Final Exam Notice

• Time and Date: 2:30 – 4:30 PM, Wednesday, Dec. 10, 08.
• Place: Classroom CHEM-102
• Coverage: All contents after midterm
• Open note
Imaging

- Imaging in the TEM
- Diffraction Contrast in TEM Image
- HRTEM (High Resolution Transmission Electron Microscopy) Imaging or phase contrast imaging
- STEM imaging
• HRSTEM imaging
• Spectroscopy
• Other technologies in TEM
• Basic SEM
• Review
the aberration wave function: $e^{-ix(u)}$

The aberrated electron probe wave function in the plane of the specimen when deflected to position $x_p$ is:

$$\psi(x, x_p) = A_p \int_0^{u_{\text{max}}} e^{-ix(u)} e^{2\pi i a(x-x_p)} du$$

$A_p$ is a normalization constant chosen to yield

$$\int \left| \psi(x, x_p) \right|^2 dx = 1$$

the electron probe passes through the specimen and
the transmission function is $t(x)$, so the transmitted wave function $\psi_t(x, x_p)$ is

$$\psi_t(x, x_p) = t(x)\psi_p(x, x_p)$$

this wave function is then diffracted onto the detector plane and
form CBED pattern

$$\Psi(u, x_p) = F[\psi_t(x, x_p)] = \int e^{2\pi iux} \psi_t(x, x_p) dx^2$$

the intensity of this wave function $|\Psi(u, x_p)|^2$ as a function of
scattering angle $\phi = \lambda u$ is the CBED pattern
The CED pattern is incoherently integrated over the detector geometry and the result is the final STEM image signal \( g(x_p) \) for one probe position \( x_p \).

\[
g(x_p) = \int |\Psi(u, x_p)|^2 D(u) du
\]

where \( D(u) \) is the detector function

\[
D(u) = \begin{cases} 
1 & u_{\text{min}} < u < u_{\text{max}} \\
0 & \text{otherwise}
\end{cases}
\]

Where \( (\lambda u_{\text{min}}) \) and \( (\lambda u_{\text{max}}) \) are the inner and outer angles of the ADF detector. This process is repeated for each position \( x_p \).

This equation is difficult to intuitively relate to any specific structure in the specimen. An approximated linear image model for thin specimens assuming an incoherent image process is
The outer dimension of ADF detector is large enough (infinite comparing to the inner dimension ADF, and then image produced by ADF is an incoherent image.

\[
g(x) = f(x) * h_{ADF}(x)
\]

where the specimen function \( f(x) \) is approximately the probability for scattering to the large angles of ADF detector

\[
f(x) \approx \int D(u) \frac{\partial \sigma(x)}{\partial u_s} du_s = \int_{u_{\text{min}}}^{u_{\text{max}}} \frac{\partial \sigma(x)}{\partial u_s} du_s
\]

\( \frac{\partial \sigma(x)}{\partial u_s} \) is the partial cross section for scattering to angle \( u_s \) at position \( x \) of the specimen.

With the incoherent image assumption an ADF-STEM image of a very thin specimen is essentially a mass thickness map of the specimen.
The point spread function is just the intensity distribution in the focused probe

\[ h_{ADF}(x) = \left| \psi_p(x) \right|^2 = A_p \left| \int_0^{u_{\text{max}}} e^{-i\chi(u)} du \right|^2 \]

ignore astigmatism and for 1-D, the probe intensity is

\[ h_{ADF}(r) = A_p \left| \int_0^{u_{\text{max}}} e^{-i\chi(u)} J_0(2\pi ur) u du \right|^2 \]

where \( J_0(x) \) is the zeroth order Bessel function, and \( r \) is the radial coordinate. This integral can only be done numerically
Circular aperture

In the 2-D, the transmission function of a circular aperture is

\[ f(x, y) = \begin{cases} 1 & \text{if } (x^2 + y^2) < (a/2)^2 \\ 0 & \text{elsewhere} \end{cases} \]

Then

\[ F(u) = \left( \frac{\pi a^2}{2} \right) \frac{J_1(\pi au)}{\pi au} \]

\( u \) is a radial coordinate and \( J_1(x) \) is the first order Bessel function.

