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XPS/ARXPS In Thin Film And Nanomaterial Process Control

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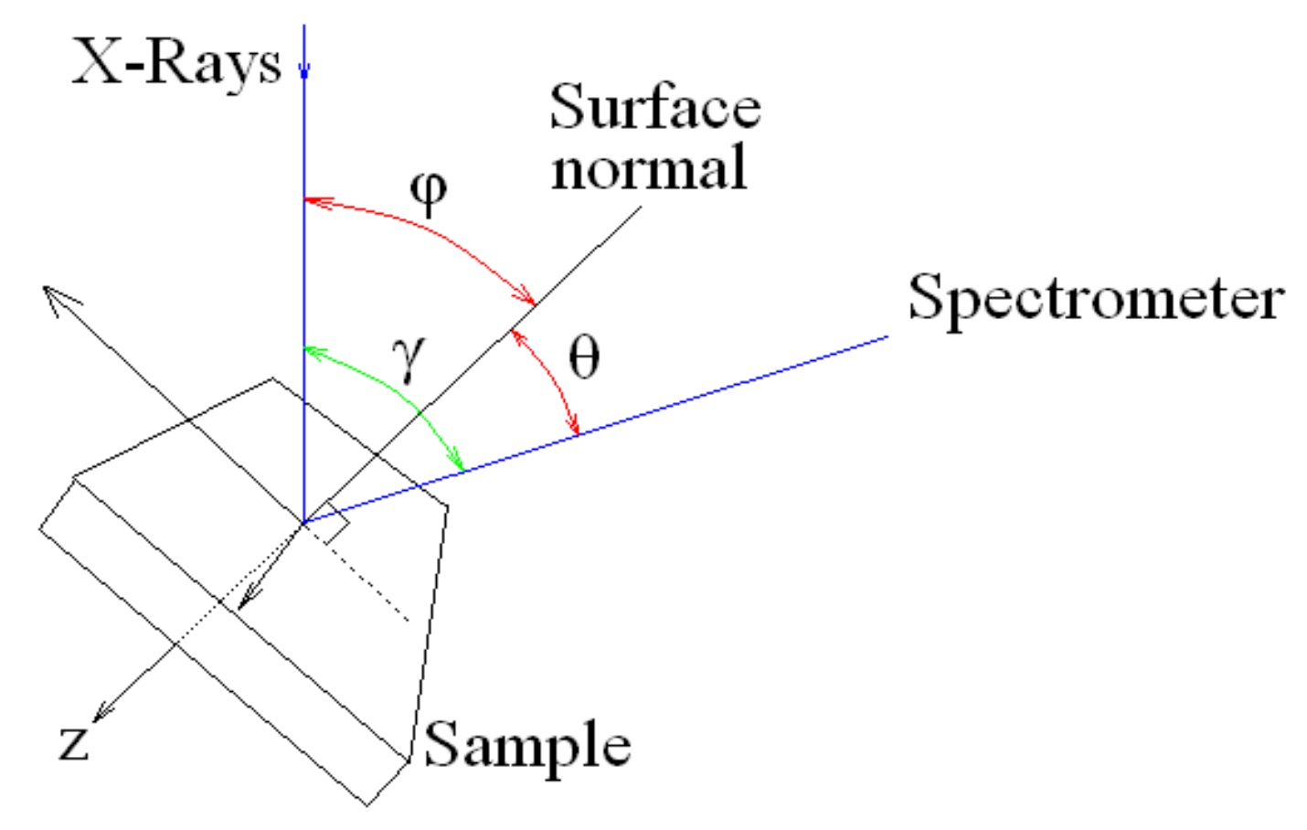
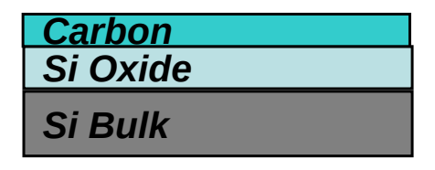
X-ray Photoelectron Spectroscopy (XPS) is an analytical technique which provides information about the chemical composition of a sample surface. The sample, typically a solid, is placed into a vacuum and exposed to X-rays. Photoelectrons emitted from the surface via the photoelectric effect are energy filtered and the energy spectrum thus formed is characteristic of the chemistry of the sample surface. The number of photoelectrons in each peak is directly proportional to the concentration of the element / chemistry from which they arose. The technique is surface sensitive due to the limited distance photoelectrons can travel in a solid, typically less than 10 nm in standard experiments. XPS can therefore provide chemical bonding and elemental depth data, illuminating the layered chemistry of thin films, including film structures on nanoparticles, yielding core shell thickness and chemical information[1]. Changing the collection angle of electrons with respect to the surface of the material (angle resolved XPS (ARXPS)) changes the sampling depth, and allows extraction of information regarding layering of the elements / chemistry over the first few nm of the sample surface.

