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# Successes and Challenges in Applications of a Laboratory-Based Scanning XPS/HAXPES Instrument

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## INTRODUCTION

X-ray Photoelectron Spectroscopy (XPS) is a widely used surface analysis technique with many well-established industrial and research applications, including nanoelectronics. The surface sensitivity (top 5-10 nm) of XPS and its ability to provide short-range chemical bonding information makes the technique extremely popular in the characterization of electronic materials. While its surface sensitivity is an important attribute, in some cases, the depth of analysis of XPS is not sufficient to analyze buried interfaces without first sputtering the sample surface. The interfaces of interest for characterization or metrology are often buried underneath metal electrodes or oxide layers and/or localized in small areas, which has been an increasing challenge for XPS.

An alternative to sputtering the sample is Hard X-ray Photoelectron Spectroscopy (HAXPES) which utilizes X-rays typically defined as having energies greater than 5 keV. By increasing the photon energy of the X-ray source, the mean free path of photoelectrons is increased, resulting in an increased information depth obtained from the sample. Depending on the energy used, these hard X-rays can provide depths of analysis three or more times greater than soft x-rays used on conventional XPS systems.

This paper describes the development and applications of a laboratory-based instrument, the PHI *Quantes*, equipped with two scanning microprobe monochromated X-ray sources, Al K $\alpha$  (1486.6 eV) and Cr K $\alpha$  (5414.8 eV), thus enabling both traditional XPS and HAXPES experiments in the same instrument.

## ADVANTAGES OF LAB-BASED HAXPES INSTRUMENT

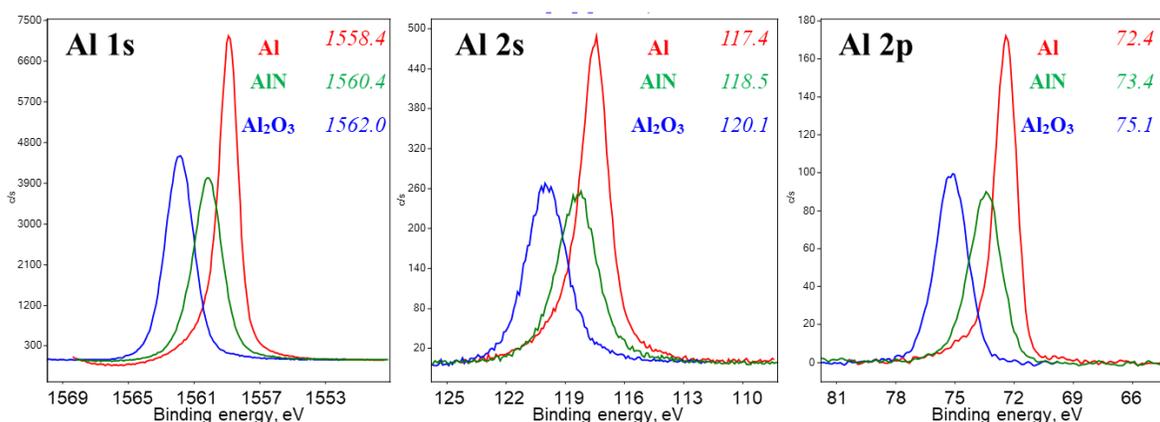
The PHI *Quantes* spectrometer combines a conventional monochromatic soft X-ray source (Aluminum K $\alpha$ ,  $h\nu = 1486.6$  eV) with a monochromatic X-ray source three times higher in energy (Chromium K $\alpha$ ,  $h\nu = 5414.8$  eV)<sup>1</sup>. The higher kinetic energy of electrons ejected using a higher-energy X-ray source results in a larger inelastic mean free path (IMFP) of electrons, making the sampling depth from which they can escape larger. For example, the inelastic mean free path for a Si 2p electron is  $\sim 9.5$  nm when the Cr X-ray source is used vs.  $\sim 3.3$  nm when an Al X-ray is used as the excitation source.

Higher escape depth of photoelectrons offers several advantages:

1. Structural investigations that are not possible with soft Al X-rays. This includes analysis of buried interfaces, such as electronic layers below a surface capping layer and compositional studies in the bulk of materials and interfaces below the sampling depth of soft X-rays.
2. Reduced effect of surface contamination on the photoelectron signal. The relative fraction of the adventitious layer with respect to the total sampling signal for Cr-induced photoelectrons is  $\sim 3$  times smaller than for Al-induced photoelectrons, resulting in much smaller signal attenuation due to contamination overlayer presence.

3. A deeper sampling depth using the Cr source allows one to probe beyond the depth of possible damage induced by ion sputtering. To take advantage of this benefit, the probing depth of the X-ray source must be deeper than the damage depth of the ion source. Damage depth is strongly dependent on ion beam sputtering parameters and material being analyzed. For commonly used ion beam settings of monatomic Ar<sup>+</sup> at 2-5 kV, the damage depth is on the order of 5-12 nm (higher for a higher energy beam), which is why we detect signs of damage in XPS spectra for ion-beam sensitive materials. For efficient and accurate chemical analysis of buried layers and interfaces, the photoelectrons analyzed must originate from below the ion beam damage depth, thus from depths of ~15 nm or more. A Cr X-ray source is well suited to meet this requirement.

