

Report on the 47th IUVSTA Workshop 'Angle-Resolved XPS: the current status and future prospects for angle-resolved XPS of nano and subnano films'

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A summary of the workshop entitled 'Angle-Resolved XPS: The Current Status and Future Prospects for Angle-resolved XPS of Nano and Subnano Films' is given, which was held at the Riviera Maya, Mexico, 26–30 March 2007, under the main sponsorship of the International Union for Vacuum Science, Technique and Applications (IUVSTA). Angle-resolved X-ray photoelectron spectroscopy (ARXPS) can provide detailed chemical as well as depth profile information about the near-surface composition of materials and thin films. This workshop was held to review the present status and level of understanding of Angle-resolved XPS, and to stimulate discussions leading to a deeper understanding of current problems and new solutions. The main goal of the workshop was to find better ways to perform experiments and, very importantly, better ways to extract information from the experimental data. This report contains summaries of presentations and discussions that were held in sessions entitled 'Basics and Present Limits of ARXPS', the Analysis of ARXPS Data, Applications of ARXPS, Equipment for ARXPS, and Future Developments in ARXPS'. There were 33 participants at the workshop. Copyright © 2009 John Wiley & Sons, Ltd.

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Introduction

X-ray photoelectron spectroscopy is an established technique for the analysis of homogeneous surfaces.^[1] Surfaces that are laterally inhomogeneous are analyzed ideally using other instruments that would be capable of measuring such lateral inhomogeneities. Changes in concentration with depth from the surface pose other challenges in determining the depth distribution of elements or the depth profile. For regions greater than 10 nm in depth from the surface, sputter depth profiling with an inert gas is the most commonly used method. This removes layers by sputtering, exposing new surfaces that are measured sequentially. Some problems with sputter depth profiling are (i) preferential sputtering of one element compared with another, (ii) sputter-induced changes in chemistry of compounds, (iii) intermixing between layers, (iv) changes in electrical charging when sputtering non-conducting materials and (v) roughening of the surface due to sputtering. Other techniques such as Rutherford Backscattering Spectrometry or backside Secondary Ion Mass Spectroscopy are also often used for depth profiling, but in general, they suffer from poor depth resolution and chemical specificity. However, the near-surface region is often of particular interest, and this region poses its own challenges for determining its depth distribution of elements. It is this region where Angle-Resolved

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Table 1. List of participants at the 47th IUVSTA Workshop 'Angle-Resolved XPS: The Current Status and Future Prospects for Angle-resolved XPS of Nano and Subnano Films'

Dr Servando Aguirre-Tostado	Richardson, TX	USA
M.C. José Alberto Armendáriz Cruz	Canahutli	Mexico
Dr Richard Brundle	Soquel, CA	USA
Dr Thierry Conard	Leuven	Belgium
Dr Giuseppina Conti	Santa Clara, CA	USA
Dr Vincent Crist	Mountain View, CA	USA
Dr Peter Cumpson	Teddington	UK
Dr Charles S. Fadley	Davis, CA/Berkeley, CA	USA
Dr Vincent Fernandez	Nantes	France
Dr Julia Fulghum	Albuquerque, NM	USA
Dr John Grant	Dayton, OH	USA
Dr Martyn Green	East Grinstead	UK
Dr John S. Hammond	Chanhassen, MN	USA
Dr Alberto Herrera-Gomez	CINVESTAV-Qro	Mexico
Dr Monika Jenko	Ljubljana	Slovenia
Dr Keisuke Kobayashi	Hyogo	Japan
Dr László Kövér	Debrecen	Hungary
Dr Sven Maehl	Berlin	Germany
Dr Chiara Marchiori	Rueschlikon	Switzerland
Dr Chris Moffitt	Chestnut Ridge, NJ	USA
Dr Stephen Muhl	IIM-UNAM	Mexico
Dr Hiroshi Nohira	Tokyo	Japan
Dr Robert Opila	Newark, DE	USA
Dr Steffen Oswald	Dresden	Germany
Dr Royston Paynter	Varenes	Canada
Dr Juan L. Peña	CINVESTAV-Merida	Mexico
Dr Carl Steinke	Bend, OR	USA
Dr Satoshi Toyoda	Tokyo	Japan
Dr Robert Wallace	Dallas, TX	USA
Dr Wolfgang S. M. Werner	Vienna	Austria
Dr John Wolstenholme	East Grinstead	UK
Dr Kent Zhuang	Boise, ID	USA
Dr Erwin Zoethout	Nieuwegein	The Netherlands

X-Ray Photoelectron Spectroscopy (ARXPS) is of great benefit for analysis.

A workshop entitled 'Angle-Resolved XPS: The Current Status and Future Prospects for Angle-resolved XPS of Nano and Subnano Films' was held at the Riviera Maya, Mexico, 26–30 March 2007, under the main sponsorship of the International Union for Vacuum Science, Technique and Applications (IUVSTA). This was the first comprehensive workshop on ARXPS and was attended by 33 invited experts who are listed in Table 1 (the group picture is shown in Fig. 1). Experts from the major equipment manufacturers were also invited to participate. The experts who attended the workshop came from 23 countries, all of which were member countries of IUVSTA, throughout Asia, Europe and North America.

The goals of the workshop were to review and discuss the present limits of ARXPS, to discuss ways of acquiring and analyzing ARXPS data, to discuss the applications of ARXPS and to consider future developments in ARXPS. The scientific program of the workshop was arranged by A. Herrera-Gomez, J.T. Grant, P. Cumpson and M. Jenko. Registration, accommodation, meals and

transportation were arranged by the Sociedad Mexicana de Ciencia y Tecnología de Superficies y Materiales. The Local Committee was formed by Martín Yáñez-Limón (CINVESTAV-Querétaro), Wilfrido Calleja (INAOE-Puebla), Juan Luis Peña (CINVESTAV-Merida), with Diana Garcia Sotelo being the Workshop Secretary.

Most of the workshop program was based on 1-h presentations followed by 20-min discussion. There were 21 invited reviews of specific topics and additional presentations by experts from the equipment manufacturers on their approaches for ARXPS. There were evening poster sessions where research areas using ARXPS were discussed at length. The workshop ran from 9:00 a.m. on Monday through 10:00 p.m. on Friday. There were 1-h breaks for lunch and 2-h breaks for dinner. There was an organized tour to Tulum on Wednesday afternoon, but otherwise the participants were kept indoors for almost the entire week.

The workshop program is shown in Table 2. The speakers prepared summaries of their presentations that could include some of the comments made during the presentations and at the discussion periods, and these are given in the following sections.

Summaries of Invited Reviews

Session 1. ARXPS current realm: perspectives from industry and academia

ARXPS use in the semiconductor wafer processing industry – a review so far (presented by C.R. Brundle, in collaboration with G. Conti and Y. Uritsky)

Owing to the match of the XPS probing depth to the film thicknesses currently in use in the wafer processing industry, XPS has become widely used for film characterization (thickness, quasi-quantitative elemental analysis and chemical state analysis). Element depth distributions can be achieved by sputter profiling, as for SIMS and the two techniques are really complementary. Sputter profiling, however, is destructive and, particularly for chemistry, can lead to artifacts; hence, there are potential advantages to the ARXPS approach to profiling for thin-film characterization (particularly ultrathin films, 1–4 nm). For metrology, the 'Holy Grail' is highly precise thickness determination, and quantitative, highly depth resolved, compositional and chemical state information, all in an automated, rapid and non-destructive mode. The question is, whether for characterization or metrology, the 'quantitative, highly depth resolved' part is achievable by ARXPS (the others are), and if so, what are the experimental and theory requirements to do this and what are the limitations.

This presentation reviews practical experience, over a 5-year period, of using the developing approaches to ARXPS analysis in the wafer processing industry. Our conclusions are as follows:

- (1) Thickness can be obtained to the required precision for 10–40 Å homogeneous composition (lateral and in-depth) films. The accuracy, or even relative accuracy (i.e. tool matching), depends on how much effort is put into calibration. For inhomogeneous films (lateral or depth), errors will occur, which will depend on the specifics. Even for homogeneous films, the variation of an effective mean free path length with thickness, and angular range sampled, (in apparently unpredictable ways for ultrathin films, ~1 nm) means that, for wide ranges of thickness, separate calibrations are needed.
- (2) At one extreme, for a first-time analysis of a new film composition, with little or no constraints on what could be the situation, you do not need to go beyond a



Figure 1. Group picture of the workshop attendees. Top, from left to right: Royston Paynter, Thierry Conard, Richard Brundle, Erwin Zoethout, László Kövér, Wolfgang S. M. Werner, Monika Jenko, Sven Maehl, Julia Fulghum, Peter Cumpson, John Grant, Vincent Fernandez, Martyn Green, Kent Zhuang, John S. Hammond, Stephen Muhl, Chris Moffitt, John Wolstenholme, Vincent Crist, Robert Wallace, Charles S. Fadley, and Steffen Oswald. Bottom, from left to right: Diana García, Keisuke Kobayashi, Satoshi Toyoda, Hiroshi Nohira, Giuseppina Conti, Servando Aguirre-Tostado, Chiara Marchiori, Robert Opila, José Alberto Armendáriz Cruz, Carl Steinke and Alberto Herrera-Gomez.

dimensionless qualitative Relative Depth Profile approach to depth distribution (which can, nevertheless, be extremely useful).

- (3) At the other extreme, where a very constrained system is involved (i.e. you either already nearly know the answer, or the depth distribution is so extreme that it is basically qualitatively obvious from the raw data), ARXPS, plus appropriate data modeling, can give depth distributions to some degree, but never, in real situations, a unique highly precise profile. There is always a temptation to over-interpret the modeling, particularly with respect to the depth resolution achievable. Effective communication of this to the customer (process engineer) is the hardest part.

The quality of the data needed to achieve (1) and (3) above, and the intellectual effort required to write (and verify) a 'recipe' for fitting/modeling the data, which then only works within a narrow confine of constraints and, even then, only provides imprecise and not highly depth resolved information, means, in our opinion, that though ARXPS has its uses for depth characterization within the wafer industry, it is not suitable for rapid metrology intended to provide *detailed information on depth distributions*. If, however, one is prepared to assume an unchanging depth distribution from site to site on a wafer, or from wafer to wafer, a simple automated approach can give rapid measurements of dose and thickness at precisions acceptable to industry for metrology (accuracy has to be calibrated). Changes in distribution from measurement point to measurement point, will, of course show up as an apparent dose change. Whether this matters depends on the accuracy and the precision demanded.

