ThinFilmsAnalysisMPEI – Software for XPS Analysis of Multilayer Multicomponent Films

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Abstract. The work presents ThinFilmsAnalysisMPEI software implementing the method of chemical and phase depth profiling based on photoelectron spectra interpretation, described in paper [1]. Efficiency and productivity of the software for the problem of chemical and depth profiling is shown on examples of synthetic and experimental spectra.

1. Introduction
One of non-destructive methods of thin films profiling is X-ray photoelectron (XPS). By means of XPS, surface chemical and phase profiling is performed. Non-destructive layer chemical and phase profiling may be carried out on the base of the method [1] enabling to obtain layer profiles with a submonolayer accuracy from XPS data.

Requirements for software for photoelectron spectra interpretation become more and more complicated. For chemical and phase depth profiling, it is necessary to solve problems of spectral lines deconvolution into partial peaks (determining of peak intensities and positions) and subtraction of background generated by multiply inelastically scattered electrons. Solution of these problems must base on the theory of multiple elastic and inelastic photoelectron scattering in an inhomogeneous multilayer medium.

The physical principles leading to shifts and broadening of peaks generated by elastically scattered electrons are not the base of the available software for photoelectron spectra treatment (e. g. CasaXPS [2], MultiQuant [3], Unifit [4]). For background subtraction, the Shirley and Tougaard methods are used. These methods don’t consider multilayer and multicomponent structures of real solid surfaces. As a result, the quality of line deconvolution into partial peaks depends on the researcher’s experience, intuition and knowledge about features of photoelectron peak generation.

This work presents ThinFilmsAnalysisMPEI software. This software implements the method for chemical and phase depth profiling based on photoelectron spectra interpretation [1].

2. Characterisation of ThinFilmsAnalysisMPEI software
ThinFilmsAnalysisMPEI consists of four cases: Analysis technique, Experimental setup, Spectrum modeling, Material characteristic (see Fig. 1).

ThinFilmsAnalysisMPEI software is written in an object-oriented language MatLab and uses MatLab matrix libraries. The graphical user interface (GUI) of ThinFilmsAnalysisMPEI (see Fig. 2) provides the user access to different objects and functions in the form of graphical on-screen components (windows, buttons, lines, etc.). Working with GUI, the user has unlimited access to all visible on-screen objects.
2.1. “Analysis technique” case
ThinFilmsAnalysisMPEI software implements the following XPS methods: Element analysis, Quantitative analysis, Depth profile analysis of chemical and phase composition.
Element analysis enables to determine elemental composition of the target on the base of binding energies corresponding to certain photoelectron peaks (see Fig. 2). The binding energy values may be chosen from the commonly accepted data sets of Handbook XPS or Bearden Burr or Gwyn Williams. The data base for binding energies used in XPS and kinetic energies used in Auger electron spectroscopy (AES) are logged in Material characteristic case.
To perform quantitative analysis of a photoelectron spectrum, after background subtraction, position of the peaks generated by elastically and inelastically scattered photoelectrons is determined. According to these peaks’ intensity, considering the sensitivity factor, relative elemental concentrations are found. The quantitative analysis may be performed within the homogeneous mixing model framework using the overview spectra or by analysis of single spectra. The sensitivity factors may be chosen from the commonly accepted data sets of Wagner or Scofield, which are available in Material characteristic case.
The method for depth profile analysis of chemical and phase composition of multi-component and multi-layer samples includes: (1) a method for background subtraction accounting for depth non-uniformity of electron energy losses; (2) a method for photoelectron line decomposition into elementary peaks, which accounts for physical nature of the decomposition parameters; (3) a joint solving of both background subtraction and photoelectron line decomposition problems; (4) a target model; (5) a simple formula for layer thickness extraction for multi-element and multi-layer sample.

2.2. “Experimental setup” case
In Experimental setup case, programs for creation and control of the photoelectron spectra database. The program can read measured spectra in formats VAMAS or SpexLab. The following experimental data hierarchy is supported: 1) Experiments, 2) Series, 3) Group, 4) Region. For each spectrum,
information on experimental condition and geometry, the X-ray gun and spectrometer parameters is recorded into the database. In Experimental setup case, programs enabling calibration of spectra and correction of peak shift are included.

Figure 2. Graphical user interface of ThinFilmsAnalysisMPEI software

2.3. “Spectrum modeling” case
A photoelectron spectrum is generated by non-scattered, multiply elastically and inelastically scattered photoelectrons. Information on chemical and phase depth profile of the target may be obtained analyzing peaks of non-scattered and elastically scattered photoelectrons (line-shape analysis). In this case, contribution of inelastically scattered photoelectrons is considered as undesirable background. Accuracy of further analysis depends on the background subtraction method. For multilayer multicomponent targets, the analysis is significantly complicated because elastically scattered electron peaks superimpose each other and inelastically scattered electron peaks.

