

Monday Afternoon, October 28, 2013

Applied Surface Science

Room: 204 - Session AS-MoA

Analyses Using Novel Ion Beams

Moderator: X. Dong, Eli Lilly and Company, W.F. Stickle, Hewlett Packard

2:00pm **AS-MoA1 Status and Prospects for ICP Focused Ion Beams**, N. Smith, P. Tesch, N. Martin, Oregon Physics LLC, R. Boswell, Oregon Physics LLC and Australian National University **INVITED**

Milling speeds with a gallium focused ion beam (FIB) are often much too slow for many sample preparation and surface engineering applications. For example, cross-sectioning stacked-die semiconductor devices, prototyping micro-mechanical structures and delayering IC's for circuit mapping are growing applications that require a milling rate that far exceeds that provided by the gallium FIB.

In the more general area of direct-write surface engineering, milling with nanometer precision is limited to volumes of $<10^4 \mu\text{m}^3$ when using gallium FIB systems. Also, engineered devices must generally be tolerant of high gallium concentrations being implanted in the near-surface region. These are major restrictions when fabricating micromechanical devices.

Furthermore, elemental secondary ion mass spectrometric imaging (SIMS-Imaging) has been limited to a lateral resolution of 200nm when using an oxygen focused ion beam for high sensitivity surface analysis. Many areas of material science could benefit from an ability to image trace level surface chemistry with $<20\text{nm}$ resolution. Example applications include, sub-cellular imaging of trace metals in the brain for neurodegenerative disease studies, analysis of trace element segregation in metal alloys and studying isotope distributions in meteorites.

Here, we review inductively coupled plasma ion source technology that can provide a focused ion beam capable of milling silicon at a rate of $>5000 \mu\text{m}^3/\text{s}$ with $<4\mu\text{m}$ milling resolution and $<25\text{nm}$ imaging resolution with 30keV xenon ions. The latest generation ICP-FIB, readily operates as a high brightness source of not only any inert ion, but also positively and negatively ionized oxygen for trace element SIMS imaging.

By transferring energy to plasma electrons via a radio frequency induction field, it is possible to create a plasma state without a cathodic electrode. This method of plasma creation can create energy normalized beam brightness values that now exceed $1 \times 10^4 \text{ Am}^2 \text{ sr}^{-1} \text{ V}^{-1}$. This high brightness can be attained with long lifetimes ($>>2000$ hours), stable beam current ($<\pm 0.5\%$ drift per 30 minutes) and an axial energy spread for the extracted ion beam of 5-6eV and for a broad array of ion species.

At Oregon Physics, we have developed the HyperionTM inductively coupled plasma ion source that is already capable of generating smaller probe diameters (Xe^+) than the liquid metal ion source (LMIS, Ga^+) FIB at beam currents in excess of 20nA. When operated with oxygen, imaging resolution, source lifetime and current stability are significantly higher than provided by a duoplasmatron.

This paper presents FIB and SIMS data from this new ion source technology, to exemplify the impact on surface science. The operating principles of the inductively coupled plasma source, the properties of the ion beam(s) being created and the projected future for this technology are also described.

2:40pm **AS-MoA3 Detection of Small Molecules on Intact Biofilms using Femtosecond Laser Desorption Postionization Mass Spectrometry**, Y. Cui, C. Bhardwaj, S. Milasinovic, R. Gordon, L. Hanley, University of Illinois at Chicago

Matrix assisted laser desorption ionization and secondary ion mass spectrometry are the two dominant mass spectrometric imaging methods, but signal stability in the former degrades when spatial resolution increases, while the latter can suffer from extensive fragmentation that complicates peak identification. Laser desorption with ultrashort pulses can remove material from a solid with minimal damage to the remaining sample [Milasinovic, *et al.*, *Anal. Chem.* 84 (2012) 3945]. Furthermore, laser desorbed neutrals can undergo soft postionization by vacuum ultraviolet (VUV) radiation for subsequent detection by MS. Here, we demonstrate the small molecule imaging capability of this method on intact microbial biofilms. Baker's yeast and *E. coli* biofilms grown on polycarbonate membranes were studied using a previously reported instrument [Cui, *et al.*, *Rev. Sci. Instrum.* 83 (2012) 093702] equipped with a long Rayleigh range focusing lens and a VUV postionization source [Bhardwaj, *et al.*, *Anal. Bioanal. Chem.* (2012) <http://dx.doi.org/10.1007/s00216-012-6454-0>].

Comparisons were made between laser desorption using direct ionization and VUV postionization. The effects of nanosecond vs. femtosecond desorption pulse lengths were also compared. The results from fs and ns pulses were similar, differing mostly in their relative peak intensities, presumably because of the dependence of the desorption mechanism on laser pulse length. Different delays between the desorption and VUV lasers were also investigated. The imaging capability was demonstrated using baker's yeast and *E. coli* cocultured biofilms. Results showed significant differences between films containing yeast, *E. coli*, and a mixture. Although these capabilities were applied here to intact biological samples, they can be extended to a wide variety of materials including polymers, metals, semiconductors, and insulators.

