High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM)

Lecture key points:

- Why are we doing HAADF-STEM?
- The reciprocity theorem of elastic electron scattering
- The origin of thermal diffuse scattering
- The electron probe
- The Ronchigram
- Quantitative HAADF-STEM imaging
  - Image simulations
  - Quantitative interpretation of atomically-resolved HAADF-STEM images

TEM microscope in the beginning…
Two basic operation modes in transmission electron microscopy (TEM):
- using stationary electron beam (conventional TEM mode)
- using scanning electron probe (STEM mode)

Combined atomically-resolved structural, compositional and chemical information:
- STEM: Scanning Transmission Electron Microscope
- HAADF: High-Angle Annular Dark-Field detector
Why are we doing HAADF-STEM?

HAADF-STEM of functional materials:
- strong compositional sensitivity

HAADF-STEM of nanoparticles:
- Cu-Ni-Pt nanoparticle in carbon-based matrix
- Ru-O nanoparticles in TiO\textsubscript{2} based matrix
Why are we doing HAADF-STEM?

HAADF-STEM of hollow structures:
- Hollow nanospheres

Combining Bright-Field (BF) and HAADF-STEM imaging:
- Compositionally complex nanotube
Why are we doing HAADF-STEM?

**Pd islands on SrTiO\(_3\) substrate**

Combining Bright-Field (BF) and HAADF-STEM imaging:
- Pd on perovskite substrate

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Why are we doing HAADF-STEM?

**Small region of polycrystalline BaTiO\(_3\) tubes**

Images were taken at SuperSTEM (Daresbury)

Combining Bright-Field (BF) and HAADF-STEM imaging:
- Atomic-scale sensitivity
- Strong chemical and structural sensitivity
Why are we doing HAADF-STEM?

Small region of polycrystalline BaTiO$_3$ tubes

Images were taken at SuperSTEM (Daresbury)

Combining Bright-Field (BF) and HAADF-STEM imaging:
- The interpretation of HAADF-STEM images is more straightforward than BF-STEM

The reciprocity theorem of elastic electron scattering

CTEM
- Electron source (far field)
- Objective lens
- Specimen
- Array of point detectors (CCD or film)

STEM
- Point detector (bright field)
- Electron source

E.J. Kirkland (1988)
The reciprocity theorem of elastic electron scattering: CTEM
The reciprocity theorem of elastic electron scattering: STEM

The origin of thermal diffuse scattering
The origin of thermal diffuse scattering

- \( Z \) : atomic number
- \( E_0 \) : electron beam energy
- \( \theta \) : scattering angle

High angle scattered electrons:
- \( \theta > 10 \) mrad
- Scattering occur on tightly bound s-type states
- Reflects chemical information

Bragg scattered electrons:
- \( \theta < 10 \) mrad
- Scattering localized on the outer shell structures
- Reflects structure

Rutherford cross section:
\[
\sigma_{\text{nucleus}} = 0.62 \times 0^{-\left(\frac{Z}{E_0}\right)} \cot^2 \frac{\theta}{2}
\]

The origin of thermal diffuse scattering
The origin of thermal diffuse scattering

Thermal diffuse scattering (TDS):
- At room temperature the atoms in the specimen vibrate slightly
- Quantum unit of energy is called phonon
- Thermal vibrations lead to a diffuse background intensity in the diffraction pattern

\[ \cot \frac{\theta}{2} = \frac{Z \cdot E}{E_0} \]

Where:
- \( Z \) : atomic number
- \( E \) : electron beam energy
- \( \theta \) : scattering angle
- \( E_0 \) : incident electron energy

Intensity of high-angle scattered electrons is related with Z
Proper setting of the detector will collect only high-angle scattered electrons, thus increase Z-contrast

coherent elastically scattered electrons
incoherent elastically scattered electrons
BF-STEM
HAADF-STEM
The electron probe

- The probe is scanning across the specimen
- The probe shape is defined by condenser (objective) lenses
- The signal is generated at a scanning point of the specimen

STEM images are not magnified by lenses, but by scanning area (pixel size).
- Pixel size is affected by aberrations of the probe

The probe functions at optimum defocus value

- $3 \text{ mrad}$
- $10 \text{ mrad}$
- $12 \text{ mrad}$
The probe functions at optimum convergence angle

How to define best probe for imaging?

Probe has to be smaller than interatomic distances
Probe has to be smaller than interatomic distances

Silicon <011>  
~ 140 pm

Silicon <112>  
~ 80 pm

- Atomic columns resolved
- Atomic columns not resolved
- Atomic columns resolved

The ronchigram

How to define best probe for imaging?
Make use of a ronchigram

Experimental image taken on JEM-2010F (15.4.2010)
The ronchigram

Perfect focus: the ideal lens

Imperfect focus: high-angle beams cross earlier than they should

Shadow image

Ronchigram
The use of ronchigram

Objective astigmatism

Atomically resolved HAADF-STEM imaging

SrTiO$_3$ bulk [001]

HAADF-STEM imaging at high spatial resolution:
- Z-contrast
- Atomic-scale combined compositional and structural sensitivity
**Atomically resolved HAADF-STEM imaging**

**SrTiO\textsubscript{3}, Ruddlesden-Popper planar fault [001]**

SrO-doped SrTiO\textsubscript{3}

Z

- Strontium (Z=38)
- Titanium (Z=22)
- Oxygen (Z=8)

**HAADF-STEM imaging at high spatial resolution:**
- Z-contrast
- Atomic-scale combined compositional and structural sensitivity

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**Atomically resolved HAADF-STEM imaging**

**CaO-doped SrTiO\textsubscript{3}**

Need for quantitative interpretation of atomically resolved HAADF-STEM images
- HAADF-STEM image simulations
HAADF-STEM image simulations

Incomplete list of HAADF-STEM image simulations softwares:

- E.J. Kirkland: Advanced Computing in Electron Microscopy
- P. Galindo: HAADF-STEM image simulations on large scale nanostructures
- V. Grillo: STEM_CELL (http://tem.s3.infm.it/software)
- http://www.hremresearch.com/ (commercial software)
Quantitative HAADF-STEM image analysis

Initial atomic structure model

Experimental HAADF-STEM image

Initial parameters

Noise filter

Multislice simulations (calculation of images)

Fitting the coordinates

Incrementation of parameters

Image matching algorithm: Cross-correlation data cube

Main parameters to vary:
- thickness
- defocus
- COMPOSITION

SrTiO$_3$ in [001] projection

BEST FIT!
Final atomic structure optimized for the composition

SrTiO$_3$ in [001] projection

Image matching algorithm: Cross-correlation data cube

SrTiO$_3$ in [001] projection

Image matching algorithm: Cross-correlation data cube

SrTiO$_3$ in [001] projection

Image matching algorithm: Cross-correlation data cube

SrTiO$_3$ in [001] projection
Quantitative HAADF-STEM

SrTiO$_3$ + 10 mol.%SrO

Experimental
Refined

Quantitative HAADF-STEM

(a) (b) (c)

Initial
Refined
Experimental

(b) 0 10 20 30 40 50 60 70 80

at.% Ca at the planar fault

Xcc

0.85 0.86 0.87 0.88 0.89 0.9 0.91 0.92