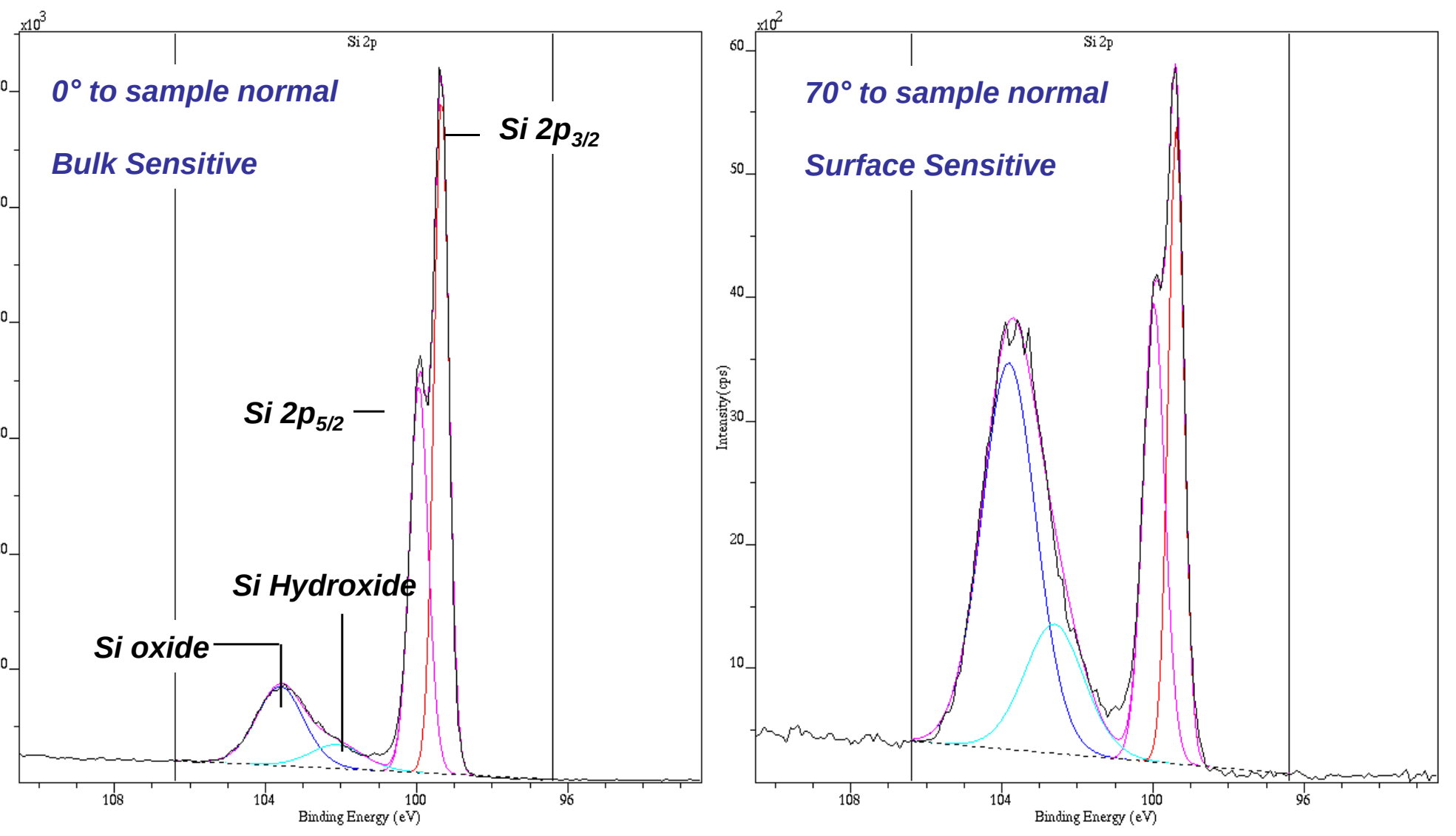
Nanoelectronics development requires careful measurement of surface chemical information for process control. Similar to how angle resolved XPS (ARXPS) became critical in the tuning of the modern transistor gate oxide structure[2], ARXPS will have a large role to play for the wide range of materials for application in nanoelectronics, measuring the various films and process results.

