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A novel technique to determine the IMFP by total reflection x-ray photoelectron spectroscopy

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The information depth λ, which is defined in x-ray photoelectron spectroscopy (XPS) in such a way that $\frac{1}{\lambda}=\frac{1}{\lambda_e}+\frac{1}{\lambda_x}$ [λ_e and λ_x are the photoelectron inelastic mean free path (IMFP) and the x-ray evanescent length in the solid, respectively], is usually 20-40 Å in XPS. To choose several information depths $\lambda = \lambda_1, \lambda_2, \ldots$, we have used the x-ray total reflection technique. The total reflection x-ray photoelectron spectroscopy was first performed by Henke [1]. Recently, Chester *et al.* [2, 3], Jach *et al.* [4, 5], and the present authors [6-8] used this to analyze surface chemical states. We have reported [9] by a numerical simulation that an XPS background was reduced when the x-rays were totally reflected. We demonstrate that how we can estimate λ_e from the reduction fuctor of backgrounds based on the Tougaard's backgrounds [10].

The sample measured was flat Ag. Total reflection XPS experiments were performed on a soft x-ray beamline (BL-11B) at the Photon Factory, KEK (Fig. 1). The electron analyzer was concentric hemispherical analyzer made by Rigaku (XPS-7000 system). The beam size was 7.0 mm (vertical) and 1.0 mm by slits.

The sample current was measured as a function of glancing angle (Fig. 2a). The glancing angle at which the sample current had a maximum was 26.0 mrad. This angle was the critical angle of the x-ray total reflection [11, 12].

We display the calculated surface x-ray intensity, $T(\phi)$, in Fig. 2b, using n tabulated in Henke *et al.* [13]. The agreement between the measured current intensity curve (Fig. 2a) and the calculated x-ray intensity curve (Fig. 2b) is satisfactory. The evanescent length λ_x of x-rays is expressed as $\lambda_x = -\frac{\Lambda}{4\pi\, Im(U)}$, where Λ is the x-ray wavelength [14]. This relation is shown in Fig. 2c for 2000.0 eV x-rays impinging on Ag. We have measured the XPS spectra at ϕ = 20, 26, and 97 mrad. The x-ray evanescent length of these glancing angles are 2.4, 3.8, and 65.7 nm, respectively, read from Fig. 2c.

The measured XPS spectra are shown in Fig. 3d. The inelastic backgrounds which extend to deeper binding energy from the Ag 3*d* peaks are weak for totally reflected x-ray excitation (20 mrad), but are strong for larger glancing angle x-ray excitation (97 mrad). The observed XPS spectra $j(E)$ of exponentially distributed emitter atoms in a solid in such a way that, (number of atoms) $\propto e^{-z/\lambda_x}$, where z is the depth from the surface, is [10],

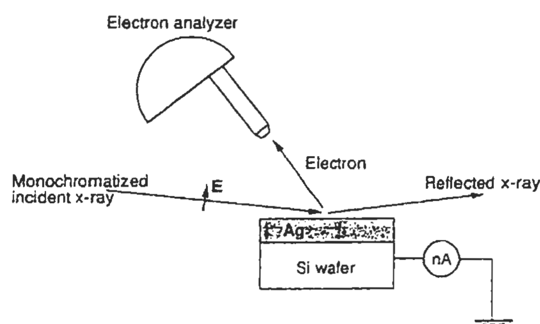

Fig. 1 Schematic illustration of the present experimental setup (top view). The electric vector (**E**) is indicated. The sample was rotated by a stepping motor. The sample was vertical.

