FYS 4340/FYS 9340

Diffraction Methods & Electron Microscopy

Lecture 2

Sandeep Gorantla
Transmission Electron Microscopy

Introduction and Basics
Part- 1

Sandeep Gorantla
Learning more about TEM!
Learning more about TEM!

http://www.matter.org.uk/tem/
Learning more about TEM!
Why learn about Transmission Electron Microscopy (TEM)?
Role of TEM in Materials Science Research and Development

Solving Materials Science problems/mysteries by probing analytically and understanding structure-property relationships at atomic scale level

Materials Science Paradigm

Courtesy: www.wikipedia.com
Allotropes of carbon

graphite

graphene

nanotube

fullerene

(Courtesy: The Royal Swedish Academy of Sciences)
1D nanomaterials modification in TEM

- Irradiation of solids with energetic particles usually leads to damage

- However, in the case of carbon nanostructures, electron irradiation was observed to have some beneficial effects

  (a) Irradiation – mediated engineering
  (b) self-assembly or self-organization

Interface: defects on outer-wall of a nanotube and fullerene

Interface: defects on outer-wall of a nanotube and fullerene

Nanohump formation (Covalent interactions of fullerene fusion)

Movie Settings:
• Frame speed: 0.6 s
• Total Frames: 48

Experimental conditions:
• Acquisition time: 1 s
• Time gap between individual frames: 1s - 30s
• Total time: 14 mins

Interface: defects on the outer-wall of a SWCNT and fullerene

Fullerene fusion with a nanohump *(Covalent interactions of fullerene fusion)*

**Movie Settings:**
- Frame speed: 0.6 s
- Total Frames: 48

**Experimental conditions:**
- Acquisition time: 1 s
- Time gap between individual frames: 1 s

*Courtesy: Gorantla, S. et al., Nanoscale, 2, 2077 (2010)*
HETEROSOLAR PROJECT
The aim of the work

Develop new solar cell devices base on ZnO/Cu$_2$O heterojunctions coupled with conventional Si based solar cells

Properties determined by the structures, faults and interfaces.

TCO

ZnO  n-type  3.4 eV

Cu$_2$O  2.17 eV  p-type

* Theoretical efficiency ~20%  
* Highest exp. efficiency 1-4%
ZnO

Cu₂O (sputtering, 300nm)

ZnO Single Crystal

Cu₂O

CuO

ZnO

50 nm

1 nm
ZnO
CuO
Transmission Electron Microscope

Brief History
Brief History: The first electron microscope

- Knoll and Ruska, first TEM in 1931
- Idea and first images published in 1932
- By 1933 they had produced a TEM with two magnetic lenses which gave 12,000 times magnification.

Ernst Ruska: Nobel Prize in physics 1986

Electron Microscope Deutsches Museum, 1933 model
Brief History: The state-of-art TEM

Electron Microscope Deutsches Museum, 1933 model

FEI Titan 60-300 TEM, NORTEM facility- UiO
Installed: 2014
**Brief History: The state-of-art TEM**

**BIG LEAP:** Introduction of **Lens Aberration Correctors** allowing atomic resolution at low accelerating voltages.

## Resolution limit

<table>
<thead>
<tr>
<th>Year</th>
<th>Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>1940s</td>
<td>~10nm</td>
</tr>
<tr>
<td>1950s</td>
<td>~0.5-2nm</td>
</tr>
<tr>
<td>1960s</td>
<td>0.3nm (transmission)</td>
</tr>
<tr>
<td></td>
<td>~15-20nm (scanning)</td>
</tr>
<tr>
<td>1970s</td>
<td>0.2nm (transmission)</td>
</tr>
<tr>
<td></td>
<td>7nm (standard scanning)</td>
</tr>
<tr>
<td>1980s</td>
<td>0.15nm (transmission)</td>
</tr>
<tr>
<td></td>
<td>5nm (scanning at 1kV)</td>
</tr>
<tr>
<td>1990s</td>
<td>0.1nm (transmission)</td>
</tr>
<tr>
<td></td>
<td>3nm (scanning at 1kV)</td>
</tr>
<tr>
<td>2000s</td>
<td>&lt;0.1 nm (Cs correctors)</td>
</tr>
</tbody>
</table>

**Typical TEM operating voltages in Materials Science Research**

- 300 kV
- 200 kV
- **80 kV**
- 60 kV

Before C<sub>s</sub> correction

![Before Cs correction](image1)

After C<sub>s</sub> correction

![After Cs correction](image2)

Core of the M100 galaxy seen through Hubble (source: NASA)

Transmission Electron Microscope Fundamentals
Electrons interaction with the specimen

Electrons have both wave and particle nature

Typical TEM operating voltages in Materials Science Research
- 300 kV
- 200 kV
- 80 kV
- 60 kV

Typical specimen thickness
~ 100 nm or less

Electron have both wave and particle nature

Courtesy: D.B. Williams & C.B. Carter, Transmission electron microscopy
Electron lenses

Any axially symmetrical electric or magnetic field have the properties of an ideal lens for paraxial rays of charged particles.

