Imaging and analysis with electrons
New developments in TEM

Facets of Electron Crystallography Talk

8th July

Emrah Yücelen

FEI Electron Optics

&

Kavli Institute for Nanoscience, Technical University of Delft
Titan Family in Nanoresearch

Titan ETEM

Titan G2 60-300

Titan^3 G2 60-300
Launch of the Titan G2 family
Technical highlights

• G2 family of Titan has been launched at M&M 2009
• Redesign includes improvements FEI learned during the TEAM project

Technical highlights

• Voltage range extended to 60kV
• Enhanced specifications in Cs-corrected STEM and TEM to 80pm level on Titan G2 60-300
to 70pm level on Titan³ G2 60-300 (see specification table in new product data sheet)
• X-FEG electron gun
• New DCOR Probe Cs-corrector and electronics improvements
• Cs-corrected field free imaging Lorentz microscopy
Flexibility: Titan G2, not only a Corrector platform
The full functionality in S/TEM application is available...

- 70pm in STEM and TEM at Titan³ G2
- SmartCam and enclosure to improve stability on Titan³ G2
- Full remote control operation with Collaboratory SW
- X-FEG with highest analytical probe currents
- Monochromator (<0.2eV)
- Best holography enabled by X-FEG
- New 3rd generation Probe Cs corrector DCOR
- Corrected Lorentz imaging
- De-scan unit
- Widest high tension range 60-300kV
- Ultimate spectroscopy performance (EDS/EELS)
- low kV applications (80 kV/60kV proven results)
- Wide S-Twin pole piece (space to do more)
- S/TEM dual axis tomography
- !!!Precession Capability (2011)!!!

Most proven stable platform
 (>100 Titans)
with large reference user base

Product data sheet available: www.fei.com
The optional X-FEG gun module on Titan G2

Essential specifications

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating voltage</td>
<td>80 to 300 kV</td>
</tr>
<tr>
<td>Energy resolution (300 kV) with mono</td>
<td>≤ 0.8 eV</td>
</tr>
<tr>
<td>chromator (300 kV)</td>
<td>≤ 0.2 eV</td>
</tr>
<tr>
<td>Brightness</td>
<td>≥ 7 x 10⁷ A/m² sr V</td>
</tr>
<tr>
<td>Current in STEM at 300 kV 0.2 nm</td>
<td>≥ 250 pA</td>
</tr>
<tr>
<td>(10 mrad)</td>
<td></td>
</tr>
<tr>
<td>Probe CS corrected current in STEM</td>
<td>≥ 2000 pA</td>
</tr>
<tr>
<td>at 300 kV 0.2 nm (30 mrad)</td>
<td></td>
</tr>
<tr>
<td>Total current</td>
<td>≤ 50 nA**</td>
</tr>
<tr>
<td>Emission stability (long and short)</td>
<td>≤ 1 %</td>
</tr>
<tr>
<td>Guaranteed emitter life time</td>
<td>≤ 1 year</td>
</tr>
</tbody>
</table>

*proven by the transfer of the 0.2 nm frequency in the Fourier transformed of an HAADF STEM image
**≤ 20 nA in combination with monochromator

- **Product introduced since M&M 2008; >8 installed**
- **Provides probe currents 250pA in a 0.2nm probe on a non Cs corrected Titans with a smaller probe convergence angles to minimize the excited volume in the sample**
  - 2000pA in a 0.2nm probe (Cs-corrected @ 300kV)
  - 1300pA in a 0.2nm probe (Cs-corrected @ 200kV)
- Life time unchanged compared to S-FEG (<1y)
- Long term emission stability is differentiator to C-FEG gun (see graph <1% a week)
- **The Brightness specified in reduced brightness due to high tension flexibility of Titan G2 60-300**

Product data sheet available: www.fei.com
Performance with X-FEG/Probe Cs-corrector Titan at 300kV
HAADF-STEM images on silicon with probe current/size measurement

Measurement of the achievable currents in dependence of probe diameter of the X-FEG
The probe current varies from <8nA in a 0.31nm probe to 0.6nA in <0.1nm probe.
New results on XFEG: outstanding holography performance