The first order Bessel function

\[ J_1(z) = \frac{z}{2} \sum_{k=0}^{\infty} \frac{(-1)^k \cdot z^{2k}}{2^{2k} \cdot k!(k+1)!} \]
Cs=1.2 mm, and E=300 kv

Transfer function

**TEM:**

\[ S(u) = A(u) \sin \chi(u) \]

where \( \chi(u) = \pi \Delta f \lambda u^2 + \frac{1}{2} \pi C_s \lambda u^4 \)

**STEM:**

\[ H_{ADF}(u) = A_p \left| \int_0^\infty h_{ADF}(r) J_0(2\pi ru) r dr \right|^2 \]
Obtaining STEM image and alignment of STEM
• forming CBED pattern in a very large aperture
• for HRSETM, orientate crystal on zone axis accurately
• focusing the probe so that a over-lapped CBED pattern (for crystalline specimen) or ronchigrams (for amorphous specimen) are formed.
• Ronchigrams is named by John Cowley, because the geometry used to obtain them is identical to that used to test optical lenses and mirrors.

Using Ronchigrams to align STEM optics
(a): Misaligned probe
(b): Astigmatic probe, x/y are not symmetric
(c): Optimized probe
Examples of STEM image

Z-contrast image

Bit Line

Capacitor

Plug

Si Base

Word Line

0.5μm
Mapped HRSTEM image of Si showing the dumbbell structure.
<110> simulated and experimental images of interfacefacial ordering of a \( (\text{Si}_{4}\text{Ge}_{8})_{24} \) superlattice grown on Ge <001> at 350C
Electron Energy Spectroscopy using STEM

- EDX: energy-dispersive X-ray spectroscopy
- EELS: Electron energy loss spectroscopy
Schematic representation of the interactions between electron beam and specimen

- The presence of the atomic and nuclear electrostatic potential affect the speed and direction of the incident electrons.
- The inelastically scattered electrons transfer their energy to the specimen and hence have less energy than their original one.
- The energy passed to the specimen is then released in different ways, and if detectable, the different signals may be collected, and then used for identify the chemical composition.
X-ray generation

• When an incident electron hits an atom in specimen, there is chance to transfer its energy to one of the bounding electron. The electron gaining that energy can be free from the nucleus, or even escape from the solid (a secondary electron). This process is called ionisation.

• The ionised atom now has an electron vacancy in a shell. The bounding electrons in higher energy levels will jump into this vacancy to restore the stationary state of atom.

• This jump has following characteristic: 1). Because of the energy difference, X-ray or other photons are released during the process; 2). This jump has a selection rule, for example, electrons in two of three energy levels in L shell may jump into K shell. They are K1 and K2 lines, or only K because of the small energy difference.

• Jumping to K shell creates K line, to L shell creates L line, and so on.

• Because the shell structure determines the unique energy differences, the X-rays such generated is characteristic. In a spectrum, this characteristic radiation is shown as a peak at a specific energy.

• When X-rays with certain energy present, it means that a certain element corresponding to these X-rays exists in the specimen.
EDX spectrum of a Zr-based metallic glass showing a fitted background and two peak areas above the background

Thin-film approximation
- determine the composition \{c_i\} from the spectrum intensity \{I_i\}

The ratio of two observed X-ray peak intensities of element A and B, \( I_A / I_B \), the corresponding weight-fraction ratio, \( c_A / c_B \)

\[
\frac{c_A}{c_B} = K_{AB} \frac{I_A}{I_B}
\]

where \( K_{AB} \) is a constant for a given accelerating voltage and \( c_A + c_B = 1 \)
EELS spectrum and mapping

- When an incident electron beam passes a specimen, electrons interact with a specimen. Some electrons are scattered elastically without losing energy, but some are scattered inelastically and losing energy.
- The inelastic scattered electron carry some valuable information, which may be used to characterize the sample.
- By collecting the electron spectrum (EELS), the optical properties (plasmons excitation), chemical composition, valence, and bounding information can be accessed.
Sample thickness

- the amount of inelastic scattering increase with specimen thickness, \( t \), rapidly.

- Mean free path, \( \lambda \), is dimension that indicates the path length inside the specimen wherein all electrons statistically will have undergone one inelastic scattering event.

