EPJ Web of Conferences **273**, 01011 (2022) https://doi.org/10.1051/epjconf/202227301011
*JNSPE 2022*

# Photoemission in microelectronic research: When technological developments allow to tackle new questions in the lab.

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**Abstract.** Photoemission has always played an important role in the development of new microelectronic devices and processes and has quickly focused on the use of monochromatized Al Kα radiation in most commercial instruments. While, for instance, ARXPS using sample tilting or the use of high-energy photoemission at synchrotron facilities were available, their use remained confidential due to technical constraints such as measurement time, repeatability of the measurements and/or access to the facilities. In this paper, we show through some examples that the implementation of these features in a user-friendly setup in the laboratory considerably enhances the information retrieved from photoemission experiments.

## 1 Introduction

Since the development of the transistor by Bardeen and Brattain[1] in 1947, the semiconductor technology has been evolving considerably. Since the introduction of integrated circuits, performances have been progressing according to Moore's law[2] which was formulated in 1965. For many years, performance improvements were achieved primarily by geometrical scaling and the technology nodes were named according to the gate length of the transistor. However, facing physical limitations, from the 45 nm node no further scaling of the gate length has occurred[3] and at the 22 nm node Intel introduced the FinFET technology shifting away from planar technology. But even within the planar technology, scaling was only possible through a different choice of materials such as the replacement of $SiO_2$ as gate oxide by oxides with higher permittivity or by the introduction of copper in interconnects. These technological evolutions also required improved capabilities in material characterisation.

This article focuses on the contribution of photoemission to the technological evolution of transistors and more specifically on the interest of Angle-Resolved X-ray Photoelectron Spectroscopy (ARXPS) and acronym Hard X-ray Photoelectron Spectroscopy, (HAXPES) to these technological developments. Both variants of PES are known for a very long time, going back to the earliest publications on XPS but were not widespread due to practical difficulties. ARXPS for instance required sequential measurements at various sample tilts leading to lengthy measurement times and difficult sample alignment. The introduction of parallel-ARXPS, allowing to get angular photoelectron information over a wide range of angles in a single measurement alleviates this limitation and is implemented by several manufacturers. Similarly, HAXPES required access to a synchrotron facility for the use of high intensity monochromatic sources, which is impractical for process development and more routine analysis. The situation changed radically when high energy monochromatic sources with photon energies ranging from ~2.98 keV to 9.25 keV were brought to the laboratory on standard XPS platforms.

## 2 Experimental

The photoemission results presented in this article are originating from three different instruments.

For ARXPS, all measurements were performed on a Theta 300 spectrometer from Thermo Fisher, using Al Kα radiation at 1486.6 eV. The exit angular range of the detected photoelectrons was between 20 and 80 degrees, as measured from the normal of the sample and intensities were binned by ~4 degrees.

For XPS, all measurements were performed either on a Physical Electronics Quantes system using Cr Kα radiation at 5414.8 eV or on a ScientaOmicron HAXPES-lab system with Ga Kα radiation at 9250 eV.

## 3 A first paradigm shift: high-k metal gate

One of the challenges faced by geometrical scaling is that the reduction of the gate oxide thickness led to an increase of leakage current due to tunnelling. This high leakage became unacceptable due to high electric consumption, which is even more critical for mobile applications. This can be improved by using higher permittivity materials which allow a larger physical thickness while keeping a low Equivalent Oxide Thickness (EOT). At first this was achieved by incorporating nitrogen into $SiO_2$, which allowed keeping the technology of *grown oxide* but the limitation of the increase of permittivity led to the use of *deposited oxides* ($Al_2O_3$, $ZrO_2$, $HfO_2$, ...) through major technological developments.

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### 3.1 Growth quality of ALD grown layer

When switching from a process of grown oxide to deposited oxide, a fundamental question is the quality of the deposited oxide in terms of uniformity both at the microscopic and macroscopic level. Indeed, very quickly, Atomic Layer Deposition (ALD) became the method of choice due to its good conformality and growth control. However, as a surface driven process, substrate surface preparation is critical and the growth quality in function of surface termination needs to be evaluated.

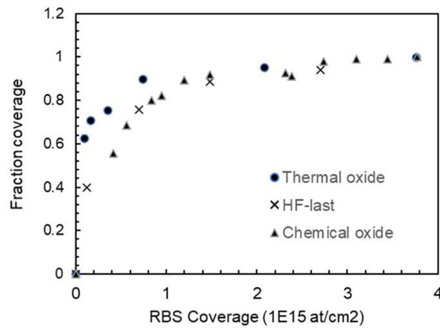


Figure 1 : Evolution of the fractional coverage of $Al_2O_3$ layer grown on various Si surfaces as a function of deposited material as measured by RBS.

