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Understanding the Environmental Transmission Electron Microscope

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Understanding the Environmental Transmission Electron Microscope

Jakob B. Wagner

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Rafal E. Dunin-Borkowski, Institute for Microstructure Research, Forschungszentrum Jülich, Germany

Jörg R. Jinschek, FEI Europe, Eindhoven, The Netherlands

DTU Cen
Center for Electron Nanoscopy

Towards Understanding the Environmental Transmission Electron Microscope

Jakob B. Wagner

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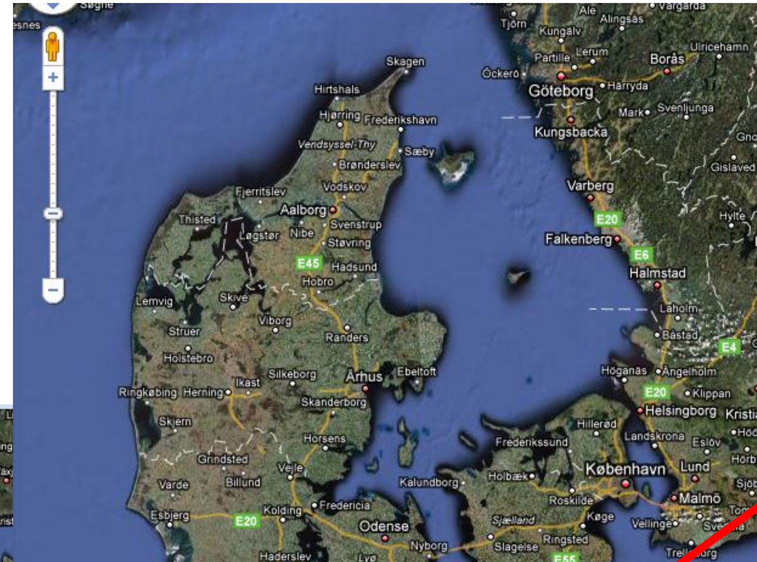
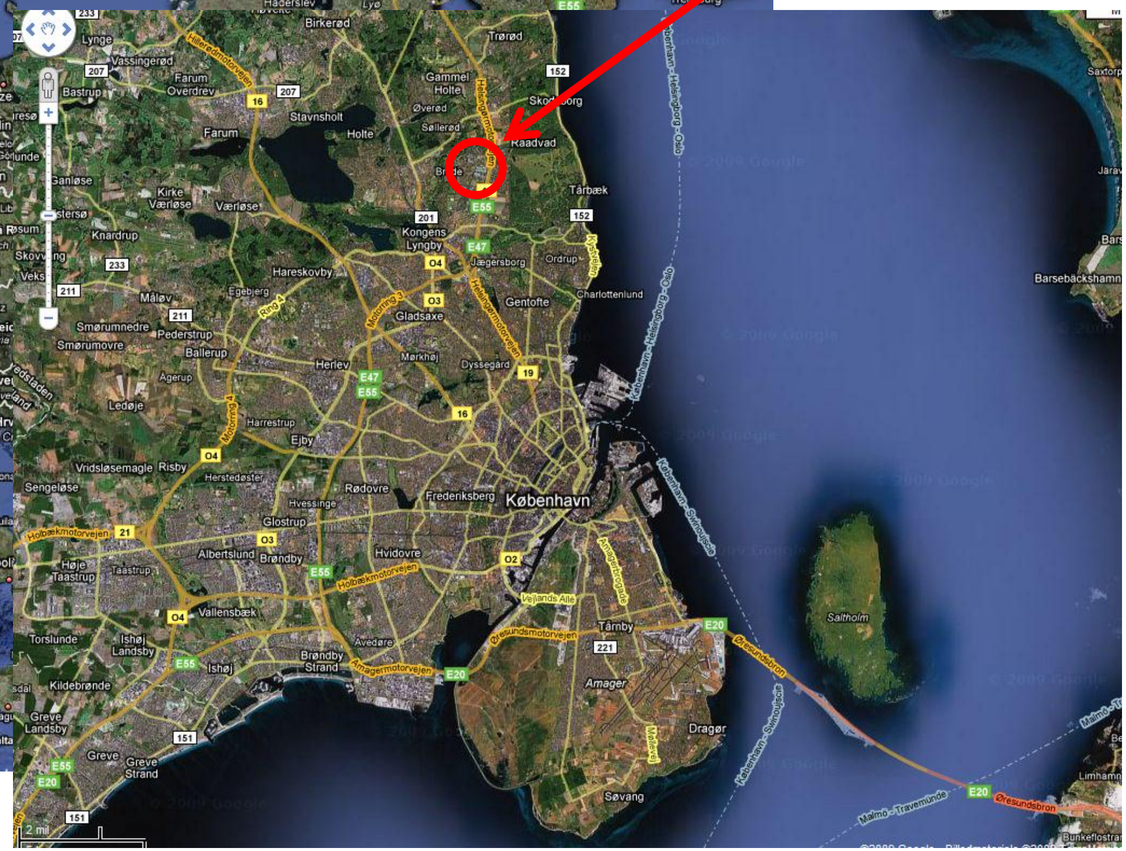
Where are We?



DTU



DTU Center for Electron Nanoscopy

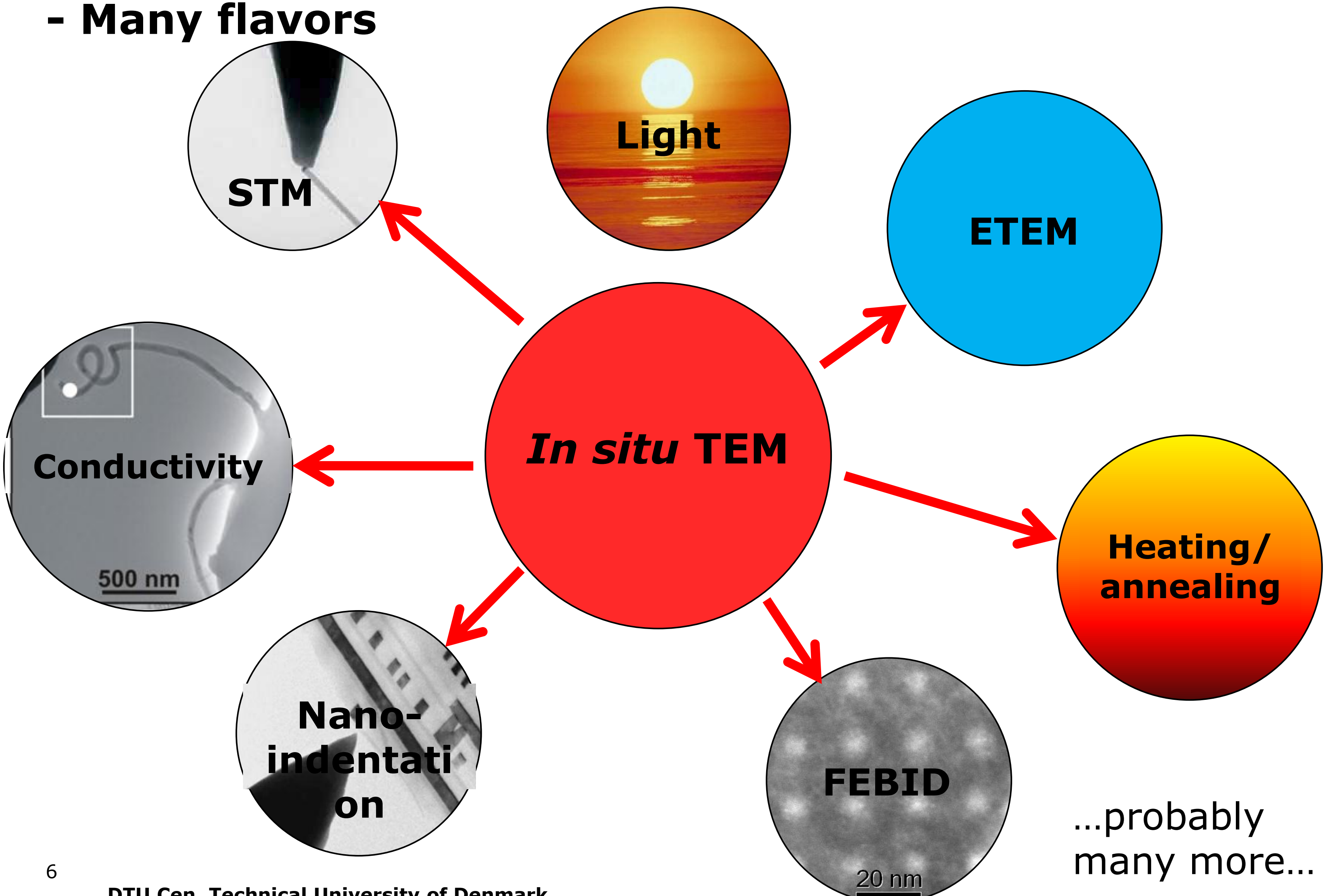
- Realized by a generous donation from the A.P. Møller og Hustru Chastine Mc-Kinney Møller's Fond til Almene Formaal
- DKK 100,000,000 ~ €14,000,000
- Grant announced in January 2006
- *"Establish a World Class Facility with a unique suite of advanced electron microscopes, in a purpose-built building"*
- Inaugurated in December 2007

- Hosting 7 electron microscopes
  - 2 high-end TEMs (1 ETEM)
  - 1 work horse TEM
  - 2 dual beam SEM/FIB
  - 2 SEM

What is *In Situ* Microscopy

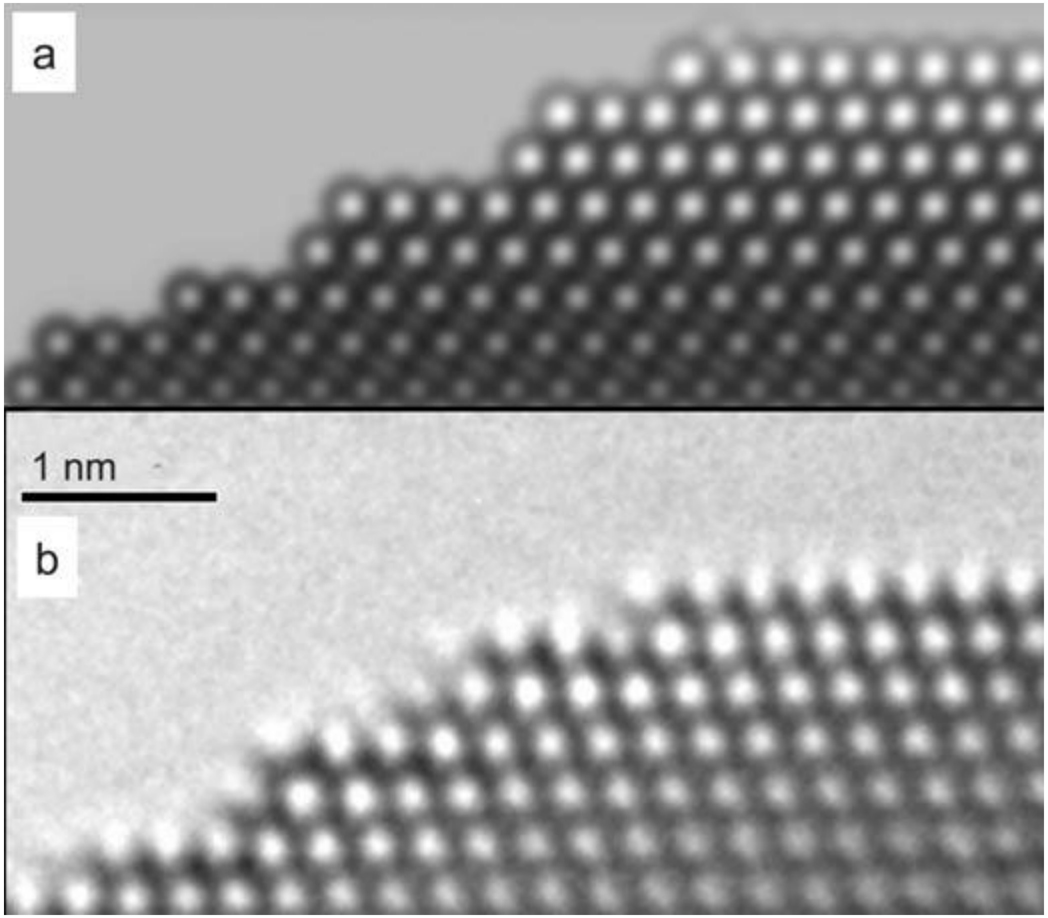
- …depends on who you ask…
- "The class of experiments allowing observations of materials' dynamic response to an externally applied stimulus as it happens inside the microscope"
- The *in situ* observations may be accompanied by simultaneous measurements of the materials' properties to directly establish structure-functionality relationships

