Application Note #250301

KeyWords
VE PARXPS, thin films, HAXPES, Non-destructive depth profiling metrology, semiconductor

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Non-destructive depth profiling by Variable Energy PARXPS (VE-PARXPS)

Parallel angle-resolved X-ray photoelectron spectroscopy (PARXPS) is a powerful tool for obtaining non-destructive depth profiles of layered thin-film samples. In this study, PARXPS was used in combination with variable energy excitation utilizing the three-color X-ray source µFOCUS 450 to probe thin oxide and nitride films in various information depths. The wide-angle AEOLOS 150 energy analyzer was used to obtain angle-resolved HAXPES data, from which concentration depth profiles were reconstructed using the ITFAP software.

Introduction

Chemical analysis of contemporary materials frequently entails the characterization of surface and bulk compositions, as well as the identification of various layers of two-dimensional (2D) materials or deposited thin films that are layered on top of each other. Achieving lateral homogeneities is imperative for ensuring reliable navigation to well-defined lateral structures. EnviroMETROS LAB and FAB provide a monochromated small spot X-ray source with up to three different photon energies giving different surface and bulk sensitivities due to the variation in kinetic energy of the emitted photoelectrons. The variable spot size and the complete software control of all parameters allow for easy lateral navigation, adaptation of information depth and count rate optimization. Furthermore the angle-resolving wide-angle electron analyzer AEOLOS 150 together with the software package enables high sensitivity and high resolution analysis with direct non-destructive depth profiling.

Metrology is key to semiconductor development and fabrication because it plays a role in material development and quality control as well. Materials surfaces and interfaces are more influential due to decreasing feature sizes and film thicknesses. So, surface analytical tools are getting more attention. Fabrication plants and pilot or research lines often work with full wafer samples, but there are only a few tools that accept complete wafers. Conducting studies on wafer coupons compromises their integrity, possibly leading to contamination and alterations in material composition.

Method

Variable Energy PARXPS (VE-PARXPS)

Variable Energy X-ray Photoelectron Spectroscopy (VE-XPS) represents a significant advancement in the field of X-ray analysis by extending the capabilities of conventional XPS. In conventional XPS, the excitation energy is fixed, typically at a photon energy such as Al Kα at 1486.6 eV. This fixed energy limitation restricts the probing depth, hindering the ability to achieve comprehensive and detailed analyses. In contrast, VE-XPS employs tunable X-ray sources, such as synchrotrons or laboratory-based monochromators, to adjust the photon energy. This adjustment enables depth profiling and enhanced sensitivity to different core-levels. By tuning the photon energy, the kinetic energy of emitted photoelectrons can be controlled, effectively changing the inelastic mean free path (IMFP). This capability allows for analysis of surface, subsurface, and bulk regions without the need for destructive sputtering. The utilization of varying photon energies can enhance the cross-section for specific core levels, thereby enhancing element-specific sensitivity.

Parallel Angle-Resolved XPS (PAR-XPS) represents a sophisticated XPS methodology in which the emission angle of photoelectrons is collected in parallel using a wide-anlge analyzer that can detect electrons at various emission angles (*cf.* Fig 1)., as opposed to the conventional sequential approach.

This innovation facilitates the concurrent acquisition of spectra from multiple angles, thereby enhancing the efficacy and precision of probing depth and electronic structure. PARXPS allows to create concentration depth

profiles from data that was taken for different photoelectron emission angles. The electron emission angle θ is defined as the angle between the sample surface normal and the emission direction of the electrons.

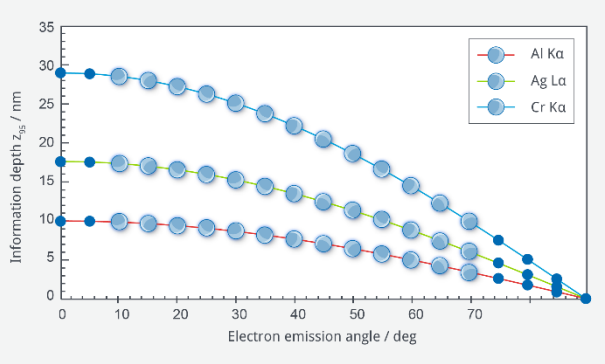

Fig. 1 The diagram illustrates the XPS information depth z_{95} for silicon photoelectrons versus the photoelectron emission angle ranging from 0° to 90° when using Al Kα, Ag Lα, or Cr Kα excitation.