3:00pm **AS-MoA4 TOF-MEIS Analysis of Nanostructured Materials**, K. Jung, DGIST, Republic of Korea, W. Min, KMAC, Republic of Korea, H. Yu, KRIS, Republic of Korea, K. Yu, KMAC, Republic of Korea, M. Sirtica, P.L. Grande, UFRGS, Brazil, D. Moon, DGIST, Republic of Korea
We report the quantitative compositional profiling with single atomic layer resolution for 0.5~3 nm CdSe/ZnS QDs with a conjugated layer and ultra shallow junctions of As and B implanted Si using a newly developed time-of-flight medium energy ion scattering (MEIS)/Direct Recoil (DR) spectroscopy, which utilizes a pulsed 70~100 keV He+ and Ne+ ion beam of $\sim 10 \mu\text{m}$ diameter for energy resolution of $\sim 5 \times 10^{-3}$.

The composition and core shell structure of CdSe cores and ZnS shells were determined with $\sim 1\%$ uncertainty and $\sim 0.1 \text{ nm}$ resolution, respectively. The number of conjugated molecules per QD can be also determined quantitatively. The composition and size of QDs estimated with TOF-MEIS were compared with XPS and HRTEM, respectively.

As depth profiles in As/Si ultra shallow junctions (USJs) were measured by TOF-MEIS for 2 keV As implantation ion energy with the nominal ion dose of $2 \times 10^{15}/\text{cm}^2$ before and after annealing. Before annealing, the As profile shows a Gaussian shaped distribution with the ion range at 4~5 nm. After annealing, the As atoms diffused out to 3~4 nm with a skewed Gaussian distribution with an extended tail to 11 nm. The dependence of the As profiles on annealing conditions were also observed. The As depth profiles measured by dynamic SIMS were compared with those from TOF-MEIS, which clearly shows the surface transient effect and ion beam mixing effect. Quantitative As depth profiles from TOF-MEIS were compared with SIMS profiles for the calibration of SIMS artifacts in USJ depth profiling. Light elements in heavy substrates can be hardly measured by ion scattering spectroscopy in general. We demonstrated that the TOF-MEIS can be used in the direct recoil mode for the depth profiling analysis of B in B/Si USJ before and after annealing.

With this new TOF-MEIS nano analysis technique, the core-shell structure with conjugated layer structure of QDs, activated As depth profiles in As/Si USJ, B depth profiles in B/Si USJ could be measured quantitatively. Progresses in TOF-MEIS analysis of other nano-structured materials and devices in various nano & bio technology will be discussed.

3:40pm **AS-MoA6 Effect of Ion Bombardment of Novel Electronic Materials**, J.D.P. Counsell, S.J. Coultas, C.J. Blomfield, S.J. Hutton, A.J. Roberts, Kratos Analytical Limited, UK

Lead zirconate titanate (PZT) is a ceramic perovskite material which exhibits piezoelectric properties. PZT is currently used in numerous applications including sensors and actuators and is currently being developed for use in memory devices. Thin-films of PZT were grown on Pt/TiO₂/SiO₂/Si substrates using CVD. Chemical analysis and stoichiometry of the surface was performed using XPS.

This paper will discuss the changes in stoichiometry and chemical states under ion bombardment. A variety of different ions (Ar^+ , $\text{C}_{24}\text{H}_{12}^+$, $\text{Ar}_{(500-2000)}^+$) and beam energies were used to gain information regarding the internal structure of this material. Depth profiling showed good compositional homogeneity through each film thickness, with some lead segregation at the film surface. Optimised conditions for depth profiling inorganic materials are proposed. Processes such as preferential sputtering, sample damage and surface charging are discussed. Previous studies have concentrated on the use of Ar^+ as the bombardment ion however we show that by using gentler ions it is possible to reduced bulk damage and preferential sputtering of the complex surface.

[1] Aleksey Etin, Gennady E. Shter, Reuven Brenner, Sioma Baltianski, and Gideon S. Grader., *J. Am. Ceram. Soc.*, 90 [12], 2007, 3800-3803.

[2] Jae-Nam Kim, Kwang-Soo Shin, Dae-Hwan Kim, Byung-Ok Park, Nam-Kyoung Kim, Sang-Hee Cho., *Appl. Surf. Sci.*, 206, [1-4], 2003, 119-128.

