Calculation of Depth Distribution Functions for CuO and SiO_2

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The emission depth distribution functions of photoelectrons for copper oxide CuO and silicon dioxide SiO_2 were calculated by the use of the first-principle quantum mechanical multiple scattering theory. The results were compared with the approximated analytical expressions from the Boltzmann equation by Tilinin et al.. The former explicitly takes the details of atomic arrangement in solids into account, while the latter does not. We show the calculated results by the use of two approaches and how the elastic scatterings affect the depth distribution function.

1. Introduction

Auger-electron spectroscopy and x-ray photoelectron spectroscopy (XPS) have developed rapidly, which are now used extensively in many different areas of science and technology. Excited electrons from solids travel some distance before they escape through the solid surface. During this transport, some electrons lose energy through inelastic scatterings. This gives rise to an attenuation of the peak intensity as well as to a background signal of inelastic electrons [1]. For any quantitative analyses of these spectra, we need procedures to correct for these spectral changes influenced by elastic scatterings.

To describe the attenuation, the inelastic mean free path (IMFP) and the emission depth distribution function (EDDF) are key factors, which are both important parameter in surface analysis. The EDDF is defined as "the probability that the electrons leaving the surface in a specified state originated from a specified depth measured normally from the surface." [2] In several theoretical and experimental studies, they have found that the EDDF of photoelectrons from s subshells leaving a surface in certain directions exhibits complex behavior, with a maximum at the depth comparable to the IMFP. For example, Tilinin et al. have obtained a peak in EDDF at the normal photoemission excited from O 1s level in Al_2O_3 grown on Al substrate. In contrast to this complicated behavior, the EDDF measured at the polar emission angle $\alpha = 60$ degrees shows a simple exponential decay as a function of the depth [3].

There are several classical approaches to calculate EDDF [1, 3], which successfully describe the EDDF in the high energy region. One of the prospective methods for deriving the analytical expressions is approximate solutions of the Boltzmann equation established by Tilinin *et al.*[3], which is a convenient method to calculate the EDDF but is fairly approximate the elastic scatterings along the electron trajectory. Another approach is the Monte Carlo method[4], which describes the elastic scatterings at any scattering center along the trajectory more precisely than the former. But they are based on the classical theory within a three-step model and approximate that the scattering centers are randomly distributed in a solid, so that they did not consider atomic structures of a solid.

Recently, we have developed a new method to calculate the EDDF based on the quantum mechanical multiple scattering theory[5-7]. In this approach, we can take the details of atomic structures and the quantum interference effects into account which has not been considered in the classical theory. It is shown that we need full multiple scattering calculations to properly evaluate the EDDF. We have discussed the EDDF only from simple metals, and normal emissions excited by a linearly polarized X-ray whose polarization is normal to the surface [6]. But it was not enough to discuss the characteristic shape of the EDDF as seen in the experiment [1], in which the X-ray polarization is parallel to the surface. Taking the experimental geometry into account, we now calculate photoelectron yield from some metal oxides and take average of it over an analyzer acceptance angle. It has been seen the EDDF shows almost exponential decay when the photoelectron is detected at 60 degrees from surface normal. We also study the angular dependence of the EDDF, and investigate the importance of the structural effect on EDDF.

In this paper, we calculate the EDDFs from copper oxide CuO and silicon dioxide SiO_2, by the use of the quantum full multiple scattering theory and also the analytical expressions from the Boltzmann equation by Tilinin et al.. And we show the advantage of our scattering theory to calculate the EDDF from a crystalline solid.

