QUASES-Tougaard
Principle of Analysis

Concept of the QUASES™ analysis procedures

This describes the principle of analysis used in QUASES-Analyze and QUASES-Generate.

1 Introduction

Quantitative surface chemical composition analysis by X-ray photoelectron or Auger electron spectroscopy (XPS or AES) relies on several factors [1-3] like for example knowledge of photoionization cross sections, inelastic electron mean free paths, and the influence of elastic electron scattering. The most serious problem in quantitative XPS, that gives the largest contribution to errors of analysis, is however 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. As a result, a meaningful interpretation of measured XPS-peak intensities can not be made unless the in-depth distribution of atoms is known. Such information is however usually not at hand in practice, because it is the purpose of the analysis to find the quantitative composition of the surface region of the solid, and if this information were available there would be no point in doing the analysis. To be able to extract quantitative information from a measured peak intensity, it is necessary to make an assumption, and for convenience it is usually assumed that the surface region is homogeneous up to a depth of a few nano-meters. This assumption does however make quantification of surface chemical compositions by XPS and AES extremely unreliable as shown below.

In view of the high and rapidly growing technological importance of reliable information on the in-depth composition of the surface region of solids on the nano-meter scale, much effort has in recent years been devoted to the development of new more accurate methods. With this goal in mind, Tougaard et al [3-8] has made systematic studies of electron transport phenomena and on this basis developed a practical technique for determination of the chemical composition of solid surfaces with nano-meter depth resolution. It relies on the phenomenon that the energy loss structure that accompanies an XPS or AES peak carries information on the depth of origin of the detected electrons. The method is non-destructive and therefore allows also studying the change in surface morphology during exposure to various treatments as, e.g., gradual annealing or chemical reaction with an ambient gas. The technique has been applied to study thin film growth mechanisms and inter-diffusion depth profiles of many systems including also several tests on the validity of the method (see ref.[8] and references in ref.[8]).

The QUASES™ software package provides a practical tool that makes application of these results possible for routine analysis work.

2 Large errors and uncertainties in traditional XPS and AES - analysis

For a meaningful quantification of measured peak intensities, assumptions on the in-depth distribution of atoms

must be made. Usually, the sample composition is taken to be homogeneous up to a depth of a few nano meters [1]. This assumption may result in enormous errors in quantification [6-8]. Thus, solids subject to surface analysis are hardly ever homogeneous up to a depth of several nano-meters. It is precisely because samples are *inhomogeneous* on the nano-meter depth scale that analysis is done with XPS or AES rather than with other well-established methods for chemical analysis that are less surface sensitive

The reason for the dramatic change in peak shape with the surface morphology is that as the electrons move on their way out of the solid, they lose energy. The longer pathlength they travel, the larger is the fraction of the electrons that have lost energy. This is illustrated in fig.1.1 where the energy spectrum is shown before and after the electrons have passed a thin solid with different thickness. For electrons that pass only a short distance in the solid, the chances that an electron will lose energy is small and the change in energy distribution is small. For electrons that pass a larger distance, a larger fraction will have lost energy and the intensity at the peak energy is diminished. These electrons are found at lower energies in the spectrum and the distortion of the energy spectrum is substantial.

