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**ENERGY LOSS FUNCTION AND SOURCE FUNCTION FOR Au 4f PHOTOELECTRONS
DERIVED BY MONTE CARLO ANALYSIS OF REFLECTION ELECTRON ENERGY LOSS
SPECTROSCOPY (REELS) AND X-RAY PHOTOELECTRON SPECTROSCOPY (XPS) SPECTRA**

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Abstract

We have derived the energy loss function of Au for 1 keV electrons by Monte Carlo analysis of the reflection electron energy loss spectroscopy (REELS) spectra. This energy loss function was significantly different from the optical loss function widely used and has revealed that the surface excitation affects the energy loss spectrum of keV electrons.

X-ray photoelectron spectroscopy (XPS) background subtraction has been recently developed by using the energy loss function derived from the transmission electron energy loss spectroscopy (TEELS). We have demonstrated that the energy loss function derived from REELS has enabled a more accurate Au 4f XPS spectrum to be obtained after subtraction of the inelastic background.

Key Words: Energy loss function, source function, X-ray photoelectron, reflection electron energy loss spectroscopy.

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Introduction

Background subtraction methods in X-ray photoelectron spectroscopy (XPS) have been widely used for quantitative surface analysis [13, 14, 17]. Tougaard's method [17] is especially worthy of note because this method takes account of the inelastic scattering processes of photoelectrons transversing a solid. It is possible with this method to obtain background-subtracted XPS spectra, called the XPS source function. The XPS source function derived by Tougaard's method depends on the accuracy of the inelastic scattering cross-section. The inelastic scattering cross-section has usually been obtained from the energy loss function data measured optically; this function is called the optical loss function.

In our previous papers [20, 21], Monte Carlo analysis revealed that the optical loss function of Au was not appropriate for reproducing the XPS background spectrum of Au 4f photoelectrons. Hence, we proposed to derive the energy loss function of Au from experimental Au 4f XPS spectra by Monte Carlo analysis [20]. We assumed that the Au 4f XPS source function was represented by a symmetrical Lorentzian curve because the expected Doniach-Sunjić asymmetry [3] was small. This energy loss function led us to more a comprehensive understanding of surface excitations produced by keV electrons emerging from a solid surface. However, it is well known that strong satellites occur in the core spectra of the chemical compounds of transition metal and rare earth metal [4, 8, 12], and this leads to the source function having an asymmetric shape associated with tailing due to shake-up effects. The energy loss function derived in the previous work, therefore, is still to be examined for further improvement.

The energy loss functions for some materials [5, 18, 22, 23] have been determined from reflection electron energy loss spectroscopy (REELS) spectra; here, the source function is free from the ambiguity caused by shake-up. To obtain the energy loss function, removal of plural inelastic scattering spectra is essential and has usually been done with the Landau formula [7]. The Landau formula basically disregards the contribution of elastic scattering events. A modified Landau formula

[17] was applied to REELS and XPS spectra in which the contribution of the elastic scattering was approximately represented by a correction factor. We also confirmed the reliability of this approximation in XPS spectra by Monte Carlo simulation [20]. However, we recognized that the contribution of elastic scattering could not be completely described by a simple correction factor in the REELS case [21] because of the significant contribution of the angular distribution of the elastic back-scattering cross-section for Au. Therefore, we have newly determined the energy loss function through the accurate evaluation of the elastic scattering contribution by Monte Carlo analysis.

We applied this energy loss function to obtain an XPS source function which may include shake-up spectra. This new energy loss function has led to the more distinct conclusion that surface excitations significantly contribute to the energy loss spectra of photoelectrons and reflected electrons.

REELS Experiment

In the present REELS experiment, 1 keV electrons impinged on the sample surface at an incident angle of 45°, and the electron spectra were observed by a 160° concentric spherical energy analyzer in the constant pass energy mode with an energy resolution 1.3 eV. The angle between the axis of the energy analyzer and the incident electron beam was set at 90°. The detector was a Channeltron operated in the pulse counting mode; we confirmed that signal electrons in the no-loss peak did not saturate the pulse counting system. Although the no-loss peak is often overlooked in most EELS measurements, we measured the no-loss peak profile as well as the energy loss spectra in order to evaluate the energy loss function. Details of the apparatus are shown in our previous paper [21].

The sample was polycrystalline Au evaporated onto a polished Au substrate. The experimental REELS spectrum is shown in Figure 1 in which a correction has been made for the transfer function. The energy loss spectrum is magnified by ten times relative to the no-loss peak, revealing characteristic energy loss peaks at 3.1, 5.9, 16.3, 24.1 and 32.5 eV. The origin of the energy loss peaks at 5.9 eV and 24.1 eV is presumed to be interband transition [6], and the energy loss peak at 3.1 eV is identified as the surface plasmon [15]. As each energy loss peak is not sharp enough to be separable from one another, it is difficult to evaluate plural inelastic scattering processes. Hence, we have used Monte Carlo simulations for deriving the single scattering spectra from the experimental REELS spectrum containing plural inelastic scattering spectra.

Monte Carlo Simulation of REELS Spectrum

Signal electrons in the REELS spectra undergo not only plural inelastic scattering events but also plural elastic scattering events. Monte Carlo simulation is a powerful tool which enables both the plural inelastic and elastic scattering events to be described accurately. The present simulation describes these scattering processes by individual elastic and inelastic cross-sections as follows. The Mott cross-section for elastic scattering is derived by the partial wave expansion method. The applicability of the Mott cross section to Au has been confirmed for sub-keV energy electrons through comparisons with experiments [2, 10].

