

Welcome

ADVANCED ANALYTICAL SCANNING TRANSMISSION ELECTRON MICROSCOPY (STEM), AND FUTURE DIRECTIONS

#### SPEAKER:

**Patrick Phillips, PhD** Asst. TEM Product Manager, JEOL USA

March 24, 2022 | 11am PT



COVALENT METROLOGY

### COVALENT ACADEMY

Advancements in Instrumentation Series

Episode 31





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



### **Covalent Technical Groups and Organization**



PCBA, Semiconductor, and Electronic Device Metrology & Failure Analysis	Electron Microscopy and Scanning Probe Microscopy	Optical Microscopy & Spectroscopy	X-Ray Characterization
<ul> <li>DPA / Mechanical Cross-section</li> <li>Dye &amp; Pry Test</li> <li>EBIC / OBIC failure analysis</li> <li>Hot Spot Detection</li> <li>IR Imaging / Emission Microscopy</li> <li>NIR Imaging</li> <li>Root-Cause Failure Analysis</li> </ul>	<ul> <li>AFM &amp; Advanced AFM Modes (EFM, KPFM, MFM, PFM)</li> <li>Scanning Acoustic Microscopy (SAM)</li> <li>SEM (+ EDS)</li> <li>FIB-SEM (+ EDS)</li> <li>S/TEM (+ EDS / + EELS )</li> <li>Nano-indent / Nano-scratch</li> </ul>	<ul> <li>Chromatic Aberration</li> <li>Digital Optical Microscopy</li> <li>FTIR and ATR-FTIR</li> <li>Laser Scanning Confocal Microscopy</li> <li>Spectral Ellipsometry</li> <li>UV-Vis-NIR Spectroscopy</li> <li>White Light Interferometry</li> </ul>	<ul> <li>X-Ray Diffraction (XRD)</li> <li>X-Ray Reflectometry (XRR)</li> <li>Micron-spot ED-XRF</li> <li>WDXRF</li> <li>Micro-computed X-ray Tomography (Micro-CT)</li> <li>2D X-ray Inspection &amp; X-ray Radiography</li> </ul>
Elemental / Chemical Composition Analysis	Particle Analysis	Material Property Characterization	Surface Spectroscopy Analysis
<ul> <li>EPMA</li> <li>GD-OES</li> <li>GC-MS</li> <li>ICP-MS and LA-ICP-MS</li> <li>Raman Microscopy &amp; Spectroscopy</li> <li>NMR (1D or 2D; solid / liquid)</li> </ul>	<ul> <li>Dynamic Light Scattering (DLS)</li> <li>Laser Diffraction Particle Size Analysis (PSA)</li> <li>Particle Zeta Potential</li> </ul>	<ul> <li>DSC</li> <li>DMA &amp; TMA</li> <li>DMA &amp; TMA</li> <li>Porosimetry / Gas Adsorption</li> <li>Rheometry</li> <li>Gas Pycnometry</li> <li>TGA</li> <li>Surface Zeta Potential</li> <li>Tap Density</li> </ul>	<ul> <li>Dynamic-SIMS</li> <li>ToF-SIMS (Static-SIMS)</li> <li>Ion Scattering Spectroscopy (ISS)</li> <li>Ultraviolet Photoelectron Spectroscopy (UPS)</li> <li>X-ray Photoelectron Spectroscopy (XPS)</li> </ul>

#### **Covalent Partners**





- **JEOL** is a global leader in cutting-edge microscopy, analytical chemistry, and materials characterization instrumentation
- New JEOL USA demonstration facility opened within Covalent's Silicon Valley lab to deepen JEOL presence in the region
  - Hosts top-of-line electron microscopes and spectrometers from JEOL, installed throughout 2021 2022
- Partners will collaborate to deepen understanding of Silicon Valley markets' analytical needs and guide the development of nextgeneration hardware, software, and applications research



