Transmission Electron Microscopy of Thin Films and 2D Materials

Paulo Ferreira

Scientific Coordinator, Advanced Electron Microscopy, Imaging and Spectroscopy
INL, Braga, Portugal

Professor
Department of Mechanical Engineering
IST, University of Lisbon, Portugal

Adjunct Professor
Materials Science & Engineering Program
The University of Texas at Austin, USA

International Iberian Nanotechnology Laboratory

+ 40 Nationalities

+ 400 People

+ 180 Ph.Ds

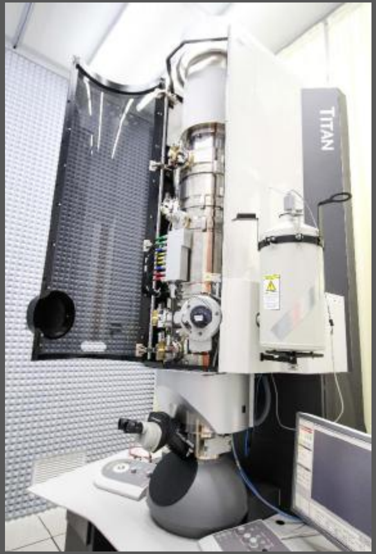
1000 m^2 Clean Room

Electron Microscopy

High Accuracy Laboratory

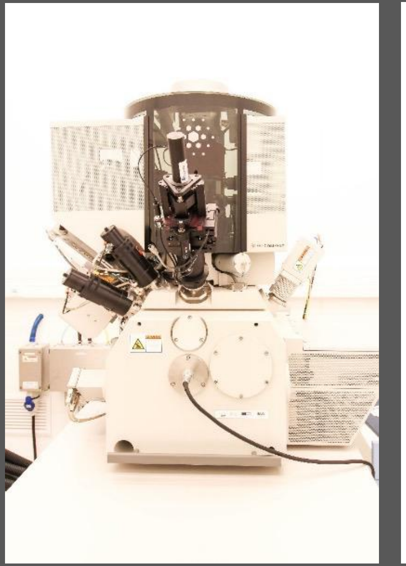
Electron Microscopy Instrumentation

Double Corrected TEM/STEM Titan Themis

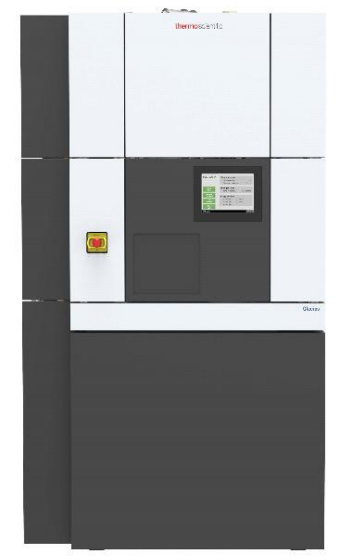


Probe Corrected STEM ChemiSTEM

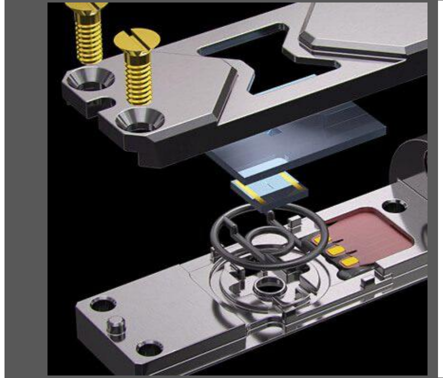
JEOL 2100 TEM/STEM



Dual Beam FIB-SEM Helios 450S



Glacios Cryo TEM



Liquid/Electrochemical Holder

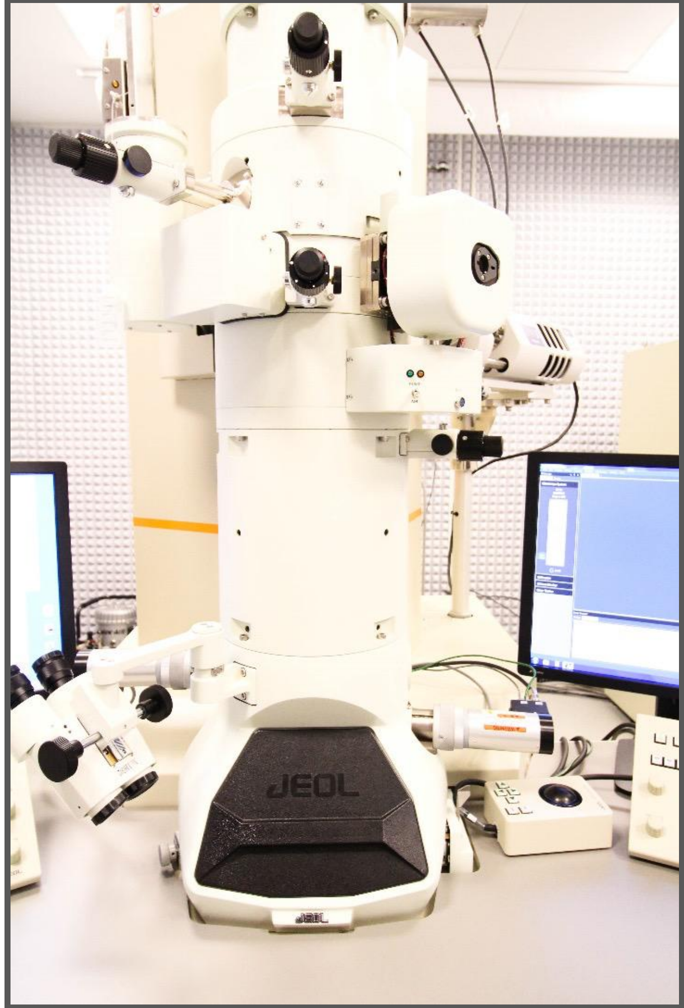
Gas Holder

Heating/Biasing Holder

Cryo Holder

Types of Microscopes

Transmission Electron Microscopes



JEOL 2100

FEI ChemiStem

FEI Themis

Which microscope shall I use?

Things to consider….

Type of sample: Biological, Polymer, Metal, Ceramic, Thin Film, 2D materials

Accelerating Voltage: 60 kV – 3 MV (TEM/STEM)

Gun Type: Tungsten, LaB_6, Field Emission

Pole-piece gap: URP, HRP, CRP

Detectors: STEM, EDS, EELS

Holders: Heating, Double-Tilt, Deformation, Tomography, Wet-Cell, etc…

Image Collection: CCD, CMOS, direct electron cameras

Aberration-correctors: spherical, chromatic

Accelerating Voltage

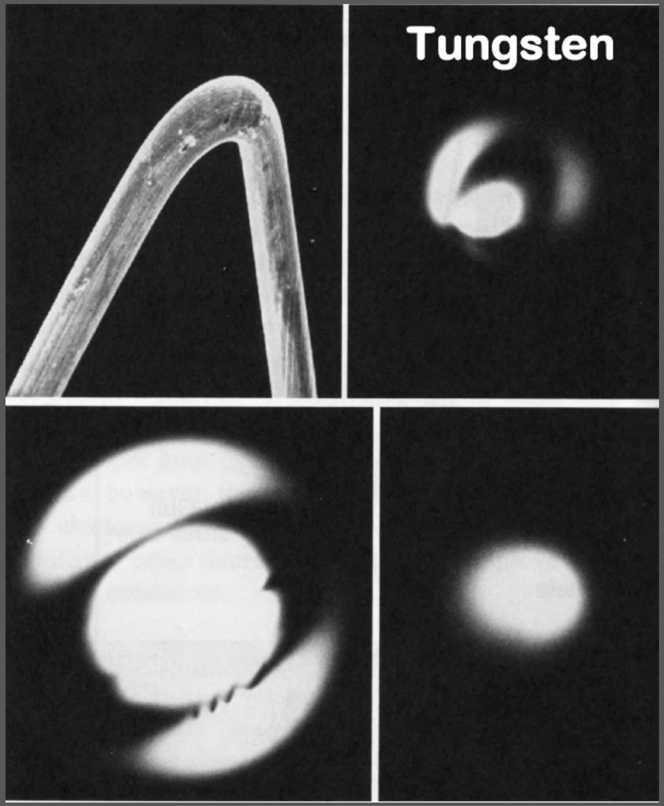
JEOL 200 kV

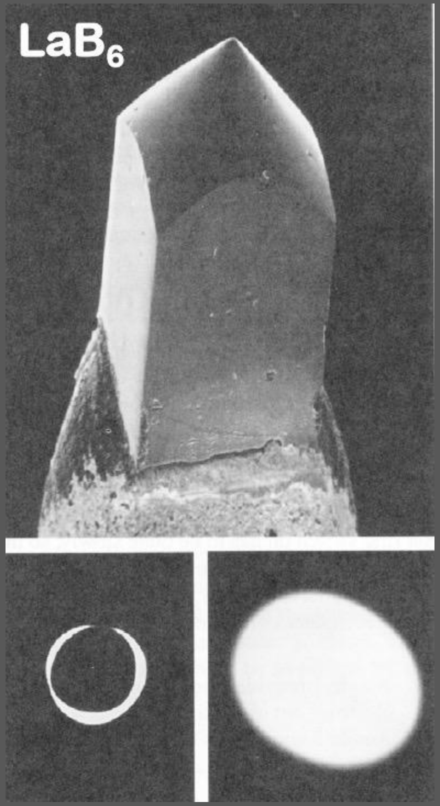
FEI 80-200 kV

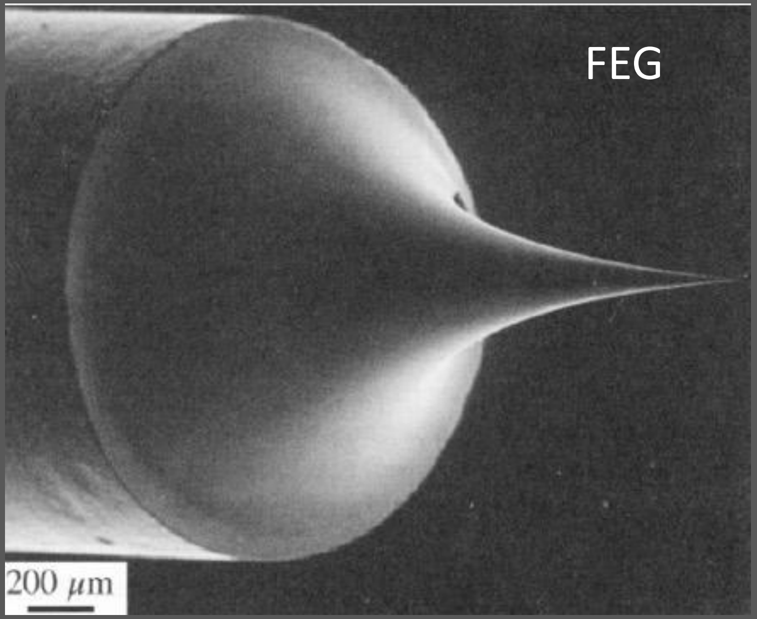
FEI 60-300 kV

Resolution and Beam damage

Gun Type

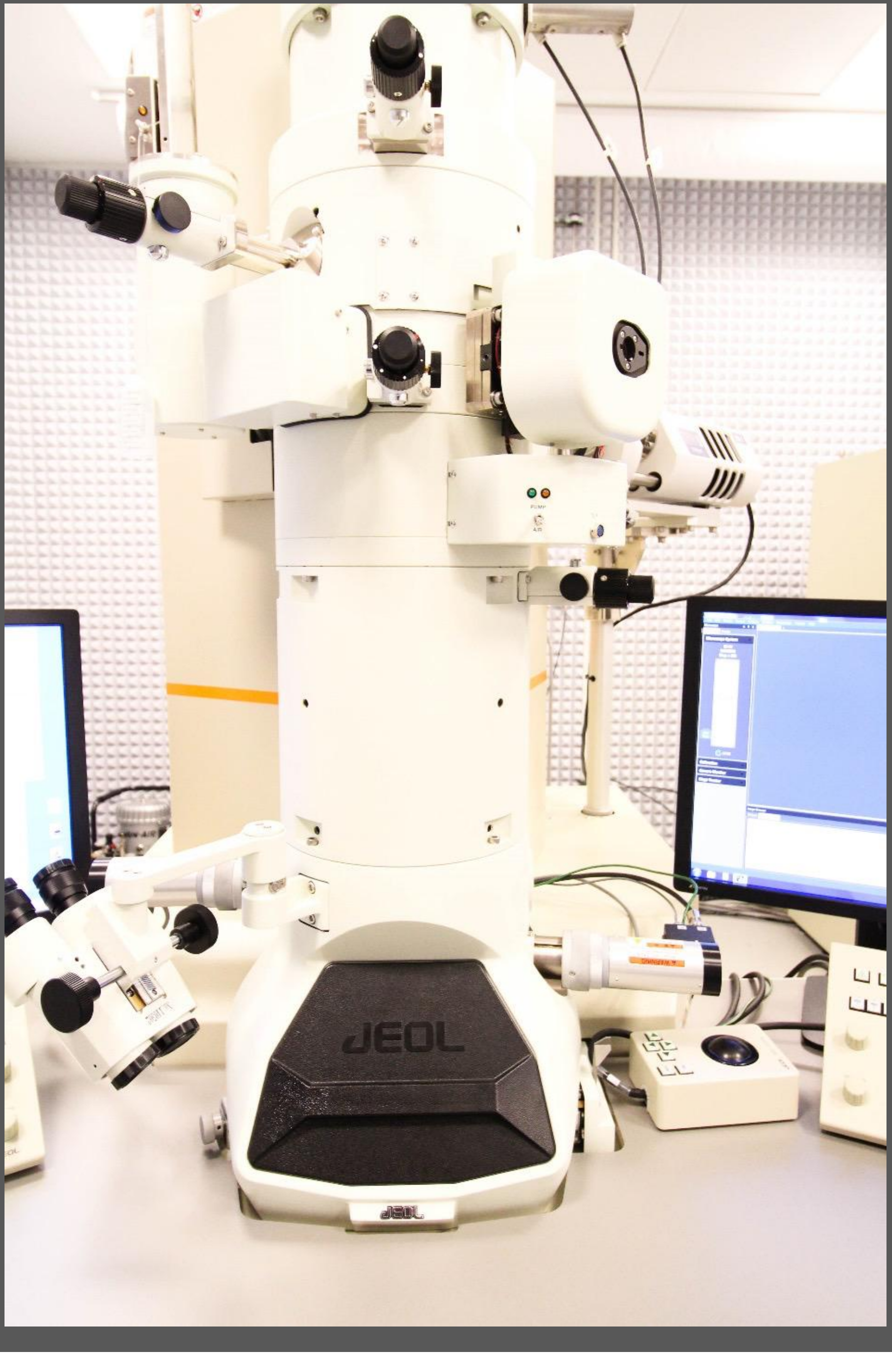


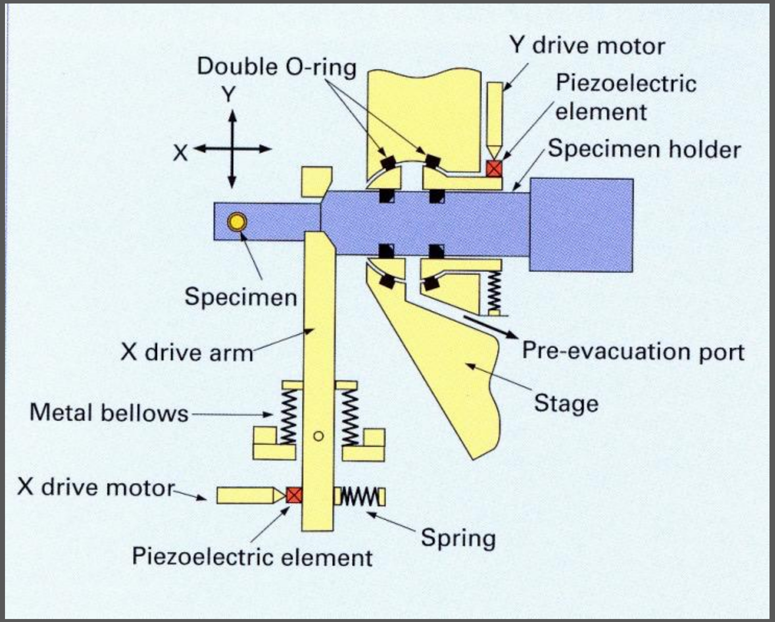


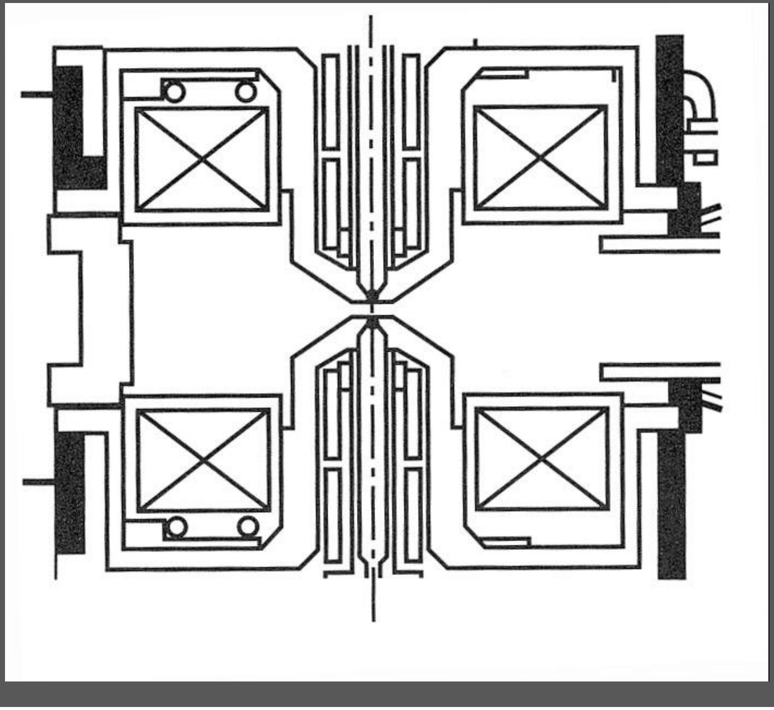


Brightness, Probe size, Temporal coherency, Spatial coherency

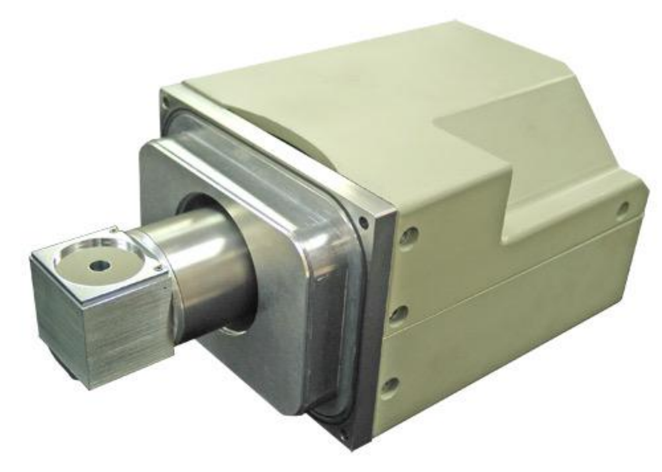
In-situ TEM: Goniometer



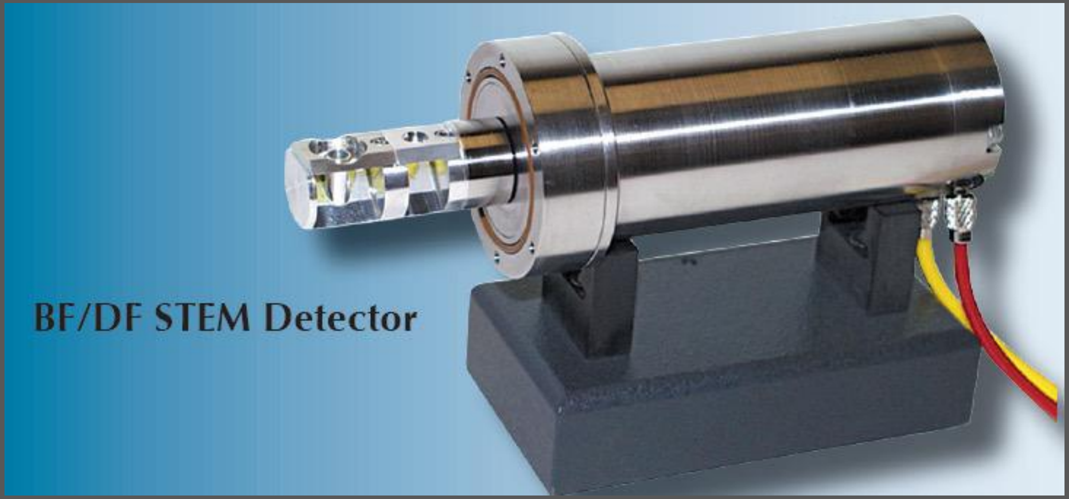


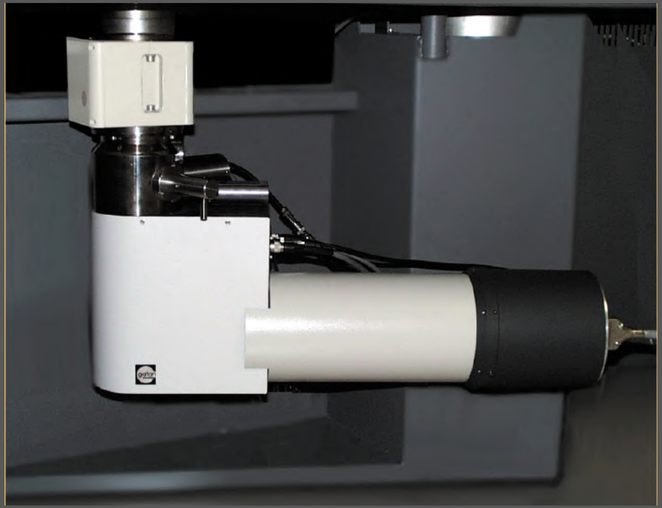


Detectors



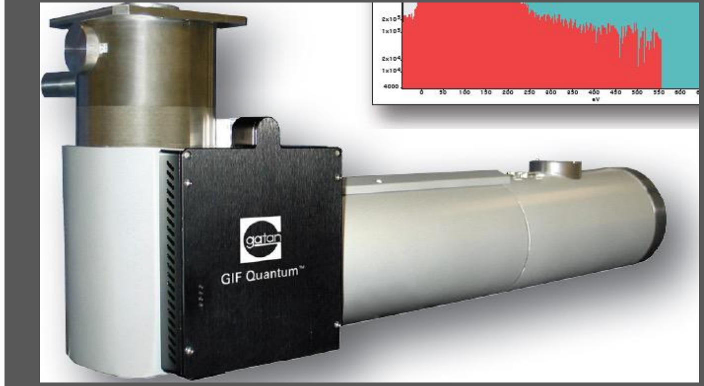
HAADF STEM





EELS Enfina

EDS



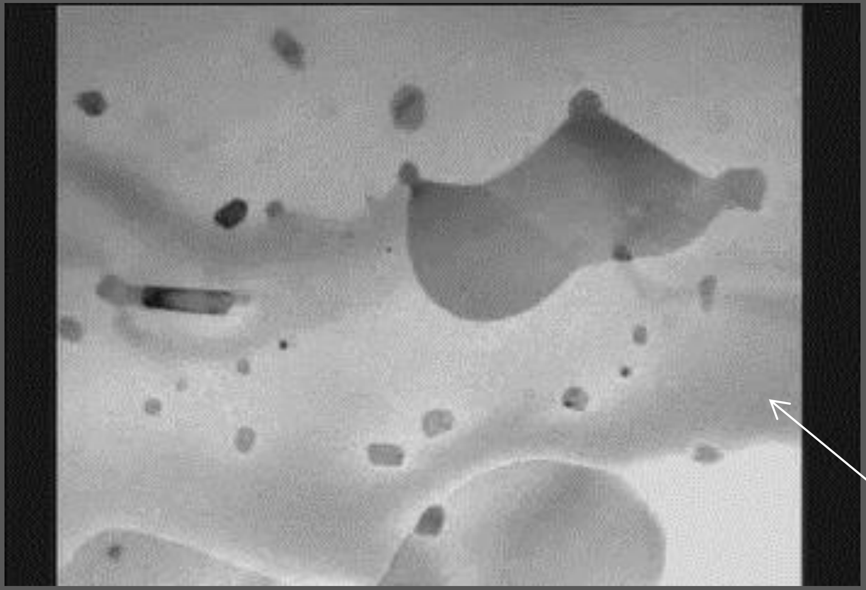
EELS Imaging GIF

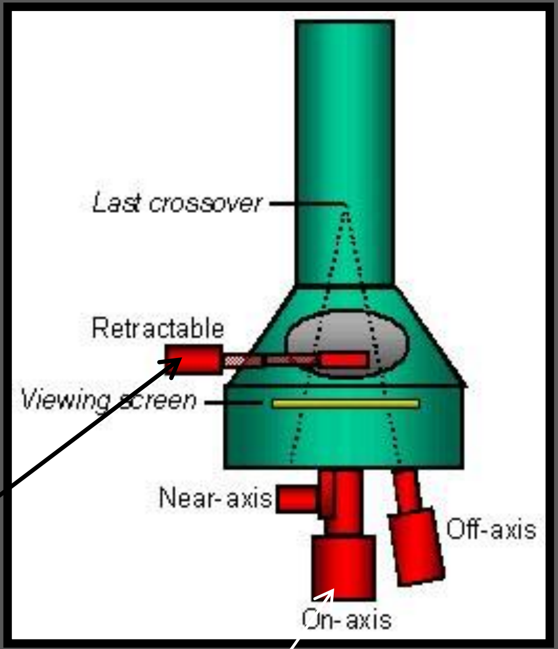
In-situ TEM Specimen Holders

Type of Holders	Possible Applications
In-situ Heating (up to 1200 C)	Thermal stresses, sintering, melting, phase transformations
In-situ Nanoindentation	Mechanical Properties of thin films and nanoparticles
In-situ Straining/Cooling (down to 5 K)	Ductile-Brittle Transition, measure lattice strains by convergent beam
In-situ STM	Electrical properties of thin films and nanoparticles
In- Situ Optical	Catholuminescence, photo catalysis
In-situ Tomography	3-D reconstruction
In-situ Liquid Cell Holder	Electroplating, electrochemical reactions
In-situ Gas holder	catalysis

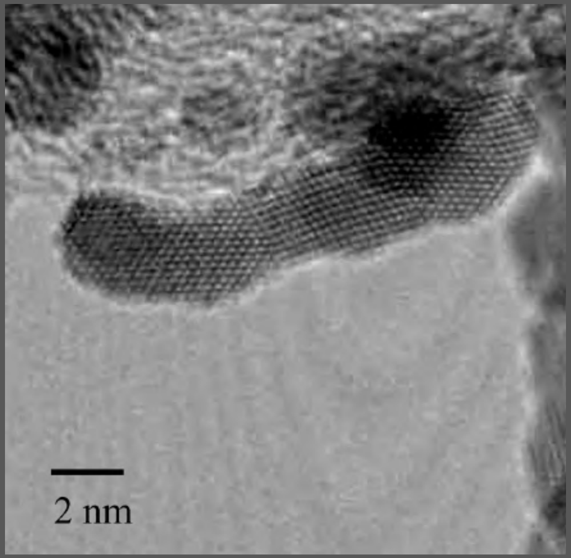
CCD Imaging

Video (courtesy from Gatan Inc.)



