



Self consistent ARXPS analysis for multilayer conformal films with abrupt interfaces

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Abstract

In this Internal Report are discussed important physical considerations for the modeling of Angle Resolved X-Ray Photoelectron Spectroscopy (ARXPS) data for multilayer conformal films. It describes a self consistent analysis method (*Multilayer Method*, or *MLM*) that properly deals with a number of issues that have prevented a richer use of the technique. The MLM is the heart of *XPSGeometry*®, a software that has been employed in a number of ARXPS studies. The method addresses simple issues such as the use of the electron transport parameters corresponding to the material in each layer, an important condition for quantitative analysis that is usually neglected. The ARXPS technique has a limit on the number of structural parameters that it can determine, and this limit is imbedded in the algorithms. The composition of the film is not imposed but quantitatively assessed from the calculations. It also allows for a meaningful estimation of the uncertainties on the structural parameters found by the technique. Some issues involving common practices in this field are also discussed.

I. Introduction

Films of thickness in the nanoscale are nowadays widely employed in a variety of products such as electronic devices (as dielectric insulators in MOS structures), hard drives (as protective films), and MEMS (as lubricants). Their performance is highly influenced not only by the composition of the film, but also by the distribution of the elements throughout the film thickness. Monitoring such composition profile requires a metrology technique that allows for its assessment as a function of the processing parameters. Angle Resolved X Ray Photoelectron Spectroscopy (ARXPS) is ideal for films thin enough to allow for the collection of signal from the substrate, that is, for films with thicknesses up to about 7nm. The XPS spectrum for each element in the film could be composed by one or more peaks. The difference in binding energy between the peaks of a certain core level is associated to different chemical environments that affect the oxidation-reduction degree. For example, in a $\text{HfO}_2/\text{SiO}_2/\text{Si}(001)$ film, the O 1s signal is composed by two peaks (species), one corresponding to oxygen in SiO_2 and another to oxygen in HfO_2 . Likewise, the Si 2p spectrum is composed by two peaks, one from the substrate and the other from the oxide layer. The depth profile information is contained in the dependence on the photoelectron take-off angle of the peak area for *each* species. This dependence is going to be referred as the “ARXPS data”. The assessment of the structure of the film from the ARXPS data is going to be referred as the “ARXPS Problem.”

The ARXPS Problem is ill-conditioned in the sense that a single ARXPS data set might correspond to a large number of different depth profiles. That is, the ARXPS data cannot be directly “inverted” to assess the depth profile. In fact, the maximum number of structural parameters (or depth profile parameters) that could be extracted from ARXPS data is three, even when the number of angles employed to generate the ARXPS data is larger than three.¹ There is a clear consensus about the value of the technique for the characterization of thin films.² However, the precise way to exploit this technique, as well as the actual amount of information that it can provide, has not yet reached such wide concordance. It is generally agreed that the thickness of simple overlayers (such as a single oxide on a parent element) could be obtained fairly accurately with ARXPS (see Peter Cumpson’s contribution in Reference 2). On the other extreme is the study of species from which no prior or little knowledge exists about its concentration-depth profile. For these situations it has been proven that the determination through ARXPS data of the depth profile holds a large uncertainty.¹

An intermediate case is represented by films composed by a series of layers with abrupt interfaces. This is an important case since the nanofilms of industrial interest usually lie under this class. For these cases there is an agreement in that the amount of information that could be obtained with ARXPS is fairly large. However, many studies only attempt to the qualitative determination of the relative depth of the different species, without determining the amount of material in each layer or the depth scale.³ Other studies that employ the Maximum Entropy (ME) method sin from getting out too much information, even more than the information inputted into the analysis, violating a basic principle of conservation of information. Another problem of the Maximum Entropy method is that the algorithm employed imposes the composition of the film in the sense that the balance of anions and cations is forced to be stoichiometric at all times during the data fitting. Then, the ME method cannot assess the composition of the films.

In this report it is described an analysis method applicable to conformal multilayer films with abrupt interfaces. It is going to be referred as “Multilayer Method” or “MLM”. As described below, it enjoys a number of advantages over the methods currently employed:

- It properly deals with the ill-conditioned nature of the ARXPS Problem by parameterizing the depth profile of each species as a layer (“square profile”). Since the number of parameters required to define a layer is three (depth, thickness and density), it also complies with the restriction found by Cumpson.¹
- The analysis is done individually for each species. The identification of a compound in the film is done a posteriori, only when the coincidence between the depths of certain species has been established from the analysis. The composition is then calculated from the relative concentrations, without the need of forcing it to stoichiometric values. This allows for the assessment of changes on composition caused by sample processing.
- The analysis is self consistent because the algorithm allows for the use of the proper electron transport parameter (attenuation length) as the electrons travel through the different layers. This is of special importance since the effective attenuation length depends strongly upon the material through which the generated photoelectrons travel. In contrast, in the ME method the film is considered as a continuum in which the composition varies smoothly with depth, obstructing the incorporation into the analysis of the dependence of the attenuation length on depth. Just because this issue, the quantitative depth profiles obtained through ME are questionable (see C.R Brundle’s contribution in Reference 2).
- The dependence of the peak signal on the take-off angle not only originates from the change on the trajectory length of the electrons inside the solid, but also from the geometry of the XPS tool. In most of the XPS equipment the change in take-off angle is achieved by tilting the sample.⁴ The x-ray spot on the sample surface change size and shape as the sample rotates. The focal spot of the analyzer undergoes similar changes. In most of the ARXPS studies this issue is handled by instead dealing with the ratio of the area of the peak of each species to the area of a peak corresponding to the substrate. This is done with the hope that the most of the geometrical issues will cancel out. As shown below, this is not the case. In the MLM method the ARXPS data is treated directly. Besides avoiding introducing unnecessary uncertainties, the results are less sensitive to the inaccuracies of the modeling (see below).
- The MLM method allows for a meaningful assessment of the uncertainties on the structural parameters (thickness and composition of the layers). Calculating uncertainties in the ME method is not possible because the solutions are very unstable, leading to artificially large numbers. With the MLM method is possible to determine, for example, the desirable degree of accuracy of the electron transport parameters.⁵
- In a related issue, through the MLM method it is possible to show that the limitations of the current transport theory applied to nanofilms. Fitting the structural parameters to the ARXPS data is not the way to go because it would lead to unphysical structures. As explained below in more detail, self consistency should be preferred over optimized data fitting.