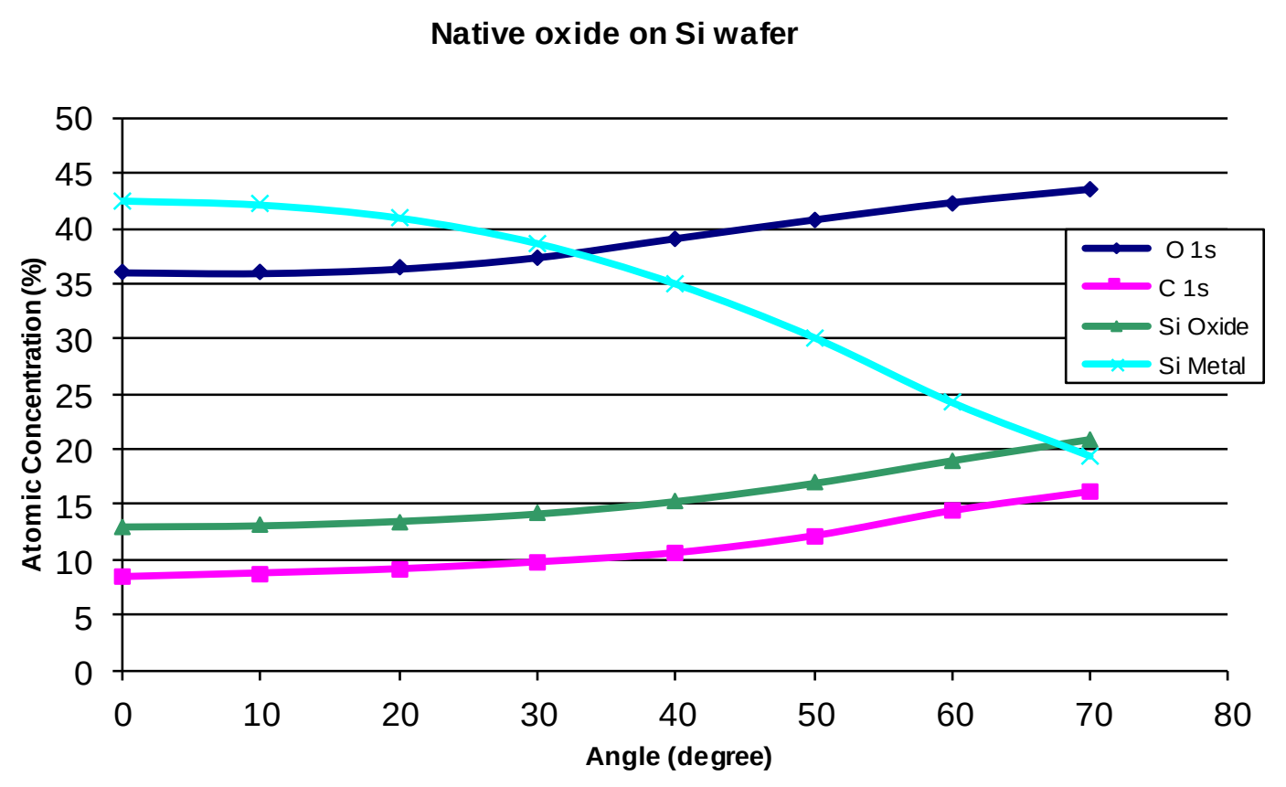
ARXPS



Si wafer with native oxide ~8Å





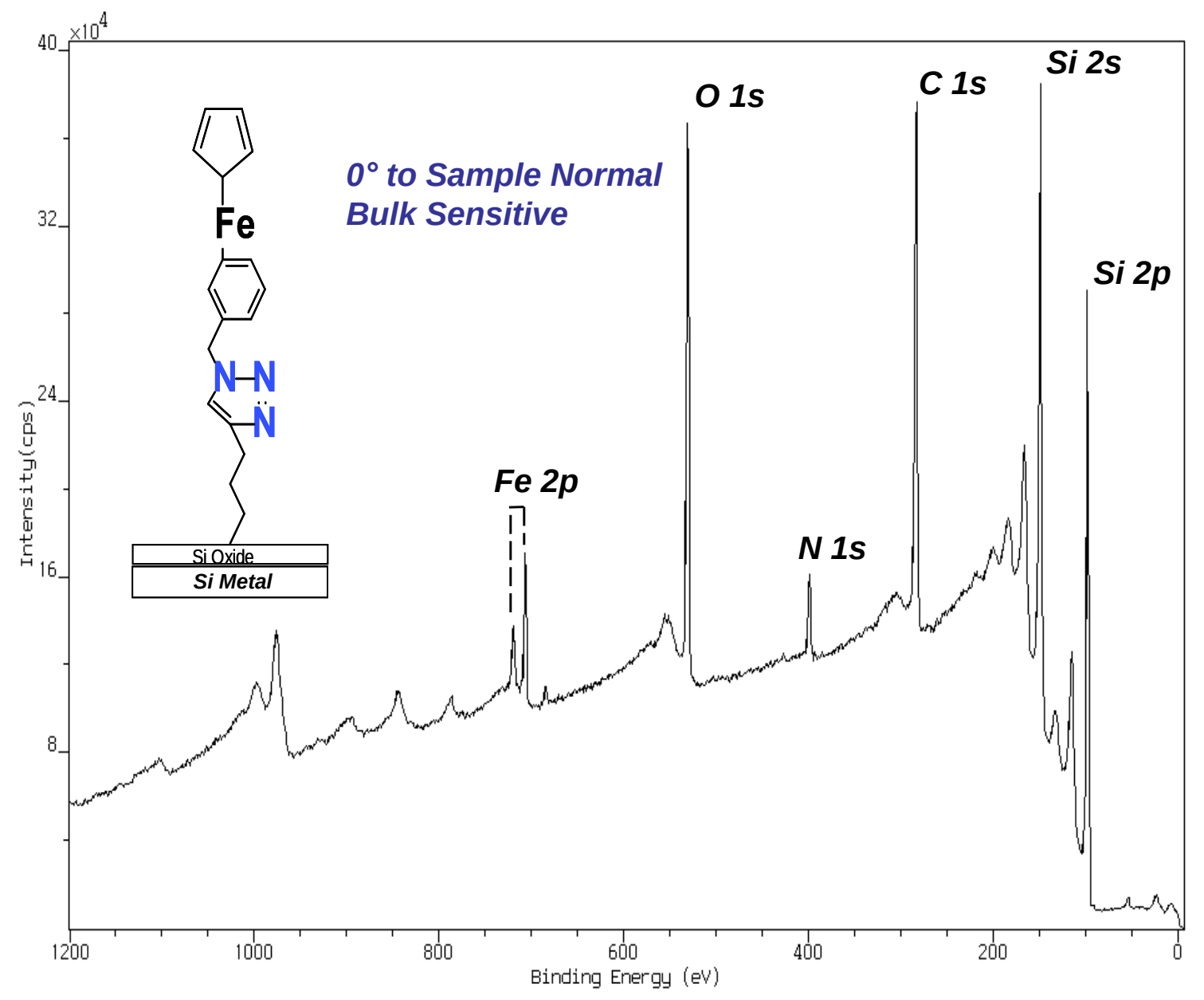


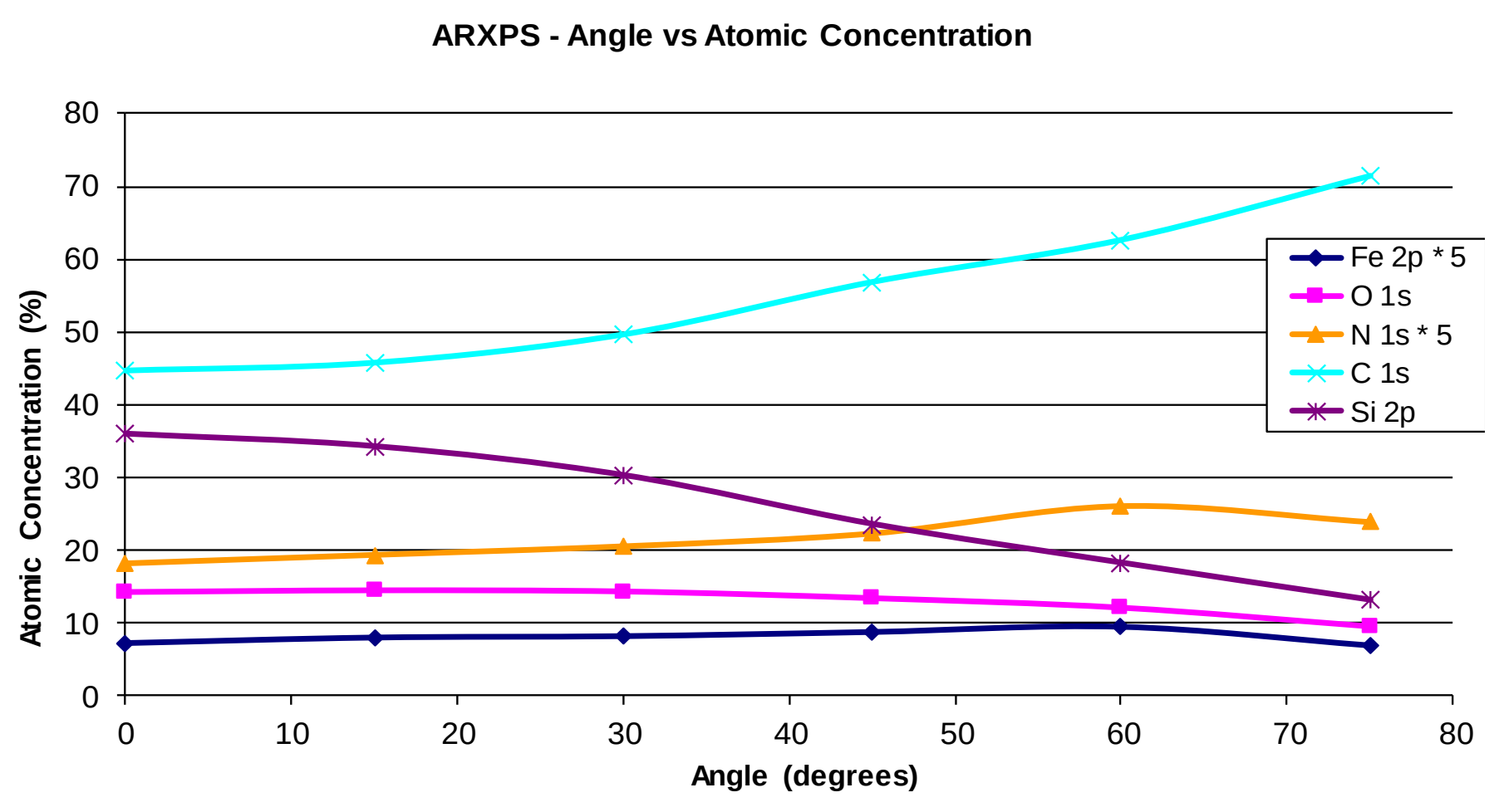
Modelling with ARXPS data reveals underlying layered structure in near surface region

