

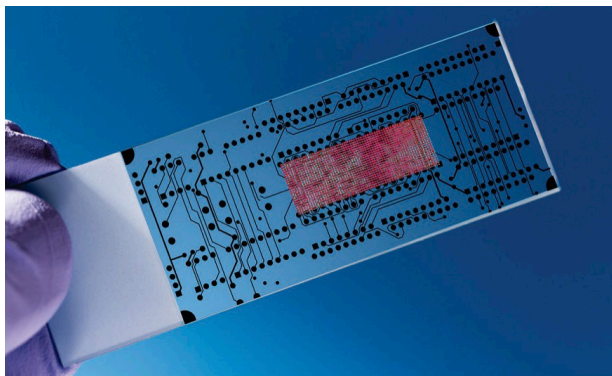
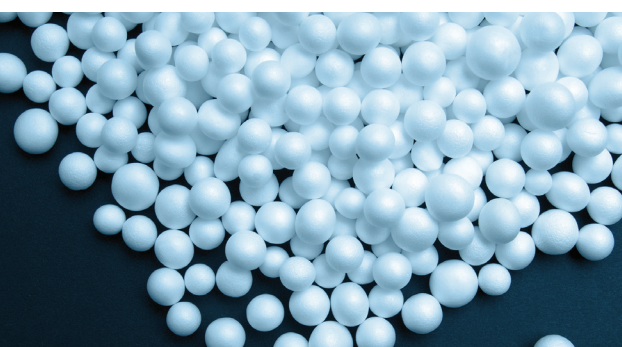
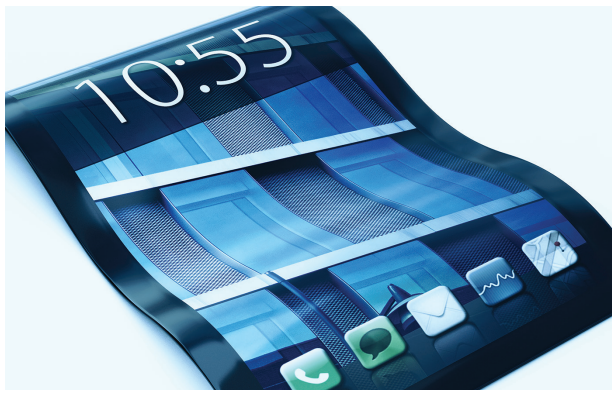
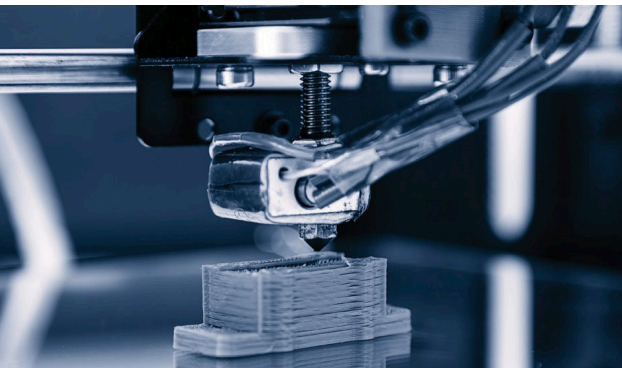
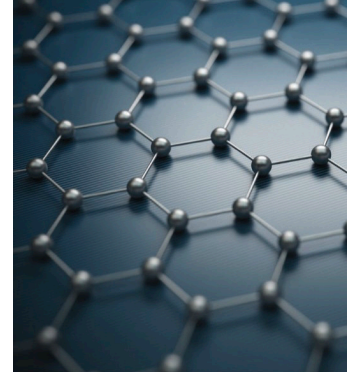
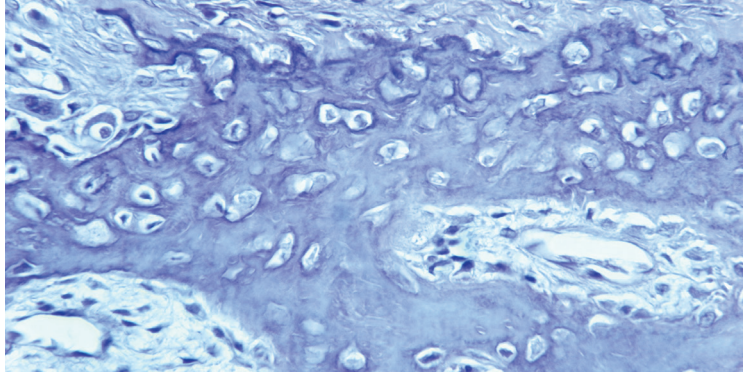
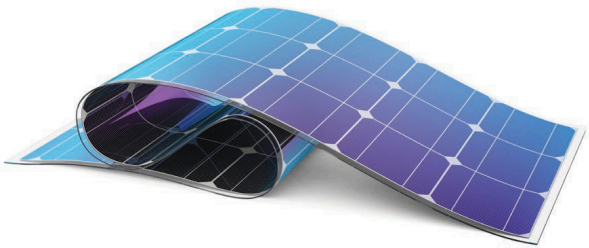