#### Introducing



# **Patrick Phillips**

Assistant TEM Product Manager, JEOL USA

- PhD in Materials Science and Engineering in 2012 from The Ohio State University
- Research Assistant Professor at the University of Illinois Chicago
- Joined JEOL USA in 2016
- Previous research projects and current interests include:
  - Cs-Corrected STEM/EELS/EDS of metals
  - Battery materials
  - Oxides
  - 2D structural characterization





# Advanced Analytical STEM and Future Directions

JEOL USA

### **Brief Outline**

- Introduction/Current Capabilities
- Critical Technology
- How Far Can We Go with "Workhorse" S/TEMs?
- Looking Beyond

Advanced Applications and Cs-correction



# Why Scanning Transmission Electron Microscopy?

- Robust to thickness and defocus changes (no contrast reversals)
- Thick specimen imaging
- Defect analysis
- Structural determination
- Changing  $\beta$  yields multitude of signals
  - HAADF (~Z<sup>2</sup> intensity)
  - LAADF (strain contrast)
  - ABF (light element contrast)
- Wealth of structural, chemical, and electronic information at the atomic scale
- Spatially-resolved analytical information with EDS/EELS

#### Simplified Lens system for STEM



# The Needs of Analytical Microscopy

- Good source of electrons
- High spatial resolution
- Analytical characterization
  - Chemical sensitivity
  - Fine structure
- Good sampling rates
- Reduced beam damage

Can we do all this in a "workhorse" S/TEM??

#### **Dislocation core in STO:**



#### **HRTEM of Nanoparticle:**

10



#### Chemical analysis of semiconductor:



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# Common Perceptions of "Workhorse" Instruments

- Low Spatial Resolution
- 200 kV only to maintain spatial resolution
- EDS Spectroscopy
  - Time consuming
  - Low magnification
  - Lack of probe current/resolution capabilities for high-mag mapping
- Electron Energy Loss
  - Core-loss mapping OK
  - Fine structure determination not possible

#### **Dislocation core in STO:**



#### Chemical analysis of semiconductor:



#### HRTEM of Nanoparticle:

- High Spatial Resolution
  - Cold FEG, redesigned electron optics, highly stabilized column
  - Conventional TEM



Overaged Al alloy, incident beam parallel to [110] 200kV

- High Spatial Resolution
  - Cold FEG, redesigned electron optics, highly stabilized column
  - Conventional TEM
  - High-resolution TEM







56.6 pm 51 pm

- High Spatial Resolution
  - Cold FEG, redesigned electron optics, highly stabilized column
  - Conventional TEM
  - High-resolution TEM
  - High-resolution STEM



Sample : Si(110) Acc. : 200 kV Probe current : 21 pA N. of pixel : 1024 x 1024

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- High Spatial Resolution
  - Cold FEG, redesigned electron optics, highly stabilized column
  - Conventional TEM
  - High-resolution TEM
  - High-resolution STEM



probe current : 1 pA





- Low kV OK ٠
  - Cold FEG helps retain spatial resolution at lower voltage





- EDS Spectroscopy
  - Flexible probe current conditions which maintain spatial resolution
  - Advanced detector technology
  - Routine, large-area maps, 3D
     Tomography reconstructions



#### Semiconductor Device





Reconstructed 3D EDS maps

#### 2D elemental Maps

- EDS Spectroscopy
  - Flexible probe current conditions which maintain spatial resolution
  - Advanced detector technology
  - Routine, large-area maps, 3D
     Tomography reconstructions

#### Semiconductor Device





**EDS Tomography Reconstruction** Volume = 313 x 313 x 100 nm<sup>3</sup>

- EDS Spectroscopy
  - Flexible probe current conditions which maintain spatial resolution
  - Advanced detector technology
  - Routine, large-area maps, 3D
     Tomography reconstructions
  - Atomic-resolution mapping



**Sr Ti+0 0** 

Sample : **SrTiO<sub>3</sub>[100]** Probe currents : 50.2 pA N. of pixels : 256 x 256 Acquisition time : 10 min



Not only Sr and Ti, but also O atomic sites can be visualized.