II. The equations for the Multilayer Model

The quantification through ARXPS of the chemical composition and distribution requires the prior knowledge of core level photoemission cross sections, which were assessed in the 1980's,⁶ as well as electron attenuation lengths, most recently estimated.⁷ In the last decade there has been significant progress towards the understanding of the scattering events of electrons inside solids and, as a result, the attenuation length values can be found in tables for most materials.⁸ In this section it is derived an expression for the photoelectron intensity proper for layered films.

According to the escape depth theory of photoemission,⁹ the photoelectron signal coming from an atom of specie S located at a depth z is attenuated by the presence of the material above by a Beer Lambert-type factor of the following form

$$\exp\left(-\int_0^z \frac{dz'}{\lambda_S(z')\sin\alpha}\right),$$

where z is the depth, λ_S is the effective attenuation length ("escape depth"), and α is the take off angle. This expression takes into account that the parameter λ_S can vary as a function of depth because the layers composing the film are constituted by different materials. Although this consideration is usually overlooked in ARXPS studies, it is of fundamental importance for quantitative analysis. When the specie S is distributed in the solid with a depth profile (atomic density as a function of depth) described by $G(z)$, the total signal is proportional to

$$\text{Equation 1} \quad \int_0^\infty dz G_S(z) \exp\left(-\int_0^z \frac{dz'}{\lambda_S(z')\sin\alpha}\right),$$

Although in many studies the depth profile is considered as continuous, it should be treated as discrete since the core levels considered are localized close to the atomic nucleus. The (discrete) depth profile for specie S located in a *locally* crystalline structure can be written in terms of its depth (d_S^a), thickness (d_S), and atomic surface concentration (s_S), as follows:

$$\text{Equation 2} \quad G_S(z) = \sum_{n=0}^{d_S/a_S} s_S \delta\left[z - \left(d_S^a + \left(n + \frac{1}{2}\right)a_S\right)\right],$$

where a_S is the atomic plane spacing. The ratio d_S/a_S corresponds to the number of atomic planes in layer S . The term $\frac{1}{2}$ has to be added since, e.g., the first atomic plane is located $\frac{1}{2}$ of a monolayer below the interface. Under this profile Equation 1 can be expressed as follows:

$$\text{Equation 3} \quad I_S(\alpha) \sim s_S \frac{1 - \exp\left(-\frac{d_S}{\lambda_S \sin\alpha}\right)}{1 - \exp\left(-\frac{a_S}{\lambda_S \sin\alpha}\right)} \exp\left(-\frac{a_S/2}{\lambda_S \sin\alpha}\right) \prod_i^{\text{layers above S}} \exp\left(-\frac{d_i}{\lambda_{S,i} \sin\alpha}\right),$$

where $\lambda_{S,i}$ is the attenuation length of the photoelectrons from species S as they travel through the layers i in the way to the surface, so the last factor is the attenuation caused by the material above the layer S . The other factor represents the sum of the signal from the atomic planes in layer S . This expression also works for the substrate species by considering that $d_S = \infty$.

Since in most studies the depth profile is treated as continuous, the next lines are dedicated to compare both approaches, discrete and continuous. In the latter instance, the depth profile can be written in the following way

$$G_S^c(z) = \begin{cases} c_S & \text{if } d_S^a < z < d_S^a + d_S \\ 0 & \text{otherwise} \end{cases},$$

where c_S is the average density and is equal to s_S/a_S . The equivalent to Equation 3 for the continuous case is the following:

$$\text{Equation 4} \quad I_S^c(\alpha) \sim c_S \lambda_S \sin \alpha \left[1 - \exp\left(-\frac{d_S}{\lambda_S \sin \alpha}\right) \right] \prod_i^{\text{layers above S}} \exp\left(-\frac{d_i}{\lambda_{S,i} \sin \alpha}\right).$$

This expression could be exactly recovered from Equation 3 by considering that $a_S/\lambda_S \ll 1$, that is, by considering that the atomic plane spacing is much smaller than the attenuation length. Physically, this corresponds to a continuous distribution of atoms in the scale of the attenuation length. The error incurred by employing this approximation is smaller for large attenuation lengths.

Going back to the discrete depth profile treatment, the XPS signal coming from the point \mathbf{r} on the sample surface can be written in the following way:¹⁰

$$\text{Equation 5} \quad I_S(\alpha, \mathbf{r}) = X(\mathbf{r}) A(\mathbf{r}) \sigma_S y_S s_S \times \frac{1 - \exp\left(-\frac{d_S}{\lambda_S \sin \alpha}\right)}{1 - \exp\left(-\frac{a_S}{\lambda_S \sin \alpha}\right)} \exp\left(-\frac{a_S/2}{\lambda_S \sin \alpha}\right) \prod_i^{\text{layers above S}} \exp\left(-\frac{d_i}{\lambda_{S,i} \sin \alpha}\right),$$

where σ_S is the x-ray absorption cross section of the core level and y_S is the efficiency to produce a photoelectron.¹¹ Both the x-ray intensity (X) and the electron analyzer efficiency (A) depend on position. These dependences can be modeled with a Gaussian curve around their axis that becomes more intense as the beam narrows, as illustrated in Figure 1.

