Simultaneous data fitting in ARXPS

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I.   Introduction

As it is reported in other studies, an appropriate analysis of Angle Resolved X-Ray Photoelectron Spectroscopy (ARXPS) data can provide very detailed information about the structure of ultra thin conformal films with abrupt interfaces.[1-6] However, the precise way to exploit this technique, as well as the actual amount of information that it can provide, has not yet reached wide consensus in the scientific community. A possible cause of this lack of consensus is that there are a number of concatenated and interdependent issues. Each one of them has to be addressed properly in order to extract the rich quantitative information that ARXPS can provide. The analysis of ultra thin films by ARXPS can be divided in the following steps:[7]

- High quality data acquisition. The development of better monochromatic x-ray sources have made nowadays possible to obtain high resolution data from commercial XPS equipment.

- Data fitting. The first part of the analysis is data fitting, which provides the take-off angular dependence of the peaks composing the spectra. The specific way to do the fitting might vary significantly from one group to another.

- Characterization of the instrument. The photoemission signal strength holds an important dependence on the shape and size of the x-ray and analyzer focal spots, as well as their overlap with the sample surface. To properly account for this dependence, it is usually necessary to perform numerical integration of the photoemission signal. The calculations require a thorough characterization of the geometrical parameters of the XPS tool. Some XPS equipment makers go out of their way to provide a geometry that dodges the need of the numerical integration, but in many cases it is unavoidable. This requirement is usually overlooked.

- Modeling. The second part of the data analysis is the modeling of the angle dependence of the peak areas to extract the composition depth profile. This is the most controversial step in the process since the methods and assumptions employed vary wildly in the community.

Failing to properly address any of these issues has as an effect that only qualitative and vague assertions could be made about the structure of the films. This Internal Report discusses the part related to XPS data fitting. It emphasizes the need of a simultaneous treatment of the spectra taken at different angles especially for those spectra where the peaks are tangled together. This is usually the case for many elements, such as oxygen and nitrogen.

II.   Data fitting and the conventional approach

The XPS spectra of each element in a film might be composed by different peaks corresponding to different chemical environments. For example, the structure on the right in the Si 2p spectra shown in Figure 1 corresponds to silicon in the substrate, while the structure on the left to silicon forming an oxide.[3] The depth profile of each component can be, in principle, obtained from the angular dependence of the area of its corresponding peak. When the peaks are clearly separated, as in this case, the take-off angular dependence of each chemical specie can be unambiguously obtained (see insert).
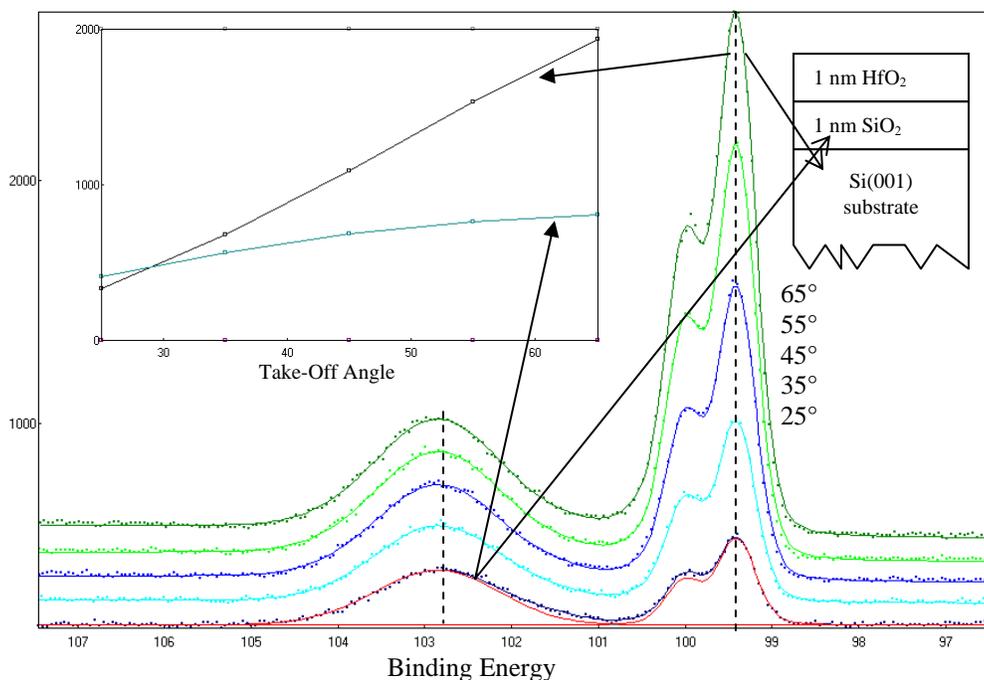

