Electron Microscopy & Spectroscopy: Window to the Nanoworld!

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“Generalized” Microscope

Radiation: *Electrons, photons, ions*...

Detector(s): *Electrons, photons, ions*..

Energy Transfer

Signal(s)
Outline

Introduction

- Why Electron Microscopy/Spectroscopy?
- Electron Microscopy in Nanoscience & Nanotechnology...duh!

Scanning Electron Microscopy (SEM):
  - Window to surfaces

Scanning/Transmission Electron Microscopy (STEM and TEM):
  - Window to the atomic world

Focused Ion Beam (FIB) System:
  - Site specific imaging, fabrication and machining

Future Challenges, and Opportunities

Nanostructures

* Dimensional and Spatial Constraints

* Zero  Nanocrystals, quantum dots
* One   Nanowires, buckytubes, DNA
* Two   Interfaces, membranes
* Three multilayers/assembled nanoxtls
Electron Microscopy: *Discovery of Carbon Nanotubes*

Key Issues in Nano-somethings

* Building Blocks: - Control, reproducibility and scaling  
  - Synthesis, architecture and design

* Block and Device Function:  
  - Functional characteristics  
  - Control and reproducibility

* Interconnect and communication:  
  - Efficiency and efficacy of connection  
  - Seamless integration

* Hierarchical Architecture:  
  - Assembly  
  - Multiple length-scales
**Why Electrons?!**

**Mass:** Dynamic interactions w/solids

*Multitude of analytical signals*

**Charge:** Trajectory manipulation

*Focusing down to 0.1 nm!*

**Wavelength:** Ultra-high resolution

*Single Atom Resolution*

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**Electron Probe (Field Emission Gun)**

~ 0.2 - 1 nm

- Secondary Electrons (SE) Image
- Backscattered Electrons (BSE) Image
- Diffraction: Structure/Crystallography
- Specimen Current/Heat
- BF/DF Imaging
- E+/−ΔE: Electronic Structure
- TDS: Z-contrast
- CL: Light
- X-rays/Auger: Chemistry

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**SEM TEM**

SS EE MM TT EE MM

50 - 100 nm

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*Focusing down to 0.1 nm!*

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*Single Atom Resolution*
Electron-Specimen Interactions

Elastic
- BSEs (Recoil, E ~ E₀)
- Diffractions (Bragg)
- Large-Angle (Rutherford) Scattering

Inelastic
- Phonon Losses (ΔE< meV)
- Plasmon Losses (ΔE1-10 eV)
- Cathodoluminescence (CL)
- SEs (E_SE ~ 1-10 eV)
- Continuum x-rays (white)
- Ionization → Leading to characteristic x-ray or Auger

Multitude of signals with specific information

Electron-Specimen Interaction: 
Interaction Volume (IV)

Resolution: Size/Shape of Interaction Volume (IV)
Sensitivity: Signal/Noise Ratio
Electron-Specimen Interactions

Cross-Section for Interactions:

\[ Q = \frac{N}{n_i n_t} \]

- \( N \) = # of events/vol
- \( n_t \) = # of target particles/area
- \( n_i \) = # of incident particles/vol

\( Q \) = events/electron/atom/cm\(^2\)

Mean-Free-Path (\( \lambda \)):

Avg distance between events

\[ \lambda = \frac{A}{N_a \rho Q} \]

- \( A \) = At wt., \( N_a \) = Avogadro’s #,
- \( \rho \) = density

Electron-Specimen Interactions:

Monte-Carlo Simulations – Do them first!

Figure 3.4. Monte Carlo electron trajectory simulations of the interaction volume in iron as a function of beam energy: (a) 10 keV, (b) 20 keV, (c) 30 keV.
Electron-Specimen Interactions: Monte-Carlo Simulations – Do them first!