The formula mostly applied for quantitative analysis by XPS and AES relies on the assumption that the average concentration in the outermost surface region of the solid is directly proportional to the measured peak intensity. To illustrate the fundamental problem with this procedure we will consider an example of model spectra calculated for different depth distributions of copper in a gold matrix. Thus, fig.1.2 shows spectra of the Cu2p peak corresponding to four different surface morphologies. The XPS-peak intensity from all four solids is exactly identical although the surface morphologies are widely different. Quantification based only on the Cu2p peak intensity cannot discriminate between these four structures. Analysis of these spectra under the assumption that the surface concentration is proportional to the peak intensity, would then result in a quantification where the concentration at the surface could be anywhere from 0 % (as in (d)) to 100 % (as in (a)). The total amount of copper material within the surface region could be anywhere from the equivalent of 1.1 Å (as in (a)) or 10 Å as in (c)) or even higher (as in (d)). Quantification based on peak intensities alone is thus subject to extremely large uncertainties and it is hard to keep the imagination of XPS and AES as quantitative techniques.
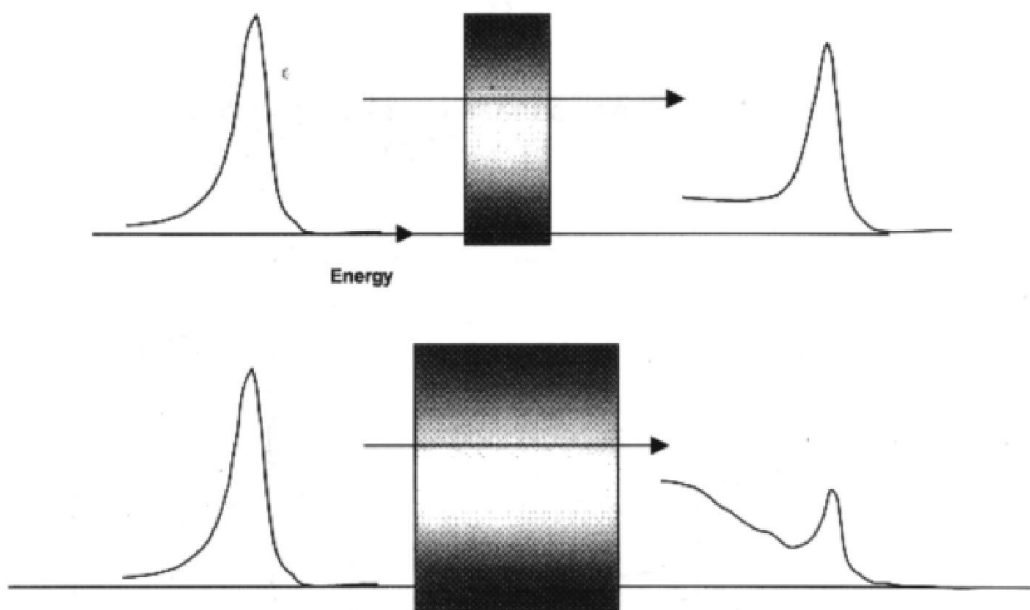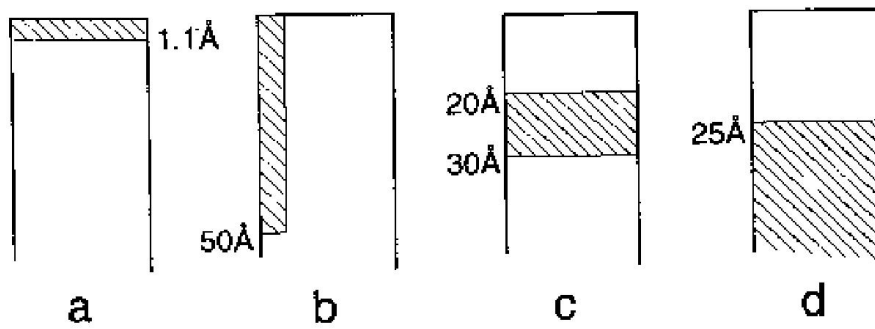

Figure 1.1

These surface morphologies all give
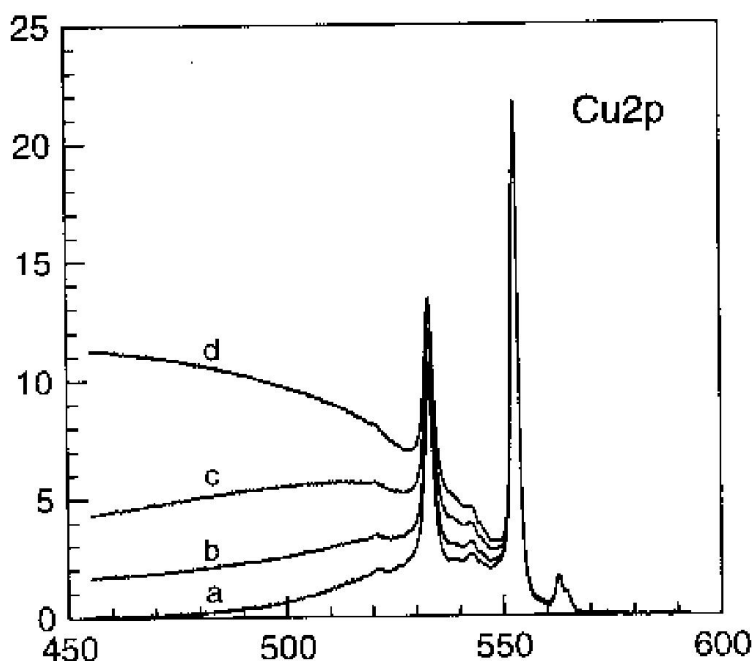the same XPS-peak intensity

Figure 1.2

In fig.1.2 (a), the electrons have traveled only a short distance before they escape through the surface, and consequently, very few have lost energy and the intensity on the low energy side of the peak is small. In Fig1.2 (c), all electrons have traveled ~20-30 Å within the solid before they reach the surface, and a larger fraction have lost energy and end up at lower energies in the spectrum. In fig.1.2 (d), there are additional electrons coming from larger depths, and these electrons will have lost further energy. This is why the intensity ~ 50 – 100 eV below the peak is considerably larger in (d) compared to
(c).