- **Electrostatic**  \[ F = -eE \]
  - Not used as imaging lenses, but are used in modern monochromators

- **ElectroMagnetic**  \[ F = -e(v \times B) \]
  - Can be made more accurately
  - Shorter focal length

*Courtesy: http://www.matter.org.uk/tem/lenses/electromagnetic_lenses.htm*
TEM Lens Aberrations

- **Spherical aberration coefficient**
  \[ d_s = 0.5MC_s\alpha^3 \]
  
  M: magnification
  \( C_s \): Spherical aberration coefficient
  \( \alpha \): angular aperture/
  angular deviation from optical axis

- **Chromatic aberration**

- **Astigmatism**

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*University of Oslo*  
Centre for Materials Science and Nanotechnology (SMN)

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TEM Lens Aberrations

Schematic of spherical aberration correction

(a) specimen
(b) Cs Correction lens system (diverging lens)

Probe-forming Cs corrector (CEOS GmbH)
Image-forming Cs corrector (CEOS GmbH)

Courtesy: Knut W. Urban, Science 321, 506, 2008; CEOS gmbh, Germany; www.globalsino.com
TEM Lens Aberrations

Why we need an aberration-corrected TEM at 80kV???

- Correcting aberrations improves the TEM resolution at 80 kV

Uncorrected 80 kV $\rightarrow$ $\sim 0.3$ nm
Corrected 80 kV $\rightarrow$ $\sim 0.14$ nm

- Improved resolution enables the possibility of imaging carbon nanostructures at atomic level

(Courtesy: NASA)
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FEG gun
Extraction Anode
Gun lens
Monochromator Aperture
Monochromator
Accelerator
Gun Shift coils
C1 aperture/mono energy slit
C1 lens
C2 lens
C2 aperture
Condenser alignment coils
C3 lens
C3 aperture
Beam shift coils
Mini condenser lens
Objective lens upper
Specimen Stage
Objective lens upper
Image Shift coils
Objective aperture
Cs Corrector
SA Aperture
Diffraction lens
Intermediate lens
Projector 1 lens
Projector 2 lens
HAADF detector
Viewing Chamber
Phosphorous Screen
BF/CCD detectors
EELS prism
GIF CCD detector

Courtesy: David Rassouw, CCEM, Canada
Electron gun

Illumination system

Imaging system

Projection and Detection system

Specimen stage

Courtesy: David Rassouw
FEG Electron gun source
Specimen Stage
TEM Specimen Holder

See also 1.4 “Holder support”
TEM Specimens

- Typically 3 mm in diameter

*Courtesy: http://asummerinscience.blogspot.no*
TEM Viewing Chamber – Phosphorous Screen
TEM Image recording CCDs and EELS Spectrometer
Transmission Electron Microscopy

Introduction and Basics
Part-2
TEM in Materials Science

The interesting objects for TEM is not the average structure or homogenous materials but local structure and inhomogeneities

- Defects
- Interfaces
- Precipitates
- Chemical composition
- Atomic Structure
- Chemical bonding
- Electronic Structure
TEM techniques

### Imaging

- Conventional TEM
- Bright/Dark-Field TEM
- High Resolution TEM (HRTEM)
- Scanning TEM (STEM)
- Energy Filtered TEM (EFTEM)

#### Main Contrast phenomena in TEM

- Mass thickness Contrast
- Diffraction contrast
- Phase Contrast
- Z-contrast

### Diffraction

- Selected Area Electron Diffraction
- Convergent Beam Electron Diffraction

Phase identification, defects, orientation relationship between different phases, nature of crystal structure (amorphous, polycrystalline, single crystal)

### Spectroscopy

- Electron Dispersive X-ray Spectroscopy (EDS)
- Electron Energy Loss Spectroscopy (EELS)

Chemical composition, electronic states, nature of chemical bonding (EDS and EELS).
Spatial and energy resolution down to the atomic level and ~0.1 eV.
Objective aperture: Contrast enhancement

All electrons contribute to the image.

Intensity: Thickness and density dependence

Mass-thickness contrast

A small aperture allows only electrons in the central beam in the back focal plane to contribute to the image.

Diffraction contrast (Amplitude contrast)

One grain seen along a low index zone axis.
TEM techniques

**Imaging**
- Conventional TEM
- Bright/Dark-Field TEM
- High Resolution TEM (HRTEM)
- Scanning TEM (STEM)
- Energy Filtered TEM (EFTEM)

**Diffraction**
- Selected Area Electron Diffraction
- Convergent Beam Electron Diffraction

**Spectroscopy**
- Electron Dispersive Spectroscopy (EDS)
- Electron Energy Loss Spectroscopy (EELS)

Simplified ray diagram of conventional TEM
Imaging

Mass thickness and diffraction contrast

Gd-Hf-Co-Al quaternary alloys

Mass thickness and Z- contrast

Z
Gd 64
Hf 72
Co 27
Al 13
Imaging

HRTEM

Phase contrast

5. nm

STEM

Z- contrast

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Raw HAADF-STEM, ABF-STEM and HRTEM image of Si in the [110] zone axis by FEI Titan 60-300 with spatial resolutions of 0.8 Å for STEM and 2.0 Å for TEM.