XPS background analysis focuses attention on the region of energy loss less than 100 eV, where the inelastic scattering cross-section in a bulk solid is described by the dielectric response theory as follows,

$$\frac{d^2\lambda_{in}^{-1}}{d(h\omega)dq} = \frac{1}{\pi a E_p} \frac{1}{q} \text{Im}\left[\frac{-1}{\epsilon(\omega, q)}\right], \quad (1)$$

where $\epsilon(\omega, q)$ is the dielectric function with $h\omega$ the energy loss and q the momentum transfer. λ_{in} is the inelastic mean free path (IMFP), a the Bohr radius, and E_p the kinetic energy of the primary electron. $\text{Im}[-1/\epsilon(\omega, q)]$ is the energy loss function which describes the inelastic scattering cross section. The q -dependence of the energy loss function is approximated by the result for plasmon dispersion. Equation (1) is then rewritten as follows,

$$\frac{d^2\lambda_{in}^{-1}}{d(h\omega)dq} = \frac{1}{\pi a E_p} \frac{1}{q} \frac{\omega_o}{\omega} \text{Im}\left[\frac{-1}{\epsilon(\omega_o)}\right] \quad (2)$$

$$\omega_o = \omega - \frac{hq^2}{2m}$$

For $q = 0$, $\text{Im}[-1/\epsilon(\omega_o)]$ is the energy loss function usually measured optically and is called the optical loss function. Figure 2 shows the optical loss function of Au [9]. We performed Monte Carlo simulations of the REELS spectrum using this optical loss function.

The result of the simulation is shown in Figure 3. This is the so-called response function provided that the primary electron beam is monoenergetic. The energy division in the present simulation is 0.2 eV, small enough to describe the no-loss peaks of reflected electrons and photoelectrons. The energy loss spectrum is magnified by one hundred times relative to the no-loss monoenergetic peak. Note that the energy loss spectrum in Figure 3 maintains the fine structure in the optical loss function (Figure 2) for energy losses less than 40

Energy loss and source functions for Au 4f Photoelectrons

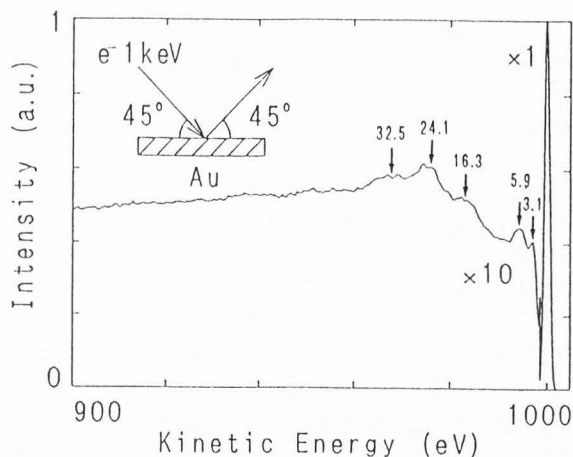


Figure 1. REELS spectrum of Au for 1 keV electrons impinging on Au sample at an incident angle of 45° and with a take-off angle of 45° . The energy loss spectrum is magnified by ten times relative to the no-loss peak.

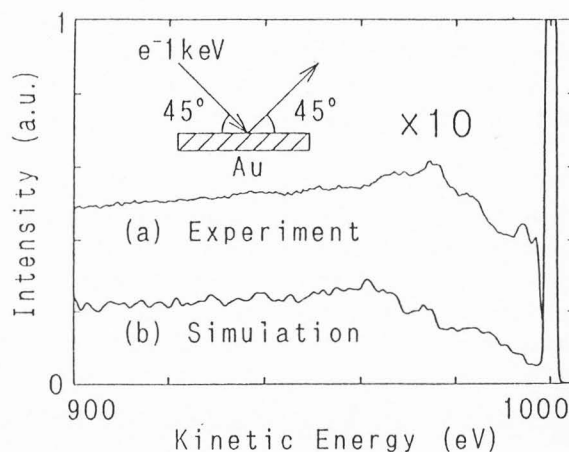


Figure 4. REELS spectra of Au obtained by the experiment (curve a) and Monte Carlo simulation (curve b). The energy loss spectra are magnified by ten times relative to the no-loss peaks.

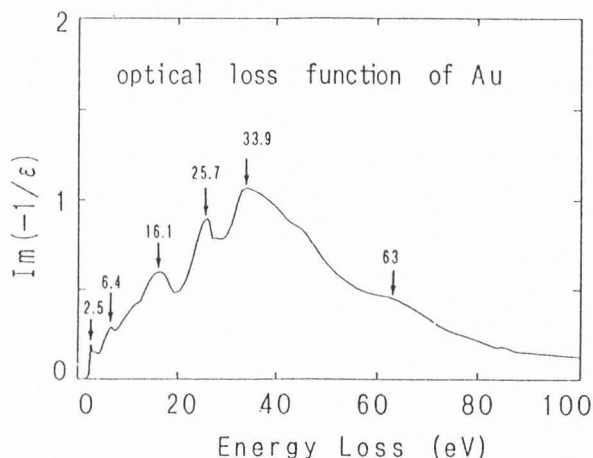


Figure 2. Energy loss function of Au obtained by optical measurements [10].

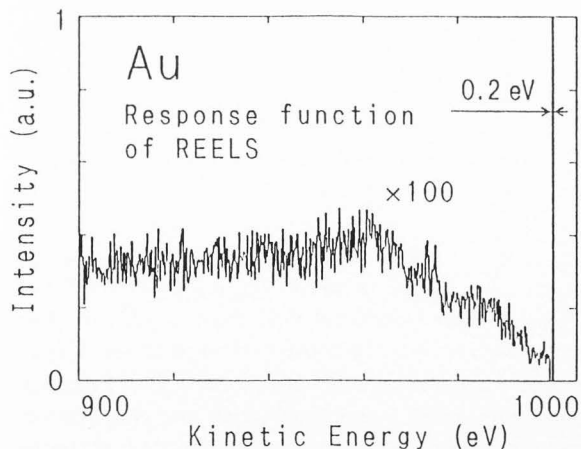


Figure 3. Response function of Au obtained by Monte Carlo simulation using the optical loss function shown in Figure 2.