The acquisition of angular data in a single operation, without the need to tilt the sample, offers numerous advantages. PARXPS characterization of a sample is based on the analysis of emitted photoelectrons over a series of emission angles. This effectively modifies the XPS information depth, which is constrained to the upper ten nanometers for Al Kα excitation as illustrated in Figure 1 for silicon as a function of photoelectron emission angles ranging from 0° to 90°.[1]
A parallel spectra collection of individual angle channels is possible with the EnviroMETROS with its wide-angle analyzer, the AEOLOS 150, developed especially for performing PARXPS measurements detecting emission angles, e.g., from 10° to 70° as highlighted in Fig. 1.

VE-XPS allows for the adjustment of penetration depth, while PARXPS provides angular-resolved data, enabling non-destructive depth profiling with enhanced accuracy. By varying the energy and emission angle, more detailed information can be extracted, which is crucial for materials such as layer stacks and semiconductors. PARXPS collects angle-resolved spectra in parallel, reducing measurement time compared to sequential methods. The combination of tunable energy with angular resolution enables the differentiation between surface, interface, and bulk states, thereby facilitating the acquisition of comprehensive structural information. The capacity to adjust depth sensitivity minimizes the occurrence of misinterpretation arising from charging effects or contributions from deeper layers, ensuring the reliability and precision of the measurement process. The combination of VE-XPS and PARXPS, allows to obtain a much richer dataset, enabling a more precise and comprehensive understanding of material surfaces and interfaces.

Results

Thin-layer Titan Nitride (TiN) Sample

Nominally, this sample consists of a 4 nm thin TiN layer grown on a zirconia substrate. With Al Kα excitation the measured angular profiles of the individual core-levels (Ti 2p, Zr 3d, N 1s, and O 1s) are fitting nicely to the reconstructed profiles if a native oxynitride film and an additional adventitious hydrocarbon layer (contamination) would be included in the layer model of this sample (Figure 2). Then the calculated film thicknesses are 2.0 nm for TiN, 1.9 nm for the native TiON layer, and 0.6 nm for the adventitious carbon layer as shown in the sample model (*cf.* inset of Fig. 2).

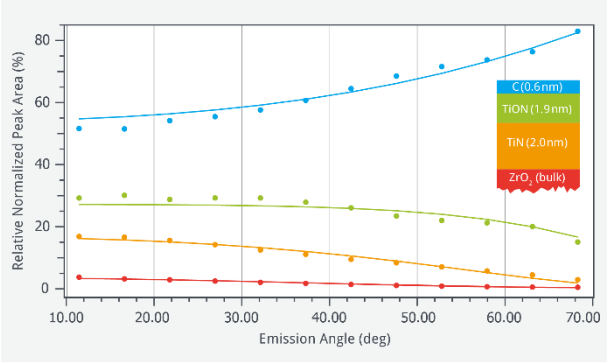

Fig. 2 Reconstructed depth-profile, layer model, and calculated thicknesses of a single-layer sample obtained from PARXPS measurements using Al Kα excitation (1487 eV).

These findings are corroborated by film thickness results that were obtained from reconstructed angular profiles of PARXPS data measured with Ag Lα excitation (2984 eV). These film thicknesses are 2.1 nm for TiN, 1.5 nm for the native TiON layer, and 0.6 nm for the adventitious carbon layer.

Thick-layer Titan Nitride (TiN) Sample

This layer stack consists of a thick titanium nitride (TiN, 12 nm) layer as shown in Figure 4. This three times thicker TiN layer was grown on a silicon substrate with a 1 nm thin intermediate SiO_2 layer. The thick-layer TiN sample was measured first with PARXPS using Al Kα

excitation and then additionally with two more excitation energies, Ag Lα and Cr Kα.
PARXPS measured with Al Kα excitation gives angular profiles (not shown) of the individual elemental core-levels (Ti 2p, N 1s, and O 1s) that can be reconstructed reliably giving a simple layer model with a 3 nm thin native oxynitride film on the thick titanium nitride, which is reasonable if one considers the information depth maximum of 10 nm for Al Kα excitation. Again, an adventitious carbon layer (0.5 nm) needs to be included in the sample model.

