KRATOS ANALYTICAL
A SHIMADZU GROUP COMPANY

Applications Note

Reconstructed Concentration Depth Profiles from Angle-Resolved XPS using MEM Software

MO454(A)

Keywords XPS, ARXPS, MEM, GCIS

Overview

XPS was used to characterize the surface chemistry of layered thin film materials, using monochromated Al Kα (1486.6 eV) X-rays to gain quantitative chemical information from the uppermost 10 nm of the surface. In this study, we illustrate how ARXPS is used as a more surface sensitive approach to probe only the topmost 1-3 nm of a material, and how one can utilize Maximum Entropy Method (MEM) software to recreate a concentration depth profile from the resulting data. How the removal of contamination effects the resulting MEM model fit is also explored following gentle sputter cleaning using the GCIS.

Introduction

The application of thin film technology is of commercial importance across a range of industries and is commonly used to influence both the physical and chemical properties of bulk materials. Ranging in thickness from tens of Angstroms to microns, their applications are used across a broad range of disciplines including the semiconductor, biomaterial and energy harvesting industries. Herein, we provide a multi-technique investigation of layered thin film and ultra-thin film coatings using a model system for gate oxide structures, in collaboration with IMEC. The combination of techniques allows one to build a complete picture of the composition of these materials and how subtle differences in chemistry and stoichiometry can influence the properties of a substrate to enhance its application specificity.

Angle-Resolved X-ray Photoelectron Spectroscopy (ARXPS) is often used to analyze thin film materials but determining the depth distribution of elements from this data to build a reconstructed depth profile is difficult. One way to approach this issue is to utilize the established Maximum Entropy Modelling (MEM) method to improve confidence in measuring elemental and chemical state depth distribution in thin films. The effect of contamination on the calculated MEM model fit can subsequently be investigated by removing the adventitious carbon overlayer using the Gas Cluster Ion Source (GCIS) and reacquiring the ARXPS data, with the hope of developing a standard approach to characterize real life thin film materials.

Experimental

Surface analysis of the layered thin film materials was performed using the state-of-the-art AXIS spectrometer fitted with a GCIS. Survey spectra were acquired over a large energy range of 0 to 1350 eV, whilst high resolution spectra were acquired over a small energy range for each particular element. The co-axial charge neutraliser was used to mitigate against the loss of photoelectrons and subsequent charge build-up.

XPS is a surface sensitive technique, with the sampling depth typically quoted as 10 nm. This surface sensitivity can be increased by rotating the sample relative to the vertical axis of the spectrometer. Spectra are acquired at a series of angles using a standard sample bar. ESCApe software uses an automated routine to tilt the sample bar whilst controlling the y/z axes to calibrate the analysis position. This ensures the same analysis location is used as the tilt angle changes during the ARXPS experiment.

ARXPS looks at changes in intensity with grazing angles, but with layered thin film materials, the analysis of this data is complicated as there is signal from several layers within the sampling depth. MEM provides a way to assess this data, being an established method which uses a simple statistical model for quantitative analysis. It is incorporated into the ESCApe software for ease of use and after recent work by K. Macak,[1] allows the inclusion of important parameters to refine the MEM model fit, such as stoichiometry, density and number/thickness of layers. This is important in layered thin film materials because it allows one to fit different chemical states for elements with different composition and densities, rather than assuming uniformity through the layers. This is extremely useful for samples with repeating, identical layers or when there are layers of the same element with a different chemical state, such as the Si substrate and SiO_2 layer(s) seen in these examples.

The multi-mode GCIS was used to gently remove adventitious carbon. It is designed to operate in both monatomic Ar^+ and cluster Ar_n^+ modes, making it suitable for sputter cleaning and depth profiling of different thin film materials. Through a combination of cluster size and acceleration voltage, a broad range of materials may be sputter cleaned or depth profiled without chemical damage to the surface. The cluster mode used here was 5 keV Ar_{2000}^+, which provides a low etch rate for gentle sputter cleaning.

Results and Discussion

Ideal Reference Sample

An ideal thin film reference sample, provided by IMEC, was initially used to develop a standard analysis workflow. With a well-determined layered structure, this sample consisted of 2 nm hafnium oxide on 1 nm silicon oxide on a silicon substrate, prepared and characterized by T. Conard *et al.*[2] The survey spectrum acquired was as expected, but also exhibited a C 1s peak resulting from adventitious carbon contamination.

