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Surface and Interface Analysis

Dependence of surface effects in photoelectron and Auger electron angular distribution on glancing incidence of X rays

Z. M. Zhang,[1]* T. Chen,[2] R. Shimizu,[3] H. Yoshikawa,[4] T. Koshikawa[5] and Z. J. Ding[2]

[1] Hefei National Laboratory for Physical Sciences at Microscale and Department of Astronomy and Applied Physics, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China
[2] Hefei National Laboratory for Physical Sciences at Microscale and Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China
[3] Department of Information Science, Osaka Institute of Technology, Osaka 573-0196, Japan
[4] National Institute for Materials Science, BL 15 SPring-8, Mikazuki, Hyogo 679-5198, Japan
[5] Fundamental Electronic Institute, Osaka Electro-Communication University, 18-8 Hatsumachi, Neyagawa, Osaka 572-8530, Japan

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On the basis of a dielectric function model, we considered the dependence of the surface excitation parameter (SEP) on incidence angle of X rays and derived a simple expression for the angular distribution of photoelectrons and Auger electrons including all surface effects. By applying the incidence-angle-dependent SEP, the discrepancy between experimental and theoretical results for the glancing incidence case was improved, and the modified theoretical result agrees with the experimental measurements.

KEYWORDS: surface excitation parameter; angular distribution; glancing incidence; X rays

INTRODUCTION

Surface-sensitive electron spectroscopic techniques, such as Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), elastic peak electron spectroscopy (EPES) and reflection electron energy loss spectroscopy (REELS), have become powerful tools for quantitative surface analyses.[1] Recent studies on these techniques have revealed that surface effects are important for low-energy electrons.[2–16] In our previous study[4–6] and in other works,[7–13] quantitative information on inelastic interaction cross sections of low-energy electrons crossing solid surfaces could be obtained from experimentally measured REELS spectra by deconvolution methods. The effective inelastic cross section extracted from the REELS spectra includes contributions due to bulk excitations as well as surface excitations. Although the effective inelastic cross section is convenient to employ, its accuracy is still not sufficient for quantitative analysis. Furthermore, the effective inelastic cross sections from measured REELS contain information on reflected electrons that cross the surface twice and, therefore, should not be applied directly to the quantitative analysis of XPS and AES for which the signal electrons cross the surface only once.

Chen[14] described the influence of surface excitations by a single parameter $P_s(E, \theta)$, the surface excitation parameter (SEP), which is defined as the average number of surface plasmons excited by electrons with energy E leaving the solid surface at an angle α, as:

$$P_s(E, \alpha) = 1/(a\sqrt{E}\cos\alpha) \tag{1}$$

where a is a constant.

The surface effects result in the spatial variation ofinelastic mean free path (IMFP) whose value strongly affects the emitted electron intensity. Chen[15] has studied the dependence of surface excitations on angular distributions of photoelectron peak intensities by applying the position-dependent IMFP in Monte Carlo (MC) simulation and obtained an X-ray photoelectron spectroscopy formalism including elastic-scattering effects and surface excitations. While the surface effects due to glancing electron emission were considered, the contribution from glancing incidence of X rays was ignored. In fact, the surface effect is strong for glancing incidence of X rays because a higher population of photoelectrons and Auger electrons are generated in surface region in this case.

Moreover, in their recent work,[2,3] Kwei *et al*. pointed out that the conservation of energy and momentum were not completely satisfied because the momentum transfer in cylindrical coordinates has no restriction on its normal component in Chen's model.[14,15] Kwei *et al*.[3] employed spherical coordinates for the momentum integration to ensure energy and momentum conservation and established the dependence of differential inverse inelastic mean free path (DIIMFP) on the crossing angle and the position of electrons with a dielectric function.

*Correspondence to: Z. M. Zhang, Department of Astronomy and Applied Physics, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China. E-mail: zzm@ustc.edu.cn

In this work, we consider the dependence of the surface excitation parameter on the angle of incidence of X rays based on Kwei's result. A close agreement has been obtained between the experiments and calculations after taking the SEP into account in the calculation to describe the surface effects for glancing incidence of X rays.

