

Processing of photoelectron spectra for advanced chemical analysis

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A procedure is proposed to process complex XPS spectra attained using a home-made X-ray photoelectron spectrometer without monochromatization of X-rays. The method includes convolution and fitting applied to Fourier transform of experimental spectrum. This spectrum is synthesized as a convolution of three functions related to Fourier transforms of natural lines, of electron analyzer instrumental function, and of exciting X-ray line shape. The validity of method has been checked by processing spectrum of gold in the region of valence band. The method has been applied to analyze composition of oxidized aluminum surface and surface of complex aluminum-magnesium oxide.

Предложен метод для обработки сложных XPS спектров, полученных с использованием рентгеновского фотоэлектронного спектрометра собственного изготовления, без монохроматизации рентгеновского излучения. Метод включает свертку и подгонку, применяемые к Фурье-образу экспериментального спектра. Этот спектр синтезируется как свертка трех функций, соответствующих Фурье-образам естественных линий, аппаратной функции анализатора электронов и формы возбуждающей линии рентгеновского излучения. Пригодность метода проверена путем обработки спектра валентной зоны золота. Метод применен для анализа состава окисленной поверхности алюминия и поверхности сложного алюминиево-магниевого оксида.

When analyzing a surface, one desires to know the elemental composition of the outermost atom layers of a solid and, if possible, a detailed information on chemical bonding states. X-ray photoelectron spectroscopy (XPS) is a well-established technique which in a principle can provide such information. This information has three levels of refinement: the simplest is the elemental and qualitative chemical analysis of the surface; the second has to provide quantitative chemical analysis of the surface; the third, and the most refined is the study of the material electronic structure (valence band, Auger parameters, etc.). To get the information corresponding to the first level, it is enough only to know the photoelectron peak position energy at an accuracy of 1 eV, but to the second and third levels, it is necessary to determine the peak position at an accuracy at least within 0.1 eV and to obtain the relative peak intensities. To meet these conditions is especially difficult when

spectra containing more than two unresolved peaks are to be treated. High advantage, in this case, is provided by using spectrometers equipped with monochromatic X-ray sources and providing total resolution of about 0.4 eV. The spectra obtained with such equipment contain no lines excited by X-ray satellites and exhibit a better signal-to-background ratio. On the other hand, when the monochromatized X-ray source is used, the positive charging of insulating materials due to photoelectron emission becomes so high that not only the acquisition of intended spectra becomes impossible but also a degradation in sensitivity and energy resolution often take place [1]. To compensate that charge which can attain 500 V for insulators, various charge compensation techniques are used. On the contrary, spectrometers without X-ray monochromator take the charging no more than 5–6 V due to wide X-ray beam and slow electrons from X-ray source window and allow to investi-

gate insulators without any additional charge compensation.

The spectra were obtained using a home-made X-ray photoelectron spectrometer equipped with a conventional Al X-ray source with a 7 μm Be foil window. The source was operated at 15 kV, with anode current of 20 mA. The analyzer was of the cylindrical mirror type with a retarding system, and was operated in constant-analyzer-resolution mode. The pass energy of the analyzer was 100 eV. The total energy resolution of spectrometer was 1.0 eV. For examinations, gold foil, naturally oxidized bulk aluminum and magnesium aluminate spinel (MgAl_2O_4) crystal preliminary etched with Ar^+ ions were used. The background pressure was better than $5 \cdot 10^{-8}$ Torr. The Shirley type inelastic background correction was applied to all experimental spectra before further treatment.

Despite of a rather large variety of high-resolution X-ray photoelectron spectrometers, the main part of the spectrometers now in use is still not equipped with X-ray monochromators. Also, even for spectra obtained with high-resolution spectrometers, the deconvolution procedure is used to improve resolution and determine areas of photoelectron lines [2]. The use of computers for photoelectron (PE) spectra processing during at least 30 years resulted in development of new algorithms and programs to get full information on physical and chemical properties of the sample surface from experimental spectrum. One class of these procedures is aimed at improvement in resolution of photoelectron spectra. Second wide class of procedures allows users to fulfill fitting of spectrum with contributing peaks.

