Surface Science 606 (2012) 644–651

Contents lists available at SciVerse ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Elastic photoelectron-scattering effects in quantitative X-ray photoelectron spectroscopy

A. Jablonski [a,*], C.J. Powell [b]

[a] Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warsaw, Poland
[b] Surface and Microanalysis Science Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8370, USA

ARTICLE INFO

Article history:
Received 22 July 2011
Accepted 7 December 2011
Available online 14 December 2011

Keywords:
Computer simulations
Electron-solid scattering and transmission – elastic
Photoelectron emission

ABSTRACT

We present improved formulae for the correction parameters Q_x and β_{eff} that are used to account for elastic scattering of photoelectrons in quantitative X-ray photoelectron spectroscopy (XPS). The new formulae are based on new Monte Carlo simulations for 584 photoelectrons in 39 elemental solids that could be excited by Mg Kα and Al Kα X-rays in 315 different XPS configurations. The new simulations differed from similar earlier calculations in that differential elastic-scattering cross sections calculated from the Dirac–Hartree–Fock potential were utilized rather than those from the Thomas–Fermi–Dirac potential, a smaller analyzer acceptance angle was chosen, and the number of trajectories in each simulation was an order of magnitude larger. New values of Q_x and β_{eff} were obtained for each photoelectron line, each X-ray source, and each XPS configuration. These Q_x and β_{eff} values could be fitted to simple two-parameter expressions, each a function of the single-scattering albedo and the photoelectron emission angle. Values of Q_x from the new predictive formula differed from the previous expression by less than 1%. Larger deviations in the values of β_{eff}, up to 2.5%, were found from the new fit to the β_{eff} parameter. The new expressions for Q_x and β_{eff} provide a convenient means for correction of elastic-scattering effects in XPS.

1. Introduction

An important application of X-ray photoelectron spectroscopy (XPS) for several decades has been determination of the composition of the surface region of a sample from measured photoelectron intensities [1]. If the sample is homogeneous within the information depths for the detected photoelectrons, simple expressions can be derived relating the photoelectron intensities to the surface composition [1]. If elastic scattering of the photoelectrons is neglected, for the moment, the photoelectron signal intensity, I_x, can be expressed as

$$I_x = C\ \Delta\Omega\ \lambda_{in} N(d\sigma_x/d\Omega), \tag{1}$$

where the constant C comprises certain instrumental parameters and settings [1], $\Delta\Omega$ is the solid acceptance angle of the analyzer, λ_{in} is the inelastic mean free path (IMFP) for the signal photoelectrons, N is the atomic density of elemental species (number of atoms in a unit volume) responsible for the detected photoelectrons, and $d\sigma_x/d\Omega$ is the differential photoelectric cross section (PCS) for the relevant subshell. This cross section, for unpolarized X-rays, is given by

$$d\sigma_x/d\Omega = \sigma_x \frac{1}{4\pi}\left[1-\frac{\beta}{4}\left(3\cos^2\psi-1\right)\right] = \sigma_x W(\beta,\psi), \tag{2}$$

where σ_x is the total PCS, β is the asymmetry parameter, and ψ is the angle between the X-ray direction and the analyzer axis (cf. Fig. 1).

It has been known for many years that elastic scattering of the photoelectrons can appreciably affect the photoelectron signal intensities [2]. Jablonski and Zemek [3] have shown, however, from Monte Carlo simulations of electron transport supported by experiment that the photoelectron intensity can still be described by Eq. (1) if the differential PCS is replaced by the expression

$$\begin{aligned}(d\sigma_x/d\Omega)_{corr} &= \sigma_x Q_x\ W\left(\beta_{eff},\psi\right)\\ &= \sigma_x\ Q_x\ \frac{1}{4\pi}\left[1-\frac{\beta_{eff}}{4}\left(3\cos^2\psi-1\right)\right],\end{aligned} \tag{3}$$

where Q_x is a parameter directly correcting the photoelectron intensity and β_{eff} is a modified asymmetry parameter. Jablonski and Powell [4] have shown that the correction parameters Q_x and β_{eff}, for a given element and photoelectron line, depend on the experimental configuration. Both correction parameters depend weakly on the photoelectron emission angle, α (see Fig. 1), up to about 50°, while this dependence becomes more pronounced at larger emission angles.

Information on the correction parameters Q_x and β_{eff} is presently available from two types of sources [4–9]:

1. values from analytical expressions that had been fitted to results of Monte Carlo calculations [4–7];
2. values derived from the kinetic Boltzmann equation within the so-called transport approximation [8,9].

* Corresponding author. Tel.: +48 22 343 3331; fax: +48 22 343 3333.
E-mail address: ajablonski@ichf.edu.pl (A. Jablonski).

0039-6028/$ – see front matter
doi:10.1016/j.susc.2011.12.003

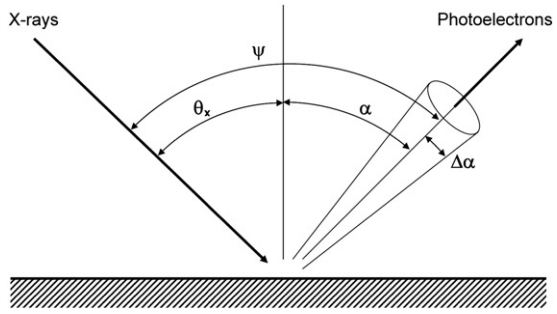

Fig. 1. Schematic of the XPS configuration considered in this work. Note that the direction of the X-ray beam, the analyzer axis, and the surface normal are located in one plane.

The former approach is expected to yield more reliable values of Q_x and β_{eff} than the latter.