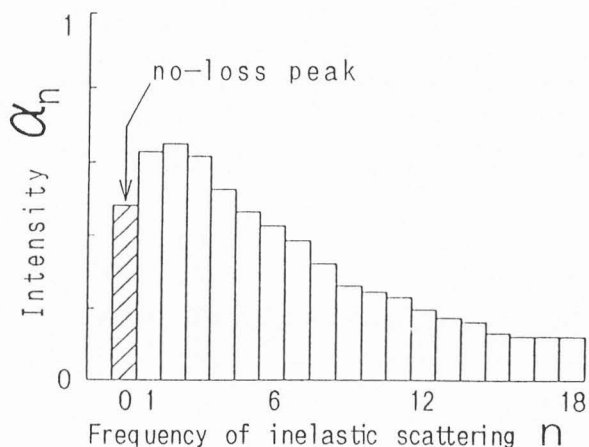


Figure 5. Frequency in occurrence of inelastic scattering in the Monte Carlo simulation of REELS spectrum of Au under the conditions shown in Figure 4.

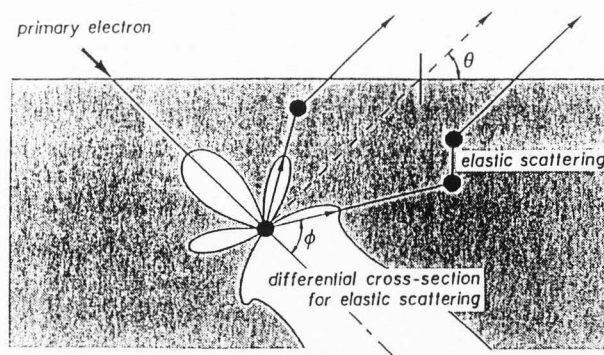


Figure 6. Monte Carlo modelling of trajectories of signal electrons contributing to the REELS spectrum for 1 keV electrons impinging on an Au sample at an angle of incidence of 45° and with a take-off angle of 45° .

eV. For larger energy losses, the fine structure in Figure 2 is smeared out by effects of plural inelastic scattering. A convolution between the response function shown in Figure 3 and the REELS source function of full width half maximum (FWHM) 1.3 eV (a Gaussian distribution describing the primary electron beam energy) is shown in Figure 4 (curve b) and compared with the experimental spectrum (curve a). The energy loss spectra are magnified by ten times relative to the no-loss peaks, and both spectra are depicted so that the no-loss peak heights coincide. The intensity of the simulated REELS spectrum is only about one-half of the experimental spectrum over the whole energy loss region except the no-loss peaks. Furthermore, there are significant differences in the shapes in low energy-loss region (less than 40 eV). Similar discrepancies between experimental and the simulated spectra have been found for other take-off angles.

As elastic scattering is described by the Monte Carlo simulation with sufficiently high accuracy [2], we believe that the discrepancy between the simulated and experimental spectra should be attributed to the optical loss function used for describing the inelastic scattering cross section. In this work, therefore, we attempted to find a more appropriate energy loss function which reproduces the experimental REELS spectrum.

Energy Loss Function Derived by Monte Carlo Analysis of the REELS Spectrum

In general, the EELS spectrum $J(\Delta E)$ including the no-loss peaks are represented by the convolution of the source function $F(\Delta E)$ and the response function shown as follows,

$$\tilde{J}(s) = \tilde{F}(s) \cdot \sum_{n=0}^{\infty} [\alpha_n \lambda_{in} \tilde{K}(s)]^n, \quad (3)$$

where a tilde means Fourier transformation and s is a Fourier variable originating from the energy loss ΔE . $K(\Delta E)$ is the differential inelastic mean free path (DIMFP) derived from equation (2) as follows,

$$\begin{aligned} \lambda_{in} K(\Delta E) &= \lambda_{in} \frac{d\lambda_{in}^{-1}}{d(\Delta E)} \\ &= \frac{\lambda_{in}}{2\pi a E_p \Delta E} \int_0^{\infty} \frac{\hbar\omega}{\Delta E - \hbar\omega} \text{Im} \left[\frac{-1}{\epsilon(\hbar\omega)} \right] d(\hbar\omega) \quad (4) \\ &\times \Theta \left[\frac{\hbar^2}{2m} (2kq - q^2) - \Delta E \right] \end{aligned}$$

where $\Theta(x)$ is the Heaviside step function required by energy and momentum conservation. In equation (3), α_n

is the coefficient for n -fold inelastic scattering events. The observed spectrum $J(s)$ and the source function $F(s)$ are given by experiment. If α_n is given, one can determine the DIMFP $K(\Delta E)$ and the successive energy loss function $\text{Im}(-1/\epsilon)$.

Figure 5 shows the coefficients α_n derived by Monte Carlo simulation of a REELS spectrum for a take-off angle of 45° . If elastic scattering was negligible, the histogram distribution of Figure 5 would be expected to be flat (i.e., all $\alpha_n = \text{constant}$). The position of maximum intensities is located not at the elastic peak but for two-fold inelastic scattering. This phenomenon is schematically explained by Figure 6 which illustrates the trajectories of those electrons contributing to the REELS spectrum. Almost all electrons for the Au REELS spectrum undergo single large-angle elastic scattering plus plural small-angle elastic scattering. This scheme was confirmed by the measurement of the angular distribution of elastically backscattered electrons from Au [2]. As the take-off angle of 45° coincides with the valley of the differential cross-section, most of the electrons detected at the take-off angle 45° are scattered just like the solid line in Figure 6 and undergo plural small-angle elastic scattering event. These plural elastic-scattering events increase the electron path length and the frequency of inelastic scattering events, as reported in detail in the previous paper [21].

The energy loss function is obtained according to the procedure of five steps as follows: first, we obtained the response function shown in Figure 7 by the deconvolution procedure $J(s)/F(s)$. Second, the coefficients α_n shown in Figure 5 are calculated by Monte Carlo simulation. Third, we obtained $\lambda_{in} \cdot K(\Delta E)$ according to equation (3), which satisfies the following relation,

$$\int_0^{\infty} \lambda_{in} K(\Delta) d(\Delta E) = 1. \quad (5)$$

This $\lambda_{in} \cdot K(\Delta E)$ is referred to as a reduced DIMFP hereafter. Then we derived the individual n -fold scattering spectrum, as labeled in Figure 7, from the response function once the reduced DIMFP was obtained. One can see the significant contribution of plural inelastic scattering processes ($n \geq 2$) to the REELS spectrum.