PHYSICAL
ELECTRONICS
A DIVISION OF ULVAC-PHI

U.S. PATENT NO.
5,128,543
ISSUED 7 JULY 1992

PHI nanoTOF 3

Parallel Imaging MS/MS

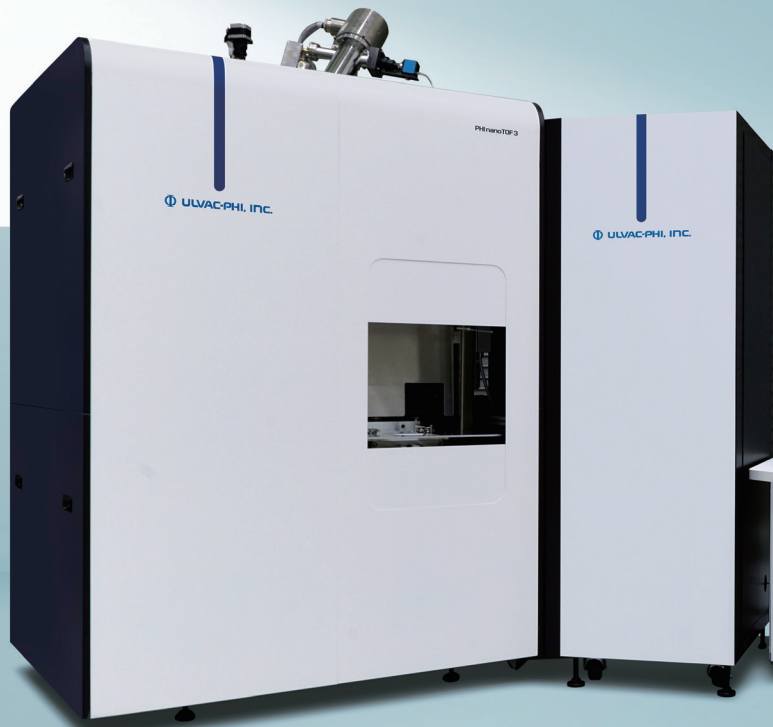


PHI nanoTOF 3

Why TOF-SIMS?

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is a key analytical technique for detecting, identifying, and imaging the distribution of both elements and molecules on the surface of materials. TOF-SIMS is the only mass spectrometry imaging technique that provides less than 50 nm spatial resolution with full mass range detection. The PHI *nanoTOF* 3 Parallel Imaging MS/MS platform has established itself as uniquely capable of providing superior analytical data, even on the most challenging samples. The *nanoTOF* 3 incorporates PHI's revolutionary Parallel Imaging MS/MS mass spectrometer technology into the base system. This patented spectrometer dramatically simplifies TOF-SIMS data interpretation and peak identification without compromising spatial resolution and speed. For the first time, confident identification is possible for high mass ions, transforming peak identification from "*I think*" to "*I know!*"

