



Correction of equipment-related and sample-related peak-energy shifts

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Abstract

This Internal Report discusses practical issues related to peak energy shifts during the acquisition of X-Ray Photoelectron Spectroscopy data. Specifically, it describes a method for correcting for this effect. The shifts could be due to stability problems of the X-ray source or the electron analyzer (equipment-related), to the sample orientation in angle-resolved XPS studies, and to changes of the relative electric potential within the film (sample-related). Some of these shifts evolve with time, so the effect on a specific peak depends on the timing of the acquisition. This can be solved by obtaining a series of complete sets of spectra, each acquired within a short period. Each set of data is composed by one scan of each of the peaks of interest, confining its acquisition time as much as possible. The scans of one set are shifted from the other sets due to time dependent shift or to angle rotation (for ARXPS studies, in its case). The scans are added to each other only after correcting for the shift (in the case of ARXPS studies, this is done individually for each angle). The shifts are found by maximizing the correlation between the scans. The algorithms for finding the shifts and adding the data are integrated to the software AFileAdder®. The application of AFileAdder results on spectra with slightly better resolution *and* on information of the time evolution of the shift for each one of the spectra of interest.

I. Equipment and sample-related instabilities

I.1. Equipment-related instabilities

Figure 1a and b shows the time evolution of the kinetic energy and the intensity of the Au 4f peak (insert) acquired on a clean gold film. The sample employed was gold because it stays clean in UHV for long periods. Its metallic character allows for effective grounding, avoiding changes on the sample potential. In this way, instabilities of the sample could be ruled out. This evolution is then related to instabilities of the equipment, which can be in part explained by the change in the chamber pressure (Figure 1c).

These equipment-related instabilities are usually smaller than those illustrated in Figure 1, which corresponds to data obtained with a newly installed monochromator. However, it is important to be aware of their presence and to correct them properly to avoid loss of resolution and incorrect binding-energy differences between peaks acquired at different times.

