COVALENT METROLOGY

# Welcome

We'll begin at 11:00 AM PT.

# NANOSIMS: HIGH SENSITIVITY IMAGING ANALYSIS FOR DEVICES

SPEAKER:

**Junichiro Sameshima, PhD**

Senior Manager of
Surface Science Laboratory,
Toray Research Center, Inc.

September 22, 2022 | 11am PT

Toray Research Center, Inc.

COVALENT METROLOGY

# COVALENT METROLOGY

Silicon Valley-based analytical labs and platform delivering quality data and expert analysis for advanced materials and device innovation

## Comprehensive Solutions Stack

- 50+ cutting-edge instruments, offering 100+ techniques
- Analytical Services
- Advanced Modeling
- Method Development
- Enterprise Metrology Solutions

## Affordable and Fast

- Fast Turnaround Times
- Volume Savings
- Instant Access to Data and Reports in Secure Portal

## Flexible Business Model

- Custom Consulting Solutions and Certified On-site Support
- Training and Certification on Instrumentation
- Co-op and Tool-Share Opportunities
- Laboratory Audits

## Rich Network of Partnerships

- Partner to the World's Leading Instrument Manufacturers and Labs
- Expanding Instrumentation, Lab Connections, and Learning

## Who We Are, Who We Serve

- 500+ Clients, 40 – 60 Added / Quarter
- 60+ Employees, 14 PhDs
- Cutting-edge Analytical Capabilities
- Silicon Valley Lab based in Sunnyvale, CA

# Covalent Analytical Services

COVALENT METROLOGY

## PCBA, Semiconductor, and Electronic Device Metrology & Failure Analysis

- DPA / Mechanical Cross-section
- Dye & Pry Test
- EBIC / OBIC failure analysis
- Hot Spot Detection
- IR Imaging / Emission Microscopy
- NIR Imaging
- Root-Cause Failure Analysis

## Electron Microscopy and Scanning Probe Microscopy

- AFM & Advanced AFM Modes (EFM, KPFM, MFM, PFM)
- Scanning Acoustic Microscopy (SAM)
- SEM (+ EDS)
- FIB-SEM ( + EDS)
- S/TEM ( + EDS / + EELS )
- Nano-indent / Nano-scratch

## Optical Microscopy & Spectroscopy

- Chromatic Aberration
- Digital Optical Microscopy
- FTIR and ATR-FTIR
- Laser Scanning Confocal Microscopy
- Spectral Ellipsometry
- UV-Vis-NIR Spectroscopy
- White Light Interferometry

## X-Ray Characterization

- X-Ray Diffraction (XRD)
- X-Ray Reflectometry (XRR)
- Micron-spot ED-XRF
- WDXRF
- Micro-computed X-ray Tomography (Micro-CT)
- 2D X-ray Inspection & X-ray Radiography

## Elemental / Chemical Composition Analysis

- EPMA
- GD-OES
- GC-MS
- ICP-MS and LA-ICP-MS
- Raman Microscopy & Spectroscopy
- NMR (1D or 2D; solid / liquid)

## Particle Analysis

- Dynamic Light Scattering (DLS)
- Laser Diffraction Particle Size Analysis (PSA)
- Particle Zeta Potential

## Material Property Characterization

- DSC
- DMA & TMA
- Rheometry
- TGA
- Surface Zeta Potential
- Porometry / Porosity
- Gas Adsorption
- Gas Pycnometry
- Foam Density
- Tap Density

## Surface Spectroscopy Analysis

- Dynamic-SIMS
- ToF-SIMS (Static-SIMS)
- Ion Scattering Spectroscopy (ISS)
- Ultraviolet Photoelectron Spectroscopy (UPS)
- X-ray Photoelectron Spectroscopy (XPS)

# Covalent Partners

*Today's webinar is in partnership with*

**Toray Research Center, Inc.**

- Partnership announced in October of 2021
- Toray Research Center, Inc. provides **unique analytical capabilities** for Covalent clients, including:
  - Rutherford Backscattering Spectroscopy (RBS)
    - High-resolution (HR-RBS) and Micro (Micro-RBS)
  - Cathodoluminescence Spectroscopy
  - **Nanoscale Secondary Ion Mass Spectroscopy (NanoSIMS)**

## Other Covalent Partners

- Rigaku
- JEOL Solutions for Innovation
- ThermoFisher Scientific
- KEYENCE
- Anton Paar
- Teledyne CETAC Technologies Everywhereyoulook
- PVA TePla
- Asylum Research an Oxford Instruments company
- HORIBA Scientific
- J.A. Woollam
- TA Instruments
- Digital Surf

# Introducing

## Dr. Junichiro Sameshima

*Senior Manager of Surface Science Laboratory,*
*Toray Research Center, Inc.*

- Joined Toray Research Center, Inc. in 1997
- 25 years working with SIMS at Toray – especially for semiconductors research
- Has managed the Surface Science Laboratory since 2012 and obtained the role of Senior Manager in 2018
- Earned Ph.D. for *"Structural analysis of SiC power device and annealing effect by Time-of-Flight Secondary Ion Mass Spectroscopy"* from Osaka University in 2019
  - Master's degree in Material Physics Engineering from OSAKA University (1997)

'TORAY'
Innovation by Chemistry

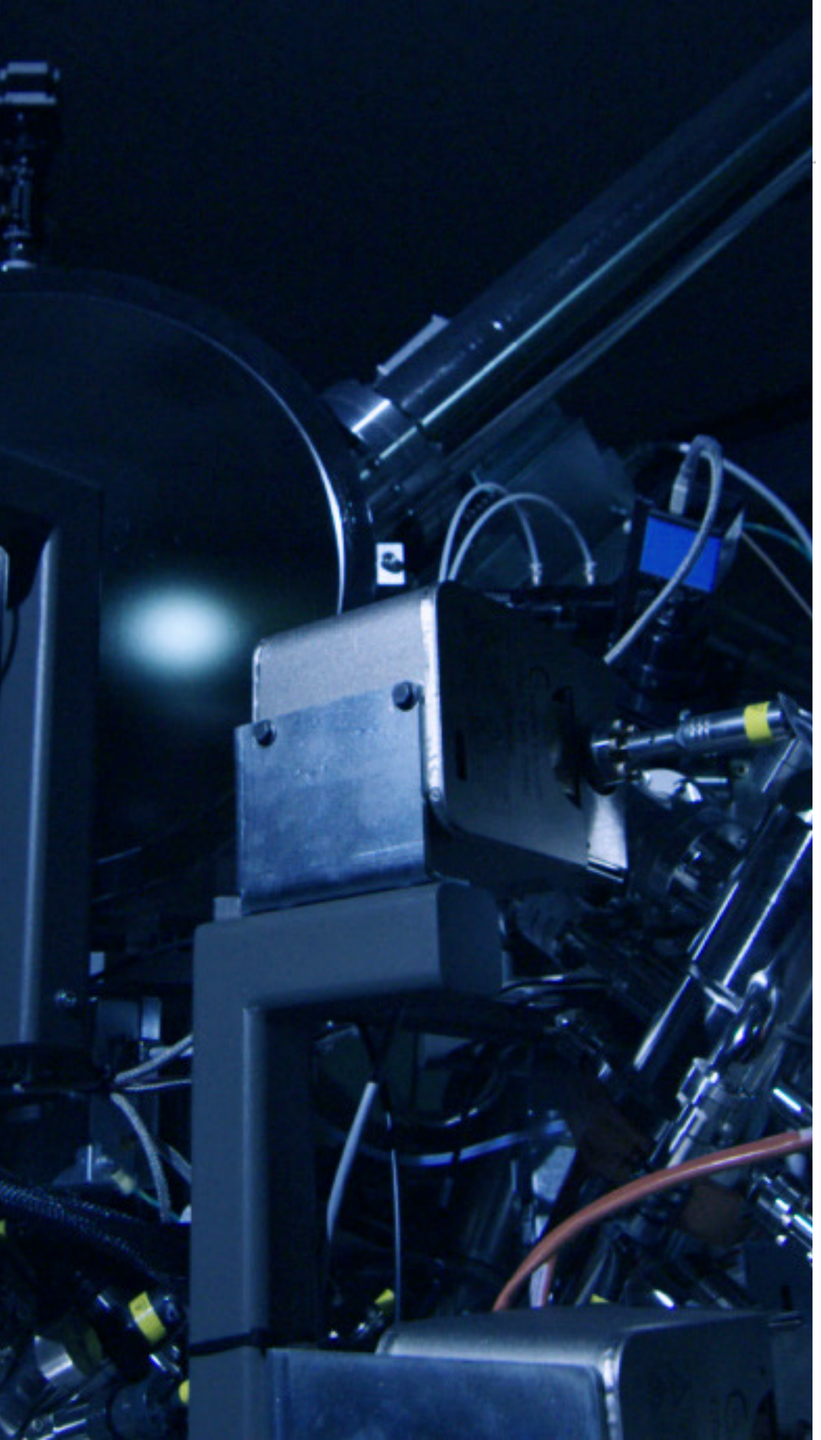
# High sensitivity imaging analysis for devices using NanoSIMS

Junichiro Sameshima, Ph.D

Surface Science Laboratory,
Toray Research Center, Inc.
Email: junichiro.sameshima.q8.trc.toray

# Contents

- Introduction to Toray Research Center
- NanoSIMS operational performance
  - Basic performance
  - Advantages over conventional SIMS and other analytical techniques
- Example NanoSIMS applications
  - Semiconductor devices (SiC-MOSFET, 3D NAND flash memory, SRAM)
  - Implanted phosphorous in Si sub.  (Quantification)
  - Li-ion Battery (LTO coating, Li-dendrite on carbon negative electrode)
- Wrap-up



# Overview

## Toray Industries, Inc.

Established in 1926 / Turnover of US$ is 22.5 billion

Developing and manufacturing advanced materials related to Organic Synthetic Chemistry, Polymer Chemistry, Nano & Biotechnology

## Toray Research Center, Inc.

Established in 1978 / Headquartered in Tokyo, Japan

Labs at Shiga (Central), Kamakura and Nagoya with 530 employees

A professional analytical service provider with 40+ years of accumulated experience

**01** Analytical Services

Using latest analytic equipment by experienced skillful specialists

**02** Contract R&D support

In the fields of Automobile, Displays, Semiconductor and Advanced materials., etc.