The evaluation of the growth quality in the first deposition cycle needs a quantitative surface analysis technique with sufficient sensitivity. Techniques that have been used/considered include Low Energy Ion Scattering (LEIS), Time-Of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), XPS and RBS (Rutherford Back Scattering), in decreasing order of surface sensitivity. As is often the case, no single technique matches all criteria. LEIS is extremely surface sensitive and a quantitative technique but has issues with detection limits due to the low counting rate. ToF-SIMS is very sensitive but has issues with quantification due to the matrix effect. XPS, has in all aspects (detection limits, surface sensitivity, quantification accuracy) characteristics similar or in between LEIS and ToF-SIMS and can thus be an adequate technique for the evaluation of the growth quality of ALD layers.

One of the limitations of photoemission is that quantification in complex systems relies on intensity modelling. This has been done for instance in the case of the deposition of $Al_2O_3$ on Si (100) with various surface preparation[4]. In that case intensity modelling was done assuming that the layers have grown in a nonuniform manner, producing island structures on the silicon dioxide. The parameters used in the modelling are the thickness of the islands and the fractional coverage. Further, it is assumed that the islands are such that shadowing of the signal emitted from the uncovered $SiO_2$ is not significant. In that case, it shown that the angular dependence of the Al 2p and Si 2p intensities is very sensitive to variation in the combination of the coverage and thickness of the islands. Using this method, a clear distinction of the growth of $Al_2O_3$ on HF-terminated Si, a thin thermal $SiO_2$ layer or a chemical surface oxide has been observed (Figure **1**). It should however be mentioned that, due to its better detection limits, ToF-SIMS allows a better discrimination of the growth quality when the surface conditions are very similar, and that the matrix effect can be neglected[5].

### 3.2 Determining composition profiles of thin layers

When good quality layers can be grown, additional parameters need to be characterised. First of all, layer thickness is critical for devices performances. For single layer on a substrate, in theory, a XPS measurement of the intensities of both the substrate and the overlayer at a single angle are sufficient for determining layer thickness. This gives excellent results and can even be considered superior to traditional ellipsometry measurements for very thin layers, the latter technique cannot discriminate between the contamination layer and the deposited layer. An example of the thickness measurement of a $HfO_2$ layer deposited on $SiO_2$ correlated to the amount of deposited material as measured by RBS is presented in Figure **2**.

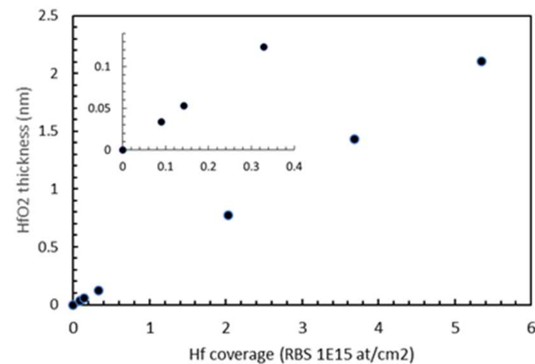


Figure 2 : Thickness calculation based on XPS data of a $HfO_2$ layer deposited on $SiO_2$ correlated to the amount of deposited material as measured by RBS

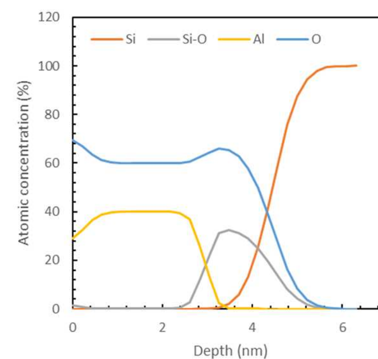


Figure 3 : ARXPS reconstructed composition profile of a $Al_2O_3/SiO_2/Si$ stack.

Next to layer thickness, it is also critical to determine the layer compositions and a composition profile. Only a few methods are available for a routine determination of composition profiles for very thin layers. Depth profiling methods such as (ToF)-SIMS can be easily applied but any sputter-based technique suffers from significant artefacts such as preferential sputtering effects. It is thus advised to rely on non-destructive methods. One of them is Medium Energy Ion Scattering

(MEIS) which is unfortunately not widely available. An interesting alternative can be found in ARXPS, which uses the strong dependence of signal intensities on material depth and, through an optimisation algorithm, allows to retrieve composition profiles from the angular difference in intensities of the different elements. An evaluation of this method has been documented in several publications[6,7,8].

