

# Surface nanostructure determination by x-ray photoemission spectroscopy peak shape analysis

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Factors that contribute to the uncertainty in quantitative analyses of surfaces by x-ray photoemission spectroscopy and Auger electron spectroscopy are considered. Quantification is usually based on the convenient but quite arbitrary assumption that the sample is homogeneous within the outermost few nanometers. This assumption can lead to uncertainties of several hundred percent in the analysis and, as a consequence, a meaningful quantification based on measured peak intensities alone is not possible. In contrast, the contribution to the uncertainty from other factors is much smaller. It is further pointed out that, when many factors contribute roughly equally to the error, even considerable improvements in the uncertainty of a single factor, have only little influence on the total error. It is therefore clear that in the future effort must be concentrated on the development of practical techniques to enhance the knowledge on the in-depth composition since, without this, no improvement can be expected even if a substantial improved accuracy of other factors is obtained. One such technique that relies on analysis of both the peak intensity and the peak shape is discussed and this technique seems to reduce the uncertainty considerably, to a typical level of 10%–20%, depending on the solid and surface morphologies. © 1996 American Vacuum Society.

## I. INTRODUCTION

The purpose of quantitative analysis by x-ray photoemission spectroscopy (XPS) is to determine the chemical composition of the outermost few nanometers of a solid. It is therefore of interest to study how accurately XPS can provide such information. This is the purpose of the present article. There are different ways to interpret measured XPS spectra with corresponding different algorithms for quantification.<sup>1,2</sup> Each procedure depends on the accuracy of various factors. When we want, in the future, to improve procedures for quantitative surface analysis by XPS and Auger electron spectroscopy (AES), it is necessary first to establish the leading factors that contribute most to the error. It is these factors that should be the focus of research because, if their accuracy is not improved, any improvement in the less important factors will have essentially no influence on the total accuracy of the quantification procedure. It is then the purpose of the present article, in view of recent experimental investigations, to compare the errors associated with these factors. It turns out that the factor that by far contributes most to the inaccuracy is the lack of knowledge of the in-depth composition of the sample.

The basis and validity of a new technique,<sup>3–7</sup> which by quantitative analysis of the peak shape takes account of the sample inhomogeneity, are also discussed. It relies on the phenomenon that the energy loss structure that accompanies an x-ray photoelectron or Auger electron peak (XPS or AES) carries information on the depth of origin of the detected electrons. The method is nondestructive and therefore also allows one to study the change in surface morphology of a given surface atomic structure during surface treatment as, e.g., gradual annealing. It has been applied to study thin film growth mechanisms and interdiffusion depth profiles of

many systems. Several tests on the validity of the method have also been done.

Another technique that also provides information on the depth distribution of atoms is angle-resolved XPS. This has been reviewed recently<sup>8–11</sup> and is not discussed here.

## II. QUANTIFICATION: GENERAL CONSIDERATIONS

Quantification by XPS and AES relies on several factors such as knowledge of photoionization cross sections, inelastic electron mean free paths, influence of elastic electron scattering, and energy dependence of the spectrometer transmission function.<sup>1,2</sup> The most serious problem that gives rise to the largest contribution to errors is, however, likely to be lack of knowledge on the in-depth distribution of atoms.<sup>5,6</sup> For a meaningful quantification, assumptions on the in-depth distribution of atoms must be made since the measured peak intensity depends critically on that. Now, in practice the in-depth atomic distribution is never known when a sample is analyzed because, if it were, it would be a waste of time and money to do the analysis. Usually, the solid composition is, for convenience, but quite arbitrarily, assumed to be homogeneous up to a depth of several nanometers and then the surface concentration will be proportional to the measured peak intensity. This assumption may result in enormous errors in quantification.<sup>5,6</sup> Thus, solids subject to surface analysis are hardly ever homogeneous up to a depth of several nanometers. It is precisely because samples are *inhomogeneous* on the nanometer depth scale that analysis is done with XPS or AES rather than with other well established but less surface sensitive techniques.<sup>11</sup>

To illustrate the fundamental problem with the assumption of homogeneous composition with depth, we will consider an example of model spectra calculated for different depth distributions. Figure 1 shows spectra of the Cu 2*p* peaks

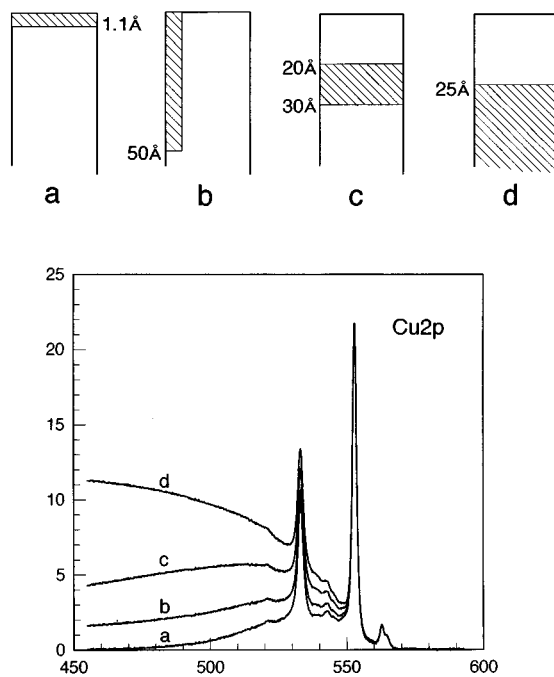


FIG. 1. Four widely different surface structures of copper in gold that give identical peak intensities.

