

Monday Morning, October 29, 2012

Applied Surface Science
Room: 20 - Session AS-MoM

Quantitative Surface Chemical Analysis, Technique Development, and Data Interpretation - Part 1

Moderator: J.A. Ohlhausen, Sandia National Laboratories, S. Suzer, Bilkent University, Turkey

8:20am AS-MoM1 2012 AVS Albert Nerken Award Lecture: Characterization of Thin-Film Nano-Structures by XPS, S. Tougaard*, University of Southern Denmark **INVITED**

This is a brief summary of the work that was involved in the development of the technique for quantitative XPS from analysis of the background of inelastically scattered electrons. About 30 years ago it became evident that these electrons must carry valuable information about the depth where the XPS electrons are excited. Theoretical modeling started and algorithms were developed. It was necessary to have an accurate description of the electron energy loss processes which at that time was not available. Theoretical calculations of inelastic cross sections based on a dielectric response description were done and a new experimental method to determine this from analysis of reflected electron energy loss spectra (REELS) was also developed.

To make these procedures for quantitative XPS analysis work in practice it is however not possible to use calculations valid only for specific sample compositions. Therefore an effort was made early on to find cross sections which can be used as an approximation for wide classes of materials and compositions. This resulted in the Universal cross sections which are now widely used and without which practical use of the formalism would have been very limited. The resulting XPS analysis technique was summarized in [1].

In the following years, much effort was then centered on applications to increasingly finer details of the morphology of nanostructures. This requires a careful data analysis since otherwise the uncertainty on the determined morphology may be large. Sometimes the detailed morphology is however not the most important issue for technological applications. Things like speed of analysis, robustness, and automation is often more important in industrial environments. It was therefore decided to develop a simpler algorithm which does not give as detailed information but which is very robust and therefore faster to use and less dependent on a meticulous analysis procedure. The resulting algorithm [2] has been shown to be very robust and therefore suitable for automation. It proved also effective in generating 3D images of nano-structures where automation is mandatory since thousands of spectra (one per pixel) must be analyzed.

Throughout, efforts were always exerted to test the validity of each step in the development of algorithms and procedures by designing and performing critical experiments. This is of utmost importance to ensure progress which does not lead to dead ends.

In this talk I will give an overview of the development of the technique and discuss some technological applications.

1. S. Tougaard, J. Vac. Sci. Technol. A14, 1415 (1996)
2. S. Tougaard, J. Vac. Sci. Technol. A23, 741 (2005)

9:00am AS-MoM3 Simulation of Electron Spectra for Surface Analysis (SESSA): (Hard) X-ray Photoelectron Spectra of Nanostructured Surfaces, W.S.M. Werner, W. Smekal, Vienna University of Technology, Austria, C.J. Powell, National Institute of Standards and Technology

The National Institute of Standards and Technology (NIST) Database for the Simulation of Electron Spectra for Surface Analysis (SESSA) [1,2] has been modified to allow a user to simulate XPS spectra of nanostructured surfaces, such as surfaces covered with rectangular islands, pyramids, spheres, layered spheres, etc. The effect of the nanomorphology of the surface on the emitted angular and energy distribution of photoelectrons is investigated. Comparison with simple models in the literature, which neglect several aspects of the physics of signal generation, such as elastic electron scattering, the dependence of the inelastic mean free path of the position of the electron in the specimen, the anisotropy of the photoelectric cross section, etc. gives good agreement when the same model assumptions are made in the simulations, but show significant deviations for more physically realistic simulations. The extent to which information on the

nanomorphology can be extracted from the photoelectron angular/energy distribution is investigated, in particular the question is addressed whether the average size of nanostructures on a surface is accessible by means of analysis of angular/energy photoelectron spectra. This is done for standard AlK α and Mg K α laboratory sources, but the possibility to gain additional information by increasing the photon energy to the hard x-ray regime is also examined.

1. <http://www.nist.gov/srd/nist100.cfm>.
2. W. Smekal, W. S. M. Werner, and C. J. Powell, Surf. Interface Anal. 37, 1059 (2005).

9:20am AS-MoM4 XPS Characterisation of InP Features Etched in Cl₂-Ar and Cl₂-H₂ Inductively Coupled Plasmas, C. Cardinaud, CNRS, France, R. Chanson, CNRS-IMN, France, S. Bouchoule, CNRS-LPN, France, A. Rhallabi, M.-C. Fernandez, Université de Nantes, France