In Situ Microscopy
- Many flavors



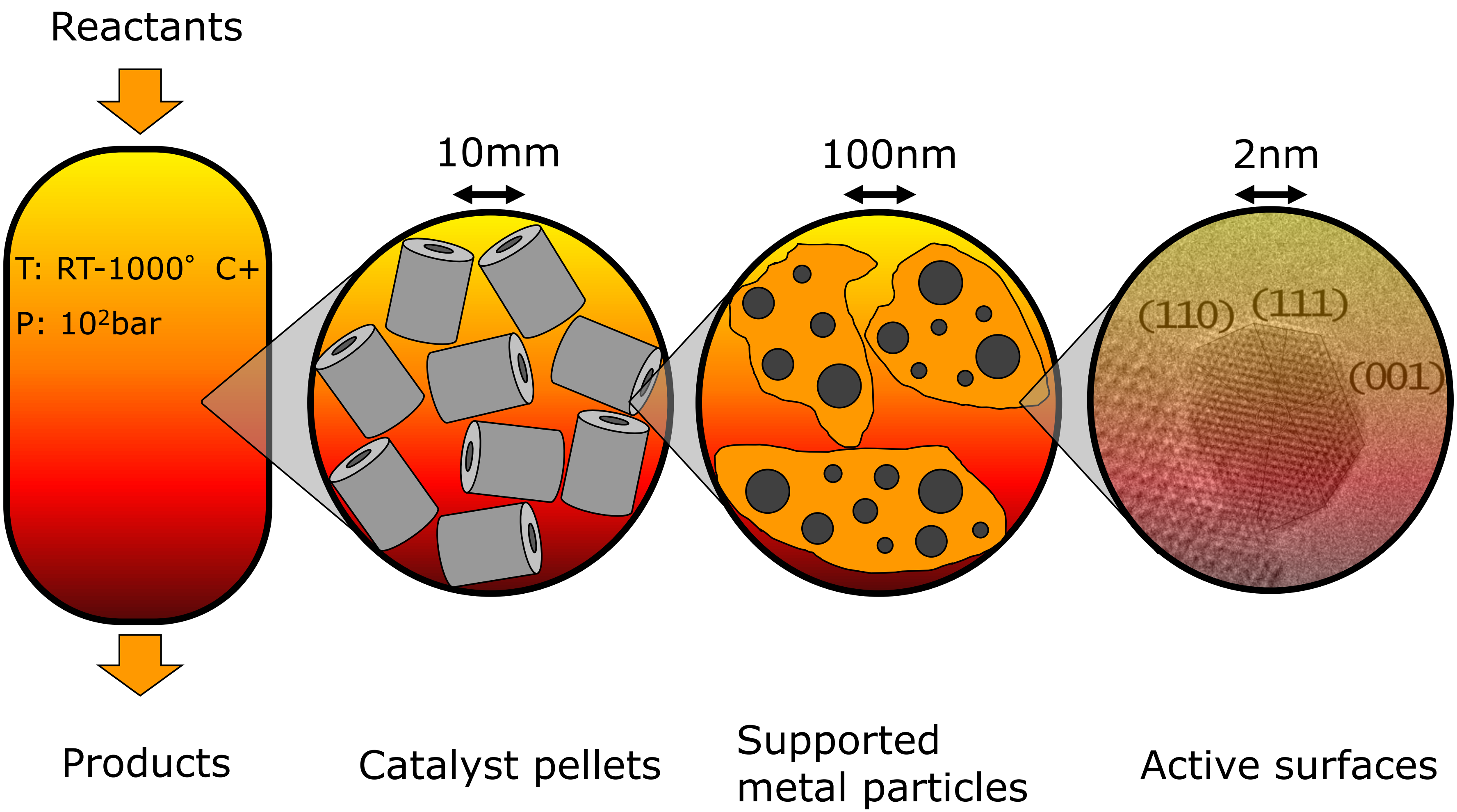
What are We Trying to Achieve?

- Obtain high-resolution information
- Dynamic responses of materials as they are exposed to reactive gases at elevated temperatures
- Surface structure of materials in various environments
- Morphology of materials in different surroundings



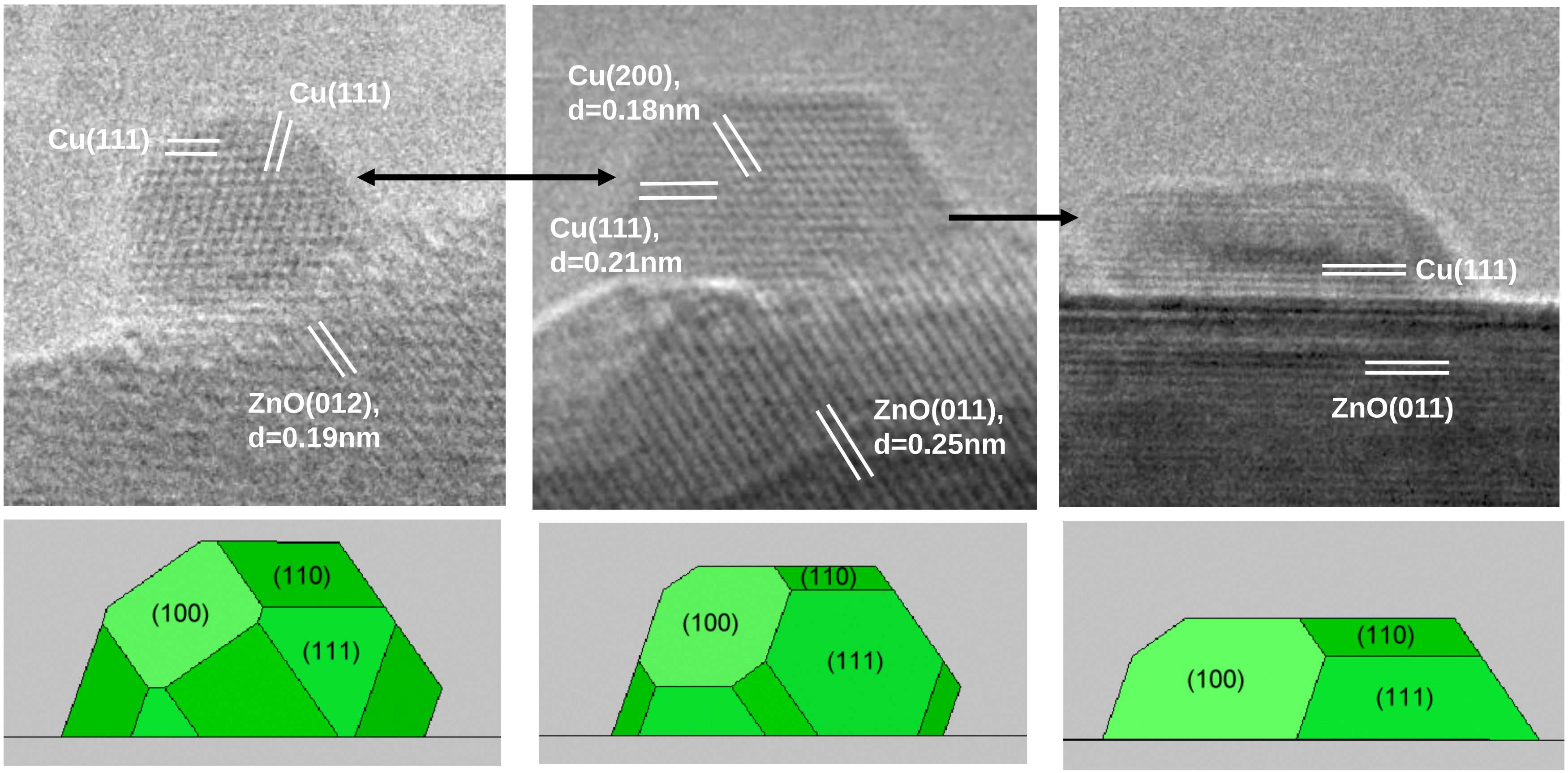
Dang Sheng Su, Timo Jacob, Thomas W. Hansen, Di Wang, Robert Schlögl, Bert Freitag, and Stephan Kujawa, *Angew. Chem.* **47**, 5005 (2008)

A Look Inside the Catalytic Reactor



Why do We Want to do *In Situ* Microscopy? Equilibrium shapes versus gas composition

H_2/H_2O | H_2 | H_2/CO

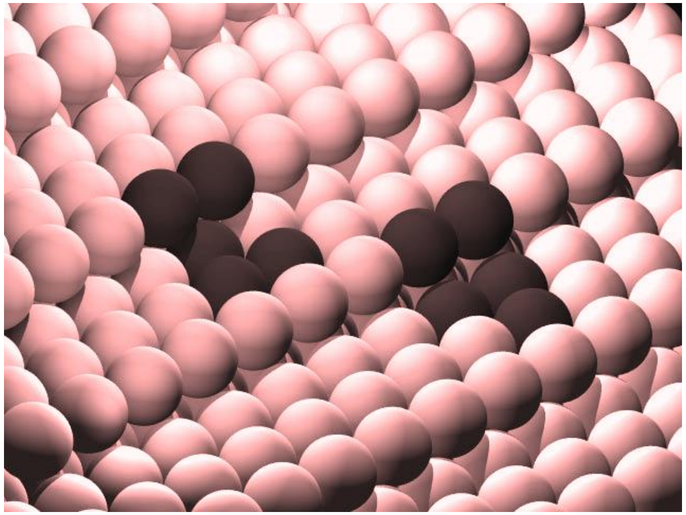


1.5mbar, H_2/H_2O=3/1, 220°C | **1.5mbar, 220°C** | **1.5mbar, H_2/CO=95/5, 220°C**

J. B. Wagner *et al. Science* **395,** 2053 (2002).

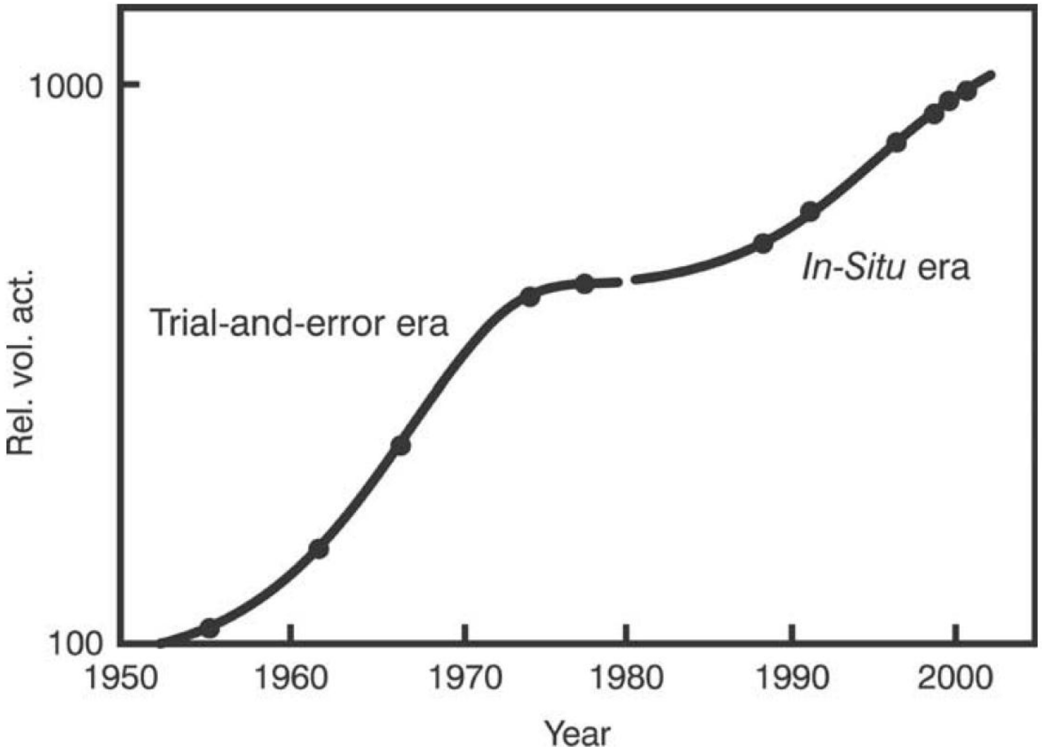
Why do We Want to do *In Situ* Microscopy? ...continued