To describe an X-ray photoelectron spectrum as a whole, photoelectron peaks (Elastic spectra) generated by non-scattered and elastically scattered electrons and background (Background) generated by inelastically scattered photoelectrons are distinguished. Elastic spectra consist of spectral lines (Lines). A line may consist of few related groups of peaks (Multiple Peaks). A spectral line structure in XPS may be complex due to spin-orbit interaction, chemical shift and various satellites. Moreover, peak shape and width depend also on many factors and the peaks themselves may overlap. For example, line Nb 3d may contain up to six related peak groups (Multiple Peaks) as far as niobium can generate five different oxides. As a result, a spectral line may contain up to 30 partial peaks. A partial peak shape (Single Peak) can be described by the following functions: Gaussian, Lorentzian, Doniach-Sunjic, a sum of Gaussian and Lorentzian, Voigt (convolution of Gaussian and Lorentzian), VoigtDS (convolution of Gaussian and Doniach-Sunjic).

For exact deconvolution of a complex measured line, parameters influencing onto shape and position of partial peaks (Single Peak) should be known: values of energy and relative doublet peak structure intensity (energy of spin-orbit interaction, ratio of spin-orbit splitting line intensities of a photoelectron level, peak asymmetry parameters, chemical shift energies), values of peak half-widths at half-heights in Multiple Peaks, relative intensities and energy shifts of satellites (these parameters depend on the X-ray gun anode material). If all this is determined, the number of varied parameters will be minimized and related peak intensities (Multiple Peaks) may be found by means of fitting algorithms, i.e. the Levenberg-Marquardt algorithm. In ThinFilmsAnalysisMPEI, parameters influencing onto shape and position of partial
peaks (Single Peak) are calculated from the physical model of a spectral line (see more details in [1]). The parameters of the physical model are determined in Material characteristic case.

The background may be composed of contribution of either a Shirley- or a Tougaard- or a Lubchenenko-type contribution. The Shirley method is purely mathematical, it doesn’t consider any features of inelastic electron scattering in solid. That leads to an unpredictable computing accuracy. The Tougaard method results from an approximate solution of the problem of multiple electron scattering in solid. This solution is based on assumption that the differential inelastic electron scattering cross-section is depth-independent. However, if even the parameters describing the inelastic electron scattering cross-section in bulk are well-fitted, this method will lead to an error because of it doesn’t consider the difference of inelastic scattering in bulk and on surface. The background subtraction method proposed by Lubchenenko [1] is based on a solution of the multiple inelastic photoelectron scattering problem considering inhomogeneity of elastic scattering in bulk and on surface. Inelastic scattering parameters and cross-sections in bulk and on surface of the substance are determined in Material characteristic case.

Spectral modelling can be performed for a semi-infinite target, multilayer multicomponent films, a target covered with islets grown by the Stranski–Krastanov or Frank-van der Merwe type.

2.4. Material characteristic case

In Material characteristic case, the databases (Database): Periodic Library (names of elements, position in the Mendeleev periodic table, the number of electrons in a neutral atom, atomic mass), Material characteristics (for each element: density, atomic concentration, number of valence electrons, forbidden band width by 300 K, plasmon energy, ionization potentials, chemical shift energy per unit of oxidation level, covalent radius, atomic radius), XPS (for all elements up to 92 amu: photoelectron binding energy, sensitivity factor), AES (for all elements up to 92 amu: Auger electron kinetic energy).

This case includes programs for calculation of integral characteristics: mean free paths — elastic (Elsepa), inelastic (Seah–Dench, Jablonski, Tanuma–Powell–Penn, Gries) and transport (Elsepa, Lubchenko); effective attenuation length (Jablonski, Jablonski–Powell, Seah–Gilmore); integral scattering cross-sections — elastic, transport and inelastic; single scattering albedo; single scattering transport albedo; mean energy losses per unit of length; photoionization cross-section (Yeh–Lindau); sensitivity factor (Scofield, Wagner), also for differential characteristics of photoelectron scattering in substance: differential cross sections — elastic end inelastic. To calculate elastic indicatrices, types Elsepa, Rutherford and HG may be chosen (Elsepa is the indicatrix calculated by the methods of Salvat; HG is the model indicatrix calculated by the Heney–Greenstein formula; Rutherford is the model indicatrix calculated for shielded Rutherford backscattering). To calculate inelastic and elastic indicatrices, types Werner, Drude, Tougaard, Model may be chosen.