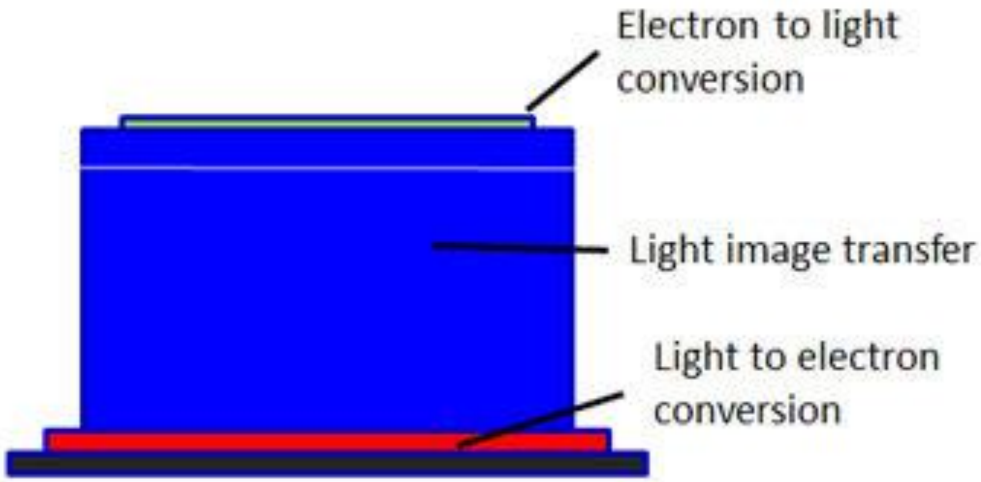


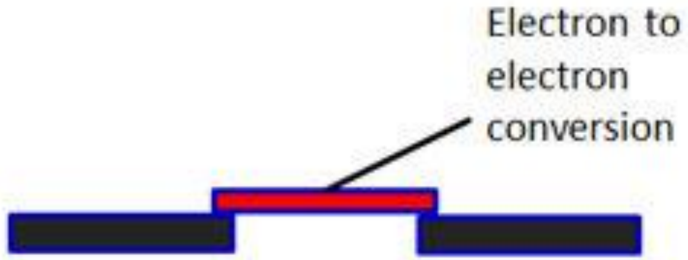
Area Imaged:
16 cm x 16 cm

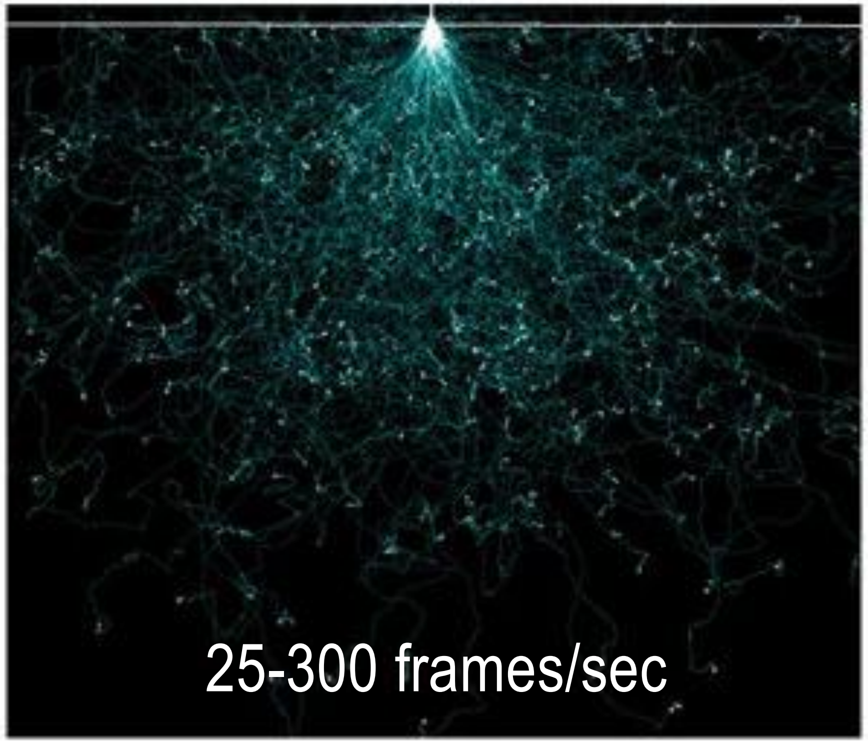


Area Imaged:
2 cm x 2 cm

Direct Detection Cameras







400-1600 frames/sec

TEM Overview

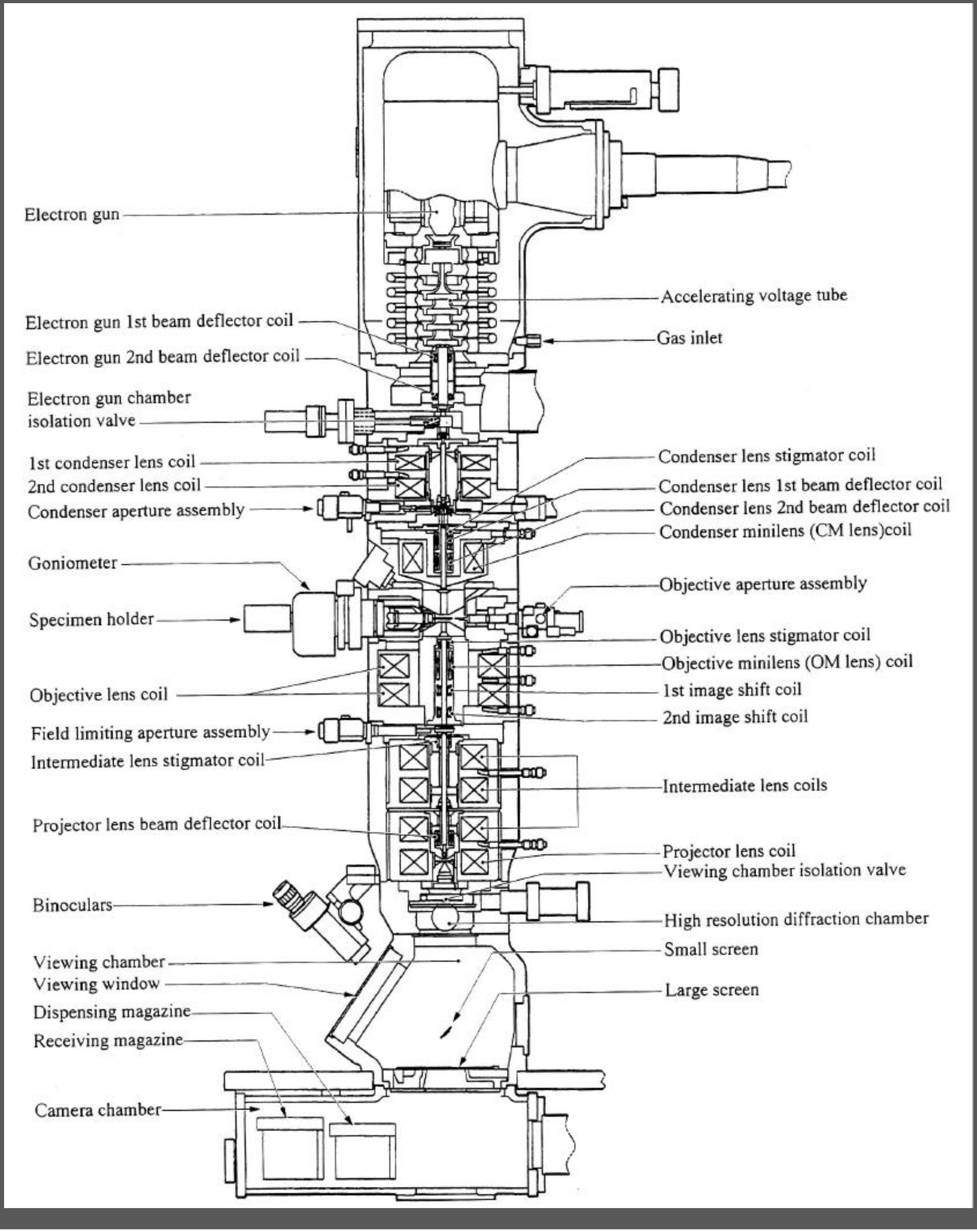
condenser aperture

objective aperture

specimen area

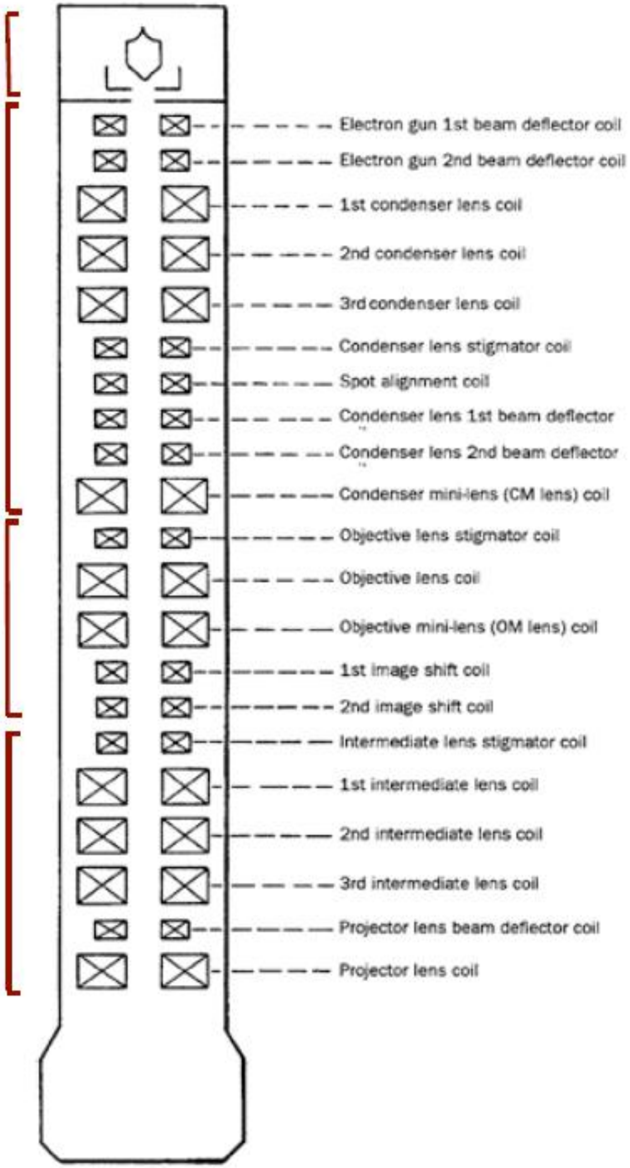
selected area aperture

TEM cross-section



TEM cross section

(simplified - somewhat)



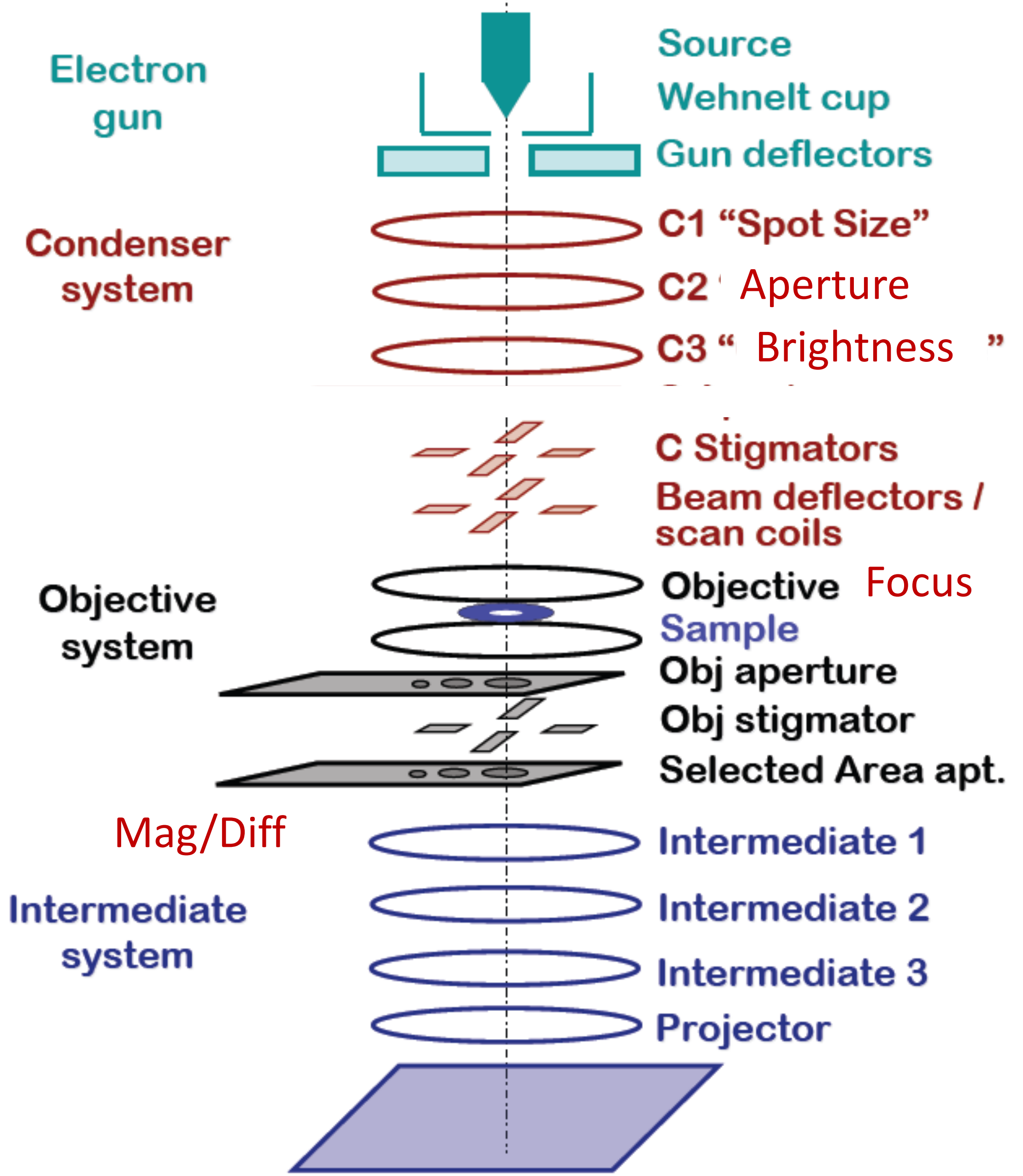
Electron Gun

Condenser System

Objective System

Projector System

TEM cross section



Electron gun

Source

Wehnelt cup

Gun deflectors

Condenser system

C1 “Spot Size”

C2 Aperture

C3 “ Brightness ”

C Stigmators

Beam deflectors / scan coils

Objective system

Objective Focus

Sample

Obj aperture

Obj stigmator

Selected Area apt.

Mag/Diff

Intermediate system

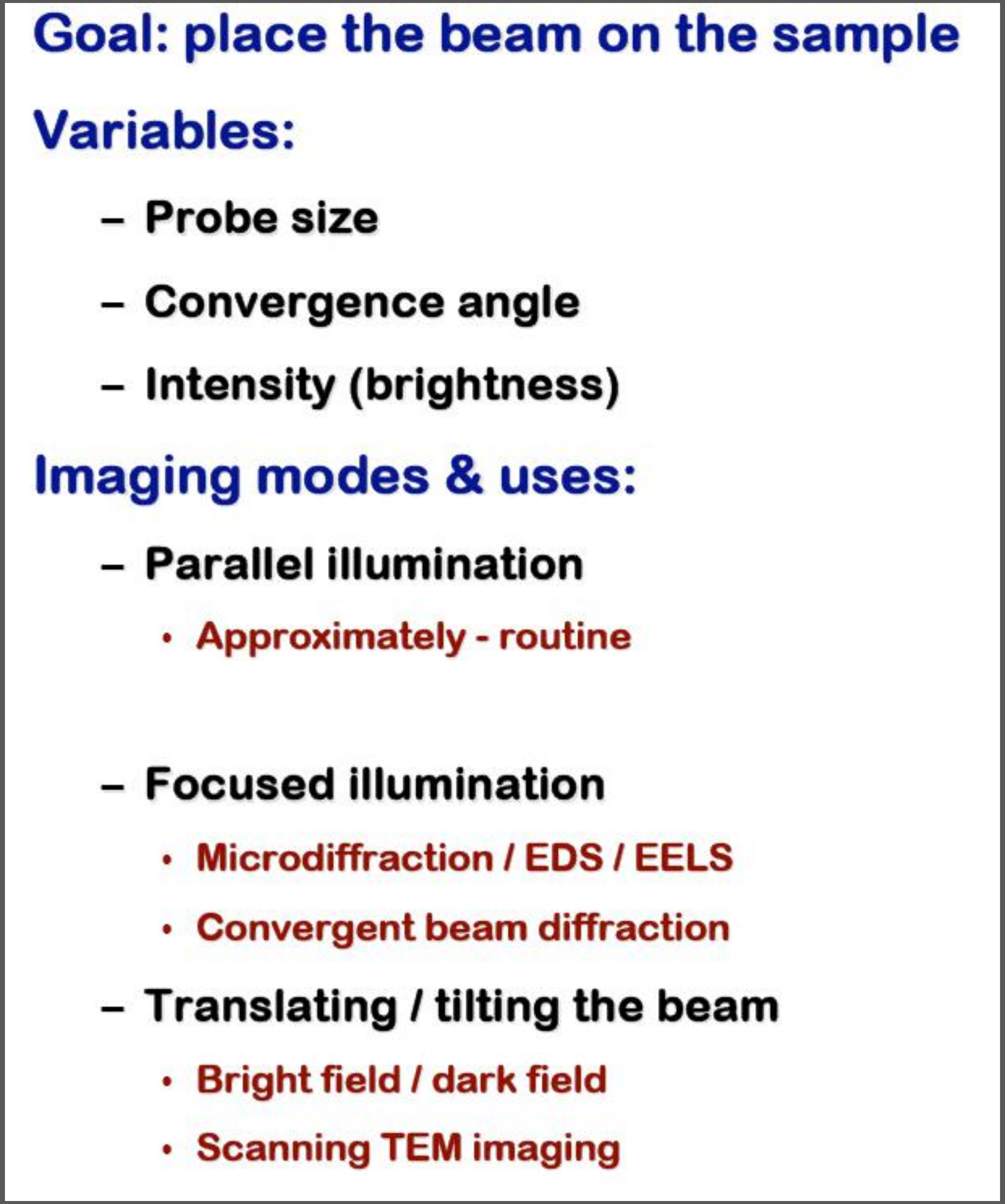
Intermediate 1

Intermediate 2

Intermediate 3

Projector

Condenser System



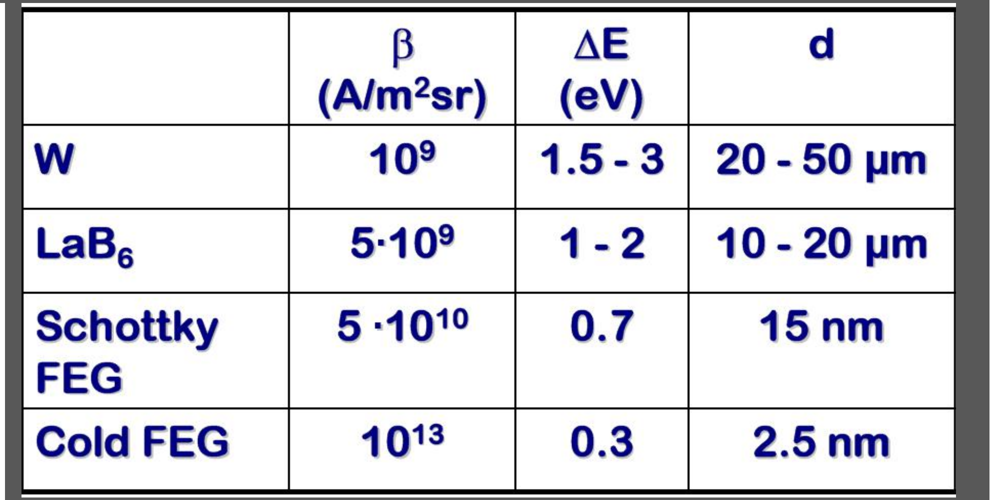
Goal: place the beam on the sample

Variables:

- Probe size
- Convergence angle
- Intensity (brightness)

Imaging modes & uses:

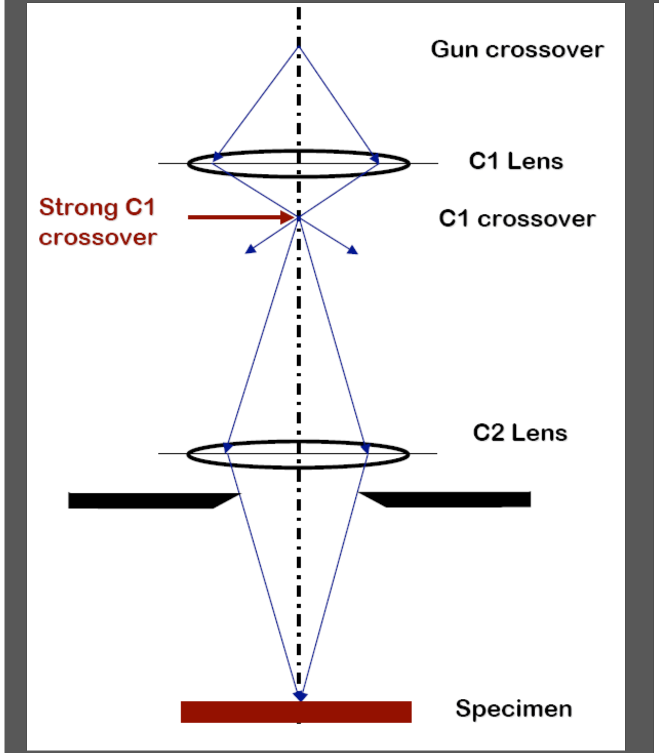
- Parallel illumination
  - Approximately - routine
- Focused illumination
  - Microdiffraction / EDS / EELS
  - Convergent beam diffraction
- Translating / tilting the beam
  - Bright field / dark field
  - Scanning TEM imaging

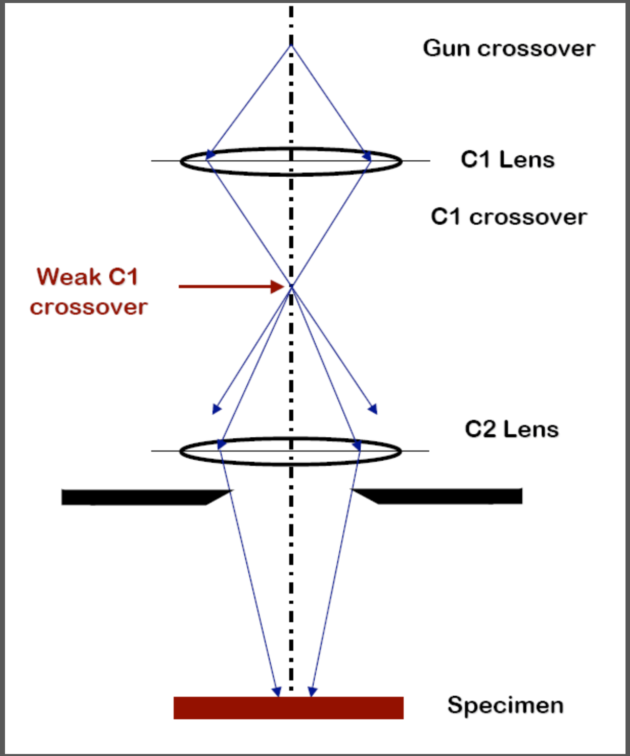


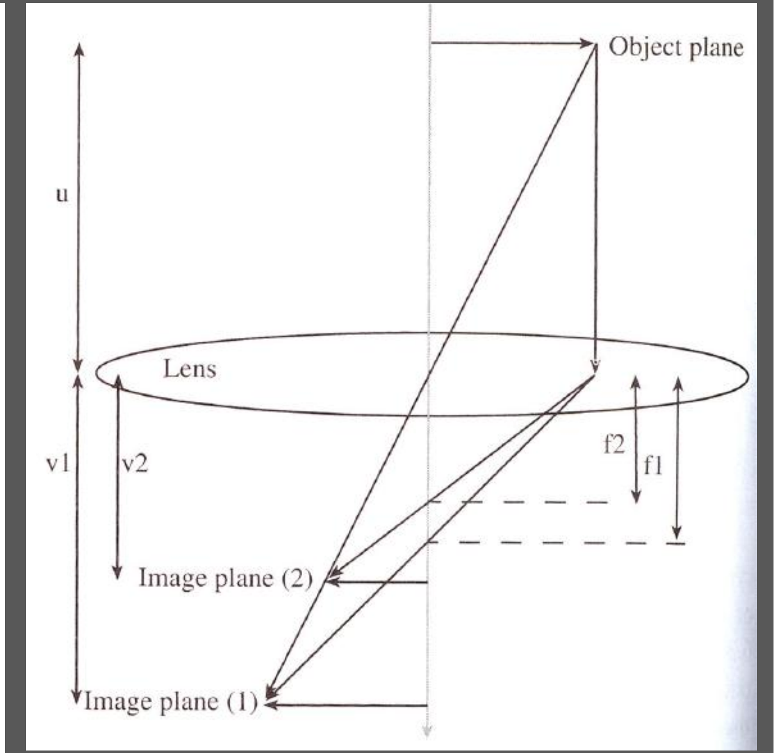
	β (A/m^{2}sr)	ΔE (eV)	d
W	10^9	1.5 - 3	20 - 50 µm
LaB_6	$5 \cdot 10^9$	1 - 2	10 - 20 µm
Schottky FEG	$5 \cdot 10^{10}$	0.7	15 nm
Cold FEG	10^{13}	0.3	2.5 nm