corresponding to four different surface morphologies of copper in a gold matrix. The XPS-peak intensity from all four solids is exactly identical although the surface compositions are widely different. Analysis of these spectra under the assumption that the surface concentration is proportional to the peak intensity would result in a quantification where the inaccuracy is such that the true concentration at the surface could be anywhere from 0% [as in (d)] to 100% [as in (a)] and the true 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)] (i.e., an uncertainty in quantification of several hundred percent). Quantification based on peak intensities alone is thus clearly subject to a large uncertainty.

From Fig. 1, it is, however, clear that the peak shape in a wider energy range below the peak depends critically on the in-depth distribution of the element. It would thus be very easy experimentally to distinguish between the peak shape of the four spectra in, say, an  $\sim 100$  eV energy region. Much more accurate quantification can therefore be achieved if the dependence of the peak shape on surface morphology can be taken into account in the analysis. This is the idea behind a new formalism, developed by Tougaard *et al.*,<sup>3-7</sup> that provides quantitative information on the surface nanostructure of the solid by analysis of XPS or AES peak shapes.

To improve procedures for quantitative surface analysis by XPS and AES, it is necessary first to establish the leading factors that contribute most to the error. It is these factors that should be the focus of research. Above it was shown that the contribution to errors in quantitative surface analysis by XPS or AES due to unknown surface morphology may well

be several hundred percent or even higher (see Fig. 1). For comparison, we will now study the level of contribution to errors from other factors in the quantification procedure.

### III. HOMOGENEOUS SOLIDS

Although in-depth compositions on the atomic scale are rarely known, and although samples are likely to be nonhomogeneous as discussed above, let us assume now the unlikely event that the solid being analyzed is homogeneous over a depth of several inelastic electron mean free paths (IMFPs). Let us first assume that the elastic electron deflection can be ignored and that the electrons move along straight line trajectories. Then, the molar fractions  $X_A$  and  $X_B$  for a solid consisting of the two elements  $A$  and  $B$  are<sup>1,12</sup>

$$\frac{X_A}{X_B} = \frac{\lambda_A(E_A) a_B^3 \lambda_{AB}(E_B) I_A / I_A^{\text{pure}}}{\lambda_B(E_B) a_A^3 \lambda_{AB}(E_A) I_B / I_B^{\text{pure}}}, \quad (1)$$

where  $I_A$  and  $I_A^{\text{pure}}$  are the measured peak intensities from element  $A$  and from a reference sample consisting exclusively of  $A$  atoms and where  $a^3$  corrects for differences in atomic densities in the two solids  $A$  and  $B$ . The terms  $\lambda_A(E_A)$  and  $\lambda_{AB}(E_A)$  are the IMFPs for electrons at energy  $E_A$  in the one element sample consisting of  $A$  atoms and in the solid being analyzed.

In Eq. (1), the contribution to errors comes primarily from the two ratios  $\lambda_A(E_A)/\lambda_B(E_B)$  and  $\lambda_{AB}(E_A)/\lambda_{AB}(E_B)$ . The uncertainty of these factors is not known.<sup>13,14</sup> However, the uncertainty of  $\lambda_{AB}(E_A)/\lambda_{AB}(E_B)$ , being a ratio of IMFPs for a single solid at two energies, will be considerably smaller than the uncertainty of  $\lambda_A(E_A)/\lambda_B(E_B)$ , which is the ratio for two energies in two different solids. To reduce the error in the analysis, one might therefore try to eliminate the factor  $\lambda_A(E_A)/\lambda_B(E_B)$ . This can be done by introducing the photoionization cross section  $\sigma_A$  and the asymmetry factor  $L_A$ . The resulting expression<sup>12</sup>

$$\frac{X_A}{X_B} = \frac{\sigma_B L_B \lambda_{AB}(E_B) I_A}{\sigma_A L_A \lambda_{AB}(E_A) I_B} \quad (2)$$

depends now on errors in  $\lambda_{AB}(E_A)/\lambda_{AB}(E_B)$  and  $\sigma_A L_A / \sigma_B L_B$ . In comparison to Eq. (1), the error on  $\lambda_A(E_A)/\lambda_B(E_B)$  has been eliminated but at the expense of the error on  $\sigma_A L_A / \sigma_B L_B$ .