Curve a in Figure 8 shows the reduced DIMFP of Au, which corresponds to the single scattering loss spectrum with $n = 1$ in Figure 7. Tougaard and Kraaer have obtained the reduced DIMFP (curve b in Figure 8) of Au from a REELS spectrum by an analytical deconvolution procedure [18]. Our reduced DIMFP is similar to their result, particularly the energy loss peaks at 3 eV and 6 eV which are remarkably intense. Their reduced DIMFP, however, shows a more rapid decrease for

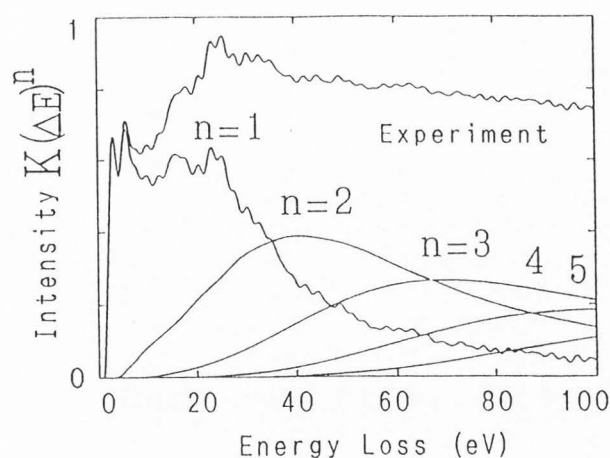


Figure 7. Components of the response function of Au derived from Monte Carlo analysis of the experimental REELS spectrum in Figure 1. n denotes the frequency of occurrence of inelastic scattering.

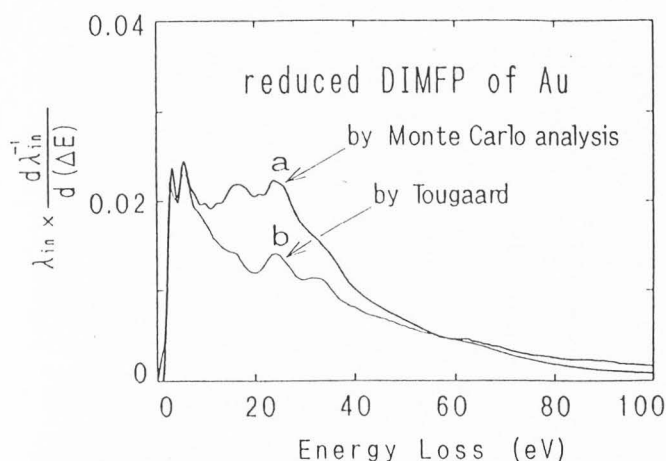


Figure 8. Reduced DIMFPs of Au for 1 kV electrons derived from REELS spectrum by Monte Carlo analysis (curve a) and by Tougaard's analytical methods (curve b) [11].

larger energy losses than ours. This difference may come from differences in the evaluation of plural inelastic scattering, i.e., the coefficient α_n . The IMFP must normally be known to obtain the DIMFP, and IMFP values have often been theoretically obtained from energy loss function data [16]. In our work, we have determined a value of the IMFP by comparison with experimental data [1].

Figure 9 shows the energy loss function obtained by an iterative procedure based on equation (4). Characteristic energy loss peaks are clearly visible at 3.1, 5.6, 16.1, 24.1, 32.1 and 61 eV, as indicated by arrows in Figure 9. We can see a significant difference between

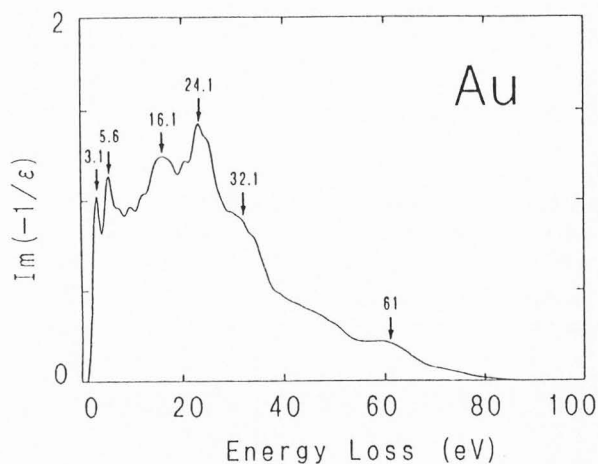


Figure 9. Energy loss function of Au derived from Figure 8. Arrows indicate characteristic energy loss peaks.

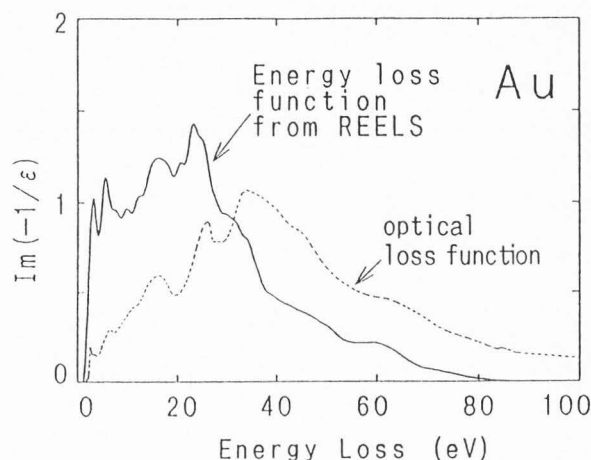


Figure 10. Comparison between the energy loss function derived Monte Carlo analysis (Figure 9) and conventional optical loss function, $\text{Im}(-1/\epsilon)$ (Figure 2).

the present result and the conventional optical loss function in Figure 10. Though the peak positions roughly coincide with each other, the intensity of the new energy loss function is considerably enhanced in the low energy loss region compared to the optical loss function. The optical loss function essentially reflects bulk excitations, but keV electrons transversing the vicinity of a solid surface undergo surface excitations as well. This result is well understood in free-electron metals like aluminum in which the surface plasmon is clearly visible and is well separated from the bulk plasmon.

