

Possibility of determining integration boundaries of a broad peak using only the Shirley Method

Masatoshi Jo

Electrotechnical Laboratory, Umezono 1-1-4, Tsukuba, Ibaraki 305-8568, Japan

(jo@etl.go.jp)

(Received October 7 1998; accepted January 11 1999)

It is shown that the integration boundaries (end points) determined by background optimization are also suitable for the Shirley method. For a couple of end points that are deduced from an optimized background, the ratio of areas of the same peak calculated by the Shirley and the optimized background is constant for all analyzer resolutions. The relative intensity ratio of different peaks from the same solid is also constant if such a couple is chosen for each peak, irrespective of the resolution. This suggests a method of determining end points by using only the Shirley method.

Introduction

The Shirley background subtraction is the most popular method to date for XPS peak analysis because the algorithm is simple and fast. At the cost of this convenience, the method has two ambiguities: one is the integration boundaries (denoted as 'end points') and the other is the algorithm itself. The latter is considered systematic because the Shirley's algorithm tends to overestimate the background compared to using a realistic loss function. On the other hand, the end points are material-dependent. Especially, it has been difficult to locate the end point at the higher binding energy side of the peak if there is a large inelastic background. In principle if possible, for quantitative analysis, the area of the primary excitation spectrum that is deduced using the material's true loss function is considered to be the best because it is directly proportional to atomic density. The end points of the primary excitation spectrum thus determined, i.e. the boundary beyond which its intensity is zero, are therefore also possible candidates for the Shirley method, though there is still some systematic difference as

mentioned above. In the present paper, it will be shown that the end points determined by background optimization are also suitable for the Shirley method. The discussion suggests how to determine suitable end points without using background optimization, but using only the Shirley method.

It is noted that the background optimization algorithm [1] used here also has an ambiguity concerning the assumed energy range of peak pair and peak tail that are fixed during the calculation. Hence, the optimized loss function may not necessarily be the true loss function. However, the optimized loss function is able to make all peak areas, not only those used for optimization but also others that are not involved, on the spectrum consistent in intensity as shown before [2] and here.

Experimental

All spectra were taken by a PHI 1600c spectrometer with a monochromatic Al $K\alpha$ source. Ag and Cu polycrystalline specimens were used. Sample treatments before the measurement are similar to those reported before [2]. Measurements

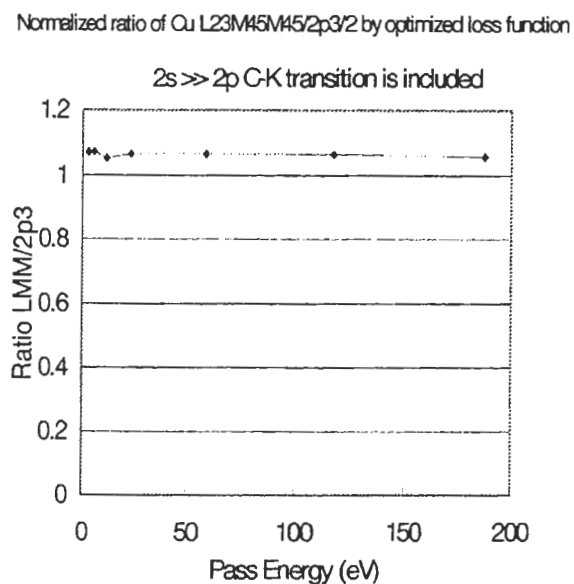


Fig.1 Area ratio of Cu ($L_{23}M_{45}M_{45}$)/($2p_{3/2}$) by optimized loss function.

were made for the following analyzer pass energies, $E_{\text{pass}} = 187.85, 117.4, 93.8, 58.7, 29.35, 23.5, 11.75, 5.85,$ and 2.95 eV.

The analyzer's transmission function was calibrated as follows. Each peak was repeatedly measured varying the E_{pass} , and the peak area for each spectrum was calculated by using the optimized loss function. The ratio of the peak area to the peak area from the spectrum with the largest E_{pass} (187.85 eV) was calculated. This ratio was used as individual transmission correction factor because for $E_{\text{pass}} = 187.85$ eV the transmission is almost constant in the measured energy range. The approximate function in the previous paper [3,4] was not used, since there is still a data scatter (Fig.2 of ref. 3), although it is better than using the Shirley method.

Details of the calculation are described in ref. 1. For Ag, the $3d_{5/2}$ and $3/2$ peak pair was used for optimization. The shape of the loss function is discussed elsewhere. For Cu, the $2p_{3/2}$ and $1/2$ peak pair was used. The loss function is shown in the previous report [2.]

For the inelastic mean-free path (IMFP), the calculation by Tanuma et al. is used [5].