- the intensity of the elastic scattered electrons \( I_0 \) depends on the sample thickness \( t \) and the mean free path \( \lambda \) of the inelastic scattering

- the total spectral intensity is \( I \)

\[
sample \text{ thickness } \: \: t = \lambda \cdot \ln \left( \frac{I}{I_0} \right)
\]
Quantification of EELS Core Edges

- The energy of absorption edges in EELS are quick and reliable indicators of the elements in a material, but quantifying the chemical composition requires more efforts.
- The absorption edge must first be isolated from the background, which originates primarily from other cores edges, sometimes the high-energy tails of plasmon peaks, and occasionally from artifacts of the spectrometer.
- As shown in figure, the atomic composition of boron and nitrogen is \( c_B \) and \( c_N \); the intensities of B and N edge are \( I_{BK} \) and \( I_{NK} \); the partial ionization cross-sections of B and N are \( \sigma_{BK} \) and \( \sigma_{NK} \)

\[
\frac{c_B}{c_N} = \frac{I_{BK}}{I_{NK}} \cdot \frac{\sigma_{NK}}{\sigma_{BK}}
\]
Energy filtered TEM imaging (EFTEM) and EELS mapping

- A conventional TEM uses all electrons that pass through the sample to form image, causing low contrast in HRTEM imaging.
- Energy-filtered TEM (EFTEM) allows image formation with electrons that have undergone selected energy losses in the specimen, detecting chemical contrast in specimen by adjusting an energy filter to pass electrons that have lost energy to core ionizations of selected elements.
- Under optimal conditions, these energy-filtered image (mapping) can reveal chemical contrast with subnanometer spatial resolution.
- Alternatively, an energy filter can pass only zero-loss electrons, thereby removing all inelastic scattering to form high contrast image and diffraction pattern image.
Instrumentation

- EDX and EELS always combine with STEM mode because of nano-probe size, low dose, and coherent beam.
Other TEM imaging techniques

• Lorentz Microscopy
• Electron holography
• In-situ TEM dynamic experiments
• Aberration (Cc/ Cs)-corrected TEM /STEM
• SEM
Lorentz Microscopy

- If the sample is magnetic, its magnetic field will deviate the electron beam as it passes through and then the electrons used for imaging will not be parallel to the optic axis. So all images will be severely aberrated and shifted when focusing.

- Using a Lorentz lens to correct the magnetic field.

- Using Fresnel imaging to see the magnetic domain well.

- If you under- or overfocus the objective lens, then the electrons coming through different domain will produce images in which the wall appears bright or dark lines.
Electron holography

- unlike conventional TEM imaging technique, the holography technique uses both the amplitude and the phase of the beam to form image. **As a result, the Cs effect can be partially corrected.** Also we can examine other phase-dependent phenomena such as magnetism.

- In conventional TEM, we treat specimen as a pure phase object and the imaginary part of \( \exp(i\chi(u)) \), i.e. the sine term, converts this information into an amplitude, which we record as the image.

- With holography, we can use the real part of the exponential too. So more information is included in holography.
Holographic image of a magnetic Co particle showing (A) the reconstructed image (B). The magnetic lines of force, and (c). The intergram (D). Lines of force in a magnetic recording medium.
Off-axis electron holography to image magnetic induction vectors in Ni nanodots.
Palladium nanocrystals sit on the surface of an amorphous silica sphere
In-situ TEM dynamic experiments

• A CCD video camera is attached to record the dynamic changes in the microstructure.
• The special sample holders are used to apply strain, cooling, and heating, etc. to foil to dynamically observe the changes of microstructure.
Environmental cell microscopy uses differential pumping and small apertures to maintain a controlled atmosphere environment in the region of the sample, thereby enabling chemical reactions to be studied in real time at close to atomic resolution.

**Possible Applications**
- real-time imaging of gas-solid reaction kinetics
- real-time study of compositional changes using EELS energy-filtered images (chemical maps) of reacted and unreacted areas

**Specimen Requirements**
Samples can be prepared by almost any method (crushing, chemical thinning, ion-beam milling) but must be thin (< 50nm) for high-resolution viewing.

Environmental TEM in The John M. Cowley Center for High Resolution Electron Microscopy, Arizona State University
In situ TEM images of hybridization
TEM double tilt heating holder, Gatan Inc.

TEM in situ heating image showing the paraelectric to ferroelectric phase transformation along grain boundary at 120 °C.
In-situ deformation of nano-structured gold film. Images shows two micro-cracks joining under applied load.
Aberration Corrected TEM/ STEM

Imaging with a perfect Lens

Objective lens

Point source

Aperture

Minimum probe diameter

Back focal plane

High-angle rays

Low-angle rays
Effect of spherical aberration, $C_s$

Real lens is limited by aberrations to ~ 50 wavelengths
Effect of chromatic aberration, Cc

Rays with different energies are focused differently
$S(u) = A(u) \sin \chi(u)$
where $A(u)$ is aperture function

$\chi(u) = \pi \Delta f \lambda u^2 + \frac{1}{2} \pi C_s \lambda^3 u^4$

$u = \theta / \lambda$, reciprocal vector

$\chi(u)$ may be called phase distortion function

We need correct $C_s$ and $\lambda$.