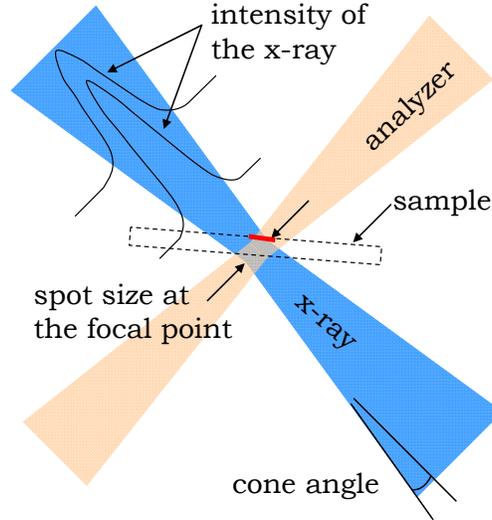


Figure 1. Diagrammatic representation of the x-ray intensity and analyzer efficiency in a XPS experiment. The red line is the region where the x-ray beam and the focal spot of the analyzer overlap with the sample surface. For monochromatic sources, the intensity of x-ray is a cylinder with a waist in the focal spot. The cone angle and the size of the waist depend on the monochromator and could be found in the user manual of the XPS tool. The efficiency of the electron analyzer could be viewed in the same way, but in addition to the cone angle and focal spot size, the acceptance angle of the analyzer should also be specified.

Although the parameters shown in the figure (cone angle, waist size and acceptance angle) are approximately provided by the vendor for both the analyzer (see, for example, Reference 12) and the x-ray source (see, for example, Reference 13), their values should be experimentally characterized for each instrument for a proper quantitative ARXPS analysis. The protocol for performing this characterization is briefly described in the Section III; a more detailed description is provided elsewhere.¹⁴

The actual measured intensity is, in fact, an integration of the Equation 5 on of the overlap on the sample surface between the x-ray beam and the electron analyzer focal spot (red region in the Figure 1):

$$\text{Equation 6} \quad I_S^T(\alpha_N) = \int_{\text{sample surface}} dr^2 \int_{\text{acceptance angle}} d\alpha f(\alpha - \alpha_N) I_S(\alpha, \mathbf{r}),$$

where α_N is the nominal take-off angle and f is a function that decay depending on the acceptance angle of the electron analyzer (lens setup). The function f is modeled as a step function. The constants in front of the Gaussian modeling of the x-ray intensity and analyzer efficiency can be enclosed into a single overall constant C that could be explicitly included in Equation 5. It is the same for all species, and is obtained from the bulk component since its structural parameters, namely thickness ($d_S = \infty$), atomic plane spacing (e.g., $a_S = 1.375 \text{ \AA}$ for Si the [001] direction) and concentration (e.g., $s_S = 8.64 \times 10^{18} \text{ cm}^{-2}$ for Si [001] planes), are known. Since the layers are usually amorphous or polycrystalline, their average atomic plane spacing and concentration should be employed in the calculations.

This integration of Equation 6 is done numerically employing *XPSGeometry*®, a piece of software developed ex professo for this purpose.¹⁵ This required a detailed knowledge of the geometrical parameters of the instrument, such as of the spread of the x-ray beam and the size of the electron analyzer focal spot. For this purpose, the XPS instrument was thoroughly characterized from knife edge experiments employing model gold samples.

III. The determination of the XPS tool geometrical parameters

The necessity of accounting for the geometrical parameters of the XPS tool is powerfully illustrated in the Figure 2. (The data shown in that figure is part of another study.¹⁴) This figure depicts ARXPS data for Au 4f obtained in an Omicron Nanotechnology system (analyzer model EA 125) with a monochromatic Al $K\alpha_1$ source. The black dots correspond to the “high magnification” mode, which is a lens mode of the analyzer in which the focal spot is small (0.7mm) and the acceptance angle large ($\pm 8^\circ$). The black curve corresponds to the calculated intensity employing the Equation 6. It can very well reproduce the behavior since the spot size of the x-ray was characterized previously with the method described below.

The red dots, on the other hand, correspond to the “low magnification” lens mode, in which the focal spot is larger (4mm) and the acceptance angle is smaller ($\pm 1^\circ$). These values, the focal spot size and the acceptance angle, are provided by the vendor.¹² To generate the red line it was only necessary to input the proper values of the focal spot size and acceptance angle into *XPSGeometry*. That is, to reproduce the experimental ARXPS data is only possible if the geometrical parameters of the XPS tool are taken into account. As it is mentioned in the Section I, in many reports the ration of the peak intensity to the bulk peak intensity, and not the actual ARXPS data, is modeled. In those cases many of these geometrical factors are cancelled out to some extent, and the effect shown in the Figure 2 is not longer apparent by visual inspection. However, as shown in Section IV.6.b, dealing with the ratio data is not convenient if full quantitative results are desired.

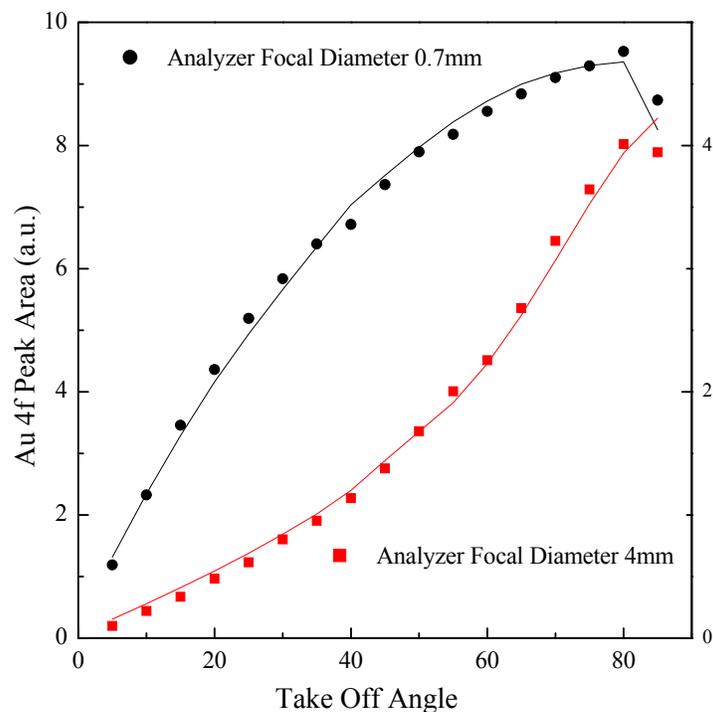


Figure 2. ARXPS data for Au 4f obtained with two lens modes. The difference in the concavity is reproduced in detail by accounting for the focal spot size and acceptance angle of the electron analyzer.