EXPERIMENTAL

The XPS and AES spectra were measured with double angular photoelectron intelligent analyzers (DAPHNIA). The beam line system was designed for coincidence measurements of photoelectrons and Auger electrons, and/or for an *in situ* depth profile analysis under conditions in which each analyzer is set independently at different take-off angles with respect to the surface plane. The two analyzers are placed on a turntable that is mounted in a large ultra-high vacuum (UHV) chamber (base pressure 6×10^{-8} Pa) of 1400 mm diameter. The take-off angle of each analyzer could be adjusted independently. The rotation axis of a sample manipulator is coincident with the rotation axis of the double analyzer, and the incident synchrotron radiation (SR) axis is in the horizontal plane in which the analyzers move. Both the analyzers of DAPHNIA are of the spherical-capacitor type with acceptance angles of $\pm 5°$ and allow measurement of emitted electrons with kinetic energies less than 4800 eV. X rays from SR are monochromatized by a YB66 [400] crystal or a Si [111] crystal. The precision for the angular measurement of the sample titling and detector was within $\pm 0.05°$.

In the experiment, a silver specimen was used because it has been widely used as a reference sample in surface analysis. The photon flux of the incident monochromatic beam was evaluated by X-ray-induced photoelectron current measured with a Au mesh (1500 lines/inch) that is placed between the monochromator and the sample, which was calibrated with a Si pin-photodiode-type X-ray detector. A detailed experimental description has been given elsewhere.[17–20] An X-ray energy of 1486.7 eV was selected which is the energy of Al Kα.

THEORETICAL

Surface excitation parameter

Kwei[2,3] and Chen[14,15] developed a semi-classical model with a dielectric response function to calculate the depth-dependent DIIMFP, IMFP and SEP for electrons crossing normally through a solid surface. On the basis of the model, they calculated the angular dependence of inelastic cross sections for electrons incident on or escaping from the solid. The dependences of DIIMFP on the crossing angle and the position of electrons were established with a dielectric function. The DIIMFP for an electron traveling from solid to vacuum is expressed as:[3]

$$
\begin{aligned}
\mu^{s\to v}(\alpha, E, \omega, r) &= \frac{2}{\pi v^2}\int_{q_-}^{q_+} dq \frac{1}{q}\mathrm{Im}\left[\frac{-1}{\varepsilon(q,\omega)}\right]\Theta(-r) \\
&- \frac{2\cos\alpha}{\pi^3}\int_{q_-}^{q_+} dq \int_0^{\pi} d\theta \int_0^{2\pi} d\varphi \frac{q\sin^2\theta\cos(q_z r\cos\alpha)\exp(-|r|Q\cos\alpha)}{\varpi^2 + Q^2 v_\perp^2} \\
&\times \mathrm{Im}\left[\frac{-1}{\varepsilon(Q,\omega)}\right]\Theta(-r) \\
&+ \frac{4\cos\alpha}{\pi^3}\int_{q_-}^{q_+} dq \int_0^{\pi} d\theta \int_0^{2\pi} d\varphi \frac{q\sin^2\theta\cos(q_z r\cos\alpha)\exp(-|r|Q\cos\alpha)}{\varpi^2 + Q^2 v_\perp^2} \\
&\times \mathrm{Im}\left[\frac{-1}{1+\varepsilon(Q,\omega)}\right]\Theta(-r) \\
&+ \frac{4\cos\alpha}{\pi^3}\int_{q_-}^{q_+} dq \int_0^{\pi} d\theta \int_0^{2\pi} d\varphi \frac{q\sin^2\theta\cos(q_z r\cos\alpha)}{\varpi^2 + Q^2 v_\perp^2} \\
&\times \left[2\cos\left(\frac{\varpi r}{v}\right) - \exp(-|r|Q\cos\alpha)\right]\mathrm{Im}\left[\frac{-1}{1+\varepsilon(Q,\omega)}\right]\Theta(r)
\end{aligned}
\quad (2)
$$

where $\varpi = \omega - qv\sin\theta\cos\varphi\sin\alpha$, $Q = q\sin\theta$, $q_z = q\cos\theta$, $v_\perp = v\cos\alpha$ and $E = v^2/2$. $\Theta(x)$ is the Heaviside step function. α is the emission angle of an electron measured from the surface normal. According to the energy–momentum conservation relations, the upper and lower limits of q are $q_\pm = \sqrt{2E} \pm \sqrt{2(E-\omega)}$. The terms including $\mathrm{Im}[-1(1+\varepsilon)]$ are due to surface excitations. The inverse IMFP for an emitting electron is obtained by:

$$\mu^{s\to v}(\alpha, E, r) = \int_0^E \mu^{s\to v}(\alpha, E, \omega, r)d\omega \quad (3)$$

