Plasmon Losses in High-Energy X-Ray Photoemission Studied by Quantum Landau Formula∗

Misato Kazama,† Hiroshi Shinotsuka, Yusuke Ohori, and Takashi Fujikawa
Graduate School of Advanced Integration Science, Chiba University, Yayoicho 1-35, Inage, Chiba 263-8522, Japan
(Received 28 December 2011; Accepted 23 June 2012; Published 7 July 2012)

Single plasmon losses associated with Al 2s photoemission have been theoretically studied on the basis of the quantum Landau formula, which describes overall features of x-ray photoelectron spectra. So far only photoelectron propagations from the emitters to the surface have been considered, and elastic scatterings have been completely neglected in studies of plasmon satellite peaks. This work takes all possible paths into account and includes elastic scatterings up to single scattering. The former causes rapid decay of the extrinsic loss intensity as a function of the emitter depth, and the latter emphasizes the photoemission from deep atomic sites.

[DOI: 10.1380/ejssnt.2012.331]

Keywords: X-ray photoelectron spectroscopy; Plasmon; Photoelectron diffraction; quantum Landau formula

I. INTRODUCTION

X-ray photoelectron spectroscopy (XPS) is now widely used for studying properties of materials. Plasmon satellites appear in the binding energy region higher than the main peaks in XPS spectra for metals and some semiconductors, notably Na, Al, Mg, and Si. The plasmon excitation mechanism has been studied since the early 1970s. The energy loss by the plasmon excitation can occur due to sudden creation of core-hole potential (intrinsinc process) or inelastic scattering during the transport of photoelectrons toward the solid surface (extrinsic process) [1]. These two excitation processes cannot be distinguished in principle: They can interfere with each other [2–5]. Numerical calculations are necessary to study the relative importance of these excitation mechanisms. For practical calculations, semi-classical approaches are often employed, where the photoelectron propagations inside the solids are described by classical trajectory [6, 7]. Starting from a first principle many-body theory, Hedin et al. have derived a quantum Landau formula, which describes overall features in core-level photoemission spectra including plasmon satellite peaks and asymmetry of main peaks due to x-ray singularity [5]. In their theory, however, elastic scatterings inside the solids are completely neglected. We have derived a quantum Landau formula, where the elastic scatterings before and after the loss are fully taken into account [8]. This formula is a powerful tool to study the plasmon losses including higher order satellites, though it is not appropriate in low kinetic energy region.

This work reports the single bulk and surface plasmon loss features associated with photoemission from Al 2s level excited by x-ray photons of 320 eV. The calculations have been performed based on our new quantum approach [8]. These calculated results are compared with those by the simple theory derived by Hedin et al [5]. The relative importance of the loss mechanisms and the elastic scattering effect are discussed.

II. THEORY

Starting from a first-principle many-body scattering theory, a quantum Landau formula with full multiple-scattering can be derived [8, 9]. The formula is written for the photoemission process measuring photoelectrons with momentum \( \mathbf{p} \) excited by x-ray photons with energy \( \omega \) as

\[
F^\infty(\mathbf{p}, \omega) = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} dt \exp[i(\omega + E_0 - E_0^\delta - \omega_p)t] \times \exp \left[ \int_{0}^{\infty} \frac{d\epsilon}{\epsilon} \left( e^{-\epsilon t} - 1 \right) \right].
\]

The detailed derivation is given in ref. [8]. The ground state energies with and without core hole are represented by \( E_0 \) and \( E_0^\delta \). The factor \( \langle \Delta | \phi_0 \rangle^2 \) describes the photoemission intensity, whereas the time integration of the exponential factor describes the loss features. The photoelectron wave \( f_p \) decays under the influence of the optical potential, and the photoemission amplitude \( \langle \Delta | \phi_0 \rangle \) can be calculated by multiple-scattering theory in practice [10, 11],

\[
\langle \Delta | \phi_0 \rangle = \sum_{\alpha} \sum_{L \leq L'} Y_{L \leq L'}(p) R_{\alpha L} Y_{L \leq L'}(p) \left[ (1 - X)^{-1} \right]_{L \leq L'}^{\alpha L} M_{L \leq L'},
\]

\[
X_{L \leq L'}^{\alpha L} = t_{\alpha L}(p) G_{L \leq L'}(p R_{\alpha L})(1 - \delta^{\alpha L}).
\]