3. Program testing with synthetic and measured spectra

3.1. Testing with synthetic spectra

In this section, testing procedure for software and demonstration of efficiency and productivity of chemical and phase profiling implemented in ThinFilmsAnalysisMPEI with the help of test spectra proposed by Seah and Brown [5] will be shown.

The following tests were performed: 1) correctness of reading in VAMAS format; 2) efficiency of background subtraction procedures; 3) ability of effective and correct peak separation in strongly overlapping peak structures by the deconvolution procedure.

First, a correct I/O (input/output) of VAMAS format in different presentations of spectra was demonstrated. Tests of accuracy for simulated C 1s peak structures were performed. Figure 3 shows line C 1s deconvolution for a PMMA (polymethylmethacrylate) target. The Shirley background was used. The spectral line was decomposed into four partial peaks. Each partial peak was described by the Voigt profile. Peak parameter fitting (binding energy, half-width at half-height, intensity) was performed by a MatLab function fit (included in Curve Fitting Toolbox). The peak parameters and relative intensities are shown in Fig. 3. The relative error of deconvolution didn’t exceed 0.5% at the full spectrum width. Computing time on a modern PC equaled fractions of a second.
3.2. Testing with measured spectra

In this section, testing procedure for software and demonstration of efficiency and productivity of chemical and phase profiling implemented in ThinFilmsAnalysisMPEI with the help of measured spectra of an air-oxidized niobium thin film (10 nm thick) on a silicon substrate will be shown.

The X-ray photoelectron spectra were recorded by the module of electron-ion spectroscopy on the base of Nanofab 25 (NT-MDT) platform. The spectra were recorded by an electrostatic hemispherical energy analyzer SPECS Phoibos 225. The X-ray gun had a Mg anode and the energy analyzer was operated in a FAT (Fixed Analyzer Transmission) mode. For survey spectra, the slowdown energy in the energy analyzer lens was set $E_{\text{pass}} = 80$ eV, for detailed spectra $E_{\text{pass}} = 20$ eV.

The following tests were performed: 1) correctness of reading in SpexLab format; 2) efficiency of background subtraction procedures; 3) ability of effective and correct peak separation in strongly overlapping peak structures by the deconvolution procedure; 4) determination of the chemical and phase depth profile.

First, a correct I/O of SpexLab format in different presentations of the spectra was demonstrated. Spectral line Nb 3d was studied (see Fig. 4). The background was subtracted using the Lubenchenko method. It was taken into consideration that a niobium oxide layer about 9 nm thick had been deposited upon the niobium layer and a hydrocarbon layer about 1 nm thick on the oxide layer. Inelastic scattering characteristics in bulk and on surface were different. By the spectral line deconvolution, a model of a related peak groups (Multiple Peaks) was used. Each group of peaks had a doublet structure and satellite peaks ($K\alpha_1$, $K\alpha_2$, $K\beta_3$, $K\beta_4$, $K\beta$) resulting from nonmonochromaticity of the X-ray gun. The number of partial peaks in a group equaled 10. Three groups of peaks were found related to niobium oxide phases: Nb$_2$O$_5$, Nb$_2$O and pure niobium. The peak parameters and relative intensities are given in Fig. 4. The relative error of deconvolution didn’t exceed 0.6% at the full spectrum width. Computing time on a modern PC equaled fractions of a second. After decomposition, the depth profile was calculated. As far as the niobium film had been air-oxidized, the oxidation level of niobium decreased with depth. The upper oxide layer was divided into two sub-layers respectively: the uppermost consisted of Nb$_2$O$_5$, the lower one of Nb$_2$O. The XPS probing depth for this target equaled 11 nm. As far as the silicon peak was not found in the spectrum, there were three layers within this probing depth: a thick niobium layer, an intermediate layer of Nb$_2$O and the upper layer of Nb$_2$O$_5$. The layer thicknesses are given in Fig. 4.
Figure 4. XPS spectra. Target: NbOx/Nb(10 nm)/Si. Line Nb 3d. Dots: experimental data. Solid line: calculation. Area: separate calculated peaks. Dotted line: Lubenchenko background. Single Peak Type: VoigtDS. The errors are shown below the curves of spectrum and components.

4. Conclusion
This work presents ThinFilmsAnalysisMPEI software. In this software, a method of chemical and phase depth profiling on the base of photoelectron spectra interpretation [1] is used. This method is based on the background subtraction method considering inhomogeneity of inelastic scattering with depth and the method of line deconvolution into partial peaks according to the physical model of photoelectron line generation.
ThinFilmsAnalysisMPEI software was tested with the help of synthetic spectra by Seah and Brown [5] and real measured spectra. Efficiency, accuracy and productivity of ThinFilmsAnalysisMPEI software was shown.

5. References
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