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Paper

Repeatability of Spectral Intensity Using an Auger Electron Spectroscopy Instrument Equipped with a Cylindrical Mirror Analyzer

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We would report the repeated survey-spectra acquisition method in order to analyze the instability of the acquired spectrum in Auger Electron Spectroscopy. The experiment followed a sequence of continuous spectral acquisition for one hour and one-hour acquisition halt, while the electron beam irradiation was continued during the acquisition halts. The sequence was repeated three times. The intensity of the survey spectra gradually decreased, and we think this was mainly due to the surface contamination. After excluding the contamination effect, we found that the intensities of spectra revealed the gradual increase by a few percent for the acquisition time less than ~500 s and for all the electron energy examined. In contrast, the rapid intensity increase by one percent was observed for the acquisition time less than ~15 s and for the energy lower than ~600 eV. After a prolonged continuous-acquisition, the stable spectrum was finally derived, however, the acquisition halt disrupted the stable state. We think the observed instability of the spectra intensity was due to the gain fluctuations of a micro-channel plate installed in a cylindrical mirror analyzer.

1. Introduction

To achieve quantitative analysis using electron spectroscopy, one of the key requirements is repeatability of the acquired spectrum. The spectrum repeatability relies on the repeatable signal intensity as well as the energy-scale accuracy of an electron energy analyzer. For the energy scale, the calibration procedures have been already described in ISO for the Auger Electron Spectroscopy (AES) analysis [1-4] and for the X-ray Photoelectron Spectroscopy (XPS) analysis [5], therefore, a well-calibrated energy scale can be derived consistently. However, for the signal intensity, the ISO defines the procedure to check the repeatability [6], but not to make a calibration. The repeatability of the signal intensity will be degraded by many factors, such as fluctuations in the beam-current, the analyzer's pass-energy, or surface contamination growth. In addition, the amplification stability of the electron detectors has remained as an un-measurable factor. A micro-channel plate (MCP) or a channel electron multiplier (CEM) is installed in most of the electron energy analyzers used for AES and XPS analysis, except for the Standard Cylindrical Mirror Analyzer (S-CMA). The S-CMA has been recognized to have the known energy-intensity response function. Therefore it is able to measure the standard spectra. So the AIST database has registered the standard spectra measured with the S-CMA[7].

The amplification characteristics of both the CEM and the MCP have been investigated independently. Many studies showed that the CEM gain varies with input electron energy [8,9], passage of time [10], multiplier voltage [11], ionic state of input ion [12-15], and gaseous adsorption [16]. For AES analysis, the energy of the electrons entering into a CEM varies with the CMA pass energy, while the energy is constant for XPS analysis. Therefore the AES measurements may have more difficulty to acquire the high-precision spectra.

In this report, we used an AES apparatus equipped with a CMA, and we will present the analysis method to evaluate the MCP gain stability by removing the effects of current fluctuations and the surface contamination. The continuous repeated acquisitions of the survey spectrum for a long period finally attained a steady spectra, however the attained steady state was immediately disrupted by an acquisition halt.

2. Experiment

The ULVAC-PHI model 680 was used, and it equipped with a MCP in a CMA. The primary electron beam had energy of 5 keV and the beam current of 11 nA. During the measurement halts the beam irradiations were continued. The beam irradiation area was set to 50 × 40 μm^2 during both the spectra acquisitions and the measurement halts.

The sample was a Molybdenum (Mo) thin film, sputter-deposited onto a soda glass with a thickness of 600 nm. The vacuum pressure of the analysis chamber was lower than 5×10^{-8} Pa. The energy scanning region was 0 to 1400 eV with step change of 1 eV, and the duration of each step was 20 ms.

The measurement procedure was as follows: The sample surface was sputter-cleaned by 3 keV Ar^+. Then the electron beam was irradiated for 1 h before the survey-spectra acquisition. The survey spectra were recorded 115 times taking approximately 1 h. It was followed by a break in acquisition for 1 h. Three sets of the spectra were recorded in total. In another experiment we examined a measurement break for 0.1 h.

It is noted that during the measurement break the electron beam was continuously irradiating, while the energy scan of the CMA was paused so as not to let the electrons enter the MCP.