ARXPS use in academia (presented by R.M. Wallace)

The use of ARXPS methods^[1] in academia is widespread and growing. Ranging from laboratory instruments offered by several

equipment vendors to dedicated beam line stations at national laboratory synchrotron facilities, the increasing importance of surface analysis on nanoscience and technology has fueled this growth as surfaces dominate the behavior of many materials at the nanometer scale. Sample analysis using *in situ* film deposition and analysis capabilities has also increased considerably in recent years, particularly in regard to large sample sizes compatible with semiconductor wafer processing interests.^[2] This talk surveyed the recent progress in using ARXPS for problems of academic interest. Some of the details of this usage are also described in the short reviews from workshop participants that follow.

Among the areas of interest applying ARXPS methods by university researchers include surface preparation, surface modification/passivation, dielectric and metal thin films, self-assembled monolayers (SAM) and polymers. The application and analysis of ARXPS to well-characterized systems such as SiO_2/Si ^[3,4] and silicon oxynitride (SiON/Si)^[5–7] have enabled the development of more accurate models for electron scattering in solids,^[8,9] and thus the extension to more complicated systems such as high-k dielectric materials.^[10–13]

Surface preparation effects are an important starting point for any surface analysis endeavor, and an important consideration is the consideration of any surface roughness effects in ARXPS studies. The work by Oswald examining the effects of surface roughness through ARXPS demonstrates the ability to use the data acquired to establish useful analysis algorithms that account for 'real world' surfaces and interfaces.^[14–16]

Surface passivation, through the controlled chemical treatment and thin-film deposition on active surfaces, remains of interest to the semiconductor community as electrical performance depends critically on such surfaces (interfaces). ARXPS has been recently applied to various systems that are technology relevant including Si ^[17] and InGaAs ^[18,19] in combination with *in situ* treatments.

Applications to SAM continue to be of interest. Since the early studies of fatty acid Langmuir-Blodgett and SAM films using

Table 2. Program for the 47th IUVESTA Workshop on 'Angle-Resolved XPS: The Current Status and Future Prospects for Angle-resolved XPS of Nano and Subnano Films'

	Sunday	Monday	Tuesday	Wednesday	Thursday	Friday
8:00 8:20	Registration	Basics and examination of the present limits of ARXPS Chair: Alberto Herrera	Analysis of ARXPS data Chair: John Grant	Analysis of ARXPS data Chair: Charles Fadley	Applications of ARXPS Chair: Monika Jenko	Future Development Chair: Laszlo Kover
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8:40 9:00						
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13:40 14:00	Registration	Basics and examination of the present limits of ARXPS Chair: Wolfgang Werner	Analysis of ARXPS data Chair: Peter Cumpson	Tour to Tulum	Equipment Developers Chair: John Grant	Workshop Conclusions Chair: Alberto Herrera
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ARXPS,^[20–22] applications to more complex molecular^[23–25] and polymer^[26–28] systems have been pursued.

Key areas for data acquisition protocol were noted to obtain consistent, high-quality data and the dependence upon the analytical system design. These include sample alignment, energy calibration and angular calibration. It seems clear that ARXPS and the ability to generate non-destructive depth profiles of thin-film constituents will remain attractive for the foreseeable future.

Session 2. ARXPS current realm: basics and examination of the present limits of ARXPS

Angle-resolved XPS-modeling of spectra (presented by W.S.M. Werner)

The need for non-destructive analysis of the first few topmost atomic layers of surfaces used for academic and industrial applications has driven the development of angle-resolved XPS in the past two decades. The information contained in the angular dependence of photoelectron intensities is limited by the photoelectron escape process. Therefore, for reliable interpretation of angle-resolved data, it is mandatory to develop a sound theory for the angular and energy distribution of photoelectrons emitted in ARXPS, which takes into account all relevant details of the photoelectron generation and, in particular, the photoelectron escape process.^[29]

In this connection, the different scattering processes the electron can participate in are of special importance. These comprise *elastic* scattering, which, for the present purpose, is

sufficiently well understood theoretically,^[30] *inelastic* scattering taking place in the interior of the solid (so-called *volume excitations*) and during the crossing of the vacuum-solid interface (so-called *surface excitations*).^[31] Inelastic excitations occur as a result of the response of the quasi-free solid-state electrons to an external perturbation that polarizes the medium and the photoelectron is decelerated in this polarization field. If the field of the moving photoelectron itself sets up the polarization, the interaction is called *extrinsic* – as it takes place along the particle's trajectory. The sudden appearance of a core hole during the photoionization process also represents a strong perturbation leading to a polarization of the solid-state electrons and a concomitant energy loss, which is referred to as *intrinsic* because it is associated with the photoionization itself. The different types of inelastic scattering also exhibit *interference* effects due to the superposition of the electromagnetic fields associated with subsequent interactions.^[32]

Presently, the investigation of reflection electron energy loss spectroscopy (REELS) so as to obtain empirical data on the response of the solid to an external perturbation is an active field of research. A method to eliminate multiple scattering from such spectra has been developed,^[31,33] and from the resulting single-scattering loss distributions the dielectric function of the solid can be extracted.^[34,35] The analysis of REELS thus not only constitutes a source for the shape of the energy loss distribution in a single surface and volume interaction in an arbitrary material, but also the (total) inelastic mean free path and the surface excitation probability as well as the dielectric function. This is

the fundamental quantity for theoretical calculations involving electron–electron correlation effects, as the electron–electron interaction is effectively reduced by screening due to the medium, and this reduction is described by the dielectric function.

The results of a REELS analysis can then be used for quantitative analysis of the energy and angular distribution of photoelectrons emitted from a sample with a given depth profile.^[29] Apart from effects due to inelastic scattering, various phenomena connected with elastic scattering need to be modeled accurately^[36] to quantitatively predict angle-resolved peak intensities and line shapes. These phenomena include the surface morphology, surface roughness,^[37] the solid angle of acceptance of the analyzer^[8] and so on.

The NIST database Simulation of Electron Spectra for Surface Analysis (SESSA) has recently been published,^[38] which quantitatively accounts for the majority of effects related to elastic and inelastic scattering mentioned above.

Angular distribution of photoelectrons excited by X-rays from solids (presented by L. Kövér)

ARXPS is increasingly applied nowadays in many fields of high practical importance, especially in the semiconductor industry. Therefore, there is an increasing need for higher accuracy and reliability of the extracted data [e.g. concentration depth profile (CDP)], with this stimulating more precise measurements and better interpretation of the experimental spectra on the basis of the deeper understanding of the underlying physical phenomena.

The fundamental phenomena affecting the angular distribution of photoelectrons excited from amorphous or polycrystalline solids (with a special attention to the emerging measurements involving photoelectrons excited by high energy – up to 10 keV-X-rays) include the nondipole contributions to photoionization, intrinsic excitations, effects of elastic electron scattering and surface excitations.

In summary, nondipole contributions to the differential cross section for photoionization tend to be significant at high (5–10 keV) photon energies.^[39–41] In the case of linearly polarized photons, octupole contributions can be non-negligible.^[42] The share of intrinsic excitations for free atoms is varying little as a function of the atomic number.^[43] However, less is known concerning the chemical and solid-state effects and the share of intrinsic plasmons (including the energy dependence).^[44–47] Accounting for effects of elastic electron scattering is important, and there are practical methods available for reducing the inaccuracies resulting from neglecting elastic scattering.^[48,49] The angular and energy dependence of surface excitations can also be important when using photoelectron lines of greatly differing kinetic energies.^[50–53]

ARXPS uncertainties and limits (presented by Peter J. Cumpson)

Introduction and some history. Angle-resolved XPS is a powerful and largely non-destructive method for depth profiling the chemical composition of thin layers, typically down to around 5–10 nm from the surface. It has a long history dating back to the early 1970s,^[54] but has come into wider use in recent years due to the emergence of some particular analytical applications for which few – if any – alternative techniques are available.

In many types of industrial or scientific samples, a layer-by-layer deposition is performed, so that one can expect the structure to be composed of discrete, homogeneous layers. In other cases, this

layer-by-layer model is not rigorously correct, but is nevertheless a valid approximation allowing differences to be identified between specimens.

Quantification of ‘easy’ samples. Quantification is straightforward if one is dealing with a single oxide layer on a parent element. The Hill equation^[55] is usually the simplest and most precise approach to quantifying the thickness of the layer and is the most widely used of all the methods for quantifying angle-resolved XPS spectra.

If there is a significant difference in energy between substrate and overlayer peaks, then the ‘Thickogram’ method is a simple and easy way to measure that thickness.^[56]

Quantification of ‘fairly easy’ samples – layer-by-layer analysis. Gries published^[57] a stepwise layer-by-layer fitting model more than 15 years ago. In 1993, Seah *et al.* published what they called the Stratification method, by which the average depth and amount of material in each layer can be calculated.^[58] It was recognized that it is not possible to plot a depth scale on these plots.

There was a good deal of discussion at the workshop about the relative merits of Stratification. Workshop members generally liked the reliability of Stratification, and its ability to show the relative amounts of the materials in the different layers, but preferred the emphasis in the ‘centre-of-gravity’ (blob plots) of layers rather than focussing on layer interfaces as does Stratification.

A good compromise may be to use the Stratification method, but to plot the results as ‘blobs’, in which:

- the depth scale shows the mean depth of the species;
- the area of each blob shows the relative amount.

Quantification of difficult samples. ‘Difficult’ samples, in this context, means samples for which little prior knowledge exists about their concentration-depth profiles. In this case, the uncertainties involved are significant and manifest themselves both as uncertainty in composition and uncertainty in depth – i.e. limited depth resolution.

Experimental origin of uncertainties. Experimental uncertainties are essentially the same as in other XPS work, except that in ARXPS analysis of difficult samples we are now much more sensitive to them than is typically the case. Particularly notable are background subtraction issues, especially when that background itself varies as a function of emission angle. In general, for older instruments ARXPS is performed by tilting the specimen, whereas in newer instruments parallel acquisition at a number of emission angles may be available. Tilting ensures that (with the exception of elastic scattering effects) terms such as emission anisotropy are constant. By comparison, acquisition at multiple angles is more rapid, and one does not need to tilt – but relies on models of emission anisotropy being accurate to a few percent for these difficult samples.

Analyzer transmission is also an issue for XPS peaks widely separated in kinetic energy; hence, a good calibration-method for multiple-channel electron multipliers, channel plate or resistive-anode detectors is essential.