In addition to higher sampling depth, higher primary X-ray source energy provides access to additional higher binding energy transitions. Compared to Al K $\alpha$ , Cr provides access to ~120 more transitions. Additional photoelectron transitions provide complementary chemical information and interpretation. The database of chemical shifts is well tabulated for transitions obtained using Al X-ray sources. A similar chemical state database is needed for higher binding energy transitions, accessible by higher energy sources. Figure 1 shows high-resolution spectra obtained using a Cr X-ray source for three reference materials – pure Al metal<sup>2</sup>, Al nitride AlN<sup>3</sup>, and Al oxide Al<sub>2</sub>O<sub>3</sub><sup>4</sup>. The chemical shift for the Al 1s transition, now accessible using a Cr source, is obtained.



**Figure 1.** High-resolution HAXPES Al 1s, Al 2s and Al 2p spectra for pure Al metal, Al nitride, and Al oxide.

Moreover, accessible transitions cover a large range of kinetic energy and, hence, sampling depth. For example, the Ti 1s photoelectron has a kinetic energy of ~444 eV originating from a sampling depth of ~ 3-4 nm, while the Ti 2p photoelectron has a much higher kinetic energy of ~4950 eV originating from as deep as 22-24 nm. Variable depth analysis can be easily performed for studying gradients, segregation, and oxidation phenomena.

Many of the Auger transitions contribute to the binding energy range of soft Al X-ray source – 0-1400 eV. When the Cr X-ray source is used, Auger transitions are shifted to a higher binding energy range clearing up the spectral range where most databases have data on chemical shifts.

## CHALLENGES IN QUANTIFICATION OF HAXPES DATA

The full benefits of the lab-based HAXPES technique are dependent on the development of parameters for accurate quantification. We at Physical Electronics have started developing experimental pure elemental relative sensitivity factors (PERSFs) for our Cr X-ray source using data obtained from ionic liquids and pure bulk elements. PERSFs were obtained by measuring the peak intensity of the selected element normalized by the peak intensity of key reference material (sputter cleaned Ag foil in our case).<sup>5</sup> Table 1 shows the results of the quantification of aluminum<sup>2-4</sup> and silicon-based compounds<sup>6-8</sup> using PERSFs. One can see that quantification is very accurate for some compounds using some transitions, while off by 5-7 % for others.

**TABLE 1.** Quantification (percent atomic) of Al- and Si-based compounds using PERSFs. Averages of 2-3 datasets per compound are shown.

| Compound  | Al 1s | Al 2s | Al 2p |
|---|-------|-------|-------|
| Al <sub>2</sub> O <sub>3</sub> (40% nominal Al) | 38.5  | 36.2  | 37.1  |
| AlN (50% nominal Al)                            | 51.4  | 50.0  | 51.2  |

| Compound  | Si 1s | Si 2s | Si 2p |
|---|-------|-------|-------|
| SiO <sub>2</sub> (33.3% nominal Si)               | 33.1  | 31.8  | 32.9  |
| SiC (50 % nominal Si)                             | 49.4  | 47.9  | 50.9  |
| Si <sub>3</sub> N <sub>4</sub> (42.8% nominal Si) | 42.8  | 47.9  | 50.9  |

The uncertainties of quantification that have been discussed in the literature for conventional Al and Mg X-ray source data<sup>9</sup> are even more significant for HAXPES data. These include the uncertainty of background subtraction, XPS peak satellite structure handling, and the accuracy of derived RSFs. Due to the much larger range of kinetic energy of photoelectrons in HAXPES data, the scattering and matrix effects on quantification may also be more significant.

## APPLICATIONS OF HAXPES

We will discuss new applications of laboratory HAXPES for the analysis of materials and interfaces used in device technology. HAXPES is of particular interest for optimizing GaN high electron mobility transistors (HEMTs) for the electronic power market because the layer thickness of the gate oxide necessarily increases well beyond the sub-5 nm values encountered in logic transistors. HAXPES is a promising technique to investigate an Al<sub>2</sub>O<sub>3</sub>/GaN interface with a thick gate oxide without the need for extensive sputtering. Another benefit of HAXPES for GaN-based structures is the elimination of overlap between the N1s core level and the Ga LMM Auger lines which occurs using a standard Al K $\alpha$  source. Recently developed software, *StrataPHI*, for thin-film structure determination from a single take-off angle HAXPES data creates an opportunity for high-throughput metrological applications for multi-layered semiconductor devices.

Operando HAXPES is a relatively new field in which a prototypical device is analyzed while an external stimulus is applied during the experiment. We will report on operando HAXPES measurements with Cr K $\alpha$  excitation on a prototypical memory device (100 $\times$ 100  $\mu$ m active area) fabricated from a Sr-doped lanthanum manganite oxide as active material showing reversible resistance changes upon biasing, also known as resistive switching (RS). To precisely understand the device's operating modes, HAXPES spectra obtained under sample bias were studied.

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## KEYWORDS

Characterization, XPS, HAXPES, operando, HEMT, thin-film structures