4:00pm **AS-MoA7 Adventures in Mass Spectrometry Imaging - From Pictures to Words**, *I.S. Gilmore*, National Physical Laboratory, UK
INVITED

The three principal mass spectrometry imaging techniques are secondary ion mass spectrometry (SIMS), matrix assisted laser desorption/ionisation mass spectrometry (MALDI MS) and the growing family of ambient mass spectrometries. These powerful techniques allow molecular imaging in 2 and 3 dimensions, from macroscale to the nanoscale and in ambient conditions in real-time. The adage says that "a picture is worth a thousand words". However, images can be seductive⁽¹⁾ but the interpretation of the picture to words of understanding requires a robust metrology framework.

In SIMS, one of the most important advances has been the use of large cluster ions, most notably, argon clusters to allow 3D imaging with a depth resolution approaching 5 nm. The metrology will be reviewed and recommendations for optimum analysis conditions provided. Important artefacts including the effect of primary and secondary ion on the relative depth position and effects of electron beam damage will be identified. The lateral resolution of SIMS for organics is two orders of magnitude worse, which is insufficient for many important applications such as measuring intracellular drug concentration. Future prospects to meet these challenges will be discussed.

Ambient mass spectrometries, such as desorption electrospray ionisation (DESI) and plasma assisted desorption ionisation (PADI) are relatively new but are growing strongly owing to their ability to analyse *in situ*. We have recently conducted a VAMAS interlaboratory study on the repeatability and constancy of the relative intensity and preliminary results will be presented. PADI has great promise for the analysis of polymers including depth profiling, however, present PADI sources are limited to the mm range. NPL and the University of Liverpool are developing novel sources with an aim to achieve 10 micrometre spatial resolution. Recent developments in PADI metrology will also be highlighted.

MALDI is a popular technique for tissue imaging since large peptides and proteins may be detected. However, the sample preparation results in a complex of the matrix, tissue and analyte. NPL has recently started a new metrology programme to support MALDI MS imaging and progress will be presented.

NPL has recently established a National Centre of Excellence in Mass Spectrometry Imaging (NiCE-MSI) including all the above techniques. An important objective of the centre is to provide the metrology and standardisation that ensures that pictures do translate to meaningful knowledge.

References:

1. J C Vickerman, *Analyst* 136, (2011) 2199

4:40pm **AS-MoA9 Argon Gas Cluster Ion Beam (GCIB) Sputter Yields: Measurements for 22 Biological and Organic Electronic Materials, Metals and Oxides**, *P. Cumpson, J. Portoles, A. Barlow, N. Sano*, Newcastle University, UK

Argon Gas Cluster-Ion Beam (GCIB) sources^[1,2] are likely to become widely-available on XPS and SIMS instruments in the next few years. Much attention has been devoted to their ability to depth-profile organic materials with minimum damage. What has not been the focus of attention (possibly because it has been very difficult to measure) is the large ratio of sputter rate for organic materials compared to inorganic materials using these sources, and the special opportunities this presents for studies of organic/inorganic interfaces. This large ratio offers a special opportunity to characterise practical organic/inorganic interfaces with near atomic resolution and high sensitivity.

Recently we published argon GCIB sputter yield measurements for 19 polymers^[3], using a combination of white-light interferometry and contact masking to provide accurate measurements of sputter crater depth. This technique overcomes the need to form a thin, uniform film of the material of interest, which can be problematic in some cases. These data showed an unexpectedly wide range, the sputter yield of PMMA being more than ten times that of PEEK when using argon ion clusters of around 4 eV/atom, with other polymers being widely distributed between these extremes.

We have extended these measurements to a further 22 materials of wide technological interest, including metals (gold, stainless steel), oxides (Si, Al, Ti oxides), biological materials (collagen, bovine serum albumen, fibronectin etc), and organic materials commonly used in organic electronics and organic photovoltaics, plus a few more polymers. Clearly there is a wide range of sputter yield across this large dataset, with inorganic materials having very low, but measurable, sputter yields. We discuss some systematic trends in these data, and the prospect of developing semi-empirical equations for estimating sputter yield in metals, oxides and molecular solids as well as polymers.

[1] S Rabbani, A M Barber, J S Fletcher, N P Lockyer, and J C Vickerman, *Anal. Chem.* 83 (2011) 3793.

[2] I Yamada, J Matsuo, N Toyoda, and A Kirkpatrick, *Mater. Sci. Eng. R.* 34 (2001) 231.