Implications of these uncertainties for the calculated depth profile. Many areas of applied physics deal with issues similar to ARXPS depth profiling, namely the recovery of the maximum possible information in the presence of noise and an imperfect

measurement process. It is possible to apply some of the theory of data transmission through noisy transmission lines to this problem – albeit modified to reflect the exponential sampling depth of XPS.^[59] Furthermore, if one can make some assumptions about the linearity of the measurement process that are reasonable for most instruments, one can calculate the fractional depth resolution, $\Delta z/z$, that should be achievable for XPS peak areas that have been measured to an uncertainty of no worse than a few percent:

$$\frac{\Delta z}{z} = 2 \sinh \left\{ \frac{\pi^2}{2 \cosh^{-1} \left[\pi(n-1) \left(\frac{I}{\sigma_I} \right)^2 \right]} \right\},$$

where I is the intensity of a typical XPS peak in the data, σ_I is the uncertainty in that peak intensity and n is the number of emission angles used.

In absolute terms, the depth resolution Δz is excellent compared with many other surface-sensitive techniques. In relative terms, the ratio $\Delta z/z$ is often disappointing, being limited to no less than approximately 0.8 in practical analyses.

Overcoming ill-conditioning in angle-resolved XPS: methods that successfully address ARXPS ill-conditioning (presented by Peter J. Cumpson)

Introduction. Usually, when fitting any set of data to a model equation, we minimize some measure of ‘badness of fit’. A common choice is the chi-squared, χ^2 , the sum of the squared residuals weighted by their standard deviations. Provided the choice of ‘badness of fit’ measure, such as chi-squared, is appropriate to the measurement statistical distribution (which is important, but difficult to get significantly wrong in most cases) then minimizing the ‘badness of fit’ gives a good fit to the data and the most probable values of the fit parameters. In the context of ARXPS, what this means is that we fit a model (typically consisting of the absolute or percentage composition of a number of layers in the specimen) to a set of measured XPS peak intensities for a number of different emission angles. We could use chi-squared as a measure of ‘badness of fit’, and this is probably appropriate to the measurement statistics (though if one looked closely one might be able to improve on it).

One approach – Minimise: ‘Badness of fit’ $\equiv \chi^2$. The really critical issue in ARXPS depth profiling is as follows: chi-squared (or something like it) does not work well as a sole measure of ‘badness of fit’ if we try to fit to a large number of layers in the model (typically more than about two or three). This is because one can reduce chi-squared further by choosing a wildly oscillating depth profile, in which alternate layers have high and low concentrations. This will reduce the residuals (and hence chi-squared) even though we know that such a depth profile is improbable or even impossible. It reduces the chi-squared by fitting to some of the experimental scatter, not just the real trend in XPS intensities with emission angle. One can hardly therefore call this a ‘better’ fit! We need to redefine our measure of ‘badness of fit’.

Maximum entropy and regularization^[60,61] address this problem by adding an extra term to chi-squared to obtain a new measure of ‘badness of fit’. Instead, we now have to minimize chi-squared plus some measure of the ‘unsmoothness’ of the depth profile.

In this approach – Minimise: ‘Badness of fit’ $\equiv \chi^2 + \alpha U$. Here U is some measure of the ‘unlikelihood’ of the depth profile, which in most cases we can take to be ‘unsmoothness’ (because in the absence of any evidence to the contrary one might expect many samples to show smooth depth profiles). Maximum Entropy, and the various types of Regularization, differ in how they choose to measure this ‘unsmoothness’, U . There is now also an issue of how one weights the relative importance of the two contributions to the ‘badness of fit’, which is determined by one’s choice of the parameter α . Choose a very small value for this parameter and one goes back to normal chi-squared fitting – and therefore a wildly oscillating depth profile that is incorrect. Choose too large a value and one obtains a very smooth depth profile that is also incorrect.

Session 3. Data processing

What photoemission can tell us about high- κ dielectrics through angle-resolved detection analyzed using the maximum entropy algorithm (presented by R.L. Opila, in collaboration with A. Mathew)

Angle-resolved photoelectron spectroscopy is an ideal probe of candidate high- κ films because the thickness of these very smooth films is comparable with the effective attenuation length (EAL) of the photoelectrons. We have analyzed SiON films of the range of thickness of 1–4 nm.^[62,63] From the N 1s spectrum, we were able to identify four binding states for N bonded to three atoms in these films: three silicon, two silicon and one oxygen atom, and one silicon and two oxygen atoms. We also identified a binding state corresponding to N bound to two silicon atoms and one dangling bond. We also converted the angle-resolved data to a compositional depth profile, effectively using the maximum entropy algorithm as applied to this problem by Livesey and Smith.^[64]

Recently we have been studying nitrided $(\text{HfO}_2)_x(\text{SiO}_2)_{1-x}$ films. The breadth observed in the N 1s peak can be attributed to N binding to varying amounts of Si and Hf. There is a tendency for N to preferentially bind to Hf in these films. We used a maximum entropy algorithm to analyze these films. Nitridation at successively higher temperatures results in more incorporation of N, and more of this N is incorporated near the oxide/Si interface. Using the maximum entropy algorithm, we were able to convert the angle-resolved data of other nitrided films to compositional depth profiles that had preferential oxidation at the outer surface and at the oxide/silicon interface, and otherwise relatively smooth Si^{+4} and Hf^{+4} compositions through the film. These results were confirmed by medium-energy ion scattering.

The maximum entropy algorithm varies the composition as a function of depth and calculates the expected photoemission intensities, given the estimated intensities and the electron EALs. The best fit to the angle-resolved data was determined by minimizing χ^2 . Because the problem is ill-posed (spectra are typically acquired at five takeoff angles and used to generate profiles taken in 0.1 nm slabs), the entropy is calculated with respect to an initial assumed profile, with a continuous film of concentration and thickness suggested by the photoelectron intensities of one of the angle-resolved films. This entropy maximization helps minimize artificial correlations (due to noise) and chooses a reconstruction that agrees with the data but has the minimum amount of extraneous information. The robustness of the solution is limited by the smoothness of the film, the knowledge of the electron EALs and sensitivity factors, and the estimate of the initial profile. The solution found using maximum entropy depends intrinsically upon the choice of the variable that

relates the dependence of the solution upon the chi-squared and entropy terms in the maximum entropy functional. This variable is chosen somewhat arbitrarily and more work will have to be done to optimize this.

Self consistent data analysis in ARXPS: getting quantitative in-depth profile analysis in ultrathin films (presented by A. Herrera-Gomez)

The performance of nanofilms is highly influenced not only by their composition but also by the distribution of the elements throughout the film thickness. Monitoring such composition profiles requires a metrology technique that allows for its assessment as a function of the processing parameters. ARXPS is ideal for films thin enough to allow for the collection of signal from the substrate, that is, for films with thicknesses up to about 7 nm. However, the precise way to exploit this technique, as well as the actual amount of information that it can provide, has not yet reached such wide concordance. In this presentation, an analysis method (MLM) applicable to conformal multilayer films with abrupt interfaces was described.^[65,66] This type of samples is important because many of the nanofilms of industrial interest lie in this class. The method enjoys a number of advantages over those currently used.^[67]

- It *attacks* the ill-conditioned nature of the ARXPS Problem (see Cumpson's contribution) by parameterizing the depth profile of each species as a layer (*square profile*). Because the number of parameters required to define a layer is three (depth, thickness and density), it complies with a restriction pointed out by Cumpson about the maximum number of structural parameters that can be obtained from ARXPS data.^[59]
- The analysis is done individually for each species. The identification of a compound in the film is done a posteriori, and only when the coincidence between the depths of certain species has been established from the analysis. The composition is then calculated from the relative concentrations, without the need of forcing it to stoichiometric values. This allows for the assessment of changes of composition caused by sample processing.
- The analysis is self consistent because the algorithm allows for the use of the proper electron transport parameter (EAL) as the electrons travel through the different layers. This is of special importance because the EAL depends strongly upon the material through which the generated photoelectrons travel. In contrast, in other methods the film is considered a continuum in which the composition varies smoothly with depth, obstructing the incorporation into the analysis of the dependence of the attenuation length on depth.
- The dependence of the peak signal on the takeoff angle not only originates from the change on the trajectory length of the electrons inside the solid, but also from the geometry of the XPS tool (see Aguirre's contribution). In most XPS equipment, the change in takeoff angle is achieved by tilting the sample (the XPS tools that allows for the simultaneous acquisition of the data at different emission angles also have problems of their own. These have to do with variations on the resolution and detection efficiency with angle). The X-ray spot on the sample surface changes size and shape as the sample rotates. The focal spot of the analyzer undergoes similar changes. In most ARXPS studies, this issue is handled by dealing instead with the ratio of the area of a peak for each species to the area of a peak from the substrate. This is done with the hope that most of the geometrical issues will cancel out. In the method

presented here, the ARXPS data are treated directly. Besides avoiding introducing unnecessary uncertainties, the results are less sensitive to the inaccuracies of the modeling.

- The method allows for a meaningful assessment of the uncertainties on the structural parameters (thickness and composition of the layers). Calculating uncertainties by inversion methods is difficult because the solutions are very unstable, leading to artificially large numbers.

A reliable quantitative assessment of the structure of the conformal film can be obtained only if these matters are addressed properly. A related issue concern XPS data fitting, which should be done simultaneously for all the angles.^[68]

Interpretation of ARXPS data – chemical resolution (presented by Royston Paynter)

The extraction of information on chemical bonding from ARXPS data was discussed with examples drawn from the speaker's work on plasma-treated polystyrene. The construction of a depth profile for a given atom in a specific chemical bonding environment amounts to the inversion of its Laplace transform based on the behavior of the intensity of the corresponding component peak as a function of the photoemission angle. Because that inversion is highly sensitive to uncertainty in the data, it is important to stabilize the fitting of the photoelectron-peak envelopes as much as possible by using the minimum number of components necessary. Two strategies were proposed for then assigning these component peaks to chemical states where ambiguities are present: comparison with other elemental peak shapes^[69] and comparing the elemental depth profiles extracted from the elemental peak data with those extracted from the component peak data.^[70]

The two basic strategies for coping with the restricted information content of ARXPS data were also discussed: the degradation of the sophistication of the extracted profile by regularization and the limitation of its complexity by the choice of a simple profile shape. It was shown that the latter approach can be useful in the verification of hypotheses, e.g. that diffusion processes control the loading of atoms into polystyrene during plasma treatment.^[71]

An important limitation of ARXPS was also discussed: the depth resolution of the extracted profile at buried interfaces. With reference to a Laplace transform based on a mathematical model of diffusion in polymers,^[72] it was shown that although the surface concentration of the diffusing species and the penetration depth in the reconstructed profile are relatively well confined by the data, the interface width at the limit of penetration is not. This is a fundamental problem that will severely restrict the usefulness of ARXPS in the study of diffusion across buried interfaces.