The analytical expressions for Q_x and β_{eff} proposed in Refs. [5–7] were based on the results of an extensive set of Monte Carlo simulations published in 1995 [5]. These simulations were performed for 396 photoelectron lines that could be excited by Mg Kα and Al Kα X-rays from the 27 elemental solids for which IMFP data were then available. For each photoelectron line, 315 different experimental configurations were considered. In total, more than 120 000 separate simulations were made. The most recent expressions for Q_x and β_{eff} [6,7] were functions of the photoelectron emission angle, the IMFP, the transport mean free path (derived from the transport cross section in Eqs. (5a) and (5b) below), and, in Ref. [6], the atomic number.

Monte Carlo simulations of photoelectron trajectories in a solid require knowledge of the differential cross section (DCS) for elastic scattering of photoelectrons for the relevant solids and photoelectron energies. In the original set of simulations, Jablonski [5] used DCSs determined from the Thomas–Fermi–Dirac (TFD) potential, an approximate description of the interaction between a photoelectron and an atom in the solid. It has been found, however, that DCSs calculated from the Dirac–Hartree–Fock (DHF) potential agree better with measured DCSs than DCSs from the TFD potential [10]. It is reasonable to assume that values of the parameters Q_x and β_{eff} derived from Monte Carlo simulations with DCSs from the DHF potential would be more accurate than the corresponding parameters obtained from the previous simulations with DCSs from the TFD potential [5]. Furthermore, values of the transport mean free path depend on the atomic potential selected for the DCS calculation.

We have performed a new series of Monte Carlo simulations with DCSs from the DHF potential. These simulations, for the same two X-ray lines and the same 315 configurations, were performed for 39 elemental solids instead of the 27 solids considered previously (solids for which IMFPs were then available [11]) since IMFPs have now been published for additional solids [12]. It was also decided to perform new calculations of the correction parameters Q_x and β_{eff} from the new simulations for a larger number of photoelectron lines.

A brief description of the strategy for the Monte Carlo simulations is presented in the next section. Our results are presented and discussed in the following section, and we conclude with a summary of our results.

2. Monte Carlo simulations

We utilized a typical Monte Carlo strategy designed for estimating the signal intensity for a given photoelectron line and experimental configuration. The relevant algorithm has been described in detail in the literature [3,4,8,13]. This algorithm provides an estimation of the photoelectron current, I_x^{MC}, which is normalized so that it is equal to the intensity I_x from Eq. (1) with $C \equiv 1$ (when elastic-scattering events are ignored in the Monte Carlo calculation). Eventually, we determined the value of the photoelectric cross section corrected for the effects of elastic scattering from

$$(d\sigma_x/d\Omega)_{corr} = \frac{I_x^{MC}}{\Delta\Omega\ \lambda_{in}\ N}. \quad (4)$$

Monte Carlo simulations were performed for the chosen solids, Al Kα and Mg Kα X-ray sources, photoelectron lines, and the 315 different experimental XPS configurations utilized previously [5]. Each configuration is characterized by the angle of X-ray incidence, θ_x, and the photoelectron emission angle, α, with respect to the surface normal, as shown in Fig. 1. We assumed that the direction of X-rays, the analyzer axis, and the surface normal were in one plane. Consequently, $\psi = \theta_x + \alpha$.

We performed simulations for 39 elemental solids for which IMFPs with satisfactory accuracy are available. We chose to disregard graphite and diamond since their IMFPs could have larger uncertainties than those of the 39 other solids [12]. We note, however, that the calculated IMFPs for diamond are consistent with IMFPs determined from elastic-peak electron spectroscopy experiments by Zemek et al. [14]. The IMFPs for most solids are also available from the National Institute of Standards and Technology (NIST) Electron IMFP database [15]. For the chosen 39 solids, we identified 584 photoelectron lines that could be excited by Mg Kα and Al Kα X-rays.

The sources of data for the parameters needed in the simulations and the choices made for the XPS configurations are summarized below:

1. The binding energies of the considered photoelectron lines, E_B, were taken from the compilation of Williams [16]. The corresponding kinetic energies of the photoelectrons could then be determined from the energy of the selected X-rays.
3. The differential and total elastic-scattering cross sections for the relevant photoelectron kinetic energies were calculated from the ELSEPA software that implements the Dirac–Hartree–Fock interaction potential between the photoelectron and a scattering atom in the selected solid [17]. These cross sections are also available from a NIST database [18].
4. For each photoelectron line, the X-ray incidence angle, θ_x, was varied between −85° and 85° in steps of 5° for a given emission angle, α. These calculations were repeated for different emission angles, α, between 0° and 80° in steps of 10°. Thus, a total of 315 experimental configurations were considered for each line.
5. The solid acceptance angle of the analyzer was assumed to be a cone with a half-cone angle of $\Delta\alpha = 5°$. This solid acceptance angle is smaller by a factor of four than the analyzer solid angle assumed in the previous calculations (that had a half-cone angle of 10°) [5].
6. For a given experimental configuration, 2×10^7 photoelectron trajectories were generated. This number of trajectories is an order of magnitude larger than the number selected previously (2×10^6 trajectories) [5].
7. An improved sampler of photoelectron polar scattering angles was used here in simulations of elastic-scattering events. The sampler used previously [5] that was implemented in the NIST Database 64 [18] did not perform correctly when the differential cross section for elastic scattering exhibited sharp features (i.e., sharp minima or maxima).

In total, 183 960 separate Monte Carlo simulations were performed. Eq. (3) was then fitted to the calculated set of values of corrected photoelectric cross section, $(d\sigma_x/d\Omega)_{corr}$, to provide values of the parameters Q_x and β_{eff} for each solid, X-ray source, photoelectron line, and XPS configuration.

3. Results and discussion

DCSs calculated from the DHF potential have been found to differ considerably from the corresponding DCSs obtained from the TFD