# Locations

## SOUTH KOREA

Anyang – KTS Global (Sales)

## UNITED STATES

Fort Wayne, IN
US Agency (Sales)

## GERMANY

Munich – AMCEU (Lab)

## JAPAN

Tokyo – Head Office, Sales Office
Shiga – Central laboratory of TRC
Comprehensive Analysis & Evaluation, Sales Office
Nagoya – Pharmaceutical(GMP) Sales Office
Kamakura – Bio & Pharmaceutical (GLP)
Fukuoka – Sales Office

## CHINA

Shanghai – TRCS (Sales, Lab)

## TAIWAN

Taichung – TITP (Sales)

# Major Targets

Materials

Semiconductor
& Packaging

Displays
& IT Equipment

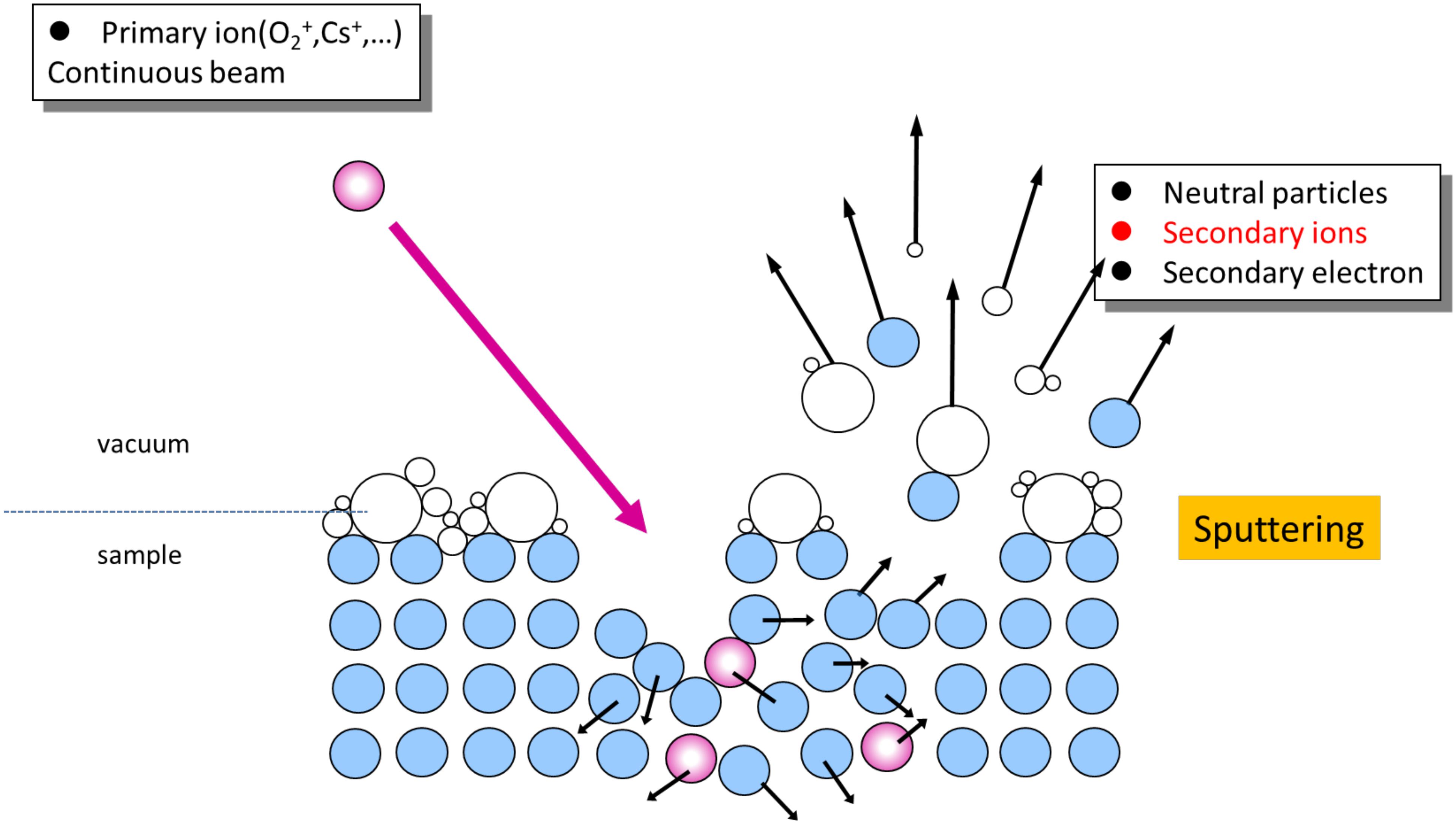
Batteries

Automobile
& Aerospace

Life Science

- Introduction to Toray Research Center
- NanoSIMS operational performance
  - Basic performance
  - Advantages over conventional SIMS and other analytical techniques
- Example NanoSIMS applications
  - Semiconductor devices (SiC-MOSFET, 3D NAND flash memory, SRAM)
  - Implanted phosphorous in Si sub. (Quantification)
  - Li-ion Battery (LTO coating, Li-dendrite on carbon negative electrode)
- Wrap-up

# Principles of SIMS



## General features of SIMS

**Pros:**

- All Elements ( from H up to U ) can be detected (in principle)
- Highest sensitivity (down to ppb levels) among other surface analytical techniques
- Both 2D and 3D ion imaging are available
- Elements contained in the sample can be quantified using a reference Standard
- Isotopic composition analysis is possible due to high mass resolution

**Cons:**

- Destructive analysis
- "Matrix effect"

  Large difference on ionization probability depending on materials and elements



'TORAY' Toray Research Center, Inc.

