

## Restoration of Loss Function in Very Difficult Case - From Poor Resolution Spectrum

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Efforts for restoration of the loss function from the XPS spectra of relatively poor resolution have been in progress. A new objective function and improving algorithm have given better convergence than reported before.

### 1. Introduction

There are two major distortion mechanisms for the XPS peaks. One is due to finite analyzer resolution and the other due to inelastic scattering inside the solid. These are entirely independent phenomena and therefore separable in principle. In the previous report [1], it was demonstrated that the loss function calculated from the spectrum of fine resolution is applicable for background correction of spectra of any resolution, finer or poorer. This indicates that the spectrum of very poor resolution also carries the same information of loss function. However the difficulty for calculating loss function increased significantly as the resolution became poorer, as expected. In the present paper, the effort to deduce the same loss function from the spectra of relatively poor resolutions by making improvements of optimization algorithm has been continued. Practically, it is convenient if one can use poorer resolution spectrum for analysis because such spectrum takes much less acquisition time and has better signal to noise ratio.

### 2. Method

Details of the present version of optimization method are described elsewhere in this issue. Only a brief summary is given here. Tougaard's formula is expressed as follows

$$j_0(E) \propto \frac{j_0(E)}{\lambda(E)} - \int_E^{\infty} j_0(E') K(E', E) dE'$$

$j_0(E)$  is the observed photoelectron energy

distribution (spectrum) with kinetic energy  $E'$ ,  $K(E, E')$  is the probability of inelastic scattering of photoelectron from  $E'$  to  $E$ ,  $\lambda(E)$  is the inelastic mean-free path of a photoelectron of kinetic energy  $E$  inside the solid, and  $j(E)$  is the spectrum after background removal. The integral represents the generated inelastic background.  $K$  is called the "loss function".

The problem is formulated such that the shape of the loss function  $K$ , which satisfies the optimum condition described below, is to be found using the observed spectrum and some general parameters.

Three quantities,  $P$ ,  $Q$ , and  $R$  are defined.  $R$  is newly introduced, others are the same as reported before [2].  $Tail$  designates the

$$P(K^0) = \left| \frac{A_1}{S_1} - \frac{A_2}{S_2} \right|$$

$$Q(K^0) = \int_{Tail} |j(E)| dE$$

$$R(K^0) = \int_{A_i} j(E) dE$$

region outside the peak.  $A_i$  is a measured intensity (area) of the  $i$ -th peak.  $S_i$  is an expected intensity of the  $i$ -th peak.  $K^0$  is the loss-energy dependent part of the loss function  $K$ ,  $K(E, E') = [1/\lambda(E')] * K^0(E', E)$ . Making  $P$  and  $Q$  small means that making peak intensity ratio  $A_1/A_2$  equal to  $S_1/S_2$ , and making intensity outside the peak zero, respectively.  $R$  is newly introduced and represents the intensity of a

particular peak. The coefficients  $S_i$ 's and the positions of boundaries of peaks and tails (fixed previously) are treated as variables for optimization, in addition to those describing the  $K^0$ . For the inelastic mean-free path, the calculation by Tanuma et al. is used.[3]

In the calculation, one of the above three is chosen as an objective function that is to be minimized. The rests are incorporated in the constraints like

$$c_P = P_0 - P > 0,$$

$$c_Q = Q_0 - Q > 0,$$

$$c_R = R_0 - R > 0.$$

This means that, during the calculation, values included in the constraints ( $P$ ,  $Q$ ,  $R$ ) are not allowed to exceed the given limits  $P_0$ ,  $Q_0$ ,  $R_0$ . Therefore these constants determine whether a reasonable solution can be reached or not.