Tabulations of IMFPs<sup>13,14</sup> and photoionization cross sections<sup>15</sup> are available. However, very little is known on the accuracy of these values and it is thus not possible to judge which of the above two formulae is more accurate for quantification of homogeneous samples. There are two additional differences between the two procedures that are of importance for their accuracy. In Eq. (1) the error from uncertainty in the energy dependence of the spectrometer transmission function is negligible because it cancels out since the reference spectra are used for normalization. The accuracy of the two equations also depends on the ability to account correctly for shakeup contributions to the peak intensity. With the use of reference spectra, one expects the analysis to be less sensitive to the procedure used for background correc-

tion, since a ratio to a reference is applied.<sup>12</sup> However, although one would normally expect this to be the case, it may also happen that the shakeup structure changes significantly due to the difference in electronic environment for the atom in the reference and the same atom in the sample being analyzed. In this case the intensity of the reference in, say, a narrow energy range around the main peak, is not a good measure, even on a relative scale, for the total peak intensity. In that case, an accurate method for background subtraction that takes into account the intrinsic excitation processes is highly important even when reference spectra are used for quantification. This effect was demonstrated to be of importance for quantitative analysis of CuAu alloys.<sup>12,16</sup>

*Validation of algorithms for homogeneous solids:* It may be a reasonable ambition to test the accuracy of a given procedure for quantitative surface analysis on the 10% level. Then it is necessary to have standard samples for which it is known that (1) the sample composition is constant to better than  $\sim 10\%$  in at least the outermost 2–3 nm and (2) that the concentration in that depth range is known by an accuracy of better than 10%. Such standards can hardly be produced with the present technology. Although alloys with very accurately known bulk composition are readily available, the composition in the first couple of atomic layers is likely to deviate from the bulk composition by an unknown amount that may well be several percent. The problem is that alternative methods for surface analysis that are more accurate than XPS and AES do not exist and, while one may have indications that the composition of the surface atomic layer of a given solid is close to that of deeper layers, this can never be known with better accuracy than the accuracy of the surface analytical technique that is applied to find the composition. The most promising experimental technique to produce such standard samples might be molecular beam epitaxy. Here, however, the crystallinity of the solid will produce strong scattering effects that may severely affect the measured peak intensity (see Sec. VI). Then, the only standard samples that meet the above two criteria are one element solids. For a more extensive discussion of strategies to validate algorithms for quantitative surface analysis, see Ref. 12.

To determine the peak intensity from a measured spectrum, the background intensity of inelastically scattered electrons must be removed. This may be done either by simplified procedures like the Shirley method<sup>1</sup> or by drawing a straight line<sup>1</sup> or a method proposed by Tougaard<sup>1,17</sup> that relies on a detailed description of the physical processes may be applied.

The validity of different procedures was studied in Ref. 12 by measuring all the peaks from seven one element solids. The peak intensity ratios were compared to a first principles calculation [Eq. (2)] based on theoretical tabulations of IMFPs<sup>13</sup> and photoionization cross sections.<sup>15</sup> When applying a method for background subtraction suggested by Tougaard,<sup>17</sup> the root-mean-square (rms) deviation from theory was found to be 11% for all ratios of peaks from the same solid and 14% for the ratios of all peak intensities to

the Au 4*d* peak intensity. The corresponding deviations from theory when the Shirley or straight line method was applied for background removal are 35% and 25%.<sup>12</sup>

The stability of XPS instruments was investigated in an intercomparison study<sup>18</sup> of data taken at eight laboratories. The transmission function of all instruments had first been calibrated to the same spectrometer at National Physical Laboratory, England, by the method developed by Seah.<sup>19</sup> The ability of the individual instruments to reproduce a spectrum taken with the same instrument at a later time was found to be 2%–6% (depending on the instrument). This means that, with the presently available XPS instruments, we can never obtain quantification with higher accuracy than the stability of the instrument, i.e., somewhere between 2% and 6%. This is true even if we assume that somehow we could find an algorithm that takes all physical processes into account with infinitely high accuracy.

It was also found in this intercomparison study<sup>18</sup> that, independent of the method applied for background correction, the root-mean-square scatter of data was higher by 3%–4% when comparing data from different laboratories than the rms scatter when comparing data taken with a single instrument. This means that we should expect an increase in the uncertainty of quantification by 3%–4% when data are being shared between laboratories, for example, by the use of a database rather than using local standards.

In Sec. III we have considered the validity of Eq. (2) which is valid when the solid is homogeneous within the outermost few nanometers and when elastic deflection of the electrons can be neglected. In the following we will discuss the changes in quantification as a result of inhomogeneity of the sample and as a result of elastic scattering.

#### IV. ELECTRON TRANSPORT EFFECTS

After the photoexcitation process, some of the electrons are transported to the surface and enter the spectrometer. Quantification relies on an accurate description of how this transport influences the energy spectrum. For inhomogeneous samples, the effect is substantial (see Fig. 1) and quantification requires a detailed and accurate description of inelastic electron scattering. In contrast, for homogeneous samples, it is just ratios of inelastic electron mean free paths that describe the effects of inelastic scattering [see Eqs. (1) and (2)]. The total energy loss of an electron moving in a solid is determined by the inelastic scattering cross section and the path length traveled and since, in typical cases, the energy spectrum includes electrons that have traveled a distance of several inelastic mean free paths, multiple scattering events are important.