3. Results and Discussions

Figure 1 shows that the intensity of the survey spectra gradually decreased across the whole range of the electron energy. The most probable reasons could be the surface contamination induced by the electron beam irradiation and the beam current fluctuation. The typical signal intensity was ~10^6 counts for every energy channel, however, the signal intensity was not much enough to evaluate the slight variation of the intensity. To reduce the statistical fluctuations, the area intensity integrated over every 50 eV, $I_E(t)$, was derived from the spectra in Fig. 1, and the results are shown in Fig. 2. It shows every reading had more than 10^7 counts.

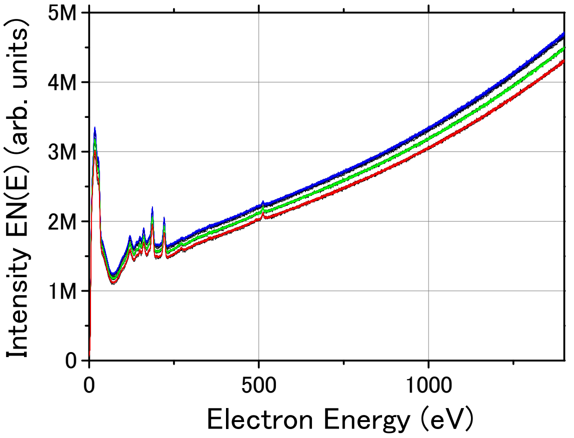

Fig. 1 Three sets of the AES survey spectra. In each set 115 spectra were continuously acquired. From the top to bottom they are the first (blue), second (green), and third (red) set of spectra.

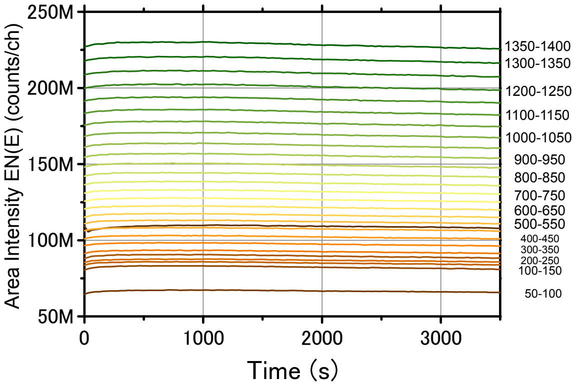

Fig. 2 Time changes of the spectral area intensities, $I_E(t)$s.

All of the area intensity, $I_E(t)$s, showed the same trends; The $I_E(t)$s increased at the initial stage (0–500 s) and gradually decreased after ~1000 s. The $I_E(t)$ varied much more for the higher electron energies.

To compare the rate of time variation among $I_E(t)$s, the normalized intensity expressed by $I_E(t)/I_E(3300s)$ were shown in Fig. 3. The anchoring points, $I_E(3300s)$, were given by the average intensity between 3000 s and 3600 s.

After ~1000 s, the change rate of the $I_E(t)/I_E(3300s)$ were similar for the entire energy. In particular, the plots for energies over 600 eV showed the same decreasing rate by ~ −3 %/h. For energies lower than ~ 300 eV, the decreasing rate was slightly larger. These phenomena can be explained by the surface contamination because the surface contamination typically reduces the spectral intensity, especially for the lower energy region.

Conversely, during the first ~500 s, the $I_E(t)/I_E(3300s)$

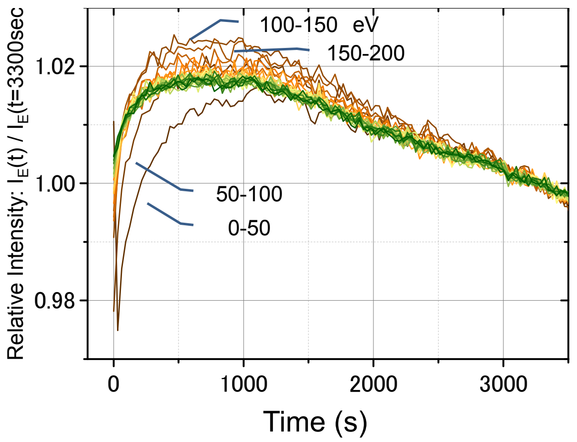

Fig. 3 The time changes of the $I_E(t)/I_E(3300\mathrm{s})$ for 0 eV to 1400 eV. The line color corresponds to the electron energy as the same in Fig. 2.

