Characterization of Thin Films and Materials

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Highlights from the 2016 Microscopy & Microanalysis Meeting in Columbus, OH. A New MS/MS Imaging ToF-SIMS Mass Spectrometer, a Very Low Cost AFM, and a Remote Plasma Cleaning System

We recently attended the 2016 Microscopy & Microanalysis (M&M) meeting held at the Columbus Convention Center in Columbus, Ohio. Columbus is a beautiful, clean city. We arrived the Saturday before the conference and that evening attended a minor league baseball game (Columbus Clippers). The home team won. Both pictures above are from the trip, and the picture of MRL was taken at the game.

The M&M conference is an excellent meeting for anyone working in the fields of microscopy, microanalysis, and thin film characterization. The conference ran from July 24 – 28, 2016 and each day featured 3 parallel sessions with topics such as advances in instrumentation and microscopy in the biological and physical sciences. There were great posters in the evenings on a myriad of topics, including microfabrication, image processing, and nanomaterials. SC gave a poster entitled: "Polyallylamine as an Adhesion Promoter for SU-8 Photoresist". MRL gave an invited talk on "New Data Analysis Tools for X-Ray Photoelectron Spectroscopy (XPS) and Spectroscopic Ellipsometry (SE): Uniqueness Plots and Width Functions in XPS, and Distance, Principal Component, and Cluster Analyses in SE". These are topics we have recently published on in the Linford group.[1-4]

Many of the sessions encouraged student participation and there were a number of student awards. In our experience, M&M 2016 drew an exceptional group of scientists and engineers. The next M&M annual meeting will be in St. Louis, MO. We hope to see you there.

In general when we go to conferences we spend some time in the exhibition hall. This is a great way to find out about what's new. Indeed, because our ability to synthesize and characterize many of the materials we work with depends on the process and analytical tools at our disposal, thin film and material characterization are never far from advanced instrumentation. Accordingly, we extended an invitation to a few of the vendors at M&M 2016 to provide us with information we might use in a ***VT&C*** article. Three of them sent us the content that we based this article on. Of course we were not able to visit most of the booths at the conference, and we do not wish any vendors to feel like the lack of an invitation to contribute to this article is in any way a judgment of their product. We are not trying to endorse any products here. Finally, in the spirit of our earlier articles, we hope to provide a technical/tutorial view and commentary of the science and technology behind the products we will be discussing.

TOF-SIMS Parallel Imaging MS/MS

Company:

Physical Electronics
(a division of ULVAC-PHI)

Company Website:

www.phi.com/physical-electronics.html

Company Contact:

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Company Overview:

According to the company, "Physical Electronics (PHI) is a subsidiary of ULVAC-PHI, the world's leading supplier of UHV surface analysis instrumentation

used for research and development of advanced materials in a number of high technology fields including: nanotechnology, microelectronics, storage media, bio-medical, and basic materials such as metals, polymers, and coatings. PHI's innovative XPS, AES, and SIMS technologies provide our customers with unique tools to solve challenging materials problems and accelerate the development of new materials and products."

Product Description:

At the time of its introduction in the 1980's, Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) was principally a surface analysis research instrument. It provided elemental ion and limited molecular fragment ion spectra and images of the outer layers of solid materials. TOF-SIMS is based on the impact of a finely focused, raster-scanned ion beam on the surface of the sample and the time-of-flight mass analysis of the ejected secondary ions (SIMS). Since its initial successes, TOF-SIMS has evolved into a more powerful technique for spectroscopy and imaging of molecular fragment ions. This has been achieved, in part, by two orders of magnitude improvement in higher mass ionization efficiencies. Improved spatial focusing of the primary ion beams has also improved the ultimate spatial resolution observed for TOF-SIMS imaging of molecular fragment ions.

All of these advances have expanded the breadth of applications, most notably the use of TOF-SIMS for analyzing organic contamination, tissue cross sections, pharmaceuticals, and polymer surfaces with sub-micron spatial resolution. Nevertheless, the limitation of organic molecular fragment compositional peak assignments, based on TOF mass resolutions of up to 16,000 m/Δm and mass accuracies of ca. 10 to 20 ppm for current state-of-the-art TOF analyzers, has created ambiguity for many of the peak assignments above 200 m/z (for either positive or negative polarity ions). That is, there is uncertainty in peak assignments because the TOF mass spectrometers have traditionally had good, but not great, mass resolution, and as the molecular weight of a fragment increases the number of possible ways the elements can be combined to make a fragment of the same mass becomes enormous. Today, analyses routinely produce secondary ion masses well over 2,000 m/z. Clearly, to further extend the technique an advance is needed in the data acquisition of higher mass molecular ion fragments in order for TOF-SIMS to reach its full potential for unambiguous compound identification and ease of data interpretation. This is particularly important for cellular and sub-cellular biological tissue analysis, as well as micro-features on polymers, biomaterials and other organic materials.

