

# Tuesday Afternoon, October 21, 2008

**Applied Surface Science**  
**Room: 207 - Session AS-TuA**

## Practical Surface Analysis

**Moderator:** J. Shallenberger, Evans Analytical Group

1:40pm **AS-TuA1 Practical Surface Analysis : Beyond Acquisition - The Human Factors**, *I.W. Fletcher, S.F. Davies*, Intertek MSG, UK  
**INVITED**

The development of modern surface analysis equipment over the past few years has changed the lot of the typical surface analyst. Indeed, acquisition of 'world-beating' data is now almost routine for many. Better quality data equates to more reliable and often novel information from analytical work to the benefit of all concerned. Also the 'turnkey' reliability of the modern equipment compared to 'the good old days' means that more time is now available to analysts to concentrate their skills and efforts into research and development, problem solving and customer service issues rather than to fault finding and instrument set-up and tuning. One factor that has remained relatively constant amidst such instrumental development, however, is the human element. Whilst surface analysts and their customers may share a common ancestry they do not always appear to share the same understanding at times. Communication is generally an issue with human nature adding extra dimensions of complication. Bringing money into the equation is also certain not to help matters either. As analysts and service providers, we need to constantly endeavour to ensure that the correct messages get received and understood. This presentation will outline several practical examples using SSIMS and XPS applied to typical 'industrial' samples and problems where the human condition has had an impact.

2:20pm **AS-TuA3 Characterization of Amine Terminated SAMs: What is with this oxygen?**, *J.E. Baio, T. Weidner*, University of Washington, *D.J. Graham, Asemblon, L.J. Gamble, D.G. Caster*, University of Washington

Self-assembled monolayers (SAMs) of alkanethiols on metal surfaces have been extensively used as model systems. In particular, amine terminated SAMs have been used to model positively charged surfaces. However, unlike simple methyl terminated SAMs, the quality of amine SAMs is harder to control. This difficulty is illustrated by the previously reported x-ray photoelectron spectroscopy (XPS) results from amine terminated SAMs, all of which describe an unusually high concentration of oxygen within the monolayer. Across a range of protocols, the amount of oxygen detected by XPS varies from 5-8 atomic %. There are two hypotheses that could explain the presence of this oxygen. The first is that the SAM is covered with oxygen containing coadsorbates, while the second assumes that the nitrogen, carbon, and sulfur species are oxidizing. To explore these hypotheses, we characterized amine terminated SAMs on gold substrates by XPS, time-of-flight secondary ion mass spectroscopy (ToF-SIMS), and sum-frequency generation (SFG) vibrational spectroscopy. XPS characterization of our amine SAMs yielded oxygen concentrations as low as 2 atomic %. High-resolution XPS results from the S(2p), C(1s) and N(1s) regions did not detect any oxidized species. However, small amounts of oxidized fragments did appear in both the positive and negative secondary ion spectra. Some of the more prominent oxidized fragments detected included  $\text{SO}_2\text{H}^+$  and  $\text{C}_2\text{H}_5\text{NO}^+$  in the positive secondary ion spectra and  $\text{SO}_3^-$  in the negative secondary ion spectra. There were two distinct stretches present in the SFG vibrational spectra: one at  $3150\text{ cm}^{-1}$  that corresponds to structured water, and a broad peak at  $2850\text{ cm}^{-1}$  indicating a high number of gauche defects within the monolayer. Nonetheless, the lack of N-O, S-O, and C-O stretches in the SFG spectra are consistent with the XPS and SIMS results that show oxidation alone cannot completely account for all of the oxygen detected by XPS on the amine SAM surfaces. Therefore, the majority of the oxygen found within these amine SAMs most likely arises from the presence of coadsorbates.

2:40pm **AS-TuA4 XPS Analyses of Patterned Samples: the Particular Case of X-ray Absorbing Compounds or Structures**, *C. Cardinaud*, IMN-CNRS, France, *S. Bouchoule*, LPN-CNRS, France, *V. Fernandez*, IMN-CNRS, France

