

## Applied Surface Science

### Room 324/325 - Session AS-FrM

#### SIMS

Moderator: D.R. Baer, Pacific Northwest National Laboratory

#### 8:20am AS-FrM1 Static ToF-SIMS - A VAMAS Interlaboratory Study, 2002, I.S. Gilmore, M.P. Seah, National Physical Laboratory, UK

The first VAMAS static SIMS inter-laboratory study was conducted by NPL in 1996. That study included 21 static SIMS instruments with a wide variety of spectrometer types. Results indicated that, whilst repeatabilities could be as good as 1%, they were on average only 10%. Additionally, the equivalence of data between all the different instruments was improved by a factor of 4 by use of a relative instrument transmission function RISR. In 2002, the second VAMAS static SIMS inter-laboratory study was conducted, this time restricted to time-of-flight instruments which now dominate static SIMS analysis. The principal objectives are (i) to determine the repeatability of instruments, (ii) to determine the reproducibility of between laboratories, (iii) to evaluate variations in spectral response between different types of SIMS instruments and, optionally, (iv) instrument compatibility with G-SIMS may also be tested. Data have now been received from 31 laboratories (10 with G-SIMS data) from 16 countries. Three reference materials were used in this study, a thin spin cast polycarbonate film, a thin layer of polystyrene oligomers on silver and PTFE. A protocol for analysis was supplied to each laboratory. Relevant details of the protocol will be discussed. Excellent repeatabilities have been demonstrated with over 90% of participants achieving average repeatabilities of better than 5% and 30% of participants with better than 1.5%. The reference materials give an average repeatability of 2% over 27 laboratories. This shows a considerable improvement from the average repeatability of 10% in the former study. An analysis of the results and the issues of conducting both SSIMS and G-SIMS using different instruments will be presented.

I S Gilmore and M P Seah, Surf. Interface Anal., 29 (2000) 624.  
I S Gilmore and M P Seah, Appl. Surf. Sci., 161 (2000) 465.

#### 8:40am AS-FrM2 TOF-SIMS with Polyatomic Primary Ion Bombardment: A Comparison Between Different Projectiles, R. Möllers, F. Kollmer, D. Rading, M. Terhorst, E. Niehuis, ION-TOF GmbH, Germany; R. Kersting, B. Hagenhoff, Tascon GmbH, Germany

In the past TOF-SIMS has been established as an analytical technique for the chemical characterization of surfaces. In particular the simultaneous detection of atomic as well as molecular ions, and the ability to obtain these information laterally resolved, makes this technique well suited for the analysis of structured molecular surfaces. Recently it was shown that polyatomic primary ion bombardment (e.g. SF<sub>5</sub><sup>+</sup>, C<sub>60</sub><sup>+</sup>, Au<sub>n</sub><sup>+</sup>-clusters,...) leads to a considerable enhancement of the secondary ion emission efficiency for organic materials. This enhancement not only increases the sensitivity for molecular species up to several orders of magnitude, but also pushes the useful lateral resolution in organic imaging down to the sub- $\mu$ m range. In this presentation we will continue our systematic investigation on the influence of different primary ion species, including monoatomic as well as polyatomic primary ions, on secondary ion parameters such as yield Y, damage cross section  $\sigma$ , efficiency  $E = Y/\sigma$ , and useful lateral resolution  $\Delta$ . Those parameters have been evaluated for a variety of different sample materials and sample preparations. Also the effect of different primary ion energies (4 to 25 keV) will be issued. The results from this investigation will be expanded by examples from routine analysis in a commercial service laboratory.

#### 9:00am AS-FrM3 Characterisation of Peptides Using TOF-SIMS with Polyatomic Primary Ion Bombardment, K. Pfitzer, E. Tallarek, R. Kersting, B. Hagenhoff, TASCAN GmbH, Germany