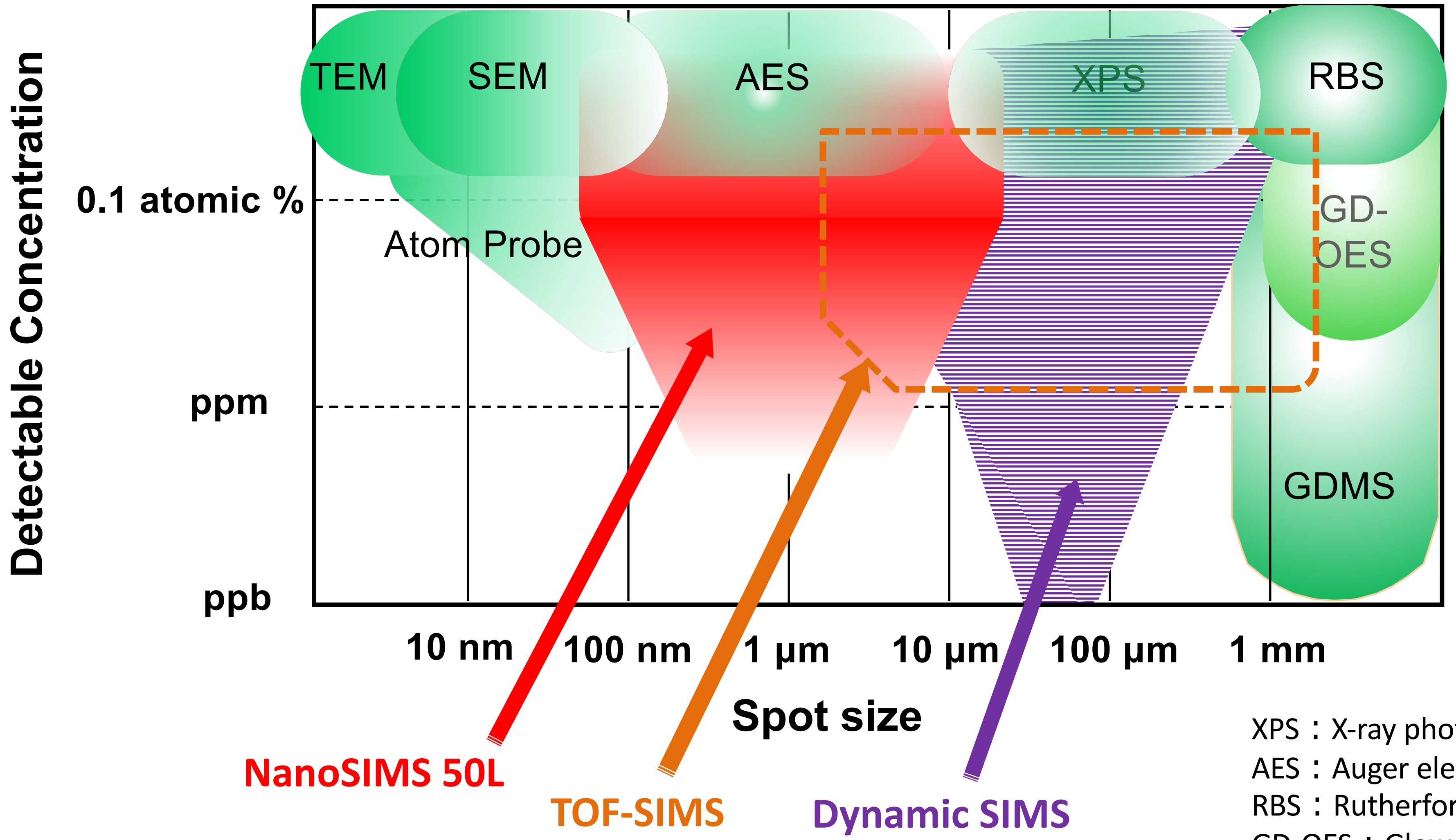
## Features of NanoSIMS 50L

- Cosmochemistry
- Geology
- Biology
- Materials
- Semiconductors / devices

### Specifications

| | NanoSIMS 50L | Conventional SIMS | TOF-SIMS |
|---|---|---|---|
| **Primary ion** | $O^-$ ; for positive ion detection<br>$Cs^+$ ; for negative ion detection | $O_2^+$ ; for positive ion detection<br>$Cs^+$ ; for negative ion detection | $Bi_n^+$<br>* $O_2^+$, $Cs^+$, GCIB as etching ions |
| **Beam size** | **50 nm** | 10 – 100 µm | 150 nm – 5 µm |
| **Detection limit** | **0.1 ppm ~** | ppb ~ | ppm ~ |
| **Mass analyzer** | Magnetic Sector | Magnetic Sector or Quadrupole | Time-of-Flight |
| **Number of detected ions** | 7 ; simultaneously | 10 -15 | (All ions within mass range) |
| **Depth capability** | 10 nm – 0.5 µm | 1 nm – 50 µm | nm – 10 µm |

# Capability - Size and Sensitivity -



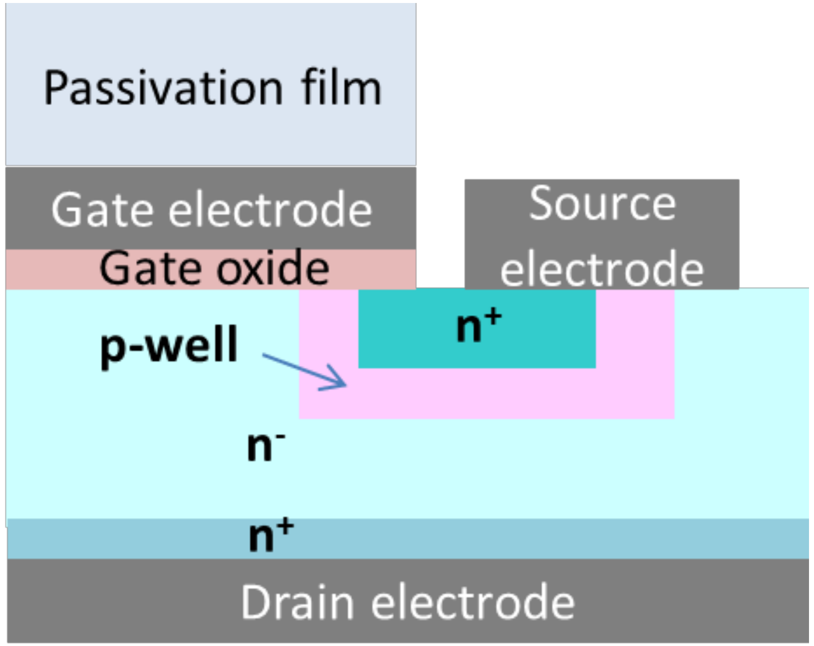

XPS：X-ray photoelectron spectroscopy
AES：Auger electron microscopy
RBS：Rutherford backscattering spectroscopy
GD-OES：Glow discharge optical emission spectrometry
GDMS：Glow discharge mass spectrometry

- Introduction to Toray Research Center
- NanoSIMS operational performance
  - Basic performance
  - Advantages over conventional SIMS and other analytical techniques
- Example NanoSIMS applications
  - Semiconductor devices (SiC-MOSFET, 3D NAND flash memory, SRAM)
  - Implanted phosphorous in Si sub.  (Quantification)
  - Li-ion Battery (LTO coating, Li-dendrite on carbon negative electrode)
- Wrap-up