2. Theory

2.1 Full Multiple Scattering Theory

First principle many-body photoemission theories give us a useful formula for X-ray photoelectron diffraction (XPD) amplitude $M(\mathbf{k})$ measuring photoelectron momentum $\mathbf{k}$ excited from the site R_A, which is written by [6, 8, 9]

$$M(\mathbf{k}) = \sum_{\alpha} e^{-\kappa D_{\alpha}(\hat{\mathbf{k}})} e^{-i\mathbf{k}\cdot\mathbf{R}_{\alpha A}} \sum_{LL'} Y_{L'}(\hat{\mathbf{k}}) \times \left[(1-X(T))^{-1}\right]^{\alpha A}_{L'L} M_{LL_c} \quad (1)$$

$$X^{\alpha\beta}(T) = t_l^{\alpha}(k) G_{LL'}(k\mathbf{R}_{\alpha\beta})(1-\delta^{\alpha\beta}) \times \exp(-k^2\sigma^2_{\alpha\beta}(T)) \quad (2)$$

where X is a matrix labeled by a set of atomic sites (A, α, β, …) and orbital angular momentum L = (l,m). The full multiple scattering is taken into account by use of the inverse matrix $(1-X)^{-1}$. $\sigma^2_{\alpha\beta}(T)$ is Debye- Waller factor at temperature T and $\mathbf{R}_{\alpha A} = \mathbf{R}_{\alpha} - \mathbf{R}_A$. The explicit formula of the the site-t matrix $t_l^{\alpha}(k)$, the propagator $G_{L'L}(k\mathbf{R}_{\alpha A})$ and the the photoexcitation matrix element M_{LL_c} excited by linearly polarized light parallel to z-axis are found in Ref. [6, 9]. Equation (1) is the basic formula to calculate the photoemission, where we can systematically include the electron attenuation in solid and the thermal vibration [6].

2.2 Geometry

The theories commonly used to calculate the EDDF, such as Tilinin's equation and the Monte-Carlo simulation, are applied only to amorphous solids where the scattering centers are randomly distributed. The multiple scattering theory, on the other hand, has a feature that it can calculate the EDDF from crystalline solids. Thus we have to define the geometrical settings explicitly. In the present paper, we calculate the photoelectron intensity from CuO (001) and SiO_2 (001) surfaces. We set [001], [100] and [010] as z-, x- and y-axis, respectively. The geometries are simply shown in the all figures below.

Table 1 Estimated effective attenuation lengths of CuO from the results of the EDDFs in Fig. 1.

	EAL (Å)
FMS	4.41
Tilinin's eq.	6.87
SLA	8.11

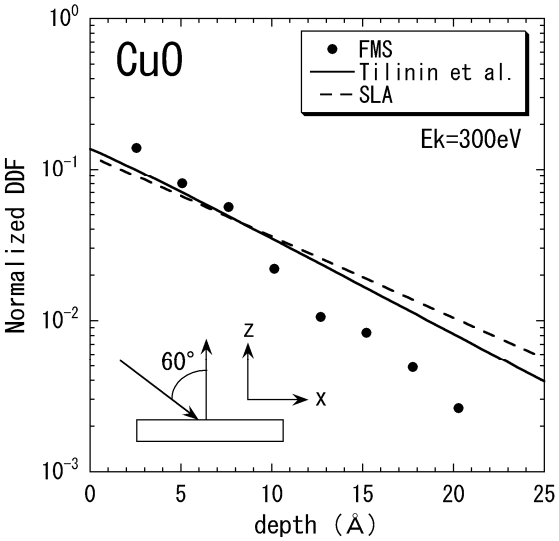

Fig. 1 Calculated EDDFs of O1s photoemission from CuO, where X-ray is irradiated from 60 degrees from the surface normal and photoelectron is detected at the surface normal. Circles, solid line and dashed line show the calculated results by full multiple scattering theory, by Tilinin's equation and by the straight line approximation, respectively.

