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Surface roughness effects in quantitative XPS: magic angle for determining overlayer thickness

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Abstract

The use of X-ray photoelectron spectroscopy (XPS) as a technique for non-destructive depth profiling of technical samples is often hindered by their roughness. In this paper, we elaborate on earlier work where we reported on the apparent existence of a ‘magic’ angle for the determination of the thickness of uniform overlayers on rough substrates. Simple calculations for fully three-dimensional model rough surfaces strongly suggest that the thickness of an overlayer on a rough substrate can be determined accurately without taking the roughness into account in the analysis of the XPS intensities, the neglect of roughness effects leading to an average error less than 10% in the determined thickness. © 1997 Elsevier Science B.V.

1. Introduction

The quantification of X-ray photoelectron spectroscopy (XPS) is a subject of great interest in relation to the characterization of surface properties of a wide variety of materials. The last years have seen much progress in this area of research, especially with respect to non-destructive depth-profiling [1], the incorporation of elastic scattering effects [2,3] and the influence of instrumentation [4]. However, quantitative XPS analyses of complex technical samples remain difficult.

Surface roughness is an example of such a difficulty that one encounters in the application of quanti-

tative XPS to technical materials. Especially in depth-profiling, surface roughness is a serious problem. The effect of roughness on the intensity of XPS signals has been studied both theoretically [5–9] and by experiment [7–11] by a number of authors. Powders are a special case, and have been considered mainly in relation to XPS analyses of catalysts (see [12] for an overview).

In previous papers [8,9], we studied the effects of substrate roughness by means of Monte Carlo calculations for the specific case of the determination of the thickness of a uniform overlayer on a rough substrate, where we modeled the roughness by means of an algorithm for simulation of fractional Brownian motion. The rather surprising result of this study was that there apparently is a ‘magic’ angle in this case: an analysis of XPS data obtained at an off-axis angle of about 35°, not accounting for the effects of

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roughness, still yields accurate values ($\pm 10\%$) of the overlayer thickness, independent of the actual magnitude of the roughness. At other angles, the error in determined thickness resulting from neglecting the substrate roughness can be quite large; at normal emission, for example, the thickness is overestimated by about the amount of 'extra' surface due to roughness, i.e., if the relative surface area R equals 1.5, the estimated overlayer thickness is 50% too large. Werner elaborated on our work and showed that our conclusions can be extended to rough substrates with arbitrary in-depth profiles [13].

The purpose of this paper is twofold. In the first place, we want to show that the magic angle effect is already visible in much simpler models of surface roughness than we considered in our previous paper. Secondly, we want to discuss the consequence of the two-dimensionality of both these simple models, Werner's model and the previous fractal model. Extending the simple models to three dimensions, we show that the angle of minimal error shifts some ten degrees towards higher values, which strongly suggests that the true magic angle (error smaller than 10%) is $\sim 45^\circ$ rather than $\sim 35^\circ$.

2. Results

Consider a flat substrate supporting a uniform overlayer with a thickness in the order of a few nanometers. An XPS spectrum of such a system will show peaks related to both the overlayer and the substrate. In the straight line approximation to electron transport, the ratio of the intensities $I_{X,ovl}$ and $I_{Y,sub}$ of two signals X and Y attributable to, respectively, the overlayer and substrate can be expressed as:

$$\frac{I_{X,ovl}}{I_{Y,sub}} = \frac{I_{X,ovl}^{ref}}{I_{Y,sub}^{ref}} \frac{1 - T_{ovl}(E_X)}{T_{ovl}(E_Y)} \quad (1)$$

where T_{ovl} is the overlayer attenuation function, which can be expressed as:

$$T_{ovl}(E) = \exp\left(-\frac{d}{\lambda_{ovl}^i(E) \cos \theta}\right) \quad (2)$$

The intensities I^{ref} in Eq. (1) are intensities that would be measured from clean, homogeneous sam-