- Conventional electron microscopy does not always tell the full story
  - Samples are (usually) not in their operational environment
- Materials respond dynamically to changes in environment
  - Surface reconstruction due to gas adsorption
  - Phase transitions
  - Growth
- Lack of temporal resolution
- Essential for establishing structure-activity correlations



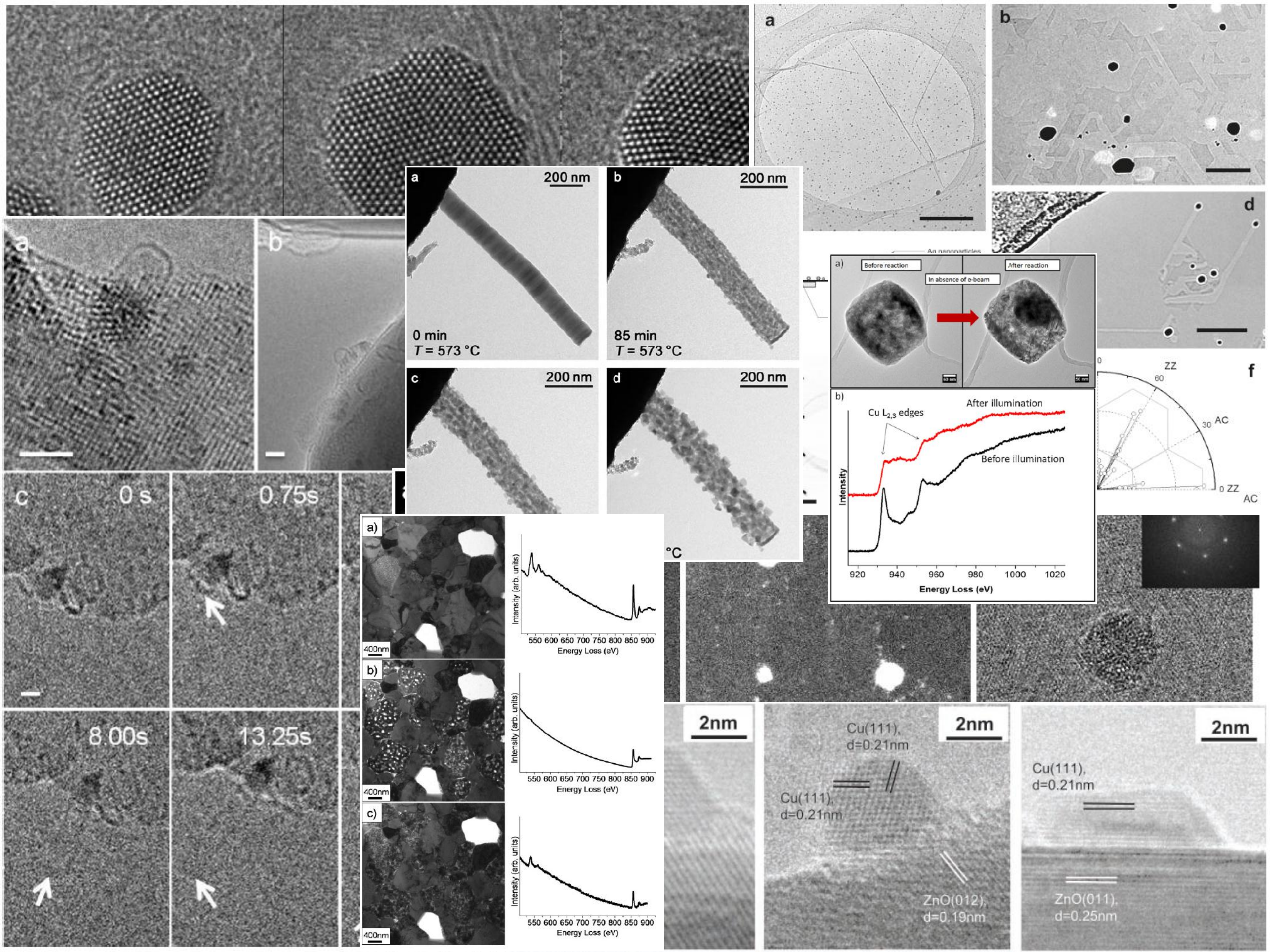
b_5 sites on the (105) surface of Ru. These sites were proposed to be the active sites for N_2 splitting (van Hardeveld and von Montfoort Surf. Sci. 4 (1966) 396. Figure from T.W. Hansen *et al. Catal Lett.* **84,** 7 (2002).

In Situ Techniques



Evolution of activity of industrial HDS catalysts,
B.M. Moyse, World Refining Jan/Feb (2001) 28
H. Topsøe, J. Catal. 216, 155 (2003)

- *In situ* XRD
  - Phase determination
  - Good for large areas
- *In situ* EXAFS, FTIR
  - Coordination
  - Chemical bonding
- Average values
  - No local information
- *In situ* TEM
  - Gives local information
- Etc…

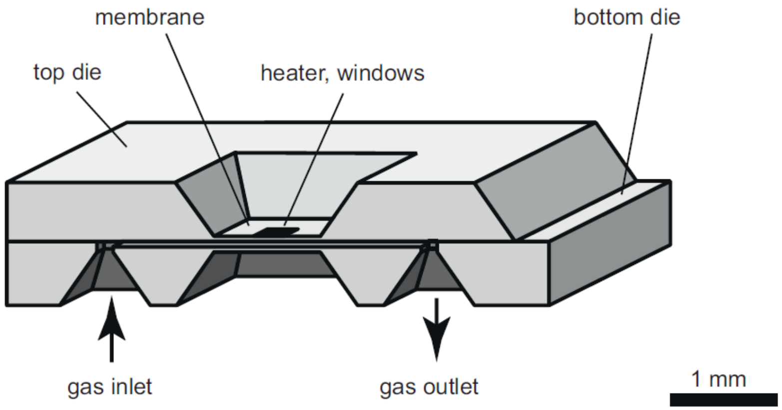


a
b
200 nm
0 min
T = 573 °C
85 min
T = 573 °C
c
d
°C
a
b
0 s
0.75s
8.00s
13.25s
c
a
b
d
f
ZZ
AC
60
30
0
0 ZZ
AC
a)
Before reaction
In absence of e-beam
After reaction
50 nm
b)
Cu L2,3 edges
After illumination
Before illumination
Intensity
Energy Loss (eV)
920
940
960
980
1000
1020
a)
b)
c)
400nm
Intensity (arb. units)
550 600 650 700 750 800 850 900
Energy Loss (eV)
2nm
Cu(111), d=0.21nm
ZnO(012), d=0.19nm
ZnO(011), d=0.25nm

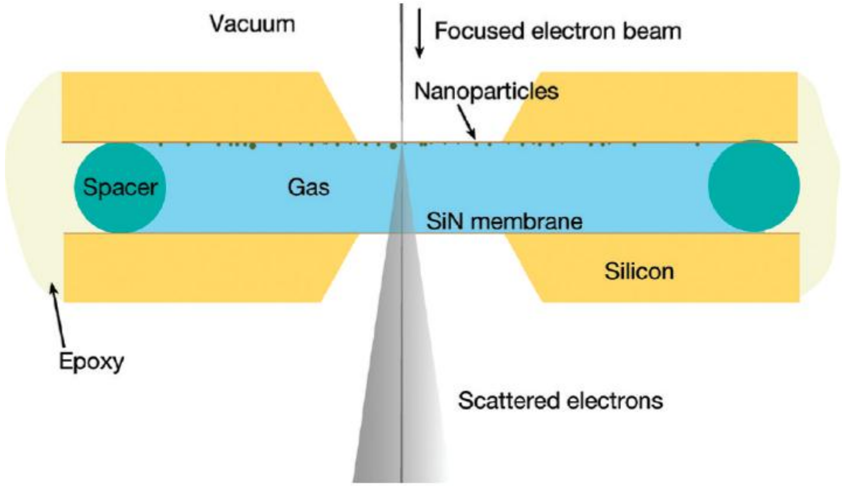
Imaging in the fog of gas

Can we get a clear view...?

Windowed Design



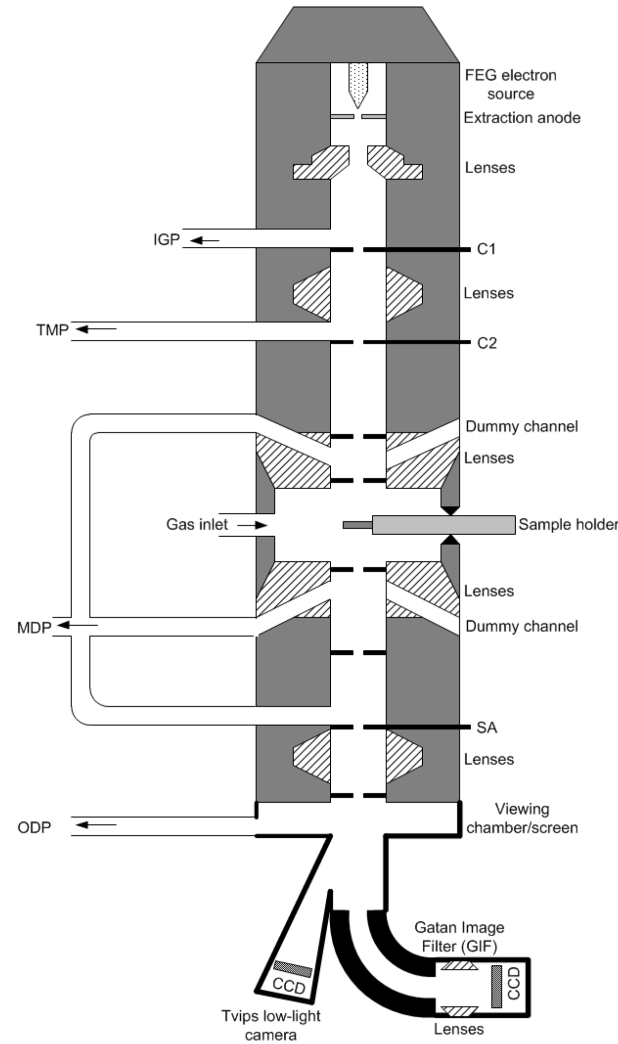
J. F. Creemer *et al.*, Ultramicroscopy 108, 993 (2008)