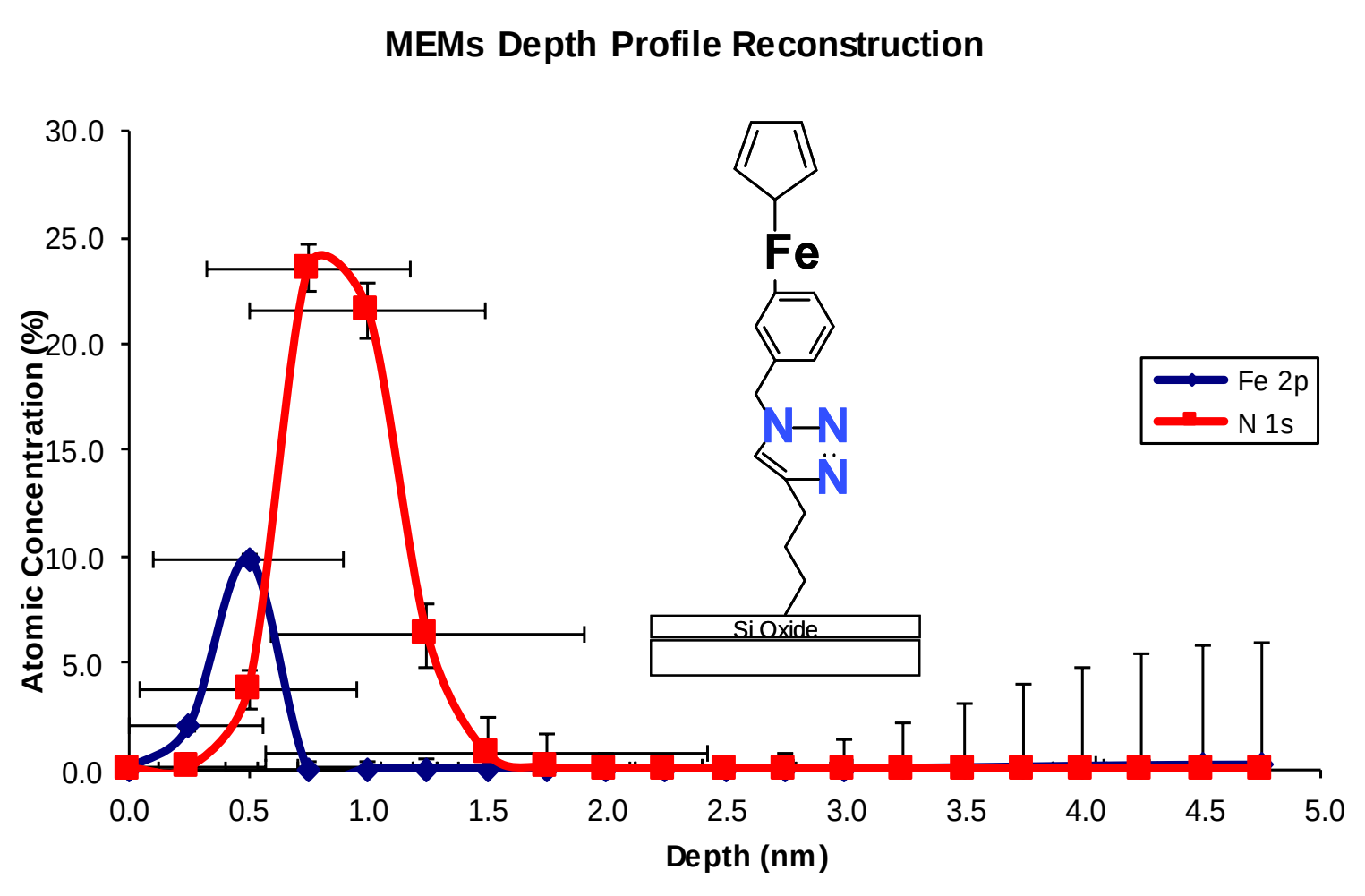
Data taken from an ARXPS experiment can be modelled based on the use of physical parameter data in algorithms that sample the solution space to find the best solutions in generating a calculated concentration depth profile. One approach to the solutions is the use of thermodynamic models in looking at the solution space, and maximizing the "entropy" of the solutions to find the best fit. While simpler models give quick information for simple systems, complex multilayer structures can require significant computational time.

Developing a model for a complex film structure can require additional samples of the same films in simpler structures, building up to the composite model for the full system.