Extraction of depth information from ARXPS data – precision and accuracy (presented by John Wolstenholme, in collaboration with Paul Mack, Bruce McIntosh and Richard G. White)

The prime purpose of making ARXPS measurements is to determine the way in which composition varies with depth in the near-surface region of a solid material. The accuracy and precision that can be achieved in the generated information will depend upon the amount of detail that is required and the amount of additional information that can justifiably be included in the calculation.

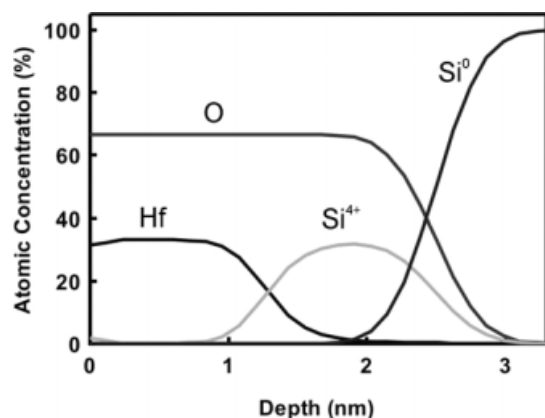


Figure 2. Non-destructive depth profile from an HfO_2 layer on SiO_2 on Si. The profile was constructed from ARXPS data using a method involving maximum entropy.

At one extreme, it is possible to determine the ordering of a stack of ultrathin layers with great confidence. Such determinations can be achieved without recourse to mathematical models and without knowledge of the physical properties of the materials. This leads to great confidence in the result but those results contain no information on layer thickness, the quantity of each component present or the distribution of components of the material within the layer.

The next stage in complexity is the determination of layer thickness. This can be achieved with very high precision (significantly better than 1%) if sufficient care is taken with the measurements. The accuracy of the method is determined by the accuracy of constants used in the calculations (e.g. the attenuation length).

The generation of CDPs is far more complex. Such determinations are required to establish, e.g. the dose of nitrogen in a gate dielectric material. Accuracy and precision here will depend upon the exact manner in which the profile is generated. It is possible to improve accuracy and precision in the profiles by the inclusion of additional information, such as stoichiometry, in the calculation. Figure 2 shows an example of a non-destructive depth profile constructed from ARXPS data using a technique based on maximum entropy but fitting the ARXPS data to stoichiometric fit units rather than the individual peak areas.

For the examples given, all of the ARXPS data were collected in parallel on a Thermo Scientific Theta Probe instrument. By using this method, the data are collected over a 60° angular range without the need to tilt the sample. This ensures that the analysis position and area are identical for each angle.

ARXPS comparison of methods for extracting information on CDPs: could the combination of different approaches lead to improvements? (presented by L. Kövér in collaboration with I. Csérny)

The increased demand concerning the extraction of more accurate and reliable CDPs from measurements and analysis of electron spectra photoexcited from thin or ultrathin film overlayers stimulates the comparison of different methods, such as those based on the analysis of the spectral shapes^[73,74] as well as those based on the analysis of the angular dependence of the line intensities (ARXPS)^[29,75,76] or on kinetic-energy effects. It is important to know whether a combination of line-shape analysis and ARXPS methods (especially when extending these methods to

the subsurface regions applying hard X-rays in the 5–10 keV range for excitation) could yield to an improvement in the performance of the non-destructive depth profiling using electron spectroscopy.

When comparing different methods for extracting CDPs, the same sample, physical quantities with model-independent definitions and values characterizing the photoionization and electron transport, and optimum experimental conditions are assumed. Regarding possibilities for combining different methods for deriving CDPs from XPS data, in the case of, e.g. a single doped overlayer and substrate system, the possible strategies include the following: (i) Determination of the overlayer thickness with one of the methods and using this thickness as an input parameter for determining a CDP with another method. (ii) Selection of the type of function describing the depth distribution of the dopant, on the basis of the comparison of the depth profiles provided by the particular methods. Selecting the type of depth profile function, a proper parameterization is determined. (iii) Introduction of further limitations for the variation of parameters characterizing the CDP – on the basis of the comparison of the results obtained with different methods – until consistency is reached. The use of reference samples for obtaining the respective source functions and the physical quantities for electron transport, derived from electron backscattering experiments and spectrum simulations, can be very helpful in selecting the type and parameters of the CDP function to be determined.

In summary, in the case of high-energy XPS or X-ray Auger Electron Spectroscopy, spectral shape analysis methods show only little effect attributable to surface excitations and elastic scattering of electrons. The comparison of different ARXPS algorithms for extracting CDPs of chemical constituents in the case of ultrathin, N-doped SiO_2 films^[77] indicates that the use of robust methods that allows introduction of prior knowledge is preferable. The combination of different methods for determining CDPs can be helpful; however, proper care should be taken concerning the consistency and the limitations of the respective physical models behind these methods. New types of experiments can lead to further improvements in the accuracy of determining CDPs.

Instrument characterization for quantitative ARXPS analysis (presented by F.S. Aguirre-Tostado, in collaboration with A. Herrera-Gomez and R.M. Wallace)

ARXPS can be used to estimate atomic concentrations at different depths. However, the accuracy of the determined depth profile depends on several key factors. The ARXPS data reduction methods assume simplistic geometries where the angular dependence of the analysis area is already known. This assumption is valid only when a careful specimen alignment has been performed. In this work, a methodology for specimen alignment to minimize the geometrical corrections was presented. The method is based on the characterization of the projected areas of the X-ray beam and analyzer spot onto the sample using a 'knife-edge' Au sample and numerical-analysis routines for the extraction of the related geometrical parameters (i.e. beam size, axis of rotation, etc.).

The sample used was a 100-nm thick Au film deposited on a Si substrate and cleaved to form a sharp straight edge (knife-edge). The Au 4f XPS data were recorded as the sample edge was swept through the focal spot. These knife-edge experiments were carried out in the dispersive (Fig. 3a) and non-dispersive (Fig. 3b) directions. Additional data were taken on the Au film by varying the sample angle (Fig. 3d) and by varying the height at a fixed takeoff angle (45° , Fig. 3c). The data were then simultaneously

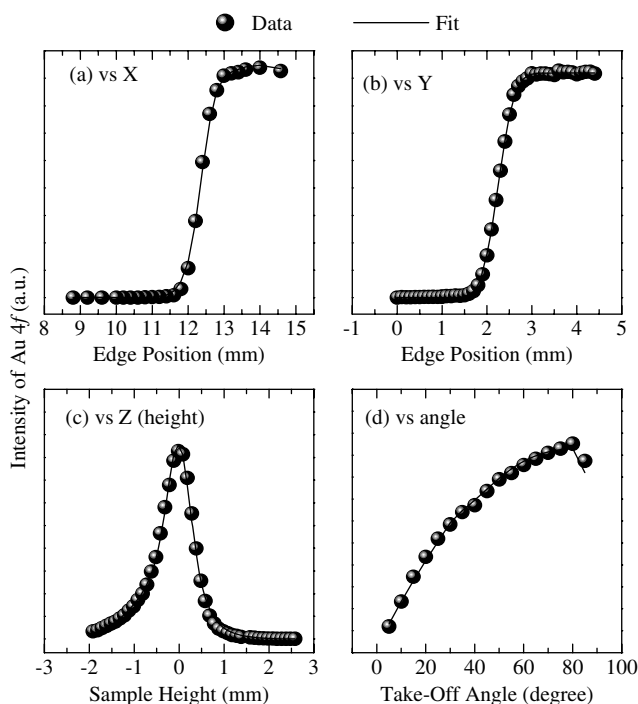


Figure 3. Au 4f peak area as function of the sample edge position in the (a) dispersive and (b) non-dispersive directions. Additional data were also obtained (c) at different heights and (d) at different takeoff angles. The solid lines are theoretical predictions of the peak intensity.

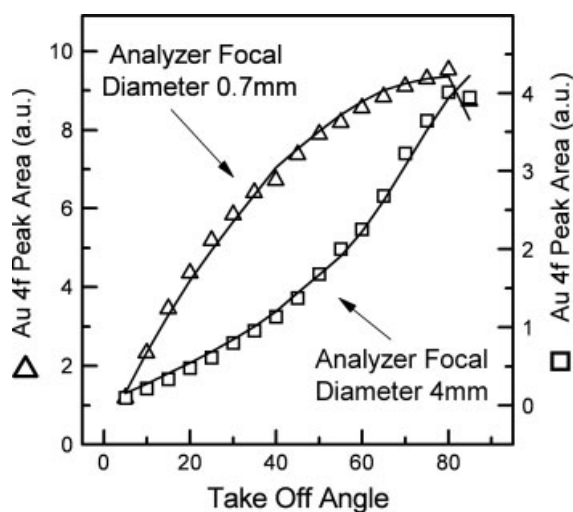


Figure 4. Experimental data and fit of the angular dependence for the Au 4f peak intensity for two different analyzer focal settings: (I) represents the case where the analyzer spot size is smaller than the X-ray illumination area, and (II) illustrates the opposite case.

analyzed using a computer algorithm to convolute the step edge with a Gaussian shape of the X-ray beam and analyzer focal spot. The experimental data acquired were then compared with the computer-generated data through least-squares fitting to extract the geometrical beam parameters.

Figure 4 shows the Au-4f intensity as a function of takeoff angle with different analyzer settings. The difference in concavity clearly shows the importance of the analyzer spot size. The solid lines are

the theoretical prediction: the sole parameter changed from one case to the other was the size of the focal spot of the analyzer.

In summary, an *ad hoc* analysis algorithm (e.g. XPSGeometry^[66,78]) for XPS geometry corrections has to be used prior to ARXPS data reduction to extract reliable elemental and chemical depth profiles regardless of the ARXPS data analysis method.