PHI nanoTOF 3



PHI nanoTOF 3

Designed for Confident Molecular Identification and Superior Imaging

The PHI *nanoTOF* 3 Parallel Imaging MS/MS instrument was designed with “*No Compromise*” in mind ensuring that there are no compromises in analytical performance. The synergistic design optimizes and combines multiple performance metrics into straight forward modes of analysis. It provides high lateral resolution and high mass resolution simultaneously in the HR² mode of analysis. The patented mass spectrometer provides superior imaging of highly topographic samples and high mass resolution spectra with excellent mass accuracy over the entire mass range. PHI’s integrated MS/MS enables confident peak identification and delivers high speed TOF-TOF mode imaging at > 8 kHz. The sample stage provides full 5-axis sample motion with active temperature control. Productivity is maximized with a high level of automation and intuitive software.

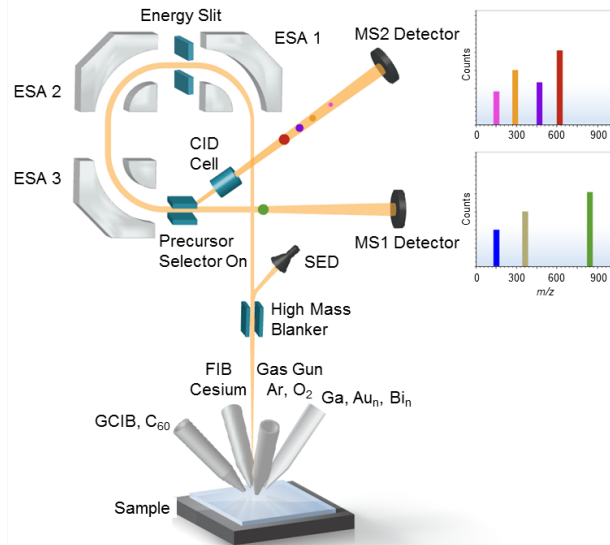
Another *REVOLUTION* from PHI. Not just functional flexibility, but confident answers!!

- Patented pulsed dual-beam charge neutralization for truly turn-key insulator analysis
- Combination of proven stage, sample parking & software queue for continuous automated measurements
- Bi cluster emitter with smaller beam diameter for improved high-throughput HR² imaging analysis
- Modern ergonomic design, reduced footprint and reduced power consumption

TANDEM MASS SPECTROMETERS

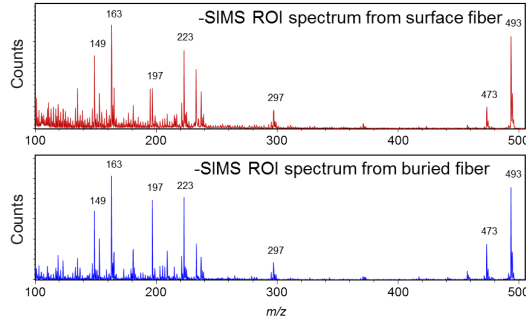
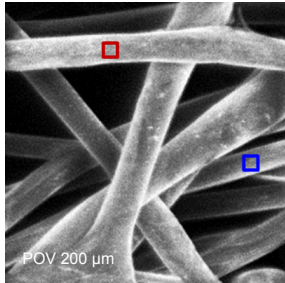
Maximum 2D/3D Information Content

No compromise provides the capability for parallel and synchronous TOF-SIMS (MS^1) and tandem MS (MS^2) imaging. Never before has tandem MS imaging been available at the < 50 nm spatial resolving power provided by TOF-SIMS. The revolutionary and patented PHI Parallel Imaging MS/MS provides the maximum mass spectrometry imaging information, with unequivocal molecular identification, from any specified analytical region. Since the TOF-SIMS and tandem MS data are collected simultaneously and from the same volume, the MS^1 and MS^2 images are always in perfect registry. The elegant and fully integrated Parallel Imaging MS/MS spectrometer provides peak identification and imaging in a single analysis.