## Commercially available SiC-MOSFET*

Silicon carbide metal-oxide-semiconductor field-effect transistor

Schematic diagram of SiC-MOSFET

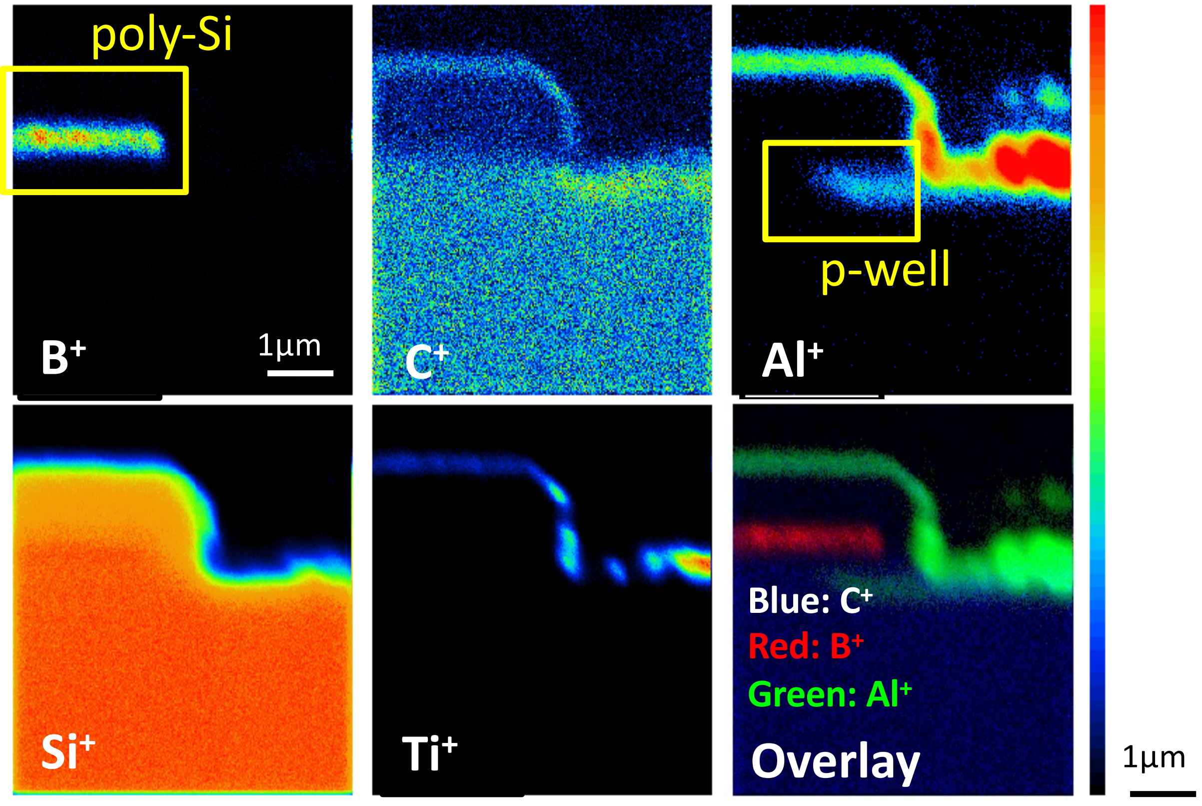



Cross-section was prepared by FIB process

# NanoSIMS Imaging for SiC-MOSFET cross-section

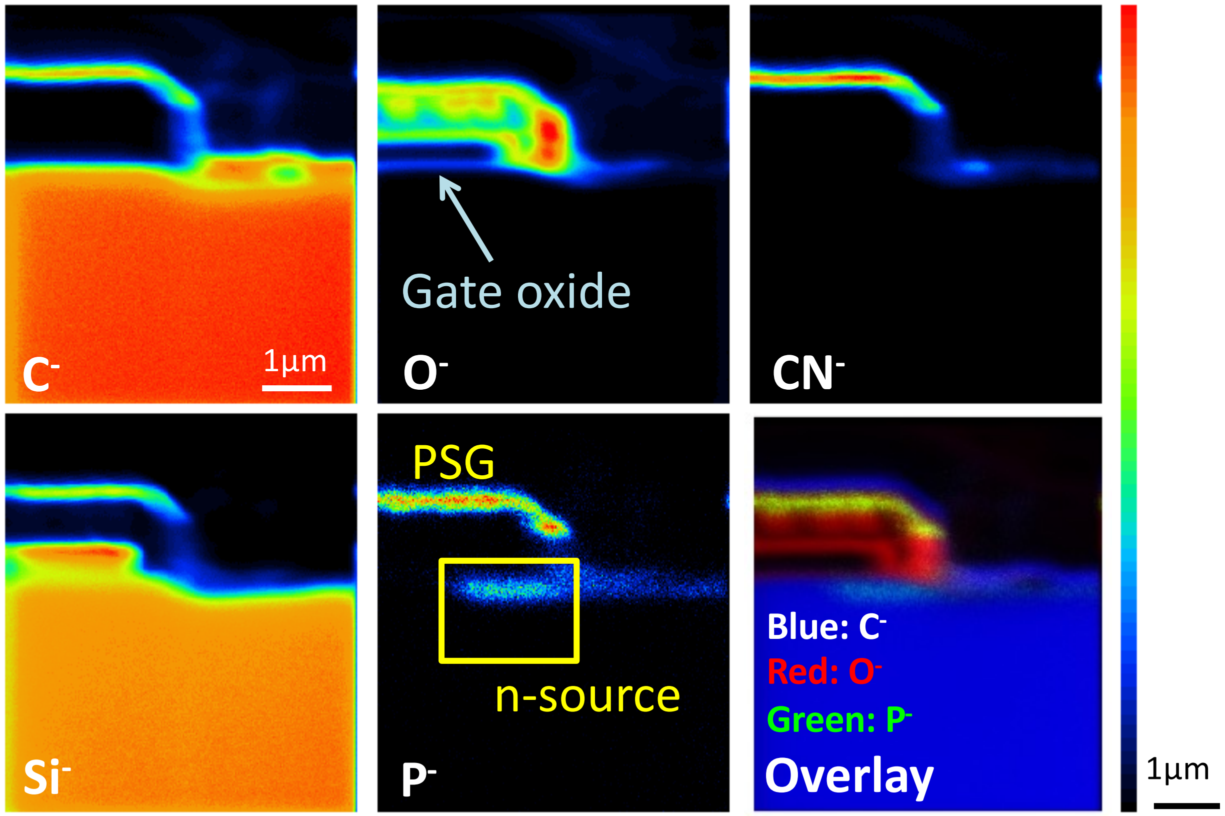
## Positive ions

Sputtered by $O^-$ primary beam




## Negative ions

Sputtered by $Cs^+$ primary beam

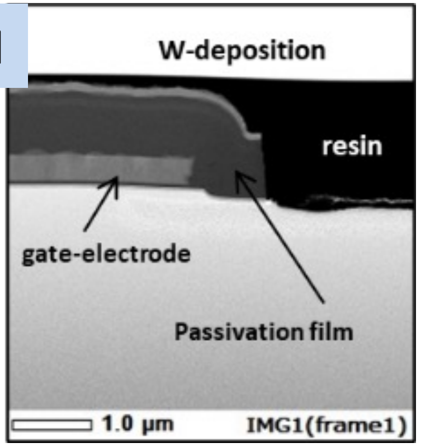



- Al: p-well
- B: poly-Si electrode

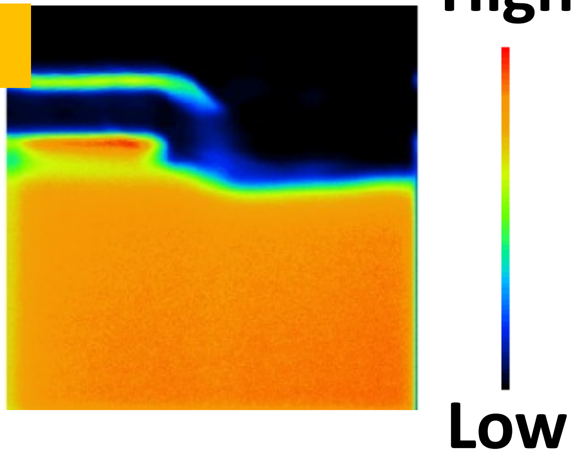
- P: PSG and n-source

# Comparison between NanoSIMS and TEM-EDX imaging for dopants

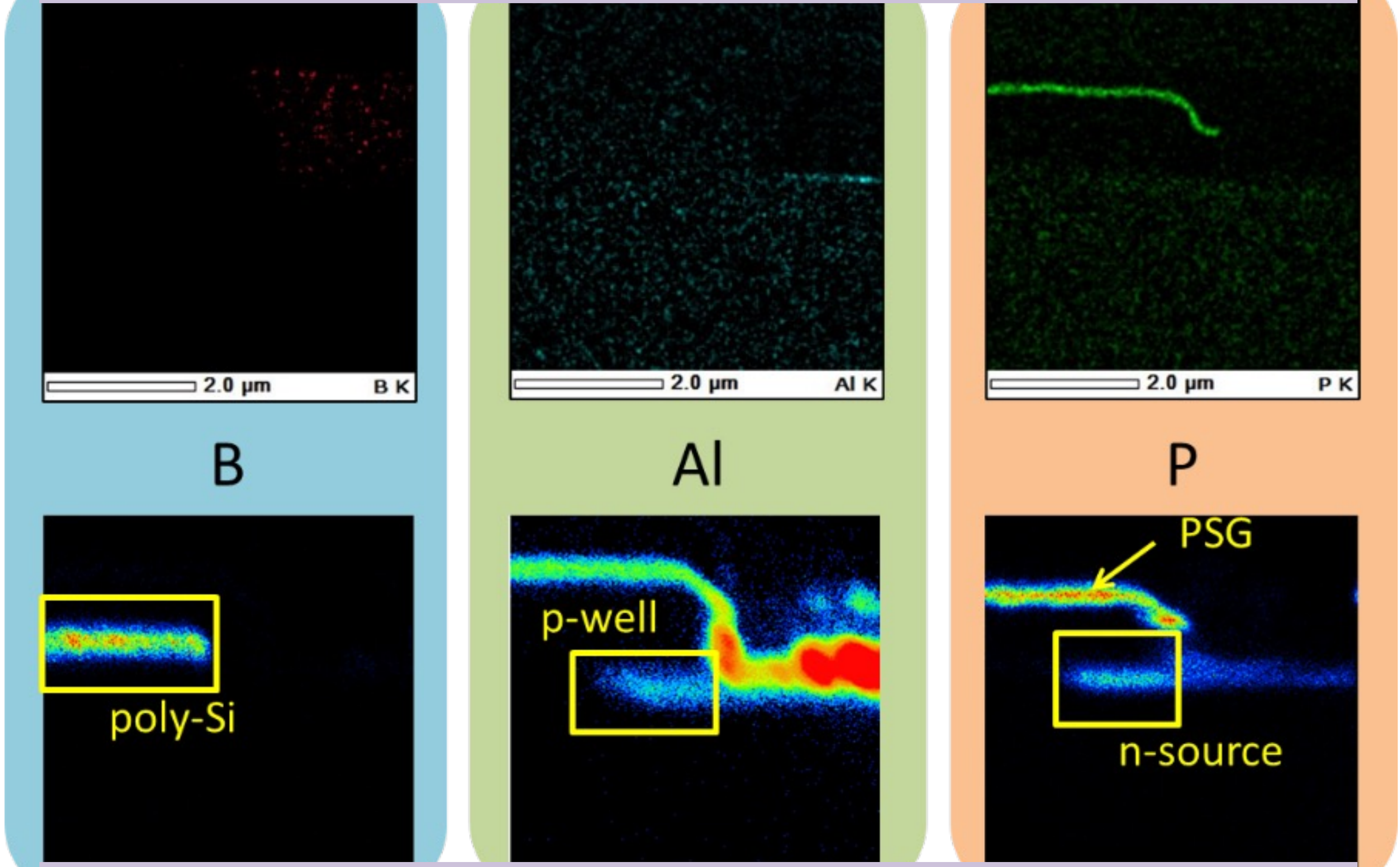
HAADF-STEM




NanoSIMS



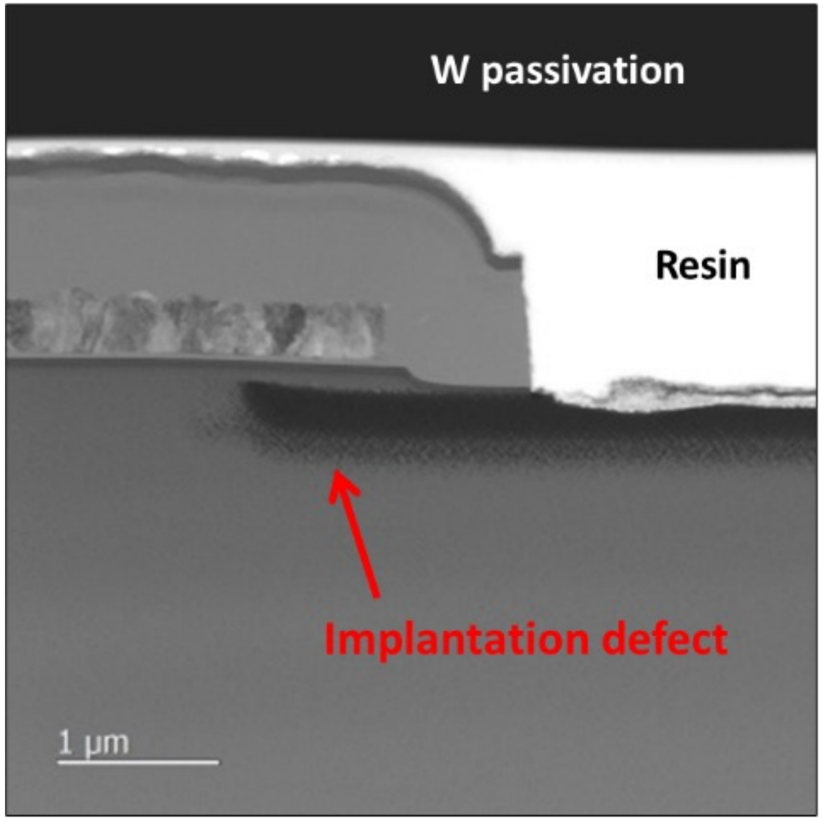

Almost no dopant was detected at all (except for P in PSG)