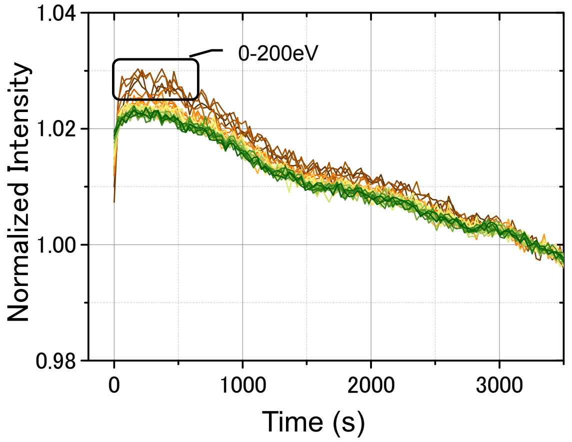

Fig. 4 The time changes of the $I_E(t)/I_E(3300\mathrm{s})$s for the second set in Fig.1. The origin of time scale is the start time of the second set acquisition.

showed the different manners. One was that all of the $I_E(t)/I_E(3300\mathrm{s})$ increased by a few percent. This phenomenon cannot be explained by the surface contamination. Another was that the increasing rates depended on the energy. The $I_E(t)/I_E(3300\mathrm{s})$ with the energies over 600 eV coincided with each other, whereas those with energies less than ~300 eV separated.

The tendencies described above were also observed in other sets of sequentially acquired spectra. As shown in Fig. 4, the second set of spectra in Fig. 1 revealed that the $I_E(t)/I_E(3300\mathrm{s})$ decreased at a rate of ~2.5 %/h after ~1000 s, while they increased for the first ~500 s. The $I_E(t)/I_E(3300\mathrm{s})$ with energies less than ~300 eV showed larger change for the first ~500 s.

The gradual decrease in the $I_E(t)/I_E(3300\mathrm{s})$s as shown in both the Figs. 3 and 4 was assigned to the beam-induced surface contamination as follows: During the period between the first and second sets of spectra (i.e. the measurement break), the probe beam continuously irradiated the sample surface. As such, the growth of the surface contamination was expected to continue during the measurement halt. Therefore, the $I_E(t)/I_E(t_o)$ of the first set can be connected smoothly to the second set of $I_E(t)/I_E(t_o)$ with the extrapolated line in accordance with the first-set decay rate of ~3 %. Figure 5 shows that the extrapolated decay line connected the $I_E(t)/I_E(10500)$ of the first set to the $I_E(t)/I_E(10500)$ of the second set, and the extrapolation line with the decay rate of ~2.5% also connected the second one to the third one smoothly.

Next we would focus on the initial increase of $I_E(t)/I_E(3300)$s appearing at the first ~500 s. To remove the gradual intensity decrease, $I_E(t)/I_E(3300)$s were normalized by the $I_{E=1350\mathrm{eV}}(t)/I_{E=1350\mathrm{eV}}(3300)$. Then the normalized $I_E^{nor}(t)$ was described as

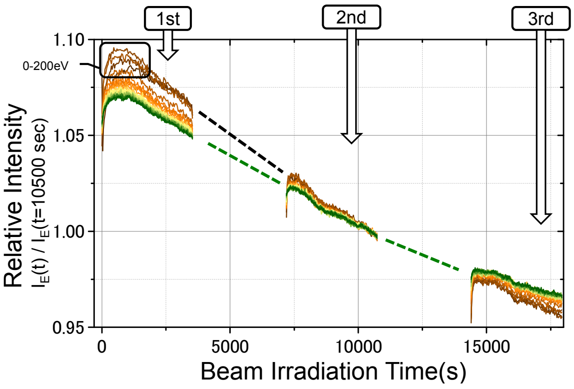

Fig. 5 The time change of the $I_E(t)/I_E(t=10500)$ for the first, second, and third sets. Dashed lines are extrapolations from the first and second sets.