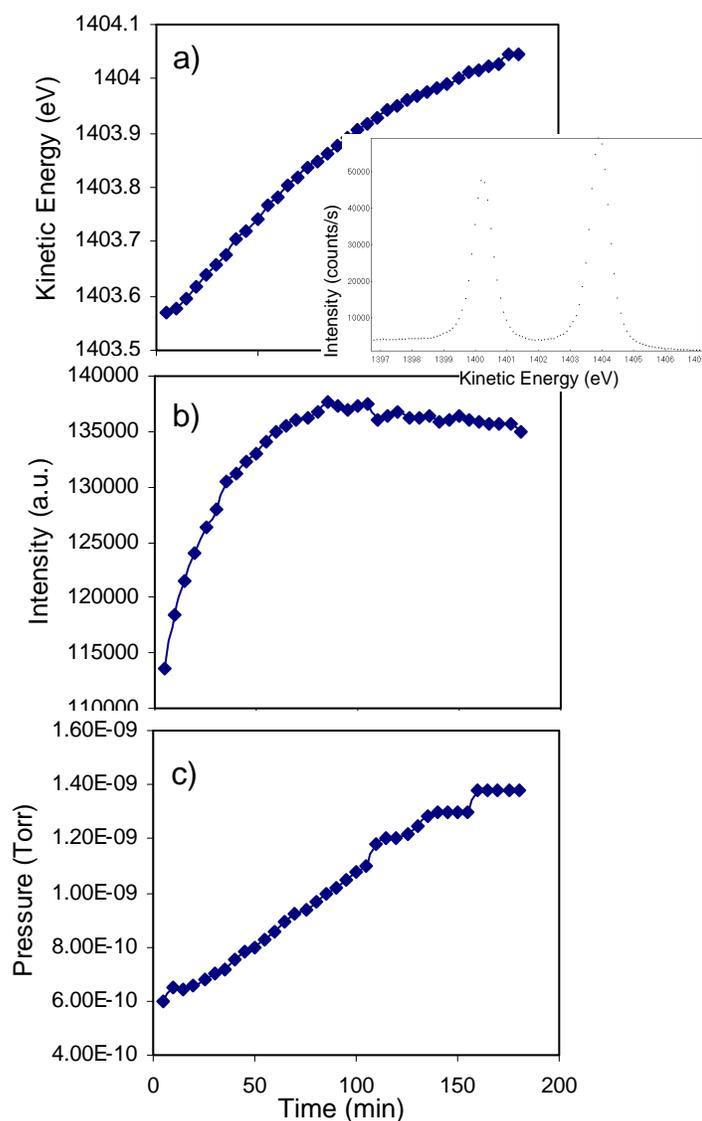


Figure 1. Time evolution of the a) kinetic energy and b) intensity of the Au 4f peak (insert) obtained from a grounded and clean gold film. c) Evolution of the chamber pressure. The behavior is related to instabilities of the equipment (the X-ray source was newly installed).

I.2. Combined sample and equipment-related instabilities

Figure 2a shows O 1s spectra obtained at different angles from a sample consisting of a ~ 2 nm silicon oxynitride layer on Si [001]. The shifts, marked with the broken line, could be due to two different phenomena:

- There is more than one oxygen species that contributes differently to the spectra at different angles. At shallow angles the contribution from the species with lower binding energy is more important, so the peak is slightly shifted to the left.
- The sample is unstable. The shifts are due to changes on the potential caused by movement, desorption, or creation of dipole or charge centers. Since the data at each angle is collected at a different time, the shift reflects the time evolution of the potential. The insert shows that,

once aligned, the shape and width of the spectra is the same, suggesting that no chemical reaction is involved.