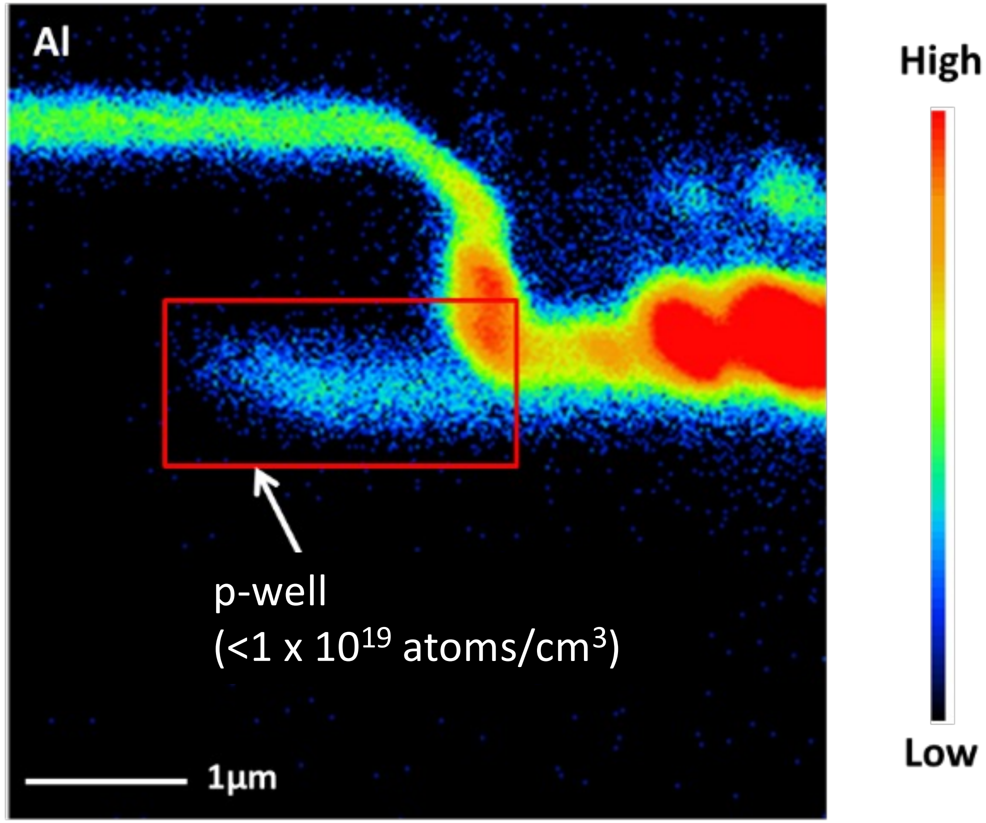

Dopant distributions are clearly captured

# Al distribution in p-well region observed by STEM and NanoSIMS

BF-STEM Image




NanoSIMS Image




- Aluminum ion distribution by NanoSIMS corresponds to crystal defect generated by ion implantation.

