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Thickness determination of uniform overlayers on rough substrates by angle-dependent XPS

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Abstract

Angle-dependent XPS thickness determinations of thin overlayers are often based on a simple model assuming a perfectly flat substrate. In this paper we analyze the errors involved in applying this method to uniform overlayers on *rough* substrates. The analysis is based on an algorithm for simulation of fractional Brownian motion to model substrate roughness and on a Monte Carlo method for electron trajectory simulation. Calculations for a SiO₂/Si and Au/Si system show that the errors strongly depend on off-axis angle, ranging from –50% to +50% and more. At ~35°, however, the error is remarkably small, and even negligible compared to errors caused by neglecting elastic scattering. Atomic Force Microscopy and XPS measurements on a roughened silicon wafer confirm these findings.

1. Introduction

Angle-dependent XPS is known for its application as a non-destructive depth-profiling technique [1,2]. In recent years a large amount of effort has been devoted to the – still difficult – direct reconstruction of depth profiles from angle-dependent XPS data [3]. Commonly, however, a model of the depth profile is used to analyze through simulation the angular dependence of XPS signals; the model is then optimized to fit the experimental data. The best known example of the latter approach is the so-called uniform overlayer model, which is often applied to determine the thickness of thin surface layers. For a uniform overlayer of thickness d covering a flat,

half-infinite substrate, the angular dependence of the intensity ratio $I_{\text{ovl}}/I_{\text{sub}}$ of overlayer and substrate signals differing not too much in energy, is given by:

$$\frac{I_{\text{ovl}}}{I_{\text{sub}}}(\theta) = \frac{n_{\text{ovl}} \sigma_{\text{ovl}} \lambda_{\text{ovl}}}{n_{\text{sub}} \sigma_{\text{sub}} \lambda_{\text{sub}}} (e^{d/\lambda_{\text{ovl}} \cos \theta} - 1). \quad (1)$$

Here, elastic scattering is assumed to be negligible. Furthermore, λ denotes the Inelastic Mean Free Path (IMFP) of the photoelectrons, n the photoelectron emitter concentration, and σ the cross section for photoelectron emission.

Our interest in layer thickness determination derives from the use of thin (3–5 nm) oxide layers of SiO₂ and Al₂O₃ as flat supports for the preparation of model catalysts. Such systems are much better accessible to study by surface science techniques than technical catalysts are [4–6].

In practical situations, one often encounters the case of a uniform overlayer (contamination, passiva-

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tion) on a substrate that is rough to some extent. Several authors have made clear, both by experiment [7–11] and by theoretical considerations [2,9–12], that the effects of surface roughness on the angular dependence of XPS and AES signals can be quite large. Hence the question, how large the errors are, that are made in applying Eq. (1) to determine the thickness of a uniform overlayer on a *rough* substrate.

In this paper we present Monte Carlo calculations of the angular dependence of the overlayer/substrate signal ratio for the case of a uniform overlayer on a rough substrate, where the substrate roughness is modeled by means of an algorithm for simulation of fractional Brownian motion. The calculated signal ratios have been used to evaluate the errors involved in determining the overlayer thickness by means of Eq. (1). The results indicate that the average local surface slope is the parameter that determines the deviations in angular dependence from the ideal case of a flat surface. These deviations are minimal for an off-axis angle of $\sim 35^\circ$, *irrespective* of the exact nature and magnitude of the roughness and the thickness of the overlayer. XPS and Atomic Force Microscopy (AFM) experiments performed on a roughened silicon wafer provide support for these findings.

2. Calculations

2.1. Generation of model rough surfaces

Fig. 1 shows a typical example of the rough substrate profiles used for the Monte Carlo calculations. To make such profiles, we have applied the

concept of fractional Brownian motion [13], which is an extension of “normal” Brownian motion, also known as random walk and $1/f^2$ noise. A fractional Brownian motion, $V_H(t)$, is a single-valued function of one variable, t , such that the following scaling law holds:

$$V_H(t_2) - V_H(t_1) \propto (t_2 - t_1)^H. \quad (2)$$

H , the Hurst exponent, is a parameter in the range $0 < H < 1$. For H close to 0, the traces $V_H(t)$ are roughest while those with H close to 1 are relatively smooth. To simulate fractional Brownian motion on a computer, one can use several methods, of which the recursive random midpoint displacement methods are the best known. In the simplest scheme, one starts with a straight line and displaces its midpoint by some Gaussian (σ_0) random offset. Subsequently, the midpoints of the two resulting straight line segments are displaced by offsets from the properly rescaled ($\sigma_{n+1} = 2^{-H}\sigma_n$) Gaussian distribution, etc. This method yields true fractional Brownian motion for $H = 1/2$ only; for other values of H more involved displacement schemes have to be used.