These functions are normalized by the area of the first peak in the list inside the program (3d5/2 for the present study), which is calculated using the initial form of  $K^0$  only once at the beginning of the calculation. This value is, though not identical to the peak area in the final solution and depends on the particular form of  $K^0$  at the beginning of the calculation, a measure for the relative accuracy of the calculated results. The constants  $P_0$ ,  $Q_0$  and  $R_0$

are determined by trials and errors as follows. First, start with appropriate guesses. If the  $K^0$  is not convergent, it is likely that the constraints are too strict. Then increase the constants in the constraint. If the  $K^0$  seems on the way to the solution, decrease the constants to make the constraints severer. Typical values used are,  $P_0 \approx 0.1$ ,  $Q_0 \approx 0.5$ ,  $R_0 \approx 1$ .

For optimization routine, the Successive Quadratic Programming method written by Fukushima [4] was used. The calculation is done on a PC with dual Pentium II Xeons. Typical computation time is between a few seconds and a few minutes depending on the data size and the number of variables.

### 3. Analysis

The same Ag3d spectra used in the previous study [1] is analyzed by an improved routine. Polycrystalline Ag sample was measured using the PHI-1600c spectrometer with Al monochromatic source. The analyzer resolution is represented by the pass energy  $E_{\text{pass}}$  for PHI-1600c. The analyzer slit No.4 was used throughout the experiment. The full-width at half maximum FWHM for Ag3d5/2 for  $E_{\text{pass}} = 2.95$  eV (highest resolution) was 0.44 eV. The "poorest" and "second poorest" cases,

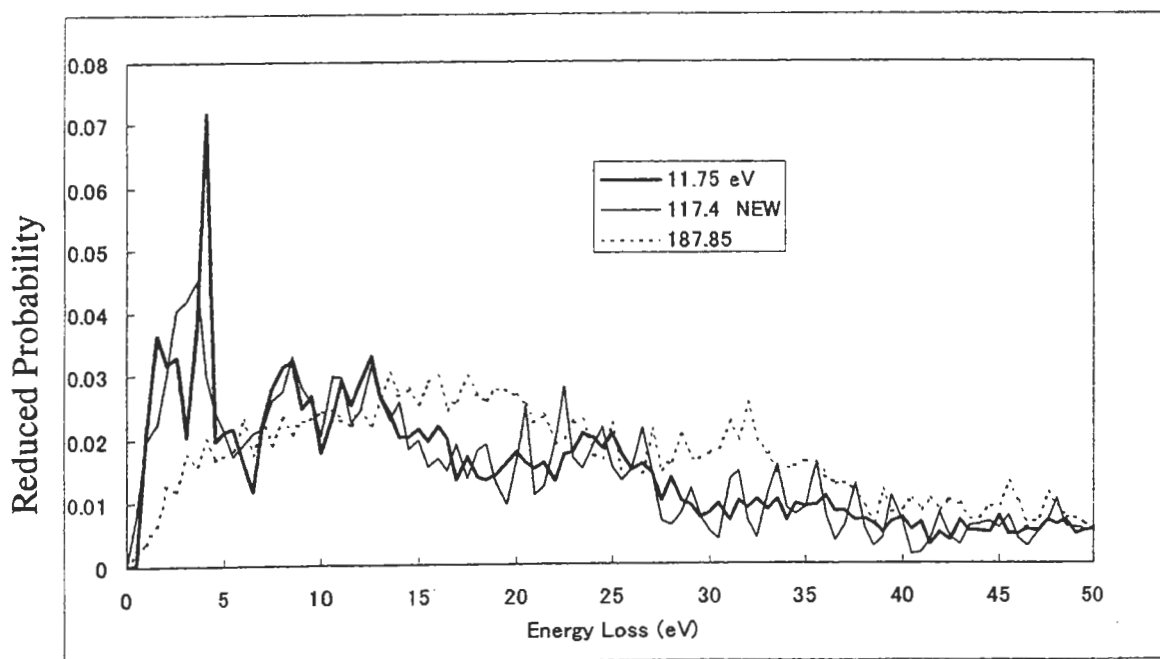


Fig. 1  $K^0$  from different resolution spectra. Bold solid line: Best  $K^0$  obtained before. Thin solid line: Present result calculated directly from universal function-like initial form for  $E_{\text{pass}} = 117.4$  eV. Dotted line: Same present result for  $E_{\text{pass}} = 187.85$  eV.

