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ARXPS, thin film, metal oxide,
Non-destructive depth profile

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Non-destructive depth profiles by Parallel Angle-Resolved XPS (PARXPS)

Parallel angle-resolved XPS is a powerful tool for obtaining non-destructive surface depth profiles of layered thin-film samples. PARXPS was used to determine the chemical composition and film thickness of two different thin layer metal oxide samples. A wide-angle analyzer was utilized to obtain angle resolved XPS data from which concentration depth profiles were created using the ITFAP software module.

Introduction

Thin films are used in many applications, especially in device technology in the semicoductor industry. The development of semiconductor devices in the 20th century considerably influenced and changed modern societies. Still semiconductor research is of great importance. Especially, there is a need to precisely analyze semiconductor surfaces and interfaces regarding their chemical composition, here X-ray Photoelectron Spectroscopy (XPS) can help to correlate device performance to materials properties in order to optimize materials choice and combinations.

XPS is commonly used in semiconductor technology, especially for characterizing gate oxide structures and other semiconductor materials. The gate oxide is a critical component in metal-oxide-semiconductor (MOS) devices, such as field-effect transistors (FETs). Understanding the electronic structure and composition of the gate oxide is essential for optimizing device performance and reliability. Some examples of how XPS is applied in semiconductor technology, particularly in the context of gate oxide structures are oxide thickness and composition, interface states, surface contamination and cleaning processes.

Method

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), provides information about the chemical composition of a material. In standard XPS, X-rays are used to irradiate a sample, causing the emission of photoelectrons from the atoms in the sample. The kinetic energy and number of emitted electrons are then measured to determine information about the chemical composition of the material.

In ARXPS, the key difference lies in the additional consideration of the emission angle of the photoelectrons. ARXPS allows to create concentration depth profiles from data that was taken for different photoelectron emission angles. This can be done by simply tilting the sample or by parallel emission angle detection using a wide anlge analyzer that can detect electrons at various emission angles (*cf.* Fig 1). The electron emission angle θ is defined as the angle between the sample surface normal and the emission direction of the electrons. The acquisition of angular data in a single operation, without the need to tilt the sample, offers a number of advantages. PARXPS can be used on very large samples that are hard to tilt, which is especially relevant for 8” or 12” semiconductor wafers. Another advantage of parallel angle acquisition is that the analysis area and position are independent of the emission angle, which is also beneficial for charge compensation of insulating sample. In contrast to this PARXPS acquisition, the analysis position must be (re)aligned at each angle and the required charge compensation conditions may change when doing ARXPS by tilting the sample.

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 z_{95}, 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]

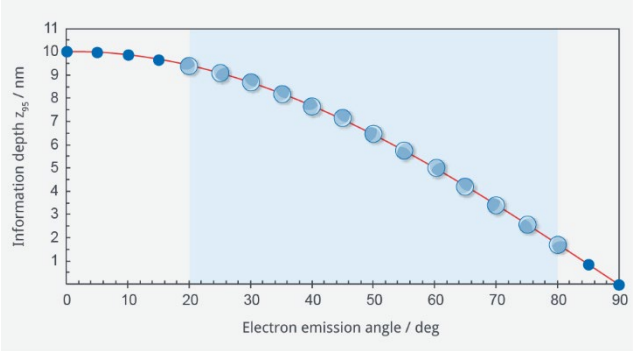

Fig. 1 The diagram illustrates the XPS information depth z_{95} for silicon photoelectrons versus the photoelectron emission angle ranging from 0° to 90° when using Al Kα excitation.

A major advantage of PARXPS is that it is a non-destructive method in contrast to standard ion sputtering procedures that abrasively remove layer by layer of a sample for depth profiling.

A parallel spectra collection of individual angle channels is possible with a wide-angle analyzer, e.g., the PHOIBOS 150 WAL or AEOLOS 150, developed especially for performing PARXPS measurements detecting emission angles, e.g., from 20° to 80° as highlighted in Fig. 1.

