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XPS MultiQuant: multimodel XPS quantification software

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A program for quantitative evaluation of x-ray photoelectron spectra has been developed to serve as a practical tool for surface chemists. The program uses the 'classic' approach of quantification and requires as input the integrated intensities of the measured XPS lines. The usual correction methods and factors can be applied and controlled independently. All necessary basic data for calculations are integrated into the main library of the program. Besides the usual 'infinitely thick homogeneous sample' geometry model, the program is able to calculate models for layered structures, both on flat and curved surfaces. Calculation for several samples or experimental data sets can be done together. Results can be presented in several forms, such as atomic %, atomic ratio, oxide molar ratio, etc., and can be stored, printed and charted. Data can be labelled and annotated. XPS MultiQuant is equipped with a user-friendly interface, full text help system and a 'wizard' for easy set-up of calculations. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: x-ray photoelectron spectroscopy; XPS; ESCA; quantification; MultiQuant

INTRODUCTION

Quantitative evaluation of x-ray photoelectron spectra is a major issue in surface characterization. Numerous methods, models and data sets have been developed and published but usually only the simplest ones are built into the data systems used for everyday work. The quantification capabilities of these programs are very limited; their supplied sensitivity factor sets do not take into account a set of factors affecting accurate quantification, like precise control of overlayer effect, variation of inelastic mean free path (IMFP) with the material of the sample, etc. The aim of developing the present XPS MultiQuant program was to give a practical tool to the surface chemist to produce reliable analytical results in most cases. The program uses the 'classic' approach of quantification and requires as input integrated intensities of the measured XPS lines. It serves as a 'toolbox' of different quantification methods where the user is responsible for applying and combining separate 'tools'.

Application of the present knowledge on quantification is based on cross-section (theoretical or experimental) values, with correcting factors for contamination, IMFP, etc., providing more accurate results. The proposed program is a tool to perform all these calculations efficiently.

Quantification models

The XPS intensity data are always sensitive to the sample geometry: implicitly or explicitly, a geometry model is applied. Two different sets of quantitative calculations can be performed using the integrated XPS intensity data.

Homogeneous model

When the chemical composition of the surface is required, usually the 'infinitely thick homogeneous sample' model is used. The applied sensitivity factor should account for corrections for the photoionization cross-section, the IMFP, angular distribution, analyser transmission and surface contamination. The results should also be normalized in various ways.

Structured models

When the surface of the sample is covered by one or more thin overlayers (the whole structure should be thinner than the information depth of the XPS measurement) and the compositions and arrangement of these layers are known, then the thickness of the layers can be calculated from the photoelectron intensities. The well-known model for planar surfaces can be extended for calculating curved (spherical or cylindrical) surfaces[1,2] and also for surfaces with non-continuous layers ('islands'). In these cases, the applied sensitivity factors should also correct for cross-section, angular distribution and analyser transmission; handling of the IMFP and contamination is explicit. The presented program can handle all of the above requirements.

EXPERIMENTAL

X-ray photoelectron spectra included in the examples were recorded on a Kratos XSAM 800 spectrometer in fixed retarding ratio mode (FRR = 20) using Mg $K_{\alpha 1,2}$ (1253.6 eV)

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excitation. The base pressure of the analysis chamber was better than 10^{-9} mbar. Peak areas were obtained by the Kratos Vision 1 software after Shirley background subtraction.

CHARACTERISTICS OF THE PROGRAM

The features of the program are summarized in Table 1. The program requires only the input of the integrated intensity values of the measured XPS lines. All necessary basic data, like theoretical and experimental cross-sections, asymmetry parameters, line energy data, etc., are provided by the attached library. One of the basic features of the program is that all terms of the sensitivity factors (cross-section, angular correction, IMFP correction, analyser transmission and contamination correction) can be selected independently and can be overridden manually at any stage of the calculation.

Cross-sections and sensitivity factors

Five sets of theoretical and experimental cross-section and sensitivity factor data are included in the library.[3–7] Any data from other sources can also be applied. When sensitivity factors are entered directly, all redundant correction features can be switched off. The applicability of the data sets is expanded by the option of splitting the cross-section of the doublet lines into its components.

Angular correction

The asymmetry parameter data of Ref. 8 for Mg K_α and Al K_α excitations are included in the library.

IMFP correction

The built-in IMFP correction methods are divided into two groups. The members of the first group supply numbers proportional to the IMFP, thus they can be used routinely for the homogeneous model calculations. The members of the other group supply the real IMFP values, thus they can be used to calculate the IMFP data for use with the structured models.