In dielectric response theory, the surface plasmon is described by $\text{Im}(-1/\epsilon+1)$. $\text{Im}(-1/\epsilon+1)$ is also deduced from the optical constants and is called the surface loss function. Hereafter, we will refer to $\text{Im}(-1/\epsilon)$ as the optical bulk loss function and $\text{Im}(-1/\epsilon+1)$ as the optical

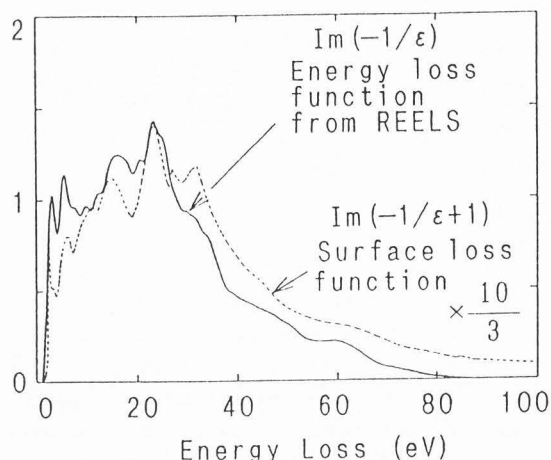


Figure 11. Comparison of the energy loss function (Figure 9) and the optical surface loss function derived from $\text{Im}(-1/\epsilon+1)$.

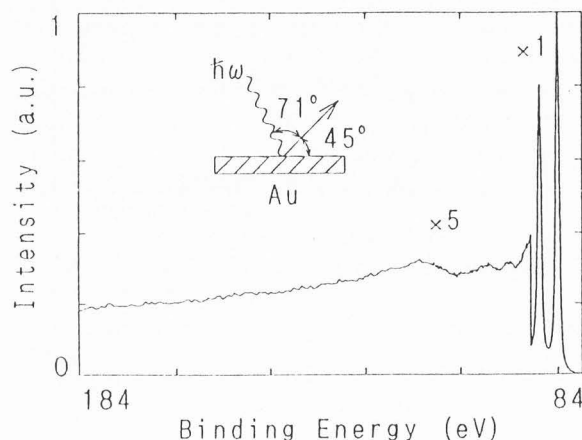


Figure 12. Experimental Au 4f XPS spectrum obtained with primary Al K_{α} X-rays at angle of incidence 71° with take-off angle 45° . The background spectrum is magnified by five times relative to $4f_{7/2}$ peak.

surface loss function for convenience. Figure 11 shows the energy loss function derived from the REELS spectrum and the optical surface loss function magnified by $10/3$ for the convenience of comparison. This optical surface loss function has turned out to be very close to the energy loss function derived from REELS; in particular, peak positions of the maximum intensity coincide with each other. This result again confirms what we have pointed out in the previous paper [20], that the surface excitation significantly contributes to the energy loss spectra of keV electrons.

It is well known that the optical loss function coincides well with the energy loss function derived by transmission electron energy loss spectroscopy (TEELS)

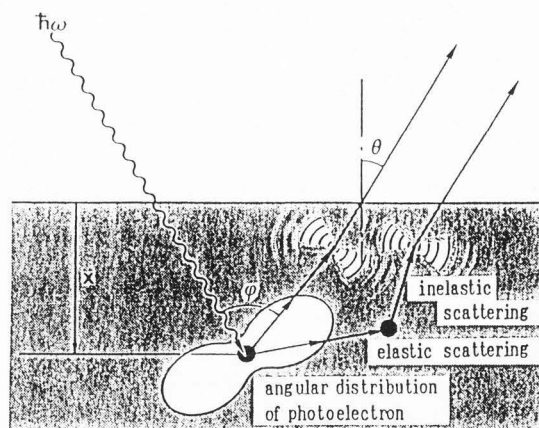


Figure 13. Schematic diagram of Monte Carlo simulation model of photoelectron trajectories with both inelastic and elastic scatterings included.

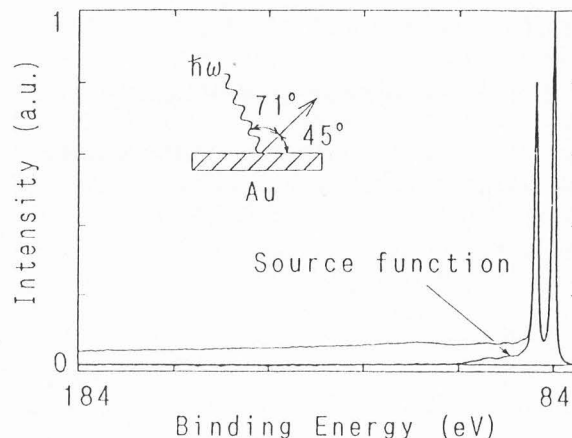


Figure 14. Au 4f XPS source function derived from the experimental spectrum (Figure 1) by Monte Carlo analysis based on use of the energy loss function (Figure 9).

for electrons of energy greater than about 10 keV. It should be noted that, even in TEELS analysis, Wehenkel [19] had to remove a slight contribution due to the surface excitations in order to obtain the energy loss function originating only from bulk excitations. Surface excitations are expected to be more significant in REELS spectra than in TEELS spectra on account of changes in the ratio of bulk to surface excitation with incident electron energy [11].