N. de Jong *et al.*, Nano Letters 10, 1028 (2010)

Differentially pumped Column

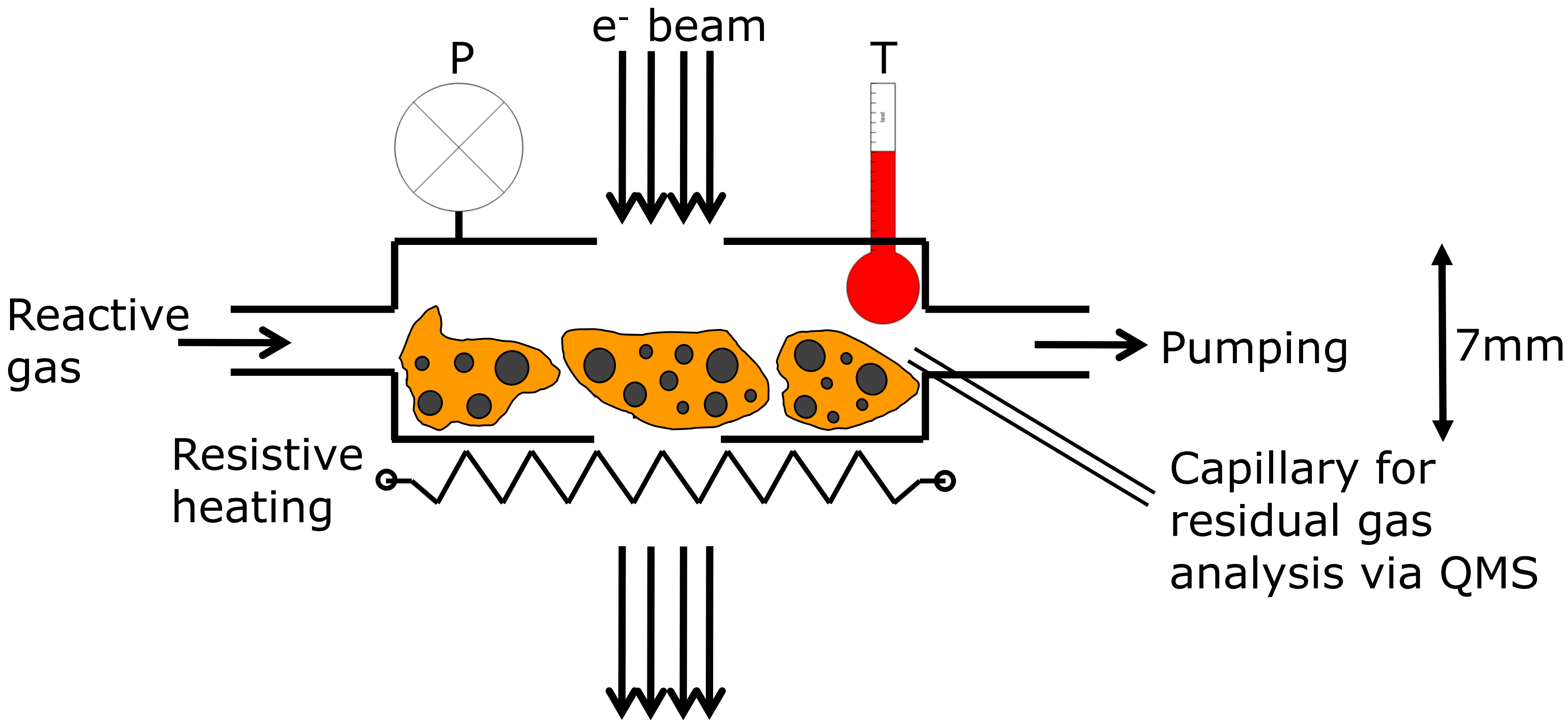
- FEI Titan 80-300
  - Highly stable platform
  - Variable high tension 80, 200, 300kV
  - Field emission electron source (XFEG)
  - Monochromator
  - Objective lens aberration corrector
  - De-contaminator (plasma cleaner)
- Differential pumping system
  - Gas is leaked in
  - Two sets of diffusion limiting apertures
  - Turbo molecular pump (TMP)
  - Ion getter pump (IGP)



T. W. Hansen, J. B. Wagner and R. E. Dunin-Borkowski, *Mater. Sci. Tecnol.*, 26, 1338 (2010)

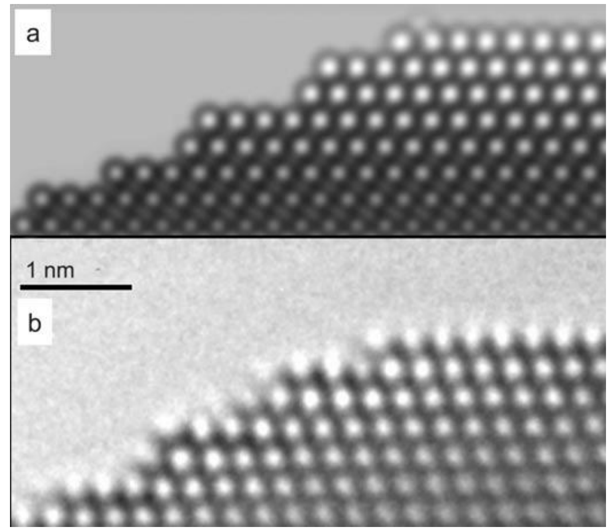
The Environmental Cell
- not really a cell…

- Main purpose: to confine the gas to the vicinity of the sample thus making the gas path length along the direction of the electrons as short as possible

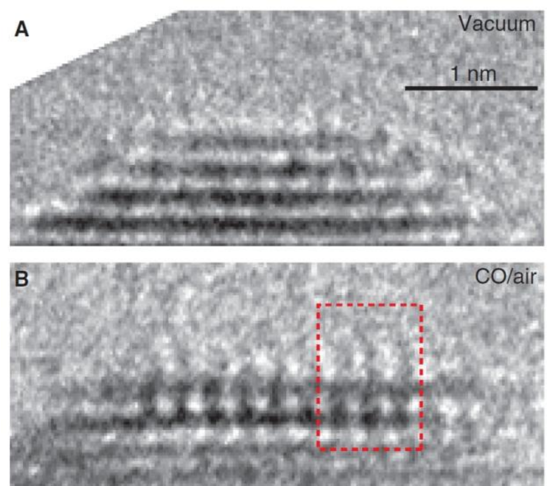


Quantitative ETEM !?

- Obtain high-resolution information
- Dynamic responses of materials as they are exposed to reactive gases at elevated temperatures
- Surface structure of materials in various environments
- Morphology of materials in different surroundings
- Adsorbed molecules



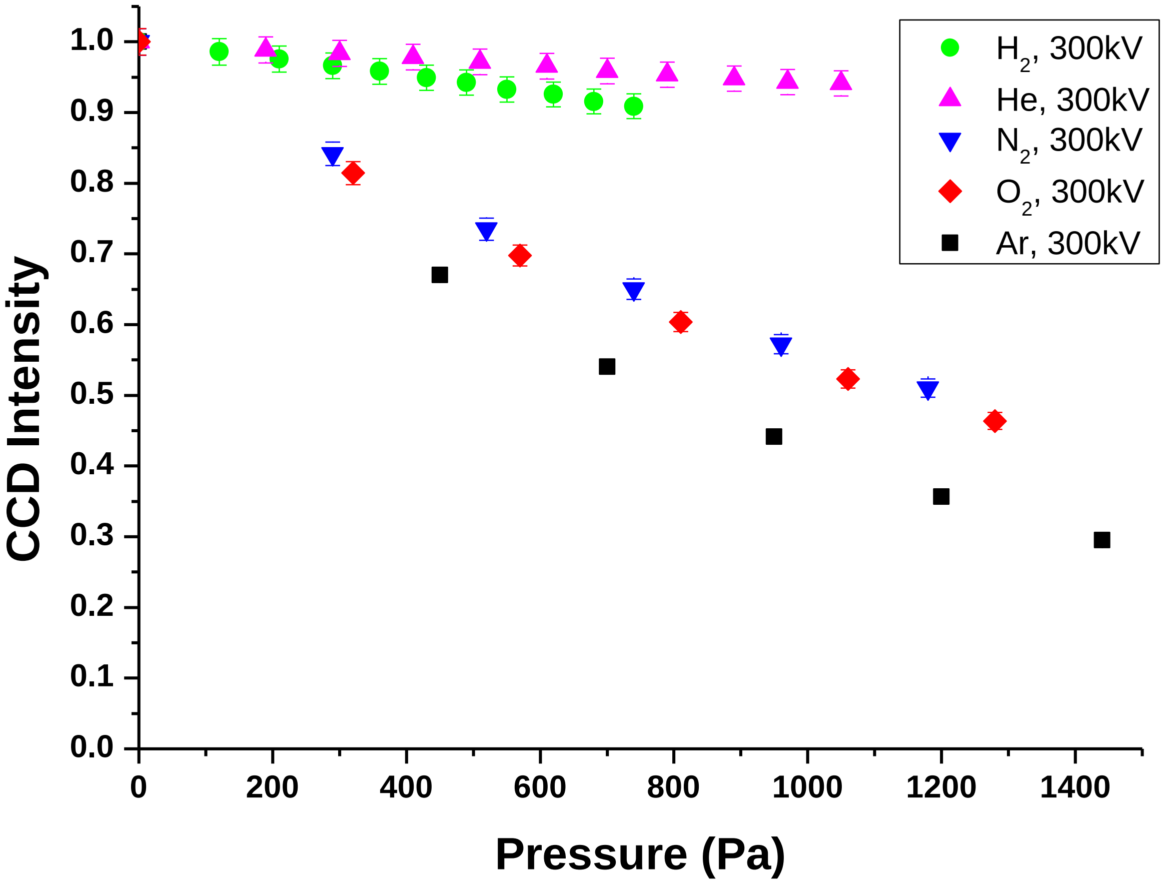
D. S. Su *et al.*, *Angew. Chem.* 47, 5005 (2008)



H. Yoshida *et al.*, *Science* 335, 317 (2012)

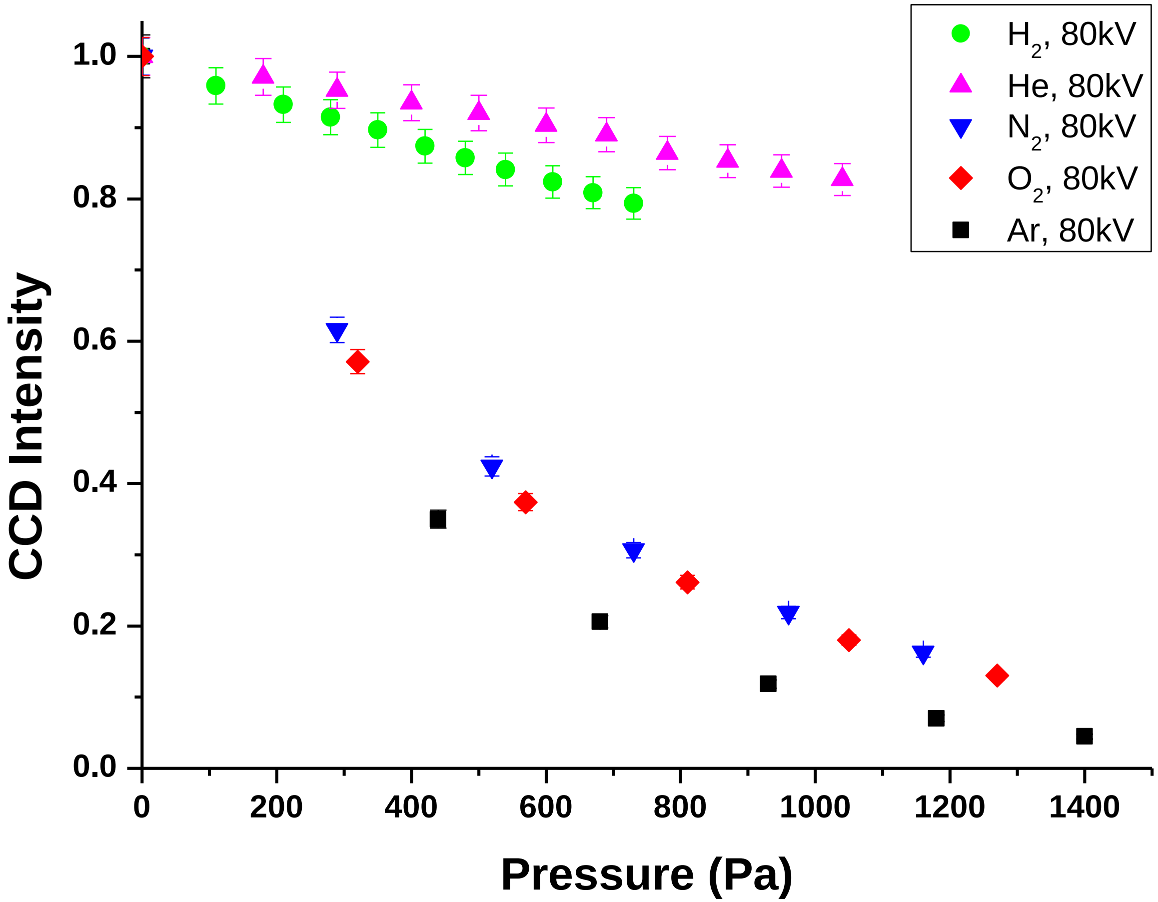
Loss of Intensity

- Main effect of imaging in gas is loss of intensity
- Intensity measured on a bottom mounted camera as a function of argon pressure in the sample region
- At high Ar pressure, >1400Pa, the intensity passing through the objective lens has decreased by more than a factor of 2 at 300kV
- Increasing pressure leads to loss of temporal resolution