The protocol that was developed to characterize the XPS tool for quantitative ARXPS analysis is described next. The parameters defining the shape and size of the x-ray spot and the focal spot of the analyzer were obtained through a series of experiments employing a model sample. It consisted of a 100 nm thick Au film deposited on a Si substrate and cleaved to form a 1.5cm×1.5cm square with sharp straight edges. The sample was clean-sputtered prior to data taking. The software developed to perform the numerical analysis, *XPSGeometry*®, is shown in the Figure 3. The page shown contains four plots, each corresponding to a different type of experiment. These experiments consisted of data collected at different angles (a), at different heights (b), and knife-edge experiments in the dispersive (c) and not-dispersive (d) directions of the x-ray beam. All the data was analyzed simultaneously to obtain the x-ray beam and electron analyzer parameters shown in (e). Similar sets of data were obtained for the low, medium and high magnification modes of the electron analyzer, allowing for the determination of the focal spot size for each lens mode. A more detailed description of the protocol is provided elsewhere.¹⁴

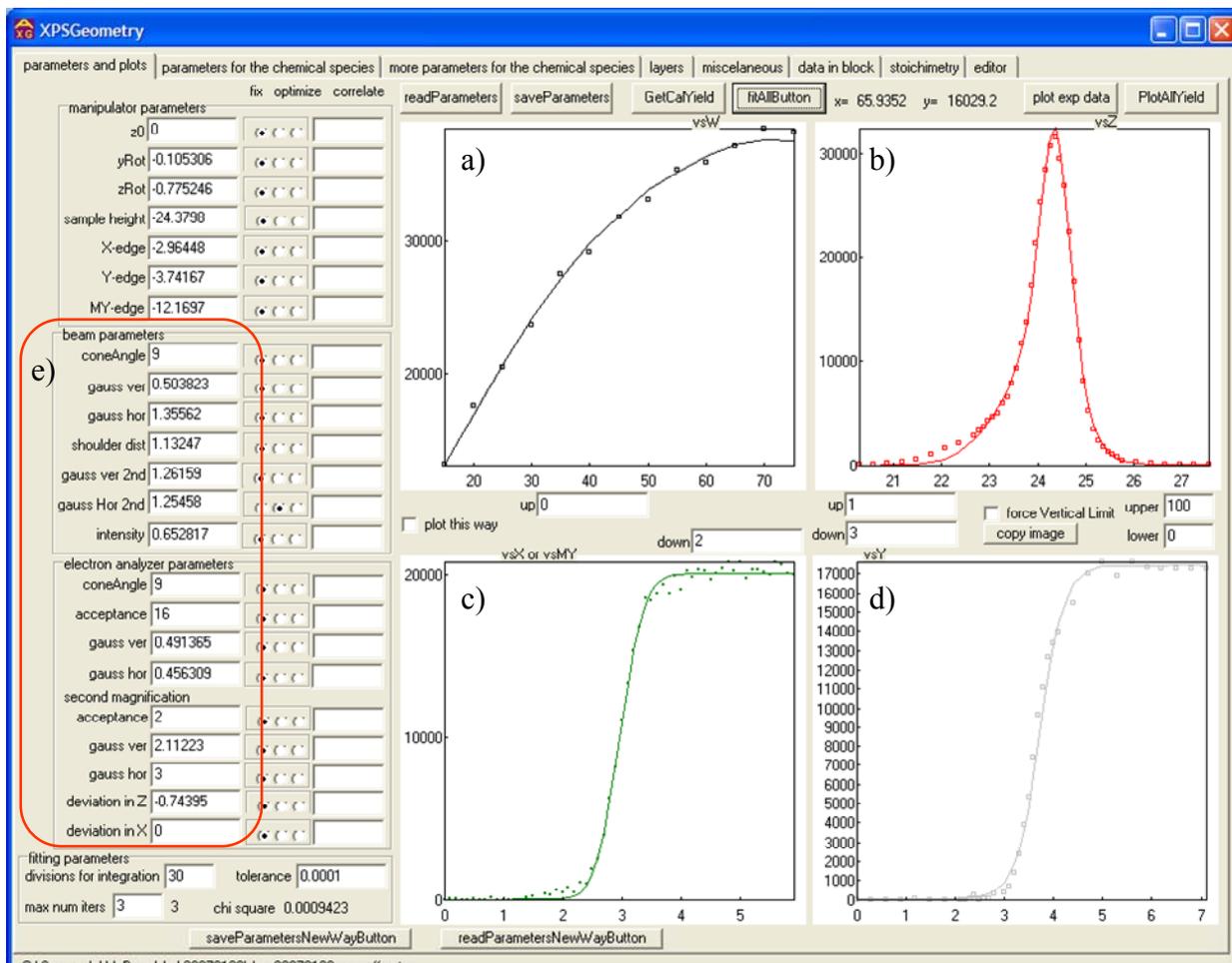


Figure 3. View of one of the pages of the software XPSGeometry. The data correspond to the XPS intensity of Au 4f taken at a) different angles, b) different heights, c) knife edge in the dispersive direction, and d) knife edge in the non-dispersive direction, all in the high magnification mode. e) Geometrical parameters of the XPS tool obtained from simultaneously fitting the four different types of experiments.

Once the beam parameters have been obtained employing a model sample, it is possible to engage into the modeling of more complex systems.