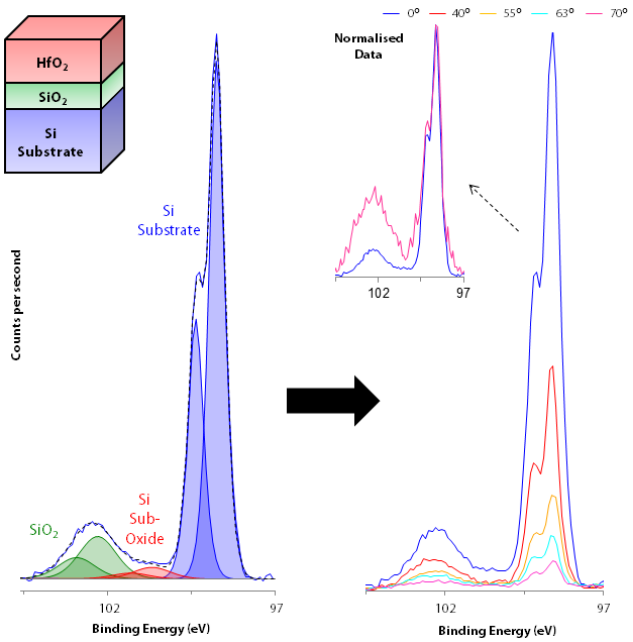

Figure 1. ARXPS Si 2p spectra for ideal reference sample (as received).

An ARXPS experiment was performed to determine elemental and chemical state concentrations as a function of depth. Figure 1 shows the ARXPS Si 2p spectra for this ideal reference sample, where the SiO_2 peak increases with grazing angle, as expected. The resulting model fit from MEM provides a calculated reconstructed concentration depth profile which is in agreement with the layer thicknesses expected for this thin film sample.

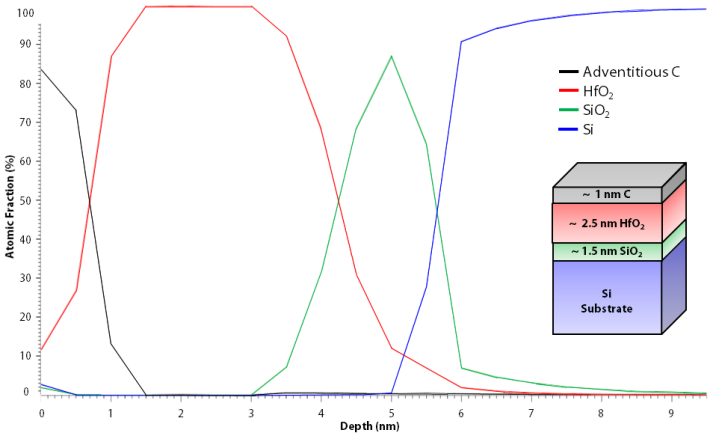

Figure 2. MEM model fit for ideal reference sample (as received).

The calculated MEM model fit is complicated by the contamination of adventitious carbon. Using the Gas Cluster Ion Source (GCIS), this overlayer was removed using the 5 keV Ar_{2000}^+ mode utilizing large clusters of a low energy. This is essential for removing carbon contamination without causing damage to the substrate, evident in Figure 3 which compares Hf 4f spectra before (blue) and after (red) argon cleaning with both monatomic and cluster modes. The 5 keV Ar_{2000}^+ cluster mode causes no damage to the substrate as the Hf 4f spectra look identical both before and after cleaning. The 0.5 keV Ar^+ monatomic mode, on the other hand, clearly damages the substrate as the Hf 4f spectra dramatically changes even when using a low energy monatomic mode.

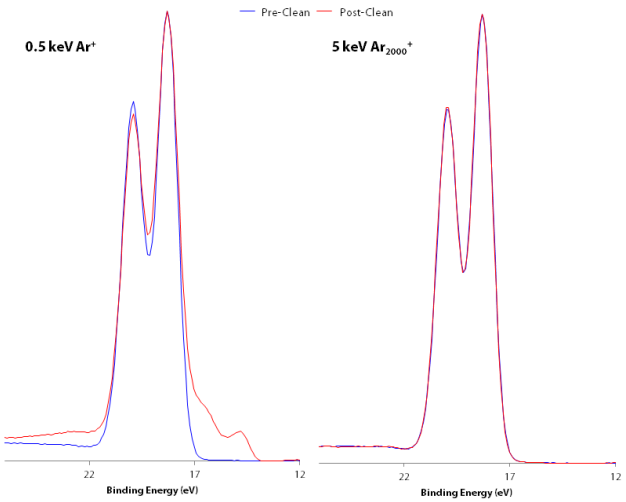

Figure 3. Comparison of Hf 4f spectra pre– (blue) and post– (red) cleaning with 0.5 keV Ar^+ monatomic and 5 keV Ar_{2000}^+ cluster modes.