The schematic highlights the triple electrostatic analyzer (ESA) design of the *nanoTOF 3*'s Parallel Imaging MS/MS spectrometer. Selected precursor ions are deflected at keV energy into a collision-induced dissociation (CID) cell for fragmentation. The product ions are collected at the MS2 detector. Any ions not within the monoisotopic precursor selection window continue on their original flight path to the MS1 detector.

UNMATCHED PERFORMANCE



A gray-scale total ion image of a non-woven fiber mat. A region-of-interest (ROI) of a surface fiber is highlighted in red, and an ROI of a buried fiber is highlighted in blue. Irrespective of the sample topography and height, the spectral performance is almost identical owing to the exceptional depth-of-field of the mass spectrometer.

Confident Chemical Analysis of All Samples

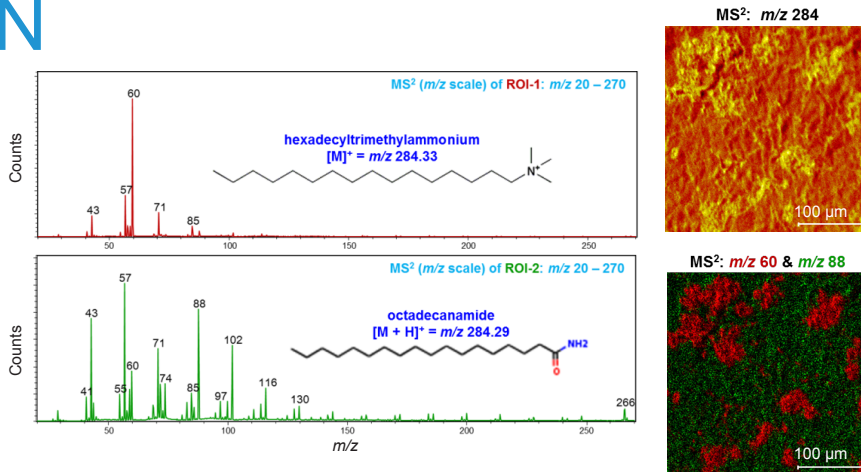
No compromise is apparent in the uncompromising performance of PHI's Parallel Imaging MS/MS spectrometer. The mass spectrometer provides high collection efficiency, high mass resolution, high mass accuracy and high signal-to-background spectra, simultaneously, for chemical imaging of flat and rough samples alike. Accurate elemental and molecular imaging of highly topographic, textured and FIB-sectioned samples is a unique capability due to the spectrometer's TOF-TOF optics design.



PARALLEL IMAGING WITH IDENTIFICATION

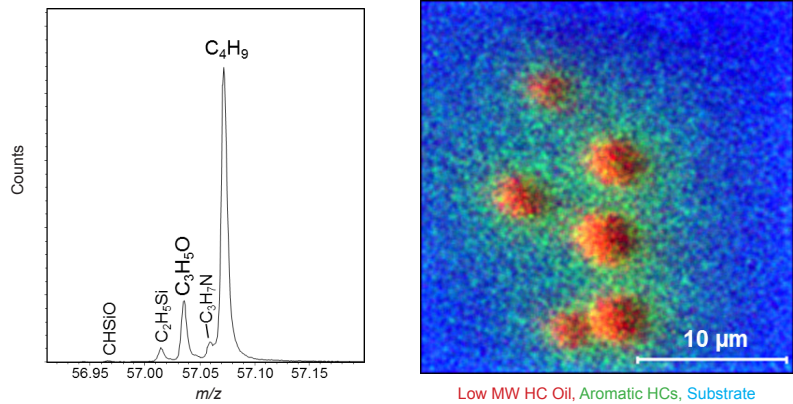
High Speed Imaging and Identification

No compromise delivers ion identification, structural elucidation, and high resolution imaging within a tandem MS analysis. PHI's TOF-TOF spectrometer enables the generation of pure, single-molecule spectra from the complex mixture spectrum which greatly simplifies data interpretation and peak identification. Molecular identification and imaging are achieved at the highest sensitivity; therefore, one-of-a-kind samples may be probed repeatedly for identification of numerous molecular precursors. PHI's Parallel Imaging MS/MS takes TOF-SIMS peak identification from "I think" to "I know!"