Microscope: “Facilitator” of electron-specimen interactions
Focused Probe Formation: *Excited Lenses*

**Dichotomy**

as \( d_b \)

so does \( i_b \)

Limits to Fine Probe Formation

*Lens Aberrations!!*

**Spherical**

**Diffraction**

**Chromatic**

\[
d_{\text{probe}} = (d_{\text{gun}}^2 + d_{\text{chr}}^2 + d_{\text{sph}}^2 + d_{\text{diff}}^2)^{1/2}
\]

Future Development: *Aberration corrections!*
Astigmatism:
**Fully Correctable!**

Symmetric
Correcting
Lenses

**Depth-of-field (DoF)**
Unique Advantage of SEM!

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*Figure 4.9.* Schematic illustration of the depth of focus (field) in an SEM image. Any portion of the specimen that lies within the range of Z (along the optic axis) defined by the planes located 1/2 from the plane of optimum focus will appear to be in focus.

*Figure 7.3.* Optical micrograph of the polished microtome specimen. An SEM micrograph of same indentation. The greater depth of focus and superior resolving capability of the SEM are apparent.

Optical Micrograph
**Advantage of FEG Source**

* Smaller source size ➔ Small probe size
  
  (Down to < 0.2 nm)

* Higher brightness ➔ Large probe current density
  
  (several nA in nm probe)

* Smaller energy spread ➔ Low Cc
  
  (Low kV operation)

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**Electron Probe**

~ 1 - 50 nm

- Ultra-high resolution from SEs (1-10 nm)
- Crystallographic information from BSEs
- Chemical analysis via x-rays
- Analysis of “softer” side of materials
  (wet and oily) via variable pressure

X-rays/Auger: Chemistry

CL: Light/Spectroscopy

Secondary Electrons (SE) Image

Backscattered Electrons (BSE) Image
Nano-cheerios! Hollow nanoparticles of Pd catalyst

Image of Ebola virus depicting the deadly thread morphology

Low-Voltage ➔ Less Damage

Direct Imaging of Active-Sites in Catalysts

Catalyst(Pt /Carbon)

20kV
Mag. : x300k – x800k
Comment: Uncoated!
“Digital” Combination of Differential Signals

Electron Diffraction in SEM: Electron Backscattered Diffraction (EBSD)

“Spot” Diffraction and Indexing

Orientational Imaging: Mapping crystallography and orientation of polycrystal grains via EBSD
**Consequences of Low kV Imaging**

* The SE yield increases significantly
* Less overall “charge” deposited in the specimen
* More “surface/sub-surface” information
* Both SEs and BSEs carry high resolution information
* Beam Damage: - More localized

**Must have FEG ➔ Low Cc!**

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**X-ray Emission Spectroscopy**

- Inner-Shell Ionization
- Inner-Shell Compensation
- Auger or x-ray
  
  \[ (1-w) \quad (w) \]

- Qualitative & Quantitative Local Microchemical Analysis
- Elemental Mapping
X-ray Emission Spectroscopy

Sample: SiO₂ Layer
Counts

Si
2.5
FEG SEM

cSEM

Elemental Mapping via x-rays
Specimen: GMR

Z-Contrast Image
Co-K
Cu-K
Si-K
Mn-K
Ni-K
Fe-K
Ta-L
Microscope: “Facilitator” of electron-specimen interactions

Scanning Electron Microscope (SEM)

- Thermionic (W/\text{LaB}_6)
- Field Emission (FE)
- Electromagnetic
- Multiple Detectors

Nano-cheerios! Hollow nanoparticles of Pd catalyst

Ultra-High Resolution

High Resolution

FEG SEM

Low-Voltage $\rightarrow$ Less Damage

Image of Ebola virus depicting the deadly thread morphology
Environmental Scanning Electron Microscope (ESEM)

- Maintenance of pristine state of sample
- No need for coating (charge-neutralization)
- Potential for dynamic, in-situ studies
- Enhanced signal due to gas ionization
- Access to all SEM signals

The Environmental Secondary Detector uses gas ionization to amplify the secondary electron signal. In nonconductive samples, positive ions are attached to the sample surface as charge accumulates from the beam. These effectively suppress charging artifacts.
Variable-pressure SEM is capable of imaging and analysis of pristine (i.e. wet/oily) materials.