HR holography on gold grain boundary

High coherence of the source

Image of a parallel probe
\[ \delta \Phi \approx \frac{2\pi}{409} \]
(5x better than Tecnai ICs)

single hydrogen atom
\[ \Phi_H \approx \frac{2\pi}{245} \]

M. Linck, B. Freitag, M. Lehmann submitted to Ultramicroscopy 2010

Martin Linck, Michael Lehmann, Bert Freitag, Stephan Kujawa, Tore Niermann:
Applied wave optics on the atomic scale: Electron holography materials characterization in a Titan TEM,
DOI 10.3217/978-3-85125-062-6-007.
Monochromator:

Comparison Monochromator TEM with X-ray synchrotron on Ba$_2$SiTi$_2$O$_8$

- Energy resolution is as good as synchrotron
- but with nanometer spatial resolution

B. Freitag, FEI, Eindhoven, Dr Thomas Hoeche, Leibniz-Institute, Leipzig
Monochromator:
EELS on polycarbonate at Helium temperature

\[ \text{Project with Hofer et al. Felmi, Graz, Austria} \]
SYNERGY

• X-FEG + Mono + $C_s$-correction powerful combination

• Ultimate...
  spatial resolution
  energy spread
  high probe current
  stability

(NB: specs are for 300kV)

⇒ TEM info limit < 70 pm
⇒ STEM resolution < 70 pm
⇒ 2 nA in 0.2 nm probe energy resolution 0.8eV
⇒ 200pA in 0.2nm energy resolution < 0.2 eV
Mono/Image Cs
TEM information limit

- X-FEG + Mono + C_s-correction
  powerful combination
- Ultimate...
  spatial resolution
  energy spread
  high probe current
  stability

(NB: specs are for 300kV)
⇒ TEM info limit < 70 pm
⇒ STEM resolution < 70 pm
⇒ 2 nA in 0.2 nm probe
⇒ energy resolution < 0.2 eV

\[ \rho_1 = \left( \frac{\pi \lambda C_c}{2} \right)^{1/2} \left[ \left( \frac{\Delta V}{V} \right)^2 + \left( \frac{\Delta E}{V} \right)^2 + 4 \left( \frac{\Delta I}{I} \right)^2 \right]^{1/4} \]

Titan with image Cs-corrector and S-FEG (ΔE=0.7eV)

Titan with image Cs-corrector and mono X-FEG (ΔE<0.2eV)

CTF Explorer by http://www.maxsidorov.com/ctfexplorer/
Titan G2 performance exemplified in results: Best S/TEM resolution, analytics, and material science

Best HR-S/TEM performance in the market (70pm)

Detailed description of the results in new applications brochure on Titan G2
Detect every signal at the same time: New FEI triple On-axis BF/DF detector

Developed by FEI and successfully introduced on Titan

One BF and two different DF detectors (DF2, DF4)

- Can be used independently, i.e. BF and DF1/DF2 simultaneously
- Optimized for combined use with EELS (signal is either collected by GIF/FS-1 or falls on DF detector)

Accommodates higher currents (~3 nA) than Gatan 805/Fishione plus simultaneous BF and DF imaging
Experimental ABF/HAADF STEM and HR-TEM images
LaB$_6$ [100] specimen

Comparison between the different imaging techniques (HR-TEM/HR-STEM) on one material

Images: S. Lazar, B. Freitag, FEI, J. Etheridge, Monash University, Australia
The new DCOR (dodecapole corrector) third generation probe Cs-corrector

Benefits:
- Includes optical elements to correct higher order aberrations
- Allows for higher opening angles:
  - Deep Sub-Ångström performance with wide pole piece gap (<5mm)
  - Especially important for low voltage application (60&80kV)
- Higher probe currents in Ångström sized probes

New User interface

electronics cabinet

New electronics cabinet with lower noise level and capability to hold both corrector electronics in one cabinet
‘theoretical’ comparison

the impact of the higher order aberrations on probe shapes

hexapole vs. DCOR

probe $C_S$ corrector

Simulations by Joerg Jinschek
program: “Dr. Probe”
by Juri Barthel (er-c, FZ Jülich)
Ronchigram & probe shape simulations on DCOR and hexapole Cs-corrector with guaranteed aberration numbers using new simulation SW Dr. Probe

Higher order aberration are higher on the hexapole than DCOR and can be tuned by DCOR