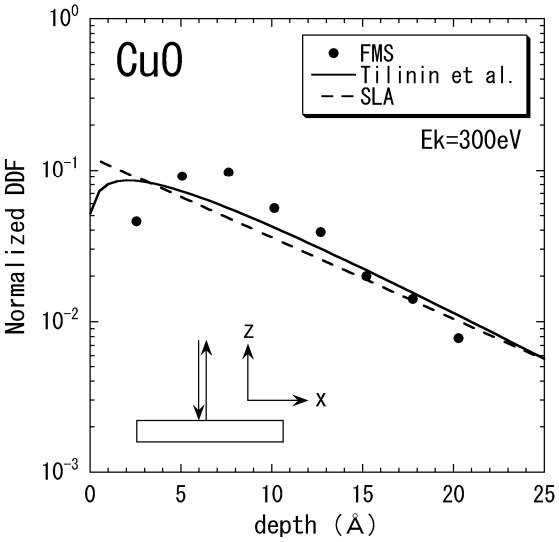

Fig. 2 The same as Fig. 1 but X-ray is irradiated from the surface normal and photoelectron is detected at the surface normal.

3. Calculated Results

3.1 CuO

In the previous papers, we have calculated the EDDFs from simple metals Cu and Al [6, 7]. We now calculate the EDDFs from more complicated solid, copper oxide, CuO so-called tenorite, which has a monoclinic structure. We assume CuO (001) surface and calculate O 1s photoemission with photoelectron kinetic energy E_k=300 eV excited by non-polarized light. The IMFP is 8.11 Å at 300 eV.

Fig. 1 shows calculated EDDFs of O1s photoemission from CuO, where unpolarized X-ray is irradiated from 60 degrees from the surface normal and photoelectron is detected at the surface normal. Circles, solid line and dashed line show the calculated results by full multiple scattering theory (FMS), by Tilinin's equation and by the straight line approximation, respectively. The EDDFs are normalized so that the depth integration to be unity. In this case, the calculated EDDFs show almost exponential decay so that we can estimate the effective attenuation length (EAL) from a slope of the fitted curve. The result is shown in Table 1. EAL from SLA is the same as the IMFP because SLA neglects elastic scatterings. Tilinin's eq. and FMS take into account the elastic scattering effects, and EALs from them are smaller than the IMFP.

Next, Fig. 2 shows the calculated EDDFs of O 1s photoemission from CuO, where unpolarized X-ray is irradiated from the surface normal and photoelectron is detected at surface normal. In SLA, detected photoelectron intensity is actually zero, but a simple exponential EDDF is written for comparison. In this case, the EDDF is no longer simple exponential decrease when the elastic scattering is taken into account. There is a peak at 2.0 Å by Tilinin's eq. and at 7.6 Å by FMS.

In Fig. 3, the EDDFs calculated in another geometry are shown, where unpolarized X-ray is irradiated from the surface normal and photoelectron is detected at 30 degrees from the surface normal. There are two results by FMS; one is detected at 30 degrees from the surface normal in xz-plane and the other is in yz-plane. The EDDF has a strong peak at 7.6 Å in xz-plane, while it shows a zigzag decrease in yz-plane. The difference may be caused by the elastic scatterings as seen in photoelectron diffraction. In SLA and Tilinin's eq., on the other hand, there is no difference between these directions because the lattice structure is not considered. Thus, the FMS theory predicts that if the EDDF is measured from a crystalline solid, this effect may appear.

Table 2 Estimated effective attenuation lengths of SiO_2 from the results of the EDDFs in Fig. 4.

	EAL (Å)
FMS	7.63
Tilinin's eq.	9.29
SLA	13.76

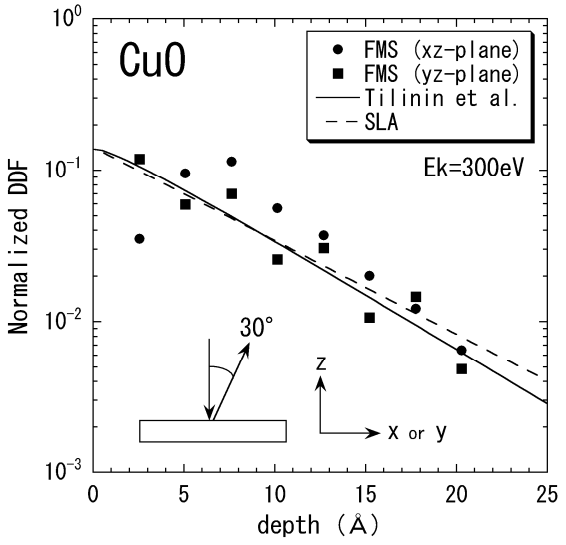

Fig. 3 The same as Fig. 1 but X-ray is irradiated from the surface normal and photoelectron is detected at 30 degrees from the surface normal. In this figure, circles and squares shows the calculated results by the full multiple scattering theory, where photoelectron is detected at xz- (circles) and yz-plane (squares) from the surface normal.