A Round-Robin on nitrogen profiling in high-k layers by ARXPS (presented by T. Conard)

Although not new, angle-resolved XPS has seen a significant increase in interest in the last years. This increase was both instrumental and application-driven. Indeed, recent instrumental developments have led to an easier use of ARXPS, and, in parallel, the semiconductor industry needed a technique able to composition-profile thin layers up to 4–5 nm thick, which falls nicely within the possibilities of ARXPS. However, as with any 'new' technique, it is important to assess the validity of the results by comparing with other techniques and also by evaluating the influence of the analyst on the results obtained.

We evaluated the long-term repeatability (18 months) of our XPS system and found relative standard deviations (RSDs) between 0.5 and 1% for the evaluated parameters (thickness of SiON film, composition of HfSiO film and nitrogen dose in a SiON film). We then produced a series of five samples with two to three individual layers. Each layer did contain some of the elements such as Hf, O, Si and N. The most complex sample was a ~ 1.6 nm SiON/2.5 nm HfO₂/0.5 nm SiON stack. These samples were distributed to 14 groups that performed analysis with the following techniques: transmission electron microscopy (TEM), ARXPS, elastic recoil detection (ERD), X-ray reflectometry (XRR), high-resolution Rutherford backscattering spectroscopy (HR-RBS) and medium-energy ion scattering (MEIS). For ARXPS, both parallel-angle detection and tilted-sample configurations were used. The stack sequences were unknown to the round-robin participants before the analysis. The choice of this system was made due to the difficulties to quantify nitrogen in Hf-containing samples, due to the presence of a loss peak of the Hf 4d photoemission peak in the N1s region. This problem was clearly evidenced on the 'as received' samples that showed large discrepancies in the nitrogen profiles obtained by the different ARXPS groups. We also observed that none of the groups performing ARXPS in the tilted-sample configuration did provide full profiles, likely due to the lack of publicly available software for this purpose.

However, once identical data treatment is performed on all measured data, good agreement is observed between the different groups. As an example, the Figs 5 and 6 present the nitrogen and silicon profiles from the ~ 1.6 nm SiON/2.5 nm HfO₂/0.5 nm SiON stack sample measured by XPS and ERD. Good agreement is then observed between the different XPS groups. The agreement with the ERD profile for the interfacial nitrogen profile is good. However, although XPS does show that nitrogen is not only present at the interface, ERD allows a better profiling of the surface nitrogen. This is likely due to the small contribution of the surface nitrogen in the N 1s XPS spectrum and to the difficulties in deconvoluting it from the Hf 4d loss peak. For larger signals, such as the Si signal, a much better agreement is observed between the XPS and ERD profiles. It has been shown that the apparently larger Si concentration in the center layer by ERD originated from an artifact of the ERD measurements. At the bottom interface, ERD cannot

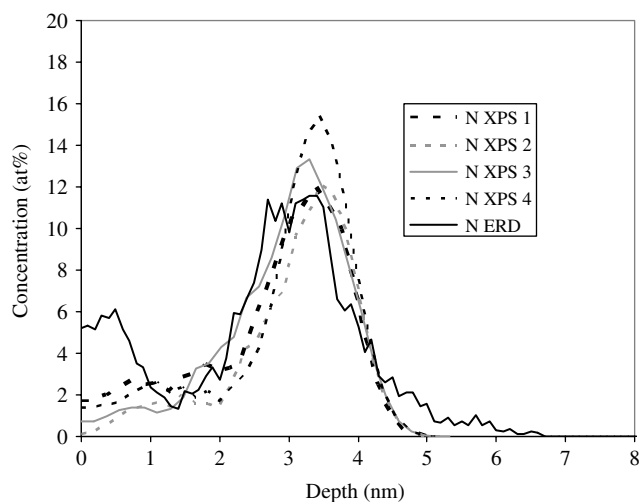


Figure 5. Nitrogen profile from the ~ 1.6 nm SiON/2.5 nm HfO₂/0.5 nm SiON stack measured by XPS and ERD (N10).

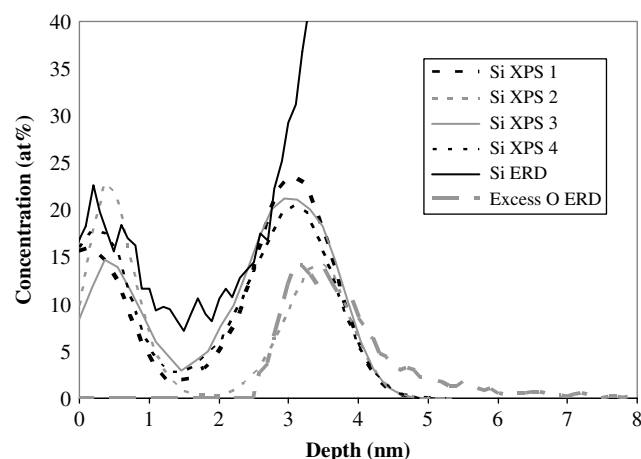


Figure 6. Silicon profile from the ~ 1.6 nm SiON/2.5 nm HfO₂/0.5 nm SiON stack measured by XPS and ERD.

distinguish between oxidized and non-oxidized Si, whereas XPS allows also chemical profiling. The reacted Si profile from ERD can be approached by calculating the excess oxygen present at the interface and gives a reasonable agreement with the XPS profiles.

In conclusion, this work showed that the qualitative concentration profile reconstruction from ARXPS works well, and that good reproducibility is obtained in the profile reconstruction, even with significant variations of the measurement conditions. Profiles can even be quantitatively reliable, even for complex samples, but care has to be taken in the data interpretation. A simple 'push-button' high-quality profile for unknown sample is not (yet) available.

Session 4. Applications of ARXPS

Non-destructive depth profile of ultrathin gate-oxide films by ARXPS (presented by G. Conti in collaboration with Y. Uritsky, and R. Brundle)

SiON has been the gate dielectric alternative to SiO₂ due to its superior interfacial composition and properties. The physical thickness of SiON for gate materials currently in development is in the range of 10–20 Å, which approaches the dielectric constant equivalent oxide thickness (EOT) of ~ 6 Å silicon dioxide.

SiON films are grown by a variety of processes such as chemical vapor deposition (CVD), atomic layer deposition (ALD), thermal oxy-nitridation and plasma-based processes (e.g. decoupled plasma nitridation or DPN). Depending upon the growth process and the process parameters, nitrogen can pile up at or near the Si/SiO₂ interface, be uniformly distributed throughout the film or be enriched at the interface of the poly-Si gate electrode. Precise control of the nitrogen content and its distribution within the gate are keys to improvements in the EOT and in reducing adverse effects such as decreased channel mobility and high leakage current.

ARXPS is a proven, effective method for providing film thickness, elemental and chemical composition. However, the characterization of varying elemental distributions with depth requires the use of reference standards to generate a reliable model.

A set of 'golden standard samples' deposited by CVD, which provide a box-like structure, was characterized by ARXPS with supportive analysis by time of flight secondary ion mass spectroscopy (TOF-SIMS), MEIS and HR-RBS. The purpose of this characterization is to develop a robust depth profile recipe based on ARXPS data and the maximum entropy algorithm, which could be transferred to SiON films deposited by processes which do not yield a well-known layer structure.

The ARXPS data were obtained using the Thermo Electron Corporation Theta 300. This instrument is capable of collecting XPS data over a wide range of emission angles (20–80°) simultaneously, without requiring tilting the wafer.

The 'golden standard' samples are: (i) CVD Si₃N₄ film deposited on Si and (ii) CVD Si₃N₄ film deposited on 10 Å SiO₂ on Si. These two films were analyzed immediately after deposition by ARXPS. In order to avoid aging effects, the same set of samples was capped with a 50 Å poly-Si layer and analyzed by MEIS, EELS-TEM and TOF-SIMS. The MEIS and EELS-TEM analyses agreed with the ARXPS results, thus confirming our ability to measure depth profiles non-destructively for films having well-defined 'box-like' layer structures. The TOF-SIMS results, however, had broad, flat profiles even for actual box-like profiles, and did not capture any distinct SiO₂ layer beneath the SiN layer. This is probably due to the ultimate limits on the resolution of TOF-SIMS for this type of study.

The recipe optimized for the SiON film golden standard was used for characterizing the depth profile of a set of SiON films deposited by thermal oxy-nitridation. These samples were analyzed by ARXPS and HR-RBS. The non-destructive depth profile for the 'golden standard samples' was reconstructed using the Maximum Entropy algorithm (ARProcess 421) provided by Thermo VG (Private communication from Thermo VG by Kevin Robinson, 2005). The depth profiles obtained by ARXPS with Maximum Entropy analysis and by HR-RBS were in a good agreement, showing that N is mostly at the Si interface. The film layer structure shows a 'broad box-like profile' with the N distribution piled up at the Si substrate.

Problems arose in transferring the recipe used for the profile of the 'golden standard samples' to plasma-based processes, which do not yield a simple layer structure. The resulting profiles for the DPN samples by ARXPS with Maximum Entropy did not agree with the MEIS, HR-RBS and TEM results. The parameters of the Maximum Entropy analysis were changed till a depth profile similar to those obtained by MEIS, HR-RBS and TEM was obtained. This new protocol was then used for determining the depth profiles of DPN samples with different process conditions. The optimum values of alpha factor range from 2.4×10^{-5} to 7×10^{-7} ; the weighting

factor was chosen based on VG algorithm where elements with lower concentration and deeper to the film have higher weighting factor. The typical weighting factors are: $w = 1$ for Si, and O and $w \geq 3$ for N. All the data were acquired collecting 16 takeoff angles; however, the spectrum corresponding to the top surface angle ($\theta = 78^\circ$) was often removed from the analysis because its high noise influenced the quality of the profile without introducing extra information. The carbon profile was used for assessing the effect of the removal of the data at that angle. Carbon is due only to adventitious surface contamination; the removal of the spectrum collected at $\theta = 78^\circ$ was often enough to confine the C profile at the film top surface. A correlation between the ARXPS depth profiles and electrical data such as leakage current, and EOT shows that the protocol provides depth profiles capable of explaining differences in electrical performance among the samples. The protocol was

We then conclude that ARXPS in conjunction with the Maximum Entropy algorithm can provide meaningful non-destructive depth profiles of thin gate-oxide films. Once an appropriate protocol has been developed, the non-destructive depth profile by ARXPS can be useful to the process engineer for tuning process conditions and discriminating among different processes.

We showed that there is not a unique Maximum Entropy analysis protocol for all types of SiON films. SiON films deposited by different processes require the development of new analysis protocols. Parameters such as spectral noise, different ranges of takeoff angles, weight factors for each element and the alpha factor play an important role.