<table>
<thead>
<tr>
<th>aberration</th>
<th>FEI Titan, S-Twin lens, DCOR 200/300k, 30 mrad</th>
</tr>
</thead>
<tbody>
<tr>
<td>B2</td>
<td>30 nm</td>
</tr>
<tr>
<td>A2</td>
<td>30 nm</td>
</tr>
<tr>
<td>C3</td>
<td>1 μm</td>
</tr>
<tr>
<td>A3</td>
<td>200 nm</td>
</tr>
<tr>
<td>S3</td>
<td>200 nm</td>
</tr>
<tr>
<td>A4</td>
<td>5 μm</td>
</tr>
<tr>
<td>B4</td>
<td>6 μm</td>
</tr>
<tr>
<td>D4</td>
<td>5 μm</td>
</tr>
<tr>
<td>C5</td>
<td>200 μm</td>
</tr>
<tr>
<td>A5</td>
<td>200 μm</td>
</tr>
</tbody>
</table>

Dr. Probe SW available via FEI for owner platform H2 2010

calculated using Dr. Probe by Juri Barthel (FZ Jülich)
sponsor: FEI Company
200kV

**B2=0 nm**
A2=0 nm
C3=±5 μm
S3=±3 μm
A3=±3 μm
A4=30 μm
B4=30 μm
D4=30 μm
C5=2000 μm
A5=800 μm

Typical specifications for hexapole correctors
$200kV$

**B2=0 nm**

A2=0 nm

C3=±1 μm

S3=±0.2 μm

A3=±0.2 μm

A4=5 μm

B4=5 μm

D4=5 μm

C5=200 μm

A5=200 μm

**DCOR probe corrector**

Confidence level values for DCOR correctors

Program: “Dr. Probe” by J. Barthel (er-c, FZ Jülich)
**200kV**

**B2=100 nm**

A2=0 nm
C3=±5 μm
S3=±3 μm
A3=±3 μm
A4=30 μm
B4=30 μm
D4=30 μm
C5=2000 μm
A5=800 μm

**Specification on B2 is 100nm**

You cannot see it in the static Ronchigram!

program: “Dr. Probe” by J. Barthel (er-c, FZ Jülich)
200kV
B2=30 nm
A2=0 nm
C3=±1 μm
S3=±0.2 μm
A3=±0.2 μm
A4=5 μm
B4=5 μm
D4=5 μm
C5=200 μm
A5=200 μm

DCOR level of confidence 30nm

program: “Dr. Probe” by J. Barthel (er-c, FZ Jülich)
AGENDA

• Flexibility
FLEXIBILITY 3 condensers + minilens

- 3-condenser zoom-system controlled by Smart Optics™
  - Beam parallelism and isoplanicity for a large range of TEM illumination
  - Full control over probe convergence in STEM, analysis, or CBED
  - NBD: parallel illumination can be restricted to 4nm diameter at 300kV

Example: NBD, CBED, SAED strain analysis
**FLEXIBILITY**

De-scan on every Titan standard

- De-scan; Why is it important?
  - EELS: no ZL-peak energy shift during SI acquisition
  - New imaging techniques going public at M&M/IMC2010
  - SCEM, confocal microscopy (atomic 3D)
FLEXIBILITY
HT range from 60 to 300kV

- Can balance effects of
  - Knock-on damage vs. radiolysis
  - Contrast vs. penetration
  - Cross-section vs. brightness
  - Energy spread vs. brightness & resolution

Bonding state analysis at 80kV

Atomic resolution at 60kV
Theoretical Consideration: Sample Penetration/interaction inelastic and inelastic scattering dependence on atomic number and high tension

Inelastic MFP dependence on HT

Mean-free-path dependence on high-tension for aluminum and carbon. The MFP increases by 20-30% from 200kV to 300kV.

Inelastic MFP dependence on z

Inelastic mean-free path calculated for amorphous materials with different average atomic number Z at 200 kV and 300kV.