IV. Example: self consistent ARXPS analysis of the $\text{HfO}_2/\text{SiO}_2/\text{Si}$ system

In this section the Multilayer Model is illustrated by its application to a real set of data from a real sample. The film chosen consist of a hafnia layer grown by ALD on a silica layer thermally grown on a Si(001) substrate.¹⁶ This is a good approximation to a multilayer conformal film since a thermally grown silica film could be very uniform, and the ALD technique provides for very uniform films. However, the conformity is just an approximation since the layers are not completely uniform. The rugosity and the lack of uniformity will not be taken into account in this analysis, neither the detailed dependence of the electron transport parameters on the particular structure of the compounds in the film, so we could only aspire to reproduce the experimental ARXPS data until a certain degree. For these reasons, the analysis should make use of independent information, such as the expected densities of the compounds constituting the

film. How to make use of this extra information is described in Section IV.5.b. To extract the rich quantitative information that ARXPS can provide it is necessary to take care of a number of concatenated and interdependent issues. How to address each one of them properly is described in the Sections IV.1.b to IV.5.

IV.1. Issues preceding the ARXPS data analysis

a. *The relevance of high resolution in XPS data*

The analysis will be exemplified with data from a sample consisting of HfO₂ deposited on top of 1nm of SiO₂ grown on a Si(001) substrate. It is almost always convenient to count with high resolution XPS data. The XPS data for Si 2p, O 1s, Hf 4f and C 1s is shown in Figure 4. The clear definition of the Si 2p^{1/2} and 2p^{3/2} branches for the bulk peak (Figure 4a) is a sign of high resolution. The high resolution is only crucial for the deconvolution of the O 1s peak because the two peaks composing the spectra lie very close to each other relative to the peak widths. In contrast, the two peaks composing the Si 2p spectra (substrate and oxide) are far enough from each other to allow for their easy deconvolution even if a lower resolution is employed during measurement. However, the data for all the core levels should be obtained with the *same* resolution to allow for a meaningful comparison of their relative intensities. This comparison is required for the assessment of the density (or width) and composition of the different layers constituting the film.

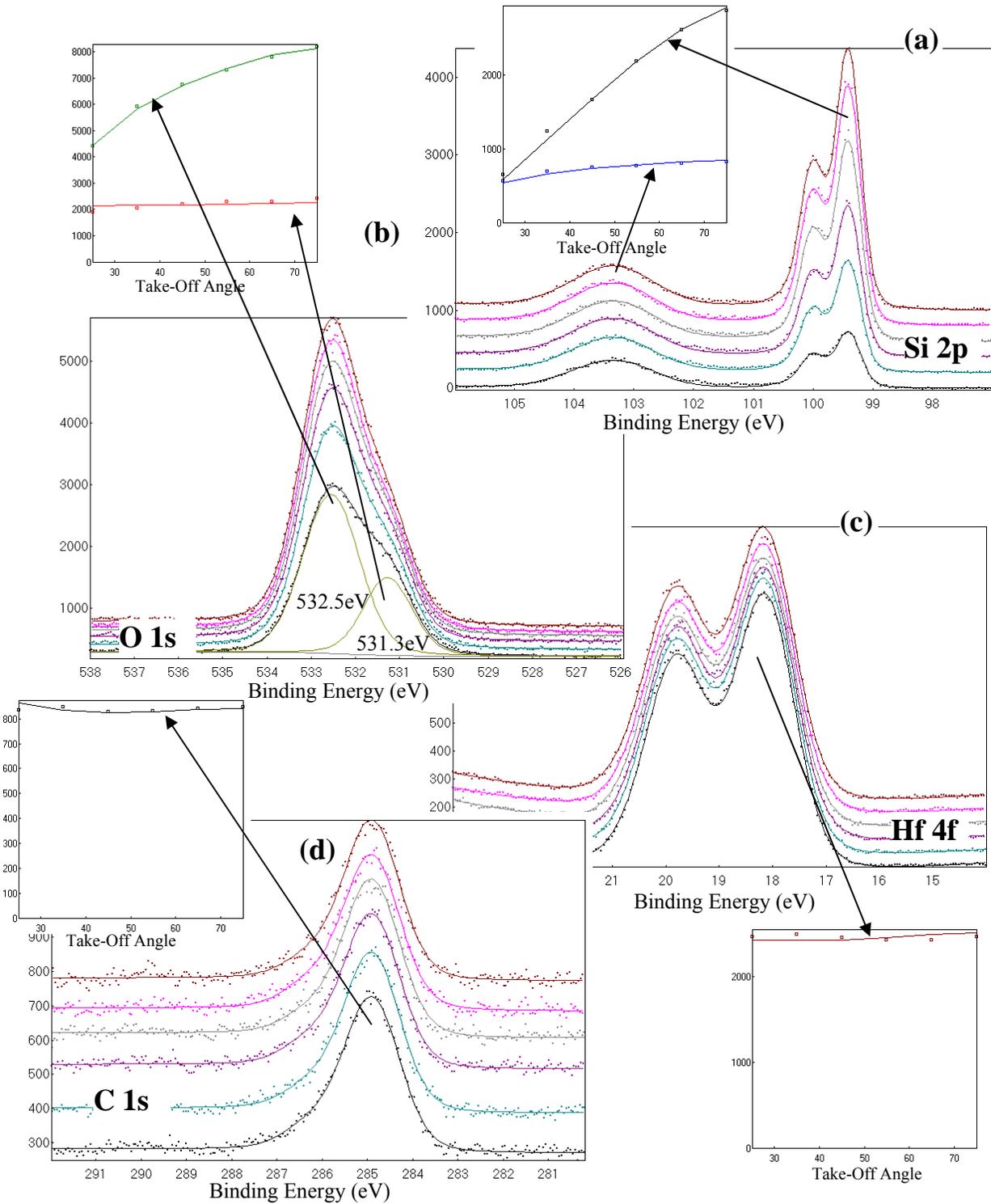


Figure 4. XPS data for a sample consisting of HfO₂ deposited on top of 1 nm of SiO₂ grown on a Si(001) substrate. The core levels considered are a) Si 2p, b) O 1s, c) Hf 4f, and d) C 1s. The take-off angle dependence of the area of each peak is shown in the inserts.

b. XPS data fitting

As described elsewhere,¹⁷ it is convenient to employ a simultaneous fitting algorithm to robustly deconvolve the two peaks in the O 1s spectra. In this way it is possible to find the take-off angle dependence of each component (see the insert in Figure 4b). It should be mentioned that in most of the reports about this type of samples, the oxygen signal is not deconvolved into the two peaks shown in Figure 4b, and only deals with the total O 1s area. Employing simultaneous fitting algorithms in high resolution data doubles the amount of information extracted from the O 1s data. Without this deconvolution it would not be possible to assess the composition of the silicon oxide and hafnium oxide layers.