Transmission correction

Beside the common predefined transmissions, like FAT or FRR, exponential and polynomial functions with separate coefficient sets for different kinetic energy ranges can be applied to describe any complicated analyser transmission.

Contamination correction

The factor for the contamination correction can be constant, as proposed in Ref. 4, or a function of the concentration of the carbonaceous contaminant.[9]

The results can be presented in various normalized forms: *atomic %, atomic ratio, oxide molar %, oxide molar ratio, mass %*, etc. When 'percentage' type results are selected, any of the elements can be omitted from the 100% sum, which is useful for direct comparison of some selected elements or for omitting the carbon of the total composition if it is only a contamination on the sample. Any of the elements can be selected as the basis for the 'ratio' type results, which directly supplies the coefficients of the chemical formulae. When an 'oxide' type normalization is selected, the oxygen balance is also calculated, which is the ratio of the measured and calculated (required by the specified chemical formula) oxygen concentration, indicating directly the relative oxygen deficiency or surplus.[10] Mass concentrations can also be calculated, which may be useful for industrial applications. Elements of the sample being present in different chemical states can be calculated separately but can be summed up easily, as necessary.

The program can handle up to 20 elements, including the different chemical states, which is satisfactory for most practical applications. Calculation of several samples or experimental data sets, up to 40 experiments (e.g., a series of ion bombardments or heat treatments, etc.), can be performed simultaneously. Several types of labels can be attached to the experiments to hold every necessary auxiliary data, such as sample name, tilt angle, temperature, time, etc. Data and results can be stored in files for further use, and exported to other programs. The set of experiments can be charted as a dependence plot of various parameters (labels), e.g., depth profiles.

Structured models

Before the thickness calculation of the structured models, the sample structure must be defined by specifying the number and compositions of the layers and other important data, like molecular weight, density and IMFP. The entered model data is thoroughly tested both for value ranges and consistency. Calculation of the layer thickness is performed either manually, by interactive iterations, providing numeric and graphical aids for comparing the calculated and measured data, or automatically, by a non-linear parameter fitting procedure using a modified Levenberg–Marquardt algorithm.

The XPS MultiQuant can run under 32-bit Windows operating systems and is equipped with a user-friendly interface (Fig. 1). A 'wizard' is available to guide unfamiliar users through the different phases of setting up a calculation by giving step-by-step instructions.

The program is also furnished with a full text, searchable online help including brief description of the built-in methods and data, literature references and application examples.

On advanced personal computers, the program is extremely fast; calculation with maximum number of input data (20 elements and 40 experiments) is done within one second. A few seconds are required to fit the parameters of the structured models calculations.

The program can be downloaded from the website: http://www.chemres.hu/aki/XMQpages/XMQhome.htm.

Relationship with other programs

XPS MultiQuant is a standalone quantification program which can be used routinely, together with the XP spectrum processing packages, to improve the flexibility and precision of the quantitative calculation. It can be applied for sophisticated calculation of layered samples (including its

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Table 1. Summary of the independently selectable features of the *XPS MultiQuant* program

Feature	Options	References	Remarks
Quantification models	Homogeneous	17, 18	
	Layers-on-plane	17, 18	
	Layers-on-sphere	1, 2	
	Layers-on-cylinder	2, 10	
	Islands-on-plane	10	
	Islands-on-sphere	10	
	Islands-on-cylinder	10	
Excitation sources	Mg K_α		[a] Excitation energy is supplied by the user.
	Al K_α		
	Other[a]		
Cross-section or sensitivity factor sets	None[a]		[a] Sensitivity factors or cross-sections are supplied by the user.
	Scofield	3	
	Evans	4	
	Wagner	5, 17	
	Nefedov	6, 7	
IMFP correction	None		[a] For homogeneous model.
	Explicit[a,b]		[b] For structured models to calculate explicit IMFP values.
	Exponential[a]		
	Seah–Dench[a,b]	17, 19	
	Jablonski[a]	20	
	Tanuma–Powell–Penn[b]	21	
	Gries[b]	21	
Angular correction	None		
	Reilman	8	
Elastic scattering correction	None		
	Ebel	22, 23	
Contamination correction[a]	None		[a] For structured models contamination correction can be implemented by defining an explicit contaminant layer.
	Explicit		
	Evans	4	
	Mohai	9	
Analyser transmission correction	None		[a] Exponential or polynomial functions with separate coefficient sets for different kinetic energy ranges.
	FRR (CAE)		
	FAT (CRR)		
	Exponential File[a]	23	
Result normalization	Atomic per cent		[a] The 'oxygen balance' is calculated.
	Atomic ratio		
	Oxide molar per cent[a]	10	
	Oxide molar ratio[a]	10	
	Mass per cent		
	Mass ratio		
	Oxide mass per cent[a]	10	
	Oxide mass ratio[a]	10	

unique curved surface models) if the structure is known and the intensity data supply sufficient information. For a lack of this information, a special approach is necessary, as performed by QUASES.[11]

