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Instrumental function of the SPECS XPS system

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ABSTRACT

A simple method for the energy resolution measurement of a spectrometer, working in the fixed analyser transmission mode, is proposed and used to determine the resolution of a SPECS Phoibos 100 spectrometer, being a part of an X-ray Photoelectron Spectroscopy (XPS) setup. The spectrometer resolution was obtained from the O 1s photoelectron line profiles, taken from the oxidized boron-doped silicon single crystal vs. the analyzer pass energy. The measurements were performed for two entrance slits having respective widths of 1 mm and 7 mm. An excellent agreement with the theoretical expectations was obtained for the narrower slit, showing linear dependence on the pass energy. As for the wider slit, agreement with theory is achieved only for lower pass energies. At higher pass energies, the resolution shows non-linear behaviour and even saturation, while the analyzer transmission continues to grow. The instrumental function of the whole XPS system is determined as a convolution of the spectrometer instrumental function and the X-ray energy profile. The usefulness of the total instrumental function for the analysis of valence band spectra was also tested. For that purpose, a novel deconvolution procedure is introduced, giving a possibility to analytically calculate the position of the valence band maximum, providing excellent agreement in the case of high resolution spectra. When the valence band spectra are taken in lower resolution, deconvolution efficiently reduces the spectrum deviations due to the lower resolution, although the valence band maximum determination is less precise.

1. Introduction

X-ray Photoelectron Spectroscopy (XPS) is nowadays probably the most widely used surface sensitive analytical technique. Due to its unique property to provide both quantitative composition analysis and information on the chemical bonds even for the non-conductive and biological samples, it became equally popular as a common tool for material characterization [1,2]. However, the interpretation of XPS spectra, based on the fitting of characteristic photoelectron lines, is far from straight forward. Although there are some attempts to make an expert system for the XPS data analysis (cf. [3] for instance), this complicated task is still mainly done by specialists, being strongly dependent on their overall skills and knowledge. Regardless the way of performing XPS spectra analysis, knowing energy resolution and other instrumental effects (detector linearity, transmission function, to mention the most important) is essential for proper data interpretation, just as it is for the optimal choice of the spectrometer parameters during the spectra acquisition.

Spectra acquisition in modern XPS systems is performed by hemispherical energy analyser operated in the fixed analyser transmission (FAT) mode. In this working mode of the spectrometer, the energy of electrons E_e is being decreased along the trajectory towards the detector: their kinetic energy is E_k at the moment of emission, and then becomes reduced to $E_e = E_{pass}$ while travelling along the optical axis of the analyser. Choice of the pass energy E_{pass} is a common way of tuning the spectrometer energy resolution. Information on instrument properties, mainly energy resolution, is necessary for making XPS measurements efficient: there is no point in increasing the energy resolution (by reducing E_{pass}) and consequently decreasing the analyser transmission if the lines are significantly broader than the instrumental function. Additionally, concerning the data analysis when a photoelectron line is resolved in several contributions by a fitting procedure, the instrumental function width should be used as a lower limit for the width of any contribution. Knowledge of the instrumental function is particularly important when XPS is used to measure valence band with the main goal to determine the position of the valence band maximum [4]. In these measurements instrumental effects introduce a broadening and thereby shift the apparent valence band onset

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towards lower binding energies. The only way to partially overcome this systematic error would be to deconvolute the instrumental function from the measured spectra.

Instrumental function of an XPS system represents a convolution of the instrumental function of an electron spectrometer, which can be very well described as a Gaussian [5], and the energy line profile of the X-ray source. The latter is typically considered to be Lorentzian, so that the instrumental function is expected to have Voigt profile. This is most probably the historical reason why pseudo-Voigt profiles are typically used for the fitting of photoelectron lines, apart from the fact that they work very well in practice. On the other hand, X-ray line profile in a SPECS XPS instrument with the monochromatic Al K_α X-ray source is actually a Gaussian, with a Full Width at Half Maximum (FWHM) equal to 167 meV [6]. Consequently, the instrumental function of this XPS system should also be a Gaussian with FWHM w_{XPS} equal to the square root of the sum of squares of the FWHMs of the X-ray beam profile (w_X) and the spectrometer instrumental function (w_S):

$$w_{XPS} = \sqrt{w_X^2 + w_S^2}. \tag{1}$$

In this paper, we measure w_S of the SPECS Phoibos 100 spectrometer for different pass energies and two entrance slits, with widths of 1 mm and 7 mm, respectively. This allows us to calculate the instrumental function of the whole XPS system, using the expression (1). Theoretical background and the corresponding experimental procedure for the measurement of w_S are presented in the forthcoming section. The experimental results, which include determination of the overall resolution of the XPS system and their discussion, are given in Section 3. Finally, a simple deconvolution procedure is introduced and employed for the data processing of valence band spectra taken from an air exposed silicon single crystal in order to demonstrate the usefulness of the determined XPS instrumental function.