The power of Parallel Imaging MS/MS for molecular identification via tandem MS imaging is demonstrated in the chemical separation of two precursor ions both having a nominal m/z of 284. In only a 10 minute acquisition, each molecular component is easily observed in the MS² overlay shown in the lower right image. Mass spectra are generated from each region-of-interest (ROI), comprised of either the red or the green pixels, and the corresponding spectra are shown to the left. The composition and identification of each molecule is made by reference library matching.

HR² IMAGING CLUSTER LMIG



The power and utility of HR² mode imaging is exemplified in the surface analysis of micro-droplets. In only a 6 minute acquisition the micron-sized droplets are spatially resolved, and the high mass resolution spectrum allows molecular identification.

Simultaneous Spatial and Spectral Resolution of Chemistry

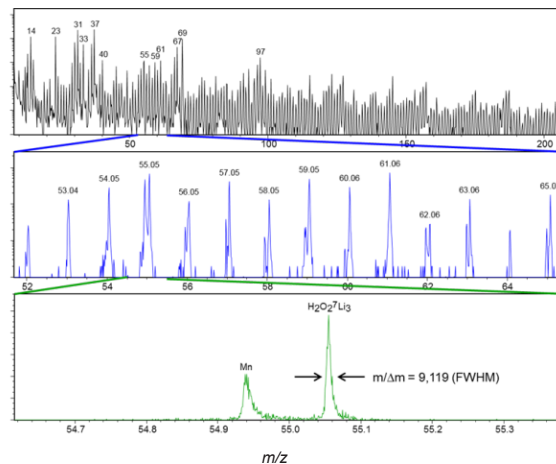
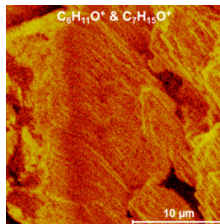
No compromise is easily illustrated by the PHI cluster liquid metal ion gun (LMIG) that is designed to optimize performance in the HR² mode of analysis. This analysis mode provides high spatial resolution imaging and high mass resolution spectra in a single analysis. What's more, the HR² mode is realized using a high analytical beam current so that a typical analysis is conducted in only a few minutes. Now it is not necessary to choose between optimized imaging or spectroscopy; PHI's unique HR² mode of operation gives you both in a single rapid analysis.



FIB-TOF IMAGING

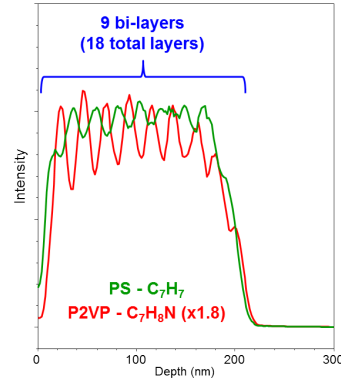
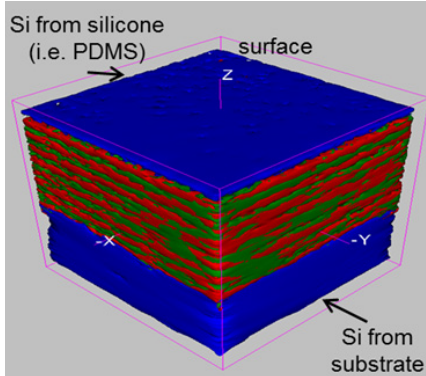
2D/3D Characterization of Challenging Specimens

No compromise spectrometer design ensures that *in situ* sectioning and 3D tomography, via the dedicated PHI FIB option, results in superior TOF-SIMS chemical imaging. Porous and multi-phase materials which are not amenable to traditional sputter depth profiling are readily characterized by FIB-TOF analysis. Full range mass spectra, collected at high mass resolution, high mass accuracy and with excellent signal-to-background (S/B), enable robust chemical imaging of the FIB sidewall. The quality of the spectrum over the entire analytical mass range, combined with uniform collection efficiency over the depth of the FIB section, provides an unmatched capability for high resolution 2D and 3D imaging.