- EDS Spectroscopy
  - Flexible probe current conditions which maintain spatial resolution
  - Advanced detector technology
  - Routine, large-area maps, 3D
     Tomography reconstructions
  - Atomic-resolution mapping

Sample : **GaAs[110]** Probe currents : 20.5 pA N. of pixel : 256 x 256 Acquisition time : 10 min



The dumbbell structure of Ga and As (0.14 nm) can be visualized by EDS.

#### • Electron Energy Loss

- CFEG energy resolution of 0.33 eV
  - 2-3x better than TFEG
  - Probe current and spatial resolution retained for mapping and fine structure
  - Core-loss



#### **Semiconductor Device**



- Electron Energy Loss
  - CFEG energy resolution of 0.33 eV
    - 2-3x better than TFEG
    - Probe current and spatial resolution retained for mapping and fine structure
    - Core-loss
    - Fine structure





Energy resolution : 0.35eV Probe current : 400pA N. Of pixels : 128 x 256 Dwell time : 0.01s



- Electron Energy Loss
  - CFEG energy resolution of 0.33 eV
    - 2-3x better than TFEG
    - Probe current and spatial resolution retained for mapping and fine structure
    - Core-loss
    - Fine structure





- Electron Energy Loss ٠
  - CFEG energy resolution of 0.33 eV
    - 2-3x better than TFEG
    - Probe current and spatial resolution retained for mapping and fine structure
    - Core-loss
    - Fine structure —
    - Plasmon resonance (low-loss regime)



#### Surface Plasmon Resonance of Ag

Courtesy of Dr. T Sannomoiya Tokyo institute of Technology



2.8 -3.3 eV



1.1 -1.3 eV



2.0 -2.4 eV

# *How Did We Get Here?*

- Introduction/Current Capabilities
- Critical Technology
- How Far Can We Go with "Workhorse" S/TEMs?
- Looking Beyond

Advanced Applications and Cs-correction



# "Workhorse" S/TEM...Where are we?

#### 1. Smart design:

Redesigned electron optics; design combining ease of use, high performance, high stability

#### 2. Quad-Lens condenser system:

Easy selection of illumination conditions; Spot size/convergence angle remain independent

#### 3. Advanced Scan system:

High stabilized multifunction STEM

#### 4. Improved Cold FEG :

High brightness with small energy spread

#### 5. Dual EDS:

Highly efficient analysis



### **STEM Detection Methods**

#### **Diffraction Pattern (STEM)**



#### ADF:

Z-contrast Robust, Easy to Understand

#### BF:

Close to conventional TEM Phase Contrast (not straightforward)

#### ABF:

Enhanced contrast for light elements Robust, Easy to Understand

#### Segmented STEM:

DPC imaging for E/B field Post-Process (limited)

#### **Pixelated STEM:**

All information of diffraction pattern Post-Process

■ Standard detector (ADF, BF, ...) gives *Integrated* signals only.
 ■ Quantitative analysis ⇒ *Fine Structure* of diffraction patterns.

More on Detectors Later...

### **STEM Detectors**

#### • HAADF

- Z-contrast
- ABF
  - BF-STEM/HR-TEM has strong dependence on thickness/defocus; suffers contrast reversals
  - ABF is more robust to these parameters;
     more directly interpretable
  - Light element imaging at atomic resolution
     (O, Li, H...)
  - Collection angle typically ½ $\theta_{\rm c}$   $\theta_{\rm c}$
- SE/BE
  - Surface-sensitive
  - Morphology



Findlay et al., Microscopy 2017 Findlay et al., Ultramicr 2010

### SE/BE Detectors

#### Detection of Surface Features...



TEM



PtRu / graphite

80 kV





# **CFEG Benefits**

- Small energy spread
  - 0.33 eV, compared to 0.8-1.0 eV for TFEG
  - Improved EELS resolution
  - Fine structure determination
- More current in smaller probe
- Improved spatial resolution; particularly low kV work
- Highly stable probe current and vacuum system



