

RECENT DEVELOPMENTS IN QUANTITATIVE XPS

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The quantitative applications of the surface sensitive spectroscopies, AES and XPS, were attempted already in late Sixties. Over the years, considerable progress has been made in quantification of both techniques. Much attention has been devoted to studies of photoelectron or Auger electron transport after being created in the surface region. Present report summarizes the recent results obtained for photoelectron transport in amorphous or polycrystalline solids.

In 1974, Fadley *et al.* [1] extensively analysed the theory relating the recorded photoelectron intensity to the concentration of atoms. The proposed formalism, with minor changes, is commonly used until present time. This issue was also addressed in more recent literature [2,3]. The common formalism is based on the assumption that the photoelectron trajectories in solid are linear, i.e. the elastic photoelectron collisions are neglected (straight line approximation). Already Fadley *et al.* [1] suggested that this assumption may not always be valid. This has been pointed out later by Baschenko and Nefedov in a series of papers [4]. These papers stimulated further extensive studies of the photoelectron transport in solids and its influence on the performance of quantitative analysis. Some of the results are briefly discussed below.

Proposition of the modified formalism

The common formalism leads to a simple relation between the measured photoelectron intensity, I_x , and the atomic density of the analysed constituent, N

$$I_x = T D I_0 A_0 \Delta\Omega N \lambda (d\sigma_x/d\Omega) \quad (1)$$

where T is the analyser transmission, D is the detector efficiency, I_0 is the flux of x-rays, A_0 is the analysed area at the detection angle normal to the surface, $\Delta\Omega$ is the solid acceptance angle of the analyser, and λ is the photoelectron inelastic mean free path (IMFP). The differential photoelectric cross section, $d\sigma_x/d\Omega$, for unpolarized radiation is given by

$$d\sigma_x/d\Omega = (\sigma_x/4\pi) [1 - (\beta/4) (3 \cos^2\psi - 1)] \quad (2)$$

where σ_x is the total photoelectric cross section, β is the asymmetry parameter, and ψ is the angle between the direction of x-rays and the direction towards the analyser. Recent theoretical and experimental studies have shown that more realistic theoretical model, taking into account the photoelectron elastic collisions, leads to photoelectron intensities which can be described by the common formalism with slightly modified photoelectric cross section [5,6,7]

$$\left(\frac{d\sigma_x}{d\Omega} \right)_{el} = (\sigma_x/4\pi) Q_x [1 - (\beta_{eff}/4) (3 \cos^2\psi - 1)] \quad (3)$$

where Q_x and β_{eff} are the parameters correcting for the elastic scattering effects. They depend on the solid, photoelectron line, and the detection angle, while they are independent of the incidence angle of x-rays. An extensive database of these corrections for about 400 photoelectron lines has been recently prepared [8]. Derivation of universal analytical formulas providing these correction factors is currently in progress.

New standards for terms describing the photoelectron transport

It has been found that the photoelectron attenuation in the solids may considerably deviate from the exponential law. On the other hand, some of the standard definitions of terms used in surface analysis are based on the assumption that the electron attenuation with the distance traversed is exponential. This refers mainly to terms defining the photoelectron transport, i.e. the attenuation length and the escape depth. Definitions of these terms are currently revised. Several new definitions are recommended in the latest issue of the ASTM Book of Standards [9]. Two of these terms are of particular importance in quantitative XPS:

1. The emission depth distribution function (DDF) - for particles or radiation emitted in a given direction, the probability that the particle or radiation leaving the surface in a specified state originated from a specific depth measured normally from the surface into the material.
2. Mean escape depth (MED) - the average depth normal to the surface from which the specified particles or radiations escape as defined by

$$D = \frac{\int_0^{\infty} z \phi(z, \alpha) dz}{\int_0^{\infty} \phi(z, \alpha) dz}$$

where $\phi(z, \alpha)$ is the DDF. The term attenuation length is presently proposed to describe the attenuation of the parallel beam of particles, and thus its use

in quantitative XPS may be limited.

The formalism of quantitative XPS and AES requires knowledge of terms defining the electron transport. In view of numerous terms and their definitions, the user of these techniques may have difficulties in selecting a proper parameter for a particular quantitative application. This problem has been recently extensively discussed [5].