To provide this needed paradigm shift, Physical Electronics has designed a revolutionary new TOF-SIMS Parallel Imaging MS/MS. Results from this unique and patented instrument[5] were presented at the Microscopy and Microanalysis Conference in Columbus, Ohio – John Hammond gave a talk on it. The newly developed TOF-TOF tandem imaging mass spectrometer system allows conventional TOF-SIMS (MS1) analysis and product ion (MS/MS or MS2) analysis to be acquired simultaneously and in parallel. Secondary ions for MS1 and MS2 analysis are produced from the same area of the surface by a pulsed and digitally raster-scanned primary ion nanoprobe. Activation of the precursor ions, defined by a 1 Da precursor selection window, is accomplished by a 1.5 keV Collision-Induced-Dissociation (CID) cell using Ar gas. Lateral resolutions produced in both MS1 and MS2 images were shown in the presented research to be < 200 nm. The MS2 fragment spectra from a sample of pure Crystal Violet demonstrates that the 1 Dalton wide precursor selection window can eliminate or select ^{13}C-containing precursor peaks, providing enhanced MS2 data from samples with complex mixtures of additives on the surface. This data bodes well for imaging of lipids and metabolites from tissue samples. The MS2 fragment ion spectra also demonstrate better than 10 ppm mass accuracy for the identified peaks. The conversion efficiency of precursor ion peaks to the spectrum of fragment ion peaks is, on average, better than 10%.

A schematic of the PHI nanoTOF II imaging MS/MS is shown in **Figure 1**. The system design allows simultaneous MS and MS/MS imaging up to 8 kHz, allowing MS1 and MS2 imaging and spectroscopy in less than 15 minutes. **Figure 2** shows a negative polarity MS2 spectrum of the Erucamide polymer additive precursor molecular ion. This spectrum allows the structural identification of the location of

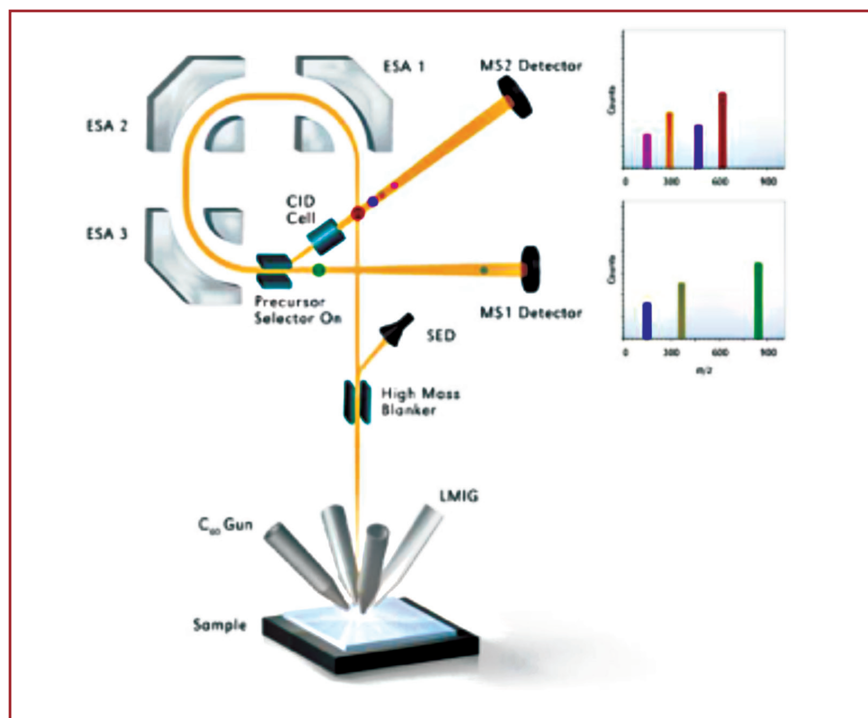

Figure 1. Schematic of the Phi TOF-SIMS Imaging MS/MS instrument. Figure obtained and used with permission from Phi (www.phi.com).