Figure 1. XPS data for Si 2p of a film described in the insert on the right. The peak at 102.8eV (silicon in SiO2) can be clearly deconvolved from the peak at 99.4eV (bulk silicon). The take-off angular dependence is very distinctive for the two peaks.

However, such deconvolution is not easily done when the different chemical components are entangled together. In such cases, as the O 1s spectra shown in Figure 2, the task for a unique and meaningful deconvolution becomes difficult.
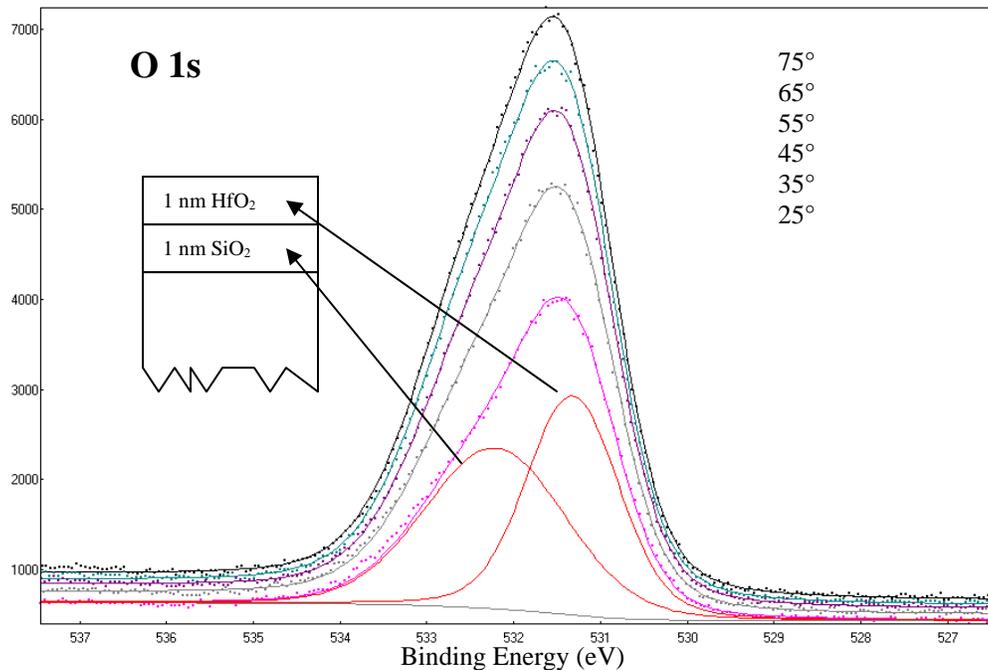
Figure 2. Oxygen 1s data as an example of overlapping peaks composing the data. The sample is HfO$_2$ on top of SiO$_2$ on a Si(001) substrate. The lines are the fits obtained by employing the two peak (red curves) with different relative intensities for the different angles. Each peak is ultimately associated to a chemical environment. For example, the peak on the left corresponds to oxygen in SiO$_2$, and the left peak to oxygen in HfO$_2$.