Quantification of pinhole density in ultrathin diamond-like-carbon films (presented by A. Herrera-Gomez, in collaboration with F.S. Aguirre-Tostado and R.M. Wallace)

The percentage of uncovered area in ultrathin diamond-like-carbon films on Si (001) wafers, which assesses the pinhole density of the carbon films, was quantified through ARXPS. The uncovered areas of the silicon substrate are oxidized upon contact with air, so the photoelectron signal from Si^{+4} could be used for this quantification. The quantification of the amount of oxide required a meaningful comparison between the photoemission signal from bulk silicon and from the oxidized silicon. For that purpose, the thickness of the carbon film responsible for attenuating the signal from bulk silicon was also quantified. The method used to analyze the ARXPS data accounts for the difference in the electron transport parameters for the various layers on the film.^[67] The three samples studied (FCA-C, DLC-E and DLC-M) were ultrathin carbon films grown under different conditions on Si(001) substrates. The FCA-C sample was prepared with the filtered cathodic arc deposition technique; whereas the DLC-E and DLC-M samples were prepared with ion-beam deposition using ethylene gas and methane gas, respectively. The slopes in the angular dependences of the peak areas attributed to silicon oxide indicated that they were at the top surface and not below the carbon film.^[78] The percentage of the surface not covered by the carbon film (2.1% for FCA-C, 1.3% for DLC-E and 5.2% for DLC-M) exhibited a strong dependence on the growth conditions, even for similar film thicknesses. These results could be qualitatively compared with the percentage of samples with pinhole count > 10 after a HCl vapor test performed on magnetic heads with similar carbon overcoats, which was 55%, 75% and 100%, respectively. The detection limit of the technique is restricted by the photoelectron signal-to-noise level and by the determination of the background signal. In the present study, the limit is better than 0.5% of the sample surface.

Application of multivariate analysis methods to angle-resolved XPS data (presented by J. Fulghum)

Multivariate data analysis (MVA) methods have obvious applications to the analysis of XPS spectral or imaging datasets, but have not previously been applied to ARXPS data.^[79–81] If a large number of samples are to be analyzed, MVA methods provide a rapid method for qualitative determination of thickness and composition differences in ARXPS sample sets, including variation in concentration with depth or overlayer thickness.

The most frequently used MVA method is principal components analysis (PCA), which can transform possible correlated variables in original data sets, such as raw spectra or data tables, into a smaller number of uncorrelated variables. PCA was applied to elemental percentage ARXPS data acquired from a set of nitrided SiO_2 layers (on Si) of 4–6 nm thickness. The results group samples by a combination of thickness and compositional variation, but do not adequately distinguish between samples of similar nitrogen distribution at slightly different depths. Similarly, PCA applied to oligonucleotides attached to diazonium-modified gold slides provides results that convolute molecular orientation and depth information. We therefore explored the use of PARAFAC, a parallel factor analysis method, appropriate for the analysis of trilinear data. In the case of ARXPS data, the dimensions are binding energy, takeoff angle and sample. Unlike bilinear methods such as PCA, trilinear methods provide a unique solution that is also easier to interpret. It is important to note, however, that multiway methods provide a model that is more robust, whereas PCA models will always provide a better fit to the data.

Figure 7 shows the results from PARAFAC analysis of nitrided SiO_2 layers on Si. The PARAFAC classifies samples based on oxide thickness and nitrogen composition. By visual analysis of the three biplots in the Fig. 7, it is possible to conclude that samples 1 through 10 have thinner nitrided layers, as the contribution of $\text{Si}(0)$ is larger in this sample group. Samples 11 through 13 have thicker nitrided Si layers. The distribution of samples along the PC1 axis shows increasing N concentration from samples 1 and 5 to sample 12.

These results indicate that PARAFAC is fast and easy to apply to ARXPS data. It is a useful classification tool for distinguishing between samples based on composition and depth distributions. When standards are available and incorporated within the sample set, semiquantitative information on thicknesses can be potentially obtained.

Session 5. Future developments

Simulation of surface roughness for ARXPS (presented by S. Oswald)

Interpretation of ARXPS data with smooth-layer models is often far from reality because at least surface and interface roughness always influence the measurement. To study such influences systematically, we introduced a computer algorithm for the simulation of ARXPS measurements of inhomogeneous surface structures,^[14,82] which can model (almost) any near-surface materials distribution. The simulated intensities are assumed to be measured ones and are analyzed afterward with a common smooth-layer approach.^[83] In this way, it is possible to study how various small-sized surface structures would be reproduced by a classical ARXPS investigation.

A number of different surface structures have been considered up to now. Starting with rough surfaces and homogeneous overlayers, we critically examined the 'magic angle concept' to

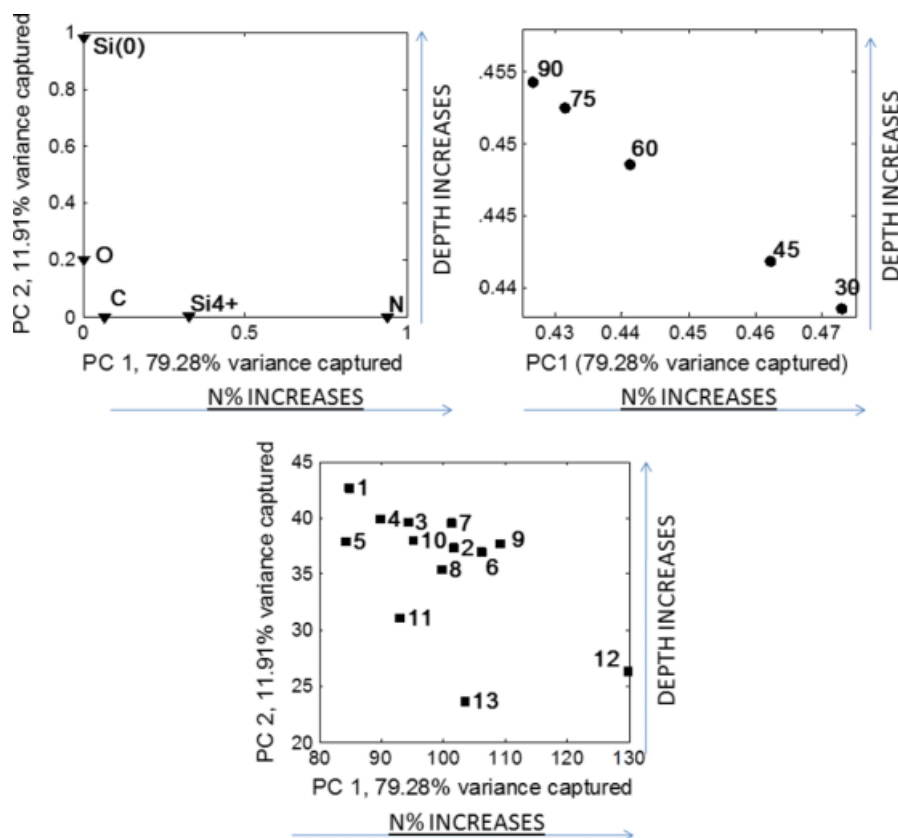


Figure 7. PARAFAC results of table combining elemental and Si 2p chemical percentages for five angles from 13 samples.

be valid only for specific roughness and showed how small-sized islands can be modeled by homogeneous smooth layers.^[14] More complex surface roughness was approximated by different inhomogeneities (islands, hollows, pores) on smooth surface overlayers.^[84,16] The dimensions of the inhomogeneities were in the range of the electron attenuation length for all the different structures. A main conclusion is that edge and shadowing effects lead to a kind of homogenization, i.e. inhomogeneous structures of different types can all be well represented by homogeneous smooth layers. In parallel, the calculated effective amount of surface overlayer material is systematically underestimated. This is shown in the Fig. 8 for islands (1-nm thick, Al oxide) of different lateral distances lp and surface coverage F on an Al sample coated with a 0.5-nm thick Al oxide overlayer. The calculated island fractions F_c (Fig. 8a) point to homogenization (increase of F_c for higher and decrease for lower nominal F); the deviation of the calculated effective island thickness from the real one (Fig. 8b) is small only for the largest islands. Often problems with the stability of the solutions occurred, but then the more homogeneous models led to the best results, too. It can be summarized that the generally limited information content of ARXPS data is further decreased drastically by this virtual homogenization.^[59]

Some new directions in angle-resolved XPS: standing wave (SW) and hard X-ray photoemission, and ambient pressure XPS (presented by C.S. Fadley)

Angle-resolved XPS has by now become a standard and well-developed tool for determining near-surface chemical states and concentration distributions, with various other presentations in this workshop exploring its applications and its limitations. I here

explore several new developments in this technique that make use of synchrotron radiation (SR).^[85,86]

In all prior ARXPS studies, the exciting radiation decays as a simple exponential away from the surface, and this decay is usually neglected, except in cases for which a total reflection geometry is used to enhance surface sensitivity and reduce inelastic backgrounds.^[87,88] The analysis of such total reflection or grazing incidence XPS (TRXPS or GIXPS) data can provide depth profile information, although using it in a more powerful way in connection with a variable electron takeoff angle requires either an analyzer that accepts a very large solid angle or a rotatable analyzer.