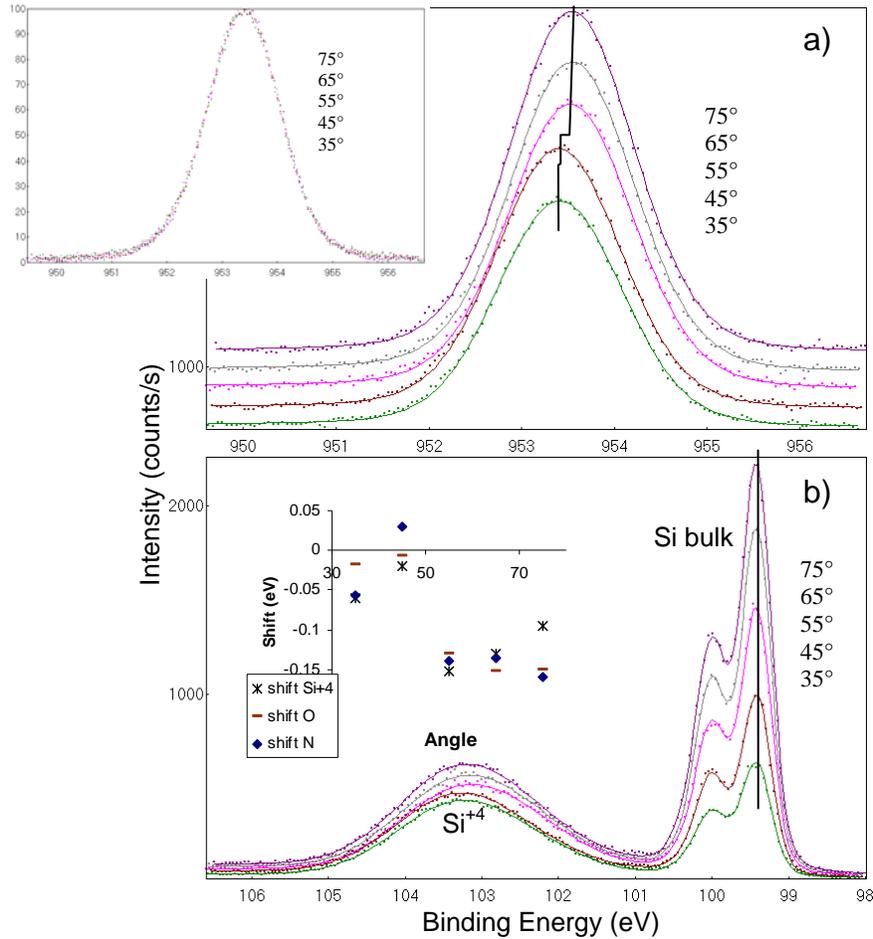


Figure 2. a) O 1s spectra obtained at various angles from a 2 nm SiON/Si[001] film. The insert shows that the shape and width of the peaks, once aligned, is the same, suggesting that there are not chemical reactions involved. b) Si 2p spectra from the same sample. The peaks corresponding to the bulk are aligned to each other. The insert shows the extra shifts that are necessary to align the Si⁺⁴, O, and N peaks.

One way to discriminate between these two possibilities is to monitor the spectra as a function of time. This involves re-taking the data with the method described in the following section.

II. Assessing shifts as a function of time

II.1. Standard method for data acquisition

A common procedure for acquiring XPS data is to take as many scans of one particular spectrum as necessary to reach the targeted noise to signal level. In this way, sequentially, each spectrum of interest is obtained. In ARXPS studies, the data for each angle is also obtained sequentially. First, a complete spectra set for one angle, then another angle, and so on in a sequential fashion. That is the way the data shown in Figure 2 in the previous section was taken. With the sample oriented at 75°, 20 scans were acquired for Si 2p. Each scan was automatically added to the

previous ones as it was taken. Then 15 scans of O 1s were obtained, followed by 20 of N 1s and then 20 for C 1s. The orientation of the sample was then changed to 65° and a similar set of spectra was acquired, all in a sequential fashion. In a similar way the data for the rest of the angles was obtained.

II.2. One-Scan method for data acquisition

The data shown in Figure 3, which corresponds to a (~ 1 nm HfO₂)/Si[001] sample, was obtained in a different way. Each scan for each spectrum was saved individually and added only after it was properly shifted. Figure 4 shows the shifts that were employed for aligning the Si 2p and the Hf 4f scans obtained at 85°. The criterion employed to find the shifts is described in Section III.