An example of PARXPS data taken on a silicon sample with a 3 nm thick oxide film is presented in Fig. 2. The Si 2p core-level spectra for emission angles from 20° to 80° show two peak components related to silicon oxide (SiO_2) and elemental silicon (Si^0) that are located at binding energies of 102.5 eV and 100 eV. The SiO_2 component becomes the main component for larger emission angles that probe only the topmost surface layers. This reflects the layered sample structure with the oxide on top of the silicon wafer.

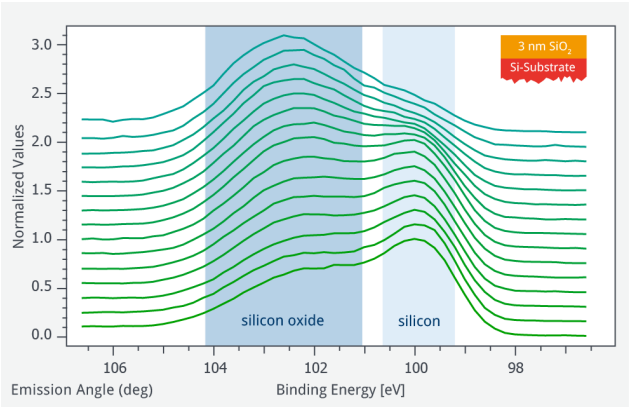

Fig. 2 The presented Si 2p data were obtained by PARXPS on a silicon sample covered with a 3 nm thick oxide film.

The SpecsLab Prodigy module *Identification of Thin Films from Angular Profiles* (ITFAP) can help the user to generate reconstructed elemental or compositional depth profiles from measured angular profiles of thin films and ultra-thin layered materials. The main capabilities of the new ITFAP module are demonstrated in this note using PARXPS data from dedicated gate oxide reference samples based on well-determined layer structures composed of HfO_2, SiO_2, and Al_2O_3 on silicon substrates.[2]

Results

PARXPS was done using a wide-angle analyzer and a monochromatized Al Kα source (14 kV, 100 W) in fixed analyzer transmission with the angle-resolved mode and a pass energy of 50 eV. Quantification was done using an angle-resolved transmission function.

Two-layer metal oxide sample

Nominally, this sample consists of 2.5 nm HfO_2 as a high-*k* layer grown on a silicon substrate with an intermediate SiO_2 layer with a nominal thickness of 1.0 nm. The measured angular profiles of the individual core-levels Hf 4f, Si 2p, and O 1s are fitting nicely to the reconstructed profiles when an additional adventitious hydrocarbon layer (contamination) is included in the layer model of this metal oxide sample, see Figure 3. Then the film thicknesses are 2.8 nm for HfO_2 and 1.2 nm for SiO_2 together with 0.4 nm for the adventitious carbon layer as shown in the sample model (*cf.* inset of Fig. 3).

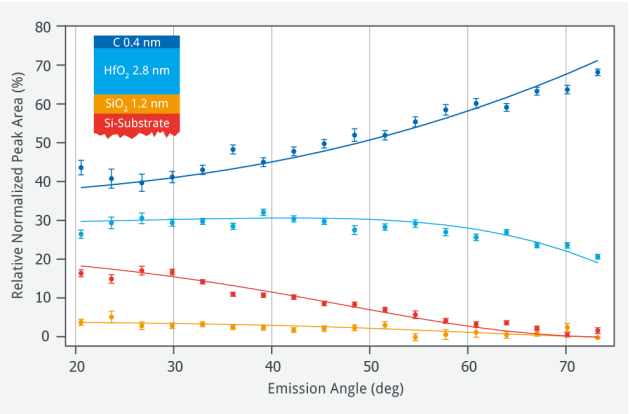

Fig. 3 Reconstructed depth-profile, layer model, and calculated thicknesses of a two-layer thin-film reference sample.

Table 1. Comparison of nominal and experimentally determined film thickness values of a four-layer gate oxide sample.

