

Non-Destructive Depth Profiling by XPS Peak Shape Analysis

Shaaker Hajati^{1,2*} and Sven Tougaard¹

¹*Department of Physics and Chemistry, University of Southern Denmark, Campusvej 55, DK-5230 Odense M, Denmark*

²*Department of Physics, Yasouj University, Yasouj 75919-353, Iran*
*hajati@ifk.sdu.dk

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It is well known that the usual procedure for quantification by electron spectroscopy that is based on measured peak intensities is highly unreliable. An improved method is to take into account that the peak shape in a wide energy range, on the low kinetic energy side of the peak varies considerably with the surface morphology on the nano-meter depth scale. This observation has in recent years been applied in the formulation of a by now well known method for quantification that is based on quantitative analysis of measured peak shapes. The technique is sensitive on the 1 - 10 nm depth scale and it is non-destructive. The method suggested for the extraction of quantitative information from the large variation of the inelastic background with atom depth distribution will be reviewed briefly here. An example of practical application of the technique is also shown.

1. Introduction

Since 1983, methods of varying degrees of complexity, for the extraction of quantitative information from the large variation of the inelastic background with atom depth distribution have been suggested and will be discussed briefly here. All information is derived from the analysis of a single spectrum and is therefore also valid for rough surfaces when the take-off angle is close to the surface normal. The technique, developed by Tougaard et al. [1-7], relies on the fact that the inelastic background in the energy distribution of emitted electrons depends strongly on the depth concentration profile (see Fig. 1).

On their way out of the solid, some electrons undergo inelastic scattering processes and the typical energy loss in a single scattering event is between 10 and 30 eV [8, 9]. This results in a fairly broad background with weak features corresponding to plasmon and interband transitions, but from a few solids (e.g. Al, Si, SiO₂) clear plasmon peaks can be observed [9]. The inelastic processes lead to a distortion of the energy distribution as compared to the original distribution at the point of excitation in the solid [1-3]. The distance between inelastic scattering events is only ~1 nm [10, 11] and the resultant shape of the background in a wide energy range, 50 to 100 eV below the characteristic peaks therefore depends critically on the atom depth distribution on the nm-scale. This phenomenon

can be used to enhance the accuracy of XPS quantification and to provide information on the depth distribution [3-6]. To interpret XPS spectra, it is important to have a good feeling for the importance of this effect and to be able intuitively to identify information on the depth distribution from simple visual inspection of the shape of the background associated with the characteristic peaks.

Fig. 1 shows the dependence on depth distribution of model spectra of Cu 2p peaks, corresponding to four different distributions of Cu atoms on and in a gold matrix [5]. The XPS peak intensity from all four solids is identical even though the concentration in the immediate surface varies between 0 and 100 %, while the actual amount of Cu within the surface region can be anywhere between the equivalent of 0.11 nm (as in (a)) or 1.0 nm (as in (c)) or even greater (as in (d)). From this it is clear that peak areas can give only qualitative compositional information unless the atom depth distribution is known, in which case it is straightforward to correct the measured intensities. For accurate quantification, the task of determining the atomic concentration therefore cannot be decoupled from the task of determining the depth distribution. These effects lead to peak shapes that are characteristic for different depth distributions. This is seen in Fig. 1 which shows spectra from different distributions of Cu atoms in and on Au. It is clear that the background

contributions to the spectra over a wide energy range below the Cu peaks depend strongly on the depth distribution of the element. It is thus very easy experimentally to distinguish between the depth distributions contributing to the backgrounds of the four spectra in Fig. 1, over a 50 eV energy region.