The key challenge is to uniquely determine the peak parameters (FWHM, position and height) of each chemical species. A possible approach, which is conventionally employed, is to incrementally obtain better fits by iterating through the following steps:

- The "best parameters" of the peaks are found for a spectrum taken at one of the angles. There is not a unique way to accomplish this, and some initial guessing is necessary.

- The values are then constrained in a small range and used to fit the rest of the data.

- By inspecting the quality of the fits, the parameters of the first file are constrained to a value that would provide a better fit for the rest of the files.

- The process is taken into a loop and repeated until a "good" fit is found for all files.

When to stop this iterative process is subjective to the judgment and patience of the operator. This is why data fitting is usually described as an art and not as a science.

III. Simultaneous fitting

Most of this ambiguity disappears when all the data is fitted simultaneously. In this alternative method all the files are fitted at the same time, and *the* best peak parameters are found for the whole set. Although the positions and widths of the peaks are shared among the files for all the angles, the heights are allowed to vary among them.

This method takes full advantage of all the information available. It is usually the case that the shape of the spectra changes with the take off angle. For example, in Figure 1 the relative intensity of the right and left Si structures change with angle. However, the change in shape is only slightly apparent to the eye for the case of Figure 2. This change in relative strength is due to depth differences of the various chemical species of each element. This, in fact, provides fiducial enlightenment about the positions of the peaks composing the spectrum. The larger the change in the shape, the less unambiguous becomes the assessment of the peak parameters. Simultaneous data fitting takes full *numerical* advantage of this phenomenon.

The take off angle dependence of the peaks in Figure 2 is shown in Figure 3. Both methods, the conventional and the simultaneous, were employed. The difference is appreciable.
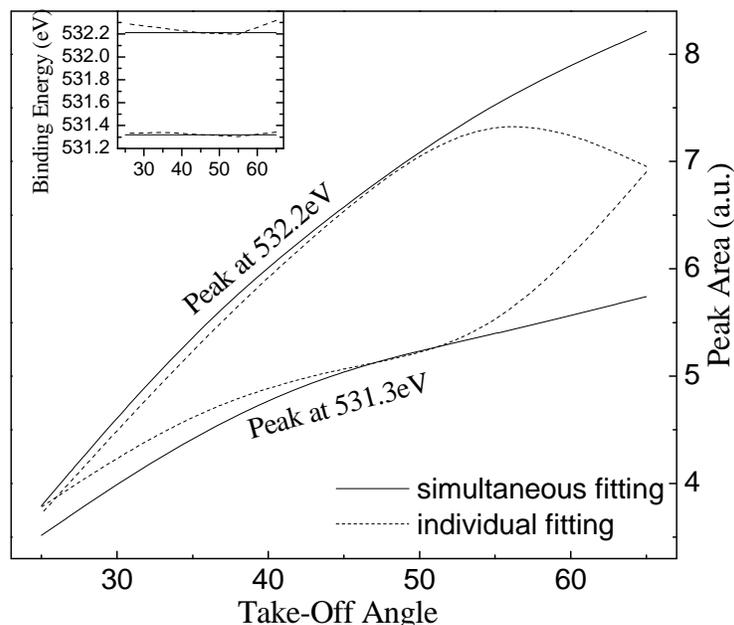

Figure 3. Take off angle dependence of the area of the two peaks in Figure 2. This is a case where simultaneous fitting is important.

The advantages of simultaneous fitting includes include:

- The use of all the information available in the XPS data at all angles to assess the parameters of the peaks (center and width).

- The assessment of the dependence of the peak areas on take off angle that can be modeled using photoemission theory, and in this way be related to depth profile.

- The assessment of the parameters of the peaks (center and width). It should be that this assessment is made under the set of underlying assumptions that are, without exception, made during every kind of analysis. This would include the number of peaks employed, the shape of the background, and the value of the intrinsic Lorentzian width.