The removal of carbon contamination was confirmed by a survey spectrum and the ARXPS experiment was repeated. The resulting MEM model fit, displayed in Figure 4, also reveals the removal of this carbon overlayer and calculates a reconstructed depth profile to give layer thicknesses in agreement with that expected for this thin film material.

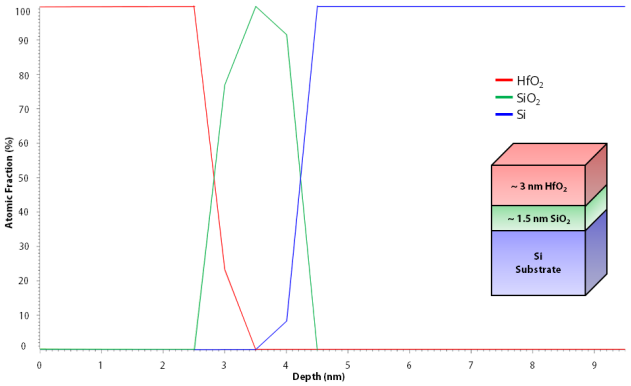

Figure 4. MEM model fit for ideal reference sample after cluster cleaning with GCIS.

A More Complex Reference Sample

With this workflow proving successful for the analysis and characterization of the ideal reference sample, it was applied to a slightly more complex reference sample with an additional silicon oxide layer. This well-defined layered thin film structure consisted of 1 nm SiO_2/2 nm HfO_2/1 nm SiO_2/ Si substrate, prepared and characterized by T.Conard *et al.*[2] The survey spectrum acquired was as expected, but again exhibited a C 1s peak as a result of carbon contamination. An ARXPS experiment was performed to determine elemental and chemical state concentration as a function of depth. Figure 5 shows the ARXPS Si 2p spectra for this more complex, ideal reference sample, where the SiO_2 peak increases with grazing angle whilst the elemental Si peak decreases, as expected when decreasing the information depth.

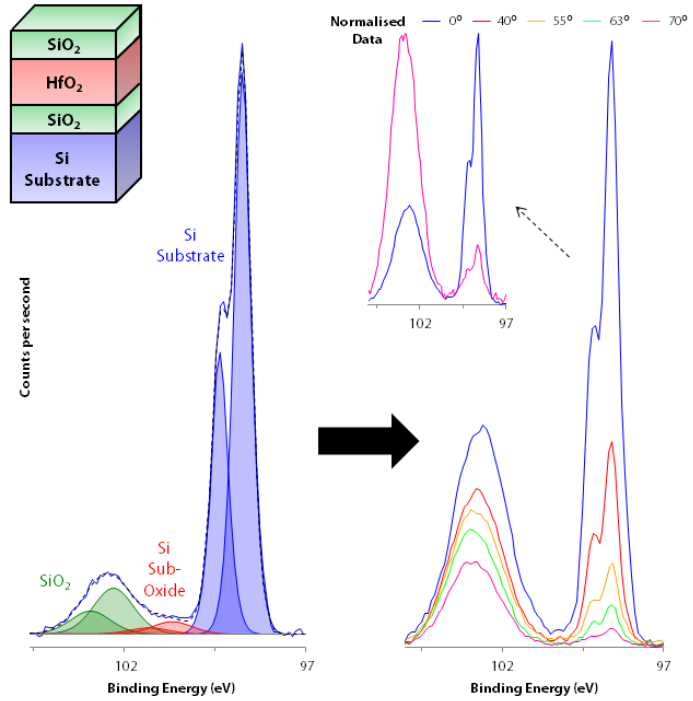

Figure 5. ARXPS Si 2p spectra for more complex ideal reference sample (as received).