Let  $F(E_0, \Omega_0, x) d^2\Omega_0 dE_0 dx$  be the flux of electrons excited at depth  $x$ ,  $dx$  in an energy interval  $E_0$ ,  $dE_0$  into the solid angle  $\Omega_0$ ,  $d\Omega_0$ , and let  $Q(E_0, \Omega_0, x; R, \Omega) dR d^2\Omega$  be the probability that an electron excited with energy  $E_0$  at depth  $x$  in direction  $\Omega_0$  will arrive at the surface in the di-

rection  $\Omega$ ,  $d^2\Omega$  after having traveled the path length  $R$ ,  $dR$ . Then the number of electrons emitted per second, per unit energy, and solid angle is

$$J(E, \Omega) = \int dE_0 \int d^2\Omega_0 \int dx F(E_0, \Omega_0, x) \times \int Q(E_0, \Omega_0, x; R, \Omega) G(E_0, R; E) dR, \quad (3)$$

where  $G(E_0, R; E)dE$  is the probability that an electron with initial energy  $E_0$  has energy in the interval  $E$ ,  $E+dE$  after having traveled the path length  $R$ .

There exists the possibility that the energy distribution at the point of excitation may vary with depth. This may arise as a result of peak shape dependence on the local chemical composition that in a typical sample will vary with depth. This effect may also appear even in a homogeneous solid because the difference in the environment of an atom present in the surface layer to that of an atom situated a few layers underneath the surface may lead to differences in electron energy levels and in the local density of electron states. This in turn will affect the response of the surrounding electrons to the excitation process and thus affect also the shakeup processes and, by that, the energy distribution of emitted electrons. Since these effects are usually small and since a complete quantitative description is not possible because of lack of detailed models of general validity, it is usually a valid and reasonable approximation to assume that the concentration of electron emitters  $f(x)$  may vary with depth  $x$  but that the energy distribution is independent of depth, i.e.,

$$F(E_0, \Omega_0, x) = f(x)F(E_0, \Omega_0), \quad (4)$$

where  $F(E_0, \Omega_0)d^2\Omega_0dE_0$  is the number of electrons per second, per atom, and per unit energy excited in an energy interval  $E_0$ ,  $dE_0$  into the solid angle  $\Omega_0, d^2\Omega_0$  and  $f(x)$  is the number of atoms per unit depth at depth  $x$ .

Elastic electron scattering enters as a path-length increasing effect and is described by the function  $Q$  in Eq. (3).

*Inelastic electron scattering:* The inelastic processes are clearly the dominating factor in interpretation of measured peak intensities and peak shapes. Quantification therefore relies heavily on accurate values for the IMFP and the inelastic scattering cross section.

The detailed energy distribution function  $G$  can be calculated provided the energy loss probability per unit path length traveled is known. Figure 1 shows that the XPS peak shape is sensitive to variations in chemical composition on the nanometer depth scale. Quantitative analysis of the peak shape may therefore provide detailed information on the distribution of the depths of origin of the detected XPS or AES electrons and by that also quantitative information on the surface nanostructure of the solid. This has led Tougaard *et al.* to formulate a new technique for quantitative XPS by peak shape analysis (see Sec. V).

If elastic scattering effects are neglected,

$$J(E, \Omega) = \int dE_0 F(E_0, \Omega) \int f(x) G(E_0, x/\cos \theta; E) dx, \quad (5)$$

where  $\theta$  is the emission angle with respect to the surface normal. The function  $G$ , which essentially gives the energy distribution of an electron as a function of path length  $x/\cos \theta$  traveled in the solid, is thus of central importance in any quantitative analysis of energy spectra of emitted electrons. It is determined by the inelastic scattering cross section.

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  $dR$ .  $K(E, T)$  usually depends strongly on  $T$  but only weakly on  $E$ .<sup>3</sup> 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

$$J(E, \Omega) = \int dE_0 F(E_0, \Omega) \int ds e^{-i2\pi s(E-E_0)} \times \int dx f(x) e^{-x\Sigma(s)\cos \theta}, \quad (6)$$

with

$$\Sigma(s) = \frac{1}{\lambda} - \int_0^\infty K(T) e^{-isT} dT. \quad (7)$$

Inelastic electron scattering is clearly the dominating first-order effect in quantitative understanding of peak intensities and peak shapes and this has been the subject of several articles.<sup>21-37</sup>

## V. QUANTITATIVE X-RAY PHOTOEMISSION SPECTROSCOPY BY PEAK SHAPE ANALYSIS

As was discussed in Sec. II, the error in quantification may be greatly reduced if the dependence of XPS-peak shape on the surface nanostructure is taken into account. This is the idea behind a new method for quantification developed by Tougaard *et al.*<sup>3-7</sup> There are two different approaches to the application of the new formalism: either algorithms are used to remove the inelastic background from the measured spectrum or they are used to calculate the peak shape of the spectrum of emitted electrons. In both cases spectral evaluation is done by formulae that depend on the in-depth concentration profile  $f(x)$ .