In a few recent studies, it has also been demonstrated that strong soft X-ray SWs in the typical XPS energy range can be created by Bragg reflection from a multilayer mirror of period d_{ML} equal to a few nanometer that is then used as the substrate for sample growth.^[89–91] If a sample is then grown on this multilayer with one of its layers in a suitable wedge form, it is possible to scan the SW, which will have a period d_{ML} , through the sample simply by moving it in the X-ray beam, as illustrated in the Fig. 9. This standing wave/wedge (swedge) technique has been used so far to study buried layers and interfaces in nanolayer structures of relevance to spintronics,^[85,90,91] but it should have broader applications to a variety of sample types in the future.^[91]

An additional important new direction in ARXPS is the use of much higher excitation energies in the 5–10 keV regime so as to probe deeper layers and interfaces,^[86] which is mentioned also in the presentations of K. Kobayashi, H. Nohira and L. Kövér in this workshop. Several simplifications result in the

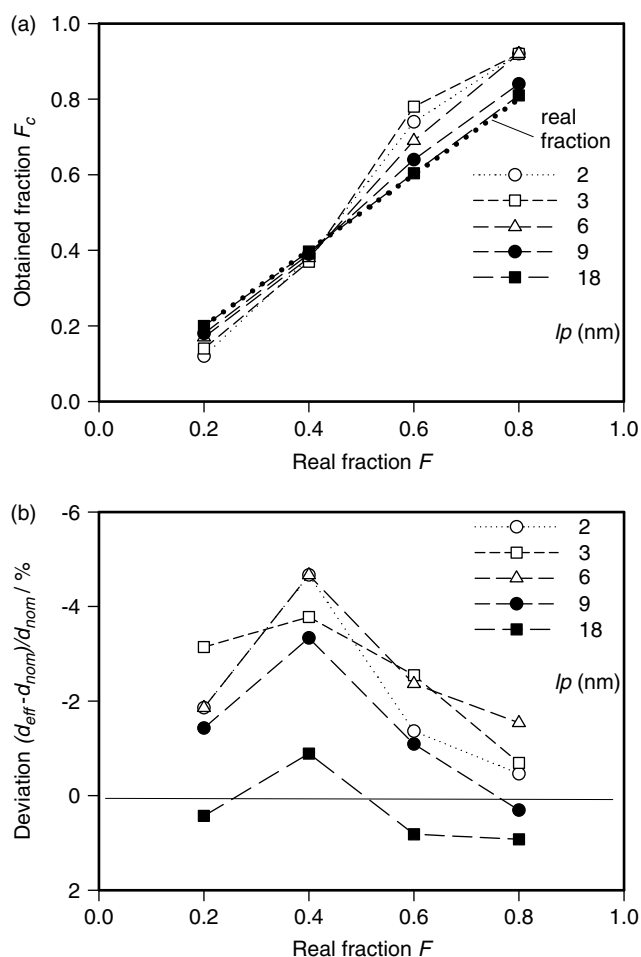


Figure 8. Calculated (a) island fraction and (b) fractional deviation as a function of coverage for 1 nm Al oxide islands in an Al sample with a 0.5 nm Al oxide overlayer for different lateral distances l_p .

interpretation of such ARXPS data: electron refraction at the surface barrier (inner potential) and elastic scattering at large angles are much reduced, permitting lower takeoff angles to be explored quantitatively; and surface inelastic scattering becomes negligible. Such measurements can thus span the range from approximately 10 nm mean emission depth to 1 nm mean depth, and various applications to buried layers and interfaces in structures of technological relevance have been reported.^[86] This type of measurement should find broad applications to surface and interface analysis in the future, and it should in certain cases be possible to combine it with the swedge technique above as an even more powerful probe of deeper layers and interfaces.^[92]

Finally, a limitation of most prior XPS studies has been the requirement of at least high vacuum, if not ultrahigh vacuum. But recently, by isolating the sample from the SR beamline with a thin window, and inserting a differentially pumped lens between the sample and the spectrometer, it has proven possible to carry out state- and time-resolved studies of surface chemical reactions at ambient pressures of up to 5 torr,^[93,94] with one recent example being the oxidation of Si at pressures up to 1 torr and temperatures up to 500 °C.^[95,96] Such high-pressure studies, both with SR and laboratory X-ray sources, and with variable takeoff angle so as to provide the additional information from ARXPS, thus open

the way to studying surface reactions under much more realistic conditions.

Development of high-resolution hard X-ray photoemission spectroscopy and its applications to nanoscale depth monitoring at SPring-8 (presented by K. Kobayashi)

Hard X-ray photoemission spectroscopy (HX-PES) with high-energy resolution using high brilliance-undulator X-rays at SPring-8 has been developed and used for the studies of various fields, including pure and applied physics, and industrial research and development.^[97–99] As schematically shown in the Fig. 10a, the X-rays obtained from a 4.5 m planar undulator are monochromatized using a beamline monochromator and a Si-channel cut post-monochromator, and focused through a Be window onto the sample surface in an analyzer chamber. The 333, 444 and 555 reflections are used to produce high-intensity radiation at about 6, 8 and 10 keV. The reduced bandwidth of these X-rays, which is estimated to be 54 meV at 6 keV, allows us high-resolution measurements. To increase the throughput as much as possible, we make the X-rays impinge into the sample surface in a glancing angle configuration to match the X-ray penetration depth to the photoelectron EAL as much as possible. A high-energy analyzer is configured so as to accept the photoelectrons emitted in the electric field direction of the X-rays, as the anisotropic factors are the largest in this direction as shown in the Fig. 10b. The X-ray beam size is reduced to less than 40 μm in both the vertical and horizontal directions by mirrors to permit accepting the highest possible acceptance solid angle for the photoelectrons at the entrance slit of the high-energy analyzer. The entrance slit is also oriented so as to be parallel to the elongated footprint of the X-rays on the sample surface as shown in the Fig. 10c. All these facilitate high throughput performance as follows. Accumulation times of typically 5 s and 30 s are required to record Au 4f and Au valence band spectra with a 230 meV resolution, respectively. The total energy resolution achieved is 55 meV at 8 keV, as estimated from Au Fermi edge measurements at low temperatures. Buried layers under 20–30 nm thick overlayers are verified to be detectable. During the past 4 years, we have developed applications of HX-PES to various fields in both basic and applied science and industrial technologies.^[98,100]

In order to show the extent of HX-PES applications, we presented several examples of investigations of chemical and electronic structure variations with depth below the surface in nanoscale surface regions and buried layers. Among them were Si-ULSI-related problems such as depth profiling of high-k gate stacks and characterization of shallow junctions in drain and source regions,^[101] which are some currently active targets of the HX-PES applications. A typical example of the application of HX-PES to depth profiling of La oxide base gate stacks was also presented by H. Nohira in this workshop (below).

We also presented other developments currently being undertaken in the Japan Synchrotron Radiation Research Institute (JASRI) and National Institute for Materials Science (NIMS) groups, including the extension of the X-ray energy down to 3 keV, and 3D chemical mapping using a focused X-ray beam and a large-acceptance objective lens, and the development of a laboratory HX-PES system using a compact Cr K α source and a newly developed large-acceptance objective lens.

Developments in HX-PES instrumentation and measurements were conducted in collaboration with various research groups, including those at SPring-8/JASRI, SPring-8/RIKEN (Rikagaku

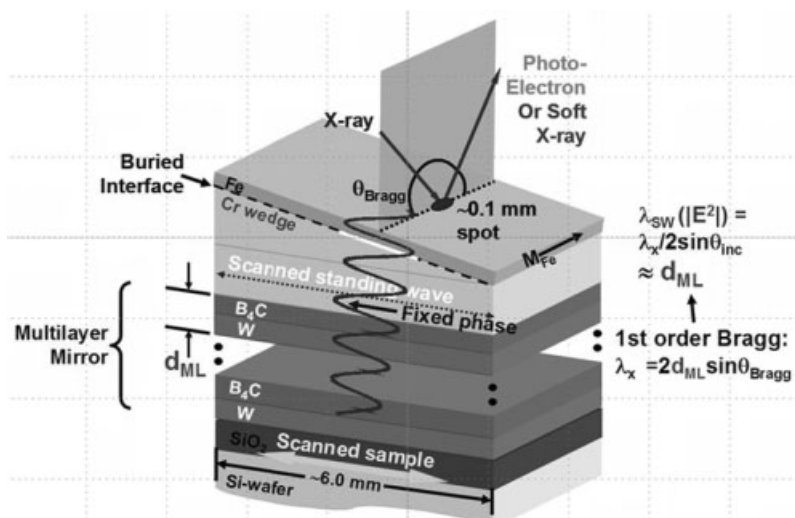


Figure 9. Illustration of the basic principles of the standing wave/wedge method for carrying out depth profiling of buried layers and interfaces.^[85,89–91] Bragg reflection of the incident SR X-ray beam creates a standing wave with the same period as the period d_{ML} of the multilayer. Scanning the sample along the slope of the wedge in effect scans the standing wave through the sample layers, leading to sinusoidal variations in intensity that can be analyzed to derive buried layer composition and magnetization profile.

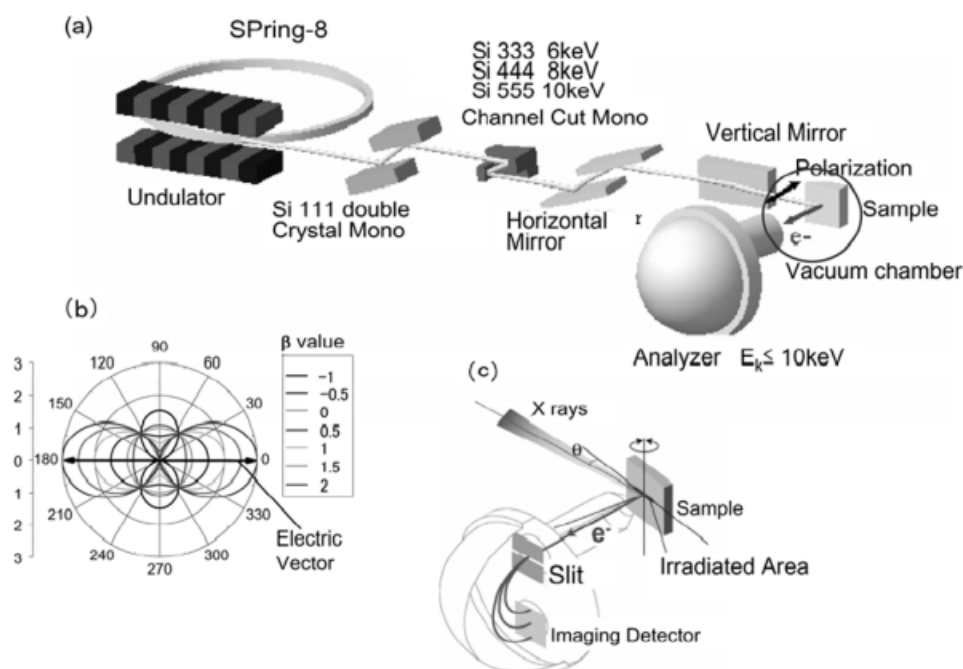


Figure 10. Schematic diagram of the experimental configuration of HX-PES at BL47XU in Spring-8. (a) Angular dependence of the anisotropy factor. (b) X-ray beam-sample-analyzer configuration.