However, for oblique incidence of X rays, the probability of the generated photoelectrons at a given depth is inversely proportional to the cosine of incidence angle of X rays. This angular dependence of photoelectron production can induce more intense surface excitation effect for the emitted photoelectrons as compared with the normal incidence case. Then the inverse IMFP involving the incidence angle ϑ of X rays measured from the surface normal may be expressed as:

$$\mu^{s\to v}(\vartheta, \alpha, E, r) = \frac{c}{\cos\vartheta}\int_0^E \mu^{s\to v}(\alpha, E, \omega, r)d\omega \quad (4)$$

For a photoelectron moving outside the solid, the SEP can be obtained by integrating the inverse IMFP over the whole path length of the photoelectron. Thus the SEP for the escaping photoelectrons is given by:

$$P_s^{s\to v}(\vartheta, \alpha, E) = \int_0^\infty \mu^{s\to v}(\vartheta, \alpha, E, r)dr \quad (5)$$

Kwei *et al*.[3] have obtained the SEP, which is independent on the incidence angle of X rays, as:

$$P_s^{s\to v}(\alpha, E) = \frac{a(E)}{\cos^b\alpha} \quad (6)$$

where $a(E)$ is the best-fitted parameter depending on the escaping electron energy. Then, the SEP, considering the incidence angle of X rays, can be written as:

$$P_s^{s\to v}(\vartheta, \alpha, E) = \frac{c}{\cos\vartheta}\frac{a(E)}{\cos^b\alpha} = \frac{d(\alpha, E)}{\cos\vartheta} \quad (7)$$

The probability for an electron leaving the solid surface without any surface excitations can be written as:

$$P_0(\vartheta, \alpha, E) = \exp[-P_s^{s\to v}(\vartheta, \alpha, E)] = \exp\{-d(\alpha, E)/\cos\vartheta\} \quad (8)$$

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Photoelectron intensity

The theoretical photoelectron intensity is expressed as follows:

$$I(\vartheta,\alpha) = \Delta\Omega T D I_0 A(\vartheta)(\lambda/\cos\vartheta) N\{\mathrm{d}\sigma(\vartheta,\alpha)/\mathrm{d}\Omega\} \quad (9)$$

where $\Delta\Omega$ is the solid acceptance angle of the analyzer, T is the analyzer transmission function, D is the detector efficiency, I_0 is the flux of incident X rays, N is the atomic density and λ is the photoelectron IMFP. $A(\vartheta) = A_0/\cos\vartheta$ and A_0 are the analysis area and the area at the normal direction of analysis, respectively. Moreover, $\mathrm{d}\sigma(\vartheta,\alpha)/\mathrm{d}\Omega$ represents the photoionization cross section. In Eqn (9), the contribution from elastic scattering to photoelectron intensity is not considered. Practically, several studies have indicated the fact that this contribution is significant. Therefore, by considering the elastic-scattering effects as well, the photoionization cross section can be written as:

$$\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_{\mathrm{el}} = \frac{\sigma_t \hat{Q}}{4\pi}\left[1 + \frac{\beta_{\mathrm{eff}}}{2}\left(\frac{3}{2}\sin^2\psi - 1\right)\right] \quad (10)$$

where σ_t is the total photoionization cross section. The parameters β_{eff} and $\hat{Q}$ are given approximately by $\beta_{\mathrm{eff}} = a_1\cos^2\alpha + a_2\cos\alpha + a_3$ and $\hat{Q} = b_1\cos^2\alpha + b_2\cos\alpha + b_3$, where the fitted coefficients a_i and b_i have been given by Jablonski.[1] $\psi = \vartheta + \alpha$ is the angle between the X rays and the emission direction of photoelectrons.