3. How QUASES solves this problem
and how QUASES gives nano-structure depth profile quantification

On closer inspection of the spectra in fig.1.2, it is clear that the peak shape in a wider energy range below the peak does depend critically on the in-depth distribution of the element. It is thus easy experimentally to distinguish between the peak shape of the four spectra in a say ~ 100 eV energy region. Much more accurate quantification can therefore be accomplished if the dependence of peak shape on surface morphology is taken into account in the analysis. It is a quantitative description of these effects that is the basic principle of surface nano-structure quantification in the QUASES™ software package.

4. QUASES Software Package
see www.quases.com

5. Samples and Downloads
see www.quases.com

6 Algorithms behind QUASES™.

This section briefly summarizes the principles used in QUASES™ to describe the variations in energy distribution of emitted electrons caused by electron transport.

The flux density of photoelectrons excited from a single atom at energy E_0 into the solid angle Ω is denoted F (E_0,Ω) and the concentration of atoms at depth x is f(x).

Then the measured spectrum of emitted electrons is

$$J(E,\Omega) = \int dE_0\, F(E_0,\Omega) \int f(x) G(E_0, x/\cos\theta; E)\, dx \quad (1.1)$$

where θ is the emission angle with respect to the surface normal. The function G, is the energy distribution of an electron as a function of path length x/cosθ traveled in the solid.

The total energy loss of an electron moving in a solid is determined by the inelastic scattering cross section and the path length traveled. Multiple scattering events are important because in typical cases, the energy spectrum includes electrons that have traveled a distance of several inelastic mean free paths.

We denote by K(E,T) the differential inelastic electron scattering cross section, i.e. K(E,T)dRdT is the probability that an electron of energy E will lose energy in the interval T, T+dT after having traveled a path length dR in the solid. For energy spectra where the total energy loss is small compared with the primary electron energy, $K(E,T) \cong K(T)$ independent of E. Then the effect of multiple scattering has a rigorous solution, and the spectrum of emitted electrons is

$$J(E,\Omega) = \int dE_0\, F(E_0, \Omega) \int ds\; e^{-i2\pi s(E-E_0)} \int dx\, f(x) e^{-x\Sigma(s)/\cos\theta} \quad (1.2)$$

with

$$\Sigma(s) = \frac{1}{\lambda} - \int_0^\infty K(T)\, e^{-isT} dT \quad (1.3)$$

where λ is the inelastic electron mean free path.

Quantification by Background Removal.

Formulae to determine the atomic excitation function F(E, Ω) from a measured spectrum were developed for different types of in-depth profiles. It was shown that the integral equation (eq.(1.2)) may be solved rigorously for the primary excitation spectrum F(E, Ω)

$$F(E,\Omega) = \frac{1}{P_1}\left[J(E,\Omega) - \int dE'\, J(E,\Omega) \int ds \exp\left[i2\pi(E'-E)\right]\left(1 - \frac{P_1}{P(s)}\right) \right] \quad (1.4)$$

where

$$P(s) = \int dx\, f(x) \exp\left(-\frac{x}{\cos\theta}\Sigma(s)\right) \quad (1.5)$$

and

$$P_1 = \int dx\, f(x) \exp\left(-\frac{x}{\lambda\cos\theta}\right) \quad (1.6)$$

Eq.(1.4) may be used to determine either F(E, Ω) if $f(x)$ is known (e.g., for a one elemental sample) or it may be used to determine $f(x)$ if F(E, Ω) is known. The exact peak shape in the energy region close to the peak energy up to ~ 10-20 eV below the peak energy is not known since it is largely determined by the chemical bond, lifetime broadening, and intrinsic excitations in the photoemission process which all may depend on the local chemical environment. However, the spectrum F(E, Ω) after background correction must be of zero intensity in an energy region beyond ~ 30eV below the primary peak energy and the spectral intensity must stay at zero intensity for all energies below the peak energy until the energy of another peak in the energy spectrum is reached. This puts a strong constraint on the function F(E,Ω) and this is applied as a criterion to determine $f(x)$ in the sense that $f(x)$ is varied until the constraint is fulfilled.

As another criterion one can use knowledge about F(E,Ω) determined from the analysis of spectra from samples with a well characterized in-depth concentration profile as, e.g., a single element solid. One should be aware of the possible peak shape changes caused by the difference in chemical environment of the atoms in the reference and the sample being investigated. To the extent that these differences can be neglected, the spectrum may be applied as a reference and $f(x)$ is varied until analysis yields a spectrum with the same absolute intensity and peak shape as the reference spectrum. If the peak shape analysis includes peaks from all the elements in a sample then the constraint that the sum of the concentration of the individual elements at any depth must add up to 100% may also be applied.

7. Inelastic electron scattering cross sections

The cross section K(T) can be described with sufficient accuracy by Universal formulas valid for different classes of materials.

Depending on the class of materials, a function with either two, or three parameters is needed to describe the cross sections of that class [9].