Depth of XPS analysis

An important information for the user of XPS is the average sampling depth of this technique in the particular case of a given experimental geometry and selected photoelectron lines. This depth is usually associated with the inelastic mean free path, λ , according to

$$\Delta = \lambda \cos \alpha$$

However, the correct parameter to use in that case is the mean escape depth. It has been found that the MED is strongly correlated with the anisotropy of photoelectron emission [10]. Furthermore, the MED may be considerable larger than Δ in some XPS configurations, which is in contrast with expectations.

Problems with the 'magic angle'

The photoelectron intensity calculated from Eqs (1) and (2) for a certain angle ψ is the same as if the photoemission were assumed to be isotropic ($\beta = 0$). This angle, equal to 54.7° , is called the 'magic angle', and is sometimes recommended for the XPS analysis since the correction associated with anisotropy of photoemission is no longer necessary. However, the value of magic angle has been derived for the straight line approximation. If the theoretical model accounting for elastic photoelectron scattering is used in the derivation [6], the magic angle is found to be no longer a constant. It depends on the photoelectron line, the solid, and the XPS configuration. These results show that no universal experimental geometry can circumvent the problems with anisotropy of photoemission.

Database of elastic scattering cross sections

Any realistic theoretical model of photoelectron transport, accounting for elastic scattering events, must be founded on the possibly reliable elastic scattering cross sections. These functions must be known for all atomic constituents of the solid and all kinetic energies of considered photoelectrons. Since the tabulations of cross sections available in the

literature are far from complete (e.g. [11]), an attempt has been made to compile a complete database of differential and total elastic scattering cross sections for all elements and energies up to 10 keV in steps of 1 eV [12]. The database has numerous options facilitating the use of cross sections: (i) quick visualisation in different coordinates, (ii) creation of files with cross sections for selected elements and energies, (iii) construction of random number generators providing the scattering angles, and (iv) testing the reliability of created generators.

Despite considerable progress in the theory of photoelectron transport, the elastic scattering effects are usually not accounted for in a routine XPS analysis. More work is still necessary to determine the correction parameters for the complex solids which are frequently submitted to quantitative analysis. Furthermore, the present database of terms describing the photoelectron transport, especially the IMFP, is also rather limited. A reliable procedure for estimating these parameters for complex solids should be elaborated.

- [1] C. S. Fadley, R. J. Baird, W. Siekhaus, T. Novakov and S. Å. L. Bergström, *J. Electron Spectrosc. Relat Phenom.* **4**, 93 (1974).
- [2] M. F. Ebel, H. Ebel and K. Hirokawa, *Spectrochimica Acta* **B37**, 461 (1982).
- [3] M. P. Seah, in: *Practical Surface Analysis*, Vol. 1, p. 201, Wiley, Salle+Sauerländer, Chichester (1990).
- [4] O. A. Baschenko and V. I. Nefedov, *J. Electron Spectrosc. Relat. Phenom.* **17**, 405 (1979); **21**, 153 (1980); **27**, 109 (1982).
- [5] A. Jablonski and C. J. Powell, *Surface and Interface Anal.* **20**, 771 (1993).
- [6] A. Jablonski and C. J. Powell, *Phys. Rev.* **B50**, 4739 (1994).
- [7] A. Jablonski and J. Zemek, *Phys. Rev.* **B48**, 4799 (1993).
- [8] A. Jablonski, *Surface Interface Anal.*, in press.
- [9] ASTM Standard E 673-93, Standard Terminology Relating to Surface Analysis, 199 Annual Book of Standards (ASTM, Philadelphia, 1994) Vol.3.06, p. 739.
- [10] A. Jablonski, *Surface Interface Anal.* **21**, 758 (1994).
- [11] M. Fink and A. C. Yates, *At. Data Nucl. Data Tables* **1**, 385 (1970); M. Fink and J. Ingram, *ibid.* **4**, 129 (1972); D. Grgory and M. Fink, *ibid.* **14**, 39 (1974); M. E. Riley, C. J. MacCallum and F. Biggs, *ibid.* **15**, 443 (1975).
- [12] A. Jablonski and S. Tougaard, *Surface Interface Anal.* **22**, 129 (1994).