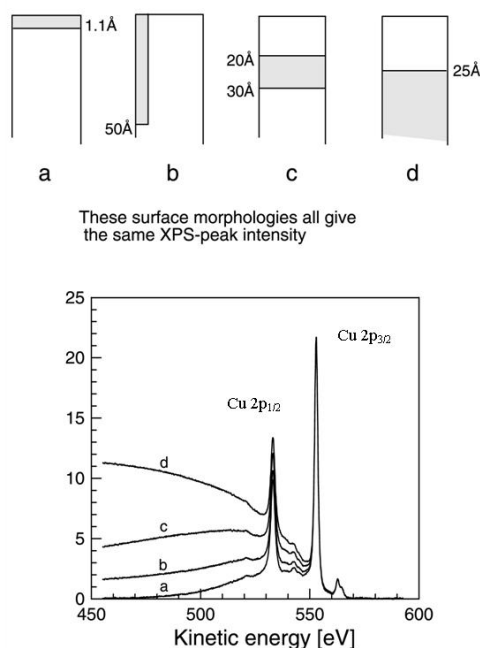


Fig. 1 Four widely different surface and near-surface distributions of Cu atoms in and on Au, that give identical Cu XPS peak intensities, but quite different inelastic backgrounds, from Ref. [1].

To make a clear description of the techniques we will take a specific example. Thus, the spectrum in Fig. 2 is from an iron sample that had been exposed to a maritime environment. Just by simple visual inspection of the Fe 2p spectrum in Fig. 2, it is evident that the depth distribution is of type (d) in Fig. 1 rather than of any of the other types. It can thus be concluded that Fe was primarily in the bulk, while the O 1s background is of type (b) or (c), indicating that the oxygen atoms were confined mostly to the outermost atomic layers. It can be concluded immediately that qualitatively the sample consisted of an iron-substrate covered with a fairly thick oxide layer. Thus, just a quick look at an XPS survey spectrum and comparing to the classes of characteristic depth profiles and corresponding peak shapes in Fig. 1 can easily give a rough qualitative picture of the depth distributions of the various elements. However, with greater effort and more elaborate algorithms it is possible to obtain an even more

accurate and detailed analysis of the near-surface elemental distribution.

2. Theory of quantification by detailed analysis of the peak shape

The underlying algorithms for this were published more than a decade ago and are summarized in Ref. (1). The validity of the technique has been established through a series of systematic experiments, some of which have been reviewed in Ref. (3). These studies showed that quite detailed information on the in-depth atom distribution on the nanometer depth scale can be extracted. The algorithms are fairly complex and a user-friendly software package, which provides tools to do the full analysis from raw spectra to the resulting distribution, was developed to make this type of analysis available for non-specialists [12]. The method is now widely used and has been applied to the study of a wide range of systems and physical phenomena, including thin-film growth mechanisms and sub-surface elemental distributions of films, nucleation, island formation, diffusion, etching, etc. [13-23]. Since the method is non-destructive, it also allows study of the changes in the surface morphology of a given surface atomic structure during surface treatment, as in chemical reaction or gradual annealing.

If the elastic scattering, diffraction and surface excitation are neglected, measured XPS spectra $J(E, \Omega)$ with atom distribution at depth (z) is described by reference [24, 25].

$$J(E, \Omega) = \int dE_0 F(E_0, \Omega) \int ds e^{-i2\pi s(E-E_0)} \times \int dz f(z) \exp\left[-\frac{z}{\cos\theta} \Sigma(s)\right] \quad (1)$$

$$\Sigma(s) = \frac{1}{\lambda} - \int_0^\infty K(T) e^{-sT} dT \quad (2)$$

where $f(z)$ is the number of atoms per unit volume at depth z , $F(E_0, \Omega)$ is true spectra excited from an atom in an energy interval dE_0 at E_0 and solid angle Ω . $K(T)$ is the differential inelastic electron scattering cross-section and T is loss energy (eV), λ is inelastic mean free path for electron scattering. And s is an integration variable without physical significance [26].

