Wednesday Afternoon, November 11, 2009

Applied Surface Science
Room: C2 - Session AS-WeA

Angle-resolved X-ray Photoelectron Spectroscopy

Moderator: A. Herrera-Gómez, CINVESTAV-Qro, Mexico

2:00pm **AS-WeA1 ARXPS: Power and Limitations in the Search for New Microelectronics Materials and Processes**, ***T. Conard***, IMEC, Belgium **INVITED**

While the concept of Angle-resolved XPS has been available since the early days of XPS, its use has always been limited both due to its demanding experimental overhead and the difficulties of data interpretation. The introduction of systems allowing recording several angles in parallel has greatly eliminated the experimental difficulties and pushed the development of more integrated software's for data interpretation. Simultaneously, the advent of use of very thin film across many industries and especially for high-k dielectric in the microelectronics industry, the ability to accurately and quickly evaluate the true composition, including species location within a layer, has become more complicated, or even impossible. Specifically, a depth profile involving ion sputtering will cause a rearrangement of species by degrading the analytical results. Non sputtering techniques such as ERD or MEIS have achieved high quality, quantitative depth profile on very thin layers. However, ERD and MEIS are complex techniques from both an instrumental and theoretical point of view. This paper will present the possibilities of composition depth profiling for thin films (<5nm) by XPS without the need for sputtering. We will however emphasize the danger of blindly applying the technique through the use of several examples. The use of ARXPS is however not limited to depth profiling of ultra-thin layers. We will also include example of application in the field of organic chemistry, bio-sensors, etching and cleaning process development, where the additional qualitative information available through angle-resolved measurement significantly simplify the interpretation of the data.

2:40pm **AS-WeA3 Effects of Elastic Scattering and Analyzer-Acceptance Angle on the Analysis of Angle-Resolved XPS Data**, ***C.J. Powell***, National Institute of Standards and Technology, *W.S.M. Werner*, *W. Smekal*, Vienna University of Technology, Austria

Angle-resolved XPS is frequently used to obtain composition-depth information. Reliable analysis of the data, however, is currently based on the validity of a number of assumptions that include neglect of elastic scattering and neglect of the analyzer-acceptance angle. We determined XPS intensities of N 1s, O 1s, Hf 4f, Si (oxide) 2p, and Si (substrate) 2p peaks at selected emission angles for $SiO_{1.6}N_{0.4}$ and $HfO_{1.9}N_{0.1}$ films on Si with thicknesses of 5 Å, 15 Å, 25 Å, 35 Å, and 45 Å. The intensities were calculated using the NIST Database for the Simulation of Electron Spectra for Surface Analysis (SESSA) [1,2]. Simulations were performed for Al Kα X-rays, sample tilting, and differential elastic-scattering cross sections from the relativistic partial-wave expansion method (Mott cross sections). We also performed simulations with the straight-line approximation (SLA) in which elastic scattering is neglected. We will report comparisons of peak intensities for four models: (a) Mott cross sections and an analyzer semi-angle of 12°, (b) Mott cross sections and a semi-angle of 0.5°, (c) the SLA and a semi-angle of 12°, and (d) the SLA and a semi-angle of 0.5°. The intensity ratios changed appreciably as elastic scattering is switched on and off, but changing the analyzer semi-angle had a smaller effect. These changes are comparable to those found in N 1s and O 1s angular distributions for different N composition profiles in SiON, thus casting doubt on the validity of N composition profiles obtained from conventional analyses of ARXPS data. We will present plots of ratios of intensities for each line obtained from Models (d) and (a) as a function of emission angle for each film thickness. The largest change occurred for the substrate Si 2p line where the ratio increased appreciably with emission angle, reached a maximum in the vicinity of 50° to 60°, and then decreased rapidly. These changes were more pronounced in the HfON films than the SiON films, indicating the stronger elastic-scattering effects in HfON than in SiON. We will report similar comparisons with Cu Kα X-rays. Although elastic-scattering effects are less pronounced than at lower energies, they are not negligible. A planned enhancement of SESSA to include polarized X-rays will make it useful for XPS applications with synchrotron radiation. [1] http://www.nist.gov/srd/nist100.htm.

