Extended Abstract of PSA-19
O-18

Automated peak fitting of XPS spectrum using information criteria

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(Received: May 30, 2019; Accepted: August 6, 2019)

We developed and implemented a fully automated method to perform X-ray photoelectron spectroscopy (XPS) spectral analysis based on the active Shirley method and information criteria. Our method searched many initial fitting models by changing the degree of smoothing, and obtained many fitting models after peak parameter optimization. The goodness of those models was evaluated using the Bayesian information criterion (BIC). As a result of applying this algorithm to measured XPS spectra, we found that using the BIC, a simple model with reasonably good agreement and a small number of peaks was selected. The model selected by the BIC was close to the results of peak fitting performed by XPS analysis experts.

1. Introduction

High-throughput measurement has become increasingly important for the efficient development of science and technology, and the accumulation of large amounts of spectral data is urgently required. Although X-ray photoelectron spectroscopy (XPS) was formerly a time-consuming characterization technique, the use of high-intensity synchrotron radiation and a high sensitivity detector enables us to obtain a large amount of spectral data over a short time period. Therefore, high throughput data processing is also required for efficient spectral data analysis. In the present work, we develop a fully automated method to perform XPS spectral analysis.

We have developed an automatic analysis tool for XPS spectra based on the active Shirley method [1]. We demonstrated that it can perform automatic peak fitting and film thickness evaluation with excellent reproducibility for SiO_2 thin film samples [2-3]. The result of peak fitting is a local solution that is strongly dependent on the initial parameters of the peak (number of peaks, energy position, height, etc.). Therefore, the peak fitting result easily changes by the initial parameters, and rarely converges to the global solution.

In this study, to make the active Shirley method applicable to XPS spectra with complicated shapes and a high degree of statistical noise, we develop a heuristic algorithm that systematically sets the initial number of peaks and automatically extracts a candidate for the global solution.

2. Calculation method

We adopt a linear combination of pseudo-Voigt functions and the Shirley background [4-5] as a model function of the XPS spectrum.

To provide a number of initial fitting models, we systematically scan the degree of smoothing applied to a given spectrum. The degree of smoothing is tuned by the parameters of the smoothing data points and the repeat count.

We subtract the initial background from the measured spectrum using the usual iterative Shirley method [2], and then calculate the smoothed third-order differential spectrum for the spectrum using the Savitzky–Golay method [6]. We use that zero point to determine the initial peak position and half width at half maximum [3]. The initial value of the Lorentz–Gauss

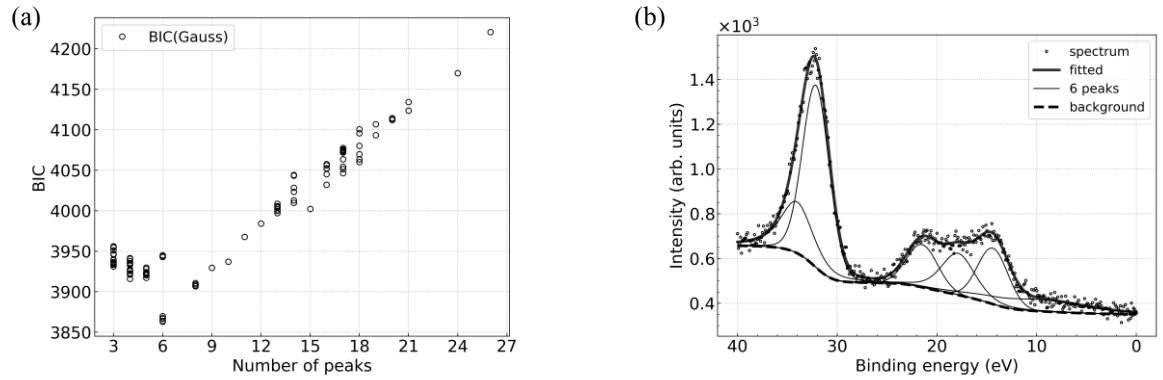

Fig. 1. (a) BIC values as a function of the number of peaks for the valence band spectrum of silicon dioxide. (b) Fitting results when minimizing BIC. Small circles are the experimental data, a thick line is a fitted spectrum, thin lines are individual peaks, and a broken line is a background, respectively.

mixing ratio is set to zero, which indicates a pure Gaussian.

After determining the initial values of the peaks and backgrounds, we optimize the peaks and backgrounds using the modified Marquardt method by Fletcher [7]. During peak optimization, we remove tiny peaks with negligible area intensity and extremely-sharp peaks.

Then, we have many optimized results. Generally, the larger the number of peaks, the smaller the difference (i.e., the error function) between the model function and measured spectrum. However, this causes overfitting, where the model function becomes too complicated, so physical interpretation is impossible. To avoid this overfitting, it is necessary to take not only the error function but also the trade-off with model complexity into consideration. As a simple method for this, we consider the Bayesian information criterion (BIC) as model selection criteria [8-9]. We calculated the BIC for 155 optimized results, and assessed that the smaller the value of the BIC, the better the model.

3. Calculation results

We applied this model selection to a valence band spectrum of silicon dioxide. The application of our method generated 155 different optimization models. The diagrams of the BIC values as a function of the number of peaks of each model in Fig. 1(a) show that there is a minimal point for both diagrams because of the tradeoff between the likelihood term and penalty term.

Fig. 1(b) shows the fitting results when the BIC were minimized. The proposed method detected the major peaks in the spectrum. There were also minor peak structures that would be difficult to determine visually by an analyst. In such cases, the minimum BIC did not recognize them as peaks.

There is another criterion, the Akaike information criteria (AIC). The AIC tended to recognize minor structures as peaks (to be submitted). Generally, the BIC adopted a model with a smaller number of peaks than the AIC.

4. Conclusions

We systematically performed round robin analysis from weak to strong smoothing on a spectrum to obtain many fitting results. Subsequently, a good model was selected by applying the BIC to the fitting results. As a result of applying the proposed algorithm to measured XPS spectra, we found that, using the BIC, a simple model with reasonably good agreement and a small number of peaks was selected. The model selected by the BIC was close to the results of peak fitting performed by XPS analysis experts.

5. References

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