$E_{\text{pass}}=187.85$  eV and  $117.4$  eV are analyzed. The Ag  $3d_{3/2}$  and  $3d_{5/2}$  doublet is used for optimization.

For expected intensity  $S$ ,  $S_{3d_{3/2}}$  is fixed and  $S_{3d_{5/2}}$  is adjusted in the calculation. (Note that only the ratio is important.) Initial values of these were given as follows. Remove background using the best loss function obtained before. The areas of  $3d_{5/2}$  and  $3d_{3/2}$  are defined as areas between two borders one of which is at the position of minimum intensity in between the two, the other is on the opposite side, as indicated in Fig.2. Initial ratio  $S_{3d_{5/2}}/S_{3d_{3/2}}$  was calculated to be 1.41 and 1.42 for  $E_{\text{pass}}=117.4$  and  $185.85$  eV, respectively. At the end of calculation the ratios are 1.41 and 1.33, measured area  $A_{3d_{5/2}}/A_{3d_{3/2}}$  ratios are 1.41 and 1.28, respectively. The energy step of optimizing loss function is  $0.5$  eV.

It is noted that the present results are obtained just in one run directly from the universal-function-like initial form in a few minutes, whereas to get the previous results took many runs of trial and error.

#### 4. Results and Discussion

Fig. 1 shows the  $K^0$  obtained directly from the initial form simulating Tougaard's universal function of  $B=3047$  and  $C=1100$ , together with the best  $K^0$  obtained before [1]. In the previous report, it was not possible to restore the structure at low

energy-loss for  $E_{\text{pass}}=117.4$  eV. In the present study it is almost reproduced, though still not

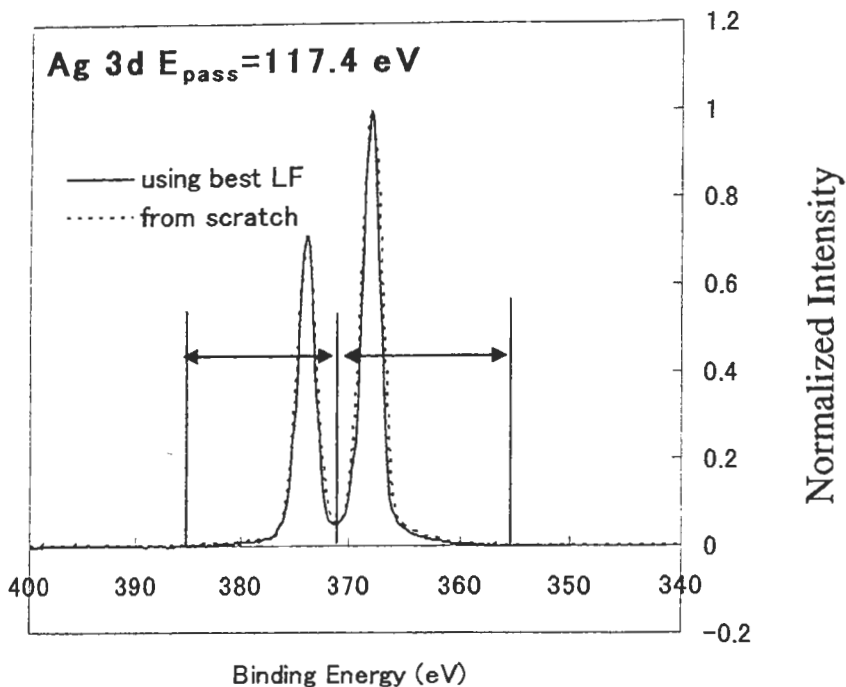


Fig.2 After background removal for  $E_{\text{pass}}=117.4$  eV. The intensity is normalized by the  $3d_{5/2}$  peak top. Solid line: using best loss function obtained before. Dotted line: Direct result from starting with universal-function-like initial form.