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

3:00pm **AS-WeA4 Combining Angle-Resolved and Inelastic Background Information into Concentration-Depth Profiles; A Massively-Parallel Algorithm and a New MEMS Electron Analyzer**, ***P. Cumpson***, Newcastle University, UK

We present new, fast algorithms for automated depth-profiling by Angle-Resolved XPS and AES, and first results from a microfabricated electron energy analyzer array optimised for use with them.

The period to 1995 saw the development of good models for simulating XPS spectra, often based on Monte Carlo simulation[1]. These helped in improving understanding, but were too slow to help analysts interpret particular spectra directly. Also these calculations were in the opposite direction to that desired - spectra were calculated from composition, whereas what we need is the reverse. Nevertheless, progress was made in speeding these calculations substantially[2].

In addition to the usual improvement in CPU speed since then, more of a surprise perhaps is the emergence of PC Graphics Processing Units ("GPUs"). No longer simple arrays of screen memory, these contain tens - often hundreds - of separate processors on one chip. Typically they are used for ray-tracing, following single rays of light back from the detector (a human eye) to their origin, including various types of scattering, reflection and refraction. They do so in parallel, and are used intensively in computer games. We can capitalise on the similarity to electron transport. We have developed algorithms to use these GPUs to simulate XPS and AES emission processes - and in the direction we need - that is, from measured spectrum back to determine the original concentration depth-profile. Most medium-power PCs typically have a suitable graphics card already installed. We have demonstrated a speed-up of roughly 20 times on a 240 processor GPU card, compared to the PC CPU alone, making the time taken for calculation of the composition-depth profile similar to the that of acquiring the spectra in many cases - so it can potentially be done in "real time".

The flexibility of these algorithms mean that the chemical information in spectra can be extracted even if analyzer performance (transmission, resolution, scattering) is poorer than that of modern analyzers, but one needs at least three emission angles[3]. Therefore we have fabricated an array of three silicon MEMS analyzers, similar to a type previously proposed for plasma measurements from spacecraft. We present initial results, though there are significant issues of low transmission and scattering compared to macroscopic hemispherical sector analyzers. We expect to improve their performance to the point where they can be used in conjunction with our GPU algorithms.

[1] A Jablonski and J Zemek, Phys Rev B 48, 4799-4805 (1993)

[2] P J Cumpson, Surf. and Interface Anal. 20, 727 (1993)

[3] P J Cumpson, J. of Elec. Spectrosc., 73 25 (1995)

4:00pm **AS-WeA7 Application and Optimization of Depth Profile Reconstruction from XPS Data using the Maximum Entropy Method**, ***G.J. Mishra***, Kratos Analytical Ltd, UK, *D.J. Surman*, Kratos Analytical, *K.C. Macak*, Kratos Analytical Ltd, UK

Angle resolved X-ray Photoelectron Spectroscopy (ARXPS) is a useful method for obtaining nondestructive quantitative information about the depth distribution of chemical components in thin (2– 8 nm) films. Modern instrumentation makes the collection of large amounts of data straight forward but determining the depth distribution of elements is more challenging. One numerical method commonly applied to this type of data is the maximum entropy method (MEM). For the MEM to be successfully applied and a depth profile reconstructed, the experimental data must be consistent with the physical model describing the electron transport in the sample. The precision of the reconstructed depth profile depends both on the noise in the experimental data and on the accuracy of the physical model. The Beer-Lambert law of electron transport which is used for routine analysis of the experimental data provides inadequate description of the elastic scattering effects and doesn't account for the finite analyser acceptance angle.

We present a more refined model of the MEM algorithm based on a depth distribution function which allows the consistent inclusion of the aforementioned effects of scattering and analyser acceptance angle into the analysis of depth profiles. Direct incorporation of the depth distribution algorithm into the MEM model also allows the utilization of the results of Monte Carlo simulations of electron transport instead of various approximate attenuation length parameters.

The effect of data collection conditions, in terms of instrument operating mode; analyser collection angles; and signal to noise, on the reliability of reconstructed profiles is also investigated. A set of optimised conditions and

minimum data quality for successful depth profiling of the materials under investigation are suggested.