We combine both, the some kind of deconvolution and fitting procedures, for the next reasons: first, these procedures are usually applied subsequently; second, the deconvolution methods do not allow to remove the broadening effects completely from spectrum, especially in spectra with low signal-to-noise ratio, i.e. spectra of chemical elements at low concentrations. In this procedure, we conducted fitting of spectra by components taking in consideration the total instrumental broadening. This allow us to omit the main problems related to application of deconvolution for real spectrum, but to obtain an improved resolution which usually could be get by deconvolution. The intrinsic, or natural, line shape of signal in X-PE spectrum can be presented by function $l(E)$, where E is the pho-

toelectron kinetic energy. The line shape actually observed, $f(E)$, is the convolution of $l(E)$ with the broadening function $k(E)$:

$$f(E) = l(E) \otimes k(E), \quad (1)$$

where \otimes denotes convolution operation, and $k(E)$ could be written:

$$k(E) = a(E) \otimes x(E), \quad (2)$$

where $a(E)$ is the electron energy analyzer instrumental function, $x(E)$ is the spectral distribution of the incident X-rays.

The analog of Eq.(1), taking into account Eq.(2) in Fourier transform theory, results in the expression:

$$F(\omega) = L(\omega) \cdot A(\omega) \cdot X(\omega), \quad (3)$$

where $F(\omega)$ is the Fourier transform of experimental spectrum:

$$F(\omega) = \int_{-\infty}^{\infty} f(E) \exp(2\pi i \cdot E\omega) dE. \quad (4)$$

At this step of treatment, we synthesized right part of Eq.(3) using analytical expressions of functions $L(\omega)$, $A(\omega)$ and $X(\omega)$.

The Fourier transform of single natural line shape was chosen in Lorentzian and Gaussian sum form

$$L(\omega) = I(\exp(-\omega \cdot (\gamma - iE_0)) \cdot (1 - \beta) + \beta \cdot \exp(-(\gamma\omega)^2)), \quad (5)$$

where γ is the FWHM of peak, E_0 is peak position, β is the coefficient of line shape.

The Fourier transform of electron analyzer instrumental function could be presented in Gaussian form by expression:

$$A(\omega) = \exp(-(\gamma_a\omega)^2), \quad (6)$$

where γ_a is Gaussian full width at half-maximum.

Finally, the Fourier transform of exciting X-ray line shape as the sum of four Lorentzian lines is

$$X(\omega) = \sum_{k=1}^4 I_k \exp(-\omega(\gamma_k - iE_k)). \quad (7)$$

Parameters used in Eq.(7) are listed in Table 1 [3] and were tested by Koenig et al. [4].

Due to procedure of spectra synthesis, we omit the main problem related to application of deconvolution: in most cases it results in nonphysical results [2]. To reduce the time needed for spectrum synthesis, we

Table 1. The energy distribution characteristics for Al K_{α} radiation. All lines assumed to be Lorentzian [3]

Line	Position relative to the α_1 line, E (eV)	FWHM, γ (eV)	Relative intensity, I
α_2	-0.416	0.50 ± 0.02	50
α_1	0	0.50 ± 0.02	100
α_3	9.65	0.83 ± 0.03	10.8 ± 0.2
α_4	11.64	0.83 ± 0.03	5.4 ± 0.1