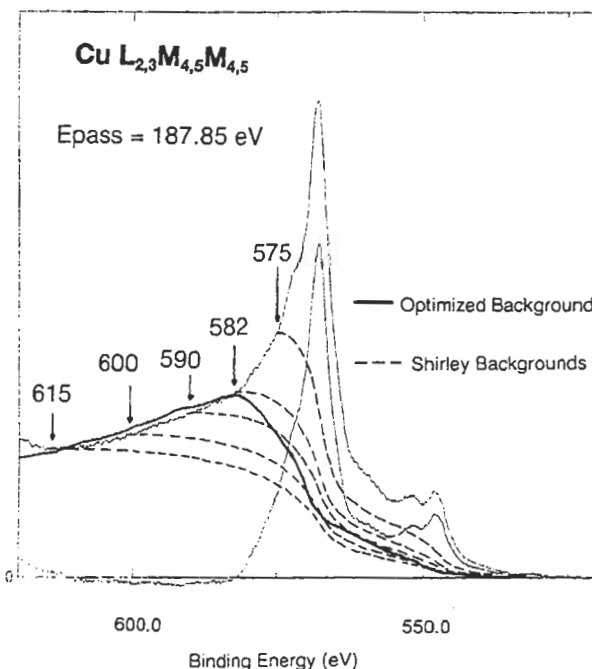


Fig.2 Cu LMM peak with backgrounds by Shirley and by optimized loss function.

Results and Discussion

In Fig. 1, the ratio of the Cu $2p_{3/2}$ and $L_{23}M_{45}M_{45}$ peak areas determined by an optimized background is plotted against analyzer pass energy, after transmission and IMFP correction, and normalization by each transition probability including Coster-Kronig transition between $L1(2s)$ and $L2,3(2p)$ [2]. The ratio should be 1 in the ideal case. Thus the optimized loss function keeps the intensity ratio of peaks on the spectrum far apart irrespective of analyzer resolution. The reason for the observed deviation in Fig.1 is not known. Anisotropy of photoelectron emission, elastic scattering, imperfection of loss function, breakdown of loss function approximation in terms of IMFP and a part independent of kinetic energy, etc. may contribute to the deviation.

In general, resolution-independence is a necessary condition for an entity to be the true property of the material, though still not a sufficient condition. These plots are used to examine whether the peak areas are consistent with this necessary condition.

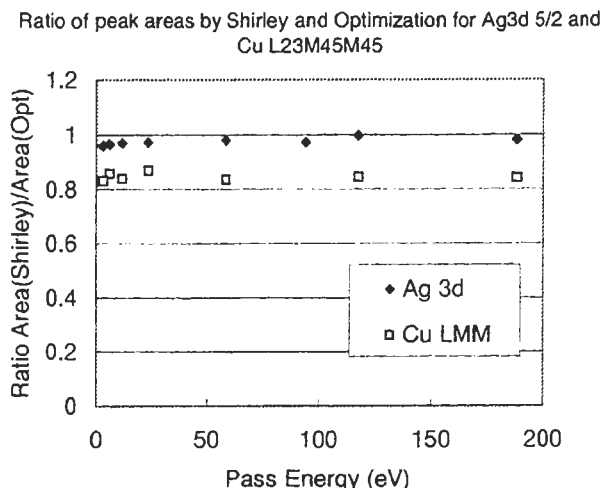


Fig. 3 Comparison of areas of the same peak by two methods

Fig.2 shows the Cu $L_{23}M_{45}M_{45}$ peak with an optimized background and Shirley backgrounds by varying the higher BE end point. The higher BE end point at 582 eV is given by the optimized background as the point at which the background-subtracted spectrum becomes zero. The lower BE end points are taken at the edge of the scanned region. In general the end points move outward as the pass energy increases. However, for higher the BE side of Cu LMM, it was difficult to trace the position because the intensity crosses zero before reaching the actual end point. This might be ascribed to those mentioned above concerning the ratio of 2p and LMM peaks. The error due to this cut-off is, however considered to be small compared to the whole area of the peak. Hence the higher BE end point of Cu LMM apparently does not move along with analyzer resolution. For the end points other than 582 eV, see the discussion below.

The optimization tends to estimate a smaller background compared to the Shirley method because the maximum of the loss function is located typically at a few eV. The ratio of the areas calculated by using these two background lines is plotted against analyzer pass energy (Fig.3). Note that, for both cases, the ratio is almost

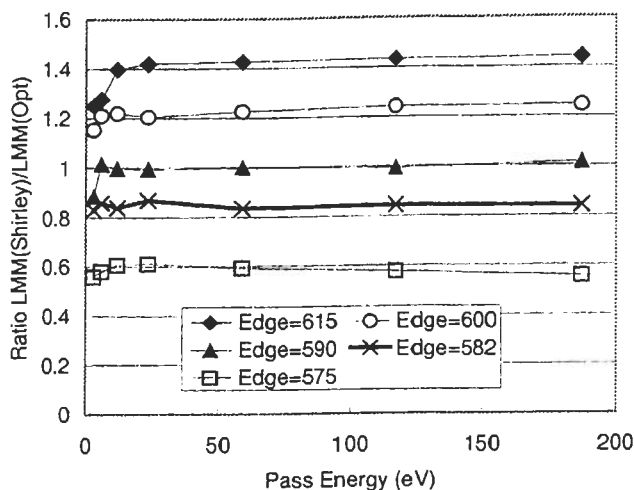


Fig.4 Ratio peak areas of Cu LMM by two methods. Higher BE end point is changed.