Application of the Energy Loss Function Derived from the REELS Spectrum to XPS Background Subtraction

In order to obtain the XPS source function, we have

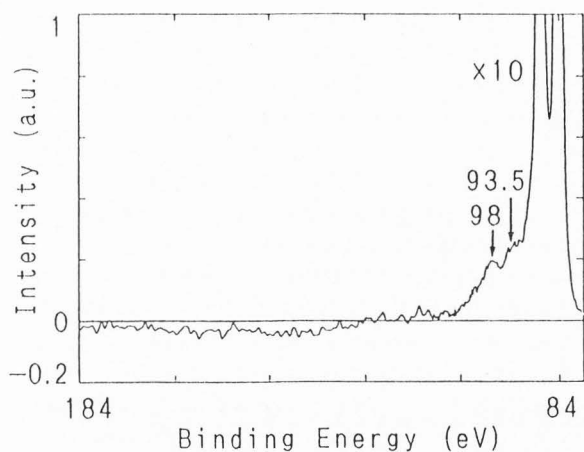


Figure 15. Tails of the Au 4f XPS source function (magnified by five times relative to the $4f_{7/2}$ peak). Two satellite peaks are observed at binding energies of 93.5 eV and 98 eV, as indicated by arrows.

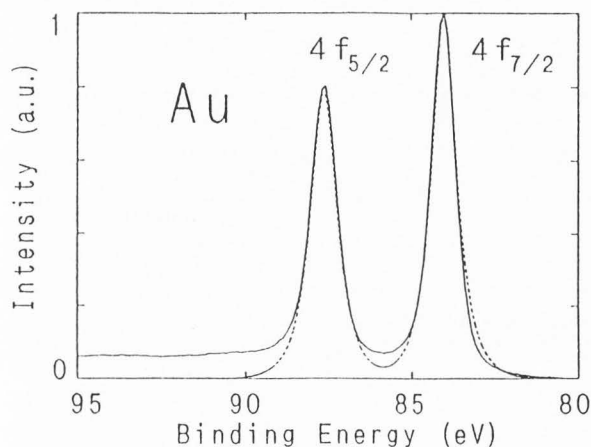


Figure 16. Comparison between Au 4f XPS source function (solid line) derived by Monte Carlo analysis (see Figure 15) and the fitted Lorentzian-Gaussian mixed function (dashed line).

applied the energy loss function derived in the preceding section to the XPS spectrum, of which signal electrons have nearly the same kinetic energy. Figure 12 shows the experimental Au 4f XPS spectrum. The energy loss spectrum is magnified by five times relative to the $4f_{7/2}$ peak. The experimental condition is depicted in the inset, K_{α} X-rays from an Al anode (1486.6 eV) impinging on the Au sample. The take-off angle of photoelectrons was 45° relative to the sample surface plane, which coincides with the REELS experimental condition. The angle between the incident X-rays and the axis of the energy analyzer was fixed at 71° . The solid angle of an input lens of the energy analyzer was 0.21 str. Details of the experimental apparatus are described

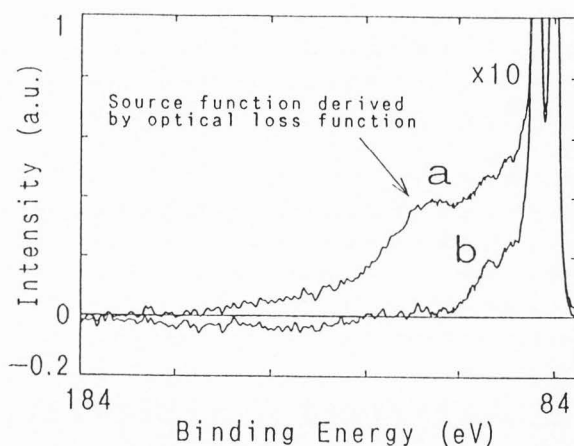


Figure 17. Au 4f XPS source functions derived by Monte Carlo analysis using the optical loss function (curve a) and by using the energy loss function in Figure 9 (curve b). The background spectra are magnified ten times relative to $4f_{7/2}$ peak.

elsewhere [20].

We have reproduced the Au 4f XPS spectrum by Monte Carlo simulation using the energy loss function in Figure 9 illustrated by the simulation model depicted in Figure 13. Photoelectrons are generated in the sample with depth up to $5\lambda_{in} \sim 90$ Å from the surface, and the initial directions of the photoelectrons are given by the photoionization differential cross-section. The generated photoelectrons then transverse a solid and undergo plural elastic and inelastic scattering processes (as do the reflected electrons).

We have, first, calculated the response function for the Au 4f photoelectrons by Monte Carlo simulation and then derived the XPS source function by the deconvolution procedure in which an experimental spectrum was divided by a response function in Fourier space. Figure 14 shows the measured XPS spectrum and the XPS source function. This XPS source function is shown magnified by ten times relative to the $4f_{7/2}$ peak. It should be noted that the background for the spectrum in Figure 15 is essentially zero for losses more than about 20 eV from the $4f_{7/2}$ peak. We can see two satellites at binding energies of 93.5 eV and 98 eV. The peak at binding energy 93.5 eV coincides with an energy loss peak of 5.9 eV originating from the $4f_{7/2}$ peak and is presumed to be due to an intrinsic interband transition. The peak at binding energy 98 eV, however, does not coincide with any loss peak in the REELS spectrum reported so far; this binding energy is also different from the expected position of the 5s peak (108 eV). This energy loss peak is observed only in the XPS spectrum and remain to be identified.

Once the XPS source function is known, we can

estimate the contribution of many-body effects such as shake-up to the XPS source function. The solid line in Figure 16 shows the XPS source function and the dashed line represents a Lorentzian-Gaussian mixed function fitted to the XPS source function. This comparison suggests that shake-up fraction of the 4f spectrum occupies about 20% of the Au 4f XPS spectral intensity. Disregard of the shakeup spectrum in previous work [20] is thus, strictly speaking, not a good approximation for accurate XPS background analysis.