Fig. 1. Two-dimensional 'triangular' rough surface. The magnitude of the roughness can be varied by means of the angle ϕ .

ples with the same composition as the overlayer or substrate. In the straight line approximation, the parameter λ^i is the inelastic mean free path (IMFP) of the electrons [14], which depends on both the material and the kinetic energy of the electrons. However, as the straight line approximation is quite crude [15], it is better to use the attenuation length λ instead of the IMFP λ^i in order to incorporate some elastic scattering effects [16]. Finally, d denotes the thickness of the overlayer, and θ the so-called off-axis angle, which is the angle between the central axis of the XPS analyzer and the surface normal of the sample.

Now Eq. (1) pertains to flat substrates only, so its application to rough surfaces will lead to errors in the determined overlayer thickness. As an example, consider the situation depicted in Fig. 1. It is straightforward to calculate that the attenuation function in this case can be expressed as follows:

$$\begin{aligned} T_{ovl} &= \frac{\cos(\theta + \phi)}{\cos(\theta + \phi) + \cos(\theta - \phi)} \\ &\times \exp\left(-\frac{d}{\lambda \cos(\theta + \phi)}\right) \\ &+ \frac{\cos(\theta - \phi)}{\cos(\theta + \phi) + \cos(\theta - \phi)} \\ &\times \exp\left(-\frac{d}{\lambda \cos(\theta - \phi)}\right) \quad \text{for } \theta < 90^\circ - \phi \\ T_{ovl} &= \exp\left(-\frac{d}{\lambda \cos(\theta - \phi)}\right) \\ &\text{for } 90^\circ - \phi < \theta < 90^\circ \end{aligned} \quad (3)$$

Here, we have assumed that the length of the segments constituting the surface is much larger than the attenuation length, so that shading (for $\theta > 90^\circ - \phi$) is complete. Using Eqs. (1) and (3), we then can calculate the relative intensities of the overlayer and

Fig. 2. Error-plot for two-dimensional surfaces like the one depicted in Fig. 1. The error in the determined thickness of the overlayer is averaged for true overlayer thicknesses ranging from 0.5 to 3 times the attenuation length. The average error is plotted as a function of off-axis angle and substrate roughness (as measured by the relative surface area R).

substrate signals as a function of overlayer thickness, off-axis angle, and surface roughness (as measured by ϕ), and use these relative intensities to determine the error we would make in applying Eqs. (1) and (2) to rough surfaces. Thus, we arrive at the plot shown in Fig. 2, where the error, averaged over values for the overlayer thickness between 0.5 and 3 times λ is given as a function of off-angle and substrate roughness. We have used the relative surface area R , i.e. the true surface area divided by the geometric or projected area, as a measure for the roughness; in this case (see Fig. 1), R can be expressed as:

$$R = 1 / \cos \phi \quad (4)$$

A remarkable feature of the plot in Fig. 2 is the valley of error values smaller than 10%, which lies at 30 to 35° off-axis angle. Apparently, the application

Fig. 3. Two-dimensional rough surface made by a method for simulation of fractional Brownian motion [11].

Fig. 4. Upside-down pyramid as a unit of the three-dimensional equivalent of the triangular surface depicted in Fig. 1.

of Eqs. (1) and (2) to rough surfaces does not lead to significant errors if data are used which are measured at these values of the off-axis angle.

Of course, one can argue that the surface depicted in Fig. 1 is a very limited model of a real rough surface. However, in previous papers [8,9] we have shown that the same 'magic' angle is found for more realistic models (see Fig. 3 for an example), which suggests that the actual orientation distribution of the flat segments constituting the rough surface is not of prime importance. Still, in both cases the models are two-dimensional, i.e. variation of the off-axis angle is carried out in the plane defined by the paper.