The modeling of *surfaces* as a generalization of traces of fractional Brownian motion was first proposed by Mandelbrot [14]. The single variable t can be replaced by coordinates x and y in the plane to give $V_H(x, y)$ as the surface altitude at position x, y . Fractional Brownian images are known [15] for their very realistic representation of natural landscapes and their use is widespread.

For our calculations it is not necessary to simulate a complete three-dimensional landscape. As explained in the next section, one can do with a two-dimensional rough profile $z_H(x)$. We have used

Fig. 1. Example of a rough profile generated by a midpoint displacement method for simulation of fractional Brownian motion. Note that the thickness of the thin surface layer is defined with respect to the local substrate surface.

an algorithm based on a midpoint displacement method with successive random addition [13] to generate profiles consisting of 100 line segments, each spanning 100 nm in the lateral direction. By means of parameters H and σ the nature and magnitude of the roughness was varied over a wide range.

2.2. Monte Carlo algorithm for calculation of XPS intensities

The Monte Carlo method used in this work to calculate overlayer/substrate intensity ratios is essentially the one discussed extensively by Cumpson [16]. It combines the trajectory reversal approach due to Gries and Werner [17] with a statistical weights method introduced by Ebel and Jablonski [18].

In the trajectory reversal approach, the depth distribution of first inelastic scattering events is determined for electrons generated outside the sample and entering it at a specified angle. This distribution is essentially equal to the depth distribution of photoelectrons detected at this angle in an experimental situation, and hence can be used to calculate XPS intensities.

The general scheme of the calculational procedure is as follows. Considering first only elastic scatter-

ing, a reversed trajectory is generated by repeatedly (i) drawing a random value from the appropriate exponential distribution of elastic step lengths and subsequently (ii) picking a new direction via the differential cross-sections for elastic scattering [19]. The twentieth elastic scattering event terminates the trajectory. On the basis of path length and IMFPs the probability is then calculated that the first inelastic scattering event for an electron following the trajectory takes place in the overlayer or the substrate. The contributions to the total overlayer and substrate signals can be calculated by multiplying these probabilities by the appropriate photoelectron-emitter densities, cross-sections for photoelectron emission, and IMFPs. Note that the angular anisotropy of photoelectron emission is not accounted for in this procedure, the reason being that emission anisotropy for 2p transitions is not very high and, moreover, elastic scattering reduces its effects on the depth distribution of photoelectrons [20,21]. Summing the contributions over some 10^4 trajectories eventually results in an overlayer/substrate intensity ratio with a standard deviation $< 1\%$.

One point deserves some special attention. As mentioned, a profile is used instead of a fully three-dimensional substrate/overlayer landscape. As the

Fig. 2. Monte Carlo results for a 2.0 nm SiO_2 overlayer on differently rough substrate profiles, characterized by their average slope s . The thickness, plotted as a function of off-axis angle, is calculated by substituting the Monte Carlo data into Eq. (1). For the right graph, the straight line approximation was applied, i.e. elastic scattering was neglected.

electron is scattered and continues in a new azimuthal direction, the profile is considered to be rotated and aligned with the new direction along the vertical axis through the scatter centre. The assumption here is that the *exact* roughness geometry is not of crucial importance because of its random nature, and therefore, that the rough profile is characteristic of any vertical cross-section. The advantage of this pseudo-3D approach is that it simplifies the localization of trajectory/interface crossings. Following Werner's [22] line of argument, these crossings are treated as forward-scattering centres, i.e. in crossing the interface, a random value is drawn from the distribution of elastic step lengths of the material the electron enters and the electron continues in its original direction. Note that this is also done for surface/vacuum crossings, so that shading effects are fully accounted for.

The values of the differential elastic scattering cross-sections and of the IMFPs are important input data for the Monte Carlo algorithm described. The results presented in this paper are based on the database of Czyzewski [23] of differential cross-sections and on the predictive IMFP formula TPP-2 of Tanuma et al. [24]. It should be noted that Tanuma et al. recently have recommended [25] a modified formula (TPP-2M) for calculation of IMFPs, which predicts remarkably higher values for some materials, including SiO₂ (viz. 3.92 nm instead of 2.83 nm at 1413 eV). This, however, has no essential consequences for the results presented here.