The result from this fitting is the ARXPS data, that is, the take-off angle dependence of the peak areas shown in the inserts. From the dependence shown in the insert of Figure 4b, it is clear that the oxygen 1s peak at 532.5eV is positioned deeper than the peak at 531.3eV, suggesting right away to which layer each component belongs.

IV.2. Identification of the arrangement of the layers

For conformal layered films it is straightforward to find out the arrangement of the compounds from the slope of the ARXPS data. As a rule, the larger the dependence on the take-off angle (i.e., the larger the slope) of the peak area, the deeper is the location in the film. The Figure 5 shows the data (dots) for the cations (Hf 4f and Si 2p). Two scenarios are considered, one with the expected order of layers and another in which the hafnia is below the silica. The solid lines are the predicted dependence according to the structure shown in the inserts. It is clear that the arrangement of the layers can be easily obtained by comparing the prediction of the models with the experimental data.

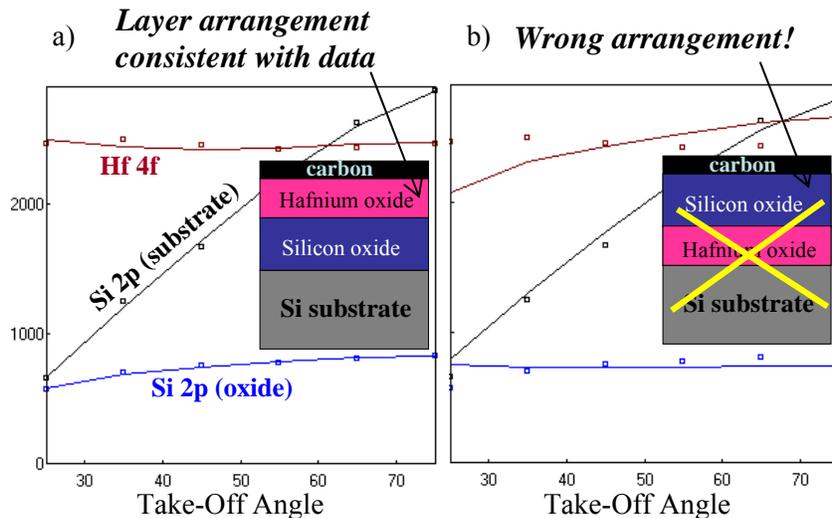


Figure 5. The order of the layers is easily obtained from the take-off angle dependence of the peak areas for Hf 4f and Si 2p. a) The solid lines are the theoretical predictions according to Equation 6 employing the model of the insert. b) The lack of consistency of the predictions with the data right away discards the model of the insert.

IV.3. Identification of compounds and correlation of structural parameters

The next step is to assign the anion peaks to the different layers. In this case there is only one anion (oxygen). However, the O 1s spectra have two peaks, so the task consists in finding out the proper assignment of each of the two peaks of oxygen to the different layers. This is done in the same way, that is, by comparing different scenarios and deciding which one is more consistent with the data. This is illustrated in Figure 6, where each one of the oxygen peaks is assigned in different ways. The scenario corresponding to the Figure 6b is clearly more consistent with the data than that in Figure 6c. The consistency between the theoretical and experimental take-off angle dependence of each peak is an independent criterion to assign the O 1s component at 532.5eV to silica and that at 531.3eV to hafnia. There are two more reasons to believe the scenario in (b). The first, which is very important, is that the binding energy of the oxygen peaks makes sense.¹⁸ The other is that the wrong assignment of the peaks represented in (c) results in completely wrong stoichiometry for both compounds.