An algorithm for removal of the inelastic background from measured spectra is effectively

solved numerically by means of discrete Fourier transformation using a fast Fourier transformation algorithm. The initial excitation energy spectrum as true spectrum, $F(E, \Omega)$ may be determined from analysis of measured spectrum $J(E, \Omega)$ [4].

$$F(E, \Omega) = \frac{1}{P_1} \left\{ J(E) - \frac{1}{2\pi} \int dE' J(E', \Omega) \right. \\ \left. \times \int ds e^{-is(E-E')} \left(1 - \frac{P_1}{P(s)} \right) \right\} \quad (3)$$

where

$$P(s) = \int f(z) e^{-\frac{z}{\cos \theta} \Sigma(s)} dz \quad (4)$$

With

$$P_1 = \int_0^\infty f(z) e^{-\frac{z}{\lambda \cos \theta}} dz \quad (5)$$

If information on $f(z)$ is known, $F(E, \Omega)$ may be determined. For specific depth profiles, $f(z)$, part of the integrals in Eqs. (4) and (5) can be done analytically. Refs. [1-7, 12, 27, 28] give expressions of P_1 and $P(s)$ for different classes of depth profiles with parameters defined in Fig.3.

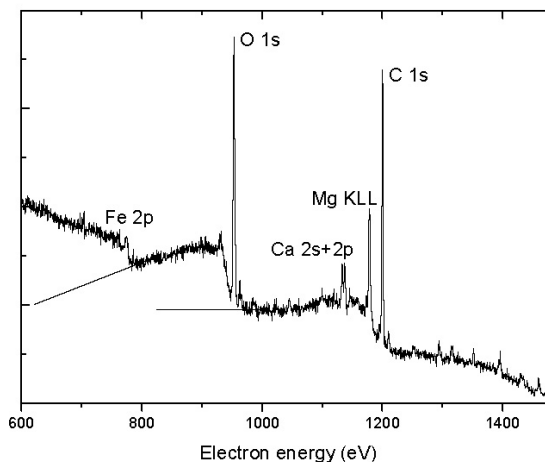


Fig. 2 Al $K\alpha$ -excited XPS spectrum from an iron sample that had been exposed to a corrosive maritime environment, from Ref. (2)

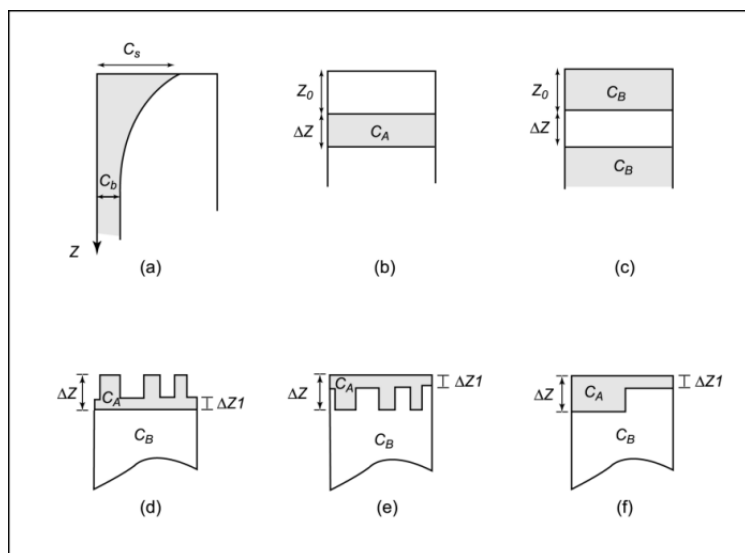


Fig. 3 Definition of parameters for some in-depth profiles. The structures in (d), (e), and (f) give identical spectra.