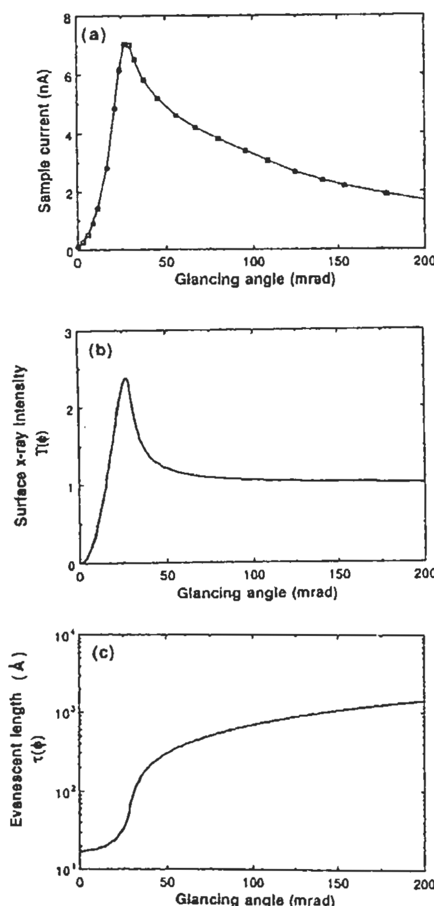

Fig. 2 (a) Measured glancing angle dependence of sample drain current. (b) Calculated x-ray intensity on Ag surface for 2000 eV x-rays. The surface x-ray intensity is normalized with respect to the incident x-ray intensity. (c) Calculated evanescent length of 2000 eV x-rays from Ag surface.

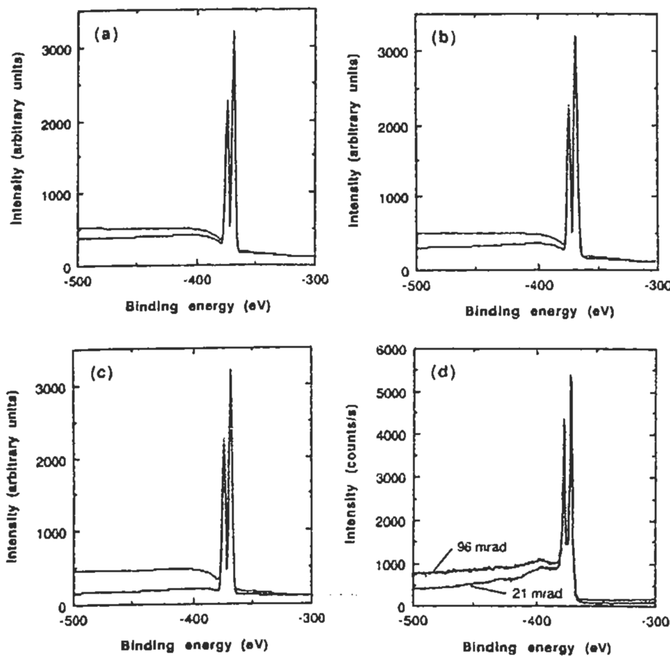

Fig. 3 Comparison between measured and calculated XPS spectra in the vicinity of Ag $3d$ peaks. Calculated XPS for λ_e = 0.50 (a), 1.00 (b), and 5.00 nm (c). Measured XPS for 20 and 97 mrad glancing angles (d).

$$j(E) = F(E) + \frac{\lambda}{\lambda_e}\int_E^{\infty} \frac{B(E' - E)}{[C + (E' - E)^2]^2} j(E')\, dE'$$

where $F(E)$ is the true XPS spectral function without energy loss, and B=2866 eV, C=1643 eV^2 for Ag [10]. We have calculated $j(E)$ for λ_x= 2.4 and 65.7 nm; λ_e is here an adjustable parameter and we varied it from 0.5 to 10 nm. Representative spectra calculated for λ_e = 0.50, 1.00, and 5.00 as well as the observed spectra are shown in Fig. 3. The observed spectral background (Fig. 3d) is reproduced in Fig. 3b. Consequently, λ_e = 1.00 nm. This λ_e is the IMFP of 1630 eV electrons (the Ag $3d$ binding energy was 370 eV and incident x-ray energy was 2000 eV). From Powell [15], the inelastic mean free path of 1600 eV electron is 2.5 nm. Tanuma *et al.* recalculated the IMFP for the same condition and obtained values of 2.01 [16] and 2.02 nm [17]. Our value is half of these calculations. The evaporated Ag layer has significantly less density than the bulk, and its surface is not perfectly flat. However, the density used for the evanescent x-ray length was that of bulk. Thus the IMFP measured in the present work is the bulk value; the inhomogeneous density effects of the sample surface were canceled out if the density dependence of l_x is similar to that of l_e.

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