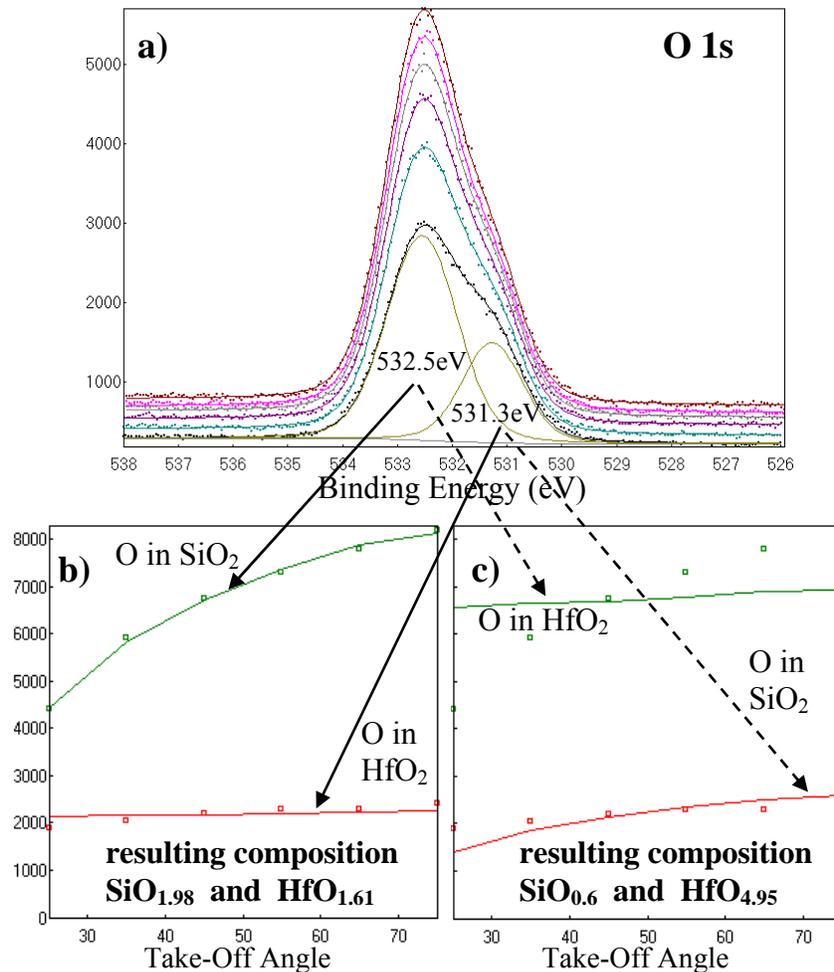


Figure 6. The task of assigning the two oxygen peaks (a) to the different layers could also be done by comparing the experimental take-off angle dependence with predictions made under different assumptions (b and c). It is clear that the experimental data is consistent with the assignments described in (b). The binding energy of the peaks also makes sense since the peak at 532.5eV is associated to oxygen in SiO₂, and the peak at 531.3eV to oxygen in HfO₂.¹⁸ In addition, the scenario shown in (c) yields to unphysical stoichiometries.

A total of six species have been considered, two from silicon (bulk and Si^{+4}), one from hafnium (Hf^{+4}), two from oxygen (O in SiO_2 and O in HfO_2) and one from carbon. Each species is modeled as a layer so requires two structural parameters (depth and thickness, except for the bulk, which thickness is known). The total number of free parameters is 11. However, it is possible to make a number of correlations. For example, the depth and thickness for Si^{+4} could be correlated to the depth and thickness of the oxygen specie with binding energy 532.5eV. It is also necessary to consider that the lower end of a layer coincides with the upper end of following layer. At the end there are only three free parameters, which are the thickness of the carbon, hafnium oxide, and silicon oxide layers.

IV.4. Consistency with the electron transport parameters

The compounds identified are $\text{SiO}_{1.98}$ and $\text{HfO}_{1.61}$. Both are close enough to stoichiometric silicon and hafnium oxide that it is possible to consider as so. Then, the electron transport parameters (effective attenuation length) employed in the calculations are those corresponding to these compounds. This is of special importance since, as shown in Table 1, the effective attenuation length depends strongly upon the material through which the generated photoelectrons travel.⁸

Table 1. Parameters employed in the angular analysis.

Core Level	Effective Attenuation Length (Å)			
	Si	SiO_2	HfO_2	C
Si 2p	29.2	35.2	17.2	33.4
O 1s		25.5	12.5	24.4
C 1s		31	15.1	29.5
Hf 4f		36.9	18	35

IV.5. Self-consistent determination of the thickness of the layers

a. *Obtaining the structure from fitting*

As mentioned at the end of Section IV.3, after all the correlations have been made the structural parameters that require being determined are the thicknesses of the carbon, hafnia and silica layers. These parameters could be chosen in such a way to better reproduce the experimental data. The comparison between the theoretical and experimental data for this case is shown in the Figure 7a.

Although the fit is good, the density of the materials differs from the expected bulk values. For silica the density is 3.2 times larger, which is a completely unphysical value. In addition, this is an inconsistency in the model calculations because the electron transport parameters depend on the density of the material. In fact, the calculations for the attenuation lengths takes into account the density of the material.⁸ If the density increases the attenuation length decreases accordingly, and vice versa. If it were going to be considered that the density of the material differs from the bulk value, then the attenuation lengths should be recalculated and the thicknesses estimated again. This would lead to new thicknesses and new densities, an iterative process that do not converge. The physical reason for this lack of convergence is that the ARXPS technique cannot assess the density of the materials: a layer twice thicker but half denser would induce the same attenuation on the photoelectron signal, and the take-off angle dependence would be indistinguishable from each other.

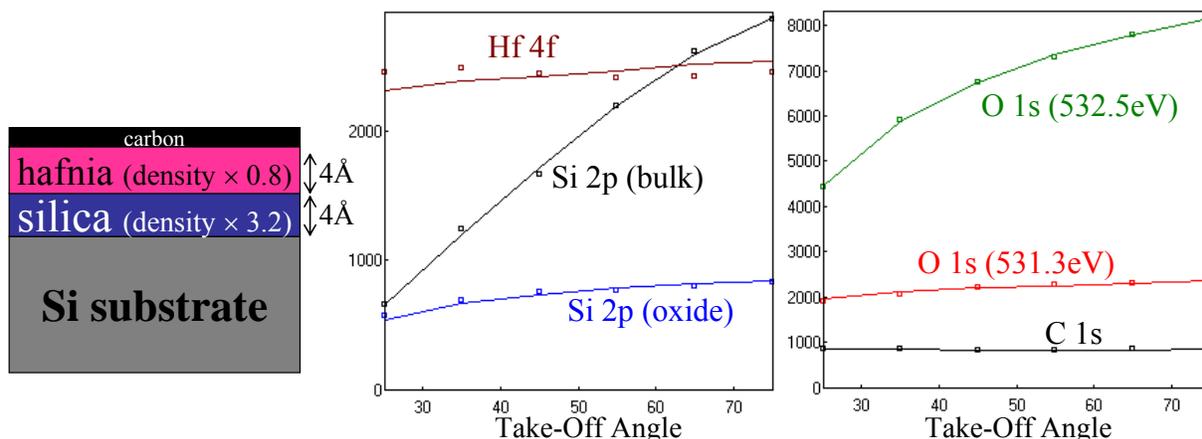


Figure 7. Comparison between the theoretical and experimental data for which the thickness of the different layers were fitted to better reproduce the experimental data.

b. Obtaining the structure by forcing consistency on density

The only way to solve this problem is to force the density of the materials to the bulk value, which is the value that is employed to estimate the attenuation lengths. In this way the calculations are self-consistent since the electron transport parameters employed do correspond to the materials in the different layers. The diagram in the Figure 8 shows the structure that is obtained in this way. The thickness of the silica layer had to be increased in a factor close to the prior overestimation of the density.