Condenser System

Effect of C1 (Spot Size)







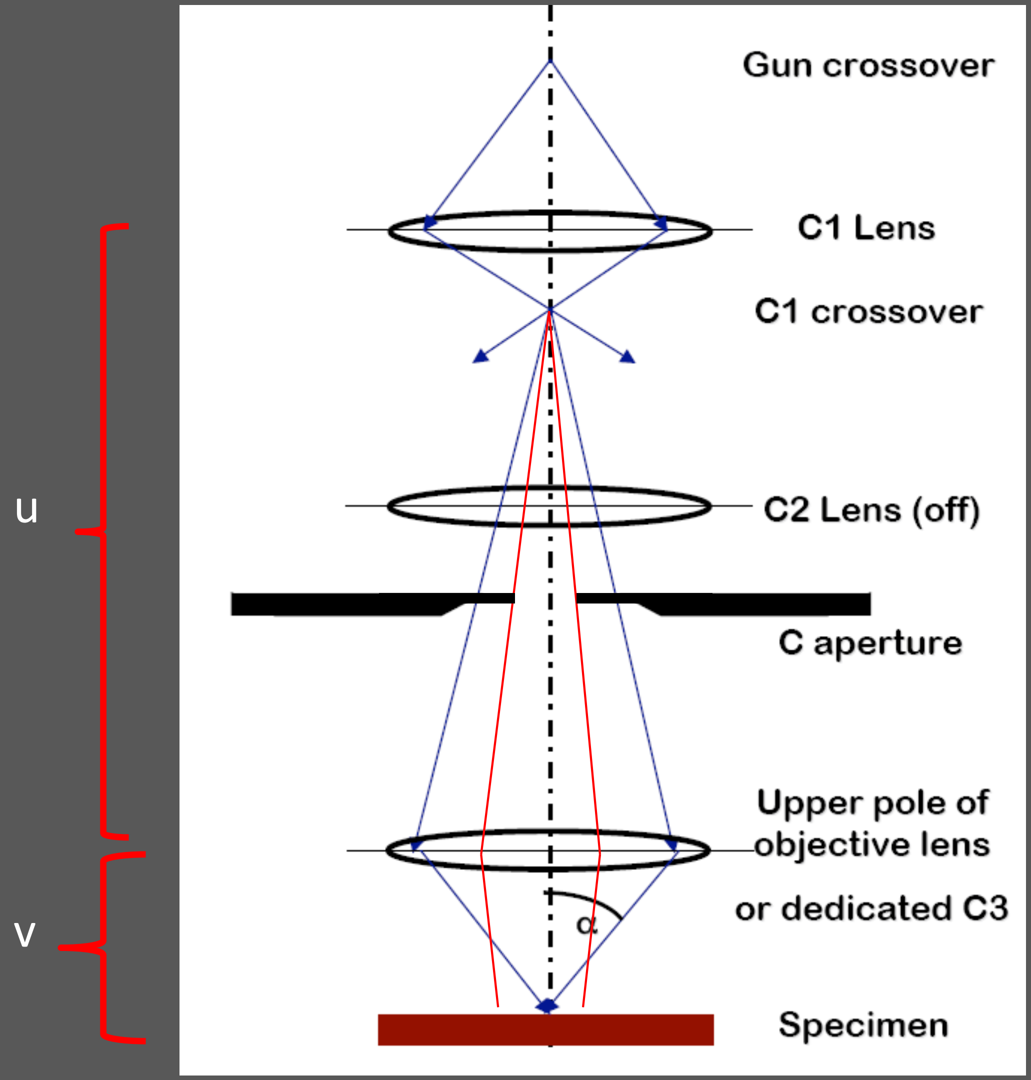
$$\alpha = \frac{\alpha_0}{M}$$

↑ lens strength, ↓ magnification (M), ↑ convergence angle (α), ↓ spot size

Condenser System

Effect of C2 (aperture)

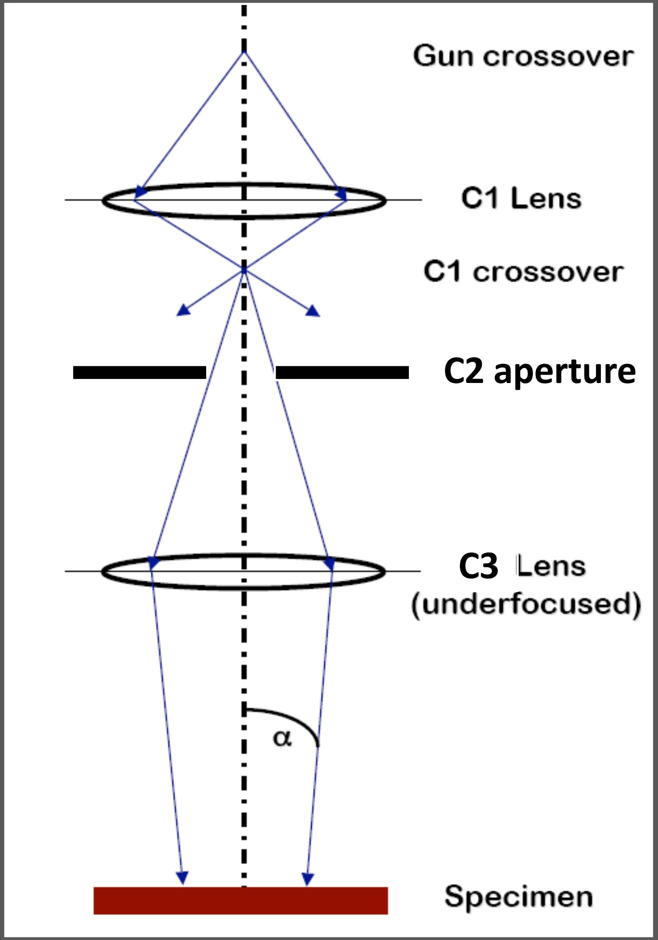
M=v/u

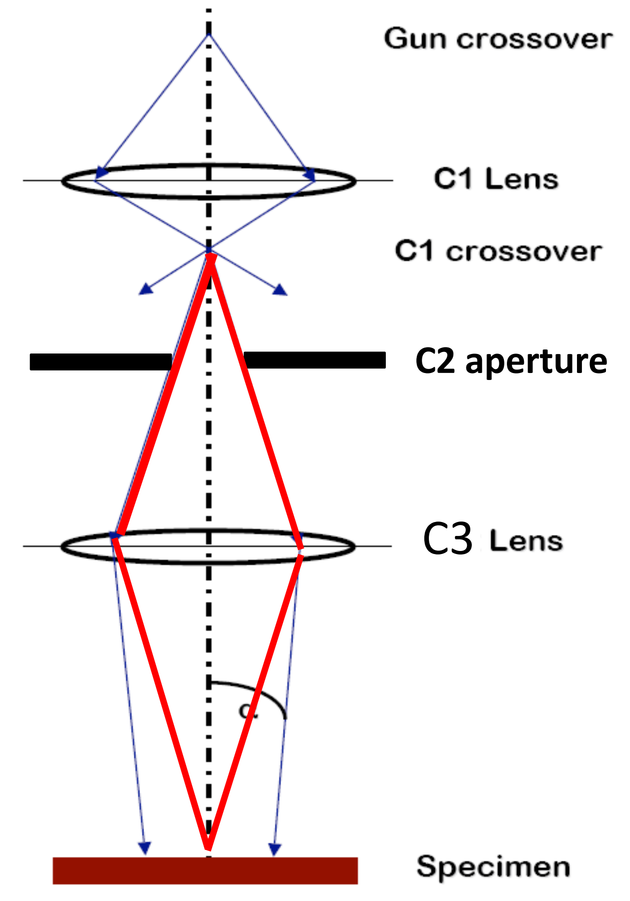


Small aperture: decrease convergence angle , thus increases coherency

Condenser System

Effect of C3 (brightness)

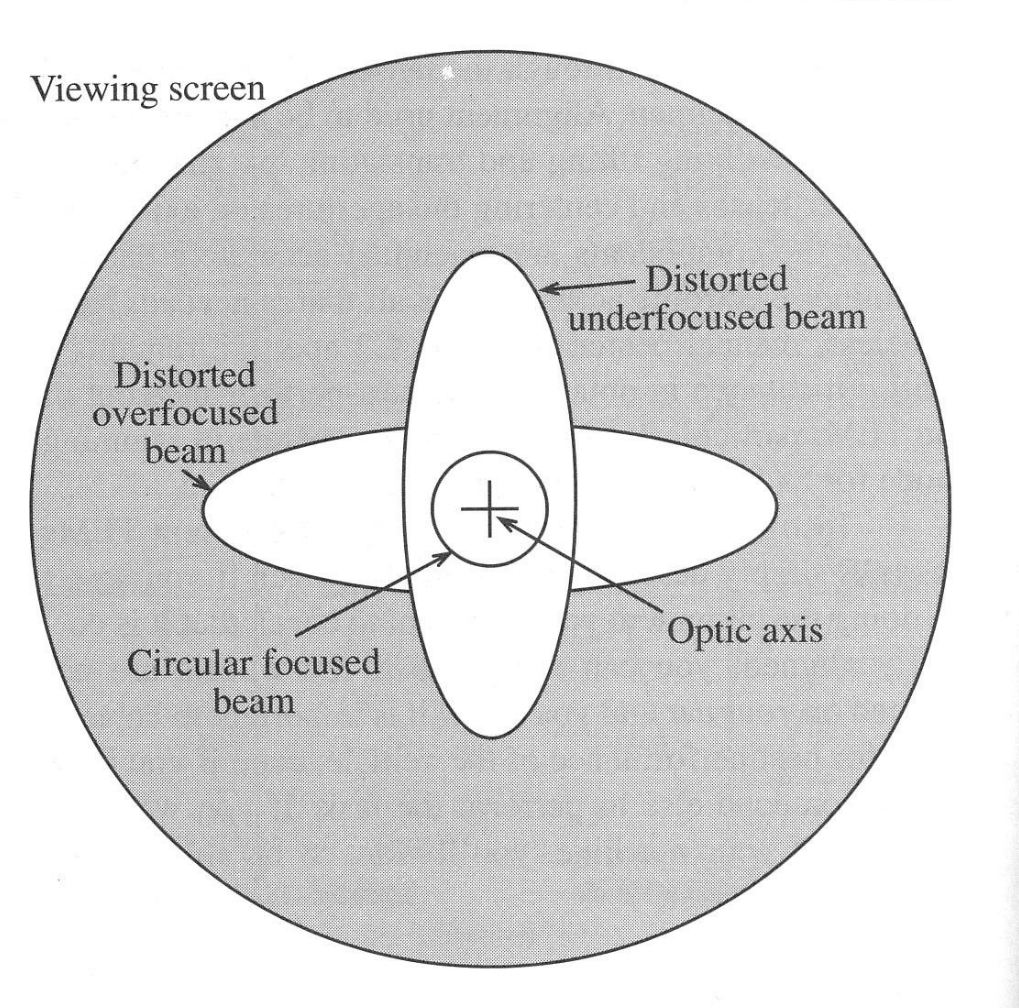




Increase C3 strength: increase convergence angle , thus decreases coherency

Condenser System

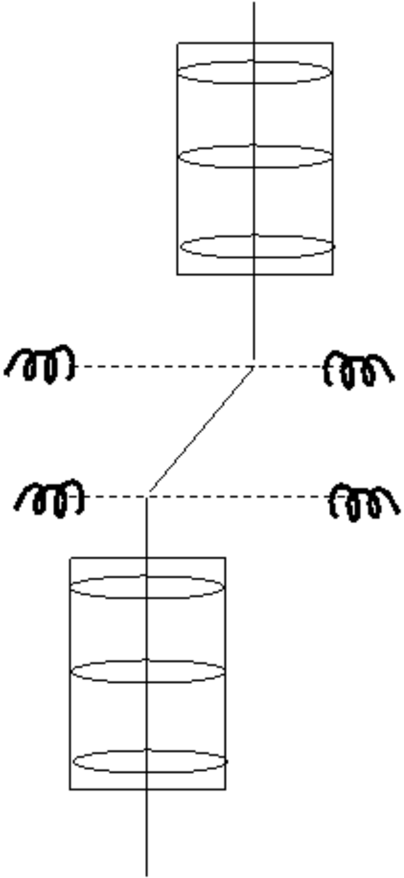
Condensor Stigmators

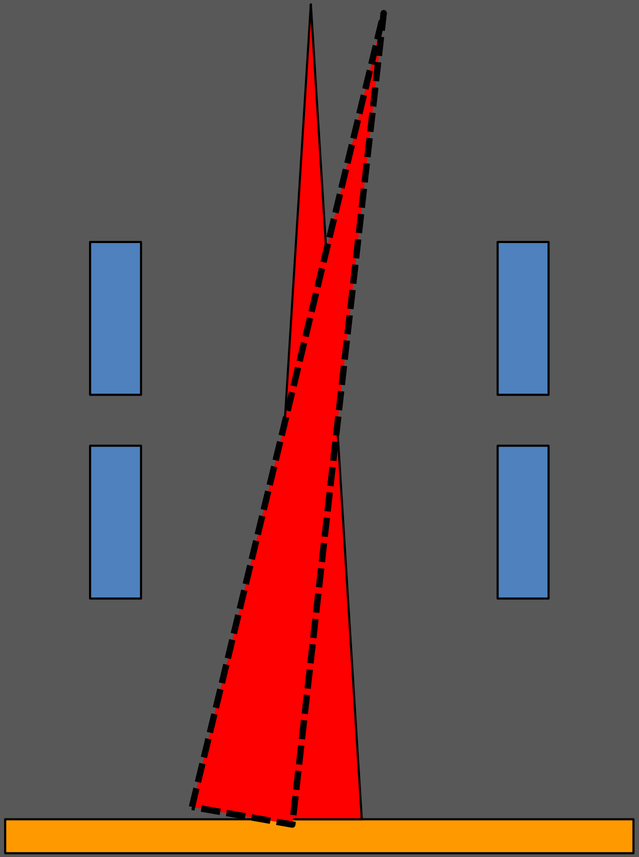


Condenser System

Beam shifts/deflectors

Beam shift

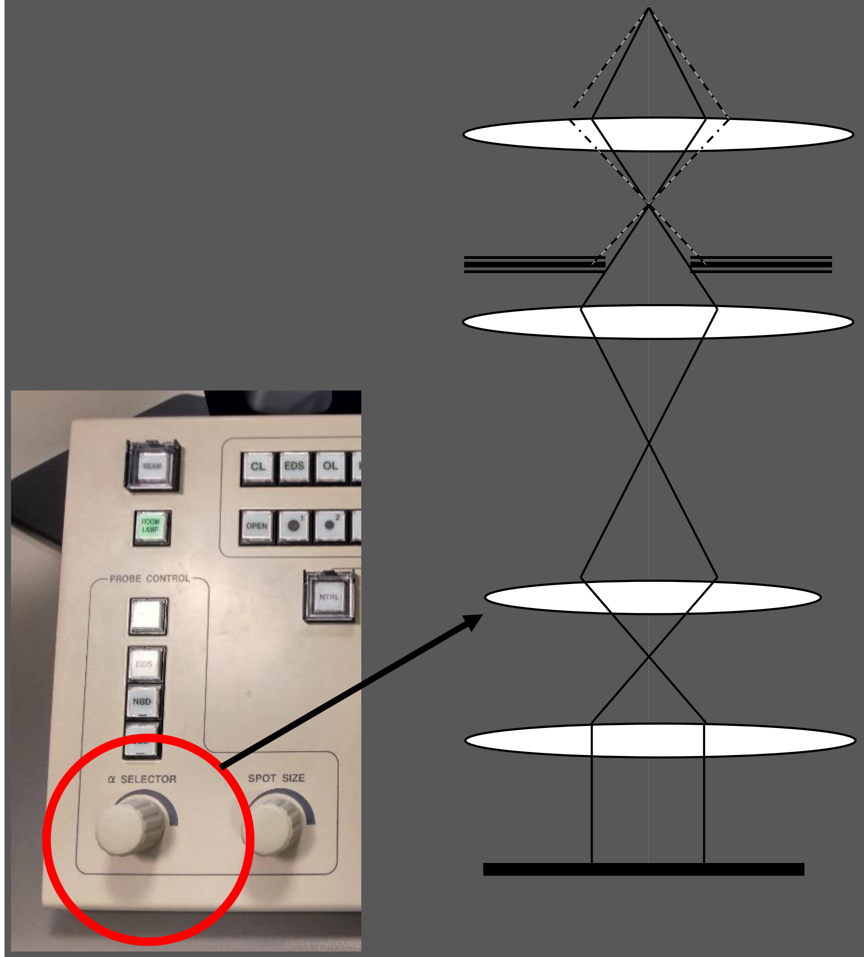




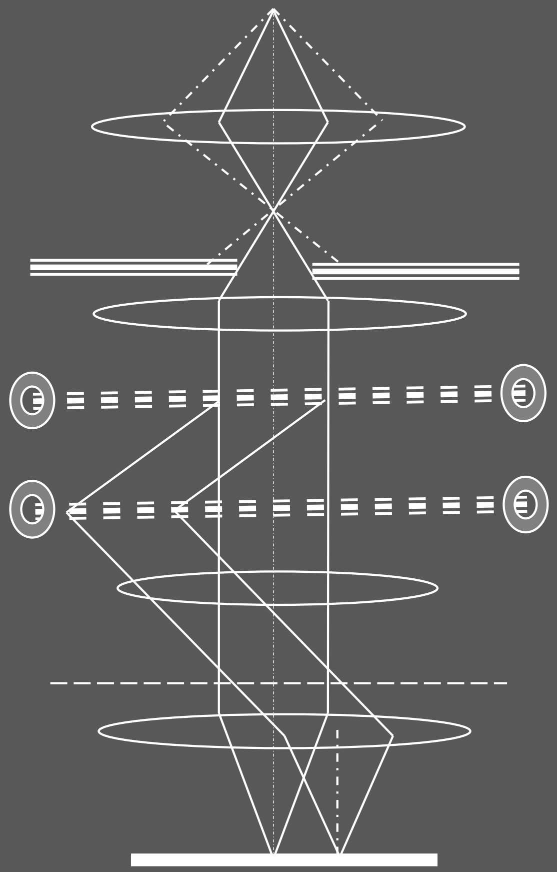
Beam tilt

Condenser System

TEM/STEM



TEM



Electron Source

Condenser 1(C1)

Aperture (C2)

Condenser 3 (C3)

Deflector Coils

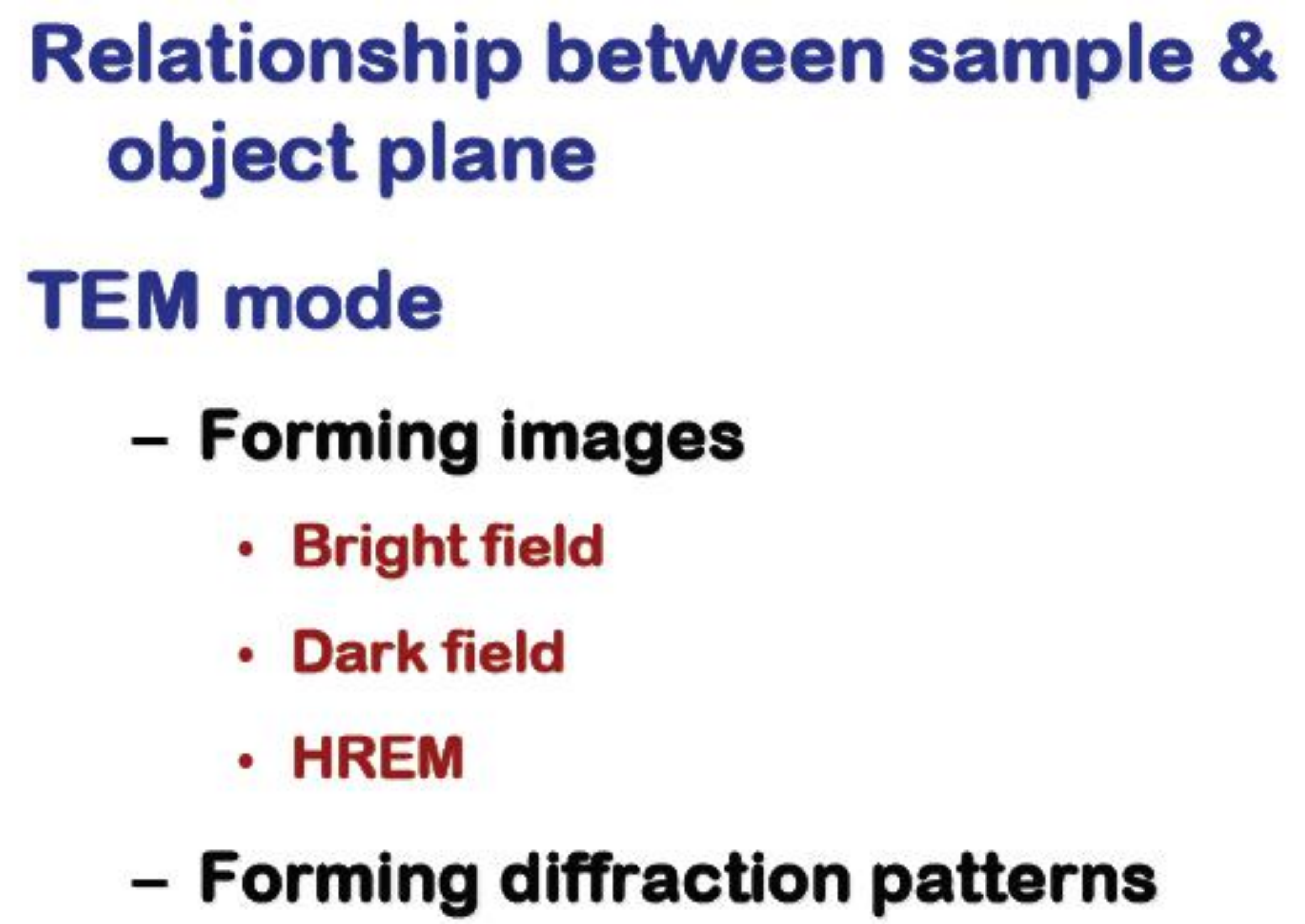
Condenser Mini (CM)