Thickness	Substrate	1st SiO_2	2nd Al_2O_3	3rd HfO_2	4th Al_2O_3	5th CH_x
Nominal	Si	1.0 nm	1.0 nm	2.0 nm	1.0 nm	–
ARXPS	Si	**0.6 nm**	**0.8 nm**	**2.6 nm**	**0.8 nm**	**0.4 nm**

These findings are corroborated by earlier results including an international interlaboratory comparison employing the same sample and using PARXPS and TEM.[2-3]

Four-layer metal oxide sample

This more complex layer stack consists of 2.0 nm HfO_2 as a high-*k* layer sandwiched in between two Al_2O_3 layers with a nominal thickness of 1.0 nm, see Table 1. And these three layers are grown on a silicon substrate with a 1.0 nm thin intermediate SiO_2 layer. The four-layered sample was measured using the same experimental setup and conditions.

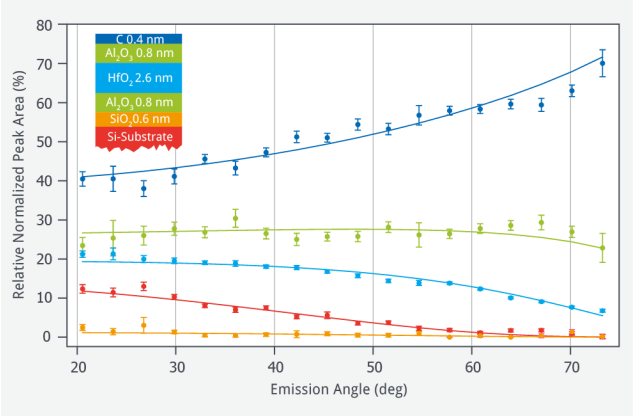

Fig. 4 Reconstructed depth-profile, relative depth plot, layer model, and calculated thicknesses of a four-layer metal oxide sample.

The measured angular profiles of the individual elemental core-levels Hf 4f, Si 2p, O 1s, and Al 2p can be reconstructed reliably giving a layer model with thicknesses of 0.8 nm for both Al_2O_3 layers, 2.6 nm for HfO_2, and 0.6 nm for SiO_2. Again, an adventitious carbon layer with a thickness of 0.4 nm needs to be included in the sample model, see Tab. 1 and inset of Fig. 4.

Conclusion

Wide-angle photoelectron analyzers PHOIBOS 150 WAL and the newly developed AEOLOS 150 with its optimized XPS transmission are ideally suited for PARXPS studies of (thin) layered samples, e.g., gate oxides used in semiconductor industry. The obtained angular profiles and reconstructions using the SpecsLab Prodigy module ITFAP show very reproducible and reliable results, which are in close agreement with earlier results employing the same samples using XPS and TEM.[1]

Obtaining angle-resolved XPS data in a single operation without tilting the sample has many advantages. PARXPS can be used on exceptionally large samples that are difficult to tilt, which is especially important for 8" and 12" wafers in semiconductor industry. Another advantage of parallel angle acquisition is that the same analysis area and position are used for each emission angle, which is also helpful when charge compensation of insulating samples is required.

All these advantages of doing PARXPS with a wide-angle analyzer are also included in the EnviroMETROS LAB and the EnviroMETROS FAB XPS tools which come 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.

[1] The 95% information depth z_{95} corresponds to the sample thickness from which 95% of the detected XPS signal originates. If elastic scattering effects are neglected it is described by $z_{95} = 3\lambda\cos\theta$, with θ the angle of emission and λ the inelastic mean free path.

[2] Conard T., Vandervorst W., Bergmaier A., Kimura K. J. *Thin layer composition profiling with angular resolved x-ray photoemission spectroscopy: Factors affecting quantitative results* Vac. Sci. Technol. A, **2012**, *30(3)*, 031509. http://dx.doi.org/10.1116/1.4704603

[3] Tasneem G., Werner W. S. M., Smekal W., Powell C. J. *Interlaboratory study comparing analyses of simulated angle-resolved X-ray photoelectron spectroscopy data* Surf. Interf. Anal. **2014**, *46(5)*, 321. https://doi.org/10.1002/sia.5482

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