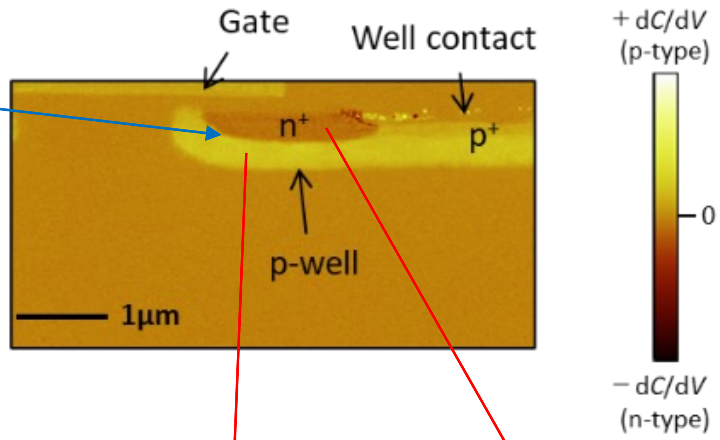
# Comparison between NanoSIMS and SCM

## SCM Image

p-n junction

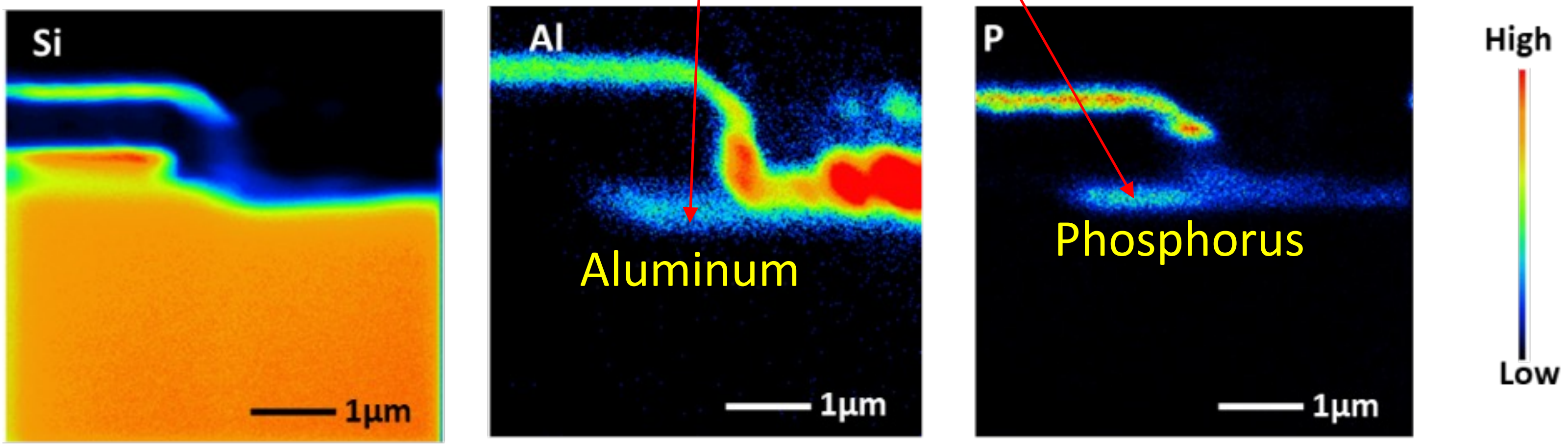
SCM：Scanning Capacitance Microscopy

- Active carrier distribution
- p-n junction



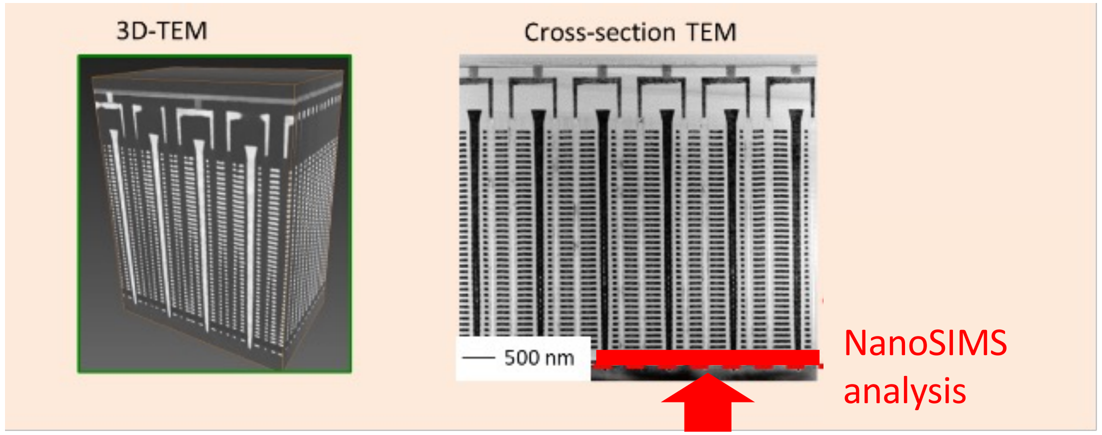

## NanoSIMS Image

- Dopant species
- Dopant distribution



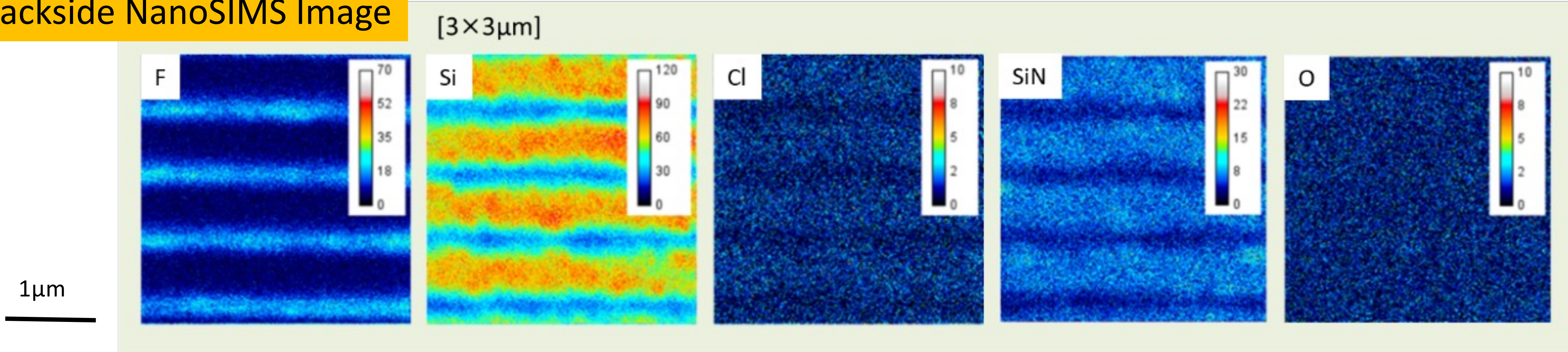
# Stack structure for NAND flash memory

## Commercially available 3D memory




Negative ions detected
Sputtered by $Cs^+$ primary beam

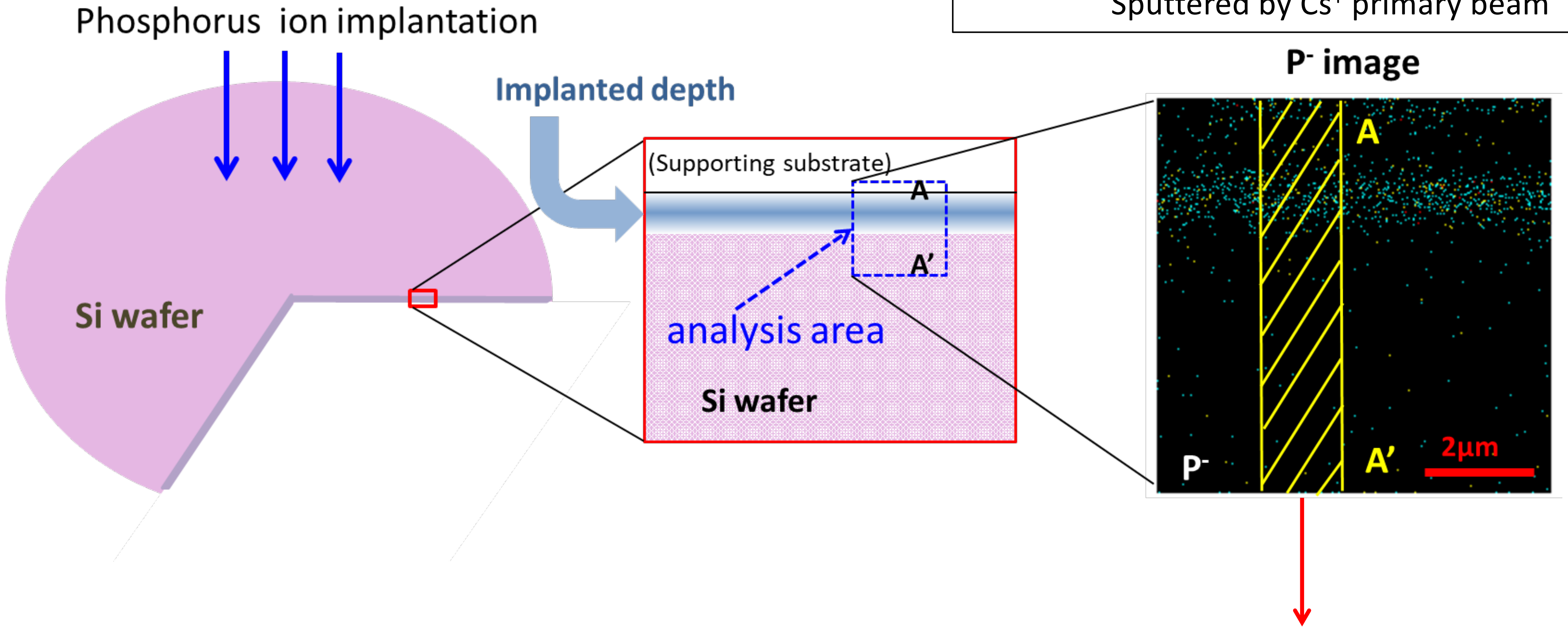
**Backside NanoSIMS Image**




- F detected in W (WF) layer - - > originated from precursor in CVD process

# Quantification and verification of detection limit - P in Si wafer -

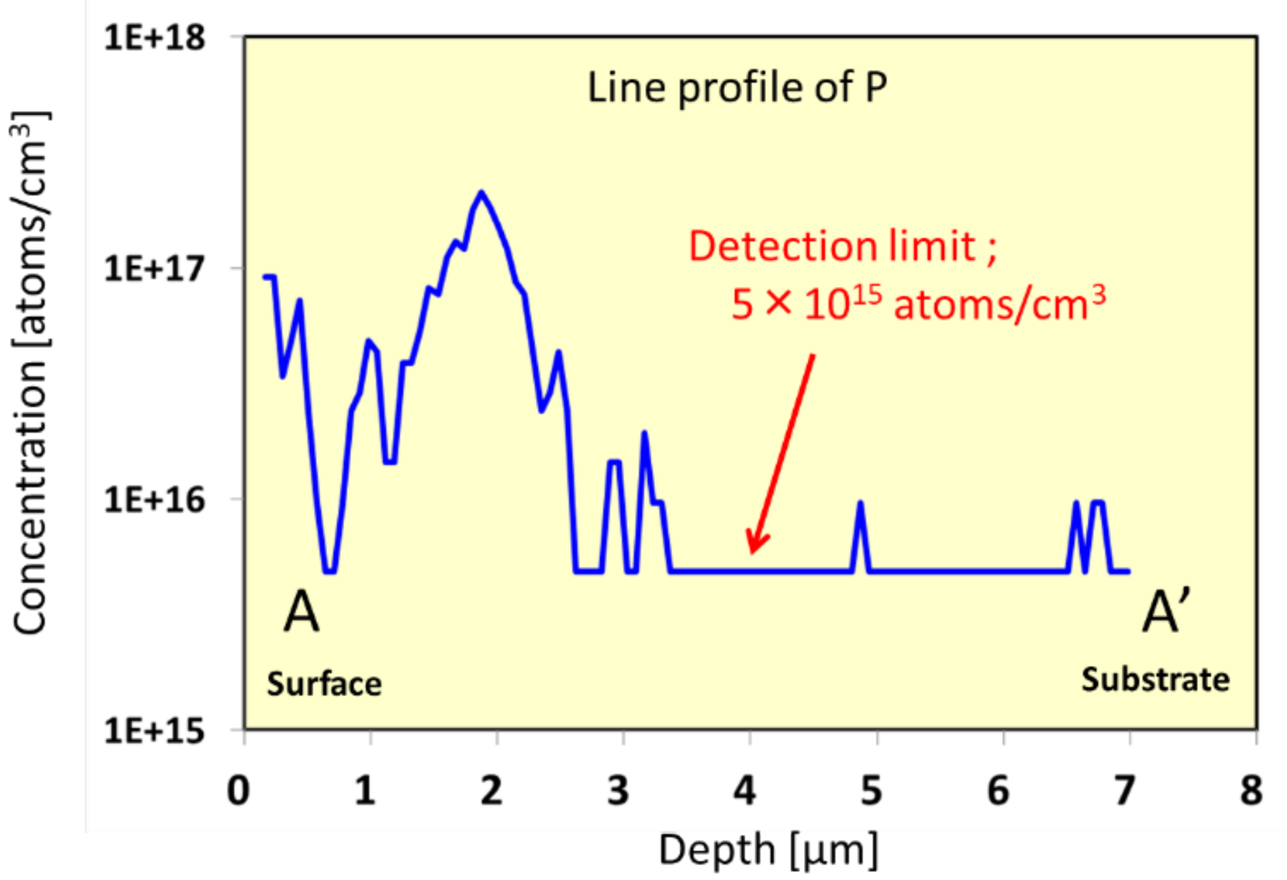
**Negative ions detection**
Sputtered by $Cs^+$ primary beam




Line profile (next page)

# Quantified line profile of Phosphorous in Si

**NanoSIMS line profiling**




*For Si device sample within less than 2 μm area*

FIB + NanoSIMS →

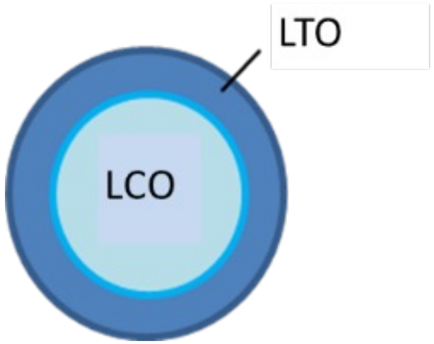
Profiles @ detection limit of $10^{15}$ atoms/$cm^3$ levels