Note that the derivation of the line shape of the XPS source function and, hence, the shake-up spectrum depends entirely upon the energy loss function used. As a demonstration to see how sensitive the source function is to the loss function, we used the conventional optical loss function of Au for the XPS deconvolution procedure. Figure 17 shows the XPS source function derived by Monte Carlo simulation using the optical loss function shown in Figure 2. The tail of the XPS source function reaches 50 eV energy loss. This type of tail is found in the XPS source function obtained by Tougaard's analytical method with the energy loss function derived from REELS spectrum. It is obvious that the optical loss function has led to overestimation of the peak area by ~55% greater than that of the energy loss function derived from the REELS spectrum. This over-estimation results in another over-estimation of the shake-up spectrum; the contribution of the shake-up spectrum to the 4f XPS source function is estimated to be ~20% from our new energy loss function newly obtained and to be ~50% from the optical loss function. The energy loss function is, therefore, the key factor for quantitative chemical composition analysis by XPS, in which accuracy depends very much on the evaluation of the peak area of the XPS source function. Furthermore, the energy loss function is crucial to clarify many-electrons effect in XPS.

Here, we propose the construction of a data base of the energy loss functions for materials by the present Monte Carlo analysis of REELS spectra and call attention to the possibility that this new type of the energy loss function for keV electrons will lead to more comprehensive understanding of many body effects, e.g., shake-up phenomena.

Conclusions

The optical loss function has been widely used to describe the energy loss process of keV electrons in XPS and AES. However, we have pointed out by Monte Carlo simulation that the optical loss function of Au reproduces only half of the background intensity of the experimental REELS spectrum. The present work has indicated that the Monte Carlo analysis leads to a new

energy loss function for Au from the REELS spectrum. This new energy loss function is significantly different from the conventional optical loss function and very close to the surface loss function derived from the optical constants. This result suggests that surface excitation plays an important role (as does the bulk excitation) for REELS and XPS spectra in which ~1 keV electrons are used as signals.

The new energy loss function enabled us to derive the original Au 4f XPS spectrum by subtracting the background, i.e., the XPS source function. This approach has revealed the existence of characteristic satellite peaks that have not been reported so far and led to the conclusion that the contribution of the shake-up spectrum to the intensity of the total XPS source function is ~20%. The peak area of the XPS source function depends entirely on the profile of the energy loss function used. The use of the conventional optical loss function lead to significant overestimation of the peak area of Au 4f XPS spectrum by about 55% compared with the result obtained by the use of the newly derived energy loss function.

References

- [1] Ding ZJ, Shimizu R (1989) Inelastic collisions of keV electrons in solids. *Surf. Sci.* **222**: 313-331.
- [2] Ding ZJ, Yoshikawa H, Shimizu R (1990) Angular distribution of elastically reflected electrons from Au. *Phys. Stat. Sol. (b)* **161**: 257-269.
- [3] Doniach S, Sunjic M (1970) Many-electron singularity in X-ray photoemission and X-ray line spectra from metal. *J. Phys. C3*: 285-291.
- [4] Fadley CS (1978) Basic concepts of X-ray photoelectron spectroscopy. In: *Electron Spectroscopy: Theory, Techniques and Applications*, Vol. 2. Brundle CR, Baker AD (eds.). Academic Press, New York, 103-131.
- [5] Ingram JC, Nebesny KW, Pemberton JE (1990) Optical properties of selected first-row transition metals determined by reflection electron energy loss spectroscopy. *Applied Surf. Sci.* **45**: 247-256.
- [6] Ingram JC, Nebesny KW, Pemberton JE (1990) Optical constants of the noble metals determined by reflection electron energy loss spectroscopy *Applied Surf. Sci.* **44**: 293-300.
- [7] Landau L (1944) On the energy loss of fast Particles by ionization. *J. Phys. (Moscow)* **8**: 201-205.
- [8] Novakov T (1971) X-ray photoelectron spectroscopy of solids: Evidence of band structure. *Phys. Rev. B3*, 2693-2698.
- [9] Palik ED (ed.) (1985) *Handbook of Optical Constants of Solids*. Academic Press, New York, 286-295.
- [10] Reichert E (1963) Die Winkelverteilung im

Bereich 30 bis 155 von elastisch an Golddampf gestreuten Elektronen mit Energien zwischen 150 und 1900 eV (The angular distribution in the region of 30°-155° of electrons elastically scattered from a gold vapor with the energy between 150 and 1900 eV). *Z. Physik* **173**: 392-401.

[11] Ritchie RH (1957) Plasma losses by fast electrons in thin films. *Phys. Rev.* **106**: 874-881.

[12] Rosencwaig A, Wertheim GK, Guggenheim HJ (1971) Origins of satellites on inner-shell photoelectron spectra. *Phys. Rev. Lett.* **27**: 479-481.

[13] Shirley DA (1972) High-resolution X-ray photoemission spectrum of the valence bands of gold. *Phys. Rev.* **B5**: 4709-4714.

[14] Sherwood PMA (1984) Data analysis in X-ray photoelectron spectroscopy. In: *Practical Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy*. Briggs D, Seah MP (eds.) Wiley, New York, 181-214.

[15] Sueoka O, Fujimoto F (1965) Plasma oscillation of electrons in alloy. II. Ag-Au alloy. *J. Phys. Soc. Jpn.* **20**: 569-573.

[16] Tanuma S, Powell CJ, Penn DR (1988) Calculations of electron inelastic mean free paths for 31 materials. *Surf. Interface Anal.* **11**: 577-589.

[17] Tougaard S (1988) Quantitative analysis of the inelastic background in surface electron spectroscopy. *Surf. Interface Anal.* **11**: 453-472.

[18] Tougaard S, Kraaer J (1991) Inelastic-electron-scattering cross sections for Si, Cu, Ag, Au, Ti, Fe, and Pd. *Phys. Rev.* **B43**: 1651-1661.

[19] Wehenkel C (1975) Mise au point d'une nouvelle méthode d'analyse quantitative des spectres de pertes d'énergie d'électrons rapides diffusés dans la direction du faisceau incident: Application à l'étude des métaux nobles (New methods of quantitative analysis of energy loss spectra of fast electrons transversing a solid in the incident direction: Application to the study of noble metals). *J. Physique* **36**: 199-213.

[20] Yoshikawa H, Shimizu R, Ding ZJ (1992) Energy loss function derived by Monte Carlo simulation from the Au 4f XPS spectrum. *Surf. Sci.* **261**: 403-411.