The suggestions for improved quantification that are presented in Secs. V A and V B were made available in the form of a software package QUASES<sup>TM</sup> (Quantitative Analysis of Surfaces by Electron Spectroscopy).<sup>7</sup>

### A. Quantification by peak shape calculation

In this approach, the spectrum  $J(E, \Omega)$  is calculated by Eq. (6). The function  $F(E, \Omega)$  may conveniently be determined, by the procedure described in Sec. V B, from a measured spectrum of a pure elemental sample. The in-depth

concentration profile  $f(x)$  is then varied until a good agreement with the measured spectrum is obtained. In this way, the detailed in-depth concentration profile  $f(x)$  is determined.

## B. Quantification by background removal

Formulae to determine the atomic excitation function  $F(E, \Omega)$  from a measured spectrum were developed for different types of in-depth profiles.<sup>3-7,20</sup> It was shown that the integral [Eq. (6)] may be solved rigorously for the primary excitation spectrum  $F(E, \Omega)$

$$F(E, \Omega) = \frac{1}{P_1} \left[ J(E, \Omega) - \int dE' J(E, \Omega) \times \int ds \exp[i2\pi s(E' - E)] \left( 1 - \frac{P_1}{P(s)} \right) \right], \quad (8)$$

where

$$P(s) = \int dx f(x) \exp\left(-\frac{x}{\cos \theta} \Sigma(s)\right) \quad (9)$$

and

$$P_1 = \int dx f(x) \exp\left(-\frac{x}{\lambda \cos \theta}\right). \quad (10)$$

Equation (8) may be used to determine either  $F(E, \Omega)$  if  $f(x)$  is known (e.g., for a one elemental sample) or it may be used to determine  $f(x)$  if  $F(E, \Omega)$  is known. It has been pointed out<sup>4-7</sup> that certain general characteristics of the  $F(E, \Omega_D)$  spectrum can be applied in this analysis. The exact peak shape in the energy region close to the peak energy say up to  $\sim 20$  eV below the peak energy is not known since it is largely determined by lifetime broadening and intrinsic excitations in the photoemission process which depends on the local chemical environment. However, the spectrum after background correction must be of zero intensity in an energy region beyond  $\sim 30$  eV below the primary peak energy. Furthermore, it was pointed out that 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  $F(E, \Omega)$  and this may be applied as a criterion to determine  $f(x)$  in the sense that  $f(x)$  must be varied until the constraint is fulfilled. As another criterion one can use knowledge on  $F(E, \Omega)$  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 the absolute intensity and peak shape of the reference spectrum. Finally, 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 be applied.

The procedures described above can be numerically speeded up considerably for those in-depth profiles  $f(x)$ , where the integral over  $x$  in  $P(s)$  and  $P_1$  can be done analytically.<sup>4,7</sup> All in-depth distributions can be considered approximately to be made up of such profiles.

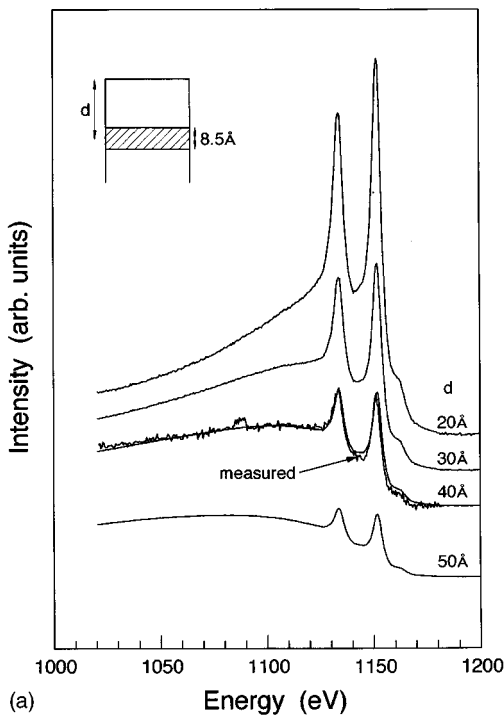
## C. Examples

The method described above has been applied in the study of many different systems<sup>21-37</sup> including surface nanostructures of metal/metal,<sup>22,29</sup> metal/silicon,<sup>33,35</sup> polymer/metal systems,<sup>30,32</sup> surface segregation,<sup>34</sup> and metal-oxide growth.<sup>21</sup> It is not possible to produce nonhomogeneous standard samples with well characterized chemical composition because no alternative technique exists which, with sufficient accuracy, can give an independent measurement of the chemical composition on the nanometer depth scale. However, the results in these previous studies point to the conclusion that, if only the peak intensity is used in quantification, the uncertainty in the analysis is several hundred percent but, if the peak shape as well as the peak intensity are used for quantification by the procedure described in Secs. V A and V B, the uncertainty is reduced considerably and amounts typically to  $\sim 10\%$ – $20\%$  depending on the solid and the surface morphology.