Fe containing SAM Film Survey Spectrum → *ARXPS Experiment* → *MEMs Depth Profile Reconstruction*



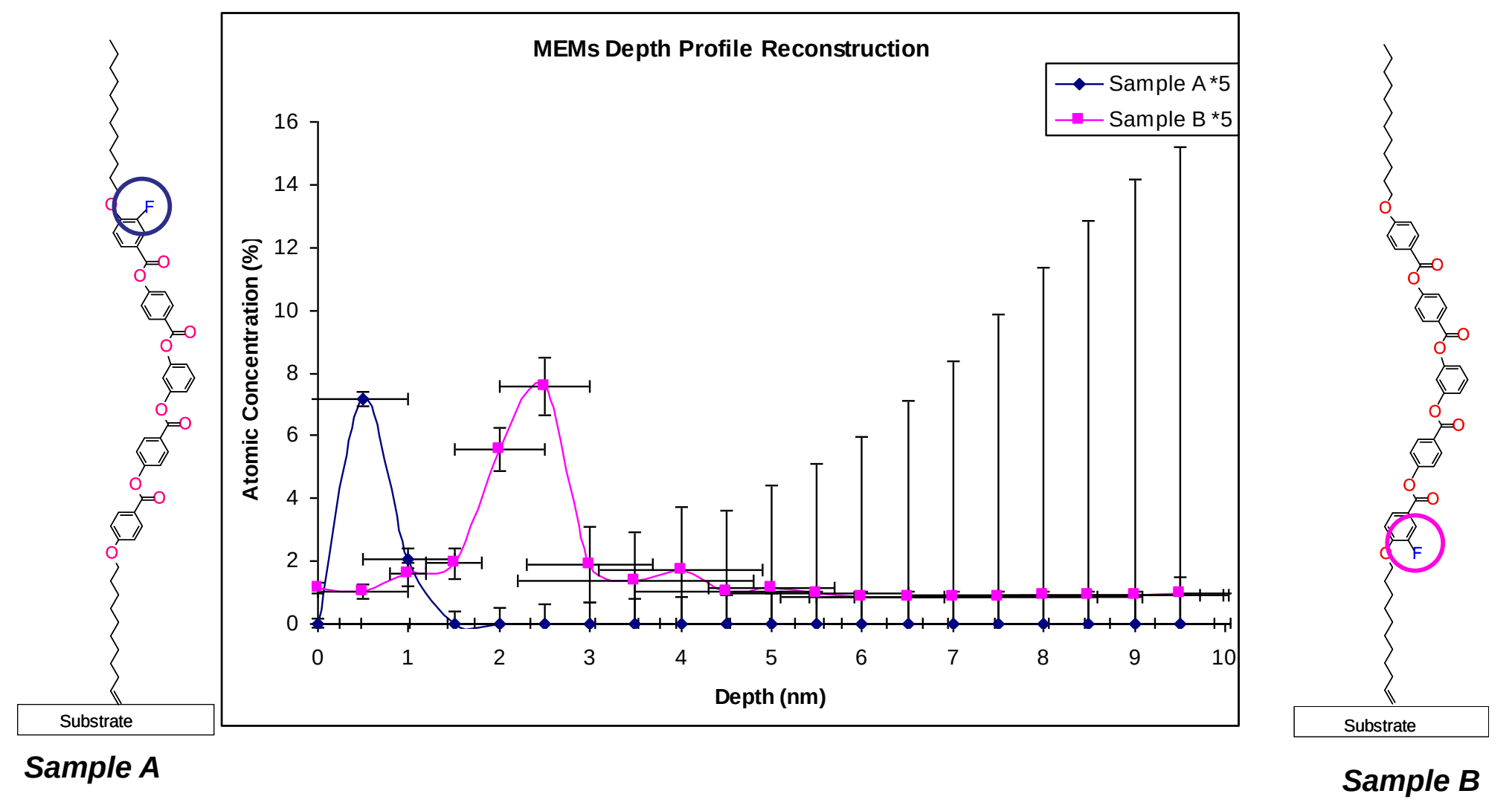




Sensitive near-surface depth information

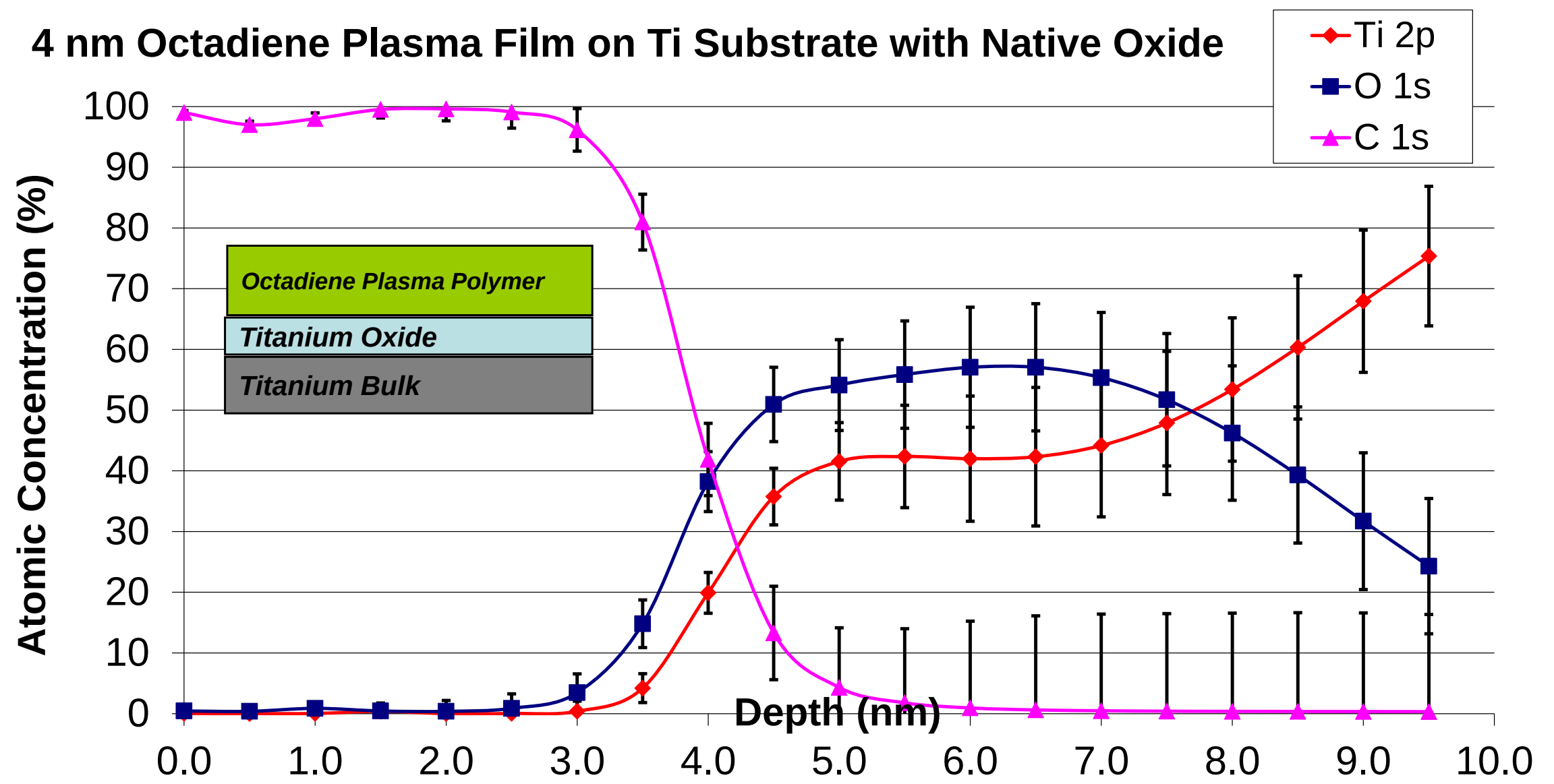
The sensitivity of ARXPS to the near surface elemental and chemical structure allows confirmation of expected structures for a wide array of applications where the state of the surface is a critical component. The nature of the surface has tremendous bearing on many electronic interface situations, as the workfunction of a material is incredibly sensitive to surface contamination, and bonding failures between layers can develop from monolayer contamination.