The MFP increases by 20-30% from 200kV to 300kV.
HR-TEM on gold nanoparticles on carbon film
TITAN image corrected with 80, 200, 300kV

- Cs-corrected images on one instrument at the same area with different acceleration voltages
- At heavy elements 300kV shows the clearest image of the surface
- At 80kV the carbon contrast is maximized and a step in thickness in the center of the particle becomes visible
Practical benefit of 300kV on carbon support film samples:
Pt clusters and single atoms on thin carbon support film
Titan 80-300 with image Cs-corrector at 300kV

Single atoms and Sub Nanometer Pt-clusters can be image artifact free due to the high penetration power of the electrons at 300kV acceleration voltage. The carbon support film is almost as invisible and as transparent as the hole in the film (upper right corner)

Only possible with 300kV

Images: Dr. R. Schneider, Laboratory for Electron Microscopy Universität Karlsruhe (TH)
Sample: Dr. A. Byier, Universität Bielefeld, Holger Blank (LEM, Universität Karlsruhe)
The Need for High Tension Flexibility

Atomic resolution images of C-single wall nano-tubes with Cul filling @ 300kV shows beam damage after ~1-2min in the e-beam.
Seeing Linked Structures: Titan at 80kV

Atomic resolution at 80kV with ultra stable conditions and high contrast for SWCNT. The delicate relationship between the tubes and the surface carbon can be studied with atomic resolution.
Atomic 3D on graphene double and single layers using new Trueimage Atlas SW at 80kV

- Carbon dumbbell can be resolved at 80kV
- Atomic positions of 2 carbon atoms and single carbon atom can be distinguished
- Atomic 3D information can be obtained
- Different heights of single atoms can be measured (3Å)

Beam damage: not everything is knock-on damage

- Grain boundary flip in gold 110 in HR-STEM imaging.
- Surface migration of gold atoms; melting of Cul crystal in SWCNT
- Mechanisms unclear...
- Knock-on damage energy is different in bulk than on grain boundary or surface
AGENDA

EELS

Chemical information on the atomic level
Atomic HR-STEM/EELS on BaTiO₃/SrTiO₃ interface

Atomically sharp interface shows minimum delocalization by atomic resolved EELS

EELS map 80kV, 46x46pix, 30ms/pix

Gianluigi A. Botton, Sorin Lazar, Christian Dwyer, Elemental mapping at the atomic scale using low accelerating voltages, Ultramicroscopy, Volume 110, Issue 8, PROCEEDINGS OF THE INTERNATIONAL WORKSHOP ON ENHANCED DATA GENERATED BY ELECTRONS, July 2010, Pages 926-934, ISSN 0304-3991,
Where does the delocalization come from?
Opening angle & sample thickness, 3D probe geometry

Average FWHM of 77 pm (in vacuum)
Filtered STEM, energy resolution of 0.15 eV

Direct measurement of the smallest probe diameter in 2D shows Sub Ångström size, but the electron probe has limited focal depth due to the opening angle, which leads to cross talk in atomic spectroscopy. Therefore the excited volume increases with opening angle and sample thickness.
Where does the cross talk come from? Bloch wave delocalization (Channeling/de-channeling) in SrTiO$_3$

**Line-scan of the image the probe across SrTiO$_3$**

Imaging the electron probe on the specimen with an image Cs-corrector shows wide distribution of electrons in the real space. The next neighboring atoms are illuminated by the electrons (channeling/de-channeling).

**Thickness ~0.38MFP**

B. Freitag, C. Mitterbauer, FEI

300kV

$\alpha = 10 \text{mrad}$
Where does the cross talk come from and how can we influence it? Spectroscopy performance: EELS map on SrTiO₃ at 80kV

**Atomic STEM/EELS map at 80kV is possible** (resolution ~0.4nm)

Lower voltage improves sensitively (cross sections), higher voltage minimizes excited volume (convergence angle)

But the ratio between elastic and inelastic scattering factor is varying greatly with atomic number

Which signal is chemical, which is elastic? Simulations & more experiments…required

Gianluigi A. Botton, Sorin Lazar, Christian Dwyer, Elemental mapping at the atomic scale using low accelerating voltages, Ultramicroscopy, Volume 110, Issue 8, PROCEEDINGS OF THE INTERNATIONAL WORKSHOP ON ENHANCED DATA GENERATED BY ELECTRONS, July 2010, Pages 926-934, ISSN 0304-3991,
Silicon Drift Detectors (SDD) replace the lithium drifted silicon (Si(Li)) detectors

FEI designed a new detector within a new pole piece for ultimate performance in EDS analysis in a S/TEM (patent pending).