[21] Yoshikawa H, Tsukamoto T, Shimizu R, Crist V (1992) Monte Carlo analysis of XPS and REELS spectra obtained at different take-off angles. *Surf. Interface Anal.* **18**: 757-764.

[22] Yubero F, Tougaard S (1992) Model for quantitative analysis of reflection-electron-energy-loss spectra. *Phys. Rev.* **46**: 2486-2497.

[23] Yubero F, Sanz JM, Elizalde E, Galan L (1991) Reflection electron energy loss spectra of silver: A quantitative analysis. *Surf. Sci.* **251/252**: 296-300.

Discussion with Reviewers

S. Tanuma: You have determined energy loss function from REELS with Monte Carlo method as shown in Figure 9. Could you separate the bulk energy loss function and the surface one from the obtained energy loss function from REELS?

Authors: We believe that it is possible to separate the bulk energy loss function and the surface one from the obtained energy loss function and that separation is important for more comprehensive understanding of energy loss function in the vicinity of a solid surface. However, we have not performed that separation yet.

K. Murata: Is it possible to reproduce the energy loss function from REELS by adding the optical loss function and the surface loss function properly?

Authors: Yes, we would suggest that one can roughly reproduce the energy loss function from REELS spectrum by adding the optical loss function and optical surface loss function. Precisely speaking, however, the energy loss function from REELS spectrum was more enhanced in the low energy loss region than the added optical loss function.

S. Tanuma: Usually, the optical energy loss function can be evaluated on the internal consistency with several sum rules. Could you evaluate the resulting energy loss function directly with sum rules?

Authors: In this paper, we did not apply such sum rules to obtain an energy loss function, since our previous XPS background analysis [20] has revealed that sum rules are inapplicable to the case where the surface excitation is involved in the energy loss function. We should evaluate the energy loss function after the separation of bulk energy loss function from the surface one.

S. Tanuma: Why is the optical energy loss function greater than the obtained energy loss function above 35 eV in Figure 10?

Authors: The curve shape of new energy loss function originated from REELS spectrum, but in this work, its curve intensity was determined so that its IMFP coincided with the IMFP derived from optical energy loss function. Therefore, the new energy loss function increases more than the optical energy loss function for low energy losses and, on the contrary, decreases more for high energy losses.

S. Tougaard: To obtain the simulated spectrum in Figure 4 from the spectrum in Figure 3, it seems that in addition to the convolution of the REELS source function, some data smoothing was also applied. Could you comment on this?

Authors: We did not apply any data smoothing in this case. The convolution between the result of Monte Carlo simulation and REELS source function does appear to smooth out the resultant spectrum.

S. Tougaard: How sensitive are the simulated spectra to the inelastic scattering mean free path, and what value was actually applied? Could part of the deviation between experiment and theory observed in Figure 4 be attributed to the uncertainty in the inelastic mean free path?

Authors: In the REELS case, we have not yet confirmed how the uncertainty in the IMFP affects the derivation between experiment and theory. But in the XPS case [20], we have confirmed that the value of IMFP do not affect its derivation. For example, we changed the IMFP twice as much, but the shape of the XPS background spectrum did not change (of course, the whole intensity of the XPS spectrum decreased).

K. Murata and C.J. Powell: Have you tried to deduce the energy loss function from REELS under other experimental conditions such as take-off angles and energies?

Authors: Yes, we have tried to deduce the energy loss function; we recognized that the energy loss function depends on take-off angle. The low energy loss region was enhanced little. But, especially at glancing angles, we have not attained reproducible data; we want to try this angle-resolved REELS experiment more precisely.

C.J. Powell: The REELS data were obtained for an incident energy of 1000 eV yet the photoelectrons of interest have energies of about 1400 eV. Why is the REELS analysis expected to be appropriate and valid for the XPS data?

Authors: For more precise discussion, we should perform REELS and XPS exactly under the same experimental conditions. This experiment has now been carried on.

C.J. Powell: In the REELS experiment, electrons transverse the interface twice while in XPS they traverse the interface once. Could the authors comment further on this difference and the corresponding two approaches of Yubero and Tougaard [(1992) *Phys. Rev. B* **46**, 2486]?

Authors: We believe that their discussion is very important to clarify the energy loss processes in the REELS case, but their point is not the main reason why the REELS spectrum increased in the low energy loss region. According to their discussion, the REELS spectrum in the low energy loss region is largely enhanced under the condition that incident angle coincides with take-off angle. However, we observed more intensity enhancement under the condition that take-off angle is

apart from incident beam and glancing to sample surface. Therefore, we recognized that this enhancement is mainly due to surface excitation rather than overlap of electron trajectory.

C.J. Powell: Is there a reason why elastic scattering events largely affect the REELS spectrum more than the XPS spectrum?

Authors: By Monte Carlo analysis, we recognized that almost all of the electrons of REELS undergo the elastic backscattering (large scattering angle) once at least, quite often followed by the plural small-angle elastic scatterings. On the contrary, most photoelectrons undergo only plural small-angle elastic scatterings. Therefore, the path length of electrons is affected by elastic scattering more in the REELS case than in the XPS case.

M. Kotera: Can you evaluate the accuracy of the expression of equation (2), especially for its q -dependence at large q , and the influence of large angle inelastic scattering events on the final spectrum?

Authors: We have not evaluated the accuracy of q -dependence in equation (2). In Monte Carlo simulation, we recognized that the REELS spectrum derived from equation (2) with the angular deflection of electrons was the same as the REELS spectrum derived from equation (4) without the angular deflection. Therefore, REELS spectra are hardly affected by the large angle inelastic scattering event.

S. Tanuma: I think the constant noise in the measured XPS spectrum may give a large contribution to the resulting source function. Does the used XPS spectrum have a constant noise caused by the instrument?

Authors: We removed the constant background noise before obtaining the XPS source function. If this background noise depends on photoelectron energy, this significantly affects our conclusion about the resulting XPS source function.