The resulting model fit from the MEM software provides a calculated reconstructed concentration depth profile which correctly models the two identical SiO_2 layers, as seen in Figure 6. This fit is however less accurate for the deeper of the two SiO_2 layers, as a consequence of only having spectral information for this deeper layer at the initial, less grazing angles. To improve the MEM model fit, the gentle removal of the 1 nm thick carbon overlayer using the GCIS is extremely useful. This results in more signal from the deeper SiO_2 layer during the more grazing angles of the ARXPS experiment.

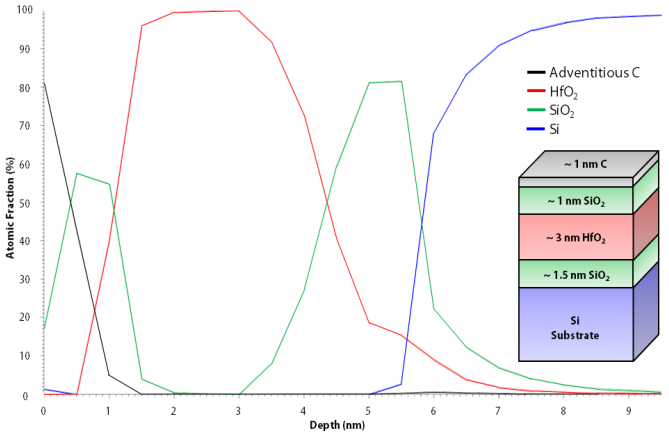

Figure 6. MEM model fit for more complex idea reference sample (as received).

Again using the low energy, large cluster 5 keV Ar_{2000}^{+} mode, the adventitious carbon overlayer was removed using the GCIS. The removal of carbon contamination was confirmed by a survey spectrum and the ARXPS experiment was repeated. The resulting MEM model fit, displayed in Figure 7, reveals the removal of the carbon overlayer and calculates a reconstructed depth profile to give layer thicknesses in agreement with that expected for this thin film material. Overall, the MEM model fit is improved, particularly at the deeper SiO_2 interface.

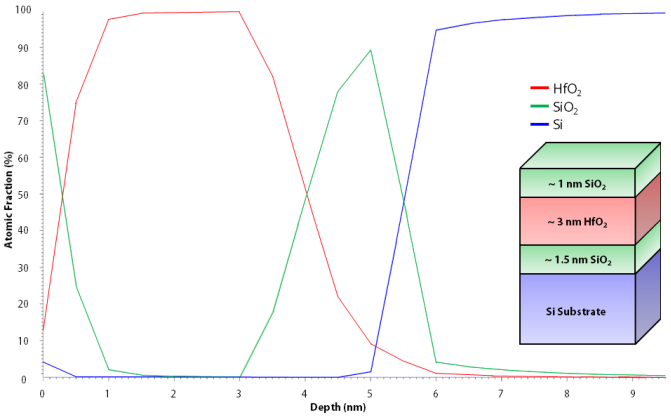

Figure 7. MEM model fit for more complex ideal reference sample after cluster cleaning with GCIS.

With the confidence that this standard analysis workflow is successful in characterizing two samples containing layered thin films, it can be used as a protocol to analyze real life thin film materials.

Conclusions

XPS was used to characterize ideal reference thin film materials which are used as model structures for gate oxides. The sampling depth for conventional monochromated Al Kα X-rays is typically quoted to be 10 nm, but this can be reduced to 1-3 nm using ARXPS which is a more surface sensitive approach. MEM was used to calculate a reconstructed depth profile from the resulting data which was found to be in agreement with the layer thicknesses expected for these thin film materials. The effect of contamination was explored after gentle cleaning using the GCIS and this was found to greatly improve the resulting MEM model fit, particularly for deeper layers where the information is limited to the initial, less grazing angles. The success of this analysis workflow has allowed it to be developed into a standard protocol to analyze real life materials and gain confidence in measuring elemental and chemical state depth distribution in thin films.

Acknowledgements

Sincere gratitude to Thierry Conard at IMEC for sample preparation.

References

[1] K. Macak, Surface and Interface Analysis, 2011, **43**, 1581-1604.
[2] T. Conard *et al.*, Journal of Vacuum Science and Technology A, 2012, **30**, 031509.

Related documents online:

MO442 Quantification of layer composition in compound semiconductors
MO427 Smart phone screen—depth analysis of alkali and alkali earth metals

KRATOS ANALYTICAL
A SHIMADZU GROUP COMPANY

Wharfside, Trafford Wharf Road, Manchester M17 1GP

Phone: +44 161 888 4400 Fax. +44 161 888 4402

www.kratos.com