A TOF-SIMS image, collected in 5 minutes using the HR² mode of analysis, of a FIB-sectioned lithium ion battery anode showing the distribution of $C_6H_{11}O^+$ (m/z 99) and $C_7H_{15}O^+$ (m/z 115) ions. The lateral resolution was measured to be ≤ 150 nm in both ion polarities. The spectra demonstrate excellent signal-to-background and high mass resolution for full chemical and isotopic characterization.

GCIB CLUSTER ION BEAM



A depth profile of a poly(styrene)/poly(2-vinyl pyridine) (PS/P2VP) copolymer blend approximately 200 nm-thick on a Si substrate. The profiles and 3D image data expose the 3-dimensional structure and composition.

Non-Destructive Organic Depth Profiling

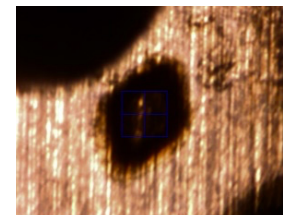
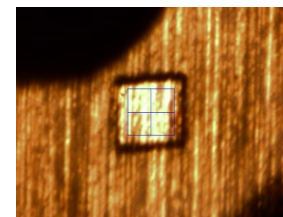
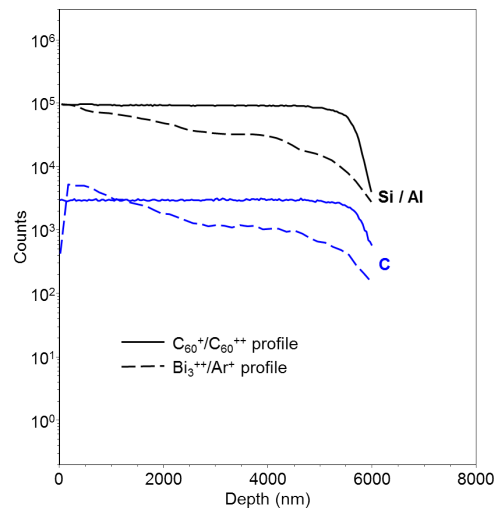
No compromise equips the analyst with tools for in-depth, non-destructive characterization of organic and molecular specimens without sacrificing resolution or molecular specificity. The PHI gas cluster ion beam (GCIB) option may be used for surface cleaning prior to analysis and for rapid 3D characterization to tens of microns in depth. For the characterization of multi-layer materials, the ultimate layer resolution may be realized while also making full use of the HR² mode for high resolution molecular imaging.



C₆₀ CLUSTER ION BEAM

Profiling and Imaging with Minimum Artifacts

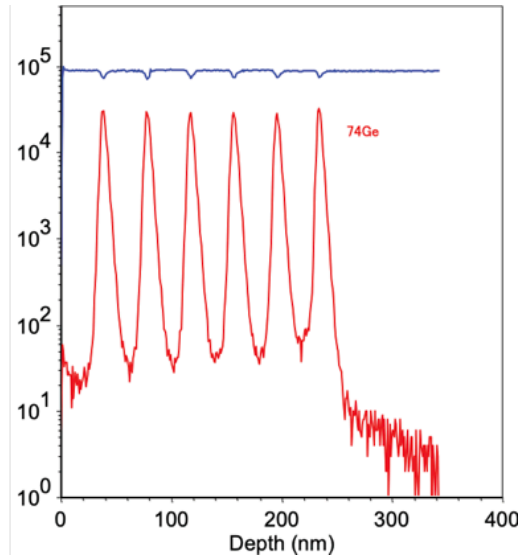
No compromise engineering provides advanced ion beams to address complex analytical problems. The PHI C₆₀ gun option is a uniquely effective beam for sputter depth profiling of inorganic and mixed composition materials and may be used in an interleaved fashion as a beam for analysis. Interface transients and differential sputtering are greatly reduced with C₆₀ compared to monatomic sputter ion beams.