Pre-field Objective Lens

Specimen

STEM

Objective and Imaging System

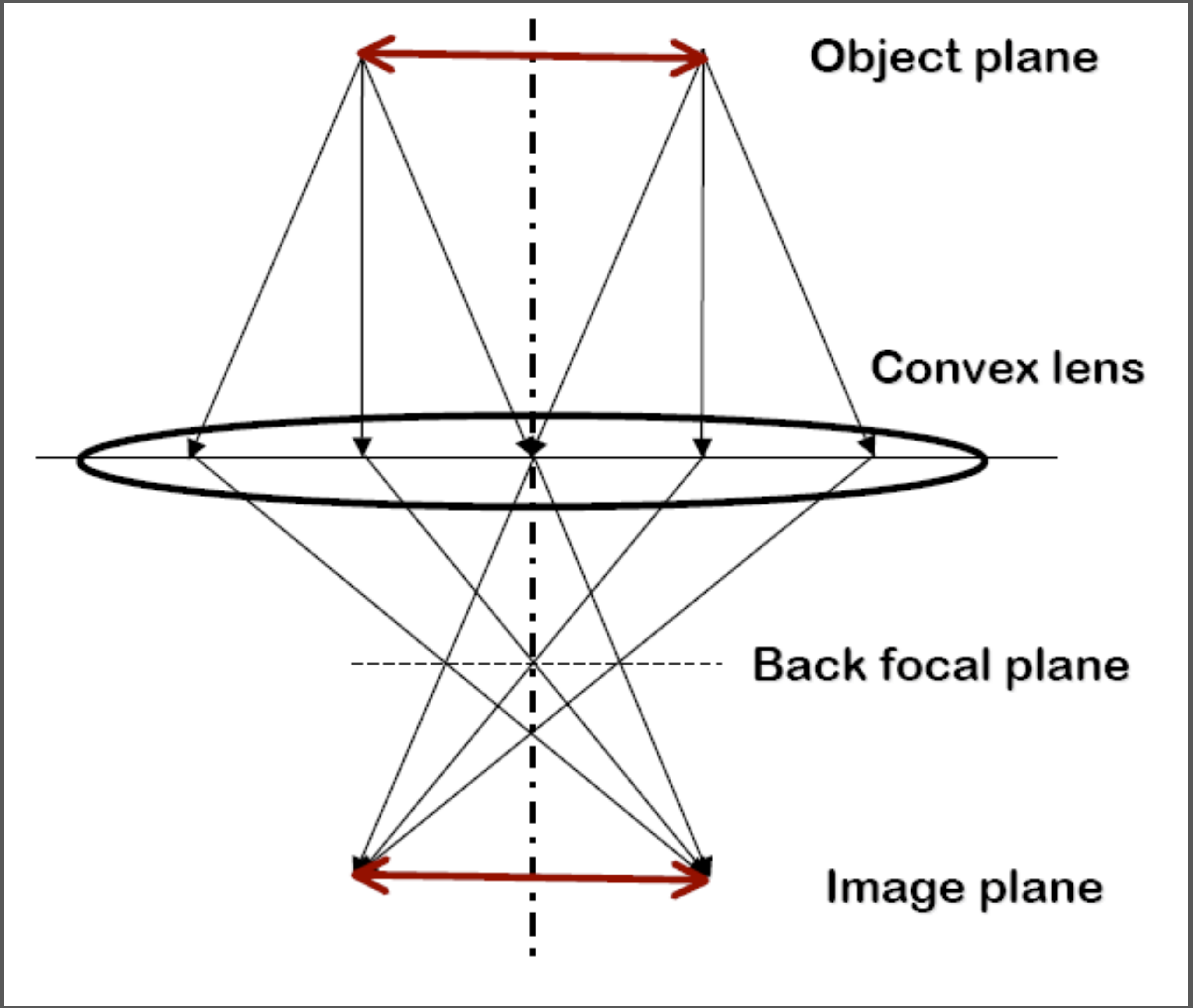


Relationship between sample & object plane

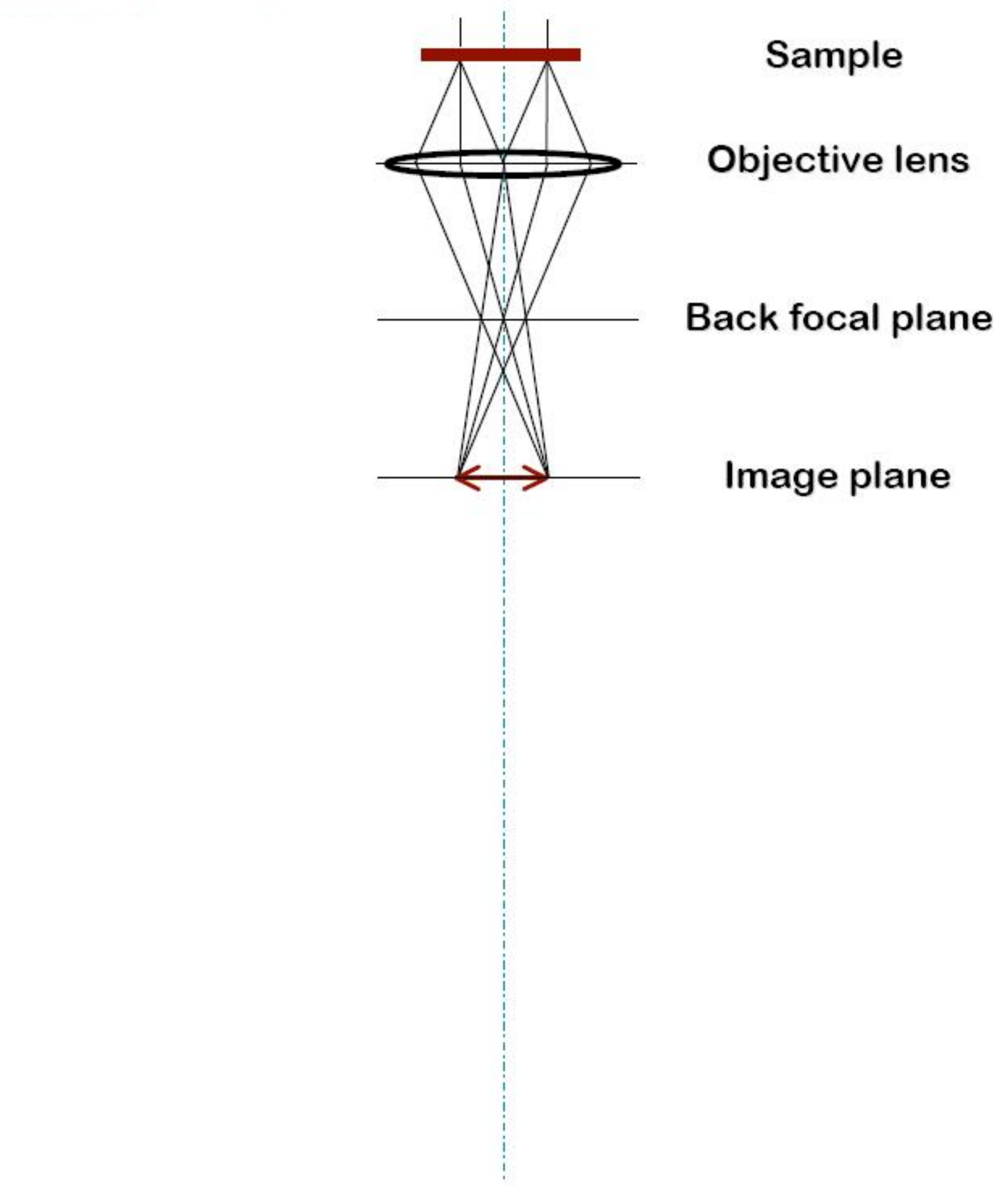
TEM mode

- Forming images
  - Bright field
  - Dark field
  - HREM
- Forming diffraction patterns

Recall

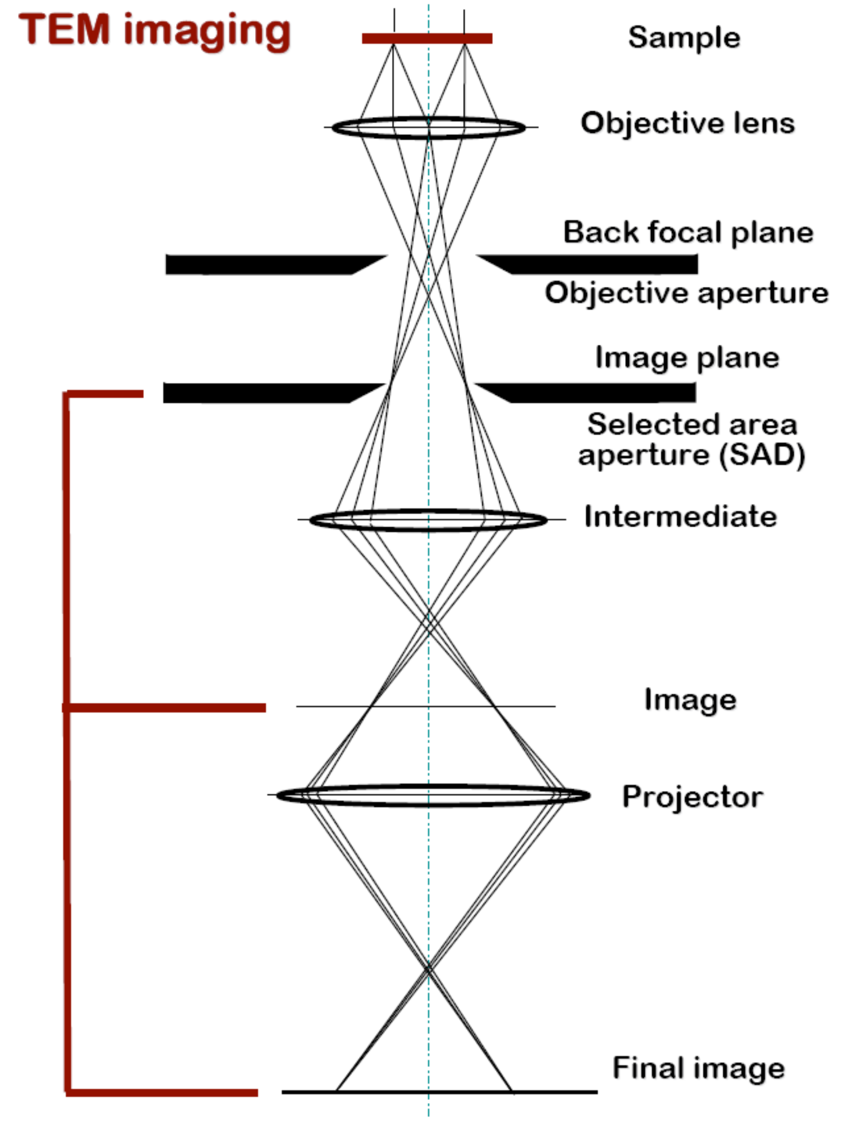


Objective System



Objective and Imaging System

Imaging vs Diffraction



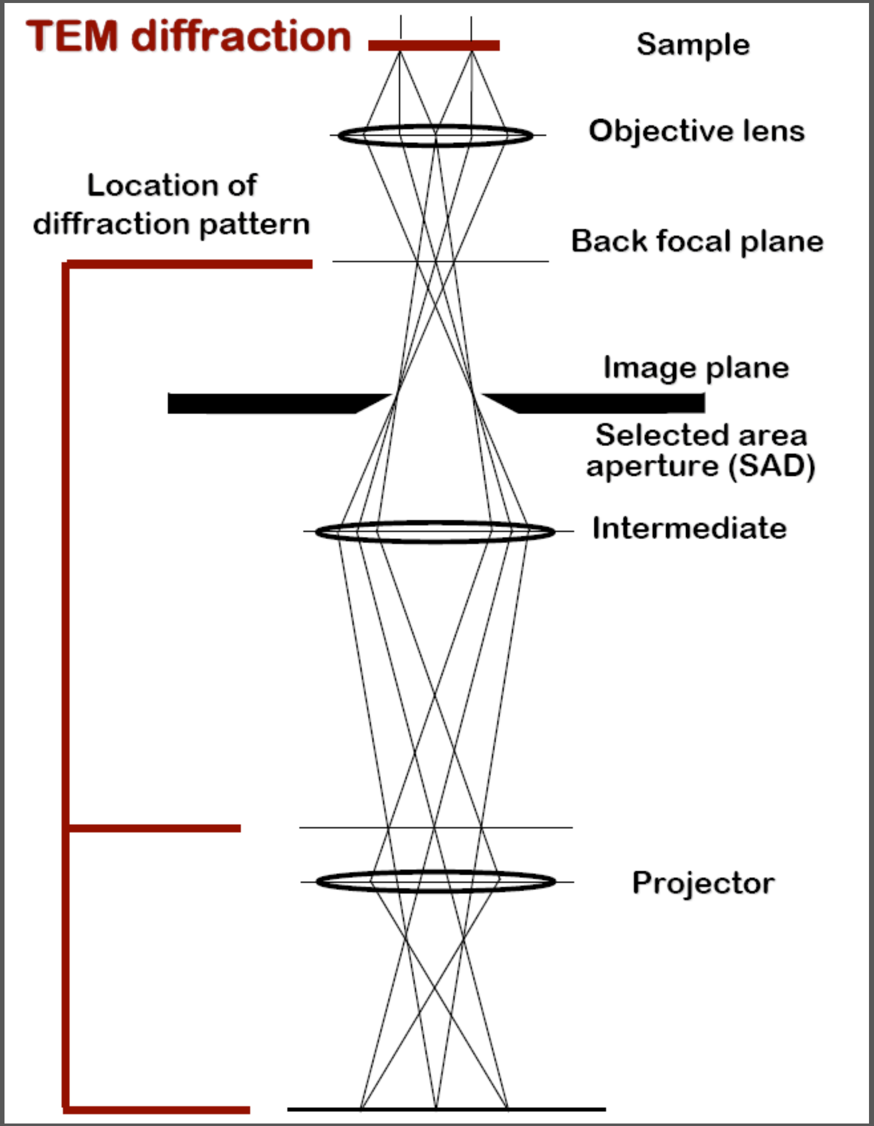
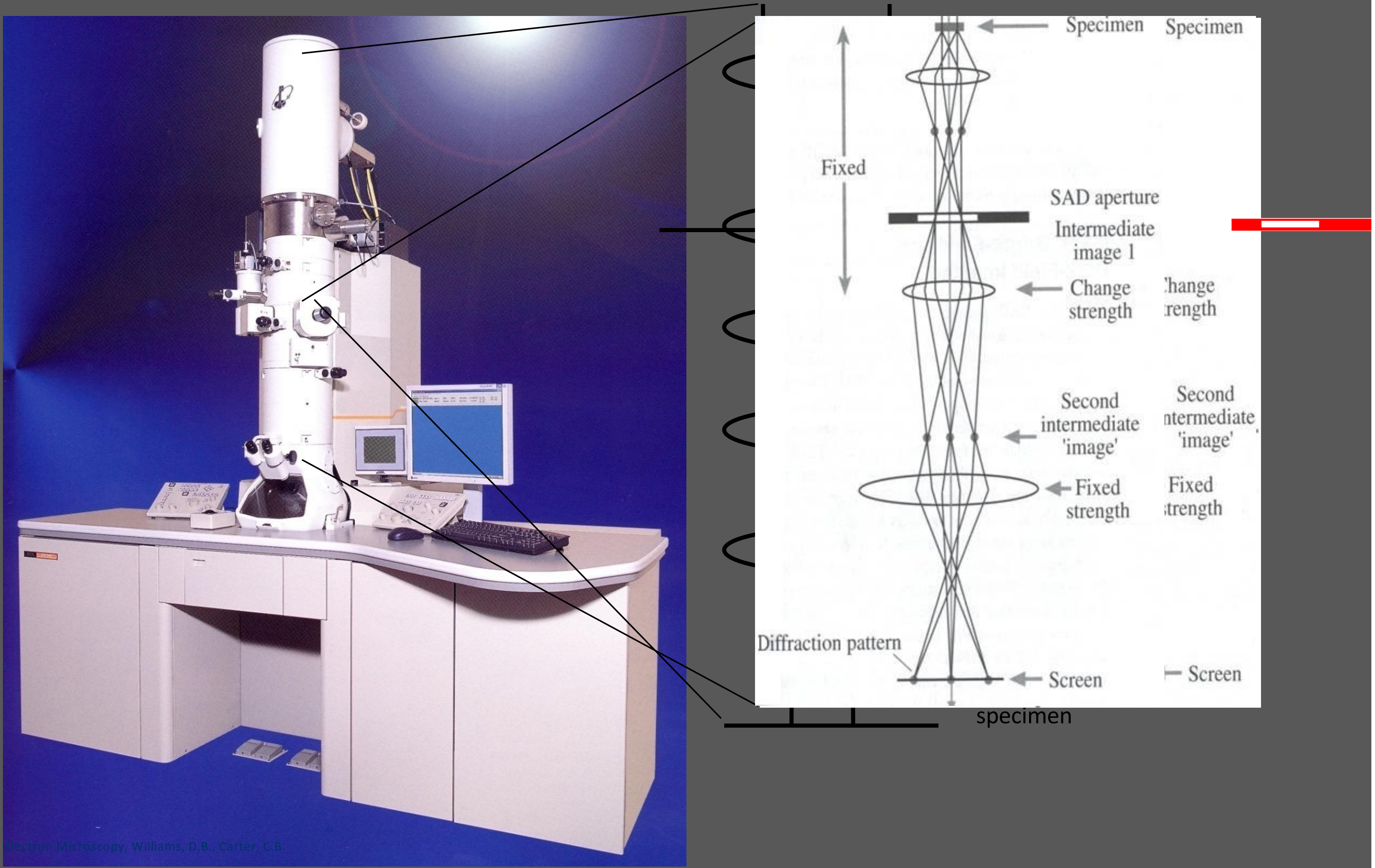
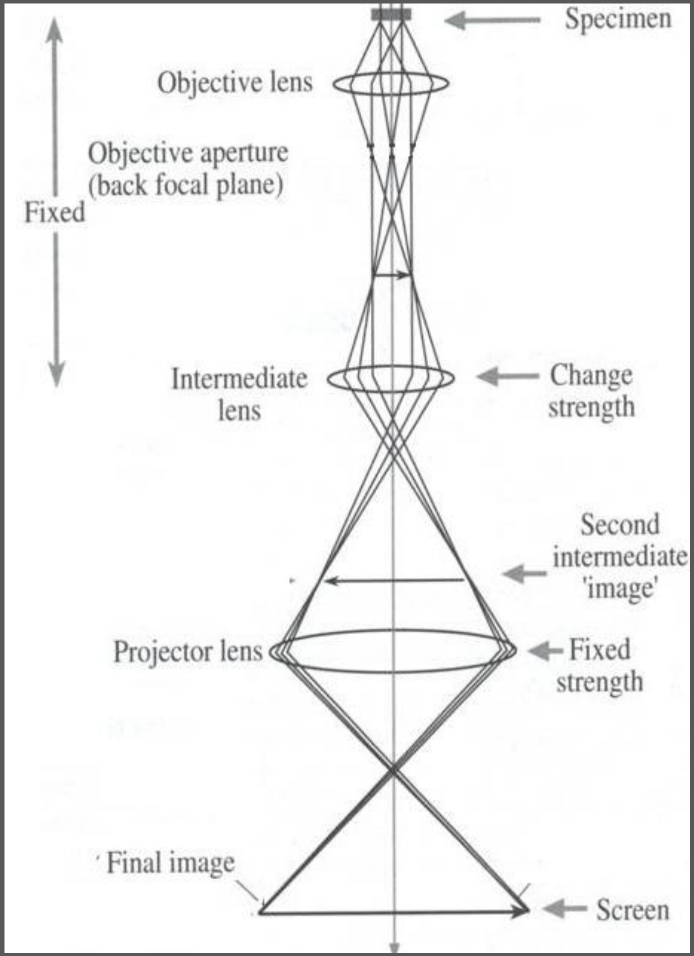


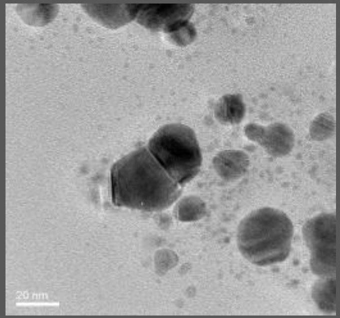
Image and Diffraction Mode



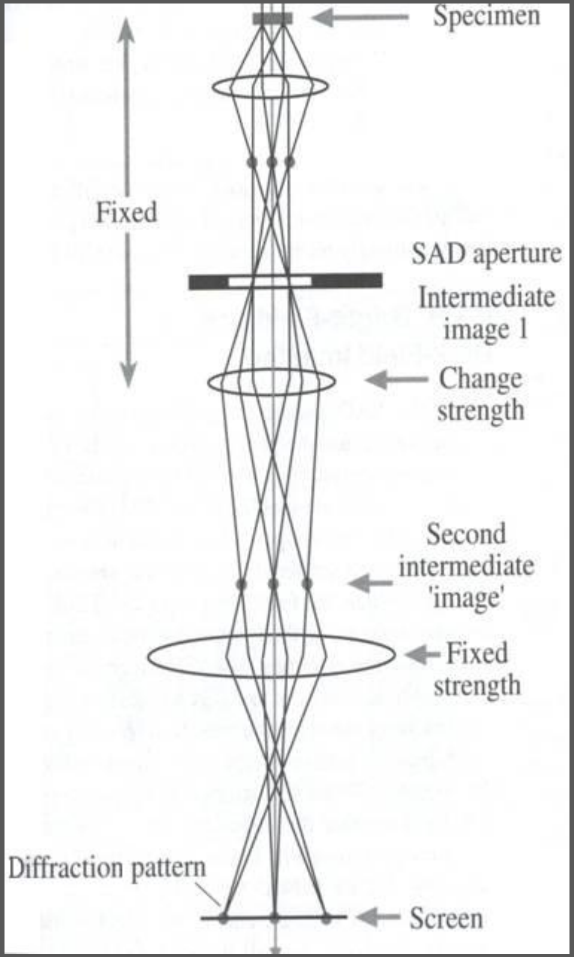
[1] Transmission Electron Microscopy, Williams, D.B., Carter, C.B.