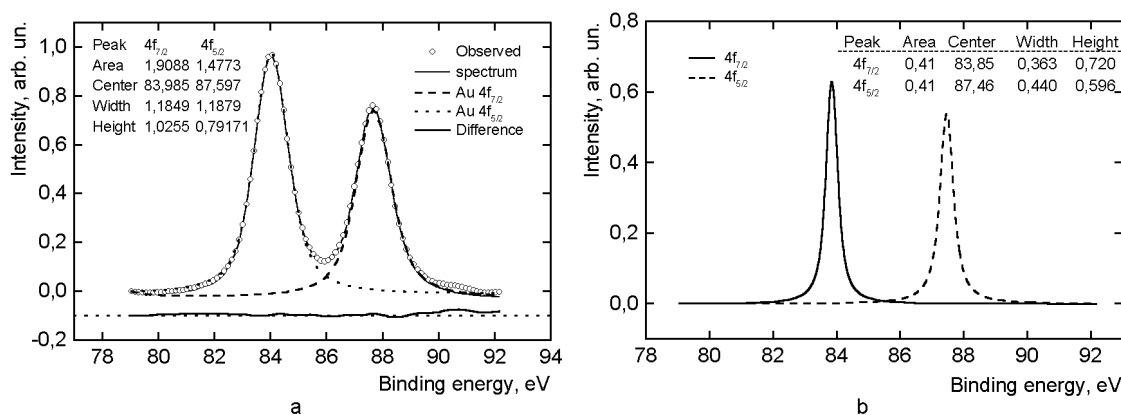


Fig. 1. Photoelectron spectrum of $4f$ gold doublet: (a), experimental with lines obtained by backward Fourier transforms of Eq.(3), (b), plotted from the analytical expression of backward Fourier transformation of function $L(\omega)$ Eq.(5).

use in fitting procedure Eq.(3) instead of Eq.(1). Moreover, since the values of functions described by Eq.(6) and Eq.(7) remain constant during fitting, those are calculated only one time before starting fitting. For additional time reduction, we apply comparison between experimental and synthetic spectra not to primary data but to their Fourier transforms. It is known from Fourier transform theory, that when we reduce number of harmonics used for backward Fourier transformation, we make least square smoothing of spectrum. This consideration and the fact that the function $A(\omega)$ decreases quickly, allow us to omit all harmonics in Eq.(4) for such ω where amplitude of $A(\omega)$ is less than 0.01 because the omitted harmonics contain only the noise.

After reaching satisfactory identity of left (experimental) and right (synthesized) parts of Eq.(3), we obtain the values of parameters in Eq.(5): I , E_0 , γ , β which describe X-ray photoelectron spectrum without instrumental broadening. Since the true instrumental function of electron energy analyzer was unknown, to get the parameter γ_a in Eq.(6), the treatment procedure was applied to well-known spectrum of gold

$4f$ doublet (Fig. 1). We have adjusted the γ_a value to obtain the FWHMs of these peaks as reported by S.Hufner and G.K.Wertheim [5]. So, we obtain value of FWHM of electron energy analyzer equal to 0.358 eV.

To check the reliability of the procedure, we carried out treatment of spectrum for gold valence band. This is a complex spectrum containing many features; it was described elsewhere [3, 5]. Fig. 2 shows result of our treatment, and the positions of spectral features (in eV) obtained by different techniques, are specified relative to the Fermi edge and shown in Table 2.

The results are in good agreement, and it should be noted that no any constraints were applied to peaks parameters.

Since this method, in general, is curve fitting method, the results, which could be obtained by this method, depend heavily on primary information involved into procedure. This information could be reflected in different types of constrains for different spectral lines, such as doublet splitting, line intensity ratios in doublets, etc. Using some of these constrains, we have treated Al2p spectrum of naturally oxidized bulk aluminum (Fig. 3). Low photoelectron Al2p lines cross-section, and the existence of carbon-