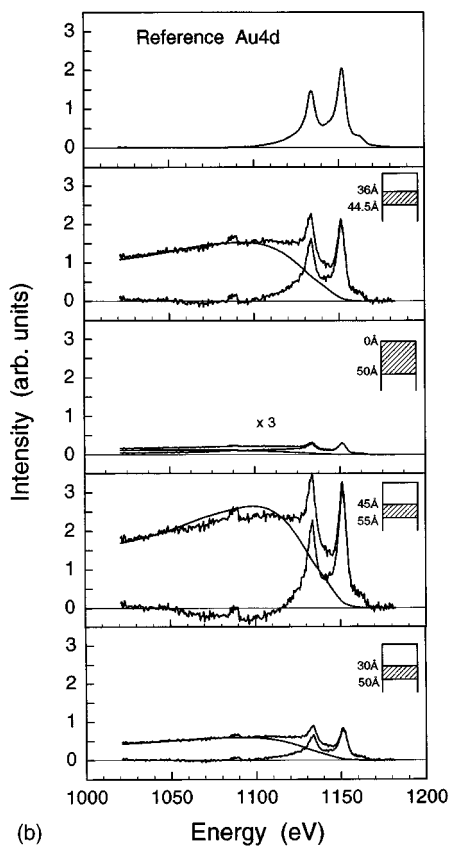
Here we will briefly illustrate the method by a practical example. Figure 2 shows analysis of an experimental Au 4d spectrum of gold. The spectrum was taken from a sample produced by evaporating a thin layer of gold on a Ni(111) substrate and then evaporating an amount of nickel on top.<sup>29</sup> In Fig. 2(a), the quantitative analysis is done by the method described in Sec. V A. Theoretical peaks corresponding to different surface structures are simulated and compared to the measured peak. Note that the peaks should be compared on an absolute scale. Clearly, the spectrum that is calculated under the assumption of a marker situated at  $40 \text{ \AA}$  depth with a width of  $8.5 \text{ \AA}$  gives the best agreement with experiment both with respect to the peak intensity and the peak shape.

In Fig. 2(b), the same spectrum is analyzed by the method of background removal described in Sec. V B. Here the spectrum is background corrected assuming different surface structures. The result is compared on an absolute scale to a reference spectrum from gold. The background corrected spectrum depends strongly on the in-depth composition and it is easy to determine from Fig. 2(b) that the best agreement with respect to intensity and shape is obtained for a layer of gold situated from  $36$ – $44.5 \text{ \AA}$ . The two methods of analysis in Figs. 2(a) and 2(b) give almost identical results as expected.

This analysis (as well as the calculation of the spectra in Fig. 1) was done with the software package QUASES<sup>7</sup> which allows essentially all possible classes of surface structures in the analysis. The space allowed here does not leave room to show a larger variety of assumed structures which, of course, are needed to unambiguously determine the correct surface structure of the gold. Such an analysis, however, shows that it is not possible to get an acceptable analysis of the same



(a)



(b)

FIG. 2. (a) Calculation of Au 4d spectral peak shape from a buried gold layer at varying depths in a nickel sample. Also shown is the experimental spectrum. The best agreement is clearly obtained for a depth of 40 Å and a layer width of 8.5 Å. (b) Background removal for the experimental spectrum in (a) assuming various surface structures. Also shown is a reference Au 4d spectrum obtained by analysis of the spectrum from a pure gold sample recorded with the same analyzer. The best agreement with both intensity and shape is obtained for a buried layer extending from 36 to 44.5 Å.

spectrum when assuming surface morphologies that differ significantly from that determined here.

In Sec. VI we will discuss some effects of elastic electron scattering in quantitative interpretation of XPS.

## VI. ELASTIC ELECTRON SCATTERING

Elastic electron scattering will cause angular electron deflection<sup>20,38</sup> and consequently it leads to an increase in the path lengths traveled by the electrons before being emitted from the solid. This affects the peak shape, the intensity, and the angular distribution of the spectrum, and thus, elastic electron scattering is important for quantitative electron spectroscopy.

Elastic scattering causes the angular distribution of emitted electrons to deviate from that of excited electrons. Consequently the fate of electrons being excited in different directions must be treated separately and the distribution of emitted electrons in a particular direction must be obtained by integrating over the angular distribution of the excited electrons.

The influence of elastic electron scattering on the effective trajectory length of emitted electrons is often described by a single parameter. Various definitions of such a parameter have been proposed,<sup>20,39-43</sup> one is the attenuation length (AL). It is the "effective distance," measured in a direction perpendicular to the direction of analysis, between successive inelastic collisions. When elastic scattering can be neglected, the AL is equal to the IMFP. It turns out that the AL depends not only on the materials involved but also on the experimental geometry as, e.g., the emission angle and to a great extent also on the concentration depth profile.<sup>38-43</sup> Considering the complex effect of elastic scattering on the angular distribution, the intensity, and the peak shape of energy spectra, and the fact that it also depends on the experimental geometry and the concentration depth profile, it is to be expected that a single parameter as, e.g., the AL, will be insufficient to describe the influence of elastic scattering on electron transport processes.