Angular X-ray Photoelectron Spectroscopy (XPS) is usually a well suited technique to obtain and discriminate chemical information from the bottom and the sidewall of periodic patterns, such as an array of ridges.<sup>1,2,3</sup> In most commercial XPS systems, 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 ( $\alpha$ ) usually close to the magic angle ( $54.7^\circ$ ). And the tilt axis is

perpendicular to the plane defined by the x-rays and the analyser. Assuming the x-rays are not significantly absorbed by the sample as it is the case for silicon, resists or dielectric materials, this setting allows to analyse the bottom of the pattern (as well as the top of the ridges). Tilting the sample towards the x-ray source to an angle  $\theta$ , allows to shadow the bottom and observe photoelectrons coming from the ridges sidewall (and the top of the ridges). Obviously the suitable value for  $\theta$  is given as  $\text{atan}(\text{space width} / \text{ridge height})$ . Problems arise whenever the ridges are sufficiently wide to absorb significantly the x-rays. This may occur for III-Vs materials such as InP or GaAs widely used in photonics. For example InP ridges having a width of  $1.8\mu\text{m}$  will absorb 99% of  $\text{AlK}\alpha$ , under  $60^\circ$  angle of incidence. Then for  $\theta=0$  the bottom is irradiated only in part, and very weakly or even not at all if  $\alpha > \text{atan}(\text{space width} / \text{ridge height})$ . In the same way, at angle  $\theta$  to obtain full irradiation of the sidewall that comes in the analyser line of sight requires that  $\theta > \alpha$ . However this may not be satisfying with regards to the pattern dimension. Taking advantage of the absorption of the x-rays, an alternative angular configuration exists: it 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. In the present communication we expose and discuss in detail the advantages, drawbacks and limits of these two configurations. The XPS system used here is a Kratos Axis Ultra, several operating modes are experienced for the surface analysis of etched InP patterns.

<sup>1</sup>C.S. Fadley, Prog.Surf.Sci. 16(1984)275

<sup>2</sup>G.S. Oehrlein, J.Appl.Phys. 64(1988)2399

<sup>3</sup>E. Pargon, J.Vac.Sci.Technol. 23(2005)1913.

3:00pm **AS-TuA5 Work Function Measurements of W-based Metal Gates by Ultraviolet Photoelectron Spectroscopy and Kelvin Force Microscopy**, *E. Martinez, F. Pierre, D. Mariolle, N. Benedetto, J.P. Barnes, R. Gassilloud, O. Renault, F. Martin, F. Bertin, A. Chabli, N. Chevalier*, CEA-LETI, France

The scaling of metal-oxide-semiconductor devices faces the challenge of metal gate integration to replace poly Silicon metallization. These metal gates will provide lower electrical resistivity and thinner EOT by removing depletion. New materials based on tungsten alloys are being investigated because of high thermal stability and corrosion resistance. W and WSi are good candidates because of a middle-gap work function that is shifted to P+ or N+ by ion implantation. Before integration in sub-45 nm nodes, the effective work function of the metal gate must be accurately evaluated. Complementary surfaces characterization techniques such as Kelvin Force Microscopy (KFM) and Ultraviolet Photoelectron Spectroscopy (UPS) can be used. Due to extreme surface sensitivity, surface preparation is mandatory before carrying out the measurements. Auger and TOF-SIMS depth profiles evidence the presence of native tungsten and silicon oxides on top of W and WSi materials, respectively. Removal of these oxides must be performed before KFM or UPS measurements, in order to estimate the real metal work function. We investigate here the impact of surface treatments, such as chemical etching, ion sputtering, and thermal annealing on the work function measurement. For WSi metal gates, HF based chemical etching is used to partially remove  $\text{SiO}_2$ . For W metal gates, annealing at  $700^\circ\text{C}$  is performed to evaporate  $\text{WO}_3$ . Subsequent X-ray Photoelectron Spectroscopy (XPS) is carried out to follow the evolution of the chemical surface composition. A detailed analysis of Si2p and W4f core levels evidences partial removal of native oxides. Gentle argon sputtering is finally performed to fully remove the superficial oxide. UPS and KFM measurements are performed after these surface treatments. A crossed study of the results obtained by these techniques will be commented. AFM and SEM results will highlight the roughness and morphology of the surface after each surface treatment.

4:00pm **AS-TuA8 Assessment of Computer-assist Automated Peak Identification in XPS (X-ray Photoelectron Spectroscopy)**, *M. Suzuki*, ULVAC-PHI, Inc., Japan, *S. Fukushima, S. Tanuma*, NIMS, Japan