In the 80s of the last century it could be shown that the optimum sample preparation for SIMS of peptides under monoatomic primary ion bombardment is a monolayer preparation on noble metal substrates. Yields from thick overlayers turned out to be distinctly lower compared to the monolayer preparation. Although many applications were possible by this type of preparation, information could not be gained from biological material directly where peptides or proteins are embedded in thick organic matrices. Now, the use of polyatomic primary ions offers new opportunities. Under such primary ion bombardment conditions molecular ions can be emitted with high secondary ion formation efficiency also from thick organic layers. Efficiency

enhancement factors can reach up to 3 orders of magnitude. We have applied Ga<sup>+</sup>, Au<sub>1</sub><sup>+</sup>, Au<sub>2</sub><sup>+</sup>, Au<sub>3</sub><sup>+</sup> as well as Au<sub>5</sub><sup>+</sup> bombardment to several peptides. The peptide masses varied from 1000u up to 3500u. Variations of the chemical structure could be tested by varying the number of basic and acidic side chains. The samples were prepared as monolayers on noble metal substrates, as thick overlayers (powders, thick layers spin coated from solutions) as well as mixed into nitrocellulose. The results show that polyatomic primary ion bombardment indeed allows to desorb peptides efficiently from thick layers. Progress can therefore be expected for SIMS imaging of peptides and proteins in biological matter.

References: A. Benninghoven; J. Vac. Sci. Technol. A3 (3), (1985), 451  
D. van Leyen, D. Greifendorf, A. Benninghoven in: A. Benninghoven, A. M. Huber, H. W. Werner (eds.); Secondary Ion Mass Spectrometry (SIMS VI); John Wiley & Sons, Chichester, 1988, 679  
D. Stapel, M. Thiemann, B. Hagenhoff, A. Benninghoven, in: A. Benninghoven, P. Bertrand, H. N. Migeon, H. W. Werner (eds.); Secondary Ion Mass Spectrometry (SIMS XII); John Wiley Sons, Chichester, 2000, 255

#### 9:20am AS-FrM4 SIMS Quantification for Depth Profiling: Overview, Recent Results for Surfaces and Insulators, and Current Problems, F.A. Stevie, C. Gu, A. Pivovarov, D.P. Griffiths, North Carolina State University; J.M. McKinley, NanoSpective; H. Francois-Saint-Cyr, University of Central Florida

##### INVITED

This paper provides an overview of quantification for SIMS depth profiling and presents recent results illustrating the importance of surfaces, matrix variations, and insulators on the quantification process. Quantification is complicated by the orders of magnitude variation of secondary ion yields over the periodic table and significant variation of these ion yields for different matrices. Since practical methods for calculation of elemental sensitivity factors using theoretical methods do not exist, a standard for each element in the matrix in which it is contained is required. However, only a few standards with high accuracy have been produced. Despite these limitations, measurement precision less than 1% can be achieved. Using ion implant standards, quantification can be achieved at surfaces, within multilayered samples, at interfaces, and in bulk materials. Implantation through a removable layer provides a known quantity at a surface that can be used as a standard by many analytical techniques. Multiple layers require an understanding of each layer. A study of O<sub>2</sub><sup>+</sup> SIMS analysis of TaN/Ta barrier penetration by Cu shows the low secondary ion yield in the barrier compared with the SiO<sub>2</sub> and Si regions complicates interpretation. Insulators present additional problems due to sample charging. Analysis of thin insulating films can be performed by using electrons with energy sufficient to penetrate the layer thus rendering the layer conductive. Magnetic sector SIMS analysis of GaN structures can be aided by the use of molecular secondary ions accompanied by the maximization of mass spectrometer secondary ion energy bandpass. Adequate O<sup>-</sup> primary beam density can be obtained to provide depth profiles in bulk insulators. Many aspects of quantification using SIMS still require additional study. It is difficult to extend the information from one matrix to another, and analysis of insulators such as porous low-k dielectrics present special problems.

#### 10:40am AS-FrM8 SIMS Backside Depth Profiling of Test Pads on PMOS Patterned Wafers, E.S. Windsor, J.G. Gillen, P.H. Chi, National Institute of Standards and Technology; J.A. Bennett, International Sematech