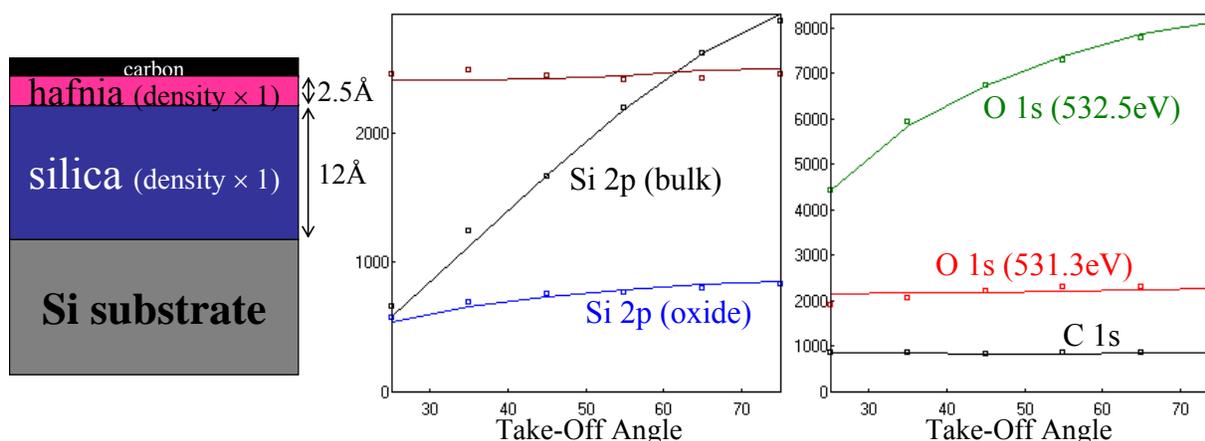


Figure 8. Final structure. The diagram shows a physically plausible structure that is consistent with the ARXPS data. The calculations are also self consistent.

The composition of the layers found with the self consistent model is $\text{HfO}_{1.65}$ and $\text{SiO}_{2.05}$, respectively. The deviation of the composition of the hafnia from stoichiometric values might be due to the fact that a good percentage of the oxygen bonded to a hafnium atom is bonded to a silicon atom. This is because the thickness of the hafnia is less of a monolayer. An O 1s peak associated to Si-O-Hf bonding was not found in the O 1s XPS spectra. A possible explanation is that this peak is closer to that associated to Si-O-Si, and could not be deconvolved from it. In

fact, the ratio of the total cation atoms ($\text{Si}^{+4} + \text{Hf}^{+4}$) to the total number of oxygen atoms is 1.97, or 2 within the uncertainty. This is remarkably close to the expected charge balance.

IV.6. Some other important analysis issues

a. *Fitting versus self-consistency: the ill-conditioning nature of the ARXPS Problem*

The theoretical prediction consistent with density does also reproduce very well the experimental data. In fact, the Hf 4f “fit” is better in this case. This is a good example of the ill-conditioned nature of the ARXPS Problem: both of the structures shown in Figures 7 and 8 reproduce fairly well the experimental data. However, one of them, that in Figure 7, corresponds to unphysical values of the density and the results are not self consistent with the calculations (a deviation on the density requires the recalculation of the attenuation lengths). The consistency of the physical model should be preferred over the optimization of the fit. This behavior is well known in ARXPS analysis since it has been observed that allowing the structural parameters to vary freely can yield to unphysical structures.

b. *Normalization by the bulk data*

As mentioned in Section I, in many ARXPS studies the ARXPS data is normalized to the bulk data in an attempt to cancel out the angular issues described in Section III. However, this approach directly leads to an increase of the uncertainties because the error on the determination of the bulk peak area should be added to the corresponding error for each species. For films thicker than 4nm the attenuation of the bulk signal compromises the accuracy of its peak area, especially for shallower angles.

The second problem associated to employing ratio data is related to modeling. As mentioned in the beginning of the Section IV, there are a number of issues not included in the model, such as rugosity and lack of uniformity. In addition, the precise value for the electron transport parameters depends on the detailed structure of the film. The experimental data could be reproduced only up to a certain degree. The treatment of the bulk signal is not an exception; there are slight deviations from the predicted value. Dealing with ratio data requires not only a close modeling of the take of area of the specie in question, but also a close modeling of the bulk data. The ratio approach imposes stronger requirements on the quality of the model.

Another important observation is that the silicon bulk signal is not as closely reproduced in the Figure 8 as it was in the Figure 7. The conclusion is that the “correct” physical model is not necessarily the model that better reproduce the bulk data, or better, the model that best reproduce the bulk peak is not necessarily physical. Fitting the structural parameters to better reproduce the ARXPS data and employing ratio data are two widely employed practices that could yield to misguided results

V. Conclusions

The most important conclusion is that through ARXPS it is possible to obtain very detailed information of the composition and thickness of each layer in multilayer conformal films with abrupt interfaces. (The film should be thin enough to allow for a clear XPS signal from the substrate.) The most important issues that should be addressed to obtain quantitative information are the following:

- The attenuation length employed should correspond to the material of the layer.
- The depth profile should be modeled with a minimum of parameters, three at the most.
- Independent extra information has to be employed to complement the ambiguity originated from the ill conditioned nature of the ARXPS Problem. The expected density of the material of each layer is a piece of such extra information. The structural parameters of the different layers should be consistent with the corresponding density employed to assess the attenuation lengths.
- Fitting the structural parameters to better reproduce the experimental data is not the most appropriate approach because it could lead to unphysical structures. The structure should be obtained by comparing different arrangements consistent with the data, and choosing the scenario that better reproduce the data.
- Dealing with data that has been divided by the area of the bulk peak could lead to appreciable errors. It is more convenient to treat the areas of the peaks directly.
- The theoretical model should consider a discrete density. The error of considering a continuous distribution could be very important.
- The theoretical prediction should include the effect of the geometrical parameters of the XPS tool (e.g., the size of the focal spot of the electron analyzer). Those parameters should be previously characterized and included in the numerical calculations of the total intensity.

In this report it was presented a method (Multilayer Method) that allows for the proper treatment of all these issues. The software *XPSGeometry*® incorporates these considerations into numerical calculations.

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