**Delta f = -10 nm, and E=300 kv**
Correction of Spherical Aberration, $C_s$

Scherzer (1936) – All round electron lenses will suffer from positive $C_s$
[Because all electric or magnetic fields must obey Laplace’s equation]

Scherzer (1947) – Combinations of non-round lenses can correct $C_s$

Non round lenses

We use multipoles, which are named according to their number of poles
Examples: Quadrupole Octupole
Correction of Spherical Aberration, $C_s$

- Scherzer (1936) – Spherical aberration unavoidable for static round lenses
- Scherzer (1947) – Combinations of non-round lenses can correct $C_s$

A corrector is a complicated system – only practical 50 years later

Quadrupole

Sextupole or Hexapole

Octupole
Quadrupole-Octupole Corrector (Nion)

Schematic only – Not to scale

Quadrupoles

Octupoles

Objective
Hexapole corrector (CEOS)

Schematic only – Not to scale

Hexapole 1

Doublet 1

Doublet 2

Hexapole 2

Objective
Measuring Aberrations in (S)TEM

- Important to accurately measure aberrations
- Zemlin tableau - bright field (S)TEM
- CEOS ADF
- Nion Ronchigram Tuning
- Ramasse and Bleloch
- Cowley Ronchigram fringes
- Yamazaki, Mitsuishi, Kuramoki et al, Sawada
Ronchigram to measure Cs (Amorphous materials)

\[
\frac{\partial \chi}{\partial \rho} = 0 \quad \frac{\partial^2 \chi}{\partial \rho^2} = 0
\]

(Cowley 1986)
Resolution implies being able to ‘resolve’ objects GaN <211>
Spots in FFT show information transfer in the image (not ‘resolution’) GaN <211>

Original sample courtesy LBNL; FIB preparation at UIUC; Images at ORNL; using FEI Titan with CEOS corrector
Progress in electron microscope resolution

- Atomic resolution of uncorrected microscopes improved from 2.0Å (1978) to approximately 1.0Å (1996) as accelerating energies increased from 100keV to 1250keV.
- Software aberration correction achieved 1.38Å at 1000keV in 1992, 1.5Å at 200keV in 1993, and 0.78Å at 300keV in 2001.
- Holography went from 1.36Å at 300keV in 1993 to 0.89Å in 2004.
- Hardware Cs correction improved resolution from 1.2Å in 1998 to 0.78Å in 2004 to the current value of 0.63Å in 2007 (STEM).

Silicon [112]

HR-TEM

http://www.sc.doe.gov/bes/scale_of_things.html

HAADF STEM

http://stem.ornl.gov/
ADF and BF STEM GaN[112]

JEOL image has 0.63Å atomic resolution

ADF image

BF image

Schottky Gun

0.063 nm
The Scanning electron microscope (SEM) is similar to the TEM in that they both employ a beam of electrons directed at the specimen.

- Certain features such as electron gun, condenser lenses and vacuum system are similar in both instruments.
- The imaging mechanisms are entirely different.
- The TEM provides information about the internal structure of thin specimens.
- The SEM is primarily used to study the surface or near surface structure of bulk specimens.
SEM image of cryptomelane
INCONEL 783 superalloy fracture surface SEM images showing the intergranular fracture and precipitates along grain boundary

(a) 300+3 trapezoid cyclic loading cracking at 650°C

(b) Sustained loading cracking at 650°C
Topographic images
- studying the surface features
- using secondary and backscattered electrons
SEM images of fracture surface of alumina
(a) Secondary electron image
(b) back scattered electron image
Backscattered coefficient varies monotonically with atomic number.

(a) Backscattered image of polished silver soldered joint. Topographic contrast arising from the different resistance to abrasion of the phase.

(b) By adding signals, the topographic contrast is suppressed and composition contrast is enhanced.
• Although we cannot obtain diffraction spot pattern in the SEM as we can in TEM, we can make use of electron channeling (the BSC electron coefficient is dependent on the orientation of a crystal with respect to the incident beam) to form diffraction patterns.

• determine the crystallographic orientation of features such as particles, grains or subgrains in a specimen.
Diffraction pattern

- Although we cannot obtain diffraction spot pattern in the SEM as we can in TEM, we can make use of electron channeling (the BSC electron coefficient is dependent on the orientation of a crystal with respect to the incident beam) to form diffraction patterns.

- determine the crystallographic orientation of features such as particles, grains or subgrains in a specimen.