(LEFT) Depth profiles of a 6 μm-thick aluminosilicate sol-gel on copper by Ar and C₆₀ sputtering. The C₆₀ ion beam does not produce the differential sputtering artifacts produced by the Ar ion beam. Additionally, the C₆₀ analysis beam does not produce the surface transient artifact that is produced by the Bi analysis beam.

(TOP-RIGHT) The 40 keV C₆₀ sputter beam provides uniform sputtering through the 6 μm-thick aluminosilicate sol-gel which is highlighted by the smooth, reflective sputter crater. (BOTTOM-RIGHT) By contrast, the 5 keV monatomic Ar sputter beam produces a rough sputter crater as indicated by the scattered light.

DEPTH PROFILING Cs⁺ BEAM



A depth profile of a multi delta layer (MDL) sample of Ge in Si was acquired using a 30 keV Bi⁺ primary ion beam (50 μm square raster) and a 1 keV Cs⁺ sputter ion beam (200 μm square raster). The Ge delta layers are 0.4 nm thick.

High Current Density with Rapid Low-Voltage Sputtering

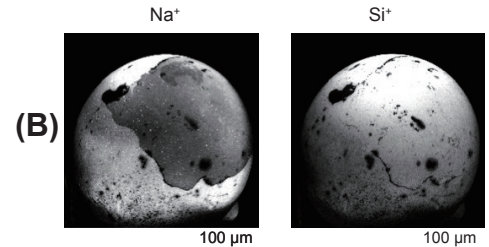
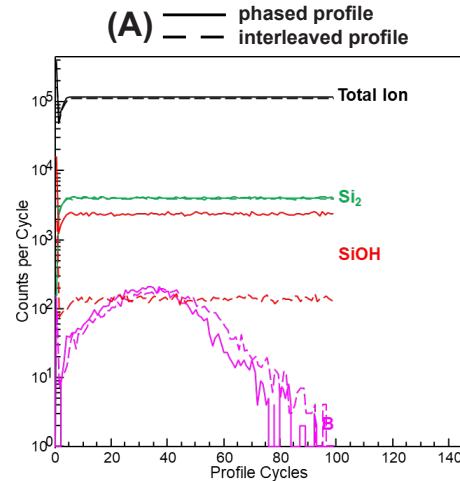
No compromise is demonstrated by PHI's 2 kV Cs⁺ sputter beam column. The column is designed and optimized to deliver maximum current at low beam voltage into a small beam diameter. The increased current density improves the sputter efficiency for rapid depth profiling even at low beam voltage. The low accelerating voltage is required for accurate characterization of today's electronic designs which incorporate shallow junctions and dopant implants because at low voltage the interlayer mixing is minimized. What's more, the improved current density enables profiling of single features, such as bond pads, without eroding nearby features.