**Processed Cheese:**
Note the fat globules!

Images of human dentinal

**High-Pressure Low-Vacuum**
**Low kV**
**SEM:**

**ESEM: Preserving Pristine Structures**

- Microbe from Antarctic ice
  Courtesy of NASA/Johnson Space Flight Center

- Asian lady bug
  Courtesy of EPIC/NUANCE

- Silverfish antennae
  Courtesy of EPIC/NUANCE

- Diatom
 Courtesy of EPIC/NUANCE
ESEM: *Seeing paint dry!*

ESEM: *Same access to analytical signals*
**Motivation for VP-EBL**

- EBL is capable of high resolution patterning - ~10nm
- EBL allows for patterning on non-planar surfaces
- EBL requires some level of sample conductivity to avoid pattern distortion
- Conventional methods to avoid charging require additional process steps or different materials
- Can the VP capability that allows for imaging of non-conductive materials be applied to EBL?
Standard EBL Process
(conductive substrate)

- Electron beam exposure
- Develop resist
- Metal evaporation
- Lift-off

Substrate (Si)

Standard EBL Process
(insulating substrate)

- Evaporate conductive layer (Al or Cr)
- Electron beam exposure
- Wet etch metal layer
- Develop resist
- Metal evaporation
- Lift-off

Substrate (Glass)
EBL on Insulating Substrates

- Problems with conventional approach
  - At least 2 additional process steps required
  - Possibility of interaction between etchant and resist, substrate or other materials
- Other solutions
  - Conductive resists
  - Ion flood
  - Low energy primary beam

FEI Quanta ESEM - Unique Capabilities:

eBL on Insulating Substrates

eBL on glass without in high vacuum

Charging/distortion on non-conductive substrates

eBL on glass at 1 Torr water vapor

Complete elimination of charging artifacts
Focused Ion Beam (FIB):
“Ion” analog of SEM

Focused Ion Beam system allows for site-specific micromachining, lithography, and Tungsten deposition.
FIB is used for sample preparation of both SEM and TEM specimens.

Site-Specific Sectioning of Brittle Composite
Nanopore Fabrication via FIB:
Converting DPN to Nano-Fountain-Tip

Conventional AFM Cantilever

Focused Ion Beam
Size ~ 20-50 nm

Field Emission Gun TEM/STEM
~ 0.2 - 1 nm Electron Probe

- Atomic resolution of lattice structures
- Crystallographic information: Diffraction
- Chemical mapping and atomic bonding
- In-situ dynamics
Samples must be thin (~100 nm) and beam energies must be high.

With crystalline samples image detail comes mostly from Bragg diffraction.

By choosing the aperture position either the diffracted beam (Dark Field) or the unscattered electrons (Bright Field) can be used to form the image.

Figure 1.1. The Basic TEM by Ruska and Knoll in Berlin in the early...
Modern TEM/STEM

Spectroscopy

Imaging

Diffraction

Spectroscopic Imaging

Nano-voids

Crystalline Films

TEM Diffraction Contrast Imaging

Defects:
Point, Line & Planar

Dislocations

Strain-Fields

TEM/STEM Imaging

Diffraction

Contrast

Defects:
Point, Line & Planar

Strain-Fields
Phase Contrast: High Resolution TEM

Interference Pattern of Diffraction Beams

Grain Boundary in SrTiO₃

Atomic resolution image of a novel form of carbon nanostructure

STEM:
Combining Best of SEM and TEM
The Unique STEM Mode: **HAADF Imaging**

- The **High Angle Annular Dark Field** image is a unique operational mode of the STEM.
- Here $\theta$ – the inner angle of the annular DF detector – is made so large (30 millirads) that no Bragg diffracted electrons are collected.
- The outer angle $\phi$ is made as large as possible.
- The images come from elastically scattered electrons which have passed very close to the atomic nucleus. High (single atom column) resolution is possible. There is zero diffraction contrast.

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**Z-contrast imaging of a crystal**

- Plane wave
- Bloch waves select s-states of the crystal
- Focused probe

When the crystal lattice is correctly oriented then the beam interaction is localized at the atom column positions (‘s’ orbitals are selected).
Z-contrast image showing maximum entropy fit to data. The HAADF Z-mode displays the actual physical positions of the atoms. TEM ‘lattice images’ are only interference effects and there is no correlation between the image positions (which vary with thickness and focus) and atom locations.