Complex models can be developed for tight control of very thin films using XPS, with high-K dielectric gate oxides in the silicon semiconductor industry being an example where the sensitivity of XPS is essential for film metrology[2].

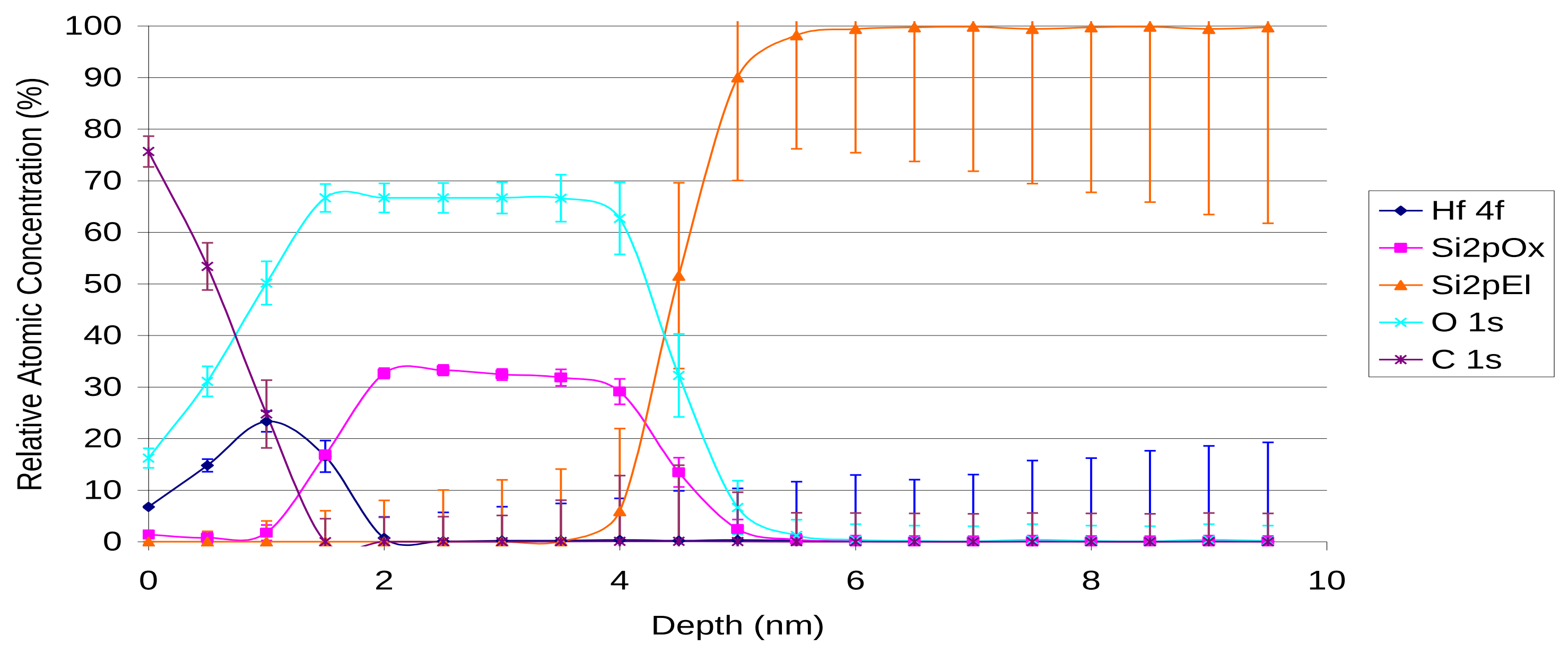


ARXPS reveals film structures

Thin films and their interfaces with substrates can be examined and compared to better understand deposition interactions and surface pre-treatment effects.