Figure 2. MS/MS spectrum of the *m/z* 336 erucamide precursor ion. Figure obtained and used with permission from Phi (www.phi.com).

Figure 3. MS1 images and MS/MS (MS2) images from positive polarity m/z 577 precursor ions from a heat treated PET film. Figure obtained and used with permission from Phi (www.phi.com).

Figure 4. (**a**) MS1 image of granulomas from the cross-section of an infected spleen of a Zebrafish, (**b**) and (**c**) the MS2 images of the fatty acid (16:0) distribution, (**d**) 0.8 micron spatial resolution of the elevated fatty acid intensities. Figure obtained and used with permission from Phi (www.phi.com).

the double bond. **Figure 3** shows the MS1 images for a heat-treated polyethylene terephthalate film and the MS2 images from the positive polarity 577 m/z precursor ions. The simultaneous MS1 and MS2 imaging of the heat-treated PET sample confirmed that the crystal structure on the surface of the PET has a cyclic trimer structure. The MS1 images and MS2 images derived from the CID activation of the positive polarity 577 m/z precursor show that the crystal images are in exact registry with one another. Line scans (80% to 20% intensity) show <200 nm spatial resolution for both modes of imaging. **Figure 4a** shows the MS1 image for the granulomas in the cross-section of the spleen of Zebrafish infected with Mycobacterium Marinum (a form of marine tuberculosis). **Figure 4b** and 4c show the elevated MS2 intensities of fatty acids (FA 16:0) around the granulomas, thought to be the result of metabolism of lipids in the macrophages trying to attack the infection in the granulomas. The spatial resolution of the elevated fatty acids observed in the MS2 image is 0.8 microns in **Figure 4d**.[6]

These results confirm that TOF-SIMS Imaging MS/MS can now provide easy and unambiguous molecular fragment ion peak identification and fast parallel imaging with MS1 and MS2 data. Further information can be obtained at www.phi.com.

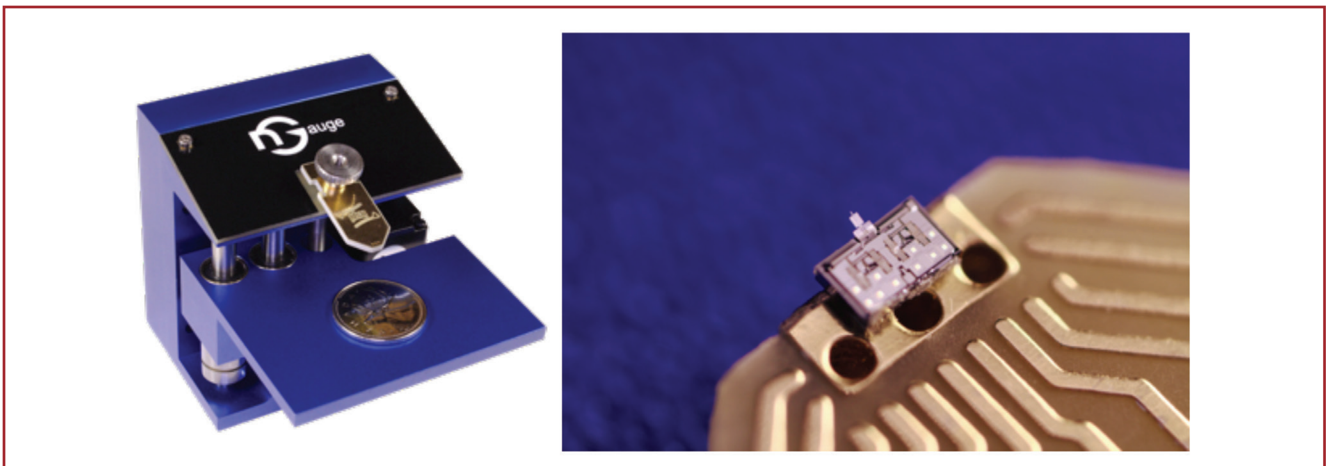

Figure 5. The nGauge AFM system (left) is a compact instrument that includes a coarse approach mechanism, an AFM chip, and integrated electronics. The CMOS-MEMS chip (right) is bonded to a printed circuit board that is easy to handle. Figure obtained and used with permission from ICSPI Corp.