Interface width
3 - 5 Å

Why STEM lattice images are better

Parallel-Collection Electron Energy-Loss Spectrometry (PEELS)

The Gatan PEELS is interfaced to a TEM after the final viewing screen. An entrance aperture selects the electrons on the optic axis and disperses them via a magnetic prism onto a cooled 1024 channel diode array.
Intensity Range in the Energy-Loss Spectrum

The energy-loss spectrum spans several orders of magnitude in intensity from >10⁹ counts in the zero-loss peak to as few as 10² - 10³ counts in ionization edges.

A Typical Low-Loss Spectrum Consists of An Intense Zero-Loss and a Smaller Plasmon peak

The diagram shows a typical low-loss spectrum with an intense zero-loss peak and a smaller plasmon peak. The spectrum is plotted against energy loss (eV) on a logarithmic scale, indicating the range of counts from low to high energy losses.
Typical High Energy Loss Spectrum

Spectrum from a small (< 50 nm thick) particle of BN showing the B and N K edges. The B K edge has a rich ELNES. The N K edge is much smaller despite N being present in equal amounts to B. The small C peak arises from the C support film - a limitation of any TEM-based technique.

Change in ELNES Upon Oxidation

When Cu is oxidized to CuO, the Fermi level is now in the 3d band rather than the metallic 4s band. The 3d band is not filled, so the preferred site for the ejected electrons is in the unfilled d states close to the Fermi level thus giving rise to intense peaks at the edge onset. These peaks are sometimes called “white lines”
The carbon K edge is very distinctive and reflects the significant differences in bonding between carbon atoms in different structures. In graphite, in which there is both sp\textsuperscript{2} and sp\textsuperscript{3} bonds there is a significant \( \pi^* \) and \( \sigma^* \) peaks reflecting the different bonds. In diamond which is completely sp\textsuperscript{3} bonded, there is only a peak for the \( \sigma^* \). So even if the details of the ELNES is not well understood it is possible to “fingerprint” different bonding types and compare unknown spectra with standards.

Electron Energy Loss Spectroscopy (EELS)  
*Clues to local bonding and E- Structure*
Sample with break through of the Permalloy layer and oxidation of the Al (and O) layer.

Electron diffraction patterns of a membrane protein: Before and after energy filtering.
**Spectrum Imaging**

A series of images of diamond-like carbon on a Si substrate. The BF image is clarified by the Si L and C K images. The amorphous interface is enriched in O.

Bonding images formed from electrons in the $\pi^*$ and $\sigma^*$ portions of the ELNES of the C K edge reveal that the amorphous region consists of two layers of $\pi$ bonding while the carbon layer is predominantly $\sigma$ bonding indicating high-quality diamond.

*Courtesy J. Bruley*

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**Cryo-TEM**

 Freeze structures in vitreous ice, cryo-TEM imaging/viewing  

- Minimize Damage  
- Preserve "pristine" state – esp bio-structures  
- Add 3-D Tomography!

* Liposome-nanoparticle assembly for drug/gene delivery  
* DNA-linked Gold Nanoparticles  

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* Image 1: BF, Si L, C K, O K, C $\alpha$, C $\pi$ images of diamond-like carbon on Si substrate.  
* Image 2: Cryo-TEM image of liposome-nanoparticle assembly and DNA-linked Gold Nanoparticles.*
3-D Tomography w/TEM: 
*Exciting New Development*

- Imaging under variation in specimen tilt
- Capture element-/density-/orientation specific images
- Reconstruct 3-D from series of projected 2-D images!

Seeing the Invisible: 
*Electron Holography*

This historic 18"x24" laser transmission, pulsed portrait of Dr. Dennis Gabor, inventor of holography, was recorded in 1971. Portrait commemorated Gabor's winning of the Nobel Prize that year. (Photo by Daniel E. Quat, 1976)
Holography was proposed by Dennis Gabor in 1948 as a way to enhance TEM performance, and first demonstrated by Haine and Mulvey in 1951. Because of the laser, the first big impact of holography was in visible light optics. But with the Field Emission Gun holography is now a routine part of electron microscopy.

"Train and Bird" is the first hologram ever made with a laser. This pioneer image was produced in 1964 by Emmett Leith and Juris Upatnieks at the University of Michigan only four years after the invention of the laser.