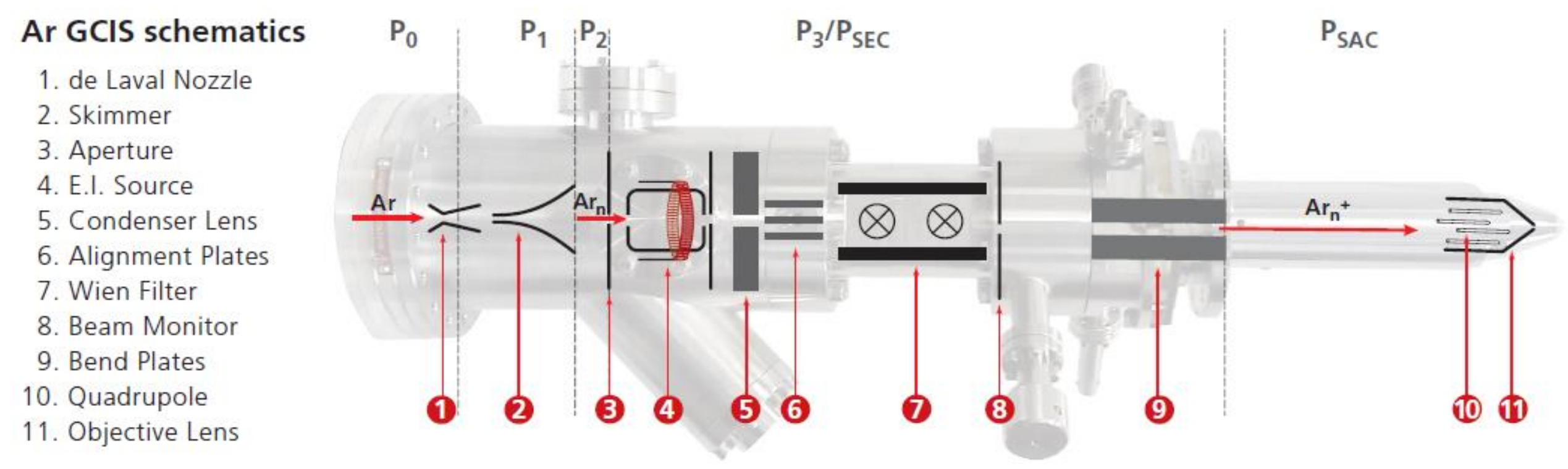


HfO2 : MEMs Depth Profile Reconstruction of ARXPS Data
Depth profile reconstruction was clearly able to separate the depth distribution of Hafnium and Oxygen on Si substrate. The MEMs reconstructed depth profile shows the adventitious carbon layer is localised in the top 1 nm of the sample surface followed by hafnium layer (~1.5 nm thick).



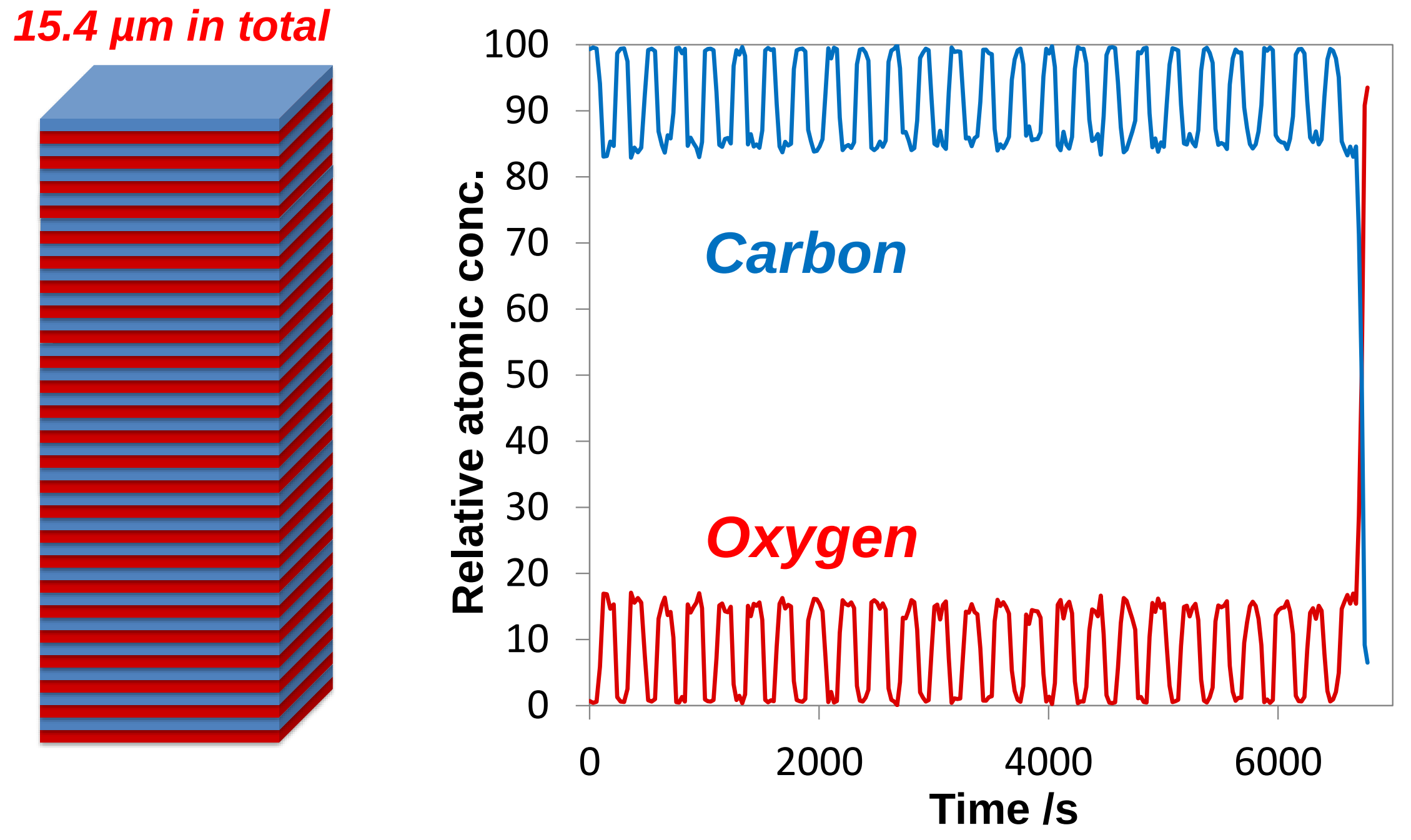
Films too thick for ARXPS

Samples thicker than ~7-10 nm generally need to be analysed using destructive analysis, such as sputter depth profiling, which involves cycling analysis with material removal via inert gas sputtering processes. New developments in sources for sputtering now allow the profiling of organic layers, that were not previously possible, as well as traditionally accessible inorganic materials. In addition to allowing sputter etching of organic materials, these same sources are showing new advantages in the etching of inorganic materials, in the lower reduction of metal oxides during the etching process when compared with monoatomic ion etching.