Loss of Intensity

- Main effect of imaging in gas is loss of intensity
- Intensity measured on a bottom mounted camera as a function of argon pressure in the sample region
- At high Ar pressure, >1400Pa, the intensity passing through the objective lens has decreased by more than a factor of 2 at 300kV
- As high a primary energy is desired due to a longer mean free path in the gas phase
- Increasing pressure leads to loss of temporal resolution



Apparent Mean Cross Sections and Mean Free Paths

- Intensities fitted to:

$$\frac{I}{I_0} = e^{-x/\lambda}$$

- Mean free path:

$$\lambda = \frac{1}{\sigma n}$$

- Assuming ideal gas:

$$pV = NRT \Rightarrow n = \frac{N}{V} = \frac{P}{RT} \Rightarrow \lambda = \frac{RT}{\sigma P}$$

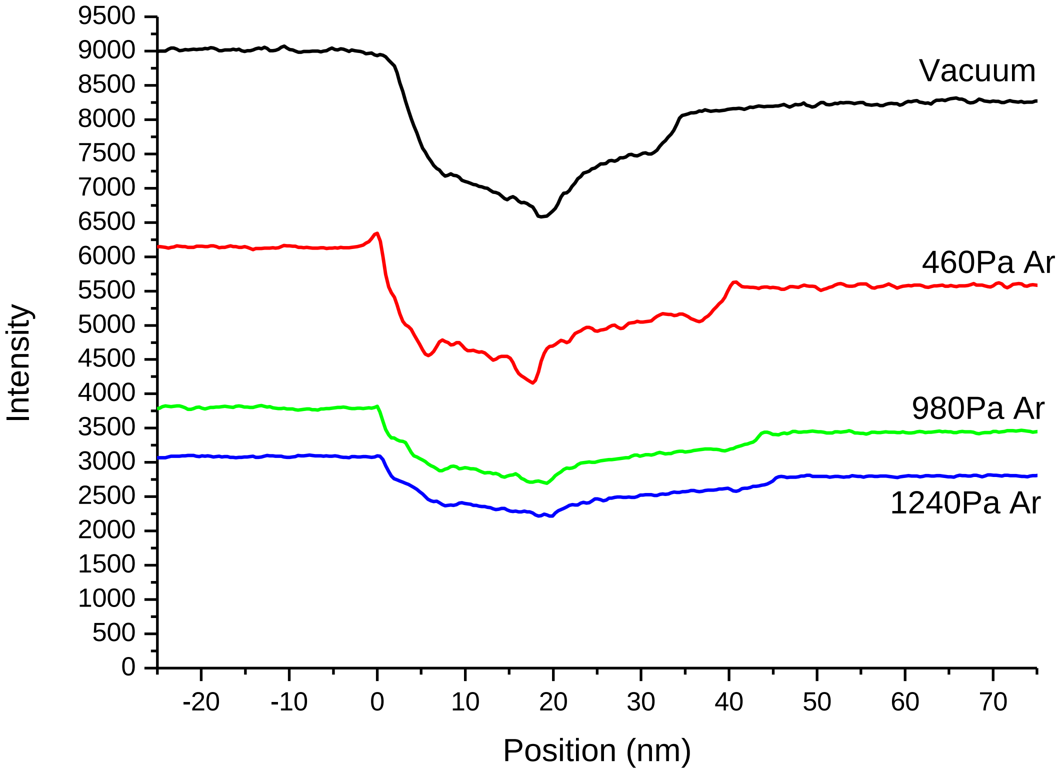
- Fit function becomes:

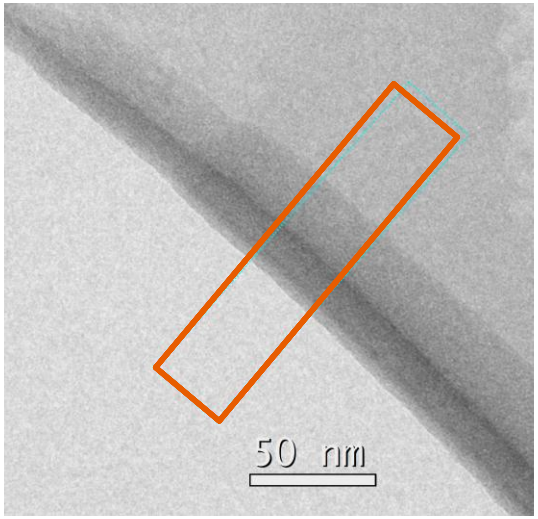
$$\frac{I}{I_0} = e^{-\frac{\sigma P}{RT}\times 7.5\times 10^{-3}\,m}$$

	σ[m²]	λ(500Pa)[10^{-3}m]
80kV, H_2	1.8E-22	46
80kV, He	9.7E-23	85
80kV, N_2	8.9E-22	9
80kV, O_2	9.1E-22	9
80kV, Ar	1.3E-21	7
200kV, N_2	4.1E-22	20
200kV, O_2	4.1E-22	20
200kV, Ar	6.0E-22	14
300kV, N_2	3.2E-22	26
300kV, O_2	3.0E-22	28
300kV, Ar	4.5E-22	19

Contrast and Loss of intensity (Bright field imaging)

- How does the contrast of BF images change with gas pressure?
- 2.7mrad objective aperture (semiangle)
- Illumination conditions kept constant





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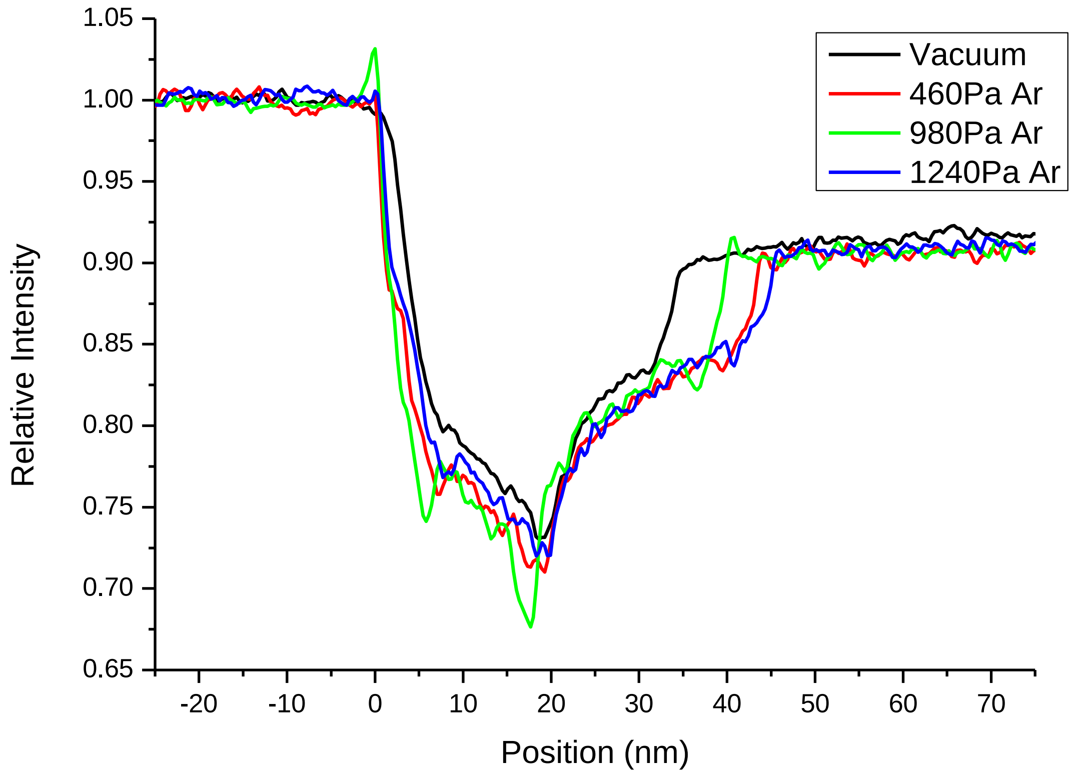
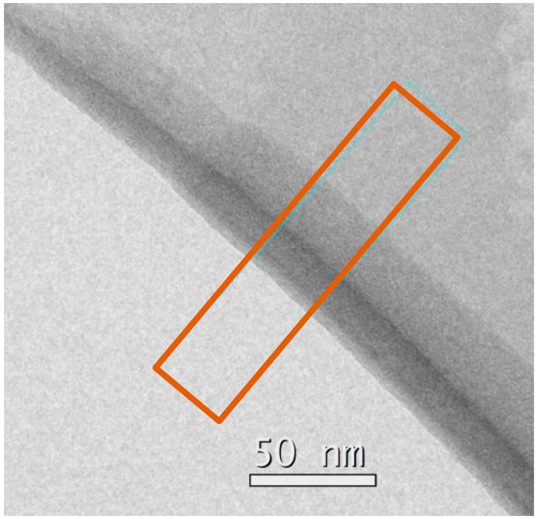
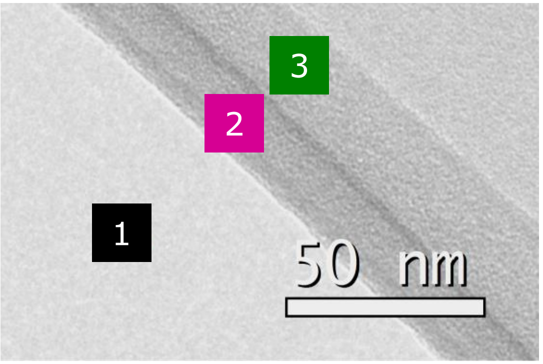
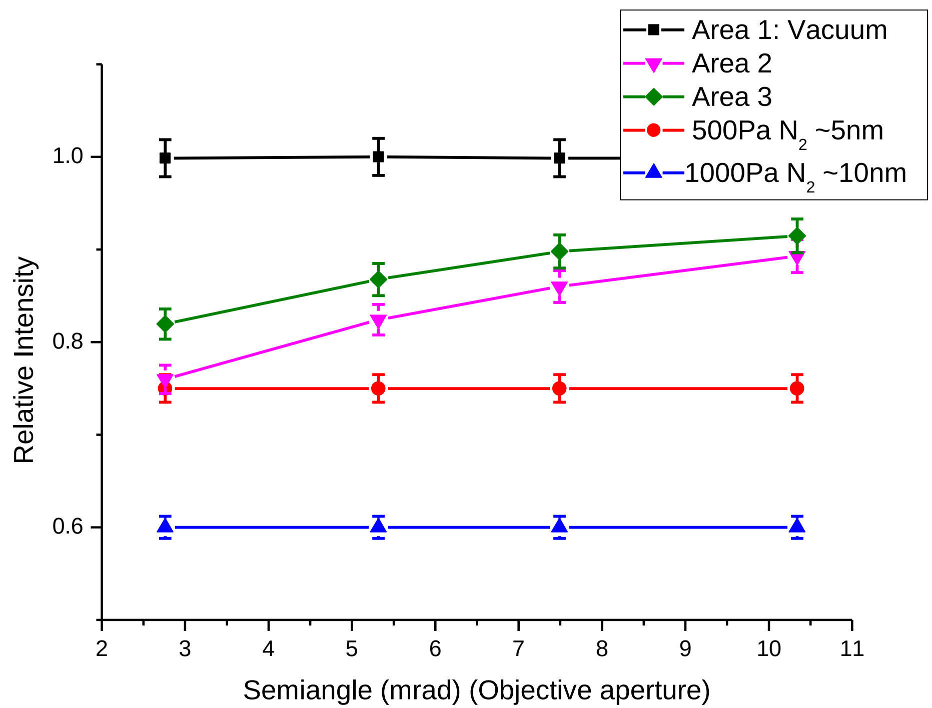