- Stability. Simultaneous fitting allows for inclusion of small peaks without the risk of destabilizing the procedure.

- Consistency. There is no physical reason to expect a significant variation of the peak's center or width for the different angles.

It is important to stress that the choice of the fitting method, individual or simultaneous, is not important when the peaks are sufficiently far enough from each other. That is the case of the data shown in Figure 1, which corresponds to the Si 2p spectra of a 1nm film of silica on top of a silicon substrate. However, when the sample consist of a film of silicon carbide on top of a silicon substrate, the deconvolution could be more difficult. The Figure 4 shows data for this system taken at different angles.[4]
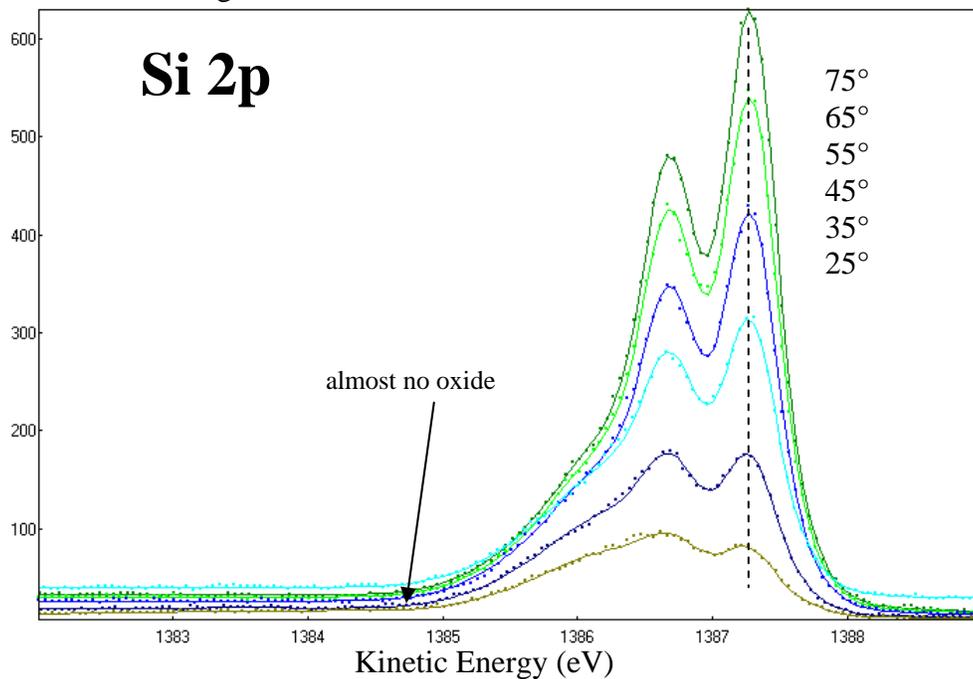

Figure 4. Silicon 2p spectra for the DLC-E 15Å film.