Kenkyusho Institute of Physical and Chemical Research, Japan), SPring-8/Japan Atomic Energy Agency (JAEA), SPring-8/NIMS and Hiroshima University Synchrotron Radiation Research Center (HiSOR). The developments of the three-dimensional chemical mapping and the Cr $K\alpha$ laboratory XPS system were undertaken by collaboration between NIMS, JASRI, Nara Institute Science and Technology (NAIST) and ULVAC PHI. VG SCIENTA also takes part in this collaboration. We owe a great deal to the earnest efforts of Drs E. Ikenaga, J. J. Kim, S. Ueda and M. Kobata of the SPring-8/JASRI HX-PES crew, Drs H. Yoshikawa and S. Ueda of SPring-8/NIMS, and Drs Y. Takeda and Y. Saitoh of SPring-8/JAEA. This work was partly supported by the Ministry of Education, Science,

Sports and Culture (MEXT) through a Grant-in-Aid for Scientific Research (A) (No. 15206006, Principal Investigator: T. Hattori), by the Nanotechnology Support Project of MEXT, and by SENTAN, JST, and also the Hyogo Prefecture Collaboration of Regional Entities for the Advancement of Technological Excellence.

Hard X-ray angle-resolved photoelectron spectroscopy study on gate insulators/Si interface (presented by H. Nohira, in collaboration with T. Hattori)

In order to achieve high performance and low power consumption in nanoscale MOSFETs, replacements of poly-Si gate with metal, SiO_2 dielectric with high- k dielectrics and Si channel with high

mobility channel and the atomic-scale control of the high- k dielectric/Si and metal/high- k dielectric interface structures are required.^[102] Angle-resolved XPS is a powerful and largely non-destructive method for depth profiling the chemical composition and the chemical structures of thin layers, typically down to around 5–10 nm from the surface. We reviewed the topics on the non-destructive characterization of three kinds of dielectric/Si interfaces using ARXPS.

The first topic is on the non-destructive depth profiling of two kinds of ultrathin oxynitride films using ARXPS.^[103–106] It was found by applying maximum entropy concept to Al- $K\alpha$ excited angle-resolved photoelectron spectra that the depth profiles of composition and chemical structure of the oxynitride film formed by plasma nitridation of wet-oxide films, followed by annealing in N_2 ambient at 950 °C, are quite different from those of the oxynitride film formed by annealing of wet-oxide films in NO ambient at 950 °C. Our results clearly imply that the distribution of nitrogen atoms and their bonding configurations in the oxynitride films formed by plasma nitridation are quite different from those in the oxynitride films formed by interface nitridation, and that the broadening observed in the depth profile determined by TOF-SIMS must be caused by the cascade collisions of ions with constituent atoms in the film.

The second topic is the depth profiling of 4-nm-HfO₂/1.0-nm-SiO₂/Si stacked structure.^[107] The hard X-ray ($h\nu = 6$ keV) excited AR photoelectron spectra arising from HfO₂/SiO₂/Si stacked structure without post-deposition annealing can be explained by the concentration of constituent atoms determined by high-resolution Rutherford backscattering (HR-RBS). However, after this structure was annealed in a N_2 atmosphere at 1000 °C for 5 s, the AR photoelectron spectra cannot be explained without considering Si-Hf bonds near the HfO₂/Si interface.

The third topic is the non-destructive depth profiling of 1.5-nm-silicon nitride/Si interfaces formed using nitrogen–hydrogen radicals produced in a microwave-excited high-density Xe/NH₃ mixture plasma.^[108] The analyses of soft X-ray ($h\nu = 1.05–1.48$ keV) excited AR-photoemission from Si 2p, N 1s and O 1s core levels yielded the same depth profile result as in the 0.5-nm-SiO₂/N/1-nm-Si₃N₄/subnitride/Si layered structure. Here, N denotes one atomic layer of nitrogen, which connects the SiO₂ and Si₃N₄ layers. Furthermore, the kinetic energies, which govern the electron EALs, were adjusted to be equal to each other by choosing appropriate photon energies for each core level so that analysis of AR photoelectron spectra is greatly simplified.

Conclusions

The scientific program ended with a session dedicated to the conclusions of the workshop. These were prepared and presented by Wolfgang Werner (basic theory), Peter Cumpson (data analysis), Robert Wallace (applications) and Charles Fadley (future development). During the Closure, Peter Cumpson presented the Workshop Resolutions.

Conclusions about the basics aspects of ARXPS

This workshop provided an excellent overview of the many efforts that have led to the at least partial fulfillment of a three-decade quest to make ARXPS 'an extremely valuable tool for near-surface chemical analysis'. At present, the basic physical phenomena associated with ARXPS are well understood, and the

limitations they pose on the resulting depth profiles are also clearly recognized. Modeling ARXPS data should incorporate phenomena associated with multiple inelastic and elastic scattering and photoelectric cross sections. Besides elastic scattering, the inelastic scattering due to surface, volume and intrinsic effects should be considered.

The analysis of the ARXPS experimental data requires construction of a limiting physical model. This is because the task of assessing the composition depth profile from the ARXPS data is an ill-conditioned problem. To maximize the number of parameters in such a model that could be obtained from the ARXPS data, the data should be of high quality, i.e. high signal-to-noise ratio and high resolution (low pass energy). The model should also be of high quality in the sense of incorporating valuable information obtained from other independent techniques. Other issues that should be included are the roughness, local inhomogeneities, photoelectron diffraction and so on. It is also desirable to take data with methods that could improve the matching between the model and the experimental data. For example, it is possible to combine information from the inelastic background with the analysis of ARXPS data.

Regarding inversion (obtaining the composition depth profile from the ARXPS data), several ARXPS data analysis algorithms have been brought to maturity in the past. Among them are regularization (Maximum Entropy), stratification and layer models. The regularization methods incorporate extra parameters whose evaluation is operator-dependent. Because it is still not possible in such analyses to allow for the calculation of error bars, this method is still not quantitative. Model-dependent analysis making use of, e.g., a maximum entropy criterion should be used with care and with a range of parameters to assess their influence on the final results. In general, it is difficult to predict the peak intensities with an error lower than 10 or 20%. A combined effort in the future should lead to good enough precision to increase the usefulness of the technique in industry and academia.

Among the most important issues regarding the quality of the data is the alignment, the electron analyzer technology and the X-ray spot size (especially for imaging). The technology developments initiated by various manufacturers have made possible the routine use of ARXPS in regular laboratories. Non-linearities in detection are often overlooked in analysis. With the increasing use of multichannel detection systems that can vastly increase data acquisition rates, it should be possible to eliminate the non-linearity.

Conclusions about data analysis

- ARXPS does not have atomic resolution – or better – if you can be confident in applying a simple model, e.g. a single homogeneous overlayer on a homogeneous substrate.
- If one does not have such (extremely) strong *a priori* information about the specimen, it does not have atomic depth resolution.
- There is much more structural information present in principle using synchrotron sources and modeling in which some phase information is present, e.g. via SWs – but this is difficult and/or very slow using laboratory-based XPS instruments.
- The critical issues remaining and where solutions are required to advance the use and reliability of ARXPS studies are:
 - Further understanding of the physics of photoemission – surface excitations, intrinsic excitations, emission anisotropy and others.

- Improvement of the instrument operating procedures (e.g. setting the sample height to lie exactly in the rotation axis), which may differ among the various types of XPS tools.
- Further development of reliable and validated fitting and depth profile software.
- Development of effective methods to incorporate into the modeling the assumptions that could be made about the specimen.

Conclusions about applications of ARXPS

Many issues regarding quantitative data analysis were discussed in the workshop. Regarding the data acquisition protocols, the importance of sometimes overlooked issues, such as simple alignment and the efficiency and linearity of the detector, was stressed. There is currently an abundance of modeling methods including Maximum Entropy, Layered Attenuation, Stratification and so on. It was emphasized that the chemical depth profiles should be physically meaningful for the ARXPS technique to be applied to practical problems.

The use of ARXPS as a metrology tool in industry remains active. However, it is used more for quality control (the criterion employed has more to do with repeatability) and less with the detailed assessment of the depth profile of the films. This is because basic issues such as peak fitting and modeling still remain as a developing field. An important application in the electronic industry is the characterization of Hf-based dielectrics and stacks with metal gates. However, there is very 'limited support' in this area for fundamental work. Other fields where the application of ARXPS is growing are polymers and coatings (effects of plasmas, synthesis routes, etc.), biological systems (thin-film sensors, SAM, DNA, etc.), and microscopy (use of multivariate analysis methods, including organic and inorganic samples).

Conclusions about future development

Some obvious future directions for development involve excitation with SR or with specially adapted laboratory systems, including:

- The use of SWs created via multilayer mirror reflection so as to provide additional phase information via rocking curves, photon energy scans or wedge scans concerning depth profiles. Provided that suitable samples can be grown or mechanically deposited on such multilayer mirrors, the standing wave approach should reduce the degree of ill-conditioning of the ARXPS measurement, providing more accurate and less model-dependent depth profiles. Although uniquely a SR type of measurement to date, laboratory systems created with the idea of making use of total X-ray reflection could have a sufficiently well-collimated beam to be used for such measurements, and this should be explored.
- The use of hard X-rays in the 5–10 keV range in both standard types of ARXPS measurements and SW-excited experiments. Hard X-ray ARXPS (HARXPS) experiments are attractive because they can probe more deeply and they can be analyzed more quantitatively over a wider range of angles due to simplifications involving elastic scattering, surface inelastic scattering and surface escape over the inner potential. Hard X-ray SW measurements add significantly to the information content available and are assisted by the fact that reflectivities and thus SW modulations are higher. Laboratory-based systems operating at about 5 keV may also become available in the near future.

Workshop resolutions

- Angle-resolved XPS is a valuable technique for in-depth analysis of surfaces in a wide range of technological applications, from semiconductors to magnetic nanostructures to biomaterials to polymer surfaces.
- The power of ARXPS makes it necessary to consider carefully what constitutes a chemically distinct layer, given that it can approach atomic depth resolution in favorable cases.
- Further research is urgently required on the reliability of depth profiling algorithms.
- The ARXPS community should agree on a standard form for the equations describing common algorithms such as Maximum Entropy, to promote clear understanding of how different implementations of those algorithms compare.
- Further research is required on the appropriate or best regularization parameter values used in Maximum Entropy or Regularization methods in ARXPS.
- Research is urgently required on combining information from ARXPS and inelastic background analysis to give more robust and easy-to-use methods of depth profiling the top 5–10 nm of specimen surfaces.
- SR measurements are promising in several ways (e.g. SWs and hard X-ray excitation), and the community should begin to exploit these more fully.
- The synchrotron photoemission community should consider standardizing acronyms for their important techniques to aid unambiguous recognition of their value by the wider surface analytical community.

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