Contrast and Loss of intensity (Bright field imaging)

- Carbon Film
- Compared to N_2 gas
- 1000 Pa N_2 between pole pieces corresponds to approx. 10nm thick solid

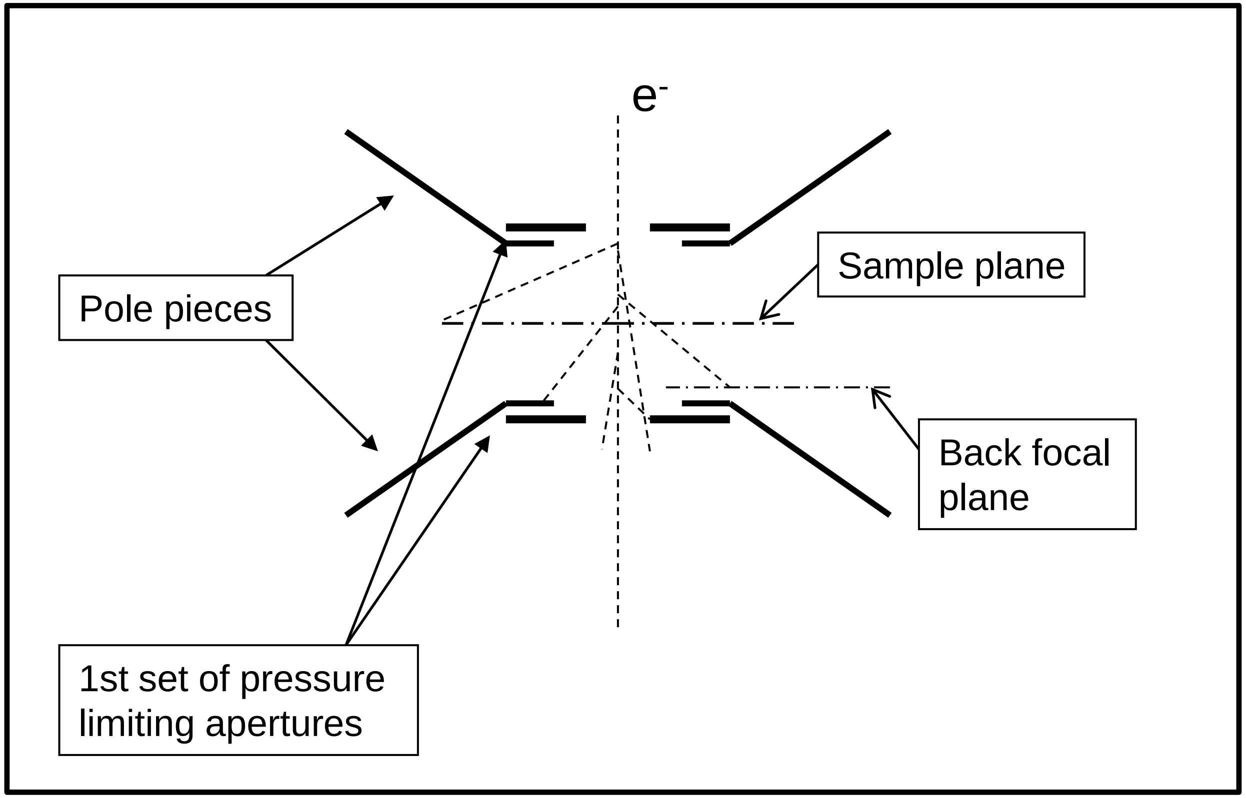




- Very little depence on the objective aperture for the gas related intensity loss
- The 'contrast' from the gas scattering appears higher than for corresponding area density of solid

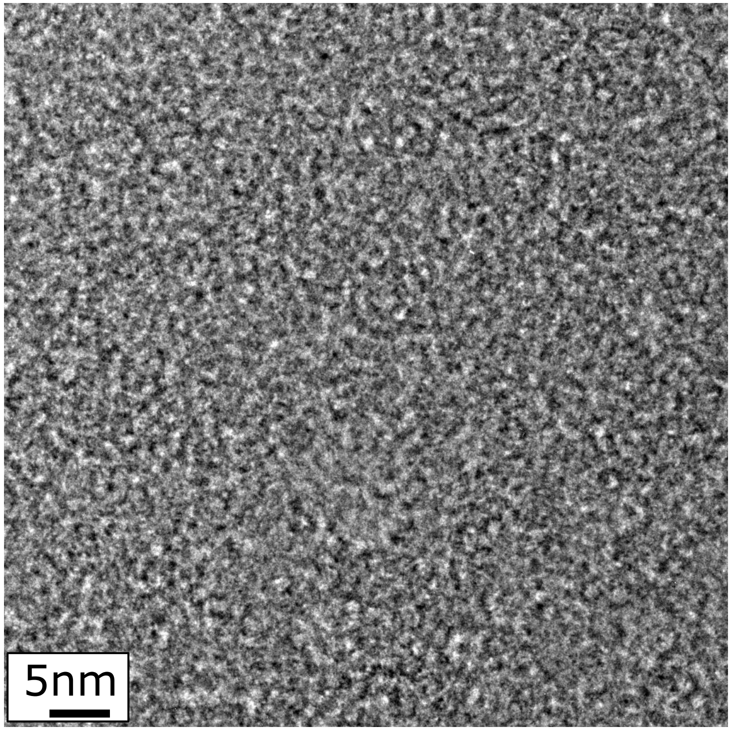
Geometry of scattering

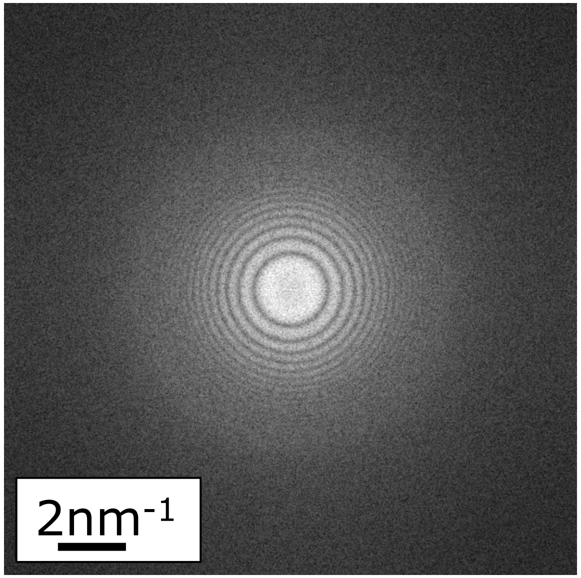
- Scattering takes place over several millimeters.
- Back focal plane and image plane not well-defined for gas scattering

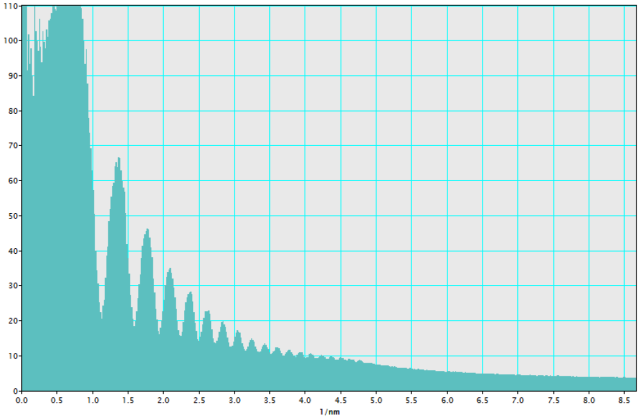


Resolution and contrast in the presence of gas (Phase contrast)

- Effects of imaging in gas can be observed from the power spectrum of amorphous carbon film