# **Probe Current Flexibility**

11500 Zero loss FWHM: 11000-0.82 eV Schottky (100 µA) 10500-0.50 eV Cold-FEG (20 µA) 10000-0.42 eV Cold-FEG(12 μA) 9500-9000-0.26 eV Cold-FEG(0.1 μA) 8500-8000-7500-7000-6500-6000-5500-5000-4500-4000-3500-3000-2500-2000-1500-1000-500-01 -1.6 -1.4 -1.2 -1.0 -0.8 -0.6 -0.4 -0.2 0.2 0.4 0.6 0.8 1.0 1.2 1.4 0.0 eV

- Highly tunable probe current and energy resolution
- Important to retain the spatial resolution

### Improved Energy Spread and Probe Size

#### Why we prefer a CFEG source for analytical work





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# **Probe Current Flexibility**



- Highly tunable probe current and energy resolution
- Important to retain spatial resolution
- Multiple avenues to change probe current/probe size/energy resolution

# EDS in the STEM

- Inherently inefficient
- Pole piece obstructions, sample proximity, etc.
- Best to avoid prolonged scanning or very high probe currents
  - Sample damage



- Solutions
  - Holders and Pole Pieces designed

specifically for EDS geometry

- Dual Silicon Drift Detectors (SDDs)
   for efficiency
- Large detectors, clean signal
  - 1.7sr solid angle
- P/B > 4000
- < 1% Spurious Peaks

#### **Top-down view of column**



# Dual SDD system



Specimen Holder



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### **Brief Outline**

-(37

- Introduction/Current Capabilities
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# Low kV - Energy Resolution and Fine Structure

Carbon - 80 kV





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# Pushing the Limits

#### **LSCO-LAO Superlattice**

High-resolution STEM and EELS/EDS Resolving O-vacancies and fine structure pre-peak changes with position





# Pushing the Limits

#### **LSCO-STO Superlattice**

High-resolution STEM and EELS/EDS Ti and O fine structure – Ti4+

Atomic-resolution spectroscopy without a Cs corrector





# Pushing the Limits

#### **LSCO-STO Superlattice**

High-resolution STEM and EELS/EDS Ti and O fine structure – Ti4+

Atomic-resolution spectroscopy without a Cs corrector







# Meteoritic Hibonite – CaAl<sub>12</sub>O<sub>19</sub>

Role of Mg/Ti in defect structure observed at atomic resolution



**Figure 1.** HAADF image from the [110] of hibonite showing stoichiometric hibonite (H) and an extended defect (D). The inset shows the distribution of heavy elements in hibonite and our model for the atomic arrangement in the defect.

L.P. Keller et al., 49<sup>th</sup> Lunar and Planetary Science Conference 2018



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### Meteoritic Hibonite – CaAl<sub>12</sub>O<sub>19</sub>

Role of Mg/Ti in defect structure observed at atomic resolution



**Figure 1.** HAADF image from the [110] of hibonite showing stoichiometric hibonite (H) and an extended defect (D). The inset shows the distribution of heavy elements in hibonite and our model for the atomic arrangement in the defect.



**Figure 3.** EELS spectra from the Ti  $L_{2,3}$  edge in meteoritic perovskite (blue) and hibonite (red). The low energy shoulders indicated by blue arrows are consistent with the presence of Ti<sup>3+</sup> in hibonite.



### **Plasmonics**

Phase-separated Ag-Cu nanoparticles







EDS Maps

Tokyo Institute of Technology J. Phys. Chem. C 2017, 121, 27029–27035



### **Plasmonics**

#### Phase-separated Ag-Cu nanoparticles



J. Phys. Chem. C 2017, 121, 27029–27035

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# DPC STEM

Differential Phase Contrast (DPC)

Detect local *Electrical / Magnetic fields* through incident beam deflections



Courtesy of Professor Naoya Shibata, University of Tokyo

#### **Electrical Field Detection**

Using STEM differential phase contrast (DPC) it is possible to directly observe the local electromagnetic fields within a material. The image on the left is an example of an analysis of the internal electric field of a pn junction in a semiconductor. The image on the right is the result of an atomic-resolution DPC observation of SrTiO<sub>3</sub>.





