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Surface sensitivity of elastic peak electron spectroscopy

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ABSTRACT

New theoretical model describing the sampling depth of elastic peak electron spectroscopy (EPES) has been proposed. Surface sensitivity of this technique can be generally identified with the maximum depth reached by trajectories of elastically backscattered electrons. A parameter called the penetration depth distribution function (PDDF) has been proposed for this description. Two further parameters are descendant from this definition: the mean penetration depth (MPD) and the information depth (ID). From the proposed theory, relatively simple analytical expressions describing the above parameters can be derived. Although the Monte Carlo simulations can be effectively used to estimate the sampling depth of EPES, this approach may require a considerable amount of computations. In contrast, the analytical model proposed here (AN) is very fast and provides the parameters PDDF, MPD and ID that very well compare with results of MC simulations. As follows from detailed comparisons performed for four elements (Al, Ni, Pd and Au), the AN model practically reproduced complicated emission angle dependences of the MPDs and the IDs, correctly indicating numerous maximum and minimum positions. In the energy range from 200 eV to 5 keV, the averaged percentage differences between MPDs obtained from the MC and the AN models were close to 4%. An important conclusion resulting from the present studies refers to the procedure of determination of the inelastic mean free path (IMFP) from EPES. Frequently, the analyzed sample is deposited as a thin overlayer on a smooth substrate. From an analysis of the presently obtained IDs, is follows that 99% of trajectories in analyzed experimental configurations reaches depth not exceeding 2.39 in units of IMFP. Thus, one can postulate that a safe minimum thickness of an overlayer should be larger than about 3 IMFPs. For example, the minimum thickness of an Al overlayer shoud be about 8 nm at 5000 eV.

1. Introduction

The surface sensitive electron spectroscopies, X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) are very useful tools for studies of nanostructures due to small sampling depths of both techniques. Analysis by XPS and AES is extended over only several atomic layers of the surface region. To quantify the thickness of the analyzed layer, we need to know a parameter that characterizes the "survival" of signal electrons in condensed matter. The relevant parameter used for that purpose, the inelastic mean free path (IMFP), is defined as ". . . average distance that an electron with a given energy travels between successive inelastic collisions" [1]. A voluminous material on the theoretical and experimental IMFP values is presently available. It has been postulated [2] that the IMFPs that are in agreement with the ISO definition can actually be obtained from two methods: (i) the IMFPs calculated from experimental optical data, and (ii) the IMFPs measured by elastic peak electron spectroscopy (EPES). A very extensive set of calculated IMFPs has been published by Tanuma and coworkers for elements [3–5], inorganic compounds [6], and organic compounds [7]. The calculated IMFPs obtained from different theoretical models are also compiled in the NIST database [8]. One should stress here that these IMFPs refer to the bulk of a solid. The IMFPs of electrons in the surface region may be different than in the bulk due to differences in the mechanism of energy losses. Consequently, the signal intensity of surface sensitive electron spectroscopies, X-ray photoelectron spectroscopy and Auger electron spectroscopy, may be affected by the surface energy losses. Quantification of XPS and AES require knowledge of the IMFPs for signal electrons. One can use the calculated IMFPs for that purpose, however it is postulated that they should be additionally corrected for surface energy losses [9–14]. Relatively simple analytical expressions were proposed for the relevant correction: the surface excitation parameter (SEP) [10–13], yet the coefficients needed for these expressions were determined for a limited number of solids. Werner et al. [12] made an attempt to derive a predictive formula

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for SEP, however its accuracy is generally unknown; it can only be considered as a useful guidance.

In contrast to the calculated IMFPs, the IMFPs obtained from EPES measurements refer to a thin surface region. We expect that the thickness of the layer sampled by backscattered electrons should be comparable to the surface sensitivity of XPS and AES, or even smaller since the elastically backscattered electrons pass the surface layer twice, and thus the probability of an energy loss is larger than that of photoelectrons and Auger electrons. An obvious question arises as to what is the actual sampling depth of EPES measurements. This problem has been approached by Jablonski and Powell [15]. It has been proposed that a convenient measure of the sampling depth of EPES is the penetration depth distribution function (PDDF) [15]. This function was defined as "... the probability that an electron incident on the surface at an angle Θ_0 will be elastically backscattered from a maximum depth z and emitted in the direction of the analyzer at an angle α and not be inelastically scattered". The PDDF, $\xi(z, \alpha, \Theta_0)$, can be normalized so that the integral over depth is equal to the elastic backscattering probability, $\eta(\Delta\Omega)$, measured within a certain solid acceptance angle of an analyzer, $\Delta\Omega$:

$$\int_0^\infty \xi(z, \alpha, \theta_0)dz = \eta(\Delta\Omega). \tag{1}$$

Two useful parameters were proposed to quantify the sampling depth of EPES, both related to the PDDF [15]. The mean penetration depth (MPD) was defined as a mean value of the PDDF:

$$G = \frac{\int_0^\infty z\xi(z, \alpha, \Theta_0)\,dz}{\int_0^\infty \xi(z, \alpha, \Theta_0)\,dz} \tag{2}$$

