Background Subtraction for Quantitative XPS

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Abstract

Potential errors (i.e. error bars) in quantitative surface analysis by XPS are extremely high unless some information is available on the in-depth concentration profile. A new formalism aimed at solving this problem will be discussed The formalism which relies on analysis of the measured XPS peak shape over a wide energy range gives non-destructively a quantitative analysis of surface nano-structures. Examples on the practical application, in the form of a commercially available software package QUASES™, is given.

1. Introduction.

Determination of the quantitative surface chemical composition by XPS relies on several factors like for example knowledge of photoionization cross sections, inelastic electron mean free paths, and influence of elastic electron scattering [1]. The most serious problem giving rise to the largest contribution to errors, is however likely to be assumptions made on the in-depth distribution of atoms. This is so because the measured peak intensity may well vary by orders of magnitude depending on the in-depth profile. Now, in practice the in-depth atomic distribution is never known when sample is analyzed, because if it were, it would be a waste of time, effort, and money to perform the analysis. It is then usually assumed that the surface region is homogeneous up to a depth of a few nano meters [1]. This assumption may result in enormous errors in quantification [2,3].

In recent years, much effort has therefore been devoted to the development of an improved formalism for quantitative surface analysis. The fact that the shape of the energy spectrum depends characteristically on the depth of origin of the x-ray excited electrons has led to the formulation, by Tougaard et al [2-6], of a new technique for quantitative XPS which also provides quantitative information on the surface nano structure of the solid.

The extent to which the peak intensity and peak shape depends on the in-depth concentration profile may be illustrated by the spectra in Fig.1. Here a thin (~1 nm thick) gold layer was evaporated onto a nickel substrate [7]. The Au4d core electrons excited by Al-Kα radiation were measured. The spectra show the development of the peak intensity and peak shape as various amounts of nickel (on the order of ~1 - 5 nm) were evaporated on top of the gold-nickel structure. From this example, it is evident that the error in quantification may easily reach several hundred

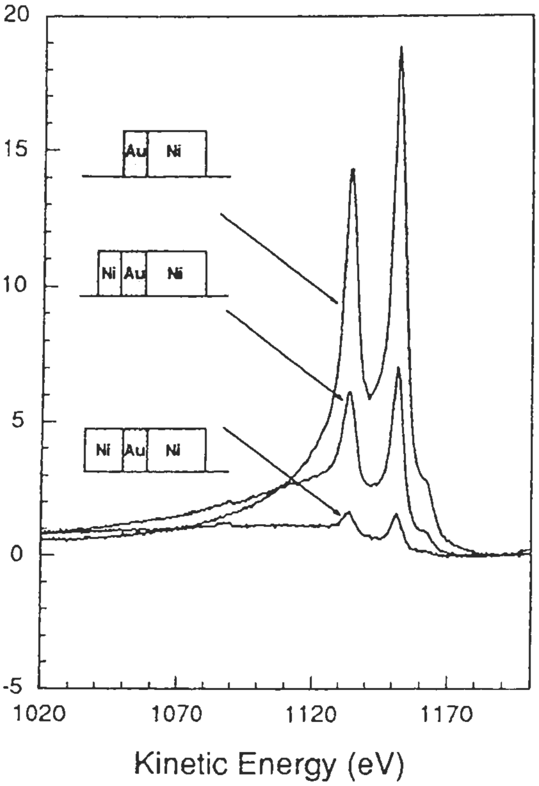


Figure 1. Spectra in the Au4d energy region from a sample produced by evaporating layers of gold and nickel on top of a nickel substrate [7].