[3] Peter J. Cumpson, Jose F. Portoles and Naoko Sano, *J. Vac. Sci. Technol.* (2013) A 31, 020605

5:00pm **AS-MoA10 Mass Imaging of Biological Samples with Focused Massive Ar Cluster Ion Beams**, *J. Matsuo*, QSEC, Kyoto University, CREST, Japan, *S. Nakagawa*, Kyoto University, CREST, Japan, *M. Fujii*, QSEC, Kyoto University, CREST, Japan, *T. Aoki*, *T. Seki*, Kyoto University, CREST, Japan

Following the development of novel primary ion beams, such as SF₅, C₆₀, Bi₃, and Ar_n, material analysis with secondary ion mass spectrometry (SIMS) has been widely used for organic and biological materials. In particular, with such ion beams the time-of-flight (TOF) SIMS system can provide whole mass spectra for the determining molecular structures on surfaces, and very recently these beams have been used in molecular depth profiling to investigate multilayer structures consisting of various organic materials. Thus, TOF-SIMS is considered to be an important surface analysis technique for organic and biological materials. Furthermore, mass spectrometric imaging with high lateral resolution can be achieved with the TOF-SIMS technique, because ion beams are easily focused down to submicrometer dimension.

However, there are still numerous challenges in applying TOF-SIMS to real biological samples. For instance, to compete with other mass spectrometry techniques, such as MALDI, DESI, DART, PADI, etc., mass resolution and sensitivity are expected to be improved. We have demonstrated that massive Ar cluster beams are quite useful as a primary beam in SIMS. Because of the high-density energy deposition and multiple collisions with low energy atoms on the surface, there are much less fragmented ions in the SIMS spectra of large organic materials. This is one of the advantages of massive Ar cluster beams, because many biological samples are crude and contain many similar but different molecules. For instance, when di-stearoyl-phosphatidyl-choline (DSPC), which is generally the most abundant lipid in animal cell membranes, is measured with SIMS, fragmented ions (184 Da) as well as protonated secondary molecular ions (791 Da) are detected. The ratio of fragmented ions to molecular ions measured with massive Ar cluster beams is around 10, which is two orders lower than the ratio measured with Bi₃ ion beam. One of the technical problems of massive Ar cluster beams was the difficulty of obtaining a short-pulsed beam, because of the large mass distribution. We have developed a TOF-SIMS mass spectro meter system with orthogonal acceleration (oa-TOF), which allows use of a continuous beam. The mass resolution of this system is better than 16,000, which is comparable to the conventional SIMS with pulsed ion beams.

The latest results of massive Ar cluster SIMS will be presented and discussed in comparison with other techniques.

Acknowledgements

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J. Matsuo, S. Ninomiya, H. Yamada, K. Ichiki, Y. Wakamatsu, M. Hada, T. Seki and T. Aoki, *Surf. Interface Anal.* (2011) 42, 1612

5:20pm **AS-MoA11 Dissociation of Argon Cluster Ions by Impact on Metal Surfaces**, *K. Mochiji*, *N. Inui*, *K. Moritani*, University of Hyogo, Japan

Argon cluster ions, typically consisting of hundreds to thousands of argon atoms, have been used in nanometer-scale fabrications such as thin film deposition or primary ion source for SIMS. The average kinetic energy per atom in the cluster ion is equal to the energy used to accelerate the cluster ion divided by the number of atoms in the cluster ion (called the cluster size). For example, when a cluster of 1000 atoms is accelerated to 5 kV, the average kinetic energy per atom of the cluster ions is only as low as 5 eV. Furthermore, when a cluster ion collides with a surface, chemical reactions such as sputtering or etching of target materials can be occurred within a very thin layer by multiple collisions among the numerous atoms constituting the cluster ion. Such characteristics of the argon cluster ion are strongly effective to low damage and high throughput processing.

In this study, we have investigated the dissociation of an argon cluster ion by the impact on material surfaces. The ion emission from the target material by the bombardment of the argon cluster ions (cluster size: 1000-5000 atoms) was analyzed by a time of flight mass analyzer. Smaller sizes of argon cluster ions were observed in the mass spectra by lowering the kinetic energy per atom of the incident cluster ion below 10 eV/atom. The prominent ions were dimer (Ar₂⁺) and trimer ions (Ar₃⁺), but monomer ions (Ar⁺) were not observed. This can be explained as follows. It was reported that the charge of an argon cluster ion is localized on the central three atoms, which forms trimeric ion core and the ion core is much more stable as compared with the shell of neutral argon atoms surrounding the ion core.

Consequently, an argon cluster ion dissociates into many neutral argon atoms and a small argon cluster ion whose size could depend on the impulsive force at the impact. We measured the mass spectra of the dissociated cluster ions by the impact on several kinds of metals. As a result, the mass spectra changed by the metal even at the same bombardment condition. As a degree of dissociation, the ion-yield ratio of $Ar_2^+ / (Ar_2^+ + Ar_3^+)$ was plotted as a function of the stress acting on the contact area between the incident cluster ion and the metal surface, which can be calculated by using the values of elastic coefficient and density of the argon cluster and the metals. The result clearly showed that the ion-yield ratio is linearly increased with the stress. Such the correlation could be used as a new method for measuring the mechanical strength such as elastic coefficient or hardness of metals.

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