Courtesy: Wei Zhan, Øystein Prytz, et al. (2015), SMN, UiO
Electron Diffraction in TEM
Simplified ray diagram

Parallel incoming electron beam

Sample

Objective lens

Diffraction plane (back focal plane)

Objective aperture

Image plane

Selected area aperture

Parallel incoming electron beam

Sample

Objective lens

Diffraction plane (back focal plane)

Objective aperture

Selected area aperture

1,1 nm

3,8 Å

Si

PowderCell 2.0

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Elastic scattered electrons
Only the direction of \( \mathbf{v} \) is changing. (Bragg scattering)

Elastic scattering is due to Coulomb interaction between the incident electrons and the electric charge of the electron clouds and the nucleus. (Rutherford scattering).

The elastic scattering is due to the average position of the atoms in the lattice.

Reflections satisfying Braggs law:

\[
2d\sin \theta = n\lambda
\]

Electrons interacts 100-1000 times stronger with matter than X-rays
- more absorption (need thin samples)
- can detect weak reflections not observed with XRD technique

Courtesy: Dr. Jürgen Thomas, IFW-Dresden, Germany
Selected area diffraction (SAD)

- Parallel incoming electron beam and a selection aperture in the image plane.

- Diffraction from a single crystal in a polycrystalline sample if the SAD aperture is small enough/crystal large enough.

- Orientation relationships between grains or different phases can be determined.

- \( \sim \) 2% accuracy of lattice parameters
  - Convergent electron beam better
Camera constant

\[ R = L \tan 2\theta_B \sim 2L \sin \theta_B \]
\[ 2d \sin \theta_B = \lambda \]
\[ \downarrow \]
\[ R = \frac{L \lambda}{d} \]

Camera constant:

\[ K = \lambda L \]
Indexing diffraction patterns

The $\mathbf{g}$ vector to a reflection is normal to the corresponding $(h\ k\ l)$ plane and $|\mathbf{g}| = 1/d_{nh\ nk\ nl}$

- Measure $R_i$ and the angles between the reflections
- Calculate $d_i$, $i=1,2,3$ (=K/R_i)
- Compare with tabulated/theoretical calculated d-values of possible phases
- Compare $R_i/R_j$ with tabulated values for cubic structure.
- $\mathbf{g}_{1,hkl} + \mathbf{g}_{2,hkl} = \mathbf{g}_{3,hkl}$ (vector sum must be ok)
- Perpendicular vectors: $\mathbf{g}_i \cdot \mathbf{g}_j = 0$
- Zone axis: $\mathbf{g}_i \times \mathbf{g}_j = [HKL]_z$
- All indexed $\mathbf{g}$ must satisfy: $\mathbf{g} \cdot [HKL]_z = 0$
Electron Diffraction in TEM

Amorphous phase

Poly crystalline sample

Single Crystals

Interface between two different phases epitaxially grown

The orientation relationship between the phases can be determined with ED.
Schematic of orientation of \( \text{Cu}_2\text{O}/\text{ZnO} \) cross section perpendicular to electron beam direction for SAED

**TEM imaging**

**Selected Area Electron Diffraction (SAED)**

- **ZnO (substrate)**
  - Image A: TEM image with SAED Tilt 1
  - B: SAED pattern with indices [002], [1-22], [1-20]

- **\( \text{Cu}_2\text{O}/\text{ZnO} \) (interface)**
  - E: TEM image with SAED Tilt 2
  - C: SAED pattern with indices [110], [11-1], [13-1], [1-10], [002] ZnO, [111] \( \text{Cu}_2\text{O} \)

- **\( \text{Cu}_2\text{O} \) (film)**
  - D: SAED pattern with indices [112], [110], [002]
  - F: SAED pattern with indices [002], [1-11], [1-10]
  - G: SAED pattern with indices [111] \( \text{Cu}_2\text{O} \), [002] ZnO
  - H: SAED pattern with indices [111], [110], [002]
Spectroscopy
We detect the X-rays generated by the sample on a spectrometer. Each element has a unique atomic structure and hence a characteristic X-ray energy.
Energy Dispersive X-ray Spectroscopy

**Layers:**
- TiO$_2$ (ALD, 10 nm)
- AZO (sputtering, ~200 nm)
- Quartz (1 mm)
Electron Energy Loss Spectroscopy (EELS)

Inelastically interacted incident electron suffers energy loss after passing through the specimen

- Phonon Excitations
- Inter and Intraband Transitions
- Plasmon Excitations
- Inner Shell Ionizations
- Cherenkov radiation

Each element has characteristic ionization energy owing to its unique atomic structure

EELS of the Oxygen K edge

The reference spectra of Cu$_2$O and CuO are from online EELS database\textsuperscript{1}. The reference spectra were shifted in energy to match the first O K peak in our experimental, and scaled by the total counts in the energy-loss 560-590 eV.

Next Lecture

• TEM Instrumentation – Part 2
  (Text book Chapters: 5 – 9)

• TEM Specimen Preparation
  (Text book Chapters: 10)