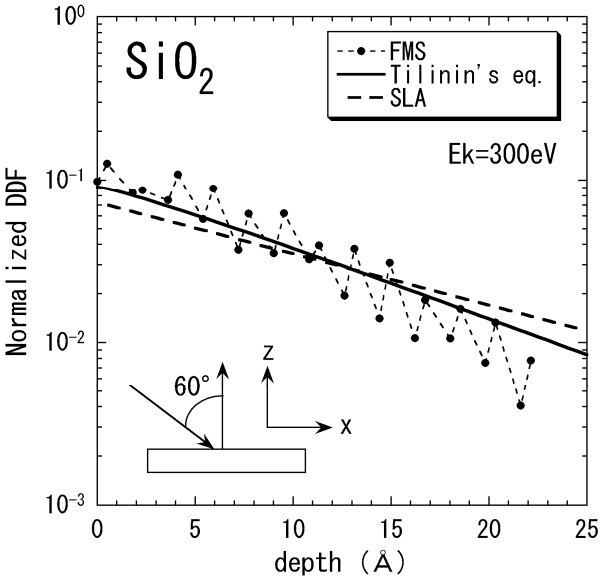

Fig. 4 The same as Fig. 1 but from SiO_2.

3.2 SiO_2

Next, we show the calculated results of EDDFs of O1s photoemission from SiO_2 (α-quartz) (001) surface with the electron kinetic energy 300 eV. The IMFP is 13.76 Å. Fig. 4 shows the EDDFs in the same geometry as Fig. 1. The EDDF by FMS from SiO_2 has more complex behavior than that from CuO because of a complex structure. Using the same manner as in CuO case, we estimate the EALs by curve fitting, which are shown in Table 2. The elastic scattering effects make the EAL smaller than IMFP. Fig. 5 shows the EDDFs from SiO_2 in the same geometry as Fig. 2. Tilinin's eq. shows a smooth EDDF curve with a peak at 3.0 Å. FMS shows a strong zigzag curve, where the strongest peak is at 4.0 Å. SiO_2 (001) has a periodic structure in depth per 6 O atoms. The different structural environment around an O atom can affect the strong and weak contribution to the EDDF.

The details of our results will be presented at the conference.

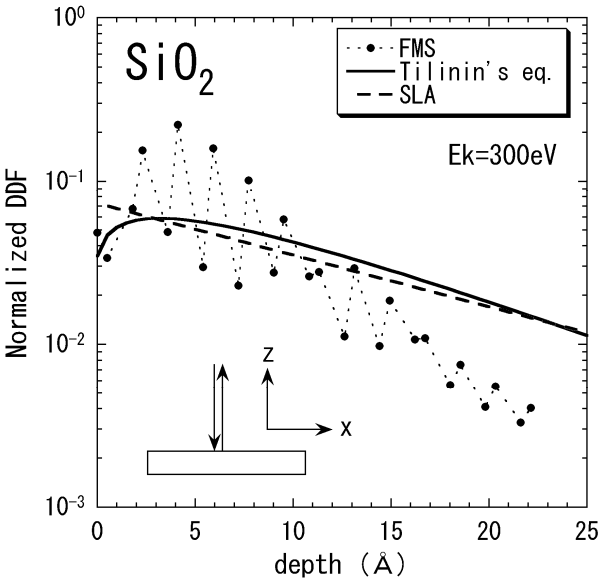

Fig. 5 The same as Fig. 2 but from SiO_2.

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