Electron Holography: Imaging Magnetic Fields

The phase image as reconstructed from a hologram. The phase image is color coded and the magnetic CoNi layer is indicated by the gray line. The MFM tip itself is too thick to be penetrated by the electron beam.

Simulation of the phase image of a MFM tip (G. Pozzi, Italy).
Quantitative 2-D Dopant Profiling with Electron Holography

E-Static Simulation

“Element-Specific” 3-D Tomography: STEM Z-contrast and Elemental Maps
The limit - Single atom imaging

CdSe/ZnS core/shell nanocrystals

Ag (Z=47) atoms on C (Z=6) foil - Crewe 1970
30keV STEM image

Dopant-Atom Imaging: HAADF

STM Image

HAADF STEM Image

Sb-doped Si Undoped Si
Can “looks” be deceiving?!

Of Course!!

Complementary Techniques

Theory/Modeling

Advanced EM

Upcoming Attractions!

* Aberration-corrected EM: New exciting frontier in EM
* Brighter, smaller and stable electron sources: Atomic-/Nano-tips
* Improved, high efficiency integrated detectors
* Real-time, in-situ microscopy with specialized specimen stages
* On-line image acquisition, processing and analysis
* Telepresence Microscopy (Remote-Microscopy)
  - Web-Based Education, Research and national/international outreach
Feynman, 1959,  
“There’s Plenty of Room at the Bottom”

“I would like to try and impress upon you while I am talking about all of these things on a small scale, the importance of improving the electron microscope by a hundred times. It is not impossible; it is not against the laws of diffraction of the electron. “just look at the thing!”

And I know that there are theorems which prove that it is impossible, with axially symmetrical stationary field lenses, to produce an f-value any bigger than so and so; and therefore the resolving power at the present time is at its theoretical maximum. But in every theorem there are assumptions. Why must the field be symmetrical?”

“just look at the thing!”

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**Correction of Spherical Aberration**

- **Corrector**
- **Quadrupoles and Octupoles**
- **Sample**
- **To Detector**
- **Source**
- **Condenser Lenses**
- **Objective Lens**
- **XZ Plane**
- **YZ Plane**

Beam cross-section: (Quadrupoles control trajectories. Correction given by Octupoles)
Probe Size is Limited by Spherical Aberration

VG Microscope’s HB501UX, 100 kV

Aberration limited
$C_s = 1.3 \text{ mm}$
$C_s = 1.3 \text{ mm}$

Significant current is lost in probe “tails”

FWHM ~ 2 Å

Aberration correction can achieve a smaller brighter probe

Stripes in Bi$_{0.38}$Ca$_{0.62}$MnO$_3$

Direct imaging of localized electrons
Pt Trimers on the $\gamma$-Al$_2$O$_3$ (110C) Surface

P.D. Nellist 1996
A. Borisevich 2004

Direct Imaging of Oxygen in SrTiO$_3$ (100)

Sr-O : 1.867Å; Ti-O: 1.894Å

Image: 034_ADF_GB_PDN35PL1p021_200M
3-D Nanomanipulation in TEM

- Nanomanipulation - can adjust tips and probes
- Polarity Reversal - control of magnitude and sign of the applied potential
- Can apply a bias to the manipulator tip to switch potentials on an object or to produce field emission

By selectively grounding or biasing the junction a reference phase image can be obtained

“Dynamic” Electron Holography with the novel 3-D Nanomanipulator (3-DNP)

Hologram of individual-isolated carbon nanostructure under bias

Reconstructed phase image showing equipotential lines.
In-situ TEM Nanomanipulation via 3-DNM

Site-Specific NT attachment

E-Beam “Nano-Cutting”

Telepresence (Remote) Microscopy:

- No need for physical presence.
- Fast, interactive and real-time
- Reduced redundancy
- Enhanced capabilities

Faculty/Director

Students, Technicians or visitors
Summary

Advanced Electron Microscopy:
(The window is becoming wide open)

- Multitude of signals and modes
- Ultra high resolution, approaching 0.1nm
- Excellent sensitivity: approaching single atom
- In-situ capabilities
- Amenable to “Telepresence”

Ideally positioned for Nanoscience and Nanotechnology