APPLICATION EXAMPLES

The methods built into the program are widely known and accepted and do not require further verification; only a few examples are given below.

Contamination correction

XPS data were measured on a thermally oxidized Si wafer. The sample was totally oxidized and no elemental silicon could be detected. It was treated by low-pressure oxygen plasma to remove residual carbon and reach the stoichiometric Si : O = 1 : 2 ratio. After measuring the clean state of the sample, hydrocarbon contamination of increasing thickness was deposited by casting of polystyrene from benzene solution in subsequent steps. The compositions of the samples (atomic ratio) were calculated with different

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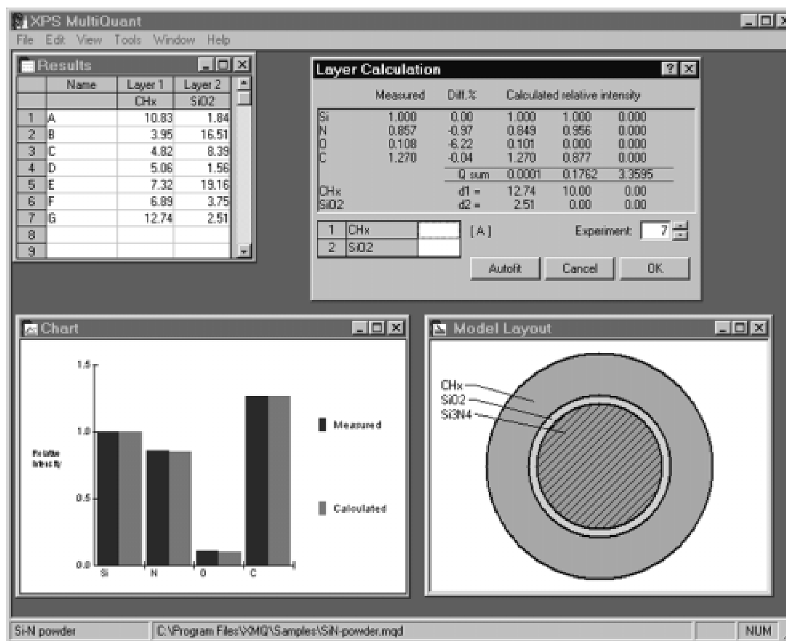

Figure 1. The window of XPS MultiQuant at fitting of layer thickness data using the *Layers-on-sphere* model. The measured and calculated intensity values are compared graphically and numerically. The layout of the model with the actual thickness values also can be displayed.

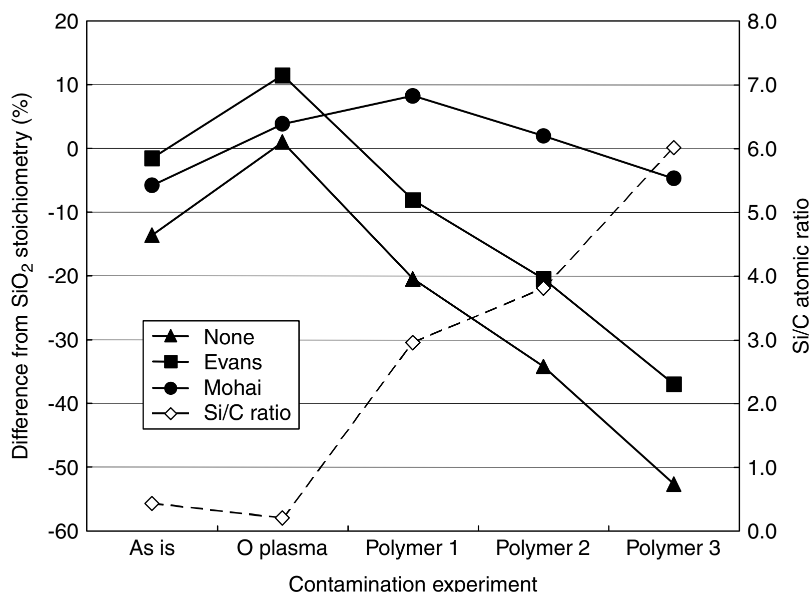

Figure 2. Comparison of the effect of different contamination correction methods on stoichiometric SiO_2 with increasing carbonaceous contamination (methods are described in Refs 4 and 9).

contamination correction methods.[9] Without applying such corrections, a substantial error is introduced as illustrated in Fig. 2.