- Introduction to Toray Research Center
- NanoSIMS operational performance
  - Basic performance
  - Advantages over conventional SIMS and other analytical techniques
- Example NanoSIMS applications
  - Semiconductor devices (SiC-MOSFET, 3D NAND flash memory, SRAM)
  - Implanted phosphorous in Si sub.  (Quantification)
  - Li-ion Battery (LTO coating, Li-dendrite on carbon negative electrode)
- Wrap-up

## Active material for Li-ion battery: evaluation of LTO coating

**Positive ions**
Sputtered by $O^-$ primary beam

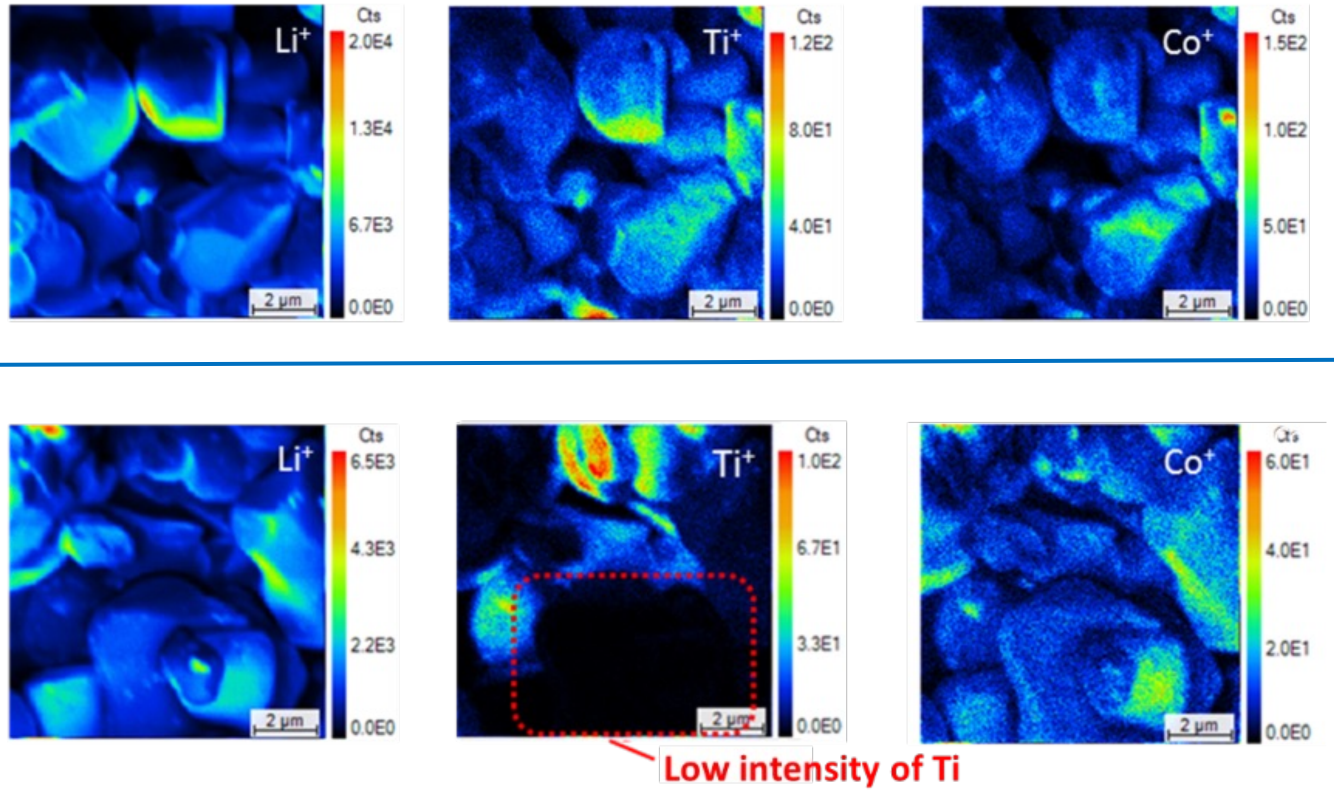
Imaging analysis of LTO layer (Field of view: 10 µm)




Uniformity of LTO coating was evaluated based on Ti and Co distributions.

LTO thick

LTO thin




**Secondary ion image of Li, Ti, Co**

"LTO thick" - Almost all LCO particles are covered with the LTO film.
"LTO thin" - Some LCO particles are not covered with the LTO film or the film thickness is thinner than the surrounding particles.

# Li-dendrite measurement on carbon negative electrode – Li-ion Battery -

## Experimental flow

- Battery disassembly in an inert atmosphere

↓

- Cross-section processing in an inert atmosphere (Cross-section polishing)

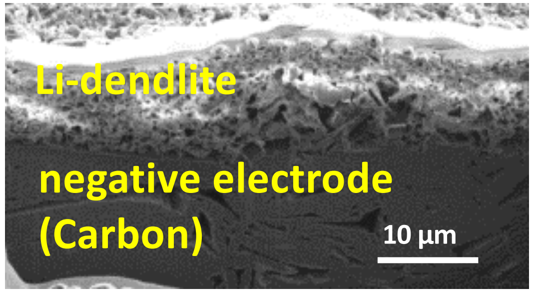
↓

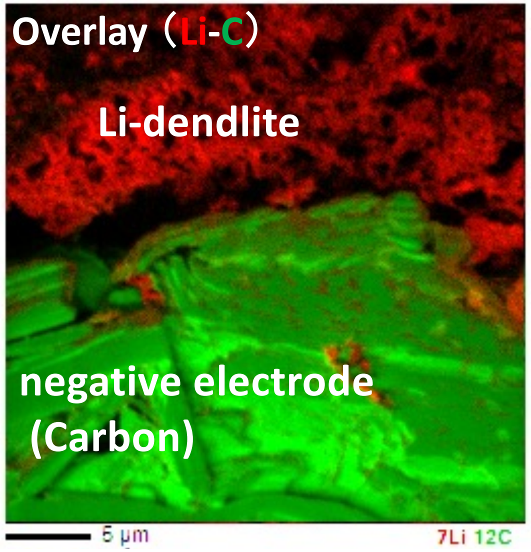
- Transport to instrument in an inert environment