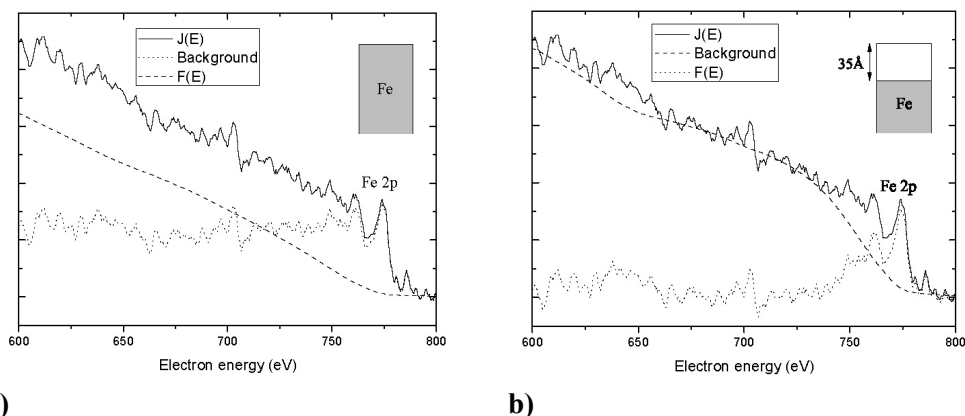


Fig. 4 Spectra from the Fe sample in Fig. 2 that had been exposed to a maritime environment. The Fe 2p peak has been analyzed with the Quases-Tougaard software [12] to determine the depth distribution of the Fe atoms [12].

3. Example

As an example of the practical application of the method the analysis of the XPS spectrum of the corroded iron sample in Fig. 2 will be described. Using the QUASES software [12], the Fe 2p and O 1s energy regions are first isolated by subtracting straight lines fitted to the intensity on the high energy sides of the peaks as shown in Fig. 2. The peaks isolated in this way are shown in Fig. 4 and Fig. 5. The spectra are then analyzed with the QUASES software by varying the assumed depth profile, and the corresponding background-subtracted spectra are calculated and plotted. In Fig. 4a Fe is assumed to be distributed homogeneously and it is clear that such a depth distribution does not account for the strong increase in background intensity. On the other hand, in Fig. 4b the assumption is that the Fe is distributed from a depth of about 3.5 nm to infinite depths, and that is clearly a much better model for the peak shape and background over a wide energy region. Fig. 5 shows a similar analysis of the O 1s peak shape.

The peak shape and background can be well described by assuming that the O atoms are distributed with constant concentration between depths of 2.5 nm and 8.0 nm. The C 1s, Mg KLL and Ca 2s and 2p peaks overlap somewhat in energy and an analysis of them is more involved and would require a spectrum with a better signal-to-noise ratio. From the analysis it is then shown that the sample consists of a Fe substrate covered first with a layer of oxide about 5.5 nm thick, on top of which is a mainly carbonaceous layer of thickness about 2.5 nm. All information was extracted from the rather noisy survey spectrum in Fig. 2. This analysis has been done without use of reference spectra. It is important to note that a

more accurate quantification can be done with use of reference spectra (see Ref. (5)) and this will also give the concentration of the elements. This is done by comparing both the area and the shape of $F(E, \Omega)$, obtained by Eq. (3), with the area and shape of $F(E, \Omega)$ obtained from analysis of a reference sample. This gives more constraints on the fitting procedure and as a result the obtained depth profiles are more accurate. This is the recommended procedure for depth profiling by XPS peak shape analysis.

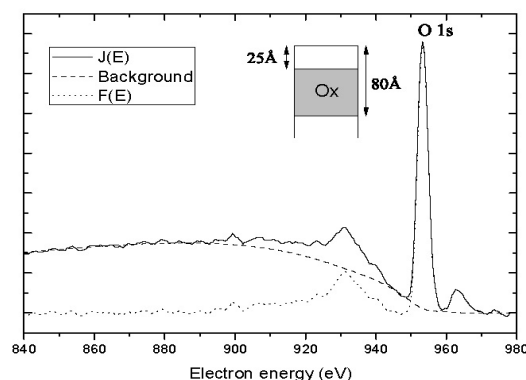


Fig. 5 Spectra from the Fe sample in Fig. 2 that had been exposed to a maritime environment. The O 1s peak has been analyzed with the Quases-Tougaard software [12] to determine the depth distribution of the O atoms [12].

In conclusion, the XPS peak shape analysis is a non-destructive, robust and simple method to determine the in-depth distribution of atoms within a few nanometer depth scale in the surface region of nanostructures.

4. References

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