XPS is widely used for the analysis of surface regions to determine elemental composition and chemical state. Peak identification is usually conducted with sophisticated software that is delivered from a manufacturer. In the VAMAS/TWA2/A9 project, we have artificially prepared basic test XPS spectra, corresponding to Au-Ag-Cu ternary alloys with three different compositions, and we also superposed noise onto them. Noise was generated by random number with amplitudes that were numerically defined from total intensity of the basic test spectra.<sup>1</sup> Three basic and noise-superposed spectra were distributed to participants in a round robin test (RRT) to evaluate visual peak detection and peak identification using software in daily use. We will demonstrate peak identification efficiency, referring the results for visual peak detection<sup>2</sup> for the test spectra. We have, first, prepared the reference sets of peak energies and elemental transitions, where we have chosen the peaks with

detectabilities more than 75% (9 persons / 12 RRT participants) or with S/N (background-subtracted peak intensity / background deviation at both peak sides) ratios more than 10. The nine persons among twelve RRT participants reported results of automated peak identification for noise-superseded test spectra. 6, 2, and one persons used software of MultiPak (ULVAC-PHI), Casa XPS (Casa Software), and Spectral Data Processor (XPS International), respectively. Analyst A (MultiPak user) showed about 60% of "positive efficiency (PE)" and several % of "negative efficiency (NE)". Here PE means the ratio of the number of identified peaks to that in a set of reference, but NE corresponds to the percentage of peak number not-included in a set of reference. Analyst J (Casa user) reported about 70% PE and 100% NE for the same test spectrum. For one other noisy test spectrum, analysts A and J answered about 60% and 70% PE, and 5-10% and 45-50% NE, respectively. These efficiencies did not depend on the noise amplitudes. The elements assigned by analyst A were only Au, Ag, and Cu, but analyst J reported several other elements. The results evidently prove the difference in design concepts of software. In the presentation, efficiencies depending on software and noise amplitude will be discussed in details.

<sup>1</sup> M. Suzuki, S. Fukushima, and S. Tanuma, *J. Surf. Anal.* 14, 104 (2007).

<sup>2</sup> M. Suzuki, S. Fukushima, and S. Tanuma, *Surf. Interface Anal.* Accepted.

**4:20pm AS-TuA9 A Novel Bismuth-Manganese Emitter for G-SIMS Spectroscopy and Imaging.** *F. Kollmer*, ION-TOF GmbH, Germany, *F.M. Green*, National Physical Laboratory, UK, *E. Niehuis*, ION-TOF GmbH, Germany, *I.S. Gilmore*, *M.P. Seah*, National Physical Laboratory, UK

Static SIMS is a well-established, powerful technique for the analysis of complex molecules on the outermost surface of a solid. However, the complexity of static SIMS spectra and the difficulties in the interpretation thereof have been significant barriers to the wider uptake of the technique. G-SIMS has been demonstrated to be a useful approach for simplifying complex static SIMS spectra of organics at surfaces leading to a direct identification of different substance classes.<sup>1</sup> G-SIMS uses two ion beams that generate high and low fragmentation conditions at the surface. This allows an extrapolation to equivalent experimental conditions with very low fragmentation. The resulting spectra are less complex, contain more structural information and are easier to interpret. A barrier for the wider uptake of G-SIMS into the community are the requirements for two ion beams producing suitably different fragmentation conditions and the need for their registration at the surface, which is especially important for heterogeneous samples. The most popular source is the liquid metal ion source, which is now sold with almost every new ToF-SIMS instrument. These produce a high brightness source of atomic and cluster ions such as  $\text{Bi}_n^+$ ,  $\text{Au}_n^+$ . Unfortunately, a preliminary study shows that the cluster primary ions are less suitable for G-SIMS. We have developed a novel emitter consisting of a mixture of bismuth and manganese that produces selectable beams of  $\text{Bi}^+$  and  $\text{Mn}^+$  for high and low fragmentation conditions respectively. The beams are automatically aligned at the surface. This combines the cluster beam capabilities of a  $\text{Bi}_n^+$  cluster source with the ability to give excellent G-SIMS imaging and spectroscopy, without significantly comprising the cluster ion performance. We investigated the fundamental fragmentation conditions of  $\text{Bi}^+$  and  $\text{Mn}^+$ , their ability to provide clear G-SIMS spectra and compared them to previously applied species as  $\text{Ar}^+$  and  $\text{Cs}^+$ . Moreover, we investigated the beam performance of the BiMn source and the possibility of high resolution imaging in combination with G-SIMS analysis.

<sup>1</sup> I. S. Gilmore, M. P. Seah, *Appl. Surf. Sci.* 161 (2000) 465.

**4:40pm AS-TuA10 Probing the Polymer-Glass Interface to Understand Adhesion in Laminate Structures.** *K.M. Stika*, *D.G. Swartzfager*, *D. Huang*, *R.L. Smith*, *D.E. Davidson*, *R.L. Agostinelli*, *D. Brill*, DuPont

Our ability to optimize and consistently control polymer-glass adhesion is an important property in many glass laminate applications. This poster will review recent rate-dependent peel testing studies that highlight significant differences in adhesion performance between polymer encapsulants and glass surfaces. Coupling quantitative AFM (Atomic Force Microscopy) with XPS (X-ray Photoelectron Spectroscopy) and ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) analyses of the debonded layers has provided new understanding linking adhesion failure mode with interfacial chemistry.