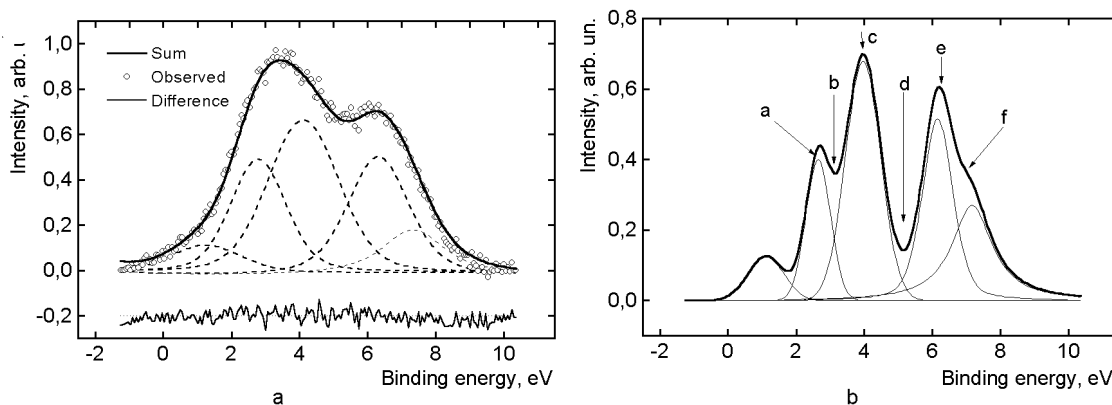


Fig. 2. Gold valence band spectrum: designations (a) and (b) are the same as in Fig. 1. Positions of spectral features in b are specified in Table 2.

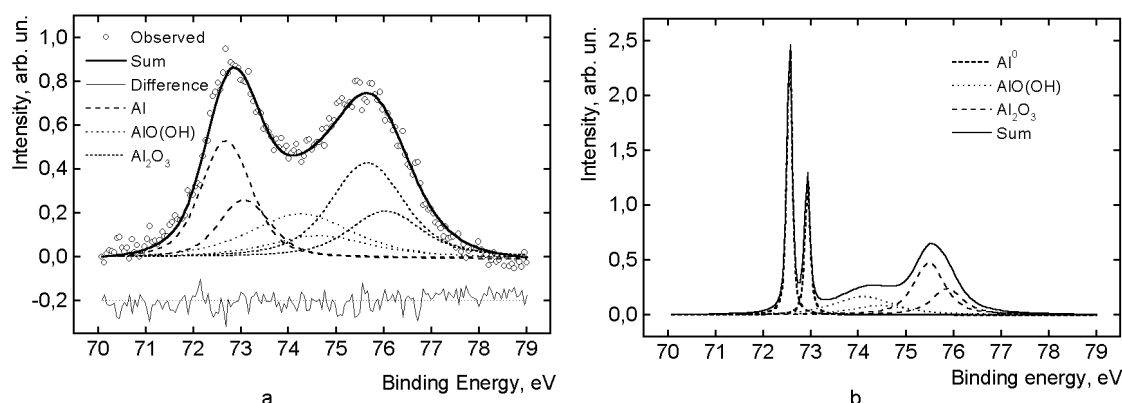


Fig. 3. Oxidized bulk aluminum Al2p spectrum, a and b are the same as for Fig. 1.

contaminated adsorbed layer have not allowed us to obtain this spectrum at a good S/N ratio.

Despite of that, the Al2p doublet with low splitting was resolved for Al metal state and FWHM of these lines was reduced to about 0.13 eV.

All deconvolution methods fail in treatment of spectra containing both photoelectron and Auger spectral lines. Using our

method which consists in convolution of intrinsic spectrum and broadening factors and constructing spectrum in line-by-line manner, we have treated the complex spectrum of Mg and Al photoelectron lines and Al KLL Auger line in MgAl₂O₄ oxide. Results of this treatment are presented in Fig. 4. This spectrum was recorded within a range wider than 100 eV and contains more than 200 points, whereas Fourier transform of

Table 2. Comparison of gold valence band features positions (in eV) in: spectrum obtained by using monochromatized X-rays, deconvoluted spectrum obtained at low resolution and spectrum fitted by proposed method

Feature	High resolution spectrum [2]	Deconvolution of low resolution spectrum [3]	Fitting of low resolution spectrum by the method proposed
a	2.6	2.6	2.7
b	3.3	3.4	3.2
c	3.8	4.0	4.0
d	5.4	5.5	5.2
e	6.2	6.05	6.2
f	7.2	7.1	7.1

