hard disk, the depth from the surface to the magnetic layer is nearly equal to the escape depth of the Auger electron, indicating it is a most suitable sample for studying the sample tilt angle dependence of the Auger electron.

Instrument configuration (JAMP-9500F) employed in the experiment and the experimental results

The instrument employed in the present experiment is the JEOL Field Emission Auger Microprobe JAMP-9500F, having a structure as shown in Fig. 3. The JAMP-9500F is equipped with a eucentric stage in the ultra-high vacuum chamber, having a feature that the detector does not miss the analyzable region even though an operator moves the sample in the x or y direction, or tilts the sample, once the operator sets the sample surface in the eucentric allocation. The sample tilt angle is the angle 0, shown in Fig. 3, between the direction of the incident electrons and the normal to the sample surface. In addition, the angle between the direction of the incident electrons and the detecting direction of the electrostatic hemispherical analyzer is fixed at 60°; in this experiment, when one tilts the sample, both the incident angle of the electron beam and the detection angle change simulta-
neously.

By using this instrument, we studied the sample tilt angle dependence of the Auger spectra in the sample of the hard disk described in the section of “Escape depth of Auger electron and the thin film structure of a hard disk.” Figure 4 shows the variation of the spectra when changing the sample tilt angle from 0 to 60°. Figure 5 shows the variation of the spectra when changing the sample tilt angle from 60 to 85°.

Looking at the spectra in Fig. 4, we can find that the C, N and Co peaks gradually grow larger and also the intensity of the entire spectrum increases as we change the sample tilt angle from 0 to 60°. At the same time, we can also find that a large bump is formed in the energy region from the Co peak (770 eV) to the lower energy side, and its size increases as the sample tilt angle increases.

Looking at the spectra in Fig. 5, we can find that the Co peak gets smaller and also the intensity of the entire spectrum decreases as the sample tilt angle increases, and that when the sample is tilted to 85°, the Co peak disappears and the F peak is detected instead. In the next section, we consider the cause for the variation of these spectra.

The cause for emerging a bump in the spectrum

In Figs 4 and 5, a bump appearing in the lower energy side than the energy of the Co peak is considered to be caused by the energy loss of the Co peak. We illustrate the reason for it in Fig. 6.

As shown in Fig. 6, if the electron beam enters into the sample and generates the Auger electron at the position of depth L, since the angle between the direction of the incident electron beam and the detector (analyzer) is 60°, the distance that the Auger electron actually passes through the inside of the sample until it is detected is Le. As this length of Le becomes the shorter, the deeper the Auger electron can be detected; when the sample is tilted to 60°, it becomes shortest. Therefore, when the sample tilt angle is 60°, the peak of Co in the magnetic layer that exists at the deepest region from the surface is most largely detected. However, not all the Auger electrons of Co are detected with their energies preserved, but some of them enter the detector by losing their energies. As a result, some of the Auger electrons of Co are not detected at the original peak energy position, but they form a bump having a broad energy distribution as shown in Fig. 6.

Sample tilt angle and its dependence on the Auger peak intensity

Next, by tilting the sample, we consider theoretically how the Auger peak intensity of each element varies [1].

For the instrument composition shown in Fig. 3, when the sample is tilted, both the incident angle of the electron beam and the detection angle of the Auger electron change simultaneously. Hence, we consider the variation of the generation amount of the Auger electrons depending on the incident angle of the electron beam and the variation of the detection amount depending on the detection angle for the surface, respectively.

Firstly, we consider the variation of the generation amount of the Auger electrons. Suppose that the sample is tilted θ for the incident angle of the electron beam, and the Auger electrons are generated from the sample element along the depth L as shown in Fig. 7 (a). If we further suppose that the Auger electrons
generated at each point of the depth L are absorbed by the sample material attenuating its intensities until they escape from the sample surface, the number of the generated Auger electrons is expressed as Equation (1). From this equation, we can find that it is proportional to 1/\cos \theta.

\[ N = \int n e^{-k \cos \theta} \, dl = \int ne^{-k \cos \theta} \, dl = \frac{n}{k \cos \theta} \]  