Note that this parameter has a close similarity to the parameter called the mean escape depth (Ref. [1], definition 4.203) which characterizes the sampling depth of AES and XPS. The emission depth distribution function in this definition is simply replaced by the PDDF. Second parameter that describes the sampling depth of EPES is the information depth (ID). This parameter, again by analogy with XPS and AES, is defined as a thickness penetrated by a specified percentage, p_{ID}, (for example, equal to 90%, 95% or 99%) of electron trajectories in particular measurement conditions. The ID designated here by T can be determined by solving the following equation:

$$\frac{\int_0^T \xi(z, \alpha, \Theta_0)\,dz}{\int_0^\infty \xi(z, \alpha, \Theta_0)\,dz} = \frac{p_{ID}}{100} \tag{3}$$

In experiments involving elastic electron backscattering, we often use samples prepared as overlayers deposited galvanically [13] or by vacuum evaporation [13,16] to ensure high smoothness of the studied surface. However, we have to make sure that an overlayer is of sufficient thickness at a given electron energy to avoid influence of the substrate on results of EPES experiments. It has been demonstrated that the sampling depth of EPES may be dramatically affected by the substrate in certain experimental configurations when the overlayer thickness is too small [17]. A safe thickness of an overlayer can be determined experimentally by measuring the elastic backscattering intensity in a given experimental geometry and for an electron energy of interest [18,19], however such experiments are very elaborate and thus are not useful as a guidance in practical EPES analysis.

An electron transport in the surface region of solids can be well characterized by Monte Carlo simulations. This computational tool is proved to accurately predict characteristics of elastically backscattered electrons (angular distribution [16,18,20], energy dependence [21,22] and overlayer thickness dependence of signal electrons [18,19]). In fact, the Monte Carlo algorithms with different simulation strategies are almost exclusively used in calculations of the IMFPs from EPES measurements [2,20,23–25]. It has been shown that, on minor modification, these algorithms can be used for estimation of the EPES sampling depth [15]. However, the Monte Carlo simulations generally require a considerable amount of computations, especially in cases when the EPES measurements are performed with analyzers having small solid acceptance angle. Consequently, such approach is impractical as a routine criterion for estimating a needed thickness of a sample material under study. On the other hand, a simple analytical model, in which only one elastic scattering event is considered, leads to the estimates of the EPES sampling depth that may dramatically deviate from predictions of the Monte Carlo approach. In the present work, an attempt is made to derive an analytical formalism that has accuracy similar to Monte Carlo simulations, however it is relatively simple to use. Furthermore, the relevant calculations are expected to be much faster than the performance of the Monte Carlo algorithms.

2. Theory

Let us consider here the theoretical models that can be used for description of the sampling depth of EPES measurements. At first, let us briefly outline the theoretical models that were used in published calculations of the MPD and EPES ID [15].

2.1. The single large-angle backscattering model

We start with the simplest model for the elastic backscattering event designated further here with the acronym SLAB. The formalism is based on two assumptions:

1. Along the trajectory of an elastically backscattered electron, only one large-angle scattering event occurs.
2. Probability of an elastic scattering event along trajectory is much smaller than the probability of inelastic interaction.

The shape of the corresponding trajectory is shown in Fig. 1. The elastically backscattered current within a small analyzer acceptance angle is then given by [15,26]

$$\eta(\Delta\Omega) = \Delta\Omega\frac{\cos\alpha}{\cos\Theta_0 + \cos\alpha}N\lambda_{in}\frac{d\sigma_{el}}{d\Omega} \tag{4}$$

where N is the atomic density, λ_{in} is the IMFP, and $d\sigma_{el}/d\Omega$ is the differential elastic scattering cross section (DCS). The PDDF is readily obtained from Eqs. (1) and (4)

$$\xi(z, \alpha, \Theta_0) = \frac{\Delta\Omega N}{\cos\Theta_0}\frac{d\sigma_{el}}{d\Omega}\exp\left[-\frac{z}{\lambda_{in}}\left(\frac{1}{\cos\Theta_0} + \frac{1}{\cos\alpha}\right)\right] \tag{5}$$

The MPD and the ID derived from Eqs. (2), (3) and (5) have the following form [15]

$$G = \lambda_{in}\frac{\cos\Theta_0\cos\alpha}{\cos\Theta_0 + \cos\alpha} \tag{6}$$

$$T = -\lambda_{in}\frac{\cos\Theta_0\cos\alpha}{\cos\Theta_0 + \cos\alpha}\ln\left(1 - \frac{p_{ID}}{100}\right). \tag{7}$$