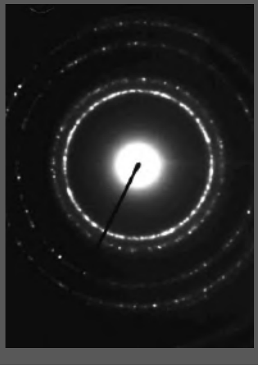
Image Mode



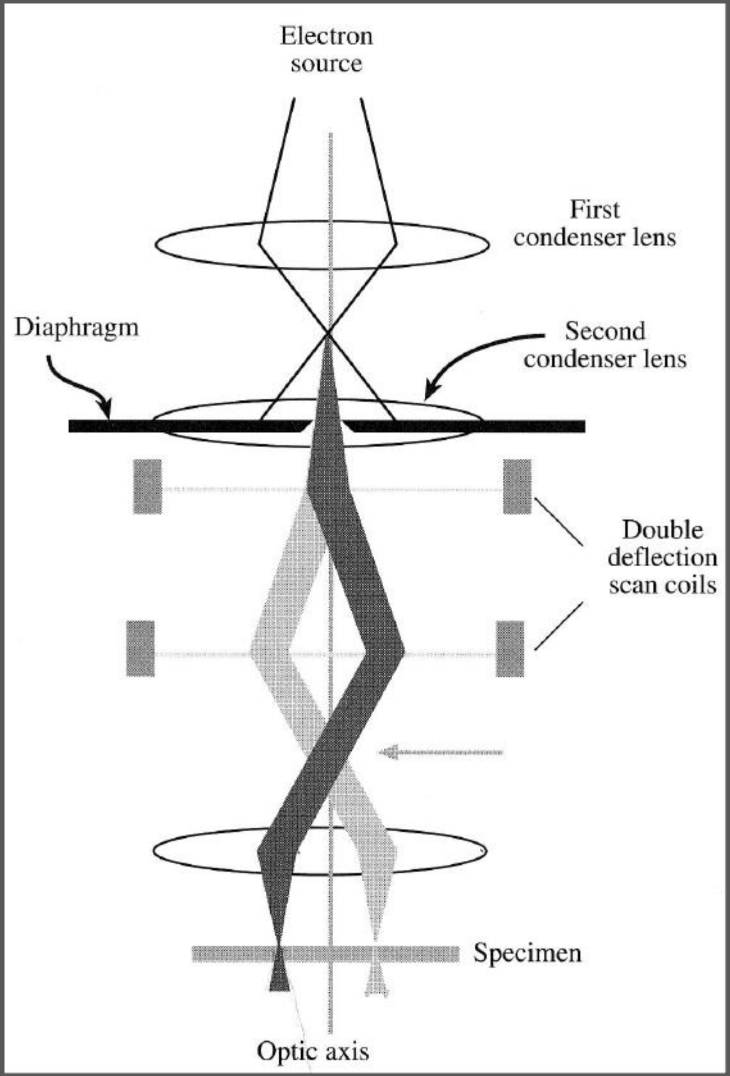


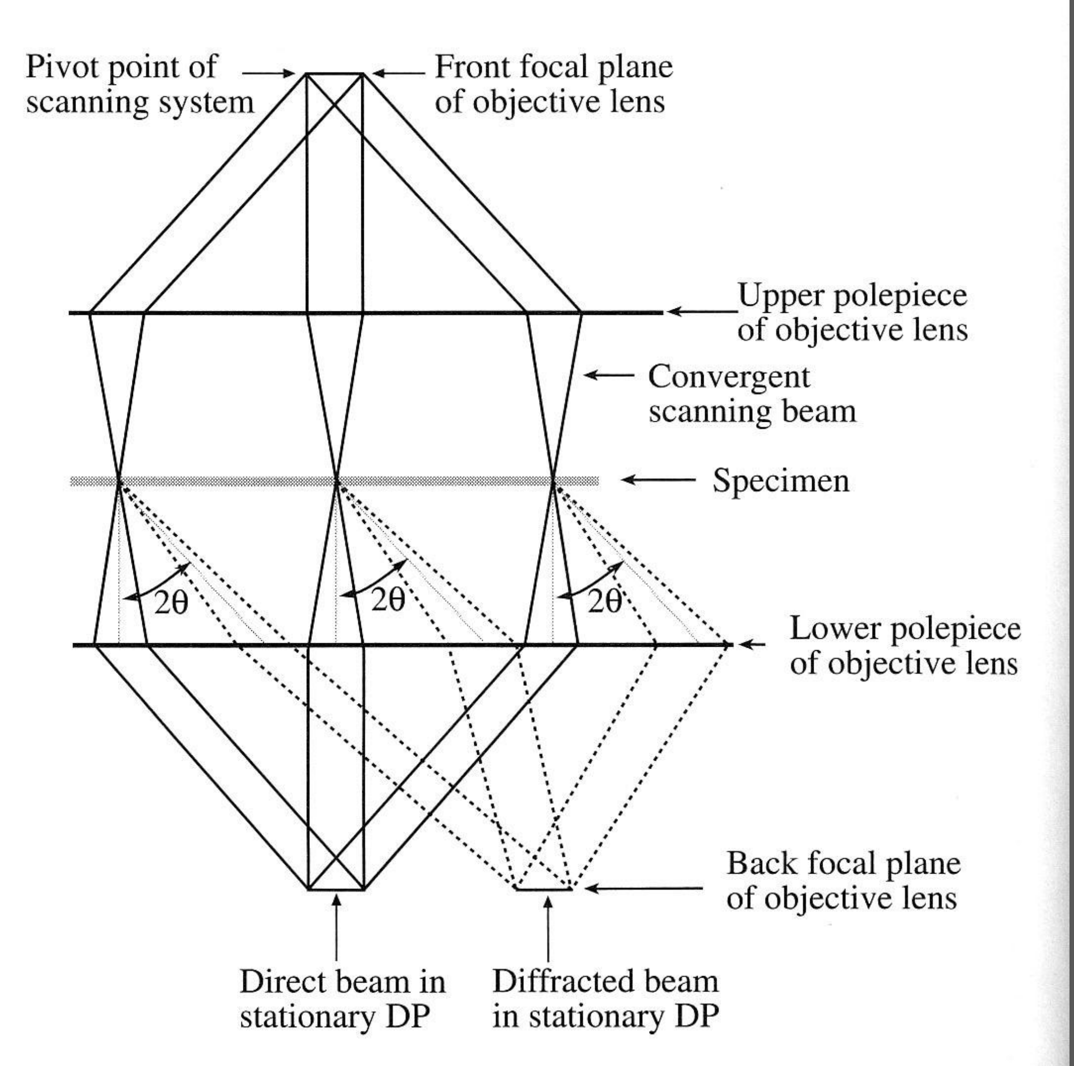
Diffraction Mode



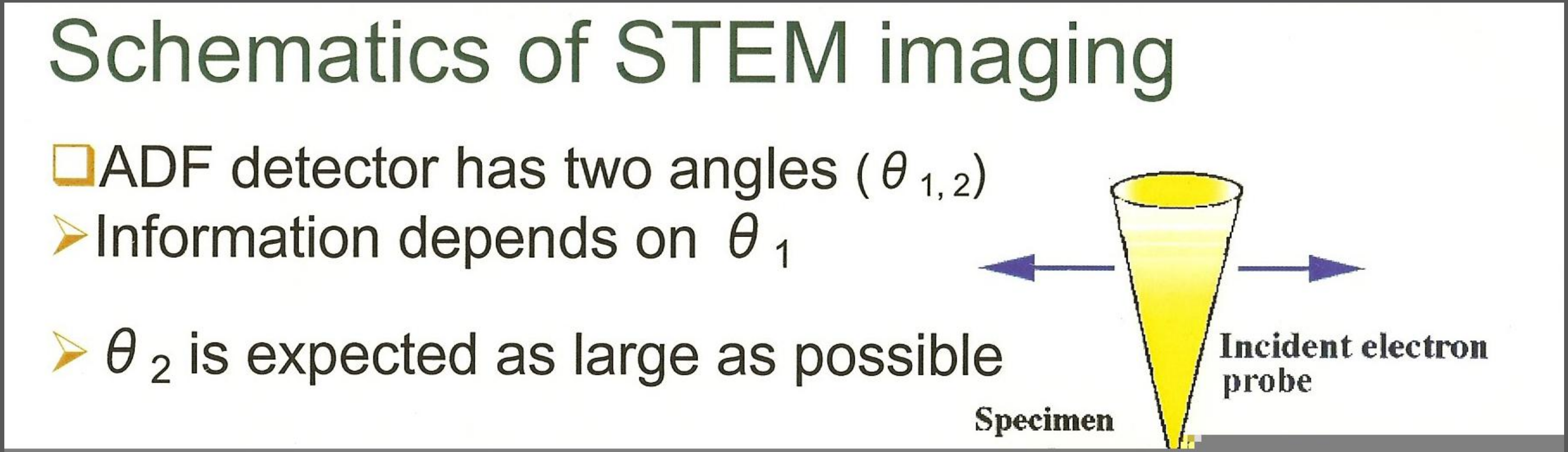


STEM Imaging System





STEM Bright/Dark/HAADF-Field

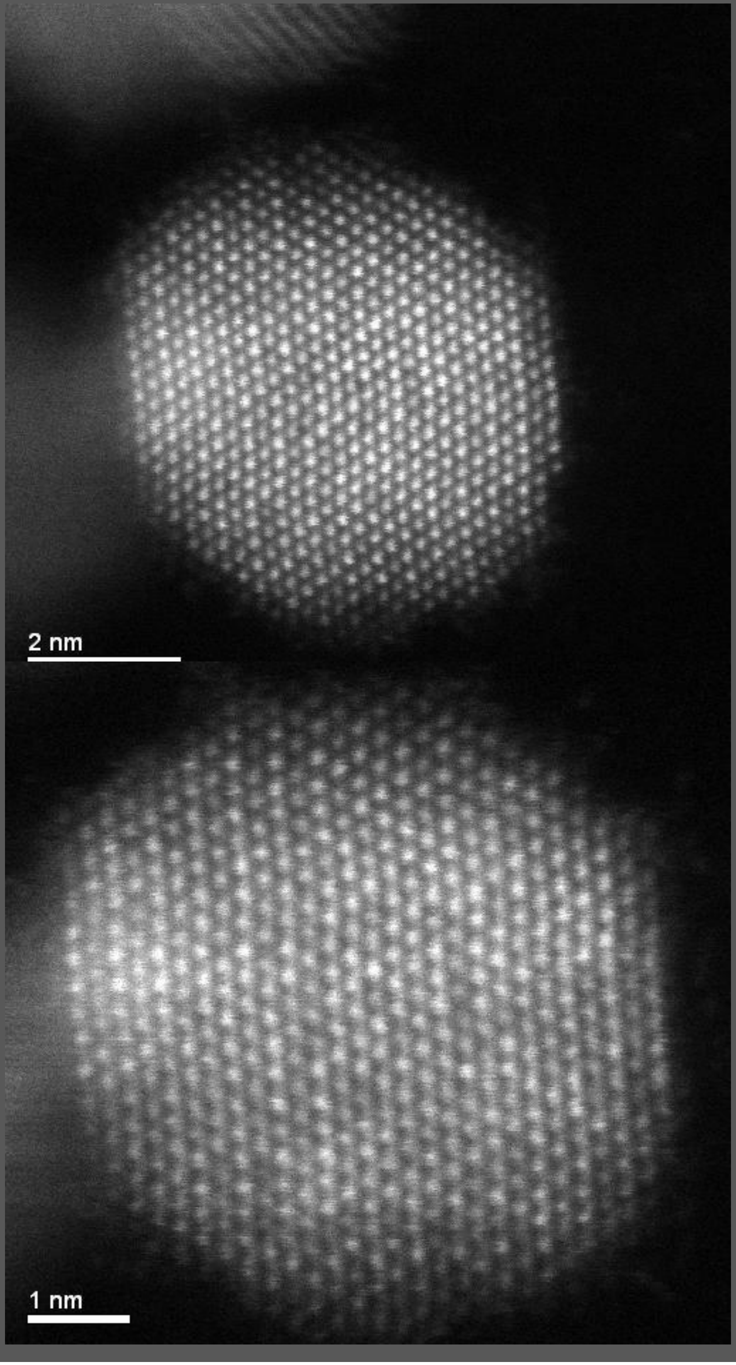


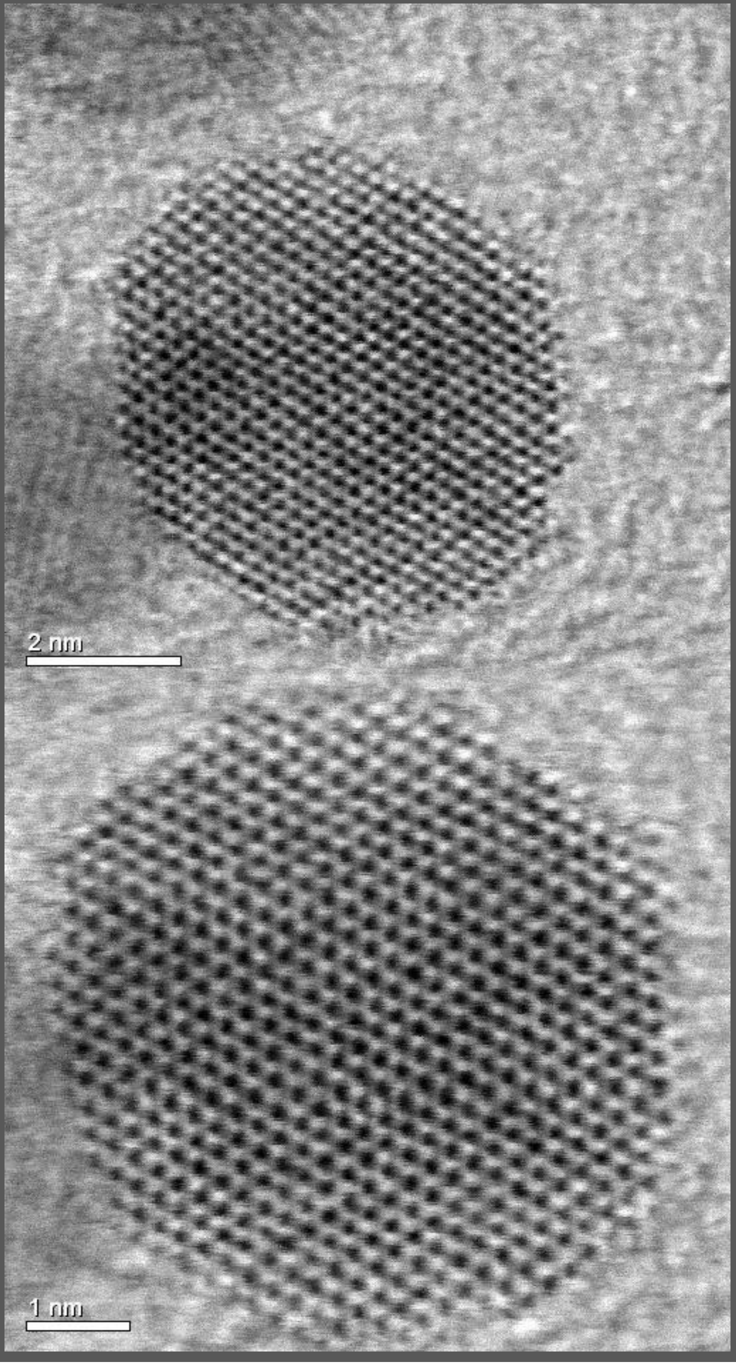
Schematics of STEM imaging

☐ADF detector has two angles ($\theta_{1,2}$)

- Information depends on θ_1
- θ_2 is expected as large as possible

Aberration-Corrected STEM: Bright/Dark-Field





Sample Preparation

Focused ion beam microscopy

Liquid metal ion source (LMIS)

Ga^+ ions incident on sample

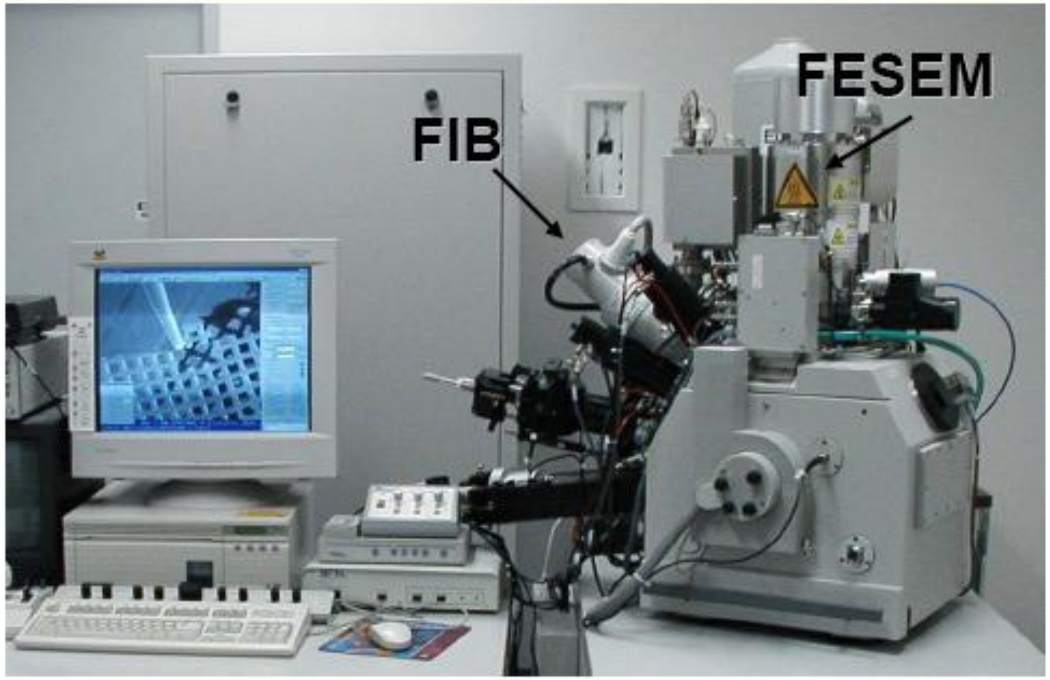
- Causes sputtering
- Causes, SE, BSE, SI emission

Rate of sputter proportional to current

- Ranges from 1 pA to 20 nA

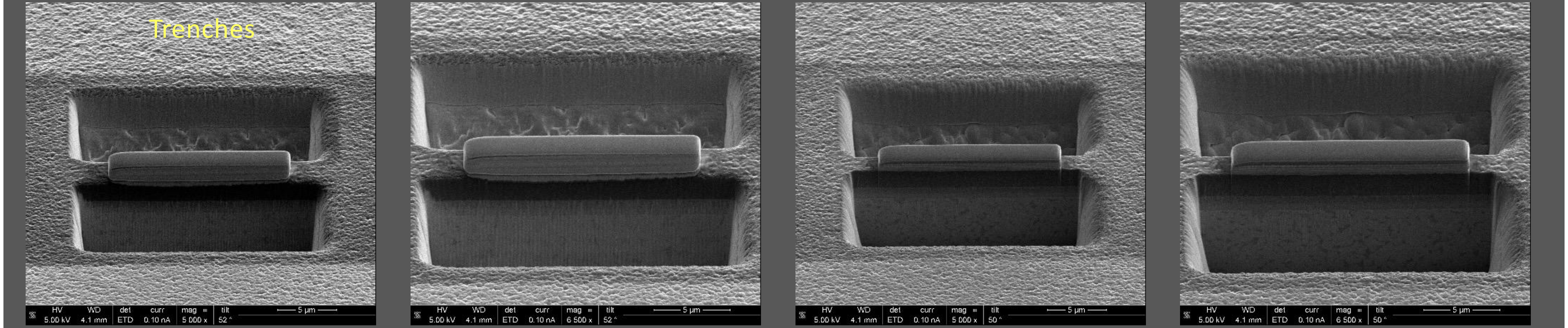
Superb for:

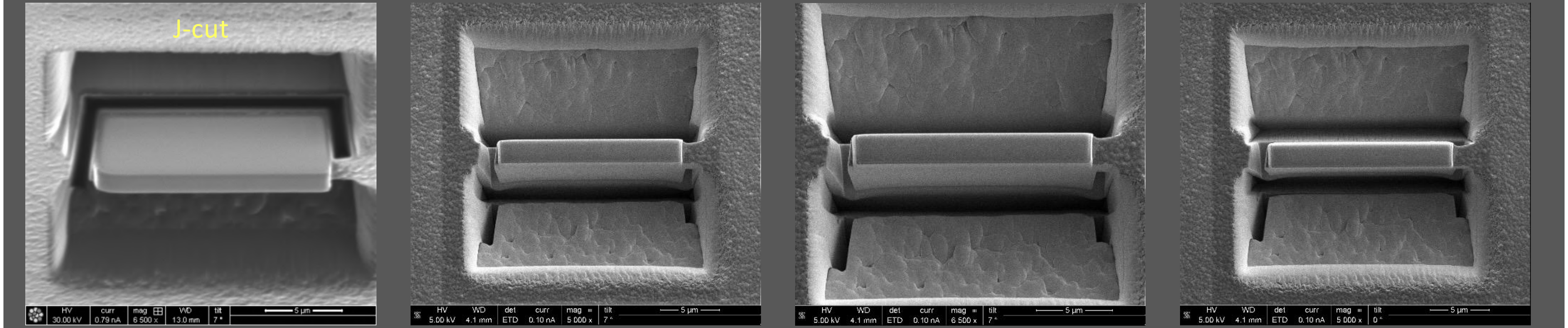
- Site specific preparation
- Cross sections & plan views of ‘difficult’ samples
- Cross sections samples with highly different hardness / ion sputtering rate