VE-XPS with all three excitation energies (Al Kα, Ag Lα, and Cr Kα) shows that the information depth can be varied in such a way that the whole 12nm thick TiN layer can be analyzed down to the silicon substrate when using Cr Kα excitation as illustrated in Figure 3, which illustrates nicely the three-fold increased information depth available with the excitation energy of 5414 eV. Moreover, even the oxidized silicon species originating from the very thin SiO_2 intermediate layer can be identified in the Si 1s core-level spectrum as small peak at 1844 eV.

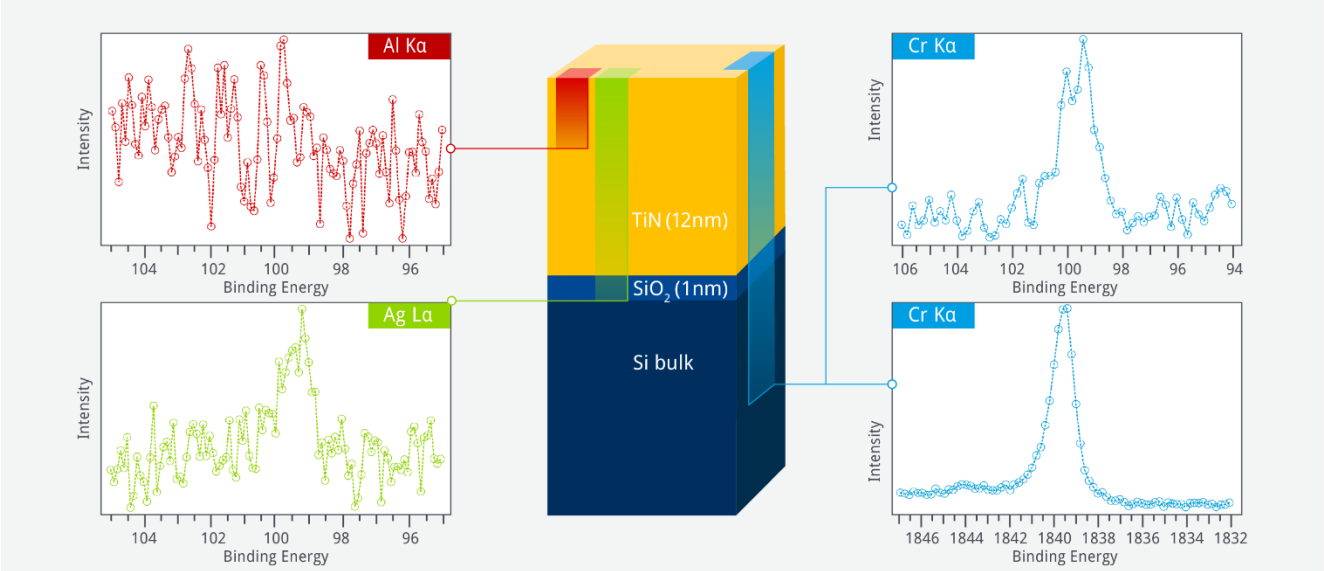

Fig. 3 High-resolution Si 2p (and Si 1s) core-level spectra of a 12 nm thick TiN sample measured with Al Kα, Ag Lα, and Cr Kα excitation.

Conclusion

Wide-angle photoelectron analyzers, e .g., the AEOLOS 150 with its optimized XPS transmission, are ideally suited for PARXPS studies of layered samples, e.g., (ultra) thin oxide and nitride films used in semiconductor industry. Reconstructions of the obtained angular profiles can be done using the ITFAP module of SpecsLab Prodigy.
The analysis of PARXPS data of a single-layer TiN sample showed very reproducible and reliable compositions and film thickness results, which are comparable for different excitation energies when employing VE-PARXPS with Al Kα and Ag Lα excitation.
Applying VE-PARXPS the information depth can be varied in such a way that a whole layer stack down to bulk silicon substrate can be analyzed when using an excitation energy of 5414 eV (Cr Ka).

Obtaining VE-PARXPS data in a single operation without tilting the sample has many advantages, e.g., for exceptionally large samples that are difficult to tilt, which is particularly important for 12" semiconductor wafers. All these advantages of doing VE-PARXPS with a wide-angle analyzer are included in the EnviroMETROS LAB and the EnviroMETROS FAB XPS tools which contain with the AEOLOS 150 analyzer and the three-color X-ray source µFOCUS 450. This unique combination allows surface chemical analysis by PARXPS with adjustable information depth using X-ray energies of 1487 eV, 2984 eV, and 5414 eV.