For most metals, their oxides and alloys, the *Universal cross section* [9]

$$\lambda_i(E)K(E,T) = \frac{B\,T}{\left(C + T^2\right)^2}$$
(1.7)

with C= 1643 eV^2 and B $\cong$ 3000 eV^2 applies with sufficient accuracy.

For solids with a narrow plasmon structure, the cross-sections can not be well described by a function with two-parameters. For these however it was shown [9] that the main characteristics of the cross section can be described by the *Three-parameter Universal cross section*

$$\lambda(E)K(E,T) = \frac{BT}{\left(C - T^2\right)^2 + DT^2}$$
(1.8)

where the three parameters B, C, and D have been determined for each class of materials (e.g. polymers, semiconductors, free-electron-like solids [9]).
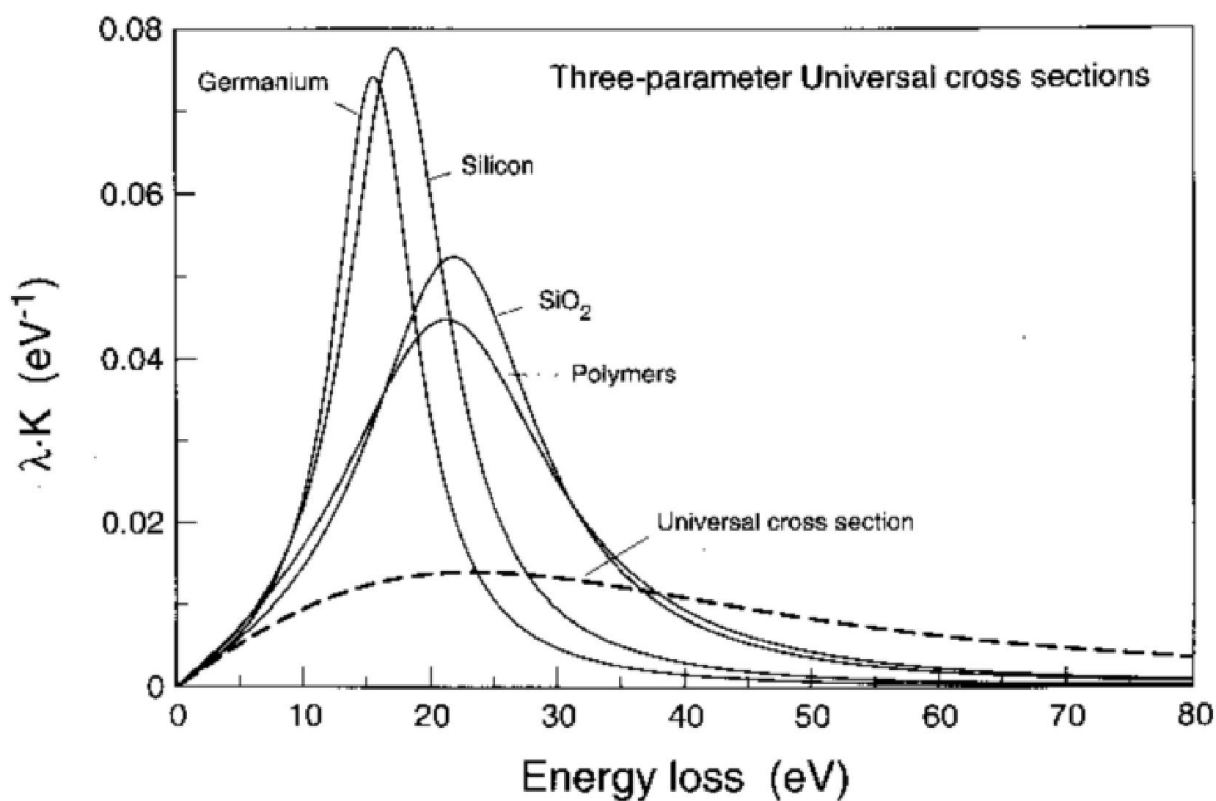
Figure 1.3

Fig 1.3 shows cross sections for various types of solids. The parameter values are given in table1. These cross sections are all included in the QUASES™ software.

TABLE 1. Parameters for the Universal cross sections in eqs.(1.7) and (1.8). B^N is the value of B for which the cross section is normalized. Some of the cross sections are plotted in Fig. 1.2 and 1.3

Universal Cross Section (eq.(5))

Class of materials	B [eV^2]	B^N [eV^2]	C [eV^2]
Metals and their oxides	2866	3286	1643

Three parameter- Universal Cross Section (eq.(6))

Class of materials	B [eV^2]	B^N [eV^2]	C [eV^2]	D [eV^2]
Polymers	434	396	551	436
Silicon-dioxide	325	299	542	275

Silicon	132	131	325	96
Germanium	73	93	260	62
Aluminum	16.5	21.4	230	4.5

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