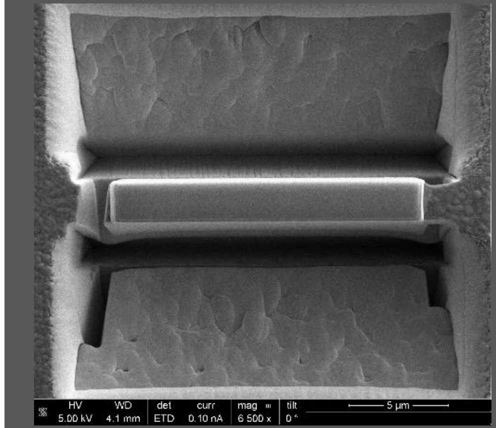
FEI DualBeam FIB / SEM

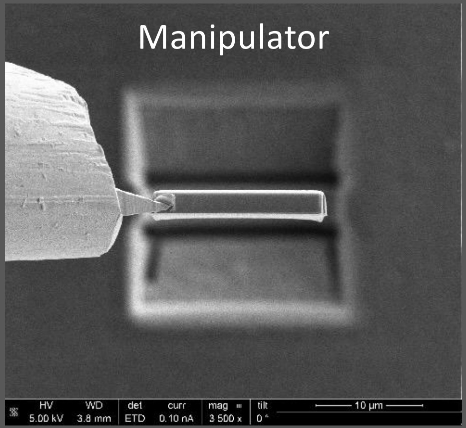
Lamella Preparation

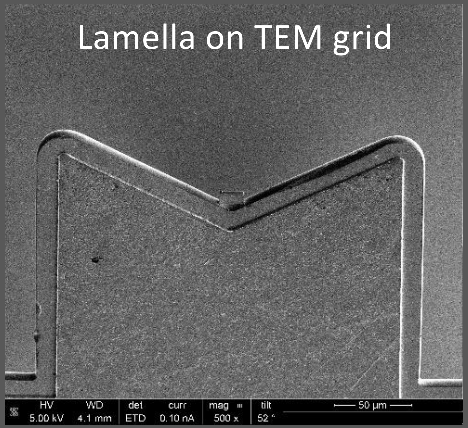


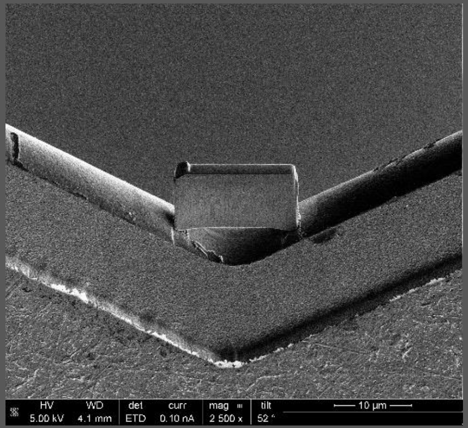


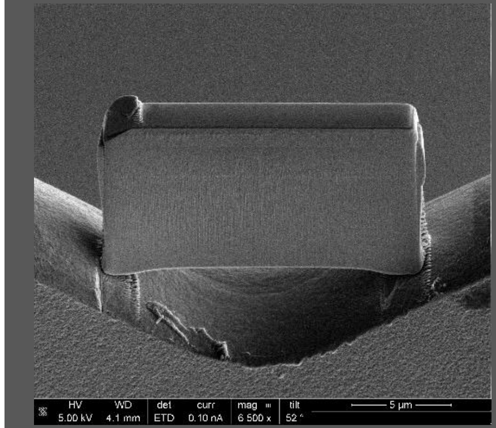
Transfer of Lamella to Grid

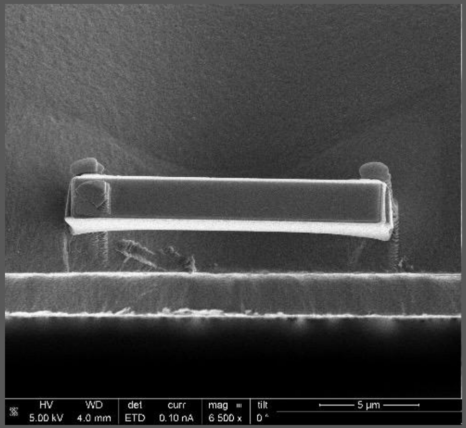


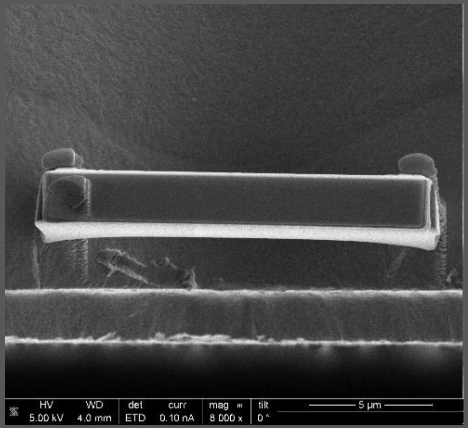


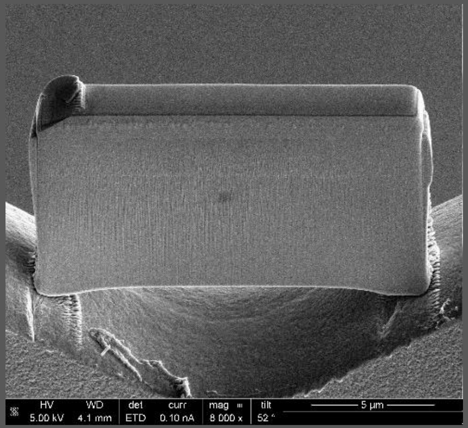




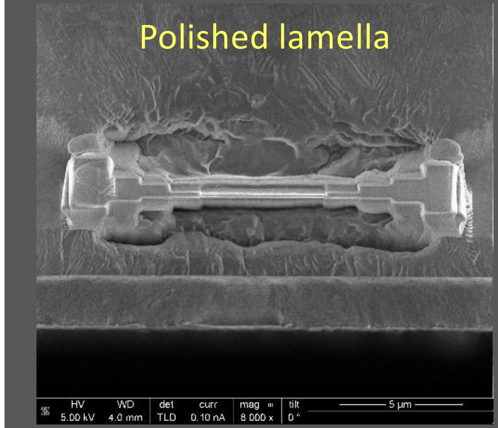


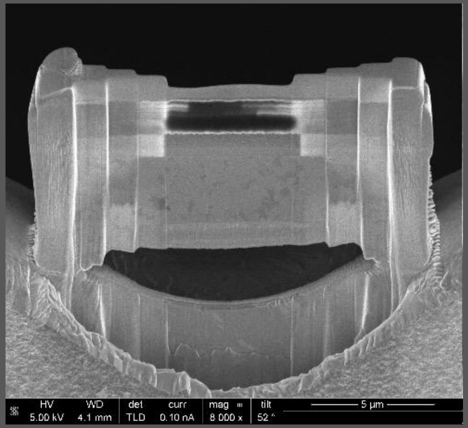


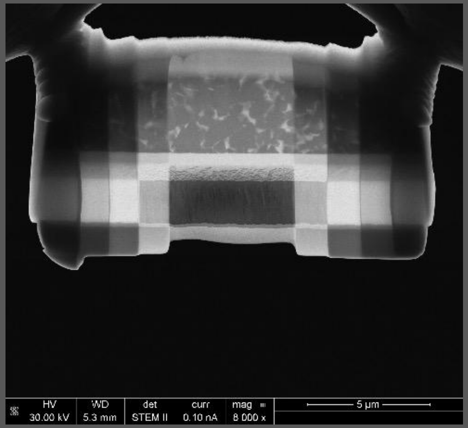


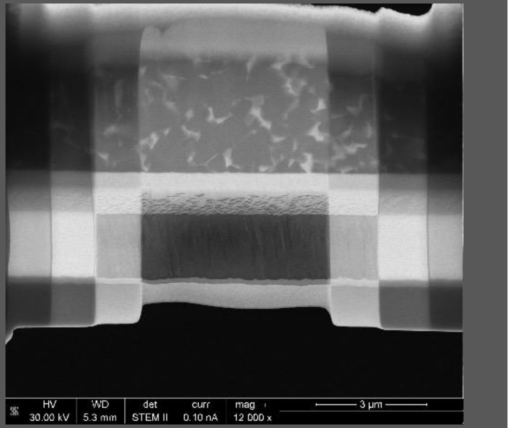


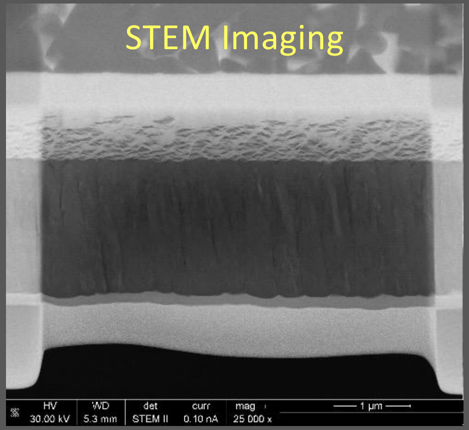
Final Thinning

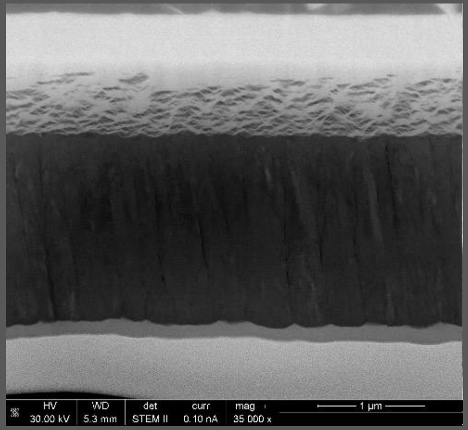




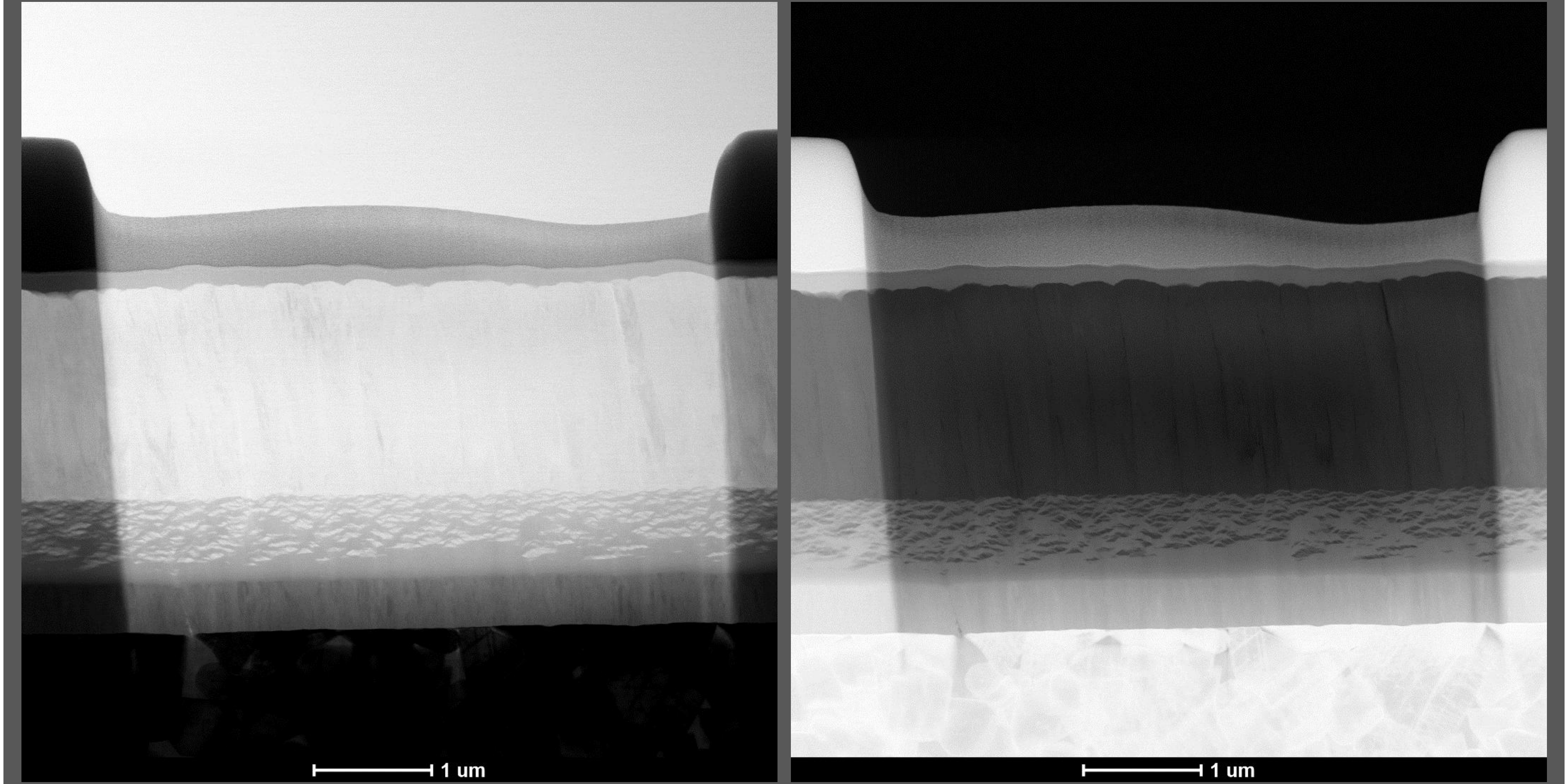




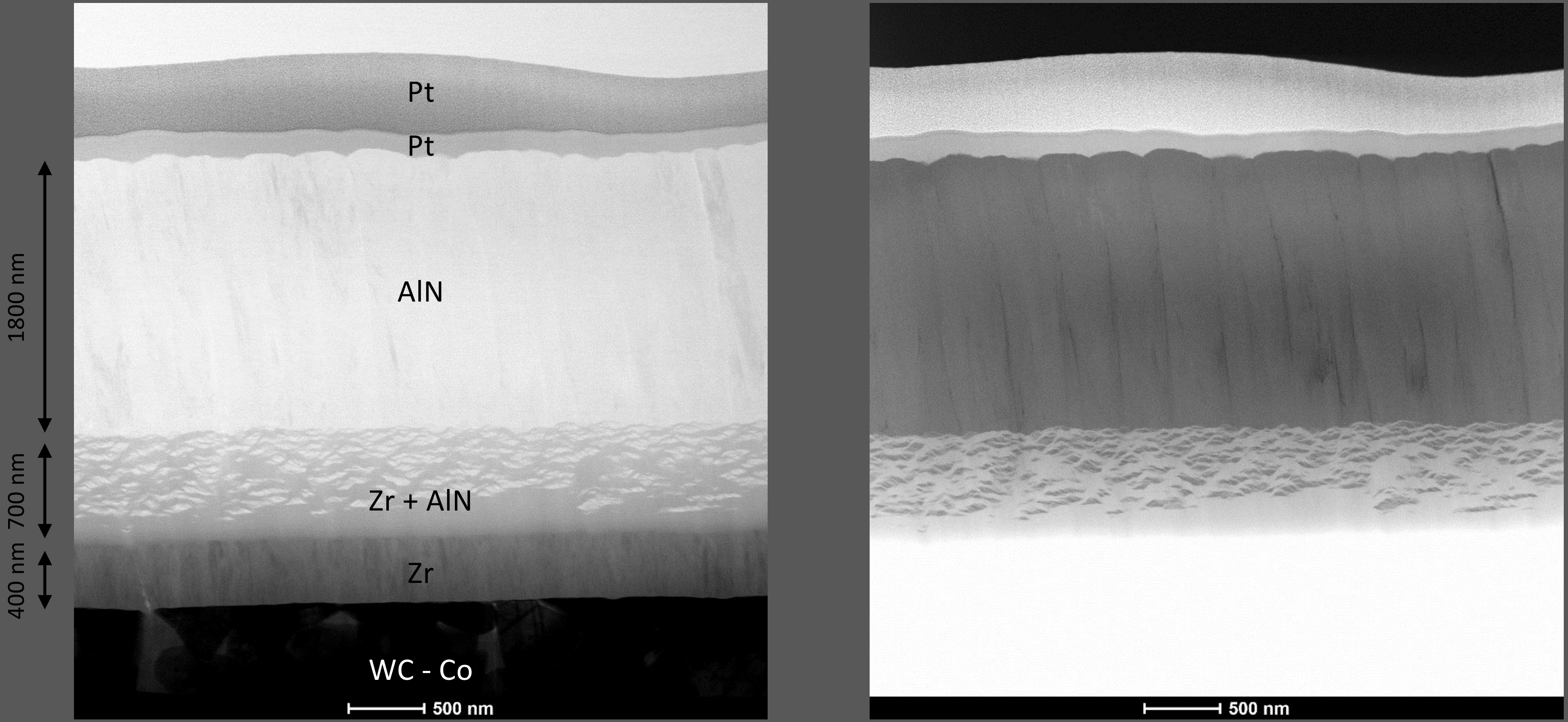




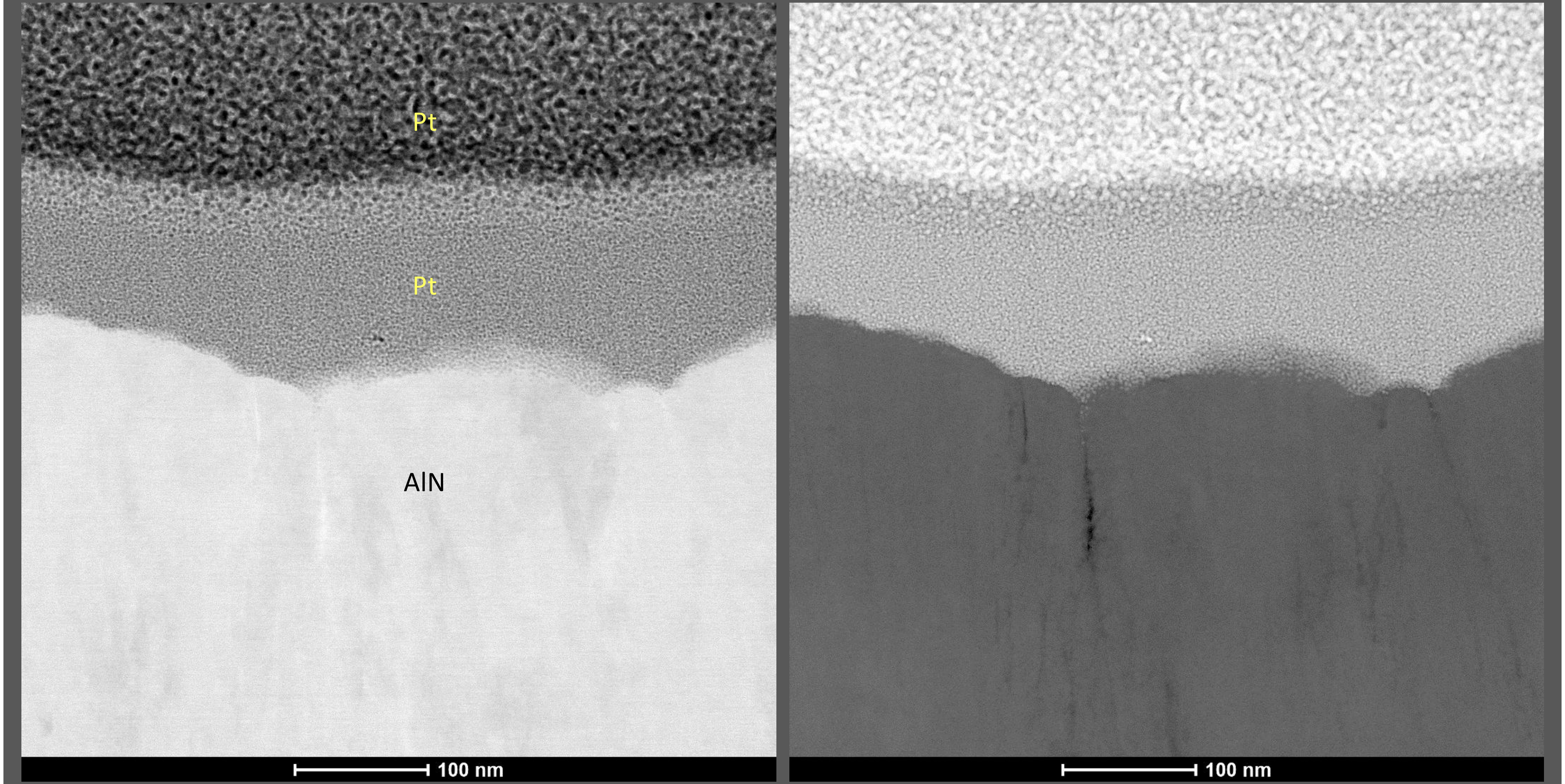
STEM Imaging – BF and HAADF



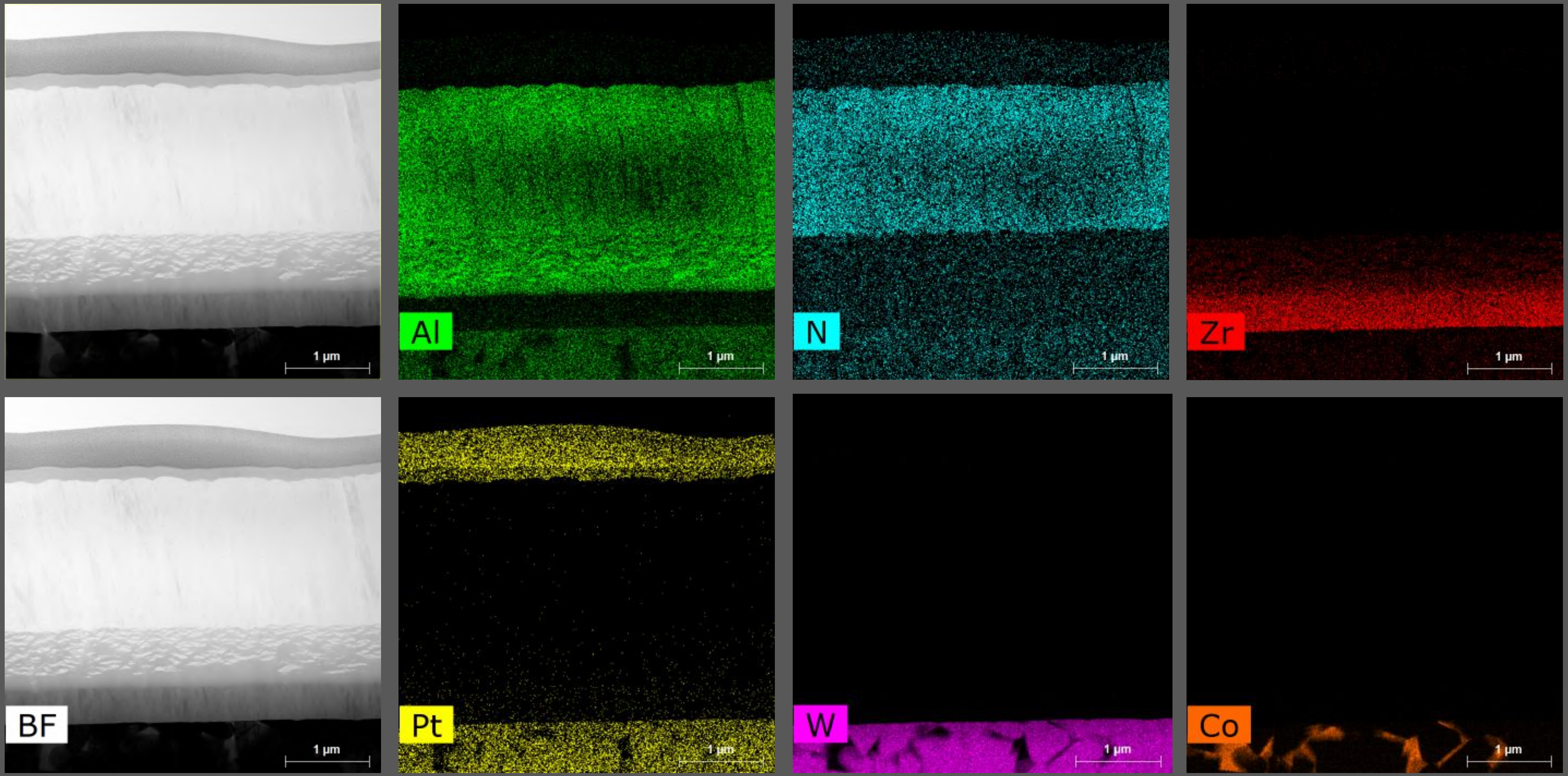
STEM Imaging – BF and HAADF



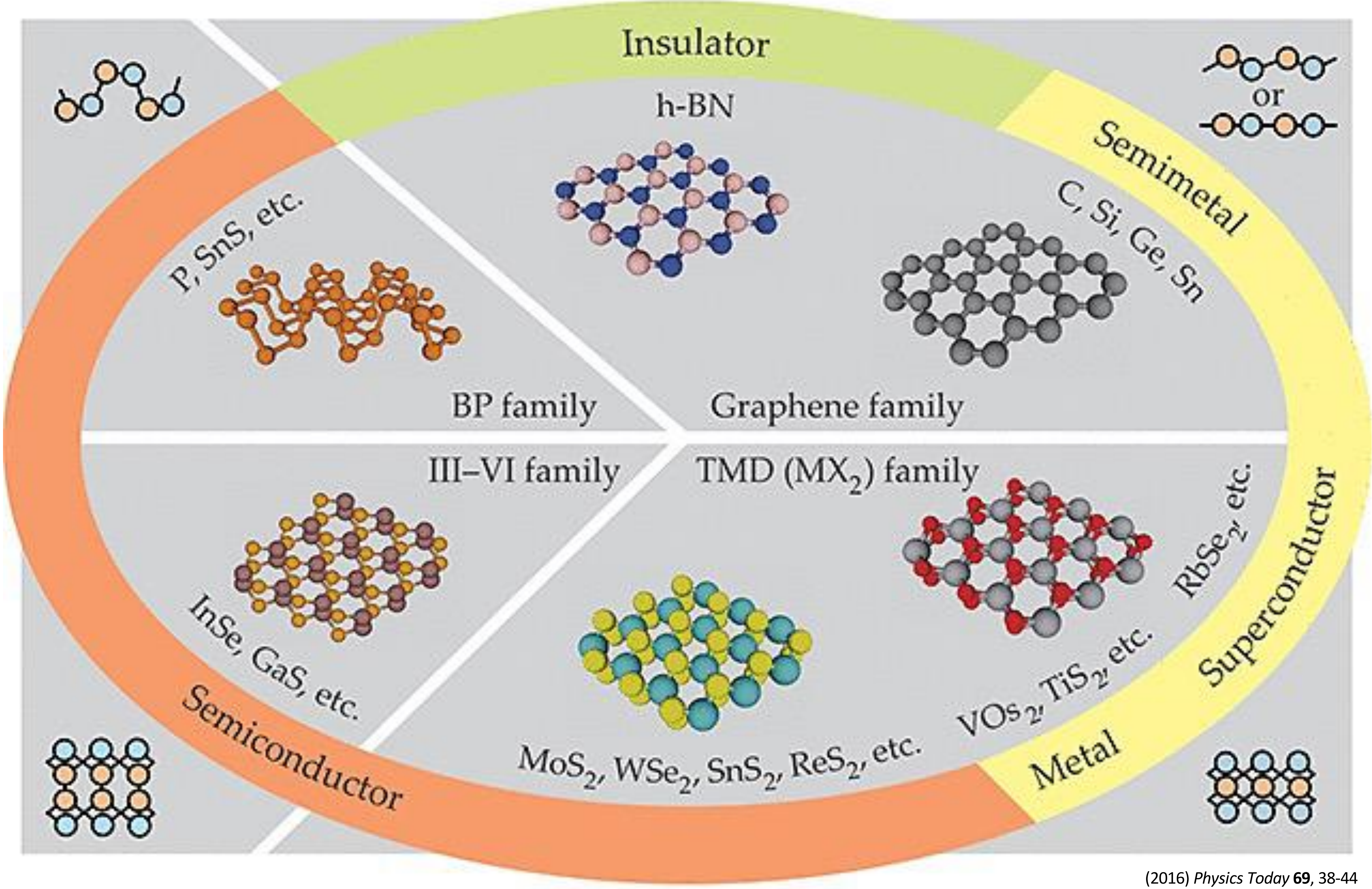
STEM Imaging – BF and HAADF



STEM-EDX



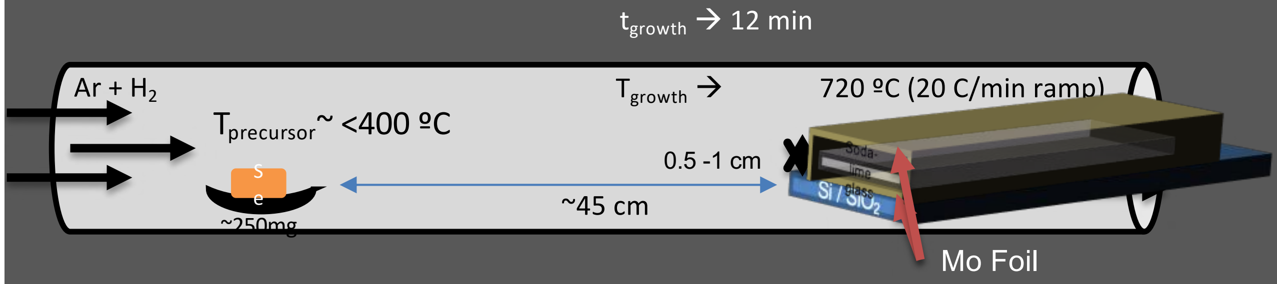
2D Materials



(2016) *Physics Today* **69**, 38-44

Growth methods of 2D materials

Synthesis of $MoSe_2$ by CVD method



t_{growth} → 12 min

Ar + H_2

$T_{precursor}$ ~ <400 ºC

T_{growth} → 720 ºC (20 C/min ramp)

0.5 -1 cm

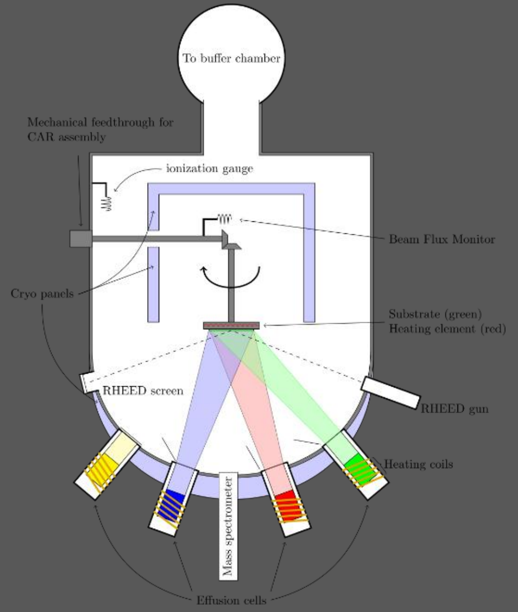
~45 cm

Mo Foil

Substrates used during CVD growth:

- SiO_2/Si
- Glass
- Mo foil

Synthesis of GaSe, InSe, In_2Se_3 by MBE method

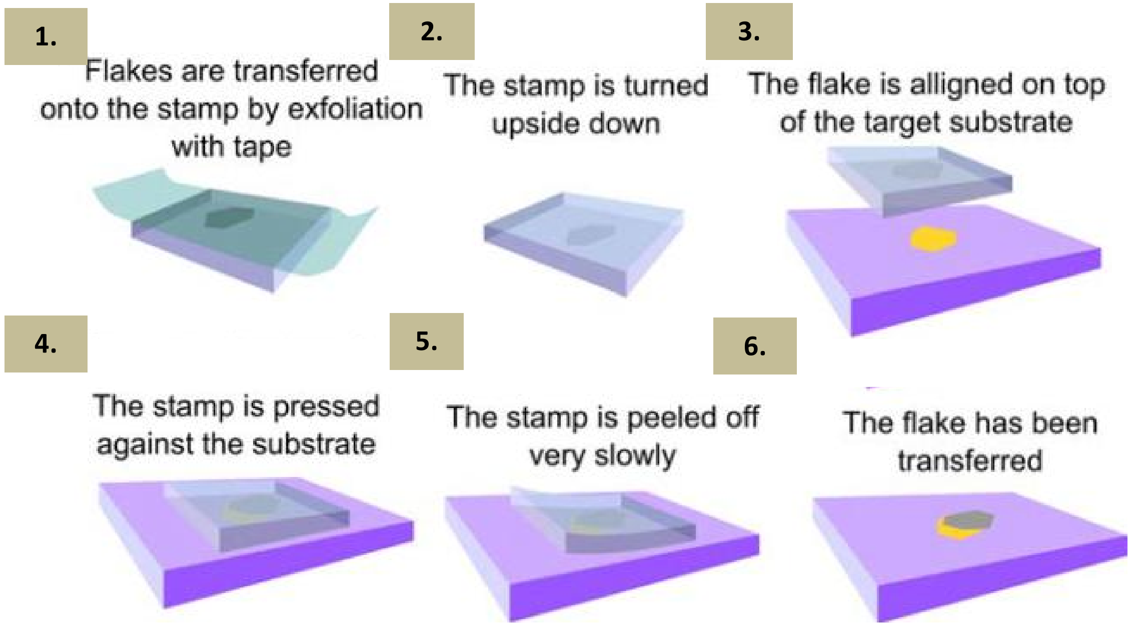


Substrates used during MBE growth:

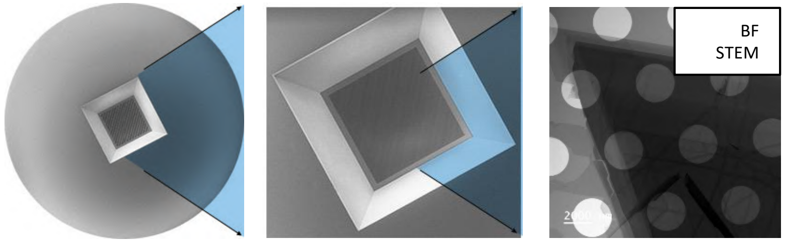
- sapphire
- silicon

Transfer of 2D materials to the TEM grid

Deterministic transfer of 2D by all-dry viscoelastic stamping

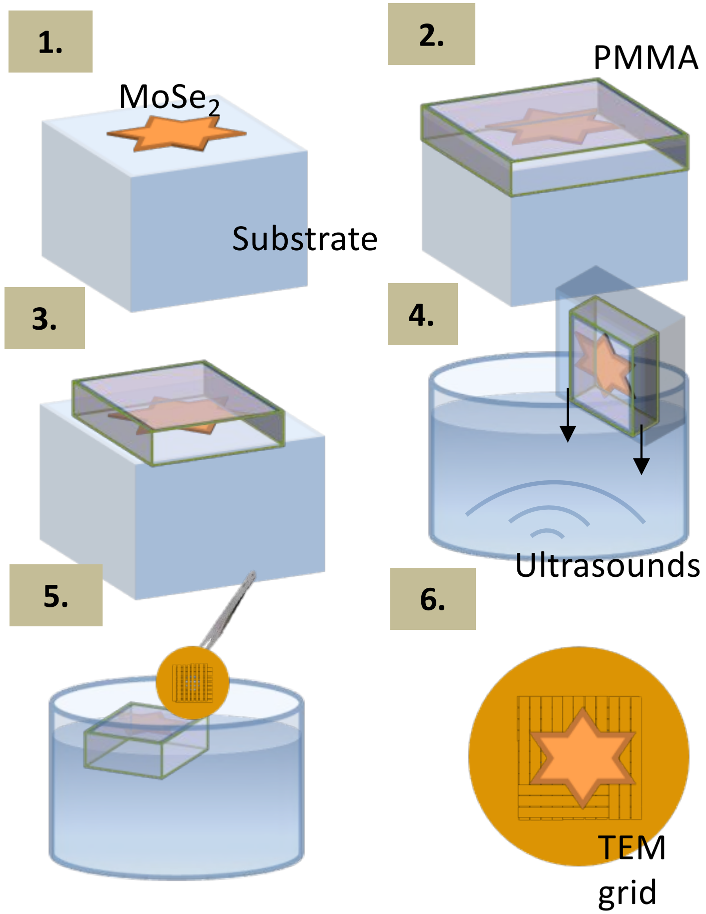


1. Flakes are transferred onto the stamp by exfoliation with tape
2. The stamp is turned upside down
3. The flake is alligned on top of the target substrate
4. The stamp is pressed against the substrate
5. The stamp is peeled off very slowly
6. The flake has been transferred