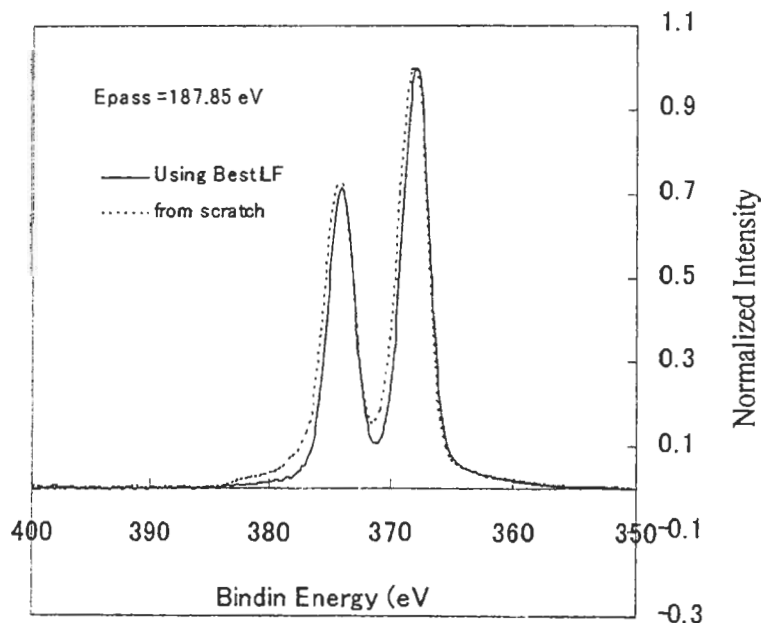


Fig.3 After background removal for  $E_{\text{pass}}=187.85$  eV. The intensity is normalized by the  $3d_{5/2}$  peak top. Solid line: using best loss function obtained before. Dotted line: Direct result from starting with universal-function-like initial form.

identical. Plasmon peak is seen at 3.5 eV, whereas the previous result shows it at 4.0 eV. It is noted that precise position of the plasmon is reported to be at 3.7 eV [5]. The agreement is much better when one compares the analyzed spectrum (Fig. 2).

The  $K^0$  of the poorest case is still not good. The Ag-specific fine structure at lower energy is not reproduced. However, the difference in background-subtracted spectra seems not very large as shown in Fig.3. Slightly larger intensity at the higher binding energy sides of the peaks corresponds to the lack of low-energy structure of the  $K^0$  compared to the best one. This suggests the possible use for quantitative analysis even if a satisfactorily good loss function is not obtained.

As was reported in ref.1, the peak positions are similar but not identical to those reported in REELS [6] experiments. It is no wonder that these are not identical, because of the following reasons.

a) REELS peak position is a result (superposition) of multiple scatterings whereas the  $K^0$  describes the probability of single scattering event.

b) In REELS the electron passes the surface twice, while the photoelectron passes the surface only once. Therefore the escaping electron sees a different medium for each case.

c) REELS results include only extrinsic effects. If one substitutes  $K^0 = \alpha \Delta E$  in the Tougaard's formula, all the spectrum becomes background. Therefore the formula itself cannot distinguish extrinsic and intrinsic parts strictly.

In order to examine all the precise peak positions of the  $K^0$ , and to exclude artifacts from stochastic noise and broadening, further analysis in a more controlled way would be necessary. This would be done by giving artificial noise and broadening to a very high precision data, and observing the calculated  $K^0$ . However, it is noted that the spectra used were not measured in *one-time*. There were at least ion bombardments and re-positioning of the sample between the measurements. Therefore, the sample alignments, the surface morphologies, the X-ray intensities, the X-ray beam positions on the sample, the signal intensities, and the signal-to-noise ratios (and of course the

resolutions) were different for all the measurements. This fact suggests that the features commonly observed in the results are very likely to be ascribed to the specific character of the material.

In summary, to restore the loss function from a spectrum with lower resolution than previously [1] has been tried. Improvement of algorithm has made it possible to restore the loss function from the second poorest resolution spectrum.

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