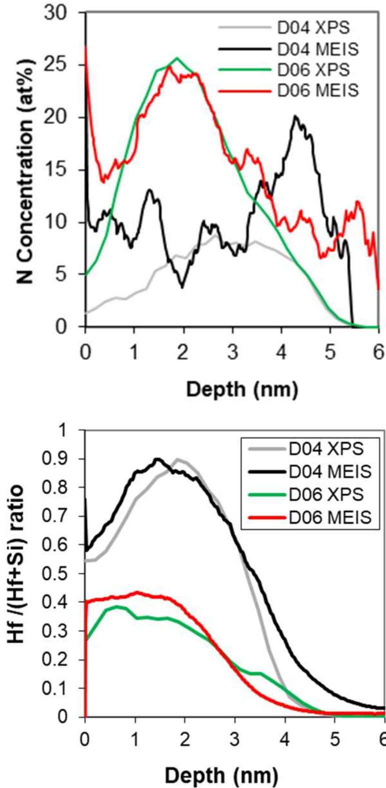


Figure 4 : ARXPS reconstructed composition profile of two nitrided HfSiO stacks.

For a simple layer structure such as the ~3.0 nm $Al_2O_3$/1.5 nm $SiO_2$/Si shown in Figure **3**, the composition profile is straightforward. However, obtaining reliable composition profiles in case of complex systems involves including some additional constraints such as stoichiometric ones. A typical complex system in gate stacks consists in the determination of composition profile of nitrided $Hf_xSi_{(1-x)}O_2$ layers deposited on Si. These types of samples have two important challenges as the Hf/(Hf+Si) may vary with depth and a peak overlap is present between the N 1s and an Hf loss peaks, making peak deconvolution challenging for low nitrogen concentration. Figure **4** presents the reconstructed profile for two stacks with different nominal Hf/Si ratios and nitridation processes. Sample D04 has a 3:1 Hf/Si ratio while sample D06 has a 1:3 ratio. Sample D04 is nitrided with a remote plasma process while sample D06 is nitrided using a $NH_3$ post-annealing process. The agreement between the Hf concentration profiles determined by ARXPS or MEIS is good. More discrepancies are observed in the Nitrogen concentration profile. The main differences are observed close to the surface and at the HfSiO/Si interface. At the interface, the main issue arises from the use of channelling during the MEIS experiment.

## 4 A second paradigm shift: Going 3D and full stack analysis

### 4.1 Analysing interfacial interactions

In the search of ultimate scaling, interfacial effects are critical, and it has been shown that the full high-k/metal gate stack needs to be considered as upon processing, the interface between the substrate and the high-k can be modified (for instance by oxygen scavenging) by the presence of the metal. Unfortunately, when the full stack is formed, the substrate/high-k interface may be beyond reach for regular photoemission measurements with Al Kα radiation[9]. At first, buried interfaces were studied using back-side XPS, i.e. by removing the substrate using polishing and etching technologies. This is however a difficult and very slow process. In addition, it is not applicable to all samples as an etch stop layer is needed under the stack to be analysed.

The alternative to back-side analysis is to use HAXPES, which with its high energy X-ray radiation allows the analysis of much deeper interfaces. HAXPES has long been limited to synchrotrons which severely limited its use for process development that requires frequent and easy access to the characterisation methods. Recently, several spectrometers were developed allowing high quality HAXPES using Ag Lα (2.98 keV)[10], Cr Kα (5.41 keV)[11] or Ga Kα (9.25 keV)[12] radiation.

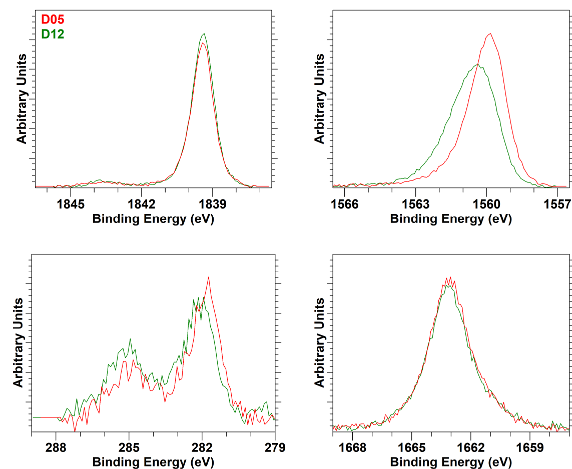


Figure 5 : Si1s (upper left), Al1s (upper right) C1s (lower left) and Hf $3d_{5/2}$ (lower right) HAXPES spectra of a ~12 nm thick TiN/TiAlC/TiN/$HfO_2$/$SiO_2$ stack on Si substrate, before (D05) and after (D12) annealing recorded with Cr Kα