2.3. Monte Carlo results for SiO₂ and Au overlayers on rough Si

We have applied the Monte Carlo algorithm to calculate the angular dependence of the Si⁴⁺ 2p/Si⁰ 2p XPS signal intensity ratio for a uniform SiO₂ overlayer covering a rough Si substrate. The thickness of the overlayer and the roughness of the substrate were varied. The calculations were repeated for a Au overlayer (Au 4f/Si 2p intensity ratio).

Fig. 2 (left) gives the results for a 2.0 nm thick SiO₂ layer on differently rough substrates. The Monte Carlo results were used to calculate the overlayer thickness by means of Eq. (1). The error due to roughness is presented in the figure as the ratio of the calculated and the real thickness. Parameter *s*

equals the averaged absolute slope of the line segments constituting the rough profile used in the calculations, i.e.

$$s = \frac{1}{N} \sum_{i=1}^N \left| \frac{z_{i+1} - z_i}{x_{i+1} - x_i} \right|, \quad (3)$$

where *x_i* and *z_i* are the coordinates of the point where line segments *i* – 1 and *i* cross. This parameter correlates very well with the influence of roughness. Note that Eq. (1) is based on the straight line approximation to photoelectron transport, i.e., that elastic scattering effects are neglected in its derivation. It is well known [26,27] that elastic scattering alone already affects thickness calculations significantly. To discriminate roughness effects from those of elastic scattering, the Monte Carlo calculations were therefore repeated in the absence of elastic scattering; the results are shown in the right graph of Fig. 2. Comparison of the “*s* = 0” curves in Fig. 2 (left and right graph) makes the effects of neglecting elastic scattering clear: The thickness is overestimated by ~ 10%, except for the higher off-axis angles, where the error due to neglect of elastic scattering can be as large as –25% for SiO₂ on Si.

As could be expected, rougher substrates (higher *s* values) lead to larger errors in calculated thickness.

Fig. 3. Error in calculated overlayer thickness at 0° off-axis angle as a function of both average slope and overlayer thickness for a uniform SiO₂ overlayer on a rough Si substrate.

Fig. 4. Error in calculated overlayer thickness at 35° off-axis angle as a function of both average slope and overlayer thickness for a uniform SiO₂ overlayer on a rough Si substrate. Note that the error at this particular angle is largely due to the neglect of elastic scattering in Eq. (1); see also Fig. 2.

The angular dependence of the error is clear. At low off-axis angles, the thickness is overestimated up to 40% for the roughest substrate; at high angles, thickness is underestimated over 50%. It is remarkable that at ~35° the error is nearly independent of the roughness of the sample. Apparently, the influence of roughness is minimal here and elastic scattering effects dominate the error made in thickness calculation.

For thinner and thicker SiO₂ overlayers, the angular dependence of the error in determined thickness is similar. In Fig. 3 the error at 0° off-axis angle is plotted as a function of both roughness and overlayer thickness. Clearly, there is some dependence on overlayer thickness, but the influence of roughness is larger. The situation at 35° is different, as can be seen in Fig. 4; the small dependence on overlayer thickness then dominates the picture. At 70° (see Fig. 5), the roughness dependence is strong again.

The overall picture is similar for the Au on Si system. However, Au is a much stronger elastic scatterer than Si and O, causing the error due to elastic scattering alone to be correspondingly larger. Fig. 6 shows the roughness and overlayer thickness dependence of the error made in thickness determi-

Fig. 5. Error in calculated overlayer thickness at 70° off-axis angle as a function of both average slope and overlayer thickness for a uniform SiO₂ overlayer on a rough Si substrate.

nation at 35° off-axis angle. As for the SiO₂/Si system, the spread in error is smallest at this particular angle. The magnitude of the error is again largely dominated by the elastic scattering contribution, especially for the thinner overlayers.

Fig. 6. Error in calculated overlayer thickness at 35° off-axis angle as a function of both average slope and overlayer thickness for a uniform Au overlayer on a rough Si substrate.

Fig. 7. Experimental XPS results for a flat Si wafer (left), and a wafer roughened with fine abrasive paper (right). The thickness of the native oxide layer, as calculated by applying Eq. (1) to the XPS data, is plotted as a function of off-axis angle. The solid lines are the best fits from the Monte Carlo data: $s = 0.0$ and $d = 0.8$ nm for the flat wafer, and $s = 0.4$, $d = 1.6$ nm for the roughened wafer.

Fig. 8. Shaded AFM image of the roughened wafer. The 500 lines in the image were scanned at a speed of $150 \mu\text{m/s}$ with a conventional pyramidal tip.