On the basis of Jablonski's result, Chen[14] considered the surface excitations and expressed the photoelectron intensity in the form:

$$I(\vartheta,\alpha) = \Delta\Omega T D I_0 A(\vartheta)(\lambda/\cos\vartheta) N\{\mathrm{d}\sigma(\vartheta,\alpha)/\mathrm{d}\Omega\}_{\mathrm{el}} \times \exp\{-P_S(\alpha,E)\} \quad (11)$$

where $P_S(\alpha, E)$ is the SEP given in Eqn (1). By considering the contribution from glancing incidence of X rays and replacing the SEP in Eqn (11) with that given by Eqn (7), the improved Eqn (11) is then given as:

$$I(\vartheta,\alpha) = \Delta\Omega T D I_0 A(\vartheta)(\lambda/\cos\vartheta) N\{\mathrm{d}\sigma(\vartheta,\alpha)/\mathrm{d}\Omega\}_{\mathrm{el}} \times \exp\{-P_s^{\mathrm{s}\to\mathrm{v}}(\vartheta,\alpha,E)\} \quad (12)$$

RESULTS AND DISCUSSION

Figure 1 shows the intensities of the no-loss Ag $3d_{5/2}$ photoelectrons at different incidence angles of X rays. Angular distribution is obtained on the basis of the peak area analysis by a Shirley integral background subtraction. The experimental data, $I(\vartheta)$, are the intensities of Ag 3d photoelectrons per photon flux measured at an incidence angle ϑ, where photon flux was assessed by X-ray-induced photo current measured with a Au mesh. Both the theoretical and experimental results in Fig. 1 are normalized for $\vartheta_0 = 40°$.

Figure 1 clearly shows a large discrepancy between experimental and theoretical angular distributions, (Eqn (11)), for the case of glancing incidence of X rays. The surface excitations become prominent for glancing incidence of X rays. The reason is that the generation probability of signal electrons (photoelectrons or Auger electrons) gets higher near the surface region in the case of glancing incidence of X rays. By taking the constant as $d = 0.027$ for the fitting, a good agreement is then obtained between the experimental data and Eqn (12). Similar results are obtained for signal electrons escaping normally from solid and are presented in Fig. 2.

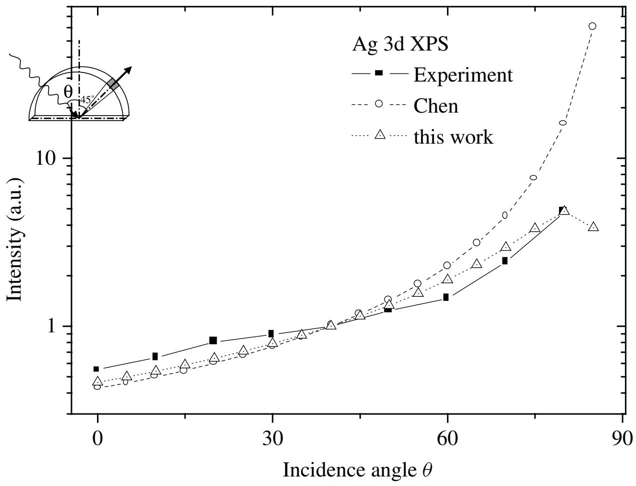

Figure 1. Dependence of the intensity of X-ray-induced photoelectrons on the incidence angle of X rays. The emission angle of photoelectrons is 45° and the intensity is normalized to incidence angle 40°.

Figures 3 and 4 show the variation of the MNN Auger electron intensity with incidence angle of X rays. Similar to the case of XPS, by taking account of surface effects for emission of electrons and for incidence of X rays, the intensity of Auger electrons was expressed in a similar form as:

$$I_A(\vartheta,\alpha) = \Delta\Omega T D I_0 A(\vartheta) P_A(\lambda/\cos\vartheta) N\cos\alpha \times \exp\{-P_s^{\mathrm{s}\to\mathrm{v}}(\vartheta,\alpha,E)\} \quad (13)$$

Using the same constant $d = 0.027$ for the fitting, a reasonably good agreement is also obtained between the