High-aspect-ratio etching of InP-based heterostructures is a critical building block for photonic device fabrication. This study is focused on the chemical characterisation of the bottom and sidewall surfaces of InP ridge patterns etched with Cl₂-Ar and Cl₂-H₂ plasmas using a SiN_x mask. Each sample contains five arrays combining various ridge widths (1.5 to 4 μ m) and space widths (5 to 16 μ m) plus four InP and mask open areas. Experiments are carried out in a Kratos-Axis-Ultra. The direction of analysis is vertical, i.e. normal to the sample surface, while the x-rays strike the surface with an angle of incidence $\alpha = 60^\circ$. The sample can be rotated in azimuth to align precisely the arrays, either parallel to or perpendicular to the plane defined by the x-source and the analyser. The first arrangement enables the analysis of the bottom (as well as the top of the ridge), whereas the second arrangement allows the analysis of the sidewall after tilting the sample. In this latter case two configurations are used. Taking advantage of the absorption of the x-rays by the InP ridges (1.8 μ m of InP absorbs 99% of AlK α under 60° of angle of incidence), the first configuration consists in tilting the sample opposite to the x-ray source until the bottom is totally screened. Simultaneously this brings the sidewall that is irradiated in the analyser line of sight. Tilting the sample towards the x-ray source to an angle $\theta = \text{atan}(\text{space width} / \text{ridge height})$ allows to shadow the bottom and observe photoelectrons coming from the sidewall (and the top of the ridges), in this case θ needs to be larger than α to obtain full irradiation of the sidewall that comes in the analyser line of sight.

For each array, the intensity of the In, P, N and Si core levels, normalised with respect to that measured on the mask and InP open spaces, are compared to the corresponding ratio calculated from the geometry of the array and the analysis arrangement or configuration. Modelling takes into account the contribution of the various surfaces (mask, InP) in the line of sight of the analyser, and the rate of irradiation according to the geometry of the array and the nature of the materials (InP ridge, mask) the x-rays pass through. This comparison points out the relation between the intensity emitted from the bottom and the aspect ratio of the array. A good agreement is obtained when including the analyser acceptance angle to the model. Concerning the sidewall the discrepancy between experiment and simulation corroborates the presence of a passivation layer. The presentation will discuss in detail the influence of the plasma chemistry on the quantitative composition of the sidewall and the bottom.

9:40am AS-MoM5 Simplified Extrinsic Background for XPS Data Fitting, A. Herrera-Gomez, UAM-Azcapotzalco and CINVESTAV-Queretaro, Mexico

In this presentation it is described a simplified form of the background for extrinsic scattering in the near-peak regime for X-Ray Photoelectron Spectroscopy (XPS) data peak-fitting. It directly accounts for the change on the slope of the background between the two sides of the core-level peak. With an approach similar to the employed for the Shirley background, it is proposed that the change on the background slope at energy E is proportional to the integrated signal above E . This functional form can be reproduced by assuming that the inelastic cross section is proportional to the energy loss. As for the Shirley background, and in contrast to the currently employed extrinsic background models, the background here introduced only employs one parameter. It has some extra advantages for XPS data peak fitting, such that its functional form is the same regardless of the core level, it account for the finiteness of the peak width in the generation of the background signal, it can be employed simultaneously with the intrinsic Shirley background, and last, but not least, it provides for good fits. Some implementations of the method are discussed.

* Albert Nerken Award Winner

10:00am **AS-MoM6 Effective Attenuation Lengths for Photoelectrons in Thin Films of Silicon Oxynitride and Hafnium Oxynitride on Silicon**, *C.J. Powell*, National Institute of Standards and Technology, *W.S.M. Werner*, *W. Smekal*, *G. Tasneem*, Vienna University of Technology, Austria We have used the National Institute of Standards and Technology (NIST) Database for the Simulation of Electron Spectra for Surface Analysis (SESSA) [1,2] to simulate photoelectron intensities for thin films of $\text{SiO}_{1.6}\text{N}_{0.4}$ and $\text{HfO}_{1.9}\text{N}_{0.1}$ on silicon with excitation by Al $K\alpha$ X-rays. We considered Si $2p_{3/2}$ photoelectrons from $\text{SiO}_{1.6}\text{N}_{0.4}$ and the substrate and Hf $4f_{7/2}$ photoelectrons from $\text{HfO}_{1.9}\text{N}_{0.1}$. The simulations were performed for ranges of film thicknesses and photoelectron emission angles and for two common configurations for X-ray photoelectron spectroscopy (XPS), the sample-tilting configuration and the Theta Probe configuration. We determined photoelectron effective attenuation lengths (EALs) by two methods, one by analyzing photoelectron intensities as a function of film thickness for each emission angle (Method 1) and the other by analyzing photoelectron intensities as a function of emission angle for each film thickness (Method 2). Our analyses were made with simple expressions that had been derived with the assumption that elastic-scattering effects were negligible. We found that EALs from both methods were systematically larger for the Theta Probe configuration, by amounts varying between 1 % and 5 %, than those for the sample-tilting configuration. These differences were attributed to anisotropy effects in the photoionization cross section that are expected to occur in the former configuration. Generally similar EALs were found by each method for each film material although larger EALs were found from Method 2 for film thicknesses less than 1.5 nm. SESSA is a useful tool for showing how elastic scattering of photoelectrons modifies EALs for particular materials, film thicknesses, and XPS configurations.