3. Experimental results

To check the validity of the Monte Carlo results, XPS and AFM measurements were performed on a piece of roughened silicon wafer. The wafer was roughened with fine abrasive paper and subsequently dipped in a 10% HF solution to remove all of the remaining native oxide. A few days of air exposure were sufficient to obtain a thin surface oxide layer again. Fig. 7 shows the results of the XPS measurements performed on this sample (right side) and on a flat reference sample, dipped in HF at the same time. The measurements were done with a VG Scientific ESCALAB 200, using a standard Al X-ray source. Spectra, measured in Constant Analyzer Energy mode at 20 eV pass-energy, were fitted with the standard VGS software to determine the Si 2p peak parts attributable to overlayer and substrate. For experimental details we refer to Refs. [10,11]. Substitution in Eq. (1) then gives the thickness d plotted in Fig. 7. The drawn curves are the best fits from the Monte Carlo results and correspond to a 0.81 nm thick SiO₂ overlayer on a flat Si substrate for the left graph, and a 1.60 nm thick SiO₂ overlayer on a rough ($s = 0.4$) Si substrate for the right graph. Apparently, the roughened surface oxidizes easier than the flat one. Note that a thickness estimate on the basis of a single measurement at 35° would have resulted in a value of 1.68 ± 0.10 nm, or 1.56 ± 0.10 if the effect of elastic scattering (see Fig. 4) had been accounted for.

Fig. 8 shows an image of a part of the roughened Si wafer, measured with a TopoMetrix TMX 2000 atomic force microscope, using a microfabricated Si₃N₄ cantilever ($k = 0.03$ N/m) with a conventional pyramidal tip. AFM allows for a quantitative analysis of surface roughness in the range from nm to μ m. With the standard TopoMetrix software, the average slope s in an AFM image can be calculated by subtraction of two laterally slightly shifted zooms, and subsequent determination of the average absolute height of the difference plot. The resolution and image size determine the range of roughness features accounted for by this procedure. For example, the size of the image in Fig. 8 is $75 \times 75 \mu\text{m}$ and the resolution 500×500 pixels. Hence, one pixel corresponds to 150 nm by 150 nm. Subtracting two parts of the image, laterally displaced by one or a few

pixels, thus results in a difference plot which reflects the slope of the sample on a scale of microns. By reducing the image size the roughness on the nanometer scale can be probed in the same way. In this particular case of roughening with abrasive paper, the sample remained rather flat on the nanometer scale. On the micron scale, however, the average slope s of the sample surface was measured to be 0.33 ± 0.09 . Hence, the agreement with the value found by fitting, viz. $s = 0.4$, is satisfactory.

4. Discussion

A remarkable result of our analysis is that the error made in thickness estimation on the basis of Eq. (1) correlates well with the average slope of the substrate profiles used for the Monte Carlo calculations. Other parameters, like the much used R_a (= average absolute departure from the mean height), do not show this correlation. The reason for this successful correlation with average slope can be understood if one considers the profiles to be a chain of flat surfaces, all with a different orientation towards the detector. This orientation determines the angular dependence of XPS signals, but of course also the local slope. Apparently, shading effects [2] only play a role at high off-axis angles. It can be questioned whether this reasoning is also valid for *real* substrates, which are clearly not a chain of flat surface parts. However, as long as the overlayer has a well defined thickness, the local orientation of the overlayer must also be well defined. From the Monte Carlo calculations we conclude that this orientation determines the angular dependence to a large amount. Therefore, the average slope of a real sample surface should be an important parameter for XPS purposes. Our AFM results strongly support this point of view.

For everyday experimental practice it is important that in determining the thickness of a uniform overlayer on a rough substrate with Eq. (1), the error caused by roughness is smallest at an off-axis angle of $\sim 35^\circ$. At this angle, the error due to the neglect of elastic scattering is larger than that due to roughness. Note, however, that the error related to the neglect of elastic scattering can be quite large, especially for heavy elements and low photoelectron energies (for Au on Si, for example, up to 35%, see

Fig. 6). Important in this respect are the attempts [28,29] to incorporate elastic scattering effects in photoelectron depth distribution functions, possibly leading to more accurate alternatives for Eq. (1) in the near future.

5. Conclusions

The use of Eq. (1) to determine the thickness of uniform overlayers on rough substrates can easily lead to errors from -50% up to $+50\%$ and more, depending on off-axis angle, roughness, overlayer thickness and elemental composition. The error in calculated thickness scales with the averaged local slope of the substrate. Remarkably, at $\sim 35^\circ$ off-axis angle, the error due to roughness is small, regardless of roughness magnitude, overlayer thickness or type of material; in most cases, it will even be negligible compared to the error caused by ignoring elastic scattering.

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