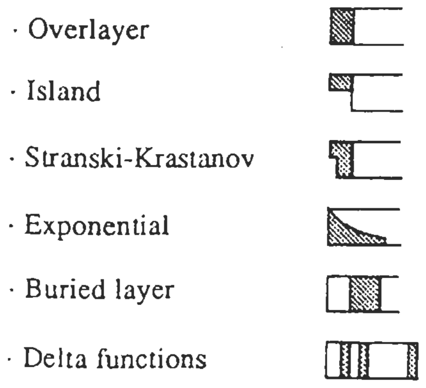


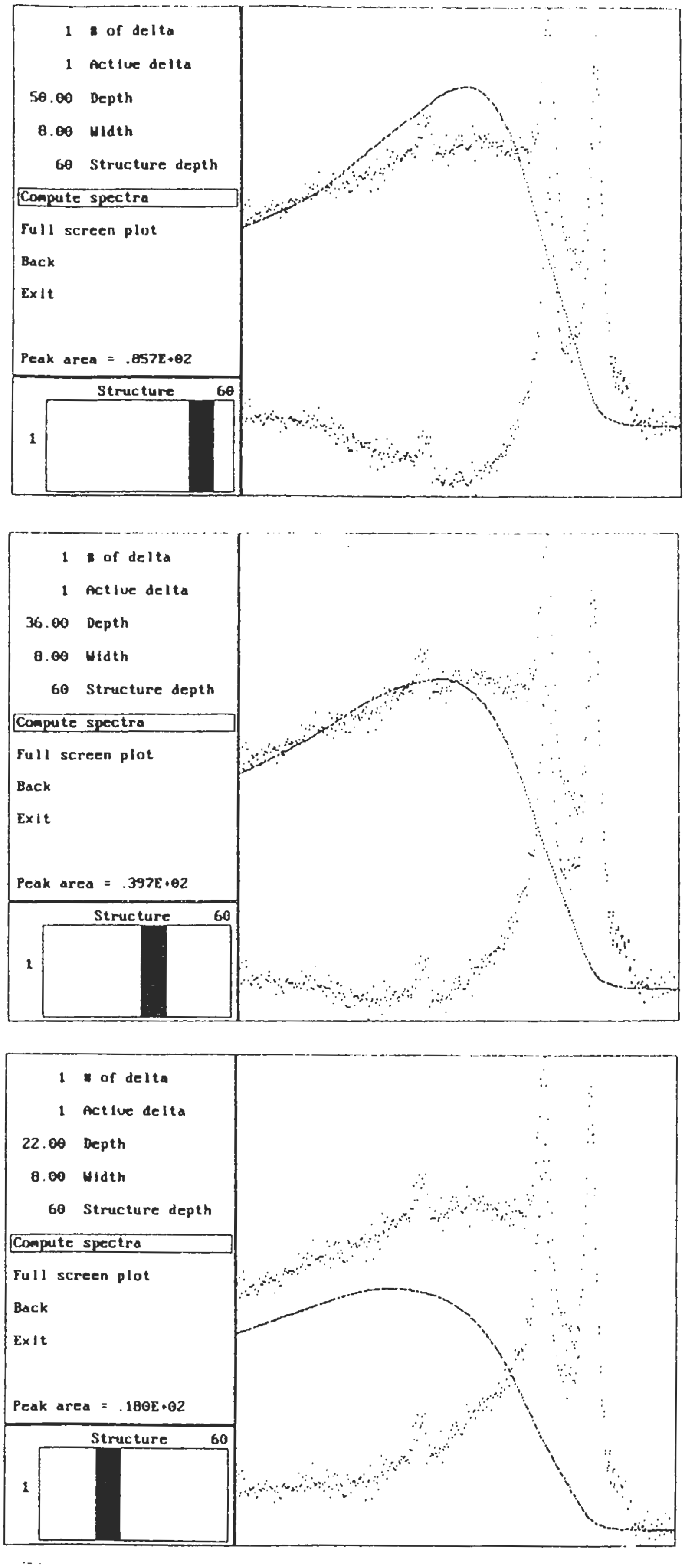
Figure 2. The surface morphologies that can be treated by the software QUASES™ [6].

percent, when as is common practice, the sample composition is assumed to be homogeneous within the surface region of the solid.

2. Software QUASES™ Implementing the Ideas in Practice.

These new ideas have been implemented in the form of a commercially available software package QUASES™ [6] (QUantitative Analysis of Surface Electron Spectra). It is a menu-oriented software which runs under DOS on any IBM or compatible PC (386 or higher) with a mathematical co-processor. All necessary data handling can be performed within the program. The software provides facilities for quantitative analysis by using either Method I or II described below. The assumed surface morphology can be changed within the types shown in Fig.2. The parameters characterizing the structure can be changed interactively. The software code has been optimized for speed and the analysis of a single spectrum takes only ~ 1 sec. As a result, several structures can quickly be tried for determination of the actual in-depth concentration profile f(x).

In practice, there are fundamentally two different approaches to the application of the new formalism for quantitative surface analysis.


1 # of delta
1 Active delta
50.00 Depth
8.00 Width
60 Structure depth

Peak area = .857E+02

1 # of delta
1 Active delta
36.00 Depth
8.00 Width
60 Structure depth

Peak area = .397E+02

1 # of delta
1 Active delta
22.00 Depth
8.00 Width
60 Structure depth

Peak area = .180E+02

Figure 3. The lower spectrum in figure 1 analyzed by the software QUASES™.

2.1 QUASES™ Method I: Background Subtraction.

In this approach, the atomic excitation spectrum F(E) is determined and the in-depth concentration profile f(x) is adjusted until F(E) is as close as possible to a reference spectrum $F_{Reference}$ (E). After this procedure, the composition of the surface of the sample on the nano-scale has been determined. The reference F(E) spectrum may conveniently be determined by analysis of the measured spectrum from a sample with known structure, for instance the spectrum from a pure elemental sample.

2.2 QUASES™ Method II: Calculation of Model Spectrum.

Here the spectrum of emitted electrons is calculated by assuming a composition profile f(x). When the best agreement with the measured spectrum is found, the in-depth composition profile f(x) has been determined. With this procedure it is necessary to know the atomic spectrum F(E). This is conveniently determined from the spectrum of a pure elemental sample as described above.

3. Example.

As an example, in Fig.3, the lower spectrum in Fig. 1 has been analyzed. The figure shows the appearance of one of the interactive graphical user interfaces of the software QUASES™ . In the menu in the left part of the screen, the surface structure can be changed and the chosen structure is also shown graphically in the lower left part. The result of the spectral analysis is shown in the right part of the picture. The three examples shown in Fig.3 correspond to the assumption of a buried layer of gold of 8 Å width centered at depths 50 Å, 36 Å, and 22 Å in the nickel matrix. It is not possible to get an acceptable analysis of the same spectrum when assuming the alternative surface morphologies (see Fig.2). From the analysis it is then clear that the gold is present as a ~ 8 Å thick layer situated roughly at a depth of 36 Å. This result is very plausible considering the sample history. Note however that no assumptions on the surface morphology was made in the analysis.

The method described in this paper has been applied in the study of many different systems including surface nano-structures of metal/metal - , metal/silicon - , and polymer/metal - systems as well as metal-oxide growth.

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