**5:00pm AS-TuA11 Process Qualification and Monitoring of Interconnect Etch Processing using In-Line Total Reflective X-ray Fluorescence Spectroscopy.** *P.S. Frankwicz*, *M. Johnson*, *T. Budri*, *T. Moutinho*, National Semiconductor Corporation

Process qualifications and monitoring serve important functions in a high volume semiconductor production environment for insuring process control and product yield. Conventional production qualifications generally involve etch rate, defect characterization and final image critical dimension metrics

and generate relatively little quantification of actual etch process excursions in the process chamber. Specifically, elevated levels of chlorine-based residual etch by-productions after interconnect etch can drastically increase the probability of corrosion of conventional Al-Cu (0.5%) metal interconnects. A new multiple parametric qualification (MPQ) has been developed that provides baseline surface composition for interconnect etch and clean process excursion detection using Total Reflective X-ray Fluorescence Spectroscopy (TRXFS). The 180nm technology node qualification includes automatic defect characterization (ADC) and electrically testable metal bridging structures for verification of electrical parametric versus interconnect design rules. TRXFS provides total chlorine content and spatial surface concentration profiling of the qualification wafers to levels of 100ppm range. In this study, total chlorine content after interconnect metal etch and clean has been correlated with high moisture atmosphere exposure tests to determine trigger levels for the start of corrosion of metal interconnect lines via HCl chemical reaction with the aluminum interconnect sidewall. Spatial surface concentrations of chlorine provide wafer maps to detect and investigate process tool variations in wafer backside helium cooling gas, process gas distribution and liquid solvent clean application. The chemical composition results have been correlated with Liquid Phase Ion Chromatograph and Secondary Ion Mass Spectroscopy to verify surface species concentrations. The TRXFS methodology provides definable metrics to compare chamber to chamber process performance and map process space. Furthermore, this surface sensitive protocol can replace cumbersome and time consuming high moisture atmosphere wafer exposure methodologies. Examples of semiconductor production excursions and process improvement investigations will be presented to illustrate the utility of the TRXFS qualification in comparison to conventional production monitoring.

**5:20pm AS-TuA12 In-situ ATR-UV Spectroscopy of Adsorption-Desorption Isotherms of Silane on Silica.** *M.A. Bratescu*, Nagoya University, Japan, *D.B. Allred*, University of Washington, *N. Saito*, Nagoya University, Japan, *M. Sarikaya*, University of Washington, *O. Takai*, Nagoya University, Japan

Ultraviolet attenuated total reflectance (UV-ATR) spectroscopy is a useful method to monitor electronic transitions of molecules at interfaces via the evanescent wave generated at a totally internally reflecting surface. Silane is a frequently used linker for functionalization and assembly on silica. Many efforts are still made to identify and to optimize the factors affecting the monolayer formation. Reaction conditions such as temperature and humidity, as well as silane and substrate chemistry influence the rate of reaction and the assembly process. We chose a silane based adsorption process to determine what insight this spectroscopic examination may yield. For this study we have used the molecule O-4-methyl-coumarinyl-N-[3-(triethoxysilyl)propyl] carbamate (Gelest, Inc.), which has the formula  $\text{C}_{20}\text{H}_{29}\text{NO}_7\text{Si}$ , and will be hereafter referred to as MCC-propylsilane. The coumarin group represents the observable chromophore in the UV spectral region, and the silane chemistry is desirable for the functionalization and possibly the assembly on silica.<sup>1</sup> Experiments were performed using a custom-made apparatus,<sup>2</sup> combining a fused quartz internal reflection element as the ATR sensor and a flow cell transparent to the light source. The measuring system was equipped with a chiller to control the interface temperature from -10°C to +60°C with 0.01°C resolution. The MCC-propylsilane concentrations were varied from 0.1 to 5.0 mM. The ATR-UV absorption spectrum of MCC-propylsilane shows two peaks at 270 and 325 nm attributed to pyrone and benzenoid groups, respectively, of the coumarin chromophore. From time-resolved spectra at different MCC-propylsilane concentrations and temperatures the adsorption-desorption isotherms were obtained. The thermodynamic properties are useful for a better understanding of the driving forces of this silane adsorption process.

<sup>1</sup> S.R. Wasserman, Y.T. Tao and G.M. Whitesides, *Langmuir* 5(1989)1074.

<sup>2</sup> M.A. Bratescu, D.B. Allred, N. Saito, M. Sarikaya and O. Takai, *Appl. Surf. Sci.*, 254(2008)2960.

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