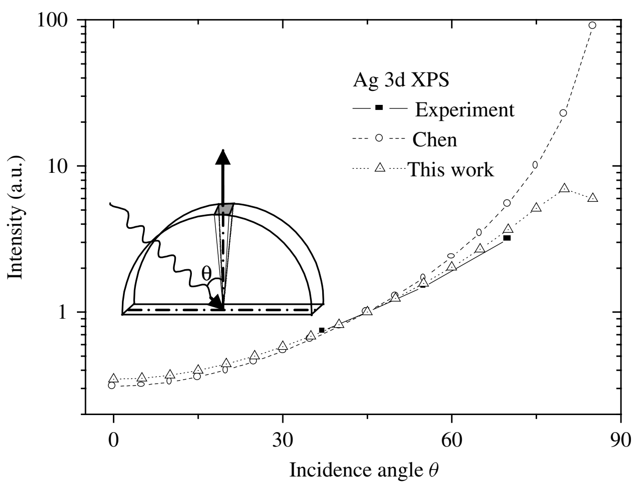

Figure 2. Dependence of the intensity of X-ray-induced photoelectrons on the incidence angle of X rays for normal emission. The intensity is normalized to incidence angle 45°.

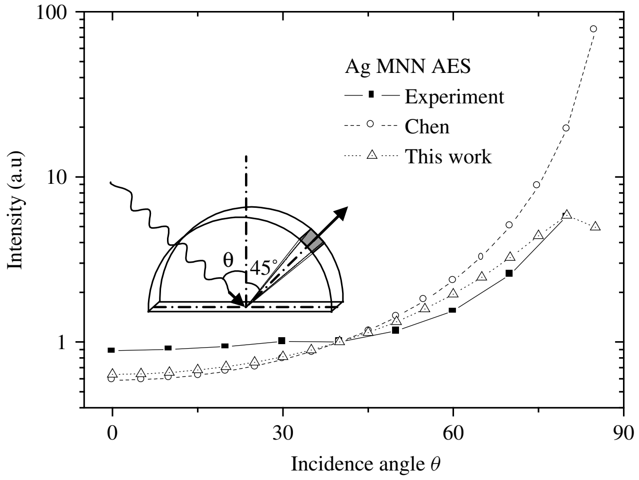

Figure 3. Dependence of Ag MNN Auger electron intensity on incidence angle of X rays for emission angle 45°. The intensity is normalized to incidence angle 40°.

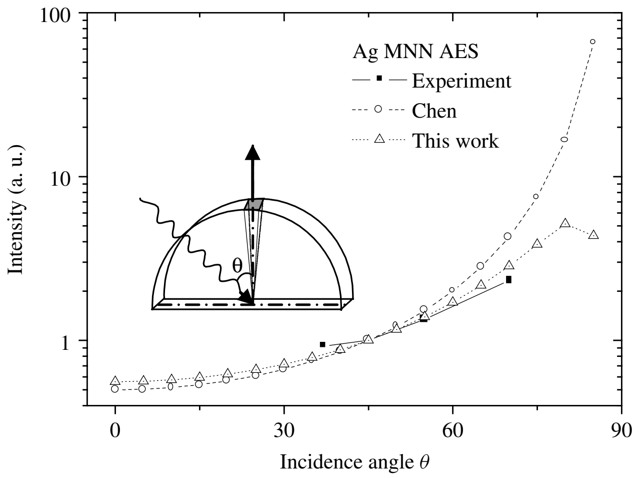

Figure 4. Dependence of Ag MNN Auger electron intensity on incidence angle of X rays for normal emission. The intensity is normalized to incidence angle 45°.

experimental data and Eqn (13), which is demonstrated in Figs 3 and 4.

For a glancing incidence of X rays (e.g. 85°), because the surface effects from glancing incidence are significant, the intensity obviously decreases as seen in Figs 1–4.

SUMMARY

On the basis of a dielectric function model, dependence of the surface excitation parameter on the incidence angle of X rays is derived. By applying the SEP, which depends on the incidence angle of X rays, the discrepancy between the experimental and theoretical results for the angular dependence of photoelectron and Auger electron signal intensities for the glancing incidence case is removed. The improved theory agrees with the experimental measurements well.

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