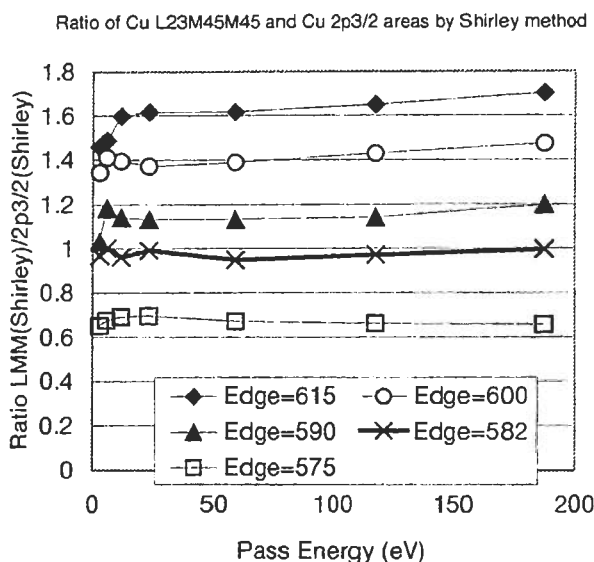


Fig.5 Ratio of Cu LMM and 2p3/2 by Shirley method.

constant irrespective of the analyzer resolution. For Ag 3d, there is little difference between the two methods. The Shirley background gives 97 % of the area by the optimized background, which is expected because both sides of the peak are flat. For Cu LMM, the ratio is about 84 %.

Fig.4 shows the ratio of areas calculated by the optimized loss function and that by the

Shirley method of Cu LMM, versus pass energy, while varying the position of the high BE end point for the Shirley method. The low BE end point is at the right edge of the spectrum. The point 582 eV is determined by the optimized loss function. The slight shift with E_{pass} is neglected as explained above. The ratio is constant only for the case of 582 eV. The change in the ratio in other cases is ascribed to the change of the inelastically scattered portion in the given integration range. It is noted that the point at 615 eV is not an appropriate point although there is a local minimum which seems suitable.

In Fig.1, the relation between Cu LMM and Cu 2p_{3/2} is given. In Fig.3 the relation of the two methods for the same end points is shown. One can thus plot Cu 2p_{3/2} (Shirley) intensity in place of Cu LMM (optimized) intensity similarly to Fig.4. Fig.5 shows the area ratios of Cu LMM and Cu 2p_{3/2} both by Shirley methods. The same tendency is shown although the deviation at 575 eV is not so clear, as in Fig.4. It is important to note that this is the relation of areas both calculated by the Shirley method.

The above discussion suggests how to determine consistent end points of a broad peak in relation to a narrow and well-defined one using *only* the Shirley method. The procedure is as follows. Choose one narrow peak whose area is easily estimated. Measure the spectra of the two (narrow and broad) peaks with different analyzer resolutions. Find the transmission factors for these peaks with the applied resolutions. For each spectrum, calculate the area by the Shirley method. For a broad peak whose end points are not known, calculate the area repeatedly by changing the positions of the end points for each resolution. (In many cases it will be sufficient to choose the lower BE side point far from the peak.) The end points by which the ratio after transmission correction becomes constant for all analyzer resolutions is the recommended choice. Though the ratio may not be different from the value determined by the loss function due to the systematic difference shown in

Fig.3, the ratio will give a correct tendency for a spectrum at any resolution.

Although the background optimization algorithm is capable of determining the detail of the realistic loss function, it is still only applicable to uniform materials. In contrast, the method proposed here has no such restrictions and therefore is expected to be more suitable for practical quantitative analyses.

Acknowledgements

The author is grateful to Dr. A. Tanaka (ULVAC-PHI), Dr. S. Ichimura, and Dr. A. Kurokawa for their stimulating discussion. Also, the continuous encouragement by Dr. K. Arai and Dr. H. Okushi is gratefully acknowledged.

References

- [1] M. Jo, Surf. Sci. **320**, 191 (1994)
- [2] M. Jo and A. Tanaka, Appl. Surf. Sci., **100/101**, 11 (1995).
- [3] M. Jo, J. Surf. Anal., **4**, 35 (1998).
- [4] K. Berresheim, M. Mattern-Klosson and M. Wilmers, Fresenius J. Anal. Chem., **341(1/2)**, 121 (1991).
- [5] S. Tanuma, C. J. Powell and D. R. Penn, Surf. Interface Anal. **11**, 577 (1988).