The matrix \( X \) is labeled by the set of atomic sites \( L \), \( \alpha \), \( \beta \), \( \ldots \), and angular momentum \( L = (l, m) \). The photoelectron emitter site is labeled \( \alpha \). \( R_{\alpha L} \) is the position vector of scatterer \( \alpha \) measured from the emitter \( L \). In eq. (2), \( \Sigma_\alpha \) means the sum over all scatterers. The propagator \( G_{L \leq L'}(p R_{\alpha L}) \) describes electron propagation from the site \( L \) with the angular momentum \( L \) to the site \( \alpha \) with \( L \). The elastic scattering at the atomic site \( \alpha \) is described by the matrix \( t_{\alpha \alpha} \). The full multiple-scattering is taken into account by the inverse matrix

---

*This paper was presented at the 6th International Symposium on Surface Science -Towards Nano, Bio and Green Innovation-, Tower Hall Funahori, Tokyo, Japan, December 11-15, 2011.
†Corresponding author: misato-k@graduate.chiba-u.jp
(1 - X)^{-1} = 1 + X + X^2 + \cdots. The dipole matrix element M_{LLc} weakly depends on the photoelectron energy.

From eq. (1), the expression for the single-loss spectra is given in terms of \( \alpha(\epsilon) \),

\[
I^1(p, \omega) = |(\langle f_p^- | \Delta | \phi_c \rangle)|^2 \epsilon \alpha(\epsilon) = e^{-\int_0^\infty d\epsilon \frac{\alpha(\epsilon)}{\epsilon}}.
\]

The function \( \alpha(\epsilon) \) is a spectral function called “asymmetric function”, which fully includes the intrinsic and the extrinsic losses [8],

\[
\alpha(\epsilon) = \frac{1}{\pi} \int d\epsilon' f_A^\ast (\epsilon') f_A (\epsilon) W (\epsilon, \epsilon'); \epsilon,
\]

where \( W (\epsilon) \) is the screened Coulomb propagator, and \( f_A (r) \) is defined as

\[
f_A (r) = \frac{[\phi_c (r)]^2}{\epsilon} + (2\pi)^{3/2} f_p^- (r) g_0 (r - R_A; \epsilon).
\]

The decay free Green’s function, and \( R_A \) represents position vector of the emitter. The solid occupies the region \( z \leq 0 \). \( \epsilon = \omega + E_0^0 - E_p^0 - \epsilon_p \) is the excitation energy measured from the photoemission threshold. The first and the second terms of \( f_A \) in eq. (5) correspond to the intrinsic and the extrinsic processes, respectively. The spectral features are primarily determined by \( \alpha(\epsilon)/\epsilon \), which can be divided into the intrinsic, extrinsic, and interference parts.

### III. RESULTS AND DISCUSSION

Here we show the calculated results for single plasmon losses associated with Al 2s photoemission. The schematic view of the geometry is shown in Fig. 1. Only the results for normal photoemission from (001) surface are reported here. Incident x-ray is linearly polarized with the tilt angle 10° away from the surface normal, and the photon energy is 320 eV.

For practical calculations, we further approximate the core function and the photoelectron wave in eq. (4) as follows:

\[
|\phi_c (r)|^2 \approx \delta (r - R_A),
\]

\[
f_p^- \approx \phi_p^0 (r) = \frac{1}{(2\pi)^{3/2}} \exp (ip_r \cdot r) \exp (ip_z).
\]

The second approximation in eq. (6) means that we neglect the elastic scatterings for the loss function \( \alpha(\epsilon) \). Note that the elastic scatterings are still taken into account in the calculation of the amplitude \( \langle f_p^- | \Delta | \phi_c \rangle \). \( \tilde{p} \) is complex number to explain the damping in photoelectron propagation along \( z \)-direction inside the solid, whereas the parallel component \( p_r \) is real. Analytical solutions for \( \alpha(\epsilon)/\epsilon \) can be obtained with the aid of above approximations. Bechstedt’s screened Coulomb potential is used to calculate \( \alpha(\epsilon)/\epsilon \) [12]. We take summation over the component of plasmon momentum parallel to the surface \( Q \) in practice, though it is not explicitly shown in eq. (4).