\( N \): Total amount of Auger electrons generated from the sample surface  
\( n \): Number of Auger electrons generated by unit length  
\( k \): Attenuation coefficient  
\( x \): Distance from the generation point of secondary electron to the sample surface (x=L \cos \theta)

Next, we consider the variation of the detection amount by changing the detection angle for the surface. As shown in Fig. 7 (b), the relationship between the detection amount of the Auger electrons and the detection angle is supposed to be compared to the situation that for a hypothetical sphere S, the chord length E at the detection angle y corresponds to the detection amount. In other words, the detection amount is largest in the direction perpendicular to the sample surface; conversely, the detection angle to the sample surface becomes the lower, the smaller the detection amount. Let \( E_0 \) (the detection amount at the tilt angle 0°) be the diameter of the hypothetical sphere S, the detection amount at the tilt angle y is expressed as Equation (2).

\[ E = E_0 \cos \psi \]  

(2)

In the actual instrument, if we suppose that there is an angle difference \( \phi \) between the directions of the incident electron beam and the detector, and let \( \theta \) be the sample tilt angle, the instrument geometry can be shown as Fig. 8. Consequently, by taking the generation amount and the detection amount of the Auger electrons into account, we define the amount of the measured Auger electrons. Calculating the product of Equation (1) and Equation (2) leads to Equation (3) as described below.

\[ I_E = N \cdot E = \frac{n}{k} \cos \theta \cdot \cos \psi \cdot \sin \phi \cdot \sin \theta \]

\[ I_E = C_1 \cos \phi \cdot \cos \theta \cdot \cos \psi \cdot \sin \theta \]

\[ I_E = \frac{N \cdot E_0}{k} \cos \theta \sin \psi \cos \phi \]  

\( C_1 \): Constant

Here, since the angle between the direction of the incident electron beam and the detector is \( \phi = 60° \), let \( I_0 \) be the detection amount at the sample tilt angle \( \theta = 0° \) and obtain the intensity ratio at the sample tilt angle \( \theta \), then \( C_0 \) is eliminated and the intensity ratio becomes as given in Equation (4).

\[ \text{(Intensity ratio)} \quad \frac{I_E}{I_0} = \frac{3 \tan \theta + 1}{\tan \theta} \]  

(4)

**Figure 9** shows the summary of the relationship between the sample tilt angle and the peak intensity by actually measuring the Auger spectra for the standard bulk samples. The measured samples are three pure metals Ag, Cu and Si; the differential Auger peak intensity ratios of Ag MNM (348 eV), Cu LMM (914 eV) and Si KLL (1614 eV) are plotted for the varied sample tilt angles.

Looking at this graph, we can find that any peak intensities satisfy Equation (4) very well up to the sample tilt angle of 60°. However, for the higher angle of 75° or more, they deviate from Equation (4). This should be considered to be due to the fact that when electrons enter the sample at a low angle for it, the fraction of the electrons that escape from the surface as backscattered electrons increase; the more they increase, the larger the atomic number of the metal composing the sample, decreasing the fraction of the electrons that excite the Auger electrons inside the sample.

Next, we calculate the peak intensity ratio from the analysis results of the hard disk described above and obtain its sample tilt angle dependence, which is shown in Fig. 10.

Looking at this result, we can find that the intensity variation of Co takes the maximum value at the tilt angle 60°, showing that the element Co exists in a deeper layer beneath the layer of C, N and O. As for the intensities of C, N and O, they take the maximum values at 80°, and they decrease at 85°, indicating that these elements exist in the secondary layer from the surface. However, the element F in the lubricant agent that exists in the 1 to 2 nm deep region from the surface is detected for the first time at such a high tilt angle as 85°, and it is not detected at any other angles. In other words, it may be considered that the element present in the top surface is detected for the first time by inserting the electron beam at such a low angle.

As is clear from this measurement result, we can find that the tilt angle dependence of the Auger electron peak intensity reflects the layer structure of the sample surface, and in particular that we can obtain the Auger spectra of the element present in the top surface by inserting the electron beam at a low incident angle. In the next chapter, we consider these issues in more detail.