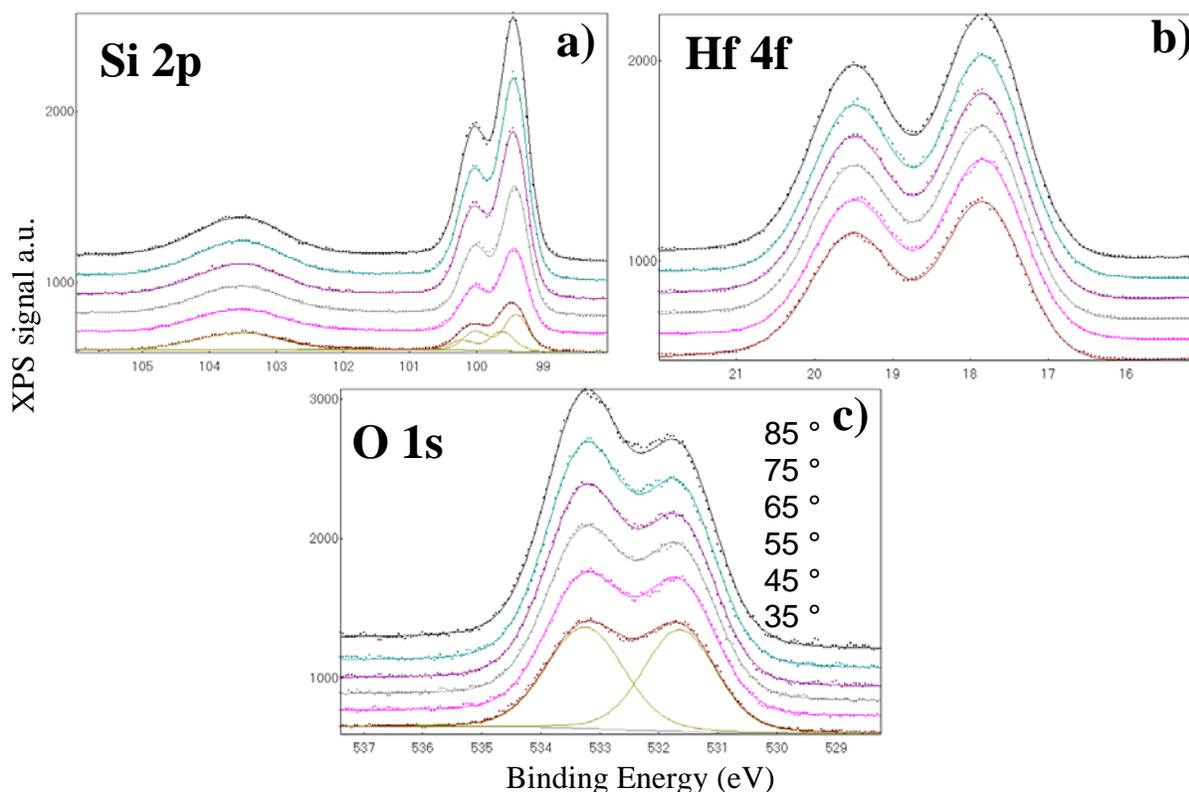


Figure 3. ARXPS data of a HfO₂/SiO₂/Si sample (10 ALD cycles on SiO₂ at 800 °C for 25 s). The spectra was acquired by individually saving each scan, shifted to maximize correlation, and then added to the rest of the scans.

The shifts shown in Figure 4 for Si 2p and Hf 4f are very similar to each other, suggesting that they were affected in the same way by equipment or sample-related instabilities. It is important to notice that the acquisition of scan *j* for Si 2p was obtained temporally very close to scan *j* for Hf 4f. One scan for Si 2p, Hf 4f, O 1s and C 1s was obtained at 85°. Then, the angle was changed to 75° and a similar set of one-scan data set was obtained. The rest of the angles were done in the same way, to then return to 75° to start over. Five sets of one-scan data was obtained in this way at the beginning (scans 1 to 5) and another five at the end (scans 41 to 45). Those in between (scans 6 to 40) were obtained by stationing the sample in one angle (85° in the case of the figure).

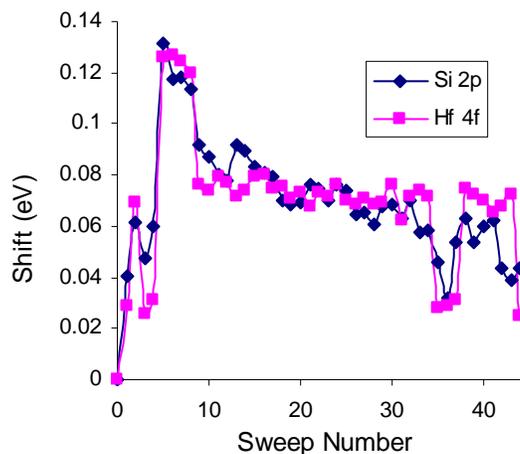


Figure 4. Shift employed to align the 45 one-scan spectra for Si 2p and Hf 4f obtained at 85° for the data shown in Figure 3. The sample corresponds to a ~ 1 nm HfO₂/Si[001] sample grown with 10 ALD cycles.

II.3. Correcting for either equipment and/or sample-related instabilities

The alignment of the data shown in Figure 3 was, in fact, done backwards. The first spectrum employed was the 45th. It is convenient to employ the last one because the sample and the equipment are usually more stable at the end of the experiment. Taking five sets of one-scan data varying the angle allows for better observation the time evolution of the shift variations as the angle is moved. It is usually found that there are no variations on the shift between the different angles at the end of the experiment.