N. Shibata et al.; 2015; Scientific Reports.

N. Shibata et al.; 2017; Nature Comm

#### Magnetic Field Detection

Using the DPC method it is possible to see the various magnetic structures as well as the quasi-particle 'skyrmions' (left), which have a vortex-like magnetic structure. The image on the right is an example of magnetic domain structures in rare earth metal dysprosium (Dy).





 $\bigcirc$ 

### Field Observations



N. Shibata et al.; 2015; Scientific Reports.



Shibata et al. Nature Comm 2017



#### Analysis for Electromagnetic Field:

- SAAF + STEM Lorentz (OL OFF)
- Semiconductor, Magnetic Material
- Easy operations as in standard STEM

#### **Atomic Resolution DPC:**

- SAAF + STEM Cs Corrector
- Atomic scale information of localized field
- No changes in optical system

#### New imaging mode – Optimum BF STEM

- Maximum S/N
- Low dose
- Light Element Detection
- Live



K. Ooe et al., Ultramicroscopy 220, 113133 (2021)

### OBF – Dose-Efficient Imaging

#### SrTiO<sub>3</sub> [001]



300kV, alpha = 24 mrad



### High Contrast – Small Convergence

#### Semiconductor material



Accelerating Voltage : 200 kV Convergence Semi-angle : 2 mrad

- High contrast under small convergence angle conditions
  - Non-corrected, Lorentz mode, etc.
- Light Element Detection



# Low Dose, Low Scattering Conditions



ARM300F2 300kV, alpha = 16 mrad Probe current = 0.5 pA



**Single Layer Graphene** NEOARM 60kV, alpha = 35 mrad



### **IDES Integrated Technology**

- IDES technology dramatically expands microscope flexibility and functionality
  - Beam damage mitigation

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- Speed
- Optical illumination
- EDM Electrostatic Dose
   Modulator



Electrostatic Dose Modulator

# EDM with Synchrony

#### **EDM** Electrostatic dose modulation

- Electrostatic shutter gives 10<sup>5</sup>x increase in beam blanking speed (50ns vs 5ms magnetic blanker)
- On-the-fly dose control without affecting imaging conditions
- Synchrony Nanosecond timing control
- STEM synchronization
- Programmable dose structuring



# EDM with Synchrony

- Single scan STEM Image
  - Si [110] HAADF, 300kV
- Changing duty ratio from
  - 90% -> 10% -> 90%
- Frequency of 500 kHz (2 µs)
- Pixel dwell time with 19 μs/pix (1024x1024 pixels)





- True Area Scan
- Integration with JEOL EDS software and scanning system
- True Area Scan automatically removes illumination during flyback
- Reduces specimen damage and coincidence loss









# EDM Synchrony



This is unprocessed STEM data showing a dose pattern programmed by EDM Synchrony that includes the JEOL IDES logo, fractal patterns, and a checkerboard pattern.







# Extreme Functionality of "Workhorse" S/TEM

- CFEG
  - High probe current
  - Maintain energy resolution for EELS fine structure analysis
- Efficient EDS
  - High-throughput
  - Decreased dwell time
- Atomic-resolution imaging and spectroscopy







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### Coming Up...



### On May 19

CHARACTERIZATION OF CLIMATE BENEFICIAL MATERIALS BY GAS SORPTION

SPEAKER: Mark Thomas, PhD Lead Scientist,

Anton Paar Quantatec

May 19, 2022 | 11am PT



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On June 23

### Nanoscale Secondary Ion Mass Spectrometry (NanoSIMS) Analysis

In partnership with Toray Research Center, Inc. 61



Thank you for joining us! To show our appreciation

We're offering attendees a Special One-time Discount

# **10% Attendee Discount**

for your next S/TEM Project

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# Q&A Session