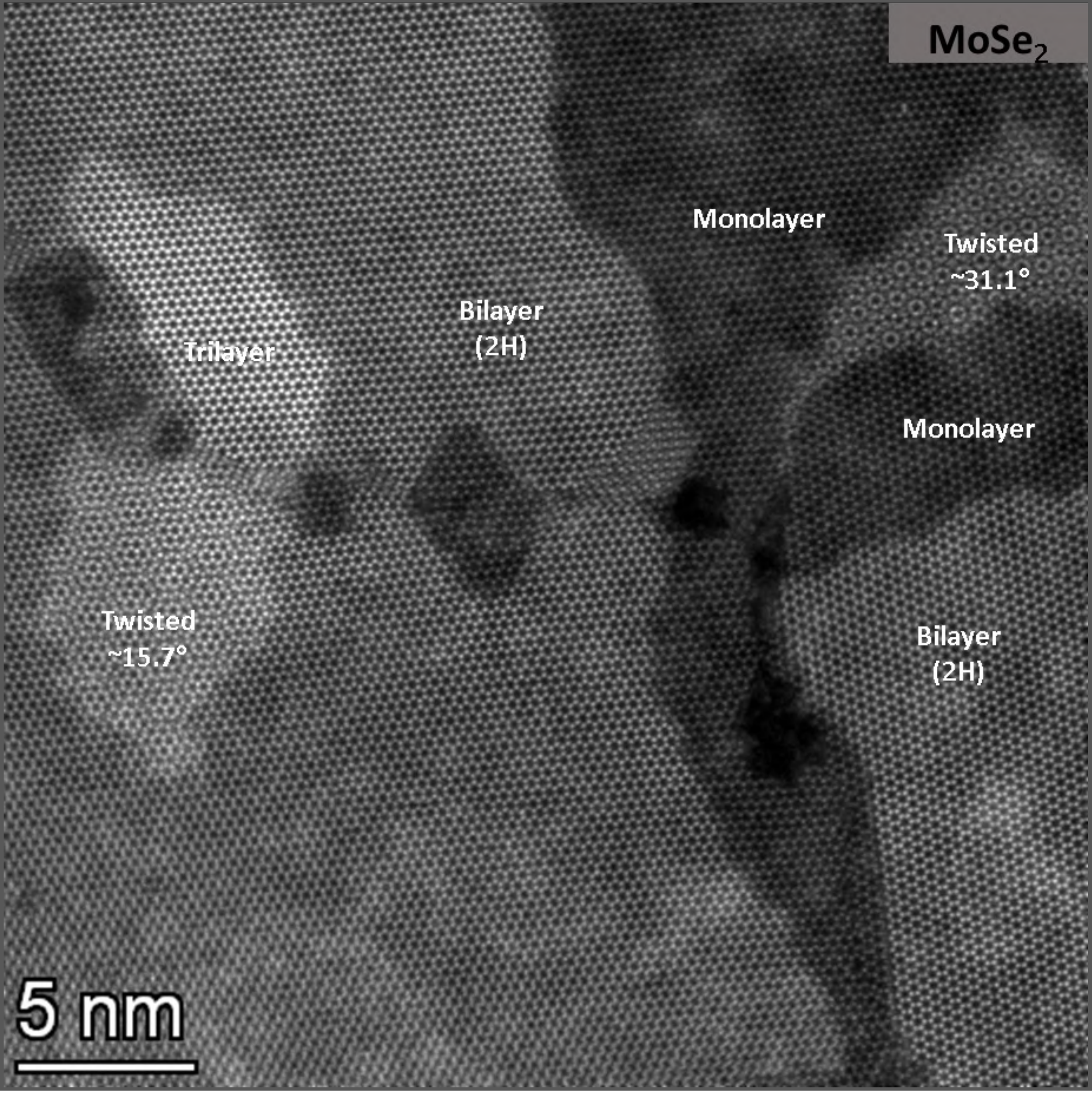
TEM Grid with Holey Silicon Nitride Support Film

Transfer with PMMA

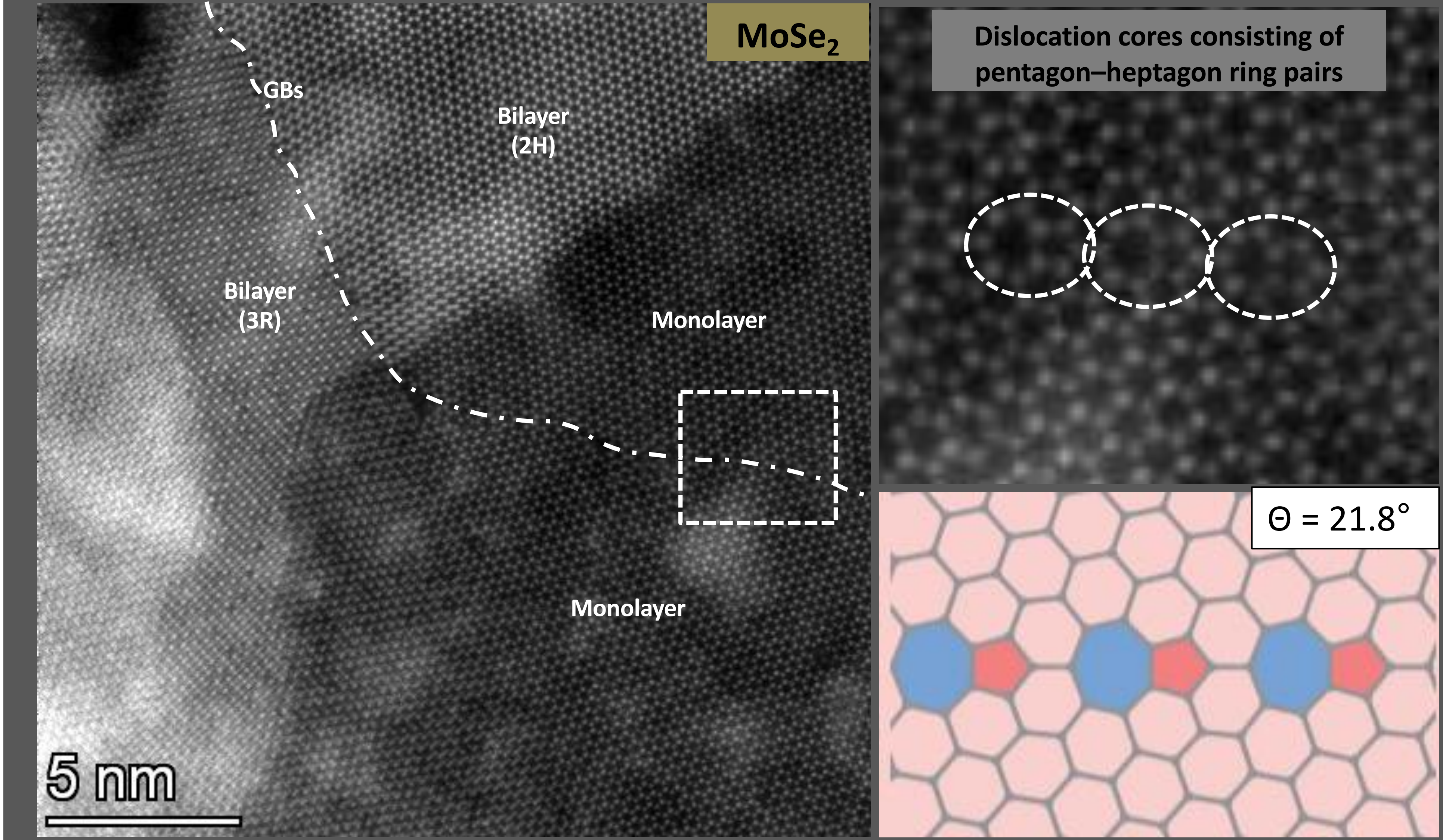


[1] Deterministic transfer of two-dimensional materials by all-dry viscoelastic stamping, Andres Castellanos-Gomez, Michele Buscema, Rianda Molenaar, Vibhor Singh, Laurens Janssen, Herre S J van der Zant and Gary A Steele, 2D Materials 1 (2014) 011002