In some cases the shifts are different for the different spectra. Figure 5 shows the required shifts for Si 2p and Hf 4f one-scan data for a (~ 2 nm HfO₂)/(~ 1 nm SiO₂)/Si[001] sample obtained at 85°. They were both affected by equipment-related instabilities. However, the difference indicates an evolution of the relative potential between the silica and the hafnia layers. No evidence of chemical reactions was found.

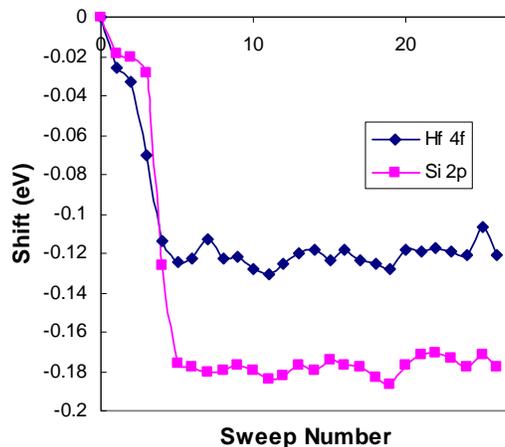


Figure 5. Shift employed to align the 26 one-scan spectra for Si 2p and Hf 4f obtained at 85°. The sample corresponds to a (~ 2 nm HfO₂)/(~ 1 nm SiO₂)/Si[001] grown with 20 ALD cycles.

III. The software *AFileAdder*

The software developed ad-hoc for finding the shifts is shown in Figure 6.¹ The input is the list of the files to be added, each file corresponding to one-scan spectrum. The output is the sum of the files after the proper shifts were done to each file, and the value of the shifts. For sample related instabilities, the shifts provide information about the phenomena that the sample is experiencing.