Oxygen balance

Cr–O–Si cermet films are widely applied in microelectronics devices. Such layers were prepared by RF-sputtering of a Cr : O : Si target with a nominal atomic ratio of 1 : 1 : 1 onto thermally oxidized silicon wafers. XP spectra of the characteristic lines (Cr 2p, Si 2p, O 1s, C 1s) were recorded.[12,13] Ion bombardments were performed by 2 keV Ar^+ ions. Composition, expressed in *Oxide molar ratio*, was calculated for assumed combinations: $Cr_2O_3 + SiO_2$, $Cr_2O_3 + Si$ and $Cr + SiO$. The *Oxygen balance*, the ratio of the measured and calculated (according to the assumed 'stoichiometric' formula) oxygen concentrations, is depicted in Fig. 3 as a function of the bombardment time. The chart revealed that the top surface is totally oxidized, i.e., $O_{obs}/O_{cal} \approx 1$ for the assumed $Cr_2O_3 + SiO_2$. After 10 min bombardment, the top layer is removed and the former composition gives unrealistic oxygen deficiency. The composition of the layer is close to either of the $Cr_2O_3 + Si$ or $Cr + SiO$ (or also $CrO + Si$) supposed structures. Further bombardment does not change the composition. Chemical shifts of the

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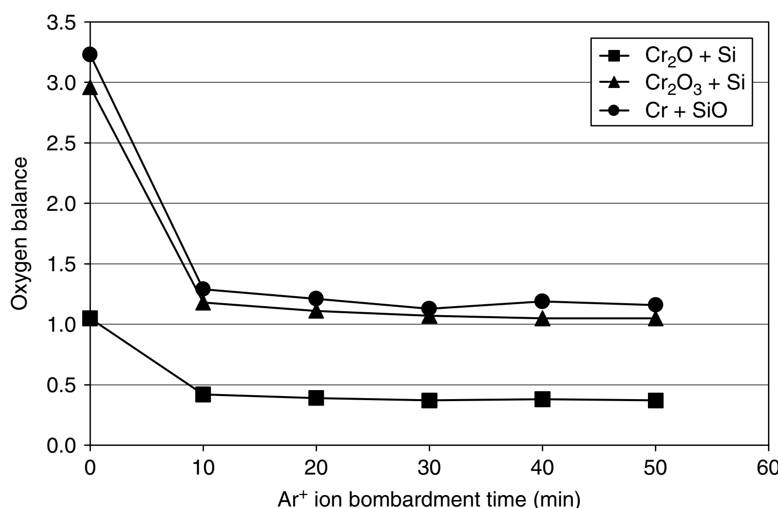

Figure 3. The oxygen balance values of the Ar^+ ion etched Cr–O–Si cermet films calculated for three different supposed surface compositions.

photoelectron lines will determine the correct chemical structure but this method can reduce the choice, discard unrealistic combinations and, by this, assist the peak decomposition procedure.

Overlayers

Lead arachidate Langmuir–Blodgett films with two monomolecular layers were deposited on trimethyl-silylated glass substrates.[14,15] XP spectra of the O 1s, C 1s, Pb 4f and Si 2p lines were recorded. The completeness of the salt formation was assessed by the normalized intensity ratio of the carboxylic (–COO–) type carbon component with C 1s BE at about 288.5 eV and that of the Pb cation. The *Layers-on-plane* model was applied with the following arrangement: the lead-arachidate monolayer was considered as two layers due to the dissimilar nature of the two parts of the molecule. The contribution of the silyl groups was neglected. The calculated monolayer thickness was 27.5 Å while the reported thickness is 28 Å.[16]

CONCLUSIONS

The XPS MultiQuant program is a fast and universal tool for the surface chemist ranging from daily routine analysis to sophisticated research measurements. A wide range of built-in methods and a library of basic data are offered together with several independently controllable correction features providing accurate results. The integral intensity values of the spectral lines are the only input required. Results can be presented in various forms.

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