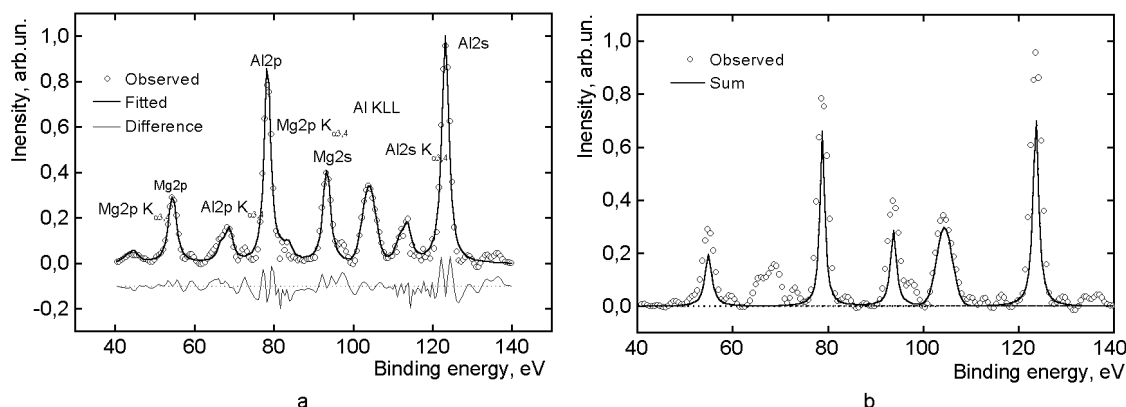


Fig. 4. Wide region spectrum of $MgAl_2O_4$ spinel crystal. a and b are the same as for Fig. 1.

this spectrum was cut to only 80 harmonics. By using the proposed techniques, we treat spectra with one exception: for Auger line, the Eq.(3) was taken without $X(\omega)$ factor. The treated spectrum is shown in Fig. 4b. From this spectrum, we obtained reliable widths of Al2s and Mg2s lines and value of Al Auger parameter is 1460 eV. The ratio of Mg and Al lines corresponds to stoichiometric composition of this oxide.

Thus, instead of usually used deconvolution of experimental spectra, we have proposed the synthesis of spectra by convolution of Fourier transforms of functions describing contributions into the width and shape of photoelectron lines and X-ray excited Auger lines to treat the complex photoelectron spectra. The Fourier transforms of synthesized spectra were compared with Fourier transforms of experimental spectra

to get fitting parameters. The developed treatment procedure was used to get reliable data on the composition and chemical states of atoms from photoelectron spectra of complex oxides.

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References

1. H.Tomizuka, A.Ayame, *Appl. Surf. Sci.*, **100/101**, 243 (1996).
2. G.K.Wertheim, *J. Electron Spectrosc. Relat. Phenom.*, **6**, 239 (1975).
3. N.Beatham, A.F.Orchard, *J. Electron Spectrosc. Relat. Phenom.*, **9**, 129 (1976).
4. M.F.Koenig, J.T.Grant, *J. Electron Spectrosc. Relat. Phenom.*, **33**, 9 (1984).
5. S.Hufner, G.K.Wetheim, *Phys. Rev.*, **B11**, 678 (1975).

Обробка фотоелектронних спектрів для поглибленого хімічного аналізу

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Запропоновано метод для обробки складних XPS спектрів, одержаних з використанням спектрометра рентгенівського фотоелектронного спектрометра власного виготовлення, без монохроматизації рентгенівського випромінювання. Метод включає згортку та підгонку, які застосовуються до Фур'є-образу експериментального спектру. Цей спектр синтезується як згортка трьох функцій, що відповідають Фур'є-образам природних ліній, апаратній функції аналізатора електронів та форми збуджувальної лінії рентгенівського випромінювання. Придатність методу перевірено шляхом обробки спектра золота в області валентної зони. Метод застосований для аналізу складу окисленої поверхні алюмінію та поверхні складного алюмінієво-магнієвого оксиду.