Low cost Atomic Force Microscope (AFM), the nGauge AFM

Company:

ICSPI Corp.

Company Contact:

info@icspicorp.com

Company Overview:

According to the company, "Integrated Circuit Scanning Probe Instruments (ICSPI, pronounced "icy spy") is a Microsystems company that was spun off from the University of Waterloo to produce the first single-chip Atomic Force Microscope (AFM). After nearly 10 years of research into CMOS-MEMS technology, the company has developed an AFM so small that one would need another microscope just to see it. Through miniaturization and integration they are making this powerful instrument more accessible to those who can benefit most from it, while enabling new applications for experienced users. This technology is being commercialized as a small, simple, affordable desktop tool called the nGauge AFM."

Product Description:

According to the company, the nGauge AFM is the smallest, simplest, and most affordable AFM on the market. The X/Y/Z scanners, the sensors, and the sharp tip of an AFM have all been integrated into a single 1 × 1 mm MEMS chip. Apart from a coarse approach mechanism, this chip is the entire AFM. Extremely precise MEMS actuators provide sub-nanometer positioning while integrated piezo resistive sensors provide precision low-noise measurements. Unlike a conventional AFM which has large external scanners, a complex laser alignment system, miniscule probes to exchange, and a large vibration isolation system, the entire nGauge AFM uses a single-chip AFM and some small, low-cost hardware to achieve results comparable to machines that cost 100x more. The software, mechanical drawings, and electrical design will be open-sourced.

Remote Plasma Cleaning System

Company:

XEI Scientific, Inc.

Company Website:

www.evactron.com

Company Contact:

sales@evactron.com

Company Overview:

According to the company "XEI invented and introduced the Evactron® Decomtaminator in 1999. It is the industry standard for remote plasma cleaning of scanning electron microscopes (SEMs), focus ion beams (FIBs), and vacuum chambers to remove hydrocarbons from chamber and specimen surfaces. Over 2400 Evactron plasma cleaners have been sold and XEI is now shipping its 4th generation of Evactron products." As an aside, we have an Evactron plasma system on our XPS at BYU.

Product Description:

The Evactron® EP model was demonstrated at the Microscopy and Microanalysis Conference. It features high vacuum start and operation, the highest Evactron hydrocarbon removal rates, dual mode UV plus oxygen radical cleaning, and a small plasma source. The plasma source has a simple on/off start and blutooth Android tablet control to call up pre-programmed recipes. Cleaning times are typically 1 – 5 minutes, and clean columns exhibit speedy pump down times.

The technical program of the M&M conference showed how Evactron® plasma cleaning has become an indispensable tool for advanced SEM technologies.[7] For example, low-energy energy dispersive X-ray spectroscopy (EDS) is now practical because there is no carbon absorption of soft x-rays in clean chambers.[8] Accurate electron energy loss (EELS) measurements also require a carbon-free environment. Electron backscatter diffraction (EBSD) sensitivity degrades if low energy backscatter signals are absorbed by carbon. Long scans must not redeposit carbon on nanoprobes from contaminated chamber or sample surfaces. Backscatter electron detectors can be cleaned by plasma instead of being replaced, saving

Figure 6. Picture of the Evactron® EP with controller. Figure obtained and used with permission from XEI Scientific.

time and money. Hydrocarbons must be prevented from condensing on specimens and interfering with imaging during cryo-SEM experiments. These examples and others have become practical on standard commercial SEMs with the easy availability of Evactron plasma cleaning. Papers mentioning plasma cleaning as a prerequisite were found in many sessions at the conference.

The Evactron EP and ES models and the more flexible Zephyr model have enabled TurboPlasma™ cleaning at the 1 to 40 millitorr range when using a turbo molecular pump (TMP) pumping system. TurboPlasma cleaning brings the "Fastest way to Pristine" using both UV light from a flowing afterglow plus the oxygen chemical etch of remote plasma cleaning. Tests with a RGA (residual gas analyzer mass spectrometer) show that heavy contamination with hydrocarbons can be removed in less than 10 minutes to less than 10^{-9} Torr. The Evactron EP is a compact and simplified model that is easy to operate and less expensive, but retains high performance cleaning.

Acknowledgments

PHI, ICSPI, and XEI have granted to VT&C the right to publish both the text and the images provided to VT&C that are published herein.

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