In the theory by Hedin et al., the current density of photon
to electron with single plasmon loss is given as follows [5].

\[ I^1(p, \omega) = \frac{|\langle \hat{p} | \Delta | e \rangle|^2}{\pi} e^{-2z_A \text{Im} \hat{p}} \times \sum_Q \int dz' dz f_A(z) f_A^\dagger(z') \times \text{Im} W(Q, z, z'; \varepsilon - \epsilon_p), \]

\[ f_A(z) = \frac{\delta(z - z_A)}{\varepsilon - \epsilon_p} + \frac{i}{\kappa} e^{i(\varepsilon - \epsilon)(z - z_A)} \theta(z_A - z). \]

The solid occupies the region \( z \geq 0 \) in their approach. The depths of the emitters are represented by \( z_A > 0 \). The photoelectron state is described by time-reversed LEED function \( \hat{p} \), which does not mean full time-reversed LEED function in their paper; \( \hat{p} \) is the same as the damping plane wave \( \phi_0^p \) shown in eq. (6). \( \kappa \) represents the photoelectron momentum before the loss. \( \varepsilon \) is defined as the photoelectron energy without the loss, and \( \varepsilon - \epsilon_p \) corresponds to the energy \(-\epsilon\) in our approach. The first term and the second term of eq. (8) describe the intrinsic loss and the extrinsic loss, respectively. Note that the extrinsic part of eq. (8) has the step function \( \theta(z_A - z) \): The photoelectrons can only travel from the emitters to the surface. In contrast, present approach eliminates the limitation \( \theta(z - z_A) \) and thus all possible paths are taken into account.

We now compare the loss spectral functions \( \beta(\epsilon) \) obtained by the two approaches:

\[ \beta(\epsilon) \equiv \alpha(\epsilon)/\epsilon. \]

Figure 2 shows the calculated results of the spectral function \( \beta(\epsilon) \) using \( f_A \) defined in eqs. (5) and (8). Bulk and surface plasmon energies are 15.8 and 11.2 eV, respectively. “Total” means “(intrinsic)+(extrinsic)+(interference)”. The intrinsic parts are the same for these two approaches. Large difference is found, however, in the extrinsic and the interference terms: These two terms calculated by eq. (5) are totally smaller than those calculated by eq. (8). As the core site becomes deeper, the difference between the two approaches becomes considerable. The results according to eq. (8) shows that when the photoelectron is emitted from deep atomic site, the contribution of the extrinsic plasmon loss becomes much larger than that of the intrinsic one. On the other hand, the results obtained by eq. (5) indicate that the extrinsic loss intensity is comparable with the intrinsic one even though the depths of the emitters become deeper. Only the photoelectron propagations from the emitters toward the surface are allowed in eq. (8); The calculations become simple owing to that treatment, but it leads to the overestimation of the extrinsic loss intensity.

Figure 3 shows the depth profiles of the single-loss spectra calculated by eqs. (5) and (8). The integrated loss intensities are shown for each depth. Calculated results by eq. (8) are shown in Fig. 3 (a), those by eq. (5) without elastic scatterings in Fig. 3 (b), and those by eq. (5) with single elastic scatterings in Fig. 3 (c). Aluminum cylinder model including 260 atoms (40 layers) is used for the calculations shown in Fig. 3 (c). In Fig. 3 (b), the extrinsic loss intensity is comparable with the intrinsic one except near the surface. The intensities of
extrinsic and interference terms rapidly decay compared with those shown in Fig. 3 (a), as a consequence of the tendency shown in Fig. 2. Figure 3 (c) shows considerably different behavior from (b) because of the elastic scatterings. The contribution of the photoemission from deep atomic sites is emphasized because of forward focusing effect: The ejected electrons are strongly scattered in the forward direction. It has been suggested on the basis of multiple-scattering calculations that if several atoms are linearly arranged along the emission direction, the destructive interference actually reduce the intensity [13, 14]. This reduction is called defocusing effect, and has also been investigated experimentally [15]. Shinotsuka et al. have extensively studied the depth distribution function (DDF) using quantum mechanical multiple-scattering calculations, and have demonstrated that inclusion of full multiple-scattering is necessary for the proper evaluation of DDF [11]. The oscillation seen in Fig. 3 (c) can be due to the photoelectron diffraction effects [16].