4:20pm **AS-WeA8 A Case Study of Depth Profile Reconstruction from Parallel ARXPS Data by Application of a Genetic Algorithm : Characterization of a Novel, Low-Energy Plasma Treatment**, *P. Mack, **R.G. White**, J. Wolstenholme,* Thermo Fisher Scientific, UK, *E.H. Lock, S.G. Walton,* Naval Research Laboratory, *D.Y. Petrovykh*, Naval Research Laboratory and University of Maryland, College Park

Maximum entropy methods are often used to reconstruct depth profiles from angle resolved XPS data. Such methods typically rely on searching a vast parameter space for potential solutions, but in the past, it has been left to the analyst to decide when the optimum solution has been identified. An undesirable side-effect of this approach is that different analysts are likely to reconstruct different depth profiles from the same ARXPS data set. By contrast, depth profile reconstruction software based on a genetic algorithm rapidly samples many thousand potential solutions in the maximum entropy parameter space, but only reports the optimum result without input from the analyst,

This approach has been applied to characterize the surfaces generated by a new, low-energy plasma treatment. Polystyrene films, modified by a variety of plasmas, were analysed using parallel angle resolved XPS (PARXPS). An evaluation of different methods of ARXPS depth profile reconstruction was performed, comparing “boxcar” and “Cumpson” models with maximum entropy method results. The maximum entropy calculations employed the genetic algorithm to search for the optimum solutions. The non-destructively measured PARXPS profiles were compared with low-energy argon sputter profiles of the polymer surfaces.

Additionally, angle resolved reflection electron energy loss spectroscopy (AREELS) measurements were performed, giving depth-dependent information on the level of carbon unsaturation in the plasma-modified regions of the surface.

This work was supported by the Office of Naval Research.

E. H. Lock is NRL/NRC Postdoctoral Research Associate.

4:40pm **AS-WeA9 Advantages of AR-Hard X-ray Photoelectron Spectroscopy (HAXPES) in the Characterization of Advanced Semiconductor films.**, ***G. Conti**, Y. Uritsky,* Applied Materials Inc., *C. Papp, C.S. Fadley*, Lawrence Berkely National Laboratory

High-dielectric constant materials such as HfO2 and metal gates such as TiN are promising materials for the fabrication of high speed, low power consumption devices.

In these systems, the control of the interfaces between the dielectric materials and the electrodes is crucial. Effects such as intermixing, chemical reactions, formation of crystalline domains, etc. require detailed investigation, especially in the new metal gate materials replacing the poly-silicon electrode. Angle –resolved soft X-ray XPS is often employed to probe chemical and structural changes of the individual dielectric and metal layer. Material intermixing, oxygen vacancies and molecular structure at the interfaces play a fundamental role in predicting the electrical performance of the final devices. Probing the entire film stack without any manipulation (spattering, FIB, etc.) is a big challenge for all the metrology presently available in the industrial analytical laboratories. Collaborations between industry and universities may greatly help in developing these advanced devices.

In this work we present the “non destructive” characterization of the total film stack by Hard X-ray AR-XPS (X-ray energy~ 6000eV). This film, under development for 32nm node technology, consists of 50A poly-Si and 100A TiN as a metal gate, of 20A HfO2 as a high dielectric constant material, of a 10A SiO2 on Si substrate.

. This paper will report recent results on chemical and structural information obtained at the TiN/HfO2 interface. Intermixing of TiN and HfO have been observed by TEM analysis, but for the first time we can show that the Hf4f is sensitive to its environments and shows a multiple peak structure probably due to Hf bonded to O and to N.

5:00pm **AS-WeA10 Evaluation of ARXPS for Thickness and Composition Determination for Typical Wafer Processing Thin Films**, ***C. Brundle,*** C. R. Brundle and Associates, *G. Conti*, Applied Materials

ARXPS can be used in two ways to obtain depth distribution information for the near surface region of materials. The first is the Relative Depth Profiling (RDP) approach, which is completely qualitative and provides a "layer ordering" under certain conditions (the material has to be genuinely approximatable by a layer structure and a given XPS resolvable species should not be present in more than one layer). Provided there is sufficient signal intensity to be observed at two angles, the method is usable, which often means qualitative information beyond 100Å depth can be obtained. The second approach is to model the data based on inelastic mean free path lengths, the Beer-Lambert law, and some degree of entropy contribution (such as the Max Entropy approach), in an attempt to produce a quantitative profile. With no constraints there are a huge number of fittable parameters (every species concentration at every depth) and reliable results cannot be obtained. Introducing reasonable constraints (as may be expected, or already known, for wafer processing thin film structures), such as sharp interfaces, known layer ordering, and fixed compound stoichiometry, can reduce the number of parameters to the point where the required accuracy of the experimental data (separation of signal intensity from background; exclusion of data where elastic scattering becomes an issue) necessary to give reliable fits can be achieved. However, owing to the exponentially decreasing contribution to the total signal strength with depth, this cannot be extended beyond about 2λ in depth (which means 40 -50Å) and, in addition, the true depth resolution possible is poor.