Now the fully three-dimensional equivalent of the surface of Fig. 1 is a surface consisting of pyramidal units, as depicted in Fig. 4. If we position the XPS analyzer along the arrow as indicated in the figure, then we can distinguish surface parts A and B. Upon

Fig. 5. Error-plot for three-dimensional surfaces consisting of pyramidal units like the one depicted in Fig. 4.

Fig. 6. A two-dimensional surface with a 'circular' distribution of surface segments. The roughness of such a surface can be varied by means of the angle ξ .

changing the off-axis angle, the orientation of surface parts A with respect to the analyzer changes sharply as in the two-dimensional case. The orientation of surface parts B, however, changes much more smoothly. The consequences can be seen in Fig. 5, which is an error plot for a surface consisting of pyramidal units with angle ϕ according to Eq. (4). Although the plot is quite similar to the one in Fig. 2, the valley of minimal errors is now positioned between 40 and 45° off-axis instead of 30 to 35°.

The shift in magic angle of about 10° in going from two- to three-dimensional surface roughness occurs for other roughness models too. As an example, consider the two-dimensional surface depicted in Fig. 6. The orientation distribution of the surface parts in the profile in the left-hand part of the figure is such, that the parts can be rearranged to form the

Fig. 7. Error-plot for two-dimensional circular surfaces like the one depicted in Fig. 6.

Fig. 8. Error-plot for three-dimensional spherical surfaces.

circular segment shown at the right-hand side. The relative roughness of the surface is the equal to:

$$R = \xi / \sin \xi \quad (5)$$

where ξ is the maximum angle in the orientation distribution of the surface parts (see Fig. 6). We have calculated the error plot for circular surfaces with ξ ranging from 0 to $\pi/2$. The results are shown in Fig. 7. Again, there is a valley of average error values smaller than 10%, which centers around 35° off-axis. Similar numerical calculations for the three-dimensional equivalent, viz. spherical segments instead of circular ones give the data presented in Fig. 8. Indeed, for this fully three-dimensional rough surface, the valley of low error values lies some 10° higher, viz. at off-axis angles of 40 to 45°.

3. Discussion and conclusions

In this paper, we extend earlier calculations for model rough surfaces from two to three dimensions. Although the three-dimensional models do represent a technical rough surface much better, one still might think of modeling a rough surface as a set of differently oriented *flat* surface parts as quite artificial. However, it is important to keep in mind that our concern here is the determination of the thickness of overlayers on rough substrates, in case that this

thickness is both well-defined and in the nanometer range. Such systems necessarily are relatively flat in the nanometer range, and can therefore be modeled realistically as sets of flat surface parts with a characteristic length scale of ~ 10 nm.

We have considered two rather different kinds of three-dimensional rough substrates, viz. a surface of upside-down pyramids and parts of a sphere. The largest difference is that the substrate consisting of upside-down pyramids has a minimal number of possible orientations of the surface parts, whereas this orientation is continuously distributed for the spherical surface. Another difference relates to shading, i.e. to the fact that because of the roughness for grazing off-axis angles the analyzer can not be seen from all parts of the surface. For a surface consisting of a set of flat segments, one can distinguish self-shading from neighbor-shading. Self-shading occurs when the orientation of a particular segment is such that the local off-axis angle exceeds 90° ; neighbor-shading occurs when a neighboring surface part blocks the view on the analyzer. For the pyramidal substrate both shading effects occur, while neighbor shading is absent in case of the spherical substrate.

For both model systems, however, we find similar error plots with valleys for off-axis angles of 40 to 45° . This strongly suggests that the position of the valley is determined by the one property that these systems have in common, viz. their three-dimensional roughness, and not by some idiosyncratic property of these systems. We therefore conclude that for systems consisting of a uniform overlayer on a rough substrate, the thickness of the overlayer can be determined accurately (error smaller than 10%)

by means of an analysis of intensity data based on Eqs. (1) and (2), provided that the data are measured with the analyzer at an off-axis angle of 40 to 45° with the macroscopic surface normal of the rough sample.

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