The simultaneous fitting of this data revealed the presence of different components that were not at all distinguishable by visual inspection. The strong dependence of the spectrum shape on the take-off angle allowed for the deconvolution.
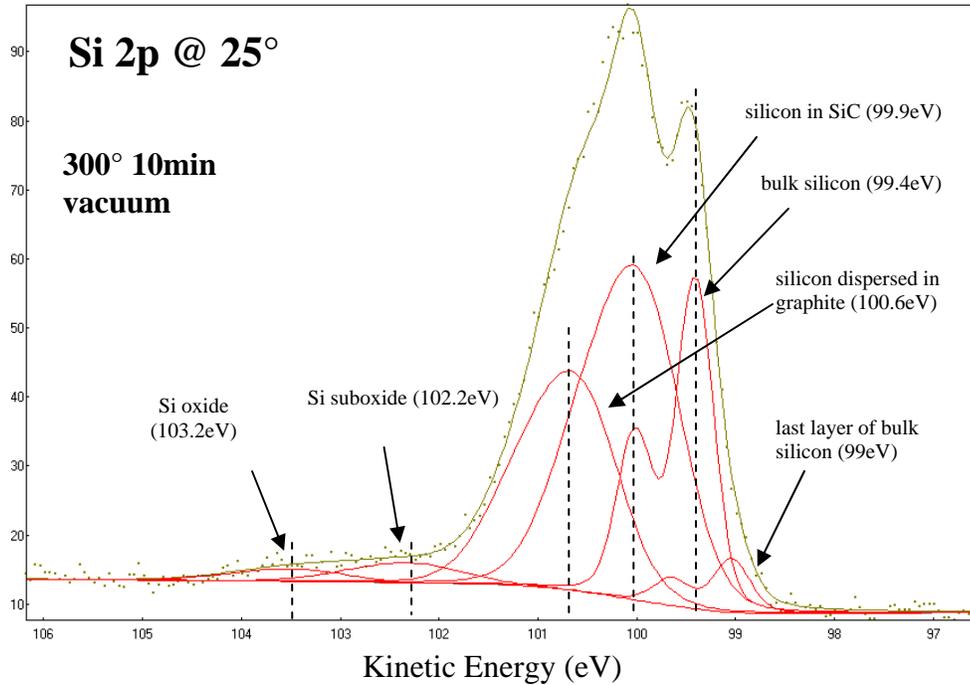
Figure 5. Silicon chemical species present in the DLC-E 15Å film.

The dependence of the shape on angle can be quantitatively observed in Figure 6, which shows the dependence of the intensity of each component on the take-off angle.
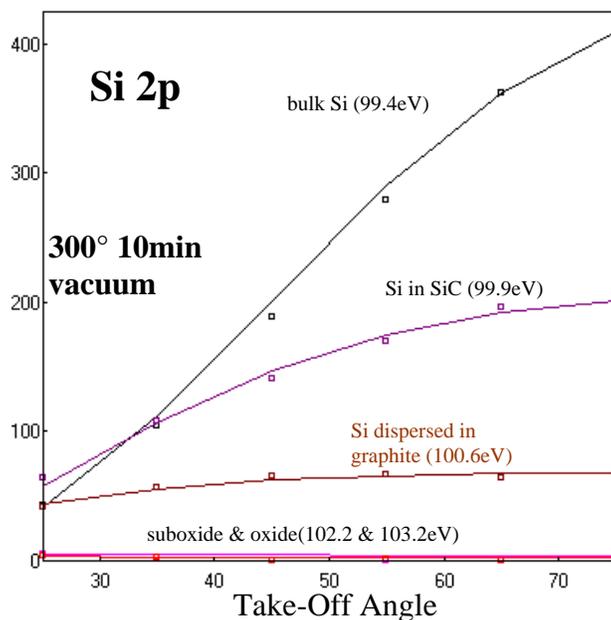

Figure 6. Angular dependence of the silicon species present in the film.

The question then becomes why multifile simultaneous fitting is not widely used. This can be partially answered by a computational difficulty. The total number of variables that has to be determined is large. In the example for oxygen mentioned above, the total number of parameters that were simultaneously optimized was 14. However, it is common to encounter cases where

the number of optimized parameters reaches 70 or even more. Take the case of the data in Figure 5 (the complete set of data is shown in Figure 4 and the take-off angular dependence is shown in Figure 6).

The spectra are composed by six peaks, which represent by themselves twelve parameters. Twelve spectra were analyzed, corresponding to six angles before and after annealing. Then, 72 areas had to be determined. This gives a total of 86 parameters to be determined from the whole data. To assess them simultaneously becomes formidable even for the most powerful algorithms, such as Levenberg. So, they are usually determined in the way described in Section III. None of the commercially available fitting software can handle this, so it was necessary to write our own algorithm. This algorithm is the heart of *AAnalyzer®*, our program for XPS data fitting.

References

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