Examples of the successful use, and the misuse, of the ARXPS approach for the types of ultra-thin film structures found in wafer processing (involving Si, SiO2, Si3N4, SiOxNy, Hf oxide based layers, and TaN) will be presented. In practical situations, where the intended recipient of the end results is not an an XPS "afficionado", communication of the data in a form that does not lead to gross over-interpretation remains an issue.

5:20pm **AS-WeA11 Development of ARHXPS System using Wide Acceptance Objective Lens and Compact Monochromatic Cr Kα X-ray Source**, ***K. Kobayashi**, M. Kobata,* NIMS Beamline Station at SPring-8, Japan, *H. Iwai,* NIMS, Japan, *H. Yamazui, H Takahashi, M. Kodama, M. Suzuki,* ULVAC PHI Inc., Japan, *E. Ikenaga, M. Machida, J.Y. Son,* SPring-8/JASRI, Japan, *H. Mastsuda, H. Daimon,* NAIST, Japan, *H. Nohira*, Tokyo City Univ., Japan

In the course of the development of hard X-ray photoemission spectroscopy (HXPS) using high flux high brilliant undulator X-rays[Nuclear Instruments and Methods in Physics Research A 601 (2009) 32–47], we were convinced that HXPS is a powerful versatile tool for the research in the basic and applied science and technology. This lead us to development of a laboratory ARHXPS system by combining a focused monochromatic CrKα X-ray source, a wide angle acceptance objective lens, and a high kinetic energy electron analyzer. The CrKα source consists of Cr target, 20 keV focused electron gun, and compact bent crystal monochromator. The X-ray spot is variable from 10 μm (1.25 W) to 200 μm (50 W). The wide acceptance objective lens using an ellipsoidal metal mesh electrode is designed by H. Matsuda and H. Daimon [Phys. Rev. E 71 (2005) 066503] . This objective lens is installed in front of a VG SCIENTA R4000 10kV hemispherical analyzer. The total resolution of 0.5 eV was verified by Au Fermi edge measurements. Angle acceptance of ±35 deg with angle resolution of 0.5 deg was confirmed by measuring Au $3d_{5/2}$ peak of Au thin strip covered with a hemi-cylindrical multi slit, in angle resolution mode. Seven times enhancement of the throughput was affirmed by comparing intensities of Au spin-orbit doublet peaks with and without the objective lens. The Si1s, Hf3d, and valence band spectra of a HfO_2(4 nm)/SiO_2 (1 nm)/Si (001) sample were measured to test the practical applicability. Acquisition times of 5 min, 10 min, and 12 hr were found enough to obtain spectra with good S/N ratio. In order to evaluate effect of overlayer on the photoelectron diffraction (XPD), polar-azimuth angle 2D mapping of Si1s intensity of Si(001) substrates was carried out in samples covered with thin natural oxide, 4 nm SiO_2, and 7 nm SiO_2. It was verified that XPD intensity modulation was clearly observed even in the 7 nm SiO_2 overlayer substrate. Another trial was to detect chemical change in buried interface of an Ir (10 nm)/HfO_2 (2.2 nm)/wedge shape SiO_2 (0-10 nm) /Si (100) sample. The Si1s (both substrate and oxides) and O1s spectral shapes were found to change along the thickness variation of the wedge.

In conclusion, the CrKα laboratory ARHXPS system was verified to be a promising tool for the investigation of bulk and thin solid film materials. The potential applicability of the system to the depth profiling of layered materials of more than 10 nm thickness is to be realized. Strong XPD modulation of the crystalline substrate may causes a certain difficulty to the depth profile analysis

We are thankful to Dr. Miyata and Dr. Abe of AIST for providing us Ir/HfO_2/SiO_2/Si(001) sample.

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