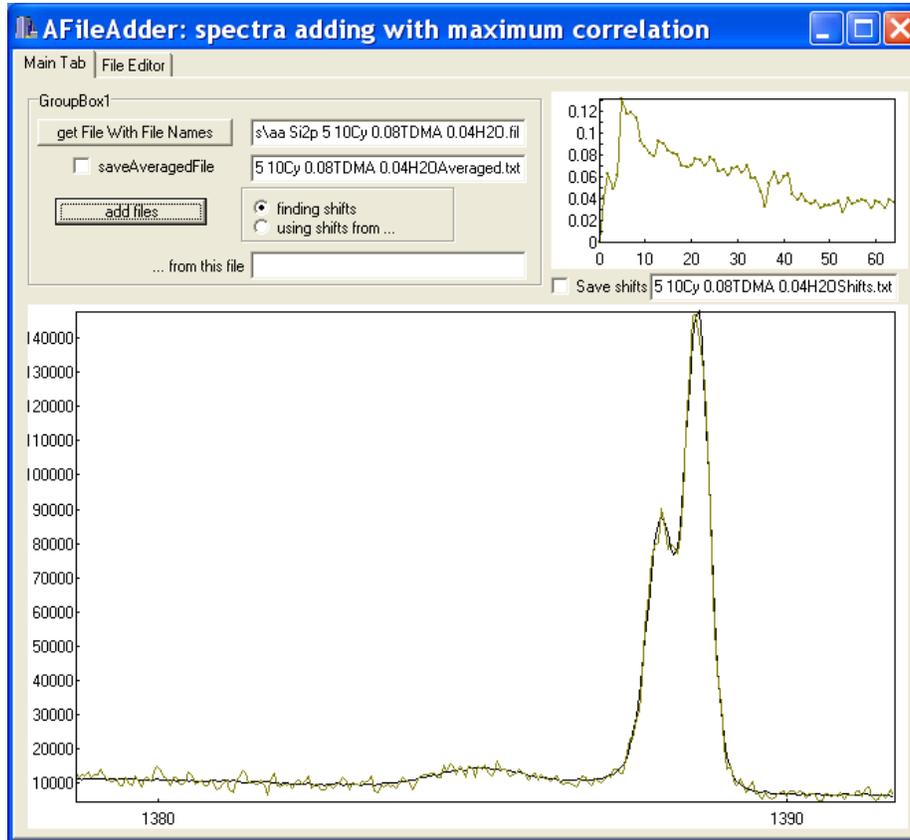


Figure 6. AFileAdder software aims to add spectra with the proper shift that maximizes the correlation between them. The graphic shows that data already added (line with lower noise) and the file that is being added (line with more noise). The shifts employed for each file (64 total) are displayed in the upper graph. It also allows for using the shifts found with another peak; this is convenient for data with high noise to signal ratio.

The criterion employed to find the proper shift for the scan j is the minimization of the difference square

$$\chi_j^2 \equiv \sum_{i=1}^N [y_t(E_i) - A_j y_j(E_i + s_j)]^2,$$

where N is the number of points of the spectrum, y_t is the added spectrum of the first $j-1$ scans, E_i is the binding energy corresponding to channel i , A_j is an optimizing constant, and s_j is the shift. s_j and A_j are chosen to minimize χ_j^2 . $y_j(E_i + s_j)$ is found by interpolation. Points are added on the left or on the right by extending the spectrum linearly.

IV. Alignment among the different angles

In ARXPS studies the data is obtained at different angles. Incorrect shifts among the same spectrum obtained at different angles can arise from both equipment and sample-related instabilities, or from the electrostatic effects of the orientation of the sample. The shifts related to the equipment and/or sample-related instabilities are fixed by the procedures described in

Section II. The electrostatic potential effect, if present, can be fixed by aligning one representative spectrum. Some times it is convenient to use the adventitious C 1s peak for alignment with the predetermined value of 284.8 eV for its binding energy. The preferred way is to provide for the necessary shift to have one of the peaks from the substrate to a predetermined value (if there are substrate peaks available, one of them should be used as reference,²) For example, for samples with a silicon substrate, it is a common practice to shift all the data in such a way that the Si 2p^{3/2} bulk peak position is at 99.4 eV.

This alignment involves fitting the data to find the position of the reference peak, and then provide with the appropriate shifts. With the software AAnalyzer this could be done very precisely by using simultaneous fitting. The procedure is iterative. It starts by first fitting the data from each angle individually, and making a first shift. These shifts are not final because the fitting is not as precise for individual fitting as for simultaneous fitting.³ Once aligned, the simultaneous fitting could be applied, and better peak parameters are obtained. With the position of the peaks fixed to each other so they move solidly, and the rest of the parameters (widths, branching ratio, and doublet splitting) fixed, each file is fitted individually. All the spectra are shifted again to get the predetermined value for the reference peak. The magnitude of this second shift is usually much smaller than the first. The procedure repeats until the shifts converge. The output is a shift for each angle, which is then applied to the rest of the data at each angle.

V. Conclusions

It is possible to correct for time-dependent shifts caused by both equipment and sample-related instabilities. To do so, the data has to be acquired one scan at a time, and only added after the proper shift is made. The shifts can be found by maximizing the correlation between the one-scan spectra. Besides eliminating artificial shifts, this procedure provides data with better resolution since the spreading due to time-dependent shifting is avoided.

References

- ¹ A trial copy of AFileAdder® is available at <http://qro.cinvestav.mx/~aanalyzer/afileadder>.
- ² ASTM-International Standard E 1523-03. "Standard Guide to Charge Control and Charge Referencing Techniques in X-Ray Photoelectron Spectroscopy."
- ³ J. Muñoz-Flores, A. Herrera-Gomez. "Resolving overlapping peaks in ARXPS data: the effect of noise and fitting method." Sent to J. Elec. Spec. Rel. Phen. (2011).