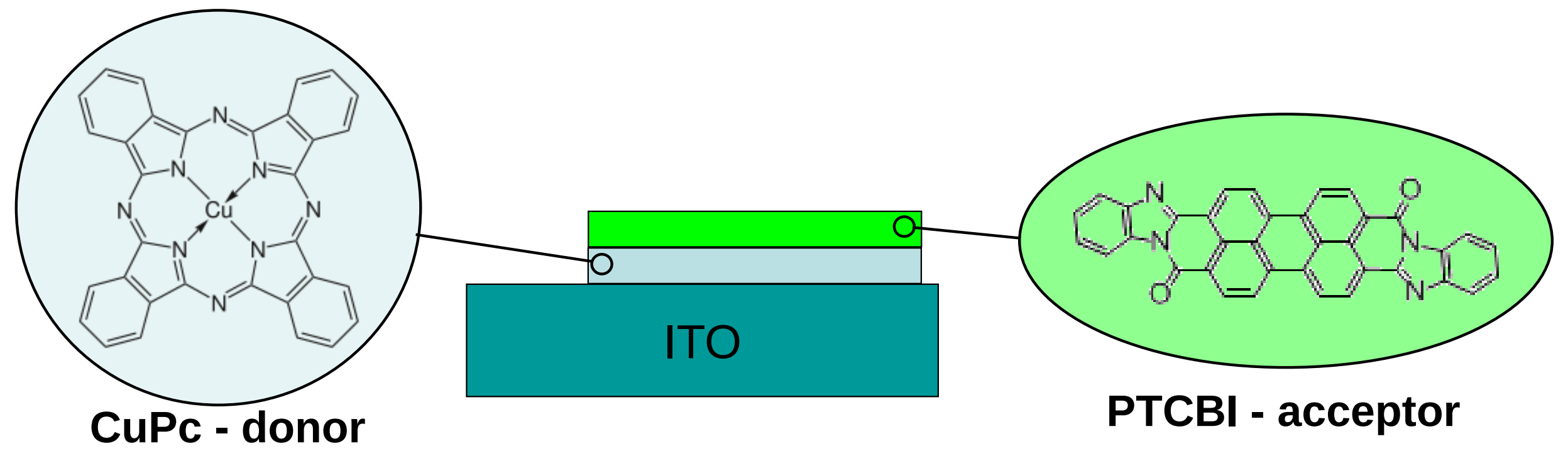
Gas Cluster Ion Source (GCIS)
Organic / Organic multilayer depth profile (Ar_{500}^+)

PS (288 nm) / PVP (328 nm) x 25
= 15.4 μm in total

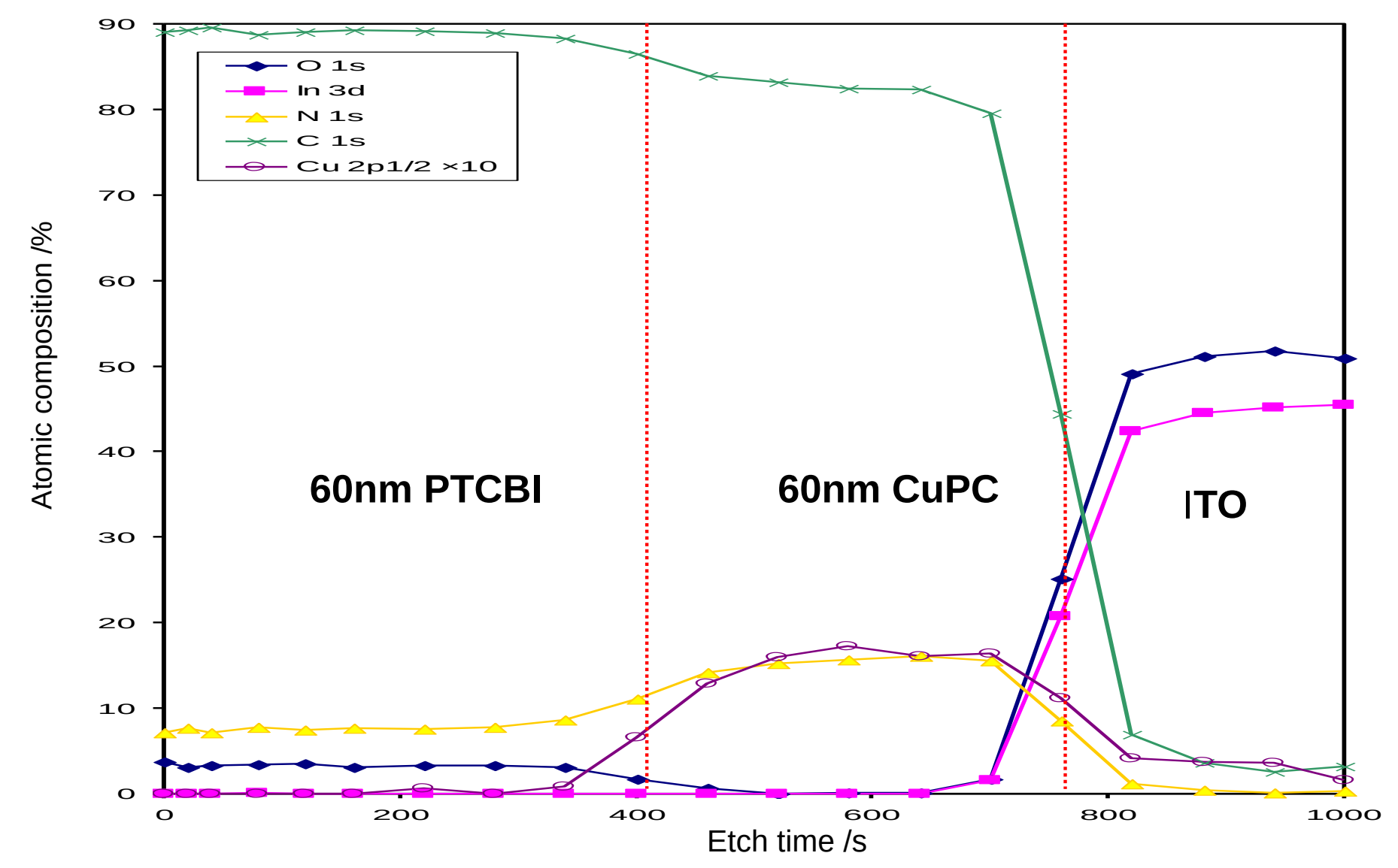


Schematic figure of organic/organic multilayer sample with concentration depth profile constructed from carbon and oxygen spectral intensities.

Organic Light Emitting Diode : Ar_N^+ Cluster Ion Depth Profile



Schematic diagram of partial OLED device with CuPu and PTCBI layers deposited on ITO on a glass substrate.



Ar_{1000}^+ 5 keV depth profile through partial OLED device.

Conclusion

Understanding the chemistry at the surface of a material is critical for any interactions with that surface. The near surface region can be investigated with XPS and ARXPS to reveal depth information through modelling of data, and information from thicker films can be obtained using XPS and sputter depth profiling. The sensitivity of XPS to the near surface chemistry will continue to expand its use as a critical measurement for nanomaterials processing.

1.A.G. Shard, J. Phys. Chem. C, 2012, 116 (31), pp 16806–16813.
2.C.R. Brundle, G. Conti, P. Mack, J. Elec. Spec. and Rel. Phen. 178, 433-448 (2010).