2. Energy resolution of a hemispherical energy analyser operated in FAT mode

Relative energy resolution $\Delta E/E$ of a hemispherical energy analyser having the equilibrium trajectory radius R, and entrance and exit slit widths s_1 and s_2, is expressed in the frame of the 2nd order approximation as

$$\frac{\Delta E}{E} = \frac{s_1 + s_2}{4R} + \frac{\alpha^2}{4}, \tag{2}$$

where α is the analyser acceptance angle in the dispersive plane, and E is the energy of electrons travelling along the optical axis of the energy analyser [7]. The absolute resolution ΔE corresponds to FWHM of the spectrometer instrumental function, assuming it has triangular profile. However, the expression (2) works equally well for the Gaussian profile [8]. Therefore, it is still valid to a very good approximation for an analyser operating in FAT regime when E and ΔE are replaced by E_{pass} and w_S, respectively.

Let us now consider a photoelectron line taken by the SPECS XPS system that can be fitted to a single Voigt profile, the latter being a convolution of a Lorentzian and a Gaussian with respective widths w_L and w_G. Lorentzian component would then originate exclusively from the energy distribution, whilst the Gaussian is a convolution of the energy distribution component and the instrumental function of the XPS system having FWHMs w_N and w_{XPS}, respectively. Therefore, the Gaussian component of the measured line represents a convolution of three Gaussians having widths w_N, w_X and w_S.

Our Phoibos spectrometer does not have the exit slit. Its SPECS 2D CCD detector system consists of two multi-channel plates mounted in a chevron assembly, a fast P43 phosphor screen and a 12 bit CCD camera. Since the magnitude s_2 represents the camera resolution, being about 0.04 mm [9], its value in expression (2) can be readily neglected. In this case $w_S \approx E_{pass} \cdot S$, where $S = s_1/(4R) + \alpha^2/4$. Finally, the width of the Gaussian component w_G can be expressed as $w_G = (w_N^2 + w_X^2 + E_{pass}^2 \cdot S^2)^{1/2}$. Therefore, w_G^2 should be directly proportional to E_{pass}^2, with the slope S^2:

$$w_G^2 = C + S^2 \cdot E_{pass}^2, \tag{3}$$

where $C = w_N^2 + w_X^2$ does not depend on E_{pass}. Even if, due to any circumstance, the dependence in some range of E_{pass} is not linear, the change of w_G with E_{pass} would still correspond only to w_S. In that case, S can be readily calculated as

$$S = \frac{\sqrt{w_G^2 - C}}{E_{pass}}, \tag{4}$$

where C is obtained from fitting of the $w_G^2(E_{pass}^2)$ linear part dependence to the Eq. (3). In any case, once S is known, the instrumental function of the XPS system will be fully determined.

It was assumed so far that s_1 equals the entrance slit width, which is generally not correct. The process of electron transport from the sample to the entrance in the energy analyser is schematically presented in Fig. 1. A spectrometer working in the FAT mode is tuned to pass through along the analyser optical axis only electrons emitted with an energy $E_e = E_k$. The sample area from which the photoelectrons that can reach the detector are emitted, here denoted as emitting area, represents a cross-section of the area irradiated by X-rays and the acceptance area of the spectrometer (cf. Fig. 1a). The size of the emitting area is characterized by its characteristic dimension r_0. A solid angle in which the electrons with the kinetic energy E_k have to be emitted in order to reach the detector is determined by the opening angle α_0. The emitting area is an object for the electron-optical column situated between the sample and the entrance slit of the energy analyser, as shown in Fig. 1b. The electron optics decelerates electrons from their initial energy E_k to E_{pass}, and forms an image onto the entrance slit plane (cf. Fig. 1c). This image is characterized by its size i.e. linear dimension r, and the maximum opening angle of trajectories of electrons reaching the detector. The latter is actually the analyser acceptance angle, α. One of the main characteristics of the electron-optical system are its linear $M_r = r/r_0$ and angular $M_\alpha = \alpha/\alpha_0$ magnifications. If the image size is larger than the entrance slit width, we may safely consider s_1 as the entrance slit width; otherwise, $s_1 = M_r \cdot r_0$ [10,11].

According to the Liouville's theorem applied to the beam of charged particles, the product of the linear and the angular magnification equals the square root of the retardation ratio: $M_r \cdot M_\alpha = (E_k/E_{pass})^{1/2}$ [10–12]. Hence, the change of the retardation ratio could strongly influence the image size, r. In that case, s_1 in Eq. (2) will not be a constant when the retardation ratio is sufficiently low. Consequently, the parameter S will not be independent on E_{pass} either; its value will be lower than expected (under the assumption s_1 equals the entrance slit width), and the spectrometer resolution $w_S = S \cdot E_{pass}$ will be improved. At the same time, the angular magnification will not affect the energy resolution since the acceptance angle is independent on E_{pass} i.e. $\alpha \approx$ const. Reduction of M_α will actually increase α_0, and therefore enhance the spectrometer transmission.

The theoretical considerations presented so far imply that experimental determination of the parameter S is straight forward: one should measure a profile of a photoelectron line for different FAT modes and perform the above described data analysis. However, there are several conditions that a convenient photoelectron line has to fulfil:

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