[1] <http://www.nist.gov/srd/nist100.cfm> .

[2] W. Smekal, W. S. M. Werner, and C. J. Powell, *Surf. Interface Anal.* 37, 1059 (2005).

10:40am **AS-MoM8 Valence Band XPS: A Valuable, but Underexploited, Tool for the Identification of Subtle Differences in Surface Chemistry**, *P.M.A. Sherwood*, Oklahoma State University **INVITED**

Valence band X-ray photoelectron spectroscopy (XPS)¹ gives spectral features (peak positions and peak intensities) that arise from different physical principles than the core spectral region. This difference leads to the valence band region providing complimentary information to that of the core region. In many cases the valence band region can be used to detect subtle chemical differences that cannot be determined in core XPS studies. The value of using valence band XPS interpreted by calculation models will be demonstrated for various systems, and the use of core and valence band XPS for the study of buried interfaces will be discussed. Examples discussed will include the formation and study of thin (less than 100Å) oxide-free phosphate films, polymer films, composite surfaces, and the identification of different oxide films (including aluminum oxides) with similar chemical composition. Studies of shallow buried interfaces will be discussed. Recent work involving the preparation of hydroxyapatite films formed on metals which were coated with a thin oxide free film of metal etidronate will be reported. The metals studied were stainless steel and titanium. The key to adhesion of the hydroxyapatite films is the initial formation of a thin, oxide free, etidronate film on the metal. It was not found possible to prepare the hydroxyapatite films directly on the metal surfaces. Since hydroxyapatite is a key component of bone and teeth, it is likely that the coated metals will have desirable biocompatible properties, and that these treated metals may find applications in the production of medical implants.

¹P.M.A. Sherwood, "XPS Valence Bands", chapter in "Surface Analysis by Auger and X-ray Photoelectron

Spectroscopy" edited by D Briggs and J T Grant, SurfaceSpectra Ltd and IM Publications, Chapter 19, 531-555,

2003.

11:20am **AS-MoM10 Multitechnique Electron Spectroscopic Characterisation of Optoelectronic Devices**, *A.E. Wright*, *P. Mack*, *R.G. White*, *A. Bushell*, Thermo Fisher Scientific, UK

Optoelectronic devices, used for inter-conversion of light and electricity (e.g. photovoltaics and displays), depend upon careful optimisation of chemical, electronic and structural properties for efficient operation and useful operating lifetime.

Characterisation of such a device will typically identify the chemical bonding states, valence band positions, band gap and work function for each component. Lateral and depth resolution may be required to evaluate cell/pixel and multilayer structures.

Electron spectroscopic surface analysis techniques are ideal for the detailed analysis of the electronic structures of optoelectronic devices. Such techniques allow full quantitative characterisation of materials with chemical state and structural information. Surface specificity of spectroscopic information ensures that thin films can be analysed without interference from deeper parts of the sample. Multilayer structures may be studied with depth profiling techniques, and imaging functionality may be used to study cell or pixel structures.

The Thermo Scientific Escalab250Xi offers several such spectroscopic techniques, which have been employed in this study. X-ray Photoelectron Spectroscopy (XPS) offers surface-sensitive, quantified chemical state analysis and imaging capabilities. Ultraviolet Photoelectron Spectroscopy (UPS) allows measurement of valence band positions. Reflected Electron Energy Loss Spectroscopy (REELS) yields information on the electronic band gap and hydrogen content of a material. These techniques are combined for a thorough characterisation of the electronic structure of optoelectronic devices.

11:40am **AS-MoM11 Chemically Resolved Electrical Characterisation of Working Devices by XPS**, *S. Suzer*, Bilkent University, Turkey

A noncontact chemical and electrical measurement technique of XPS is performed to investigate a CdS based Photoresistor and a Si-Diode during their operation. The main aim of the technique is to trace chemical and location specified surface potential variations as shifts of the XPS peak positions under operating conditions. For the Photoresistor Cd3d and for the Diode (p-n junction) Si2p peaks positions have been recorded, respectively. The variations in the Cd3d peak without and under photoillumination with 4 different lasers is extracted to yield the location dependent resistance values, which are represented; (i) two dimensionally for line scans, and (ii) three dimensionally for area measurements. In both cases one of the dimensions is the binding energy. For the Si p-n junction the variations in the Si2p peak position under normal and reverse bias are recorded to differentiate and identify the nature of the doping (p- or n-). The main advantage of the technique is its ability to assess element-specific surface electrical potentials of devices under operation based on the energy deviation of core level peaks in surface domains/structures. Detection of the variations in electrical potentials and especially their responses to the energy of the illuminating source *in operando*, is also shown to be capable of detecting, locating, and identifying the chemical nature of structural and other types of defects.

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