**Auger Analyses Using the Low Angle Incident Electron Beam**

**Incident angle of the electron beam and the scattering region**

As is shown in the previous chapter, when...
using a low angle incident electron beam, it is possible to detect the elements present in a top surface region of the sample. Hence, we study the diffusion region of the electron beam when inserting it at a low angle by using the Monte Carlo simulation. Figure 11 and Table 1 show the results.

Figure 11 shows the scattering regions of the electron beam when the 10 kV electron beam enters the sample surface that is tilted to 0° and 80°. Looking at the results of this Monte Carlo simulation, we can assume that the region where the electron beam is scattered is a sphere, making it possible to regard the center of the sphere as the scattering center. Table 1 shows the distance from the surface to the scattering center. At the same time, we show the fraction of the electrons that escaped from the surface as the backscattered electrons among the incident electrons.

Looking at this result, we can find that as the tilt angle increases more, the nearer the scattering center of the electron beam approaches the surface, resulting in the electron beam running the shallow region of the surface. When the sample is tilted to 85°, the scattering center comes to about 6 nm from the surface. This is the same escape depth of the Auger electron in this state, since the Auger electron is more effectively generated and detected than that of the tilt angle 0°, it may be possible to obtain a spectrum sensitive to the surface element. In addition, it may also be evident from the fraction of the backscattered electron generation that the more the tilt angle increases, the greater the probability that electrons will escape from the surface as backscattered electrons among the incident electrons, decreasing the electrons diffusing inside the sample. With this, the number of high energy electrons that generate secondary electrons may decrease, conceivably resulting in reducing the background and enhancing the SN.

Figure 12 shows the comparison of spectra at 30° and 85° shown in Figs 4 and 5, respectively in the section of “Instrument configuration (JAMP-9500) employed in the experiment and the experimental results.”

As this result shows, the spectra at 30° and 85° appear quite differently from each other, even though they are measured with the same sample. When we compare these spectra, we can find that the spectrum measured using the low angle incident electron beam at the sample tilt angles of 85° has a lower background, and the peak of element F present near the surface is detected more intensely.

Low angle incident Auger analysis using a thin film sample (Cr/Si)

We have found that using the low angle incident electron beam makes it possible to excite the top surface element more effectively, enabling us to perform a more sensitive Auger analysis. Here, in order to check what kind of analysis is effective for a thin film sample, we fabricated the sample experimentally and studied the performance of the analysis.

We used a natural oxide removed Si wafer on which the Cr thin film is uniformly coated using the GATAN Precise Coating System (PECS) as a sample. We fabricated four kinds of Cr thin film by controlling the film thickness with the coating time of the PECS varied to 10 s, 20 s, 1 min and 2 min. Figures 13 and 14 show the sample tilt angle dependence for the Auger spectra of the Si sample on which Cr is coated for 20 s and 2 min, respectively.

Looking at these results, we can find that although for the spectrum with the Cr film of 20 s, the substrate Si is detected at any tilt angles, for the spectrum with the Cr film of 2 min, only a bump is finally formed at the tilt angle 0° min, only a bump is finally formed at the tilt angle 0°.

Figure 15 shows the summary of the tilt angle dependence for the peak intensity of each detected element. The vertical axis of the graph shown in Fig. 15 is the normalized peak intensity ratio based on the peak intensity at
the sample tilt angle of 0°. The theoretical curve shown here represents Equation (4) for the peak intensity ratio that is obtained for the bulk sample as shown in Fig. 9.

The sample tilt angle dependence of C draws the same curve as the theoretical curve for any sample. This shows that the element C is present at the top surface without any layer above it.

Elements O and Cr draw the same curve, indicating that both elements exist in the same layer. We can infer from this that the sample may have been oxidized while coating Cr on it under an inappropriate environment. In addition, the maximum intensities of O and Cr appear near at 85° for any samples, indicating that the thicknesses of contamination (C) adhered to the surfaces are roughly the same.

The sample tilt angle dependence of the substrate Si differs largely by the film thickness of Cr present on the substrate. As the substrate becomes thicker, the smaller the tilt angle at which the maximum intensity is obtained. However, as mentioned above, since the detection angle of the analyzer is 60°, the tilt angle of 60° is the lower limit; therefore, if the maximum intensity is obtained at the tilt angle of 60°, as the film thickness increases, the tilt angle at which the maximum intensity is obtained cannot decrease, but the detection intensity decreases.