Atomic Structure of 2D Materials

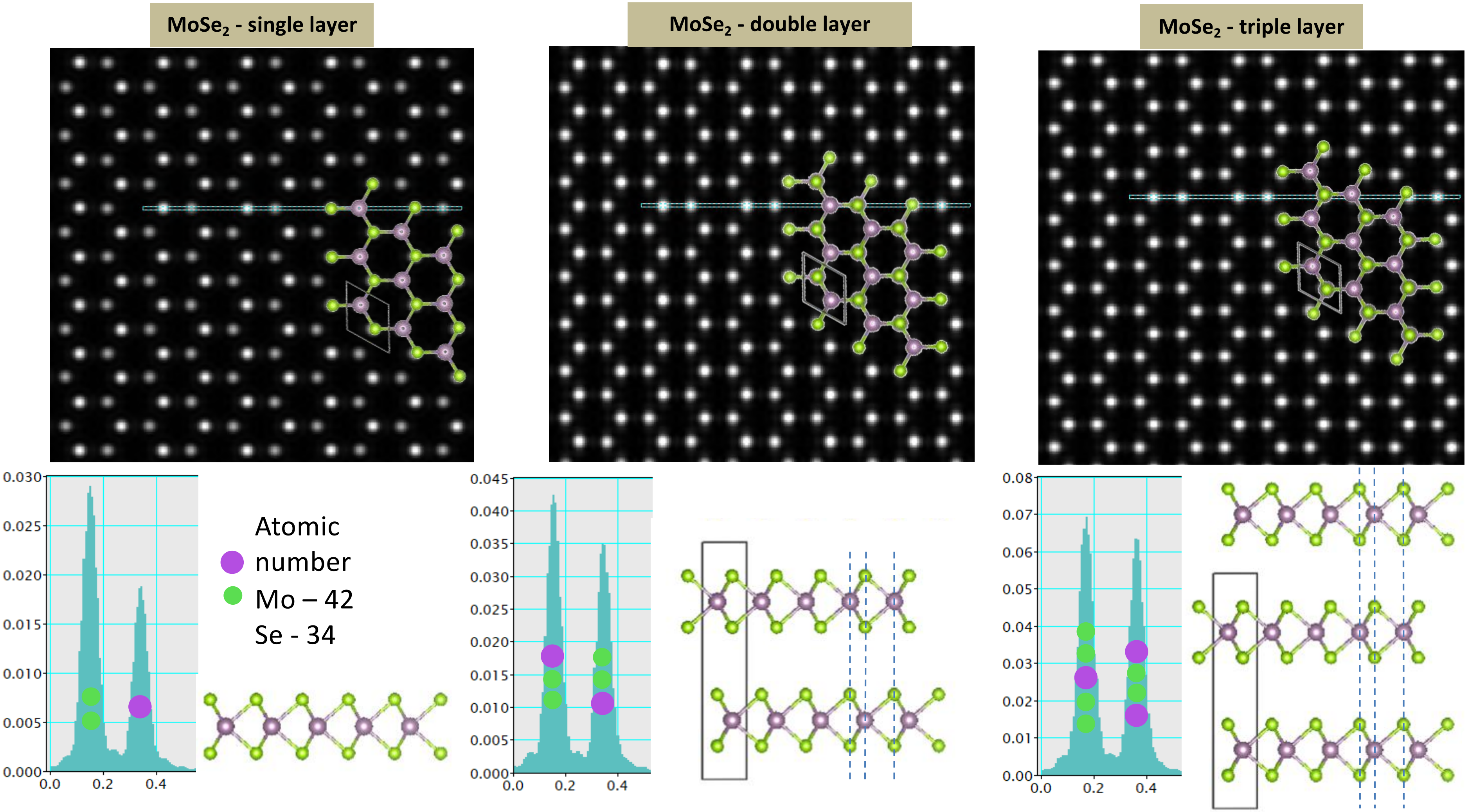


Atomic Structure of 2D Materials



Dislocation cores consisting of pentagon–heptagon ring pairs

2H stacking



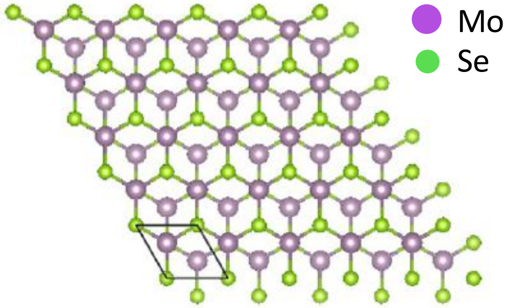
MoSe$_2$ - single layer

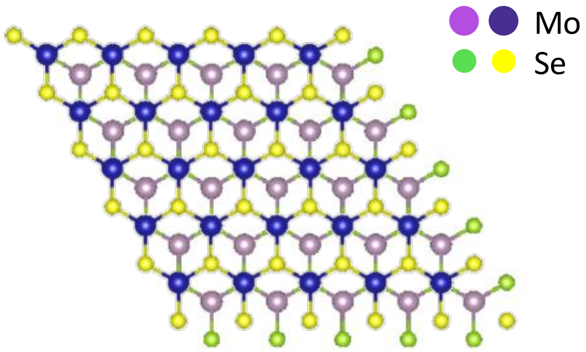
MoSe$_2$ - double layer

MoSe$_2$ - triple layer

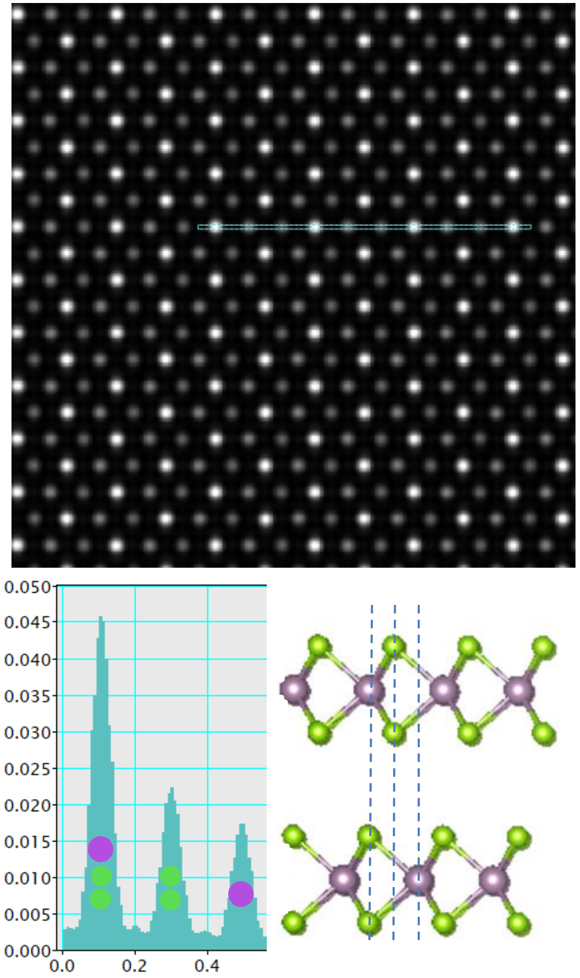
3R stacking

Model of $MoSe_2$ – 3R stacking

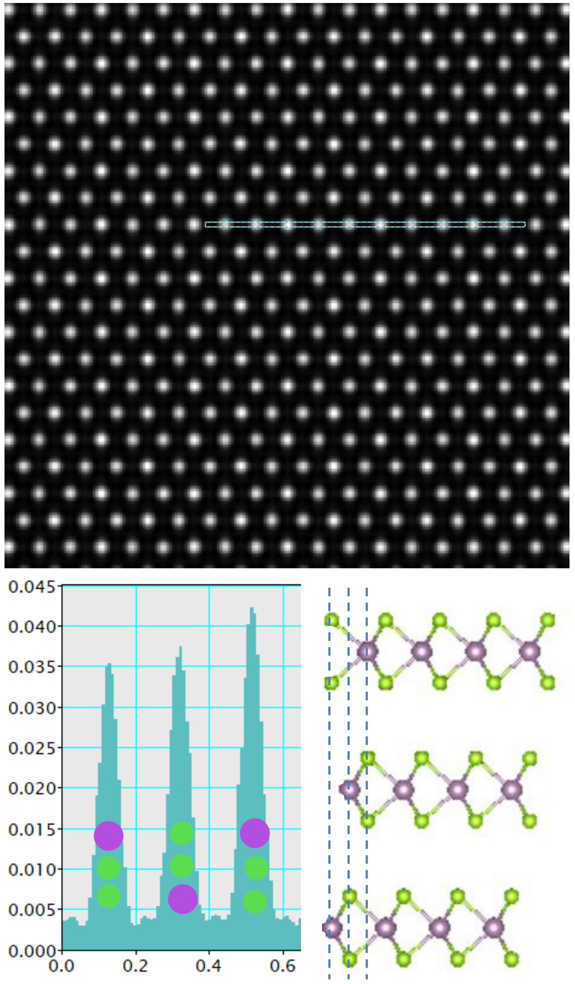




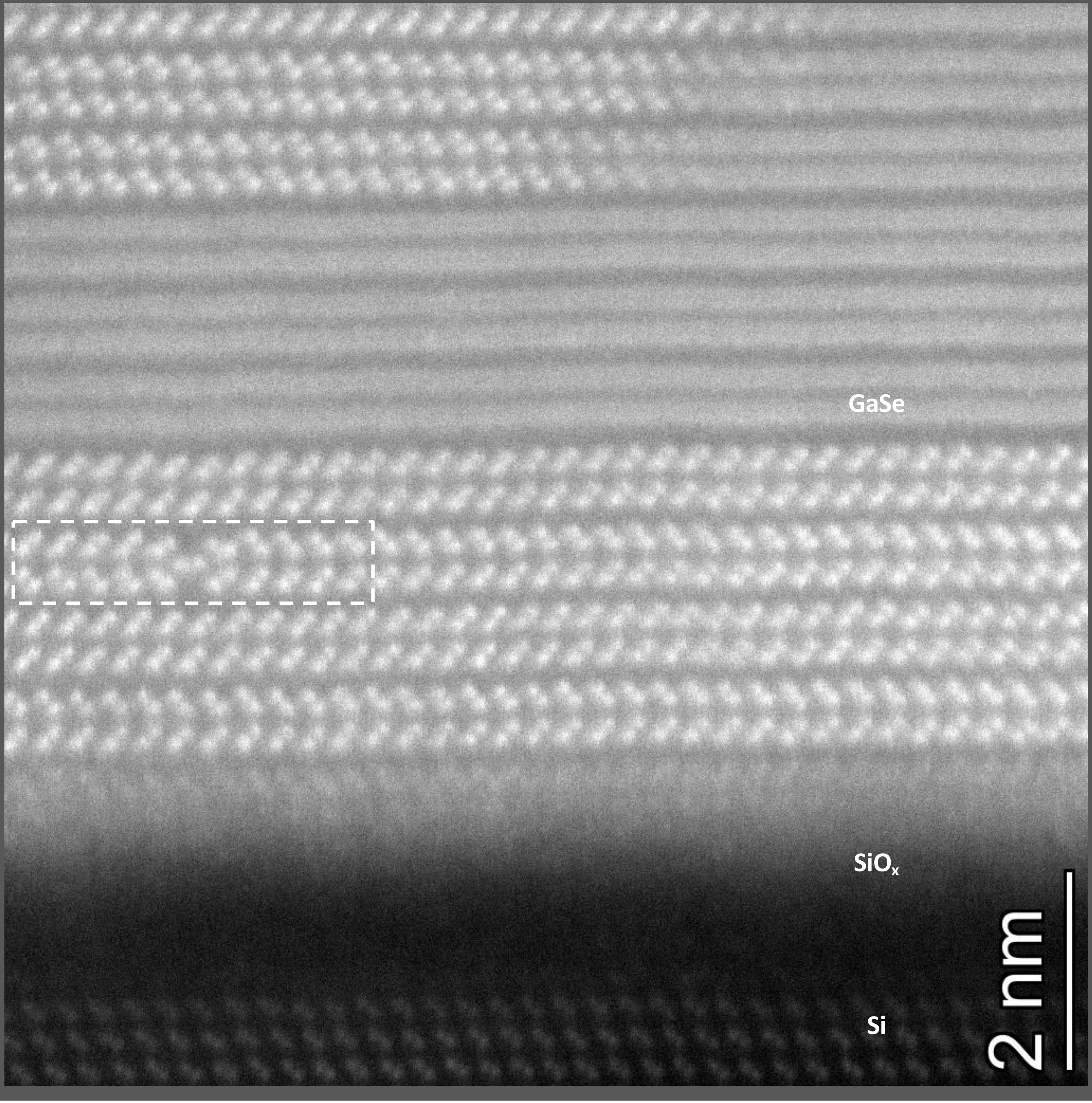
$MoSe_2$ - double layer



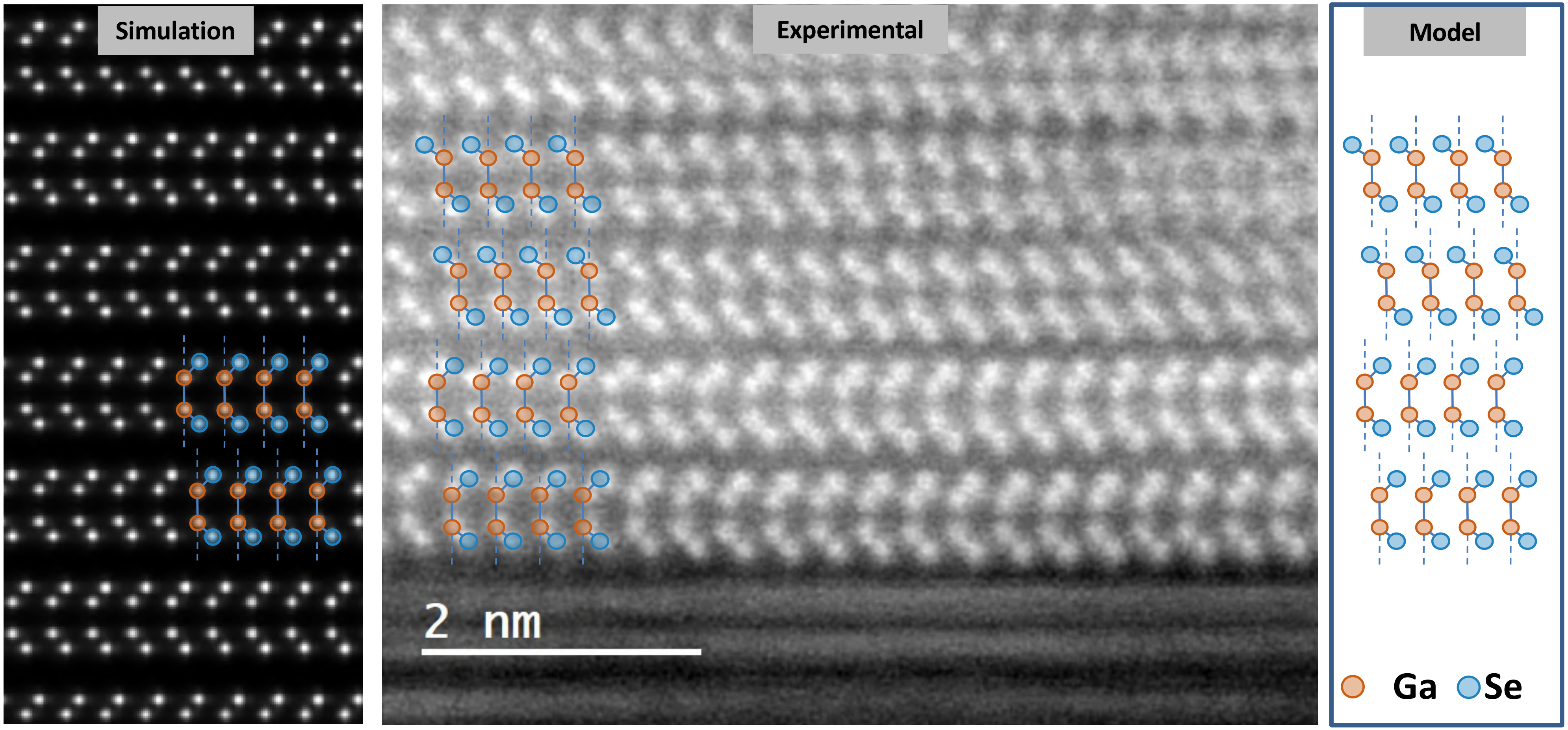
$MoSe_2$ - triple layer



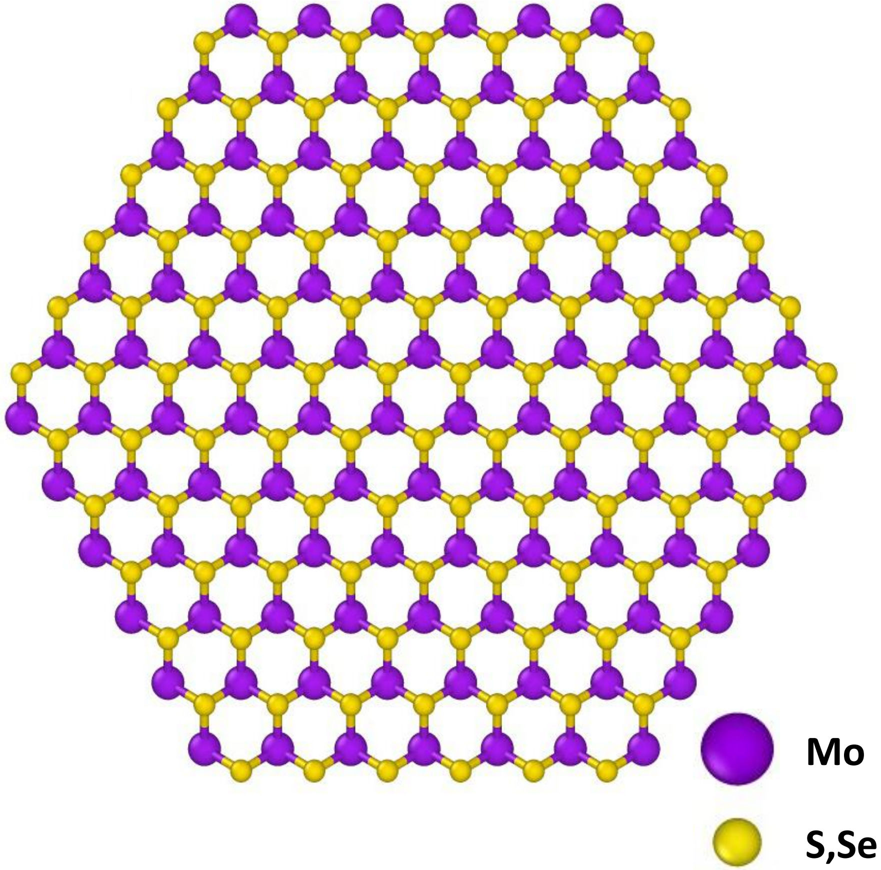
Atomic structure of defects in GaSe

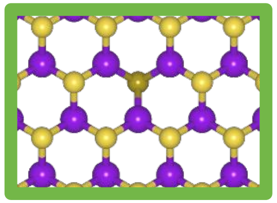


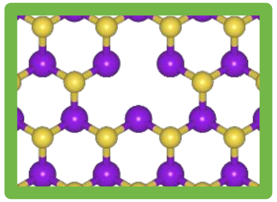
Atomic structure of defects in GaSe

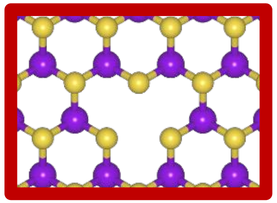


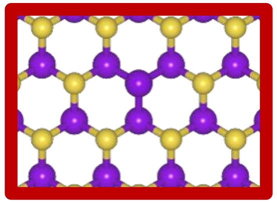
Transition Metal Dichalcogenides

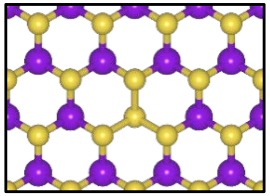


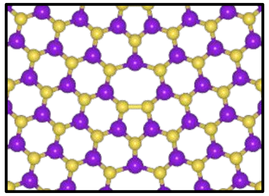

V_S,V_{Se}

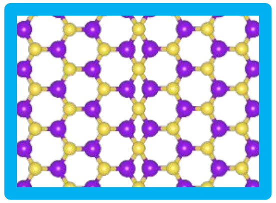

V_{S2},V_{Se2}


V_{Mo}

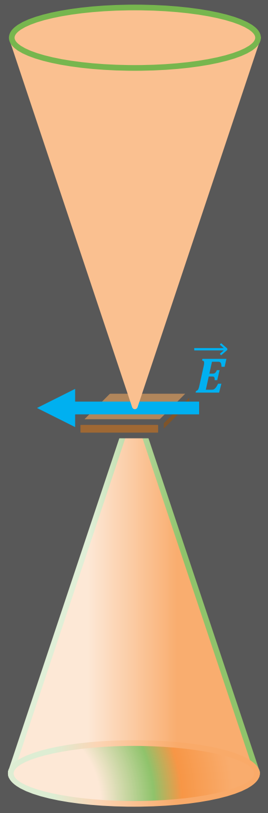

Mo_S,Mo_{S2},Mo_{Se},Mo_{Se2}

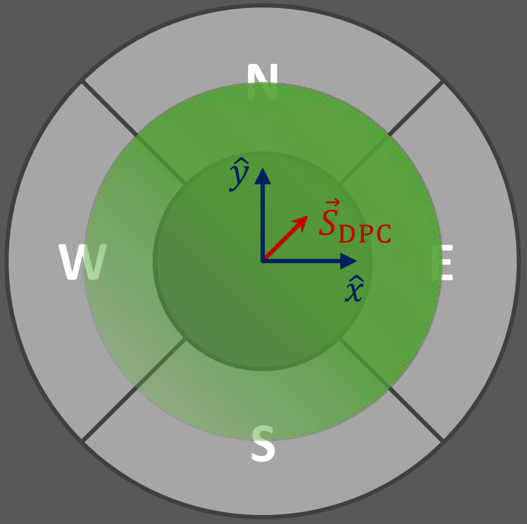

S_{Mo},Se_{Mo}


Mirror twin boundary (~20°)


Tilted grain boundary (60°)

DPC - Probing Atomic Electric Fields

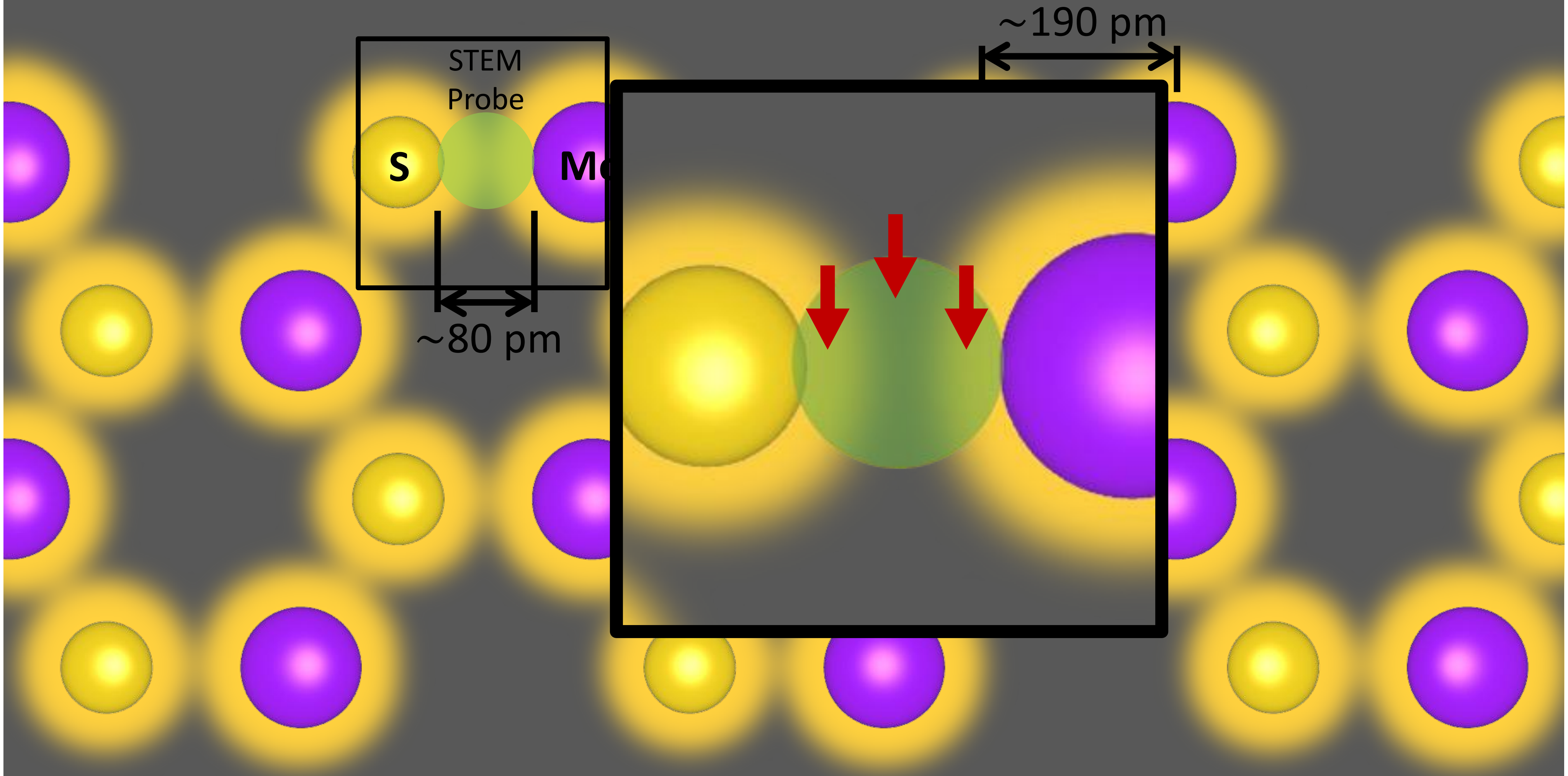




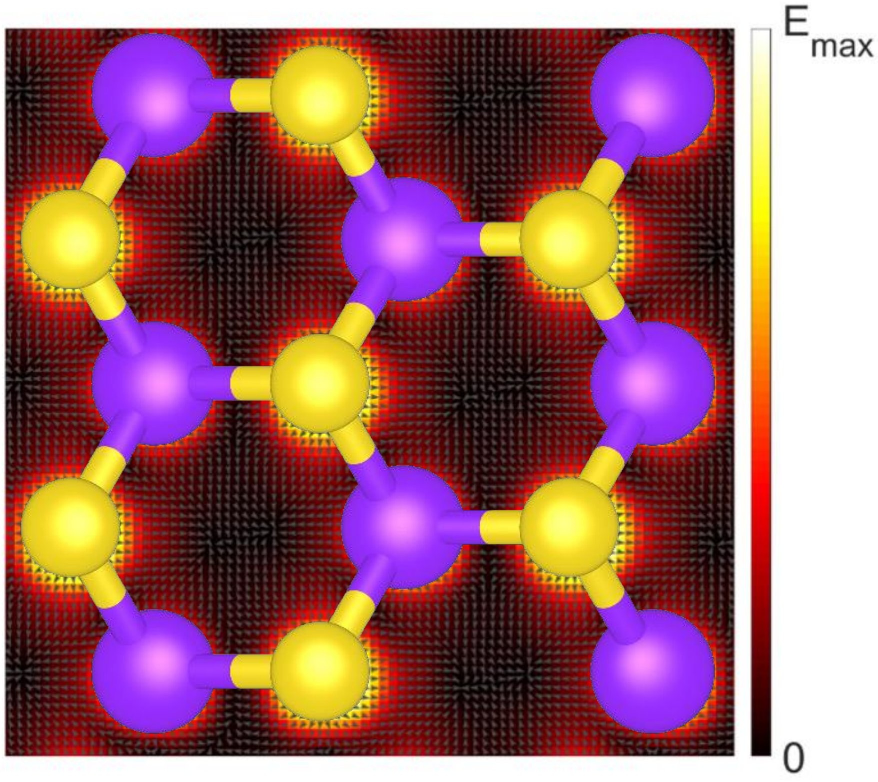
$$\vec{S}_{\mathrm{DPC}} = (E - W)\hat{x} + (N - S)\hat{y}$$

$$\vec{S}_{\mathrm{DPC}}(\vec{R}) = -\frac{e}{v}\Delta z \cdot \vec{E}_{\mathrm{PC}}(\vec{R})$$

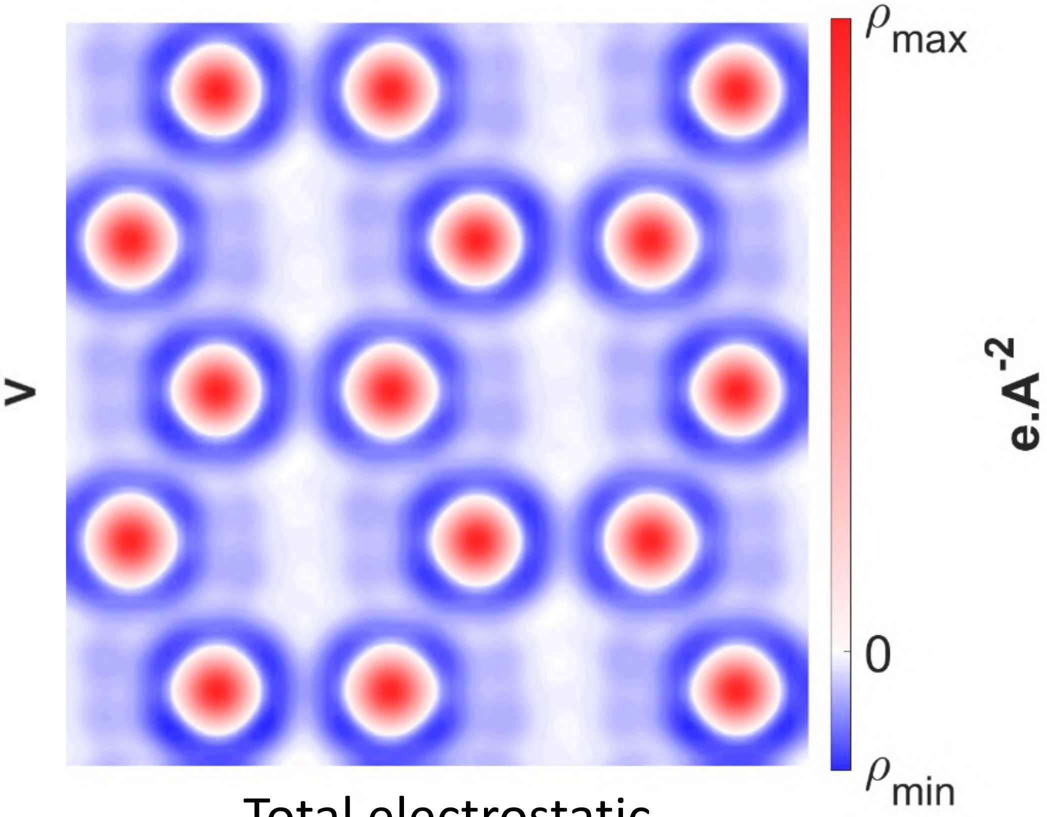
Probing Atomic Electric Fields



DPC - Electrostatic Information



Electrostatic field map
(magnitude + direction)



Total electrostatic
charge distribution map

Segmented vs Pixelated Detectors

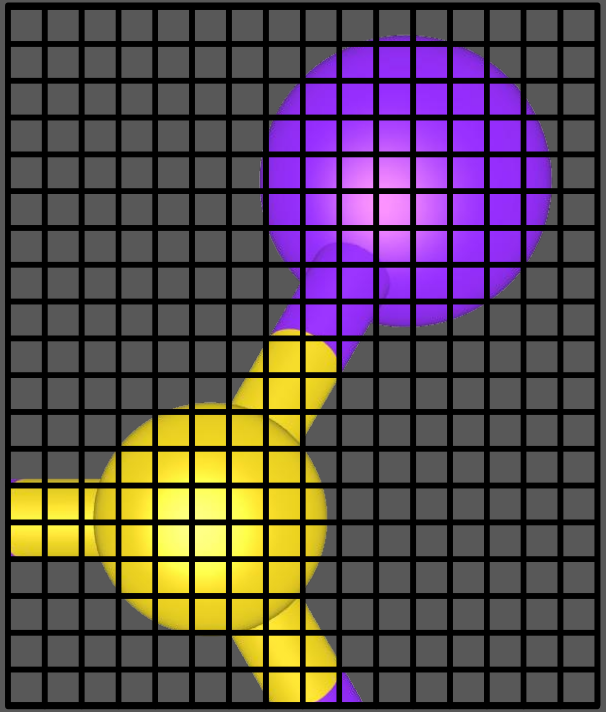
Segmented detector

- Lighter datasets
- Readout speeds < 1 µs/scan point
- Larger fields of view are more manageable
- Suited for series acquisitions
- Real-time DPC-STEM observations

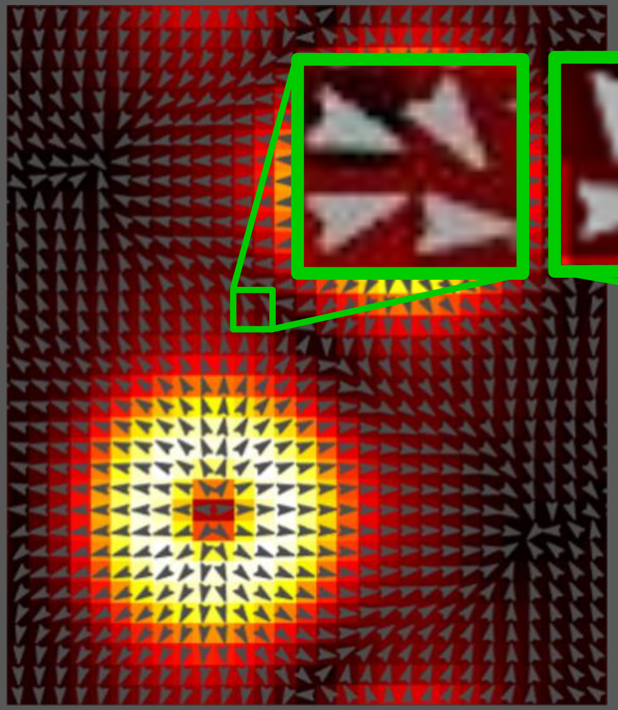
Pixelated detector

- Simpler configuration
- Readout speeds ≈ 100 µs/scan point
- Higher resolution acquisitions
- Better accuracy

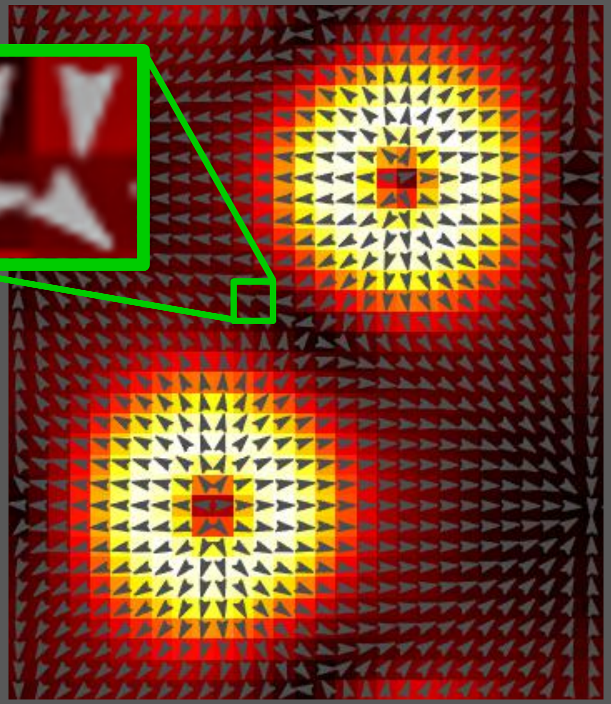
Segmented vs Pixelated Detectors



STEM Scan Grid

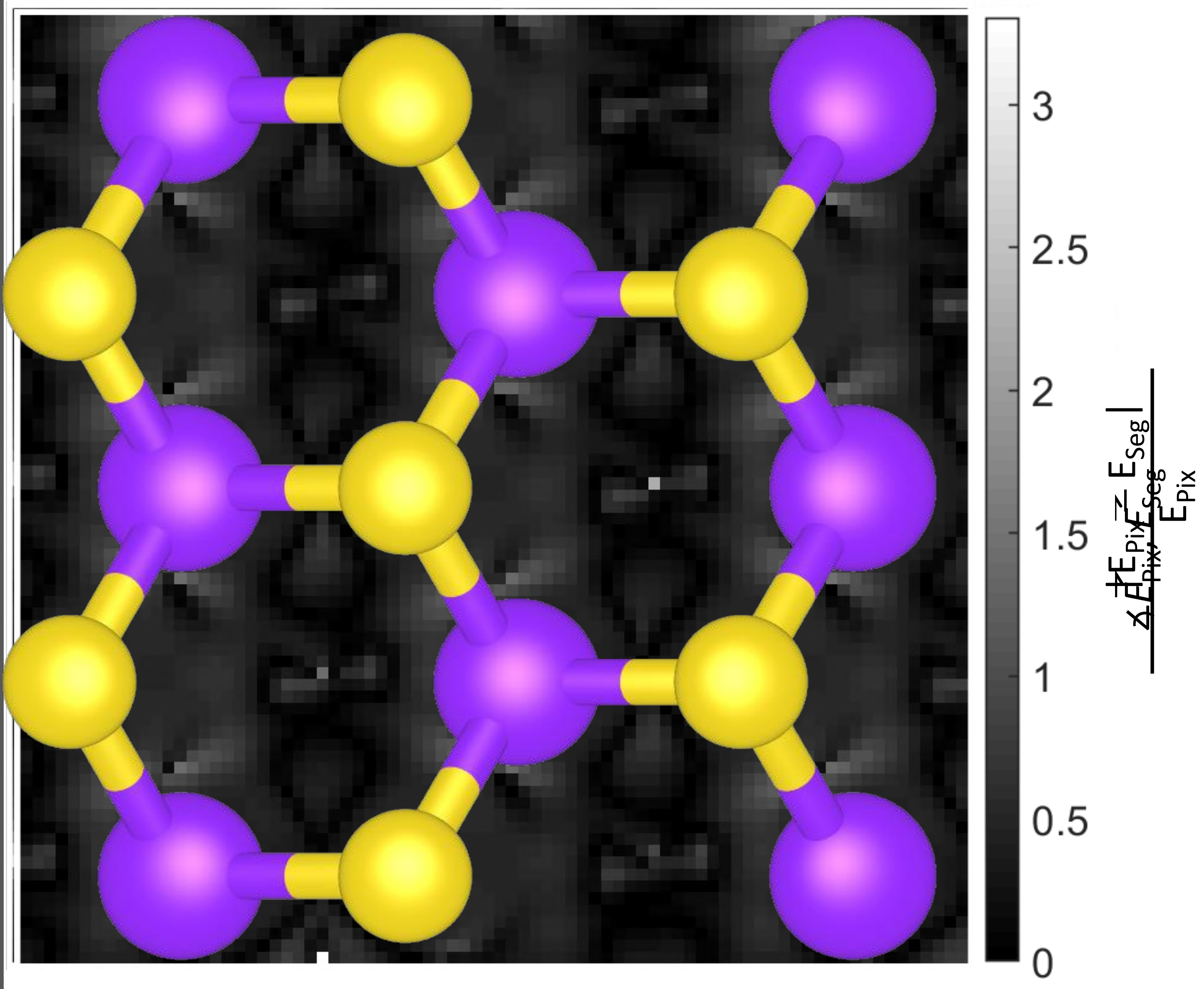


Segmented Detector



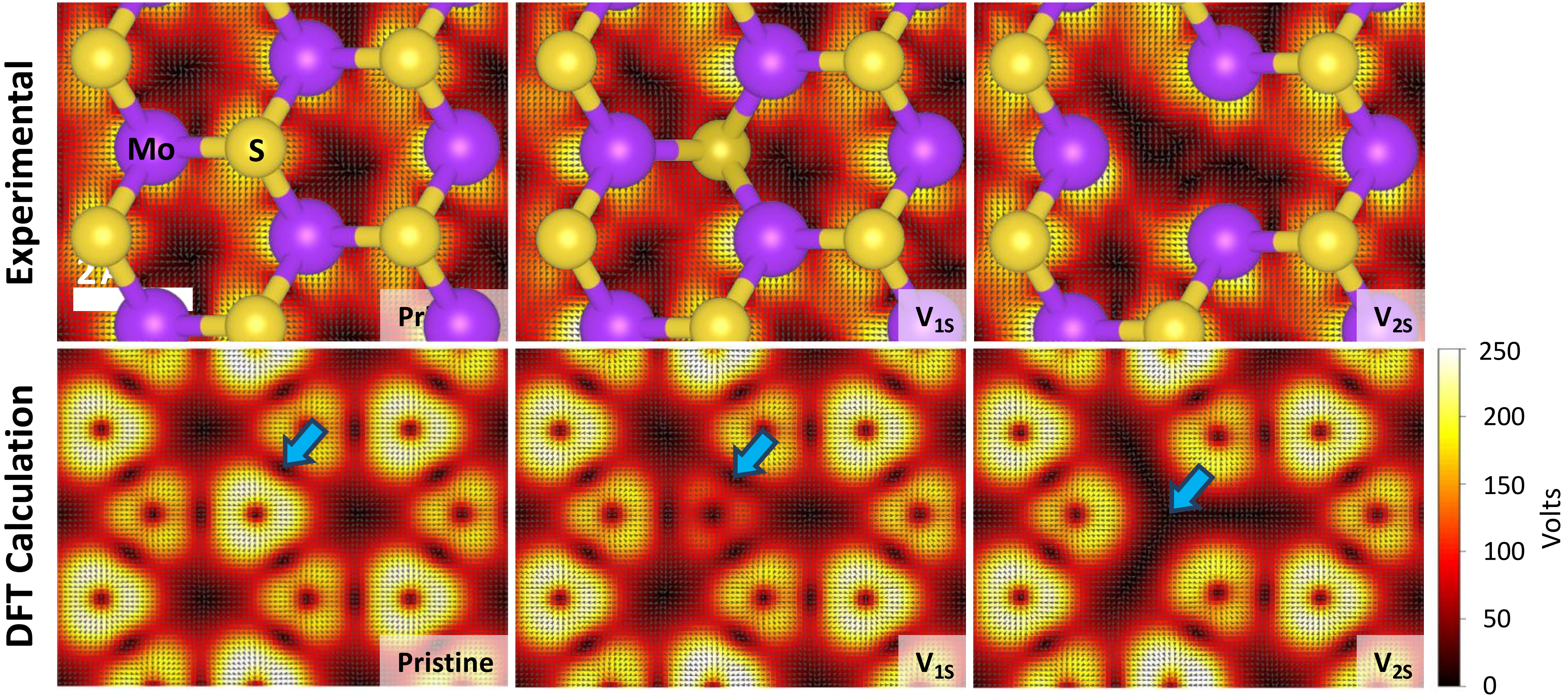
Pixelated Detector

Segmented vs Pixelated Detectors



(2021) *Nano Lett.* **21(24)**, 10157–10164

S mono- and divacancies in MoS_2



(2021) *Nano Lett.* **21(24)**, 10157–10164