

Extended Abstract of PSA-19

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Chemical State Quantification of X-ray Auger Electron Spectrum with Top-Hat Filtering

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The chemical state quantification of elements, especially transition metals and their compounds from X-ray Auger electron spectrum, is generally difficult due to the complexity of spectra resulting from peak asymmetries and overlapped binding energies. Moreover, background shape which contains information on surface contamination and roughness affects comparability of spectral fitting data on the element of interest.

To promote practical use of spectral fitting for the chemical state quantification, the top-hat filtering (THF) was applied to Cu LMM Auger electron spectra. It was found that the THF suppressed the difference of background shapes derived from surface contamination and that oxidation states of Cu was quantified plausibly by least square fitting of standard spectra. Thus, it is suggested that the combination of the THF and least square fitting is a practical method for the chemical state quantification of X-ray Auger electron spectrum.

1. Introduction

XPS is one of the essential tools for understanding the nature of material surfaces because it can provide information on elemental composition and chemical state of each element. In case of some transition elements such as Ni, Cu and Zn, X-ray Auger electron spectra are often used for chemical state analysis because spectral line-shapes and positions vary with their oxidation states. However, it is generally difficult to quantify the chemical states from X-ray Auger electron spectrum due to the complexity of spectra resulting from peak asymmetries and overlapped binding energies [1, 2]. Moreover, background shape which contains information on surface contamination and roughness adversely affects the quantification of the chemical states. Although the active Shirley method which can adjust the background intensities automatically has been developed to suppress peak area fluctuation [3], proper spectral fitting is not always achieved due to the curvature of calculated background.

Here, we focused on the top-hat filtering (THF) which is often applied as a data processing method for X-ray spectrum [4].

The THF is the convolution of the top-hat function and a spectrum. When M and N represent the arbitrary numbers of channels on the spectrum, the top-hat function is described in Fig. 1.

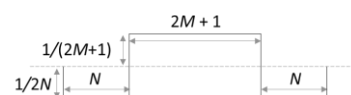


Fig. 1 The top-hat function. A weighting function is zero on a horizontal dotted line.

It should be noted that top-hat takes the average over $2M + 1$ channels about the channel of interest and subtract the averages over N channels on both sides of this central region. Thus, a symmetrical peak is transformed into a central positive lobe with negative lobes on either side. As a result, the THF effectively suppresses the difference of background, especially a linear one, numerically. Besides, it enables to enhance the separation of overlapped peaks on the spectrum with reducing statistical noise by using suitable M and N values which are empirically estimated at less than 70% of full width at half maximum (FWHM) against data points of the peak. The Gaussian peaks with various backgrounds before and after the THF

preprocessing are shown in Fig. 2.

To improve the comparability of quantitative results by the spectral fitting, we introduced the THF preprocessing to X-ray Auger electron spectra with different background shapes.

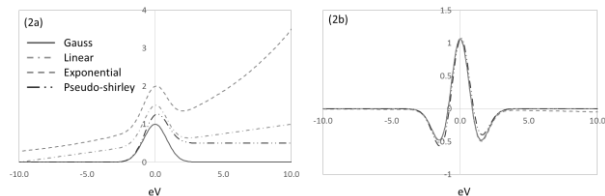


Fig. 2 Gaussian peaks with linear, exponential and pseudo-shirley backgrounds before (2a) and after (2b) the THF preprocessing. On the assumption of X-ray Auger electron spectrum, FWHM and energy step of the peak were 2 eV and 0.1 eV, respectively. M and N values were 3.

2. Experimental

The spectra of CuO powders with/without C coating (around 3 nm thickness) were used as sample data. Least squares fitting was carried out against these spectra using standard ones of Cu metal, Cu₂O, CuO and Cu(OH)₂.

All spectra were obtained by VersaProbe (ULvac-Phi, Inc., Chigasaki, Japan) operated with Al X-ray at 250 W. Energy steps and pass energy were 0.1 eV and 23.5 eV, respectively. Spot size was 100 μm in diameter and the take of angle was 45 degrees.

On the THF preprocessing, N was defined as the same value as M in this study and 7 was chosen for both values, assuming that FWHM of the sharpest peak is around 1 eV.

3. Results and discussion

Firstly, spectral shapes were thoroughly compared between Cu LMM Auger electron spectra of CuO powder samples with and without C coating (Fig. 3). Spectral shape of the CuO powder with C coating was slightly different between 570 and 574 eV compared to the one without C coating. This difference is supposed to be derived from coated C.

Then, the THF was applied to the LMM spectra of CuO powder samples. The fitting result of raw data (without the THF preprocessing) identified the spectrum as a mixture of Cu metal and CuO (Fig. 4a). In contrast, the fitting result after the THF preprocessing explained the spectrum as only CuO (Fig. 4b). This indicates that the THF suppressed the

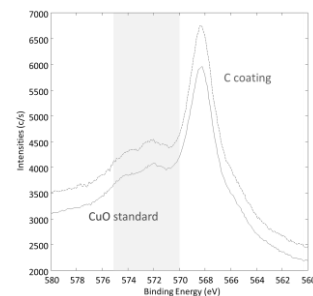


Fig. 3 LMM spectra of CuO powders with (solid line) and without (dotted line) C coating.

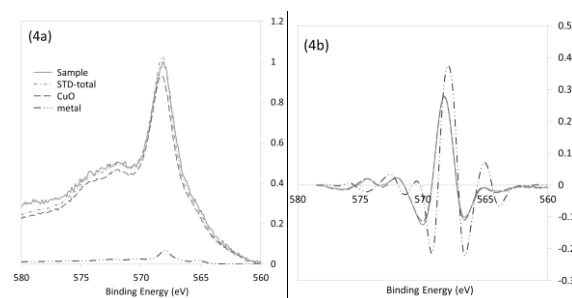


Fig. 4 Least squares fitting results of CuO LMM spectra (4a) raw data, (4b) THF preprocessing data.

background derived from the contamination. Although some information on the surface might be lost because the THF is not based on physical model, chemical states were plausibly quantified by least square fitting of standard spectra.

4. Conclusion

In this study, we investigated a practical method for spectral fitting of X-ray Auger electron spectra using the THF.

It was found that the THF improves the comparability of least squares fitting for Cu LMM Auger electron spectra by suppressing the difference of the background shapes. Therefore, it is suggested that the combination of the THF and least squares fitting is useful for the chemical state quantification from X-ray Auger electron spectra.

5. References

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