As mentioned above, it is found that if the sample tilt angle is larger than 60°, the thin film sample also gives the similar tilt angle dependence as is obtained using the XPS. The quantitative analysis like discussions such as obtaining the film thickness or other values from the graph that has the tilt angle dependence are left to future research challenges.

Resolution of depth profile in the low angle incident Auger analysis

In the previous sections, we have shown that utilizing a low angle incident electron beam enables one to perform a more sensitive Auger analysis. In this section, we study how much depth resolution is obtained if we apply this method to depth profile.

The sample used in the experiment is a 20 nm thick SiO$_2$ film that is formed on a Si substrate. As is generally known, a SiO$_2$ film formed on a Si wafer has not only a precise film thickness but also a very steep interface between SiO$_2$ and Si at the atomic level: so it is widely used as a reference sample for measuring the sputtering rate. For this SiO$_2$/Si interface, we studied how much the resolution of the depth profiles improves when using the tilt angle (30°) of normal measurement condition and when using the low angle incident electron beam (85°). Figure 16 shows the result. In this experiment, we measured the depth profiles with a high energy resolution (ΔE/E=0.05%), and by splitting the metal and oxide peaks in chemically different states from the Si KLL and LVV peaks, we plotted these depth profiles independently.

Figure 16 shows that the depth profile using the low angle incident electron beam at the tilt angle of 85° is clearly more improved in the steepness of the interface than the other depth profile. When we obtain the difference between depths that become 16% and 84% of the maximum intensity for each peak, and define the width as the resolution of the depth profile, we can summarize the results as Table 2. When we compare these results, in the Si KLL (metal) peak of the depth profile with the worst resolution, the resolution at the tilt angle of 85° becomes 60% of that of 30°. Particularly, for the peaks in the high energy side, since the resolution of the depth profile deteriorates because the Auger electrons that escaped from the deep region with a long mean free path are detected, the effect of improvement by this method is significant.

As mentioned above, we proved that if we utilize the low angle incident electron beam, we can measure a higher resolution depth profile.

Comparing with X-ray photoelectron spectroscopy (XPS)

Before implementing the surface structure analysis using the low angle incident electron beam, we compared it with the already launched Angular Resolved X-ray Photoelectron Spectroscopy (ARXPS). We used the Si substrate with Cr film coated on it as the sample that is used in the section of “Low angle incident Auger analysis using a thin film sample (Cr/Si)” employed the JEOL JPS-9010MX for the ARXPS, and compared the quantitative analysis results at each tilt angle. Figures 17 and 18 show the compared results for Cr film (20 s) and Cr film (1 min), respectively. The left figure shows the result of the ARXPS and the right figure shows the result of the angle tilted Auger analysis.

Looking at each result, it shows that in the ARXPS as the tilt angle varies, the intensity of each element gradually varies; on the other hand, in the angle tilted Auger analysis, it varies rapidly near from 70°. Insofar as this
Fig. 16 Difference of depth profiles at the tilt angle of 30° and 85°.

Table 2 Variation of the resolution of depth profile in each peak (width of 16% - 84%).

<table>
<thead>
<tr>
<th>Sample tilt angle</th>
<th>Tilt = 30deg. (49.5°)</th>
<th>Tilt = 85deg. (35°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si LVV (oxide)</td>
<td>76eV</td>
<td>2.2 nm</td>
</tr>
<tr>
<td>Si LVV (metal)</td>
<td>92eV</td>
<td>2.0 nm</td>
</tr>
<tr>
<td>O KLL</td>
<td>510eV</td>
<td>2.6 nm</td>
</tr>
<tr>
<td>Si KLL (oxide)</td>
<td>1604eV</td>
<td>5.6 nm</td>
</tr>
<tr>
<td>Si KLL (metal)</td>
<td>1615eV</td>
<td>6.2 nm</td>
</tr>
</tbody>
</table>

Fig. 17 Comparison of the quantitative results for the Si sample on which Cr is coated for 20 s.

Fig. 18 Comparison of the quantitative results for the Si sample on which Cr is coated for 1 min.