In order to evidence the advantages of HAXPES, a multilayer sample with a total thickness of ~12 nm was processed and analysed before and after annealing. The analysed stack consists of 3 nm TiN/5 nm TiAlC/1 nm TiN/1.7 nm $HfO_2$/1 nm $SiO_2$/Si substrate and the corresponding Si 1s, Al 1s, C 1s, Hf $3d_{5/2}$ HAXPES curves before (D05) and after (D12) annealing are presented in Figure **5**. The Si and Hf spectra are not modified upon annealing showing a good chemical stability of the layers. However, significant changes are observed on the Al 1s spectra. A significant broadening and a shift towards high binding energy are observed,

which is a clear indicator of chemical changes in the TiAlC layer.

### 4.2 3D-device technology

In present technologies such as FinFET, devices are developed in 3D and more complex structures are considered. As an example, Figure **6** shows a nanosheet structure with progressive lateral etching of the SiGe layers in repetitive Si/SiGe stacks. In order to avoid registering time consuming Transmission Electron Microscope (TEM) images for the monitoring of the SiGe etch, several top-down techniques were investigated, one of them being HAXPES using Cr Kα radiation. Thanks to the larger electron escape depth of HAXPES compared to XPS this type of analysis is within reach of PES. When monitoring Ge signal intensities, a good correlation between the measured Ge signal and the etch depth is observed, at the condition that the top $SiO_2$/SiN stack was first removed.

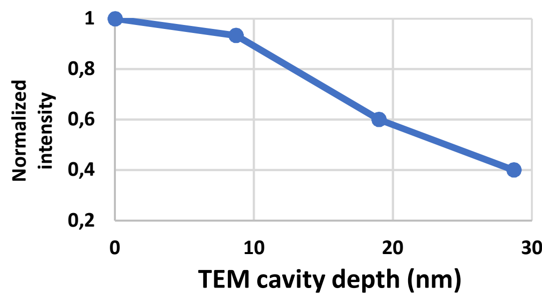


Figure 6 : Nanosheet structures (top) etched to various lateral depths and corresponding changes of the Ge 2p HAXPES curve intensities as measured with Cr Kα radiation

## 5 Future technologies

Future performance improvements along the path of Moore's law will imply further development in material integration and process capabilities.
For instance, the ability to pattern ever-smaller feature sizes and denser pitches is significantly challenged due to the lack of a fundamental understanding of EUV sub-picosecond exposure processes. Getting this understanding requires developments in analytical capabilities, including time resolved capabilities. Similar to the evolution of HAXPES from synchrotron to lab environment, time-resolved photoemission by use of a laser set-up will become readily available. Such a set-up is now available within imec and a more profound understanding on photoresist chemical modifications is developing through comparison of recorded spectra with theoretically modelled photoemission spectra. An example of modifications to experimental resist spectra upon photon exposure is shown in Figure 7.

These time-resolved capabilities will allow the characterization of the molecular and quantum dynamics of materials within the attosecond to picosecond for instance in 2D-materials or topological insulators.

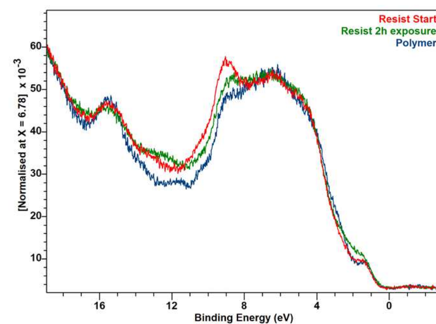


Figure 7 : UPS spectra from a non-exposed polymer-based resist (red), the base polymer (blue) and the exposed resist (green).

## 6 Conclusion

Photoemission is a very versatile characterisation technique that developed into a "must have" in the semiconductor industry. The technological evolution in instrumentation at lab-scale has led to a widening of the application field throughout the years. First, the introduction of parallel ARXPS allowed to easily retrieve depth information and composition depth profiling. Then, the introduction of high-quality HAXPES systems allowed to characterise buried interfaces in realistic systems as well as getting bulk-information. In the future, a laser-based system will allow time-resolved analysis, paving the road to a fundamental understanding of photoresist modifications and new materials.

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