The Al 2s single-loss spectra obtained by summing up the contributions from all depths are shown in Fig. 4. These spectra have been normalized so that the areas of “Total” are unity. The relative importance of the intrinsic and the extrinsic plasmon losses is distinctly different between Fig. 4 (a) and (b), though the total loss features are rather similar. Figure 4 (c) shows strong bulk plasmon loss peak (15.8 eV) compared with the surface loss (11.2 eV) as a consequence of the enhancement of bulk contribution shown in Fig. 3 (c). The relative importance of the bulk plasmon loss should become lower, however, with the inclusion of full multiple-scattering, because of the defocusing effect: This problem will be discussed elsewhere.

IV. CONCLUDING REMARKS

We have calculated bulk and surface single plasmon losses associated with Al 2s photoemission on the basis of the quantum Landau formula. In this paper two factors which had not been considered are taken into account: photoelectron propagation from the emitter to deeper sites of the solid and single elastic scatterings. The former causes rapid decay of the extrinsic loss intensity as a function of the emitter depth $|z_A|$, and the latter causes overestimation of the contribution from the photoemission from deep atomic sites. This overestimation will be improved by inclusion of full multiple-scattering.

The applicability of the quantum Landau formula has recently been reported by Ohori et al [17]. Their study has shown that the formula can be safely used even in the intermediate energy region (say, several hundred eV) as far as the photoelectron momentum $p$ is nearly parallel to the x-ray polarization vector.

Acknowledgments

M. Kazama is grateful to the financial support of Grant-in-Aid for JSPS Fellows. Y. Ohori is grateful to the financial support of Global COE program.

[1] C. N. Berglund and W. E. Spicer, Phys. Rev. 136, A1030 (1964).
[2] J. E. Inglesfield, J. Phys. C 16, 403 (1983).
[3] W. Bardyszewski and L. Hedin, Physica Scripta 32, 439 (1985).
[4] T. Fujikawa, in: Core-Level Spectroscopy in Condensed Systems, Eds. J. Kanamori and A. Kotani (Springer-Berlin, 1988) p. 213.
[5] L. Hedin, J. Michiels, and J. Inglesfield, Phys. Rev. B 58, 15565 (1998).
[6] S. Tougaard, Surf. Sci. 464, 233 (2000).
[7] W. S. M. Werner, L. Kovér, S. Egri, J. Tóth, and D. Varga, Surf. Sci. 585, 85 (2005).
[8] T. Fujikawa, M. Kazama, and H. Shinotsuka, e-J. Surf. Sci. Nanotech. 6, 263 (2008).
[9] T. Fujikawa and H. Arai, J. Electro. Spect. Relat. Phenom. 123, 19 (2002).
[10] T. Fujikawa, J. Phys. Soc. Jpn. 50, 1321 (1981).
[11] H. Shinotsuka, H. Arai, and T. Fujikawa, Phys. Rev. B 77, 085404 (2008).
[12] F. Bechstedt, R. Enderlein, and D. Reichardt, Phys. Status Solidi B 117, 261 (1983).
[13] S. Y. Tong, H. C. Poon, and D. R. Snider, Phys. Rev. B 32, 2096 (1985).
[14] M.-L. Xu, J. J. Barton, and M. A. Van Hove, Phys. Rev. B 39, 8275 (1989).
[15] S. Valeri, A. di Bona, and F. Borgatti, Surf. Sci. 371, 143 (1997).
[16] M. Kazama, J. Adachi, H. Shinotsuka, M. Yamazaki, Y. Ohori, and T. Fujikawa, Chem. Phys. 373, 261 (2010).
[17] Y. Ohori, H. Shinotsuka, M. Kazama, and T. Fujikawa, e-J. Surf. Sci. Nanotech. 10, 145 (2012).