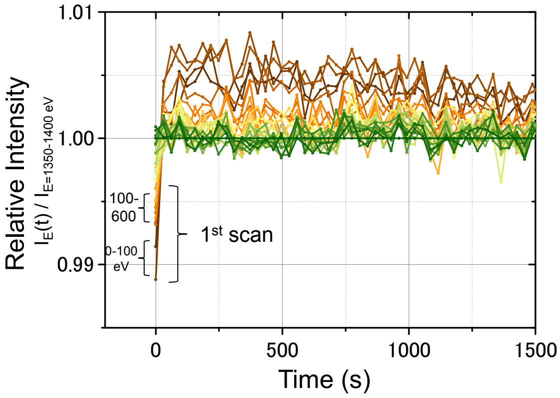

Fig. 6 Initial change of $I_E^{nor}(t)$ for the second set of acquired spectra. The line color corresponds to the electron energy as the same in Fig. 2

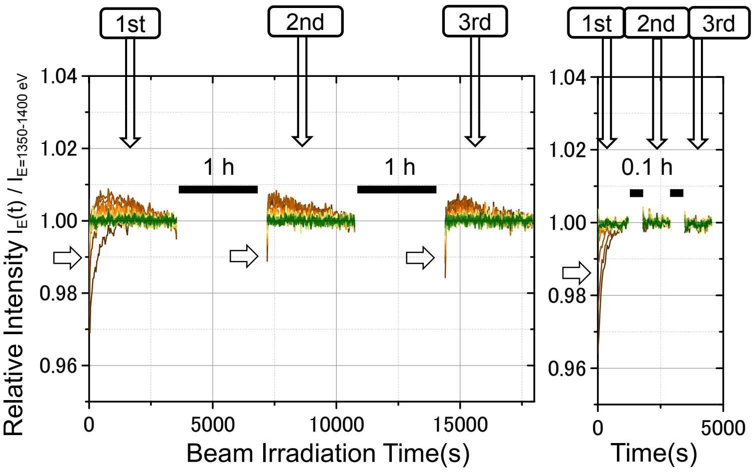

Fig. 7 Time changes of the relative intensity for the measurement halts of 1 h (left) and of 0.1 h (right) respectively. The scanning of the kinetic electron energy was carried out from low to high energy (left) and from high to low energy (right).

$$I_E^{nor}(t)=\left[I_E(t)/I_E(3300)\right]/\left[I_{E=1350}(t)/I_{E=1350}(3300)\right]. \quad (1)$$

The $I_E^{nor}(t)$ s for the second set spectra are shown in Fig. 6. Only the first acquired spectrum, $I_E^{nor}(0)$, had notably different characteristics. They showed that the $I_E^{nor}(0)$ s with the energy less than ~600 eV were less than unity. The $I_{E=0-50eV}^{nor}(0)$ had the minimum value among the $I_E^{nor}(0)$ s, and it was 0.99. However, the intensity of the secondly-acquired spectrum, $I_E^{nor}(t=30s)$ s, were around unity. Since the acquisition time for the first spectrum with the energy less than 600 eV was ~15 s, we believed that the spectra lost its intensity at the beginning of the acquisition.

The other important finding was that the acquisition halt caused the instability of the acquitted spectra. Fig. 3 showed that after the repeated acquisition for ~1000 s, the steady spectra with similar shape were derived. However, the acquisition halt disrupted the steady state, and as shown in Fig. 4, it needed ~ 500 s to derive the steady spectra again.

We think that the instability of the spectra intensity as mentioned above, reflected the instability of a MCP amplification. The input electrons are multiplied at the MCP wall surface. However the electron yield can be changed, if surface conditions are modified due to surface charging, gas adsorption, temperature, and so on. As one explanation for the experimental results, we may speculate that the MCP needs ~15 s to make its channel surface be stably-charged, and the MCP needs more than ~500 s to desorb the gas adsorbed on the channel wall, or to stabilize the wall temperature.

The instability of the first spectrum could be improved by shortening the measurement halt as shown in Fig.7. We think that the shorter period of measurement halt might reduce the gas adsorption on the channel walls.

According to the experimental results, we would suggest that when one checks the spectrum repeatability according to the ISO 24236 [6], the spectra taken within the first 10 min. be discarded, because they may lose their intensity by a few percent.

4. Summary

Repeated acquisitions of survey spectra and the removal of the gradual intensity variation revealed the instability of the MCP amplification. The instability caused the spectrum-intensity lost by a few percent. The intensity lost appeared after every measurement-halt.

The typical electron analyzer has equipped a MCP or a CEM. To achieve the high-accuracy analyses with an electron spectroscopy, we need to clarify how the MCP gain stability will be disrupted. Further study on the MCP gain stability is necessary as well as the investigations with other instruments.

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