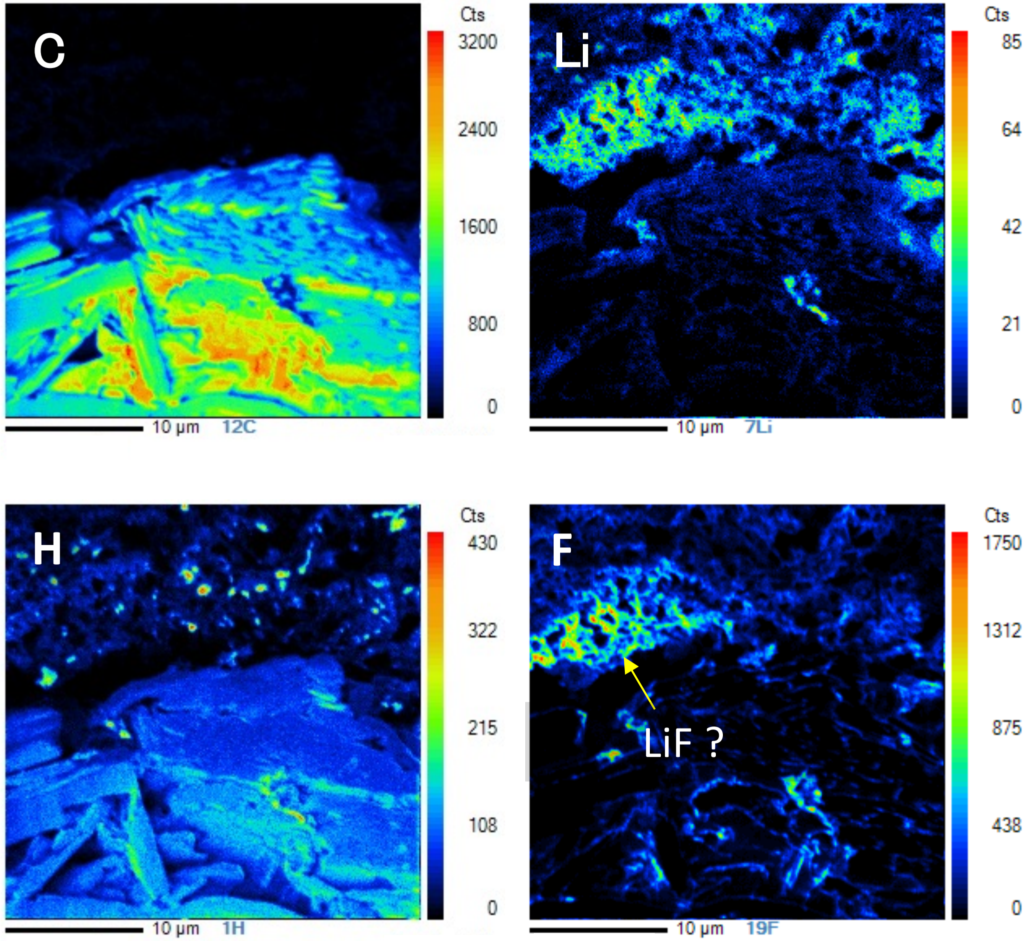
↓

- Mapping by NanoSIMS

FIB-SEM（Cross-Sectional view）



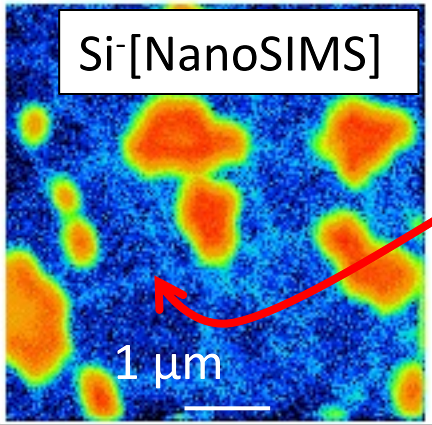




Evaluation of Li, which is hard to detect by EDX, is enabled by NanoSIMS

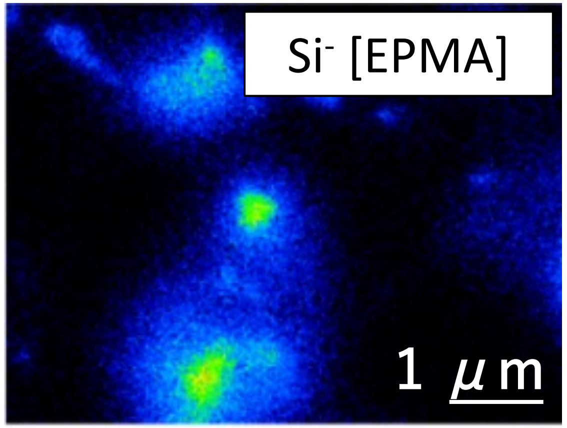
# Comparison – NanoSIMS, SEM-EDX, EPMA -

STD: Standard Materials

| | NanoSIMS 50L | SEM-EDX | EPMA |
|---|---|---|---|
| Probe | Ion beam （$Cs^+$, $O^-$） | Electron beam | Electron beam |
| Special resolution | **～50 nm** | 20～100 nm | ～100 nm |
| Detection limit | **～ppm** | sub wt% | 0.05～0.1 % |
| Detectable elements | **H**～U | B～U | B～U |
| Qualitative analysis | No (7 elements have to decided in advance) | Yes | Yes |
| quantification | Yes (STD needed) | Yes (for semi-quantification, STD not needed) | |
| Other Pros. | - **Highest sensitivity** | - short measurement time | - Higher sensitivity than SEM-EDX |




NanoSIMS is capable of detecting Si along with grain boundary in ceramics, contrary to SEM-EDX, EPMA



- Introduction of Toray Research Center
- NanoSIMS performance
  - Basic performance
  - Advantage towards conventional SIMS or other analytical techniques
- NanoSIMS applications
  - Semiconductor devices (SiC-MOSFET, 3D NAND flash memory, SRAM)
  - Implanted phosphorous in Si sub.  (quantification)
  - Li-ion Battery (LTO coating, Li-dendrite on carbon negative electrode)
  - Organic Coating layer
- Wrap-up

# Summary

- NanoSIMS is optimized for high sensitivity elemental imaging analysis.
- NanoSIMS can provide
  - 2D and 3D Imaging
  - Line profiles (which can be quantified with a reference sample)
- NanoSIMS can *measure* dopant / impurities contained at *lower levels*, which are invisible to TEM-EDX, SEM-EDX, EPMA
- NanoSIMS often works better by combining it with other analytical methods.

# Summary

- NanoSIMS is a great choice in case you need:
  - dopant imaging [implantation, diffusion, additive, etc. ]
  - impurities imaging [contamination, segregation, coexistence, etc. ]
  - depth profiles [p-/n-type dopant in semiconductor]

  on devices, small target areas, powders, etc.

- Toray Research Center has developed not only the NanoSIMS analytical technique, but also sample preparation for analyses across manifold fields for various analytical methods. By taking advantage of this, we can get out of the best NanoSIMS performance for the field below
  - Semiconductor devices
  - Li-ion Battery, SOFC
  - Materials including layer films, powder
  - Tissues, Cells [not shown in this seminar]

Toray Research Center hopes to help promote your R&D with you.


Thank you for your attention.

# Some Quick Housekeeping…

COVALENT METROLOGY

**Stay Tuned!**

We'll announce the next episode soon on our website at:

https://covalentmetrology.com

**Thank you for attending!**

To show our appreciation, we're offering all attendees a **special limited-time discount**

## Up to 15% Attendee Discount*

### On Your Next NanoSIMS Project

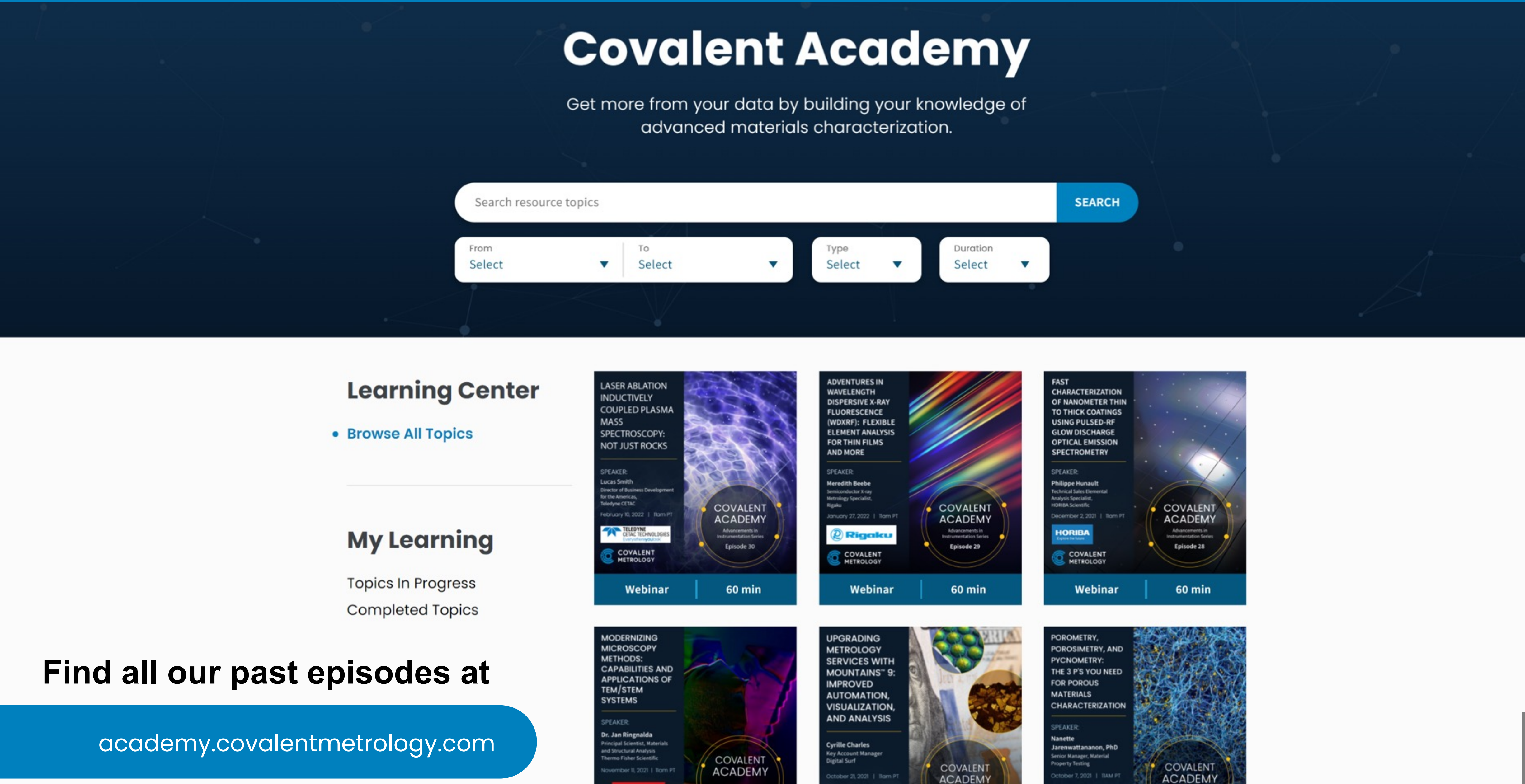
**10% discount for jobs quoted at $1,500 - $2,999; jobs over $3,000 qualify for the 15% discount*

Schedule a **Free Discovery Consult Appointment** to discuss your needs with a Covalent expert

Calendly Link in the Chat

# All Episodes On-Demand in the Covalent Academy

COVALENT METROLOGY




**Find all our past episodes at**

academy.covalentmetrology.com

# Q & A Session

COVALENT METROLOGY

# Thank You

For Q and A

# Sample Preparation for cross-section for semiconductor or materials

| The way to make sample | Sample | Pros. | Concerns and solution |
|---|---|---|---|
| FIB preparation | Specific area in device | Pick up an interested are | Damage due to Ga ion beam<br>- - > pre-sputtering |
| Broad Ion Beam Etching | Materials | Clean | Curved sample<br>- - > keep wide area |
| cleavage | Semiconductor wafer | As it is, intact | Roughness or line at surface<br>- - > additional polish etc. |

*This slide could be removed*

# NanoSIMS 50L synopsis