PULSED Ar^+/O_2^+ FOR PROFILING & NEUTRALIZATION

Pulsed Gas Gun for Low-Voltage Sputtering and Turn-key Insulator Analysis

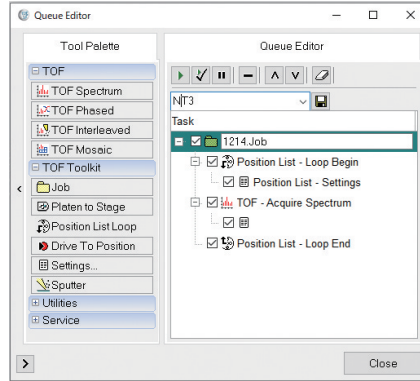
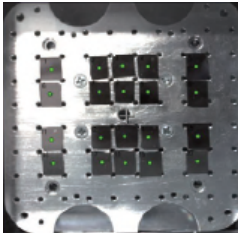
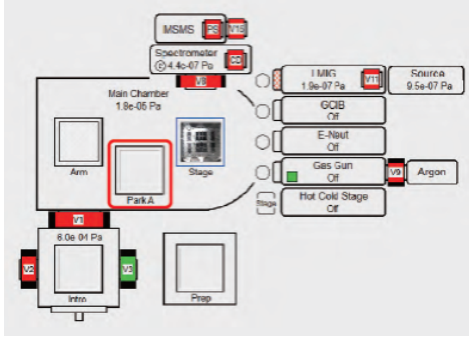
No compromise is demonstrated by the new pulsed Gas Gun column which can be used for both interleaved (interlaced) depth profiling and pulsed charge neutralization. The column is configured to deliver maximum current at low beam voltage into a small beam diameter. The increased current density improves the sputter efficiency for rapid depth profiling even at low beam voltage. The high frequency pulsing of the sputter beam improves the sensitivity toward, and data density across, ultra-thin interfaces. The high frequency pulsing also enables robust and truly turn-key charge neutralization even in the negative ion polarity.



(A) A depth profile comparison of a B-implant reference acquired using a Bi^+ primary ion beam and an O_2^+ sputter ion beam. The phased (noninterlaced) profiles are shown in solid lines, and the interleaved (interlaced) profiles are shown in dashed lines. Note that the Si_2^+ matrix signal is the same for both profiles, as expected, but the interleaved SiOH^+ signal (dashed red) is reduced owing to the reduced adsorption of hydrogen from the background gases.

(B) In a separate experiment the entire 420 μm -diameter of an insulating sapphire sphere is observed with uniform signal collection due, in part, to the pulsed dual-beam charge neutralizers. The distribution of the Na^+ and Si^+ ions are shown in the gray-scaled ion images.

CONTINUOUS AUTOMATED TOF-SIMS MEASUREMENT



The system glyph (top-left) indicates the sample stage position and the navigational image of the active sample platen. The navigational image (bottom-left) shows each sample and each analysis position. The Queue Editor (right) is used to specify the analysis, or analyses, at each position of each specimen loaded onto the sample platen.

Automated Sample Stage, *in vacuo* Sample Parking, & Software Control

No compromise enables the continuous and automated measurement of large numbers of samples. The *nanoTOF 3* is equipped with a robust sample stage and automatic sample transfer mechanism that has been proven in more than 300 of PHI's Q-series XPS instruments. The accommodated sample sizes can be up to 100 mm × 100 mm, and the analysis chamber includes a built-in sample park. The Queue Editor allows creation and editing of depth profile, 2D imaging and 3D imaging measurements. The Queue Editor recipes, which may be saved and recalled, include information on the measurement conditions and measurement locations, enabling automated multi-sample and multi-point analysis.



Standard Features

- Parallel Imaging MS/MS mass analyzer
- 30 kV LMIG with Bi, Au, or Ga emitter & HR² imaging
- Pulsed dual-beam charged neutralizers
- *In situ* optical viewing
- Integrated bakeout facilities
- Secondary electron detector
- 5 kV gas gun (Ar only)
- Oxygen flood module
- SmartSoft-TOF instrument control and TOF-DR data reduction software packages
- 5 axis sample stage with in vacuum parking
- Analysis chamber with four ion beam ports & high-throughput turbo molecular pumping

Optional Accessories

- 20 kV C₆₀ ion gun
- 20 kV Ar₂₅₀₀ gas cluster ion gun
- 2 kV Cs ion gun
- 5 kV gas gun (O₂ option)
- 30 kV Ga-FIB gun
- Dual-LMIG operation (for Ga-FIB)
- Hot/Cold stage & intro module
- High temperature stage & intro module
- 25 mm XPS/AES transfer vessel & adapter
- Intro chamber glove box
- Sample preparation chambers