Differential elastic scattering cross sections vary strongly with scattering angle and, while small-angle scattering is clearly most probably for all elements, the heavier elements show large scattering angle variations with several maxima and minima in the scattering cross section.<sup>38,41</sup> The fact that elastic scattering in the forward direction is always dominating means that the major part of the electrons moves along approximately straight lines over the distance between inelastic scattering events. This is the reason that complete neglect of elastic scattering effects is often a reasonable approximation. For example, spectral peak intensities from homogeneous samples were found to be more accurately described when the inelastic mean free path rather than the attenuation length is used in the evaluation of peak intensities for quantitative surface analysis.<sup>43</sup> The reason that elastic scattering effects are less important in the analysis of spectra from homogeneous samples is that the flux of emitted electrons in the energy region around a peak is dominated by electrons that have traveled a small distance in the sample. In

other cases, angular deflection does, however, play a non-negligible role. As an example, the spectrum of electrons from a substrate covered with an overlayer has only contributions from electrons that have passed a minimum distance equal to the overlayer thickness. Then all electrons have traveled a large distance in the sample and the effect of elastic scattering can, for thick overlayers, be substantial.<sup>42</sup> For reflected electron energy loss spectroscopy (REELS), only those electrons that are being backscattered through large angles (either in a single scattering event or because of multiple scattering) are being detected. Although elastic scattering processes are then highly important, a very simple approximation, where the backscattering probability in a given direction is assumed constant for all path lengths traveled by the emitted electrons, is a reasonable approximation. This is so because the probability for large angle scattering is very small and, hence, the intensity in the primary electron beam stays constant as a function of the depth that the primary beam has reached in the surface region of the solid.

The effect of elastic scattering in XPS and AES is often small, and this has led to the consideration of simplified approximate analytical solutions to the Boltzmann transport equation.<sup>20,44–46</sup> The general problem with these models is that the elastic scattering cross section varies strongly with both angle and element and this causes difficulties for a general analytical description of multiple scattering. These approximate analytical models are expected to give a reasonable description of the general trend and may be a valid qualitative approximation for experimental situations where the effect of elastic scattering is small. However, they completely fail to describe the effects quantitatively in situations where the effect of elastic scattering is strong. For example, in a REELS experiment,<sup>47</sup> it was found that an analytical model based on the *P1* approximation to the Boltzmann transport equation gives large quantitative deviations from experiment, and it completely fails to describe the angular distribution of elastically backscattered electrons.<sup>47</sup>

The Monte Carlo approach has been used extensively over the past decade to study the effect of elastic scattering for the XPS and Auger peak intensities;<sup>38,47–53</sup> now more accurate cross sections are used and algorithms that apply for more involved experimental geometries and for inhomogeneous samples are being developed. The intensity distribution of elastically backscattered electrons in the above-mentioned REELS experiment was found to be well described by application of a Monte Carlo algorithm based on differential cross sections calculated within the partial-wave expansion method.<sup>47</sup> Most of these studies have been done for homogeneous samples. The problem is that a Monte Carlo description of elastic scattering for a solid with a general in-depth composition is complicated and requires large computational times.

From Eq. (3) it is seen that elastic electron scattering not only affects the intensity in the emitted energy spectrum at the peak energy  $E_0$  but it does also at lower energies. The distribution of inelastically scattered electrons below the peak energy and thereby the peak shape are thus also af-

ected by angular deflections caused by elastic electron scattering. The function  $Q$  in Eq. (3) can be evaluated by Monte Carlo simulations. Although such calculations are in principle straightforward, they require considerably longer computing times compared to calculations of the effect of elastic scattering on the intensity at the peak energy alone. In recent years, several interesting articles have been published<sup>49–53</sup> where various methods have been developed to speed up the efficiency of the Monte Carlo calculations considerably. A complete database, which should be useful as a starting point for Monte Carlo calculations, of elastic scattering cross sections for all elements and relevant energies was also made available.<sup>41</sup>

A new and highly promising analytical approach valid for homogeneous solids was recently developed by Tilinin and Werner.<sup>54–56</sup> It relies on an analytical solution of the Boltzmann kinetic equation with appropriate boundary conditions and is considerably more accurate than the *P1* approximation. The solution can be obtained in the transport approximation and is valid provided that the angular distribution of emitted electrons is not highly anisotropic. In Ref. 57 this approach was applied to evaluate path length distribution functions for XPS electrons emitted from various elemental samples. There, this analytical solution was compared to Monte Carlo calculations using Mott differential elastic-scattering cross sections for photoelectron lines in Al, Cu, and Au (which have quite different elastic-scattering cross sections). A systematic comparison was done considering a range of experimental geometries, asymmetry parameters, and photoelectron energies. It was found that within about 10% accuracy, the path length distribution function is a universal function of the path length divided by the transport mean free path. The advantage of this approach is that computational times are several orders of magnitudes faster than the Monte Carlo calculations. Having calculated the path length distribution function, simulated spectra can be calculated by Eq. (3). This was done in Ref. 57, and the results were compared to the spectra obtained when elastic-scattering effects are ignored and the transport approximation was found to give spectra that are in close agreement with the more accurate Monte Carlo calculation.

The effect of elastic electron scattering on quantitative XPS was studied in Ref. 58, where ratios of experimental XPS peaks were compared to two first-principle theories corresponding to neglecting and including the effects of elastic electron scattering. Elastic electron scattering was simulated by a Monte Carlo calculation. The theoretical peak intensities were found to change by an average of 14% as a result of elastic scattering. Surprisingly, however, the standard deviation from experiment was practically unchanged, namely, ~15%, in both cases (i.e., whether neglecting or including elastic-scattering effects).