In semiconductor electronics, the diffusion of elements from one layer to another can lead to poor performance or device failure. Interlayer diffusion is of particular interest in process design where experimentation with films of varying composition and thickness is common. In this study, we investigate a patterned PMOS wafer containing hafnium oxide as an experimental gate dielectric. The question arises as to whether boron from the overlying polysilicon layer has diffused through the dielectric down into the silicon substrate below. We use Secondary Ion Mass Spectrometry (SIMS) to investigate possible boron diffusion because of the high analytical sensitivity and excellent depth resolution of the SIMS technique. Front-side SIMS analyses of these patterned wafers can be limited by: (1) difficulty sputtering patterned (non-planar) surfaces, (2) initial or sputter induced topography of the sample surface and (3) degraded depth resolution caused by ion mixing when sputtering from high to low concentrations of the element(s) of interest. To minimize these effects, it is often desirable to sputter (analyze) from the backside of the wafer. Backside analysis requires the removal of the majority of the silicon substrate (final substrate thickness less than 1 micron). This is accomplished by mechanical grinding and polishing. Since the features of interest (test pads in this study) can not

# Friday Morning, November 7, 2003

be observed from the backside, they must be marked from the front side prior to mechanical preparation. Marking is accomplished by ion sputtering, and we sputter both holes and raster craters. Holes mark the features of interest while the larger raster craters are used to aid thickness determinations and adjust planarity during mechanical preparation. Also investigated are factors that limit the usefulness of mechanical backthinning preparation such as polished surface roughness and sample polishing planarity.

11:20am **AS-FrM10 Development and its Application of Multiple as Delta Layer Si Reference Thin Film for Shallow Junction SIMS Profiling**, *D.W. Moon*, Korea Research Institute of Standards and Science, South Korea; *H.K. Kim, K.J. Kim*, Korea Research Institute of Standards and Science; *H.K. Shon, J.Y. Won, J.C. Lee*, Samsung Advanced Institute of Technology, Korea; *F. Toujou*, Matsushita Technoresearch, Inc., Japan

To meet the demand for shallow junction SIMS profiling, the surface transient Si sputtering effect should be corrected in addition to the improvement of depth resolution. With low energy grazing incident ions, the SIMS depth resolution could be improved better than 1 nm. For the correction of the surface transient effect, we report that multiple As delta-layer Si thin films characterized with HRTEM and MEIS can be used as a reference thin film. With the reference thin films, the depth scale shift in the surface transient region can be calibrated under each analysis condition. For low energy  $O^{2+}$  and  $Cs^{+}$  ion bombardment, the average Si sputtering yield in the first surface 5 nm layer can be 50~70% higher than that in the steady state for typical incidence angles around 45°. However, for incidence angle above 60°, the surface transient effect enhanced significantly with the increase of the sputtering yield up to 150% and the extension of the surface transient region up to 15 nm for low energy  $Cs^{+}$  bombardment. Preliminary understanding for the enhanced surface transient effect will be discussed.

## Author Index

### Bold page numbers indicate presenter

— B —

Bennett, J.A.: AS-FrM8, **1**

— C —

Chi, P.H.: AS-FrM8, **1**

— F —

Francois-Saint-Cyr, H.: AS-FrM4, **1**

— G —

Gillen, J.G.: AS-FrM8, **1**

Gilmore, I.S.: AS-FrM1, **1**

Griffis, D.P.: AS-FrM4, **1**

Gu, C.: AS-FrM4, **1**

— H —

Hagenhoff, B.: AS-FrM2, **1**; AS-FrM3, **1**

— K —

Kersting, R.: AS-FrM2, **1**; AS-FrM3, **1**

Kim, H.K.: AS-FrM10, **2**

Kim, K.J.: AS-FrM10, **2**

Kollmer, F.: AS-FrM2, **1**

— L —

Lee, J.C.: AS-FrM10, **2**

— M —

McKinley, J.M.: AS-FrM4, **1**

Möllers, R.: AS-FrM2, **1**

Moon, D.W.: AS-FrM10, **2**

— N —

Niehuis, E.: AS-FrM2, **1**

— P —

Pfitzer, K.: AS-FrM3, **1**

Pivovarov, A.: AS-FrM4, **1**

— R —

Rading, D.: AS-FrM2, **1**

— S —

Seah, M.P.: AS-FrM1, **1**

Shon, H.K.: AS-FrM10, **2**

Stevie, F.A.: AS-FrM4, **1**

— T —

Tallarek, E.: AS-FrM3, **1**

Terhorst, M.: AS-FrM2, **1**

Toujou, F.: AS-FrM10, **2**

— W —

Windsor, E.S.: AS-FrM8, **1**

Won, J.Y.: AS-FrM10, **2**