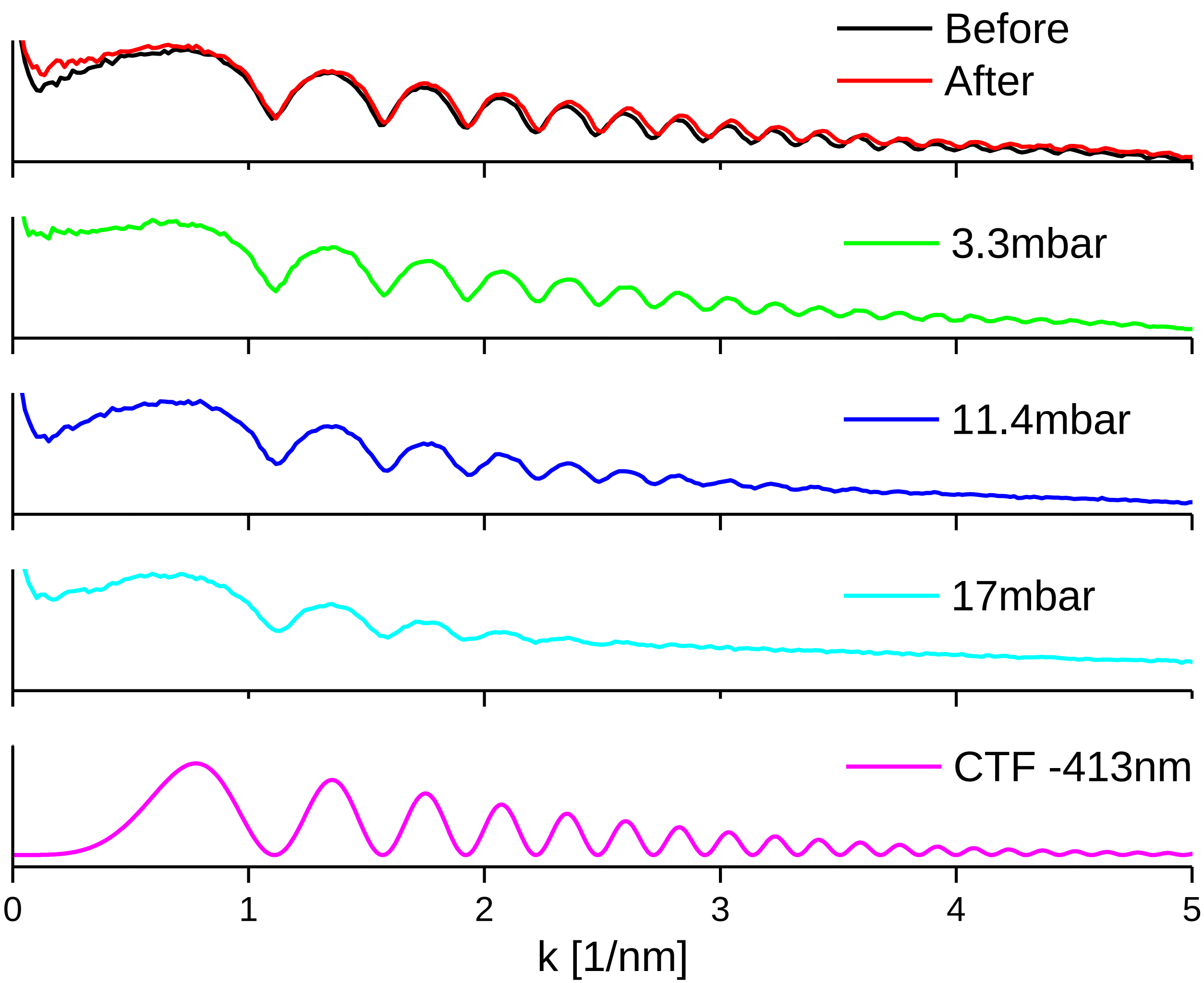






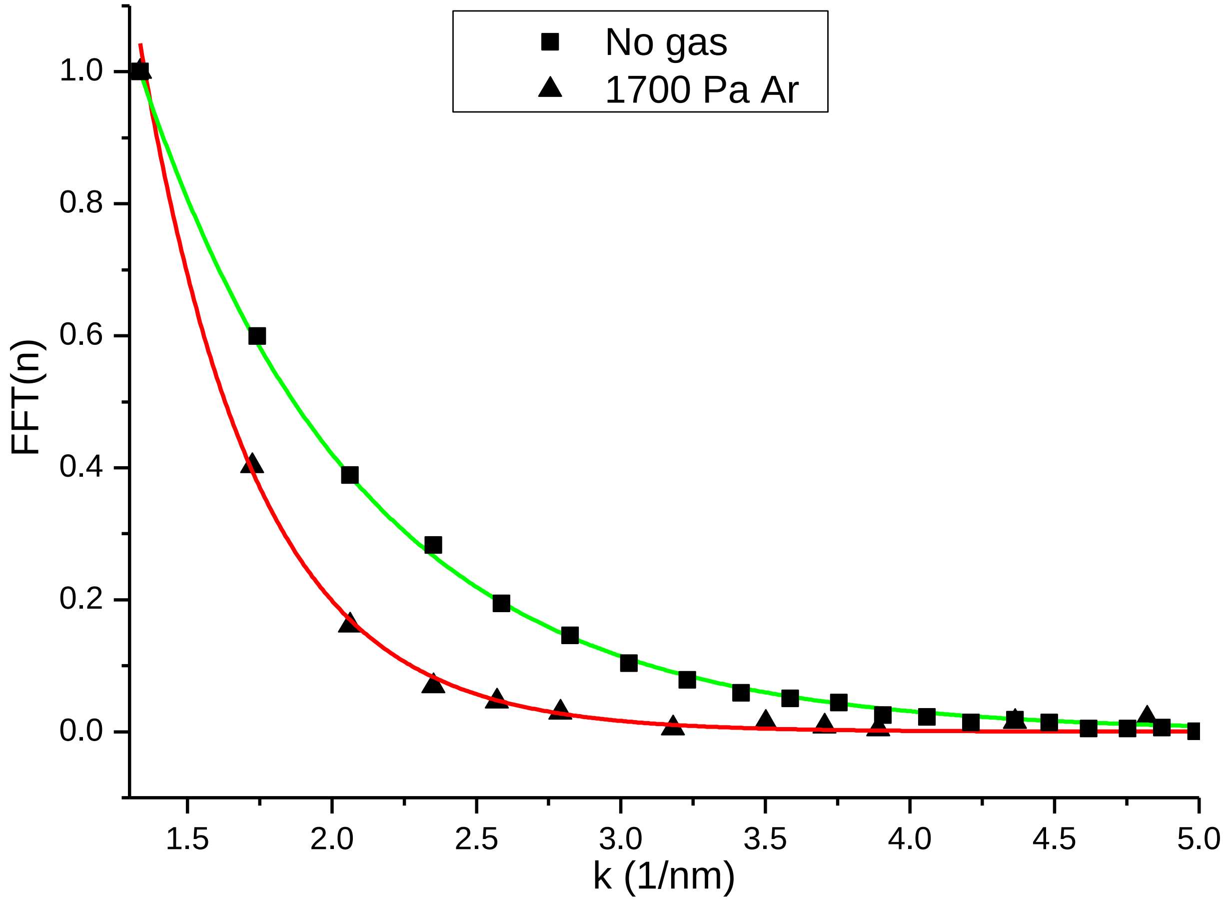
CTF in the Presence of Ar (300kV)

- In high vacuum (red), the power spectrum is almost identical to that calculated from ctfExplorer (purple)
- At low pressures, the effect is not observable (green)
- With increasing pressure, the damping becomes increasingly visible (blue and cyan)
- With lighter gas molecules, this effect is significantly lower
- An image was acquired in vacuum after the series (red) to ensure that the aC was not significantly damaged



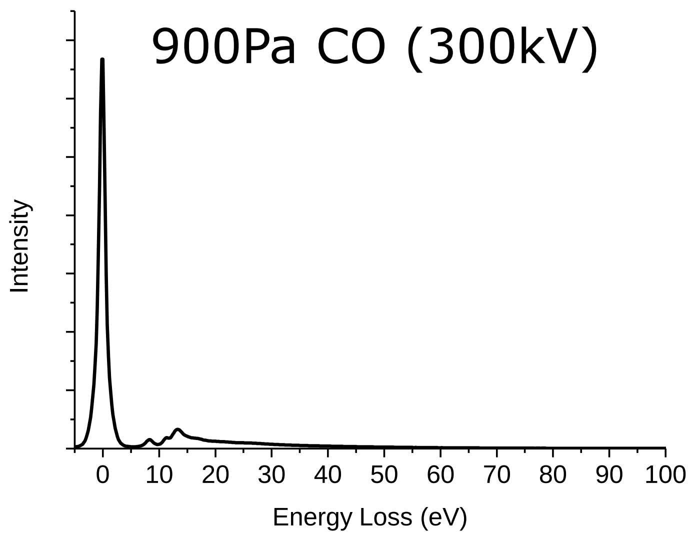
Fitting of Damping of FFTs in Ar (300kV)

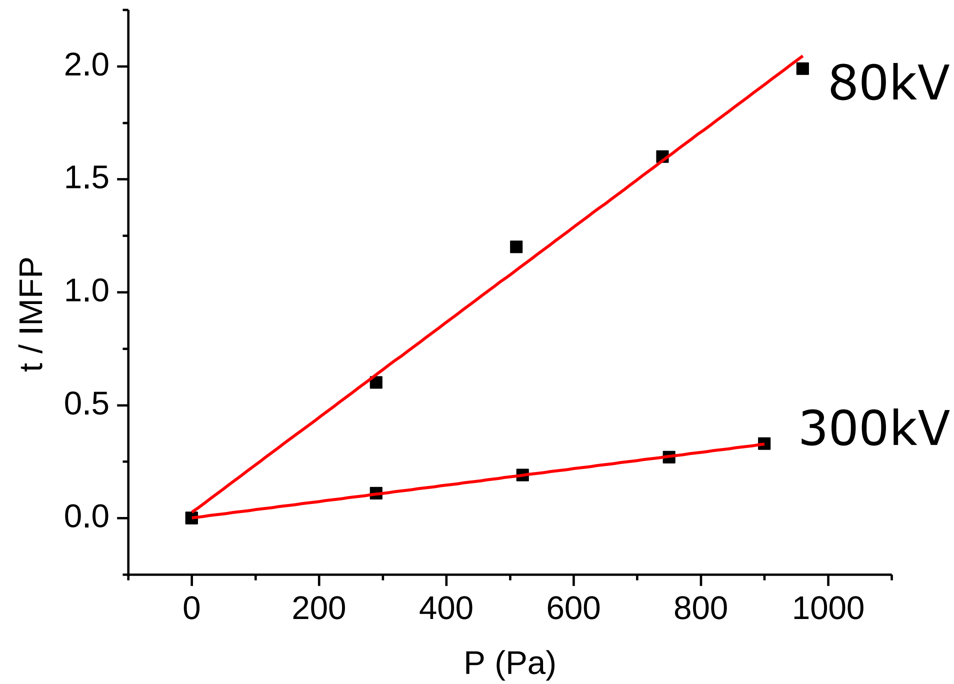
- The step height in the power spectrum is plotted as a function of k
- Each plot is fitted to an exponential decay
- At increased pressure, the step height decreases considerably faster



Gas composition and pressure by EELS

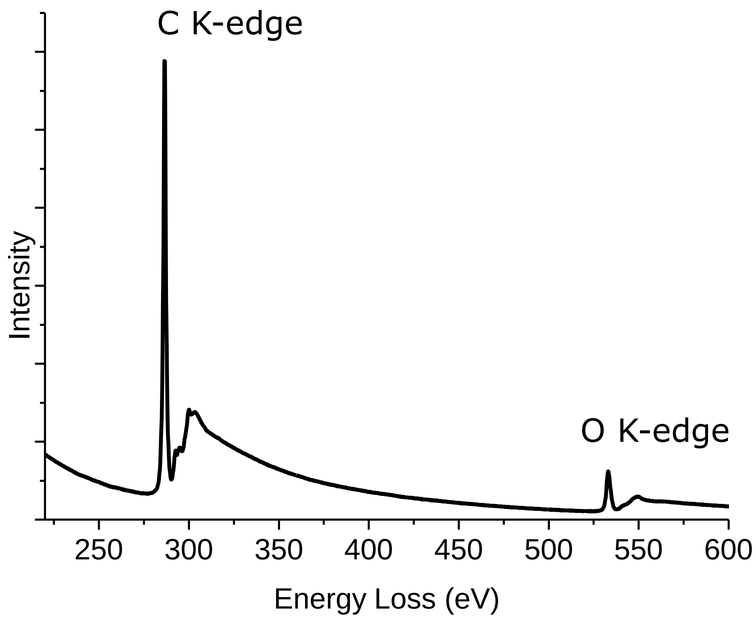
- Pressure (Low-loss EELS)
- Gas composition (Core-loss EELS)
- CO – EELS acquired in image mode
- IMFP is collection angle dependent

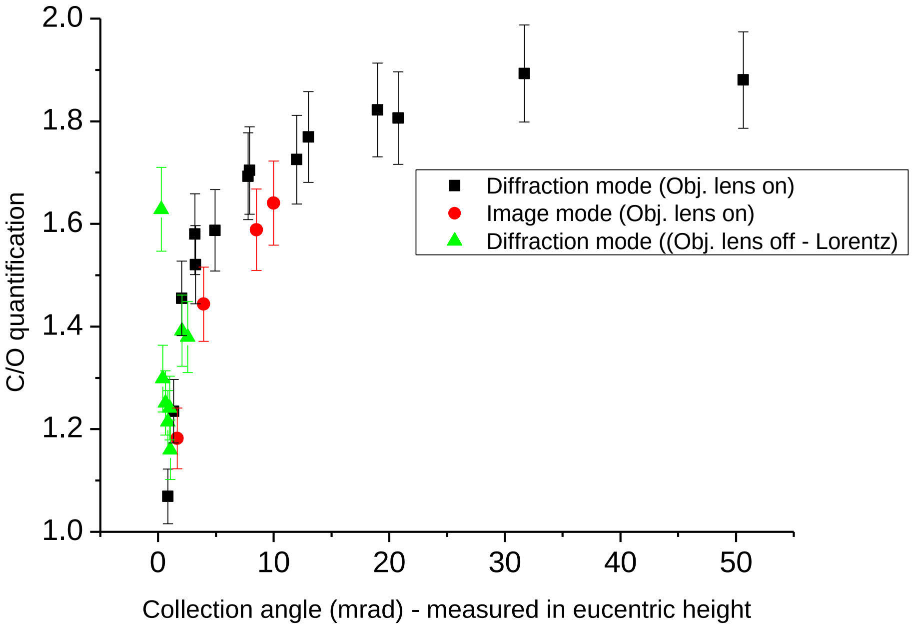




Gas composition and pressure by EELS

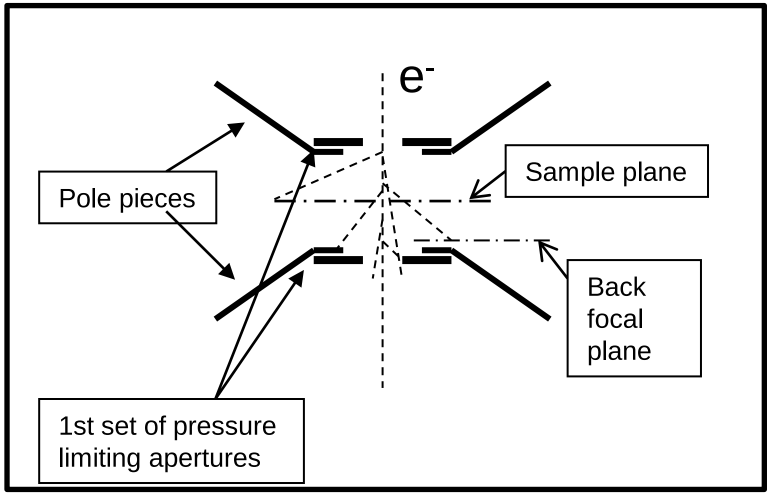
- CO – EELS acquired in image mode
- The collection angle is measured in the eucentric height