This result can be understood from the following consideration. The error on quantification for the peaks from the pure elemental samples depends mainly on the accuracy of six factors: the ratio of IMFPs, the ratio of photoionization

cross sections, the procedure for peak intensity determination (i.e., the method used for inelastic background correction), the influence of elastic electron scattering, the stability of the instrument, and the energy dependence of the electron spectrometer transmission function (other factors will also contribute to the error as, for example, the role of surface roughness and surface plasmon excitations but, for simplicity, we assume that the error comes from the above-mentioned six factors). Let us assume that all factors contribute with the same amount to the error and let us assume that this is 6% for each factor (this number is chosen just to illustrate a point and is quite arbitrary but probably not too far from reality). The total relative error due to these six factors is 14.7% [close to what was observed in the comparison of XPS peak intensity ratios to theory<sup>58</sup> (see above)]. Let us then assume that somehow we are able to completely eliminate the uncertainty from one of these six factors. Then we have five factors each contributing 6% to the error and this results in a relative error of 13.4%. This is only slightly smaller than 14.7% and illustrates that, when several factors contribute roughly equally to the error, even a considerable improvement in the uncertainty from a single factor has only little influence on the total error.

*Forward focusing and diffraction effects:* Since elastic scattering of electrons on atoms is highly forward directed, structure in measured spectra as a function of emission angle is frequently observed with maxima occurring in directions corresponding to emitted electrons being scattered on neighboring atoms.<sup>59–63</sup> Variations as high as 30%–50% in measured peak intensities as a function of takeoff angle have been observed.<sup>59–63</sup> The enhanced intensity is caused by focusing in the forward direction of the emitted electrons by the attractive Coulomb potential on neighboring atoms. In a simple qualitative picture, this leads to enhanced intensity in directions that directly correspond to the near neighbors of the electron emitting atom. In XPS of Al(001)<sup>62</sup> and of NiO, MnO, CoO,<sup>63</sup> this forward focusing effect was investigated within the energy region of the peak and also in the energy loss region below the peak energy. By observing the intensity variation as a function of both the emission angle and the energy distance to the peak, it was found that the further the energy distance to the main peak, the less structure is observed in the measured intensity. This was interpreted as being due to a substantial reduction in the forward focusing for the electrons that originate from deeper layers. Thus, electrons below a peak energy have traveled a typical distance roughly in proportion to the energy loss. The mean energy lost per inelastic mean free path traveled is  $\sim 15$ – $30$  eV.<sup>64</sup> Features due to forward focusing observed experimentally are then concluded to originate predominantly from electron emitters within the outermost two to four layers of atoms.<sup>59</sup> Several examples of the forward focusing effect have been reported.<sup>59–63,65,66</sup> To account quantitatively for the effect as well as for the finer details in the intensity variations with takeoff angle, detailed models are being used with considerable success.<sup>60,61,65</sup> Analysis of the preferred angular directions of Auger or photoelectrons gives therefore very direct

information on the geometric arrangement of the outermost atoms and has led to the development of a powerful technique for surface structural investigations.<sup>60,61</sup>

Being an advantage for investigations of the geometrical structure of surface atoms, forward focusing effects have, however, severe negative implications for quantitative surface composition analysis of single crystalline substrates by AES and XPS. It can lead to errors as high as  $\pm 50\%$  in determined stoichiometries.<sup>60–63,67</sup> Averaging over several directions will reduce the effect.<sup>60,63,67</sup> This is, however, often impractical since total data collection time thereby is severely increased or it may even be impossible since many instruments do not allow for variations of both azimuthal and polar angles of the electron energy analyzer. The effects are largely avoided in polycrystalline and amorphous materials, as long as the polycrystalline material is free of preferential crystal orientation.<sup>67</sup> In any case, ion bombardment used, e.g., for sample cleaning will to some extent destroy the crystal structure in the outermost 2–4 atomic layers and will thus tend to reduce forward focusing and diffraction effects.

## VII. CONCLUSIONS

We have considered the leading factors that contribute to the uncertainty in quantitative analysis of surfaces by XPS and AES. The main contribution to errors comes from the fact that peak intensities are extremely sensitive to the surface structure on the nanometer depth scale. A meaningful quantification based on peak intensities alone is thus not possible.

Quantification has usually been based on the arbitrary assumption that the sample is homogeneous within the outermost few nanometers. Although this assumption is convenient since it leads to a simple algorithm, it can result in uncertainties in the analysis of several hundred percent. In contrast, the contribution to the uncertainty from other factors is much smaller.

It was further pointed out that when several factors contribute roughly equally to the error, even a considerable improvement in the uncertainty from a single factor has essentially no influence on the total error.

It is therefore clear that in the future effort should be concentrated on procedures to enhance the knowledge on the in-depth composition since without this no improvement in the reliability of quantitative XPS and AES can be achieved even from a substantially more accurate description of other factors.

A new technique for quantitative XPS and AES that relies on analysis of both the peak intensity and the peak shape was discussed and this method seems to reduce the uncertainty considerably to a typical level of 10%–20% depending on the solid and the surface morphology.

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