Apparent / mean collection angle (300kV)

- The measured collection angle makes little sense as the scattering occurs all over the pressurized volume



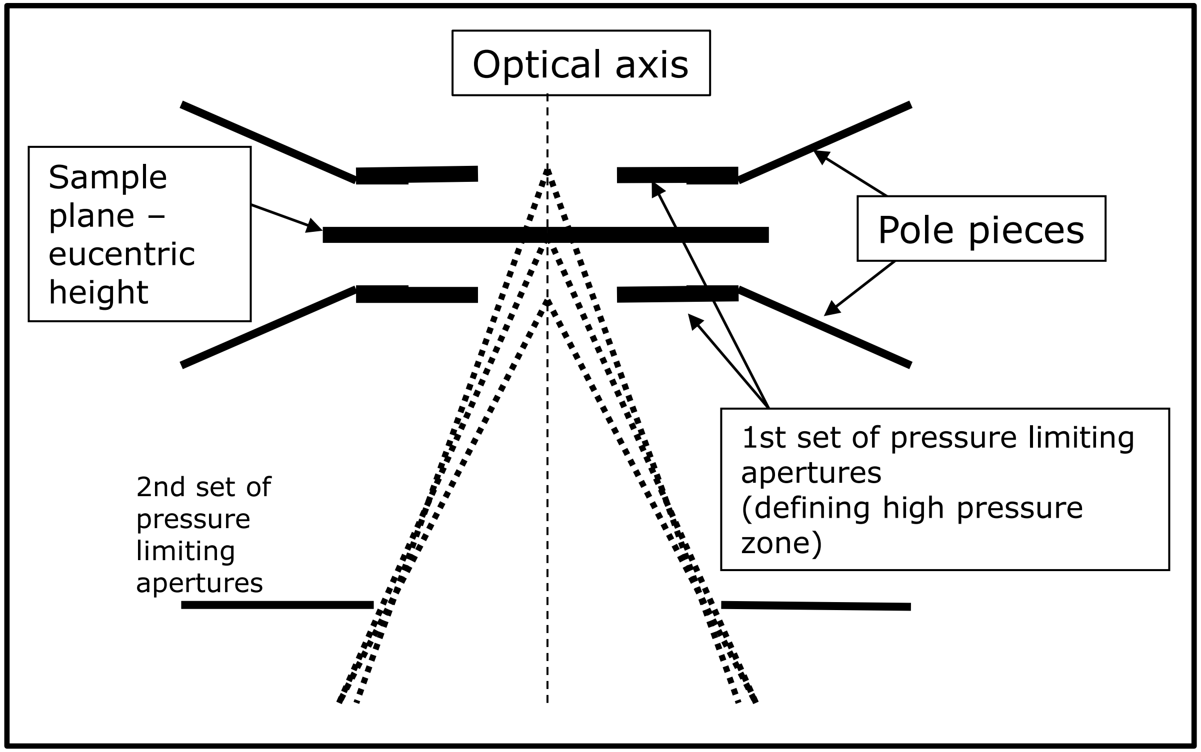
- The atomic ratio between carbon and oxygen calculated from the acquired spectra fits the theoretical value for small (~1 mrad) collection angles

- Consistent with the small 'scattered contribution' of gas to the image intensity – 'high contrast of gas'

Angle resolved EELS

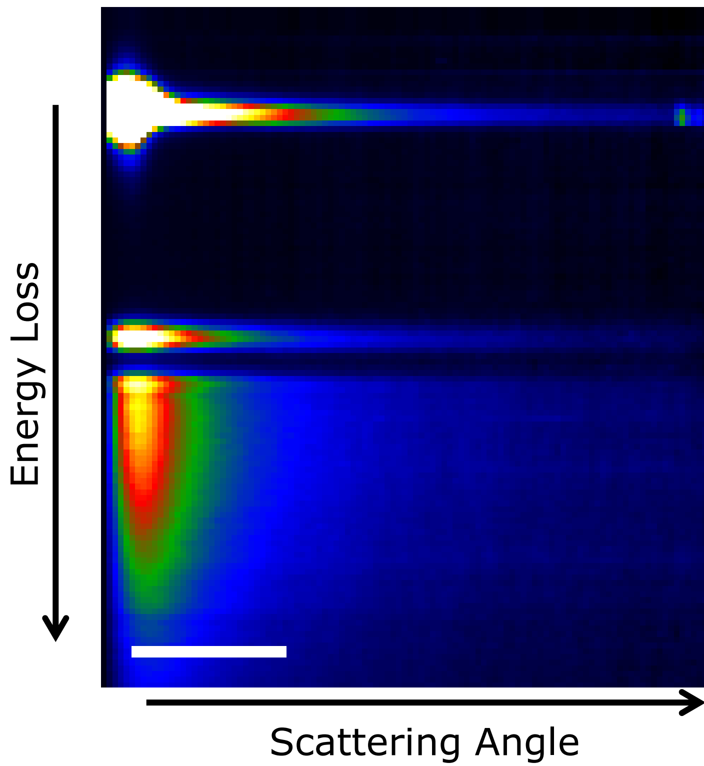
- Angle resolved EELS are acquired in Lorentz mode (objective lens off) to simplify scattering geometry

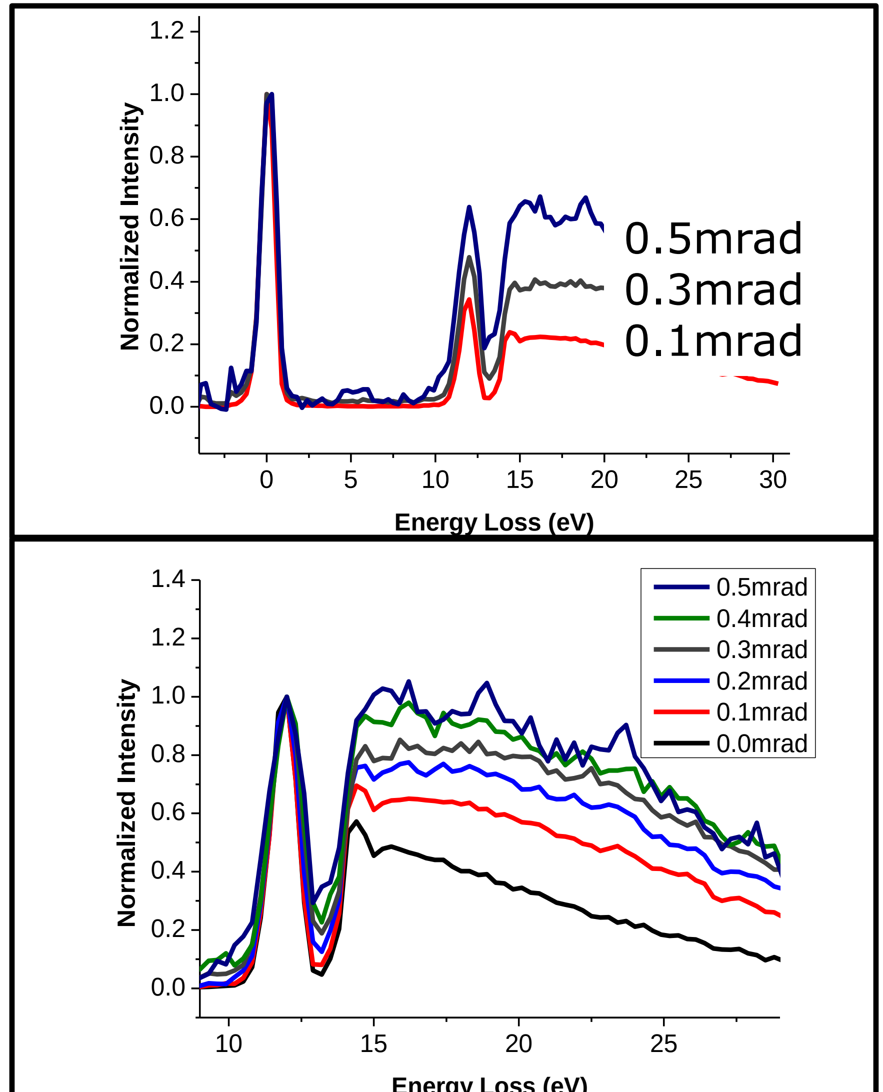
Broadening of scattering is usually less than 5%



Spectrum imaging (300kV) - Argon

- 1100Pa of Argon – no specimen
- Spectrum imaging with 0.3eV energy-selecting slit width
- Rotationally averaged





Beam Effects

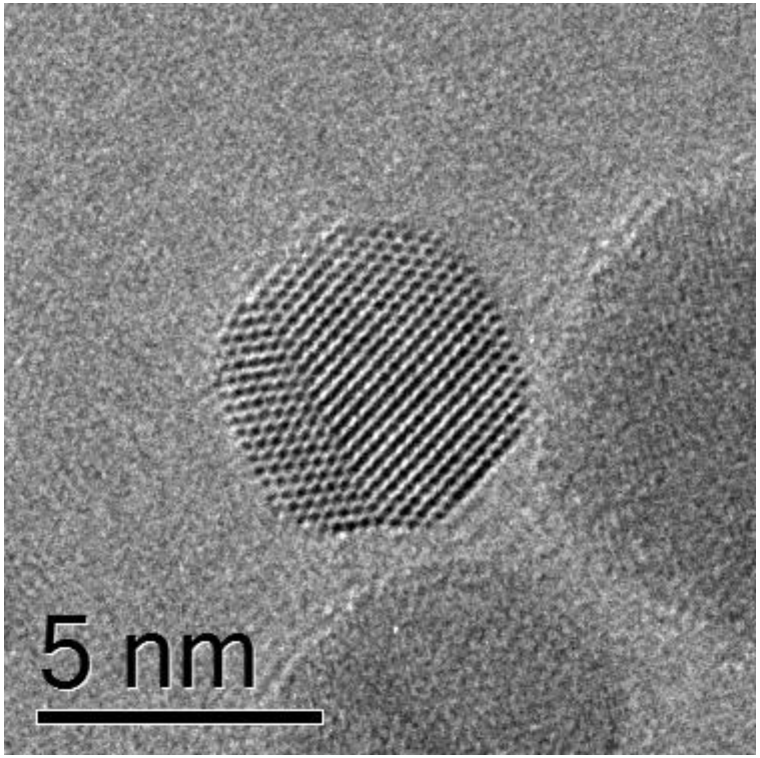
- Electrons can ionize gas molecules making them more reactive
- Surfaces can be etched by reactive gas atoms, ions and molecules
  - S. Helveg *et al. J. Am. Chem. Soc.* **132**, 7968 (2010)
- Local heating in the electron beam
  - V. G. Gryaznov *et al. Phil. Mag. Lett.* **63**, 275 (1991)
- Knock-on damage altering atomic structure
- Sample ionization
- Sample charging and de-charging
  - Removal of charge from sample as in ESEM

Is abberration correction needed / useful in Environmental TEM?

- Yes, as interface regions (including surface regions) are not disturbed by delocalisation

- Au on graphene, P_{H_2} = 430Pa, RT

- Dynamics at interface / surface



Outlook and Challenges (Wish list)

- More to be done to understand the gas-electron interaction in the imaging process
- Detector efficiency
- Sample heating holders
  - Drift-free environment
  - Investigations while ON the heating ramp
  - Interference with electron beam
- Sealing technology
- Complementary *in situ* techniques
  - Light (Visible, IR, UV)
  - XRD (Transfer system)
- Sample heating and local temperature
  - The local temperature is a multi-parameter problem involving multiple sources and sinks