Benefits of new FEI design:
- Collection angle: 0.9 srad
- Throughput rate >240 kcps
- Pixel dwell time for mapping down to 10 μs/pixel
- Windowless design (with shutters)
- Energy resolution

3-7 times more than existing
~5 times more
>1000x faster
Higher sensitivity for light elements (N,O,B, etc.)
<136 eV at Mn-Kα and 10,000 cps
Super-X™ Detector: SDD Basics

Detector design

- concept patented by Kemmer & Lutz in 1989

SDD max. output count rate is much higher than for standard Si(Li)

SDD advantage:
- low capacitance = high throughput
  = low dead time at high count rates

An integrated multiple silicon drift detector system for transmission electron microscopes
Super-X™ Detector on Osiris

- 4 Silicon Drift Detectors (SDD) symmetrically around sample: 120 mm² detector area
- 0.9 srad collection angle with symmetric design allowing for tilt flexibility in EDS
- Enhanced sensitivity for light elements
- 200,000 cps (output) were measured
- Dwell times per pixel down to 10 µs, i.e. 100,000 spectra/sec

**Relative count rate at 200kV, NiOx film, constant probe current**

- **SuperX**
- **Si(Li) 0.3 sr**

**Graph details:**
- X-axis: Alpha tilt angle
- Y-axis: Normalised count rate
- Legend:
  - SuperX
  - Si(Li) 0.3 sr

Super-X Performance on Tecnai Osiris

The benefit of collection angle improvement and higher throughput of SSD technology

In both experiments the same FIB-cut InP sample was used with a thickness of about 200 nm.

Higher sensitivity of the design allow for more X-ray counts per electron (nA) than any other EDS detector on a S/TEM
Super-X™: SDD Technology and Fast Mapping

• Enhanced sensitivity for light elements
• 300,000 cps (output) were measured
• Dwell times per pixel down to 10 µs, i.e. 100,000 spectra/sec
• Mapping time reduced from 2 hr to 2 minutes
• Speed can also be traded in for larger maps (more pixels): larger field-of-view
Super-X™ Detector: Light Element Detection

Windowless detector has more transmissivity for low-energy X-rays, e.g. ~3x more signal for O-K than with Moxtek window

NiO_x film on carbon, 200 kV

Microscopy Today (2010), 18:14-20 Cambridge University Press
Fast Mapping with Super-X™: FinFET Comparison of Tecnai Osiris with TF20 XT

**Tecnai TF20XT**
- 100 x 100 pixel
- 500 msec dwell time
- ~0.7 nm spot, 0.4 nA
- 1 h 54 min total time ~ 2 hrs
- Full quantification

Images and maps by A. Carlsson, FEI

**Tecnai Osiris (X-FEG, Super-X)**
- 100 x 100 pixel
- 5 msec dwell time
- ~0.3 nm spot, 1 nA
- 115 sec total time ~ 2 min
- Fully quantified (binning 2)

Sample courtesy of NXP Research
Images and maps by D. Klenov, FEI

Super_X: Minimum mass fraction (MMF) limits

New record on certified NIST steel No 461

Fig. 2 Top: Super-X spectrum of NIST steel standard NBS No.461 (log scale). Bottom: zoomed spectra showing minor elements of vanadium (0.024wt.%), arsenic (0.028wt.%) and tin (0.022wt.%). Ga and Pt peaks are due to FIB preparation.

Beat the best AEM results of Watanabe&Williams UM 78 (1999) in MMF on Cu 0.12wt%Mn
**MMF performance versus spatial resolution**

Example chemical detection of As dopant profile in silicon

$$MMF \propto \frac{1}{\sqrt{P(P/B)\tau}}$$

Semi conducting device

**Osiris**

Estimate:

- 1 atom in a volume exited
- With a 1nm probe size
- of a 100nm thick sample
  will become detectable!!!

As dopant $\sim 10^{-19}$ $\sim 0.03$ wt%

Lateral resolution $\sim 5$ nm

600x600 pix, 50 $\mu$sec dwell time, multiple frames,
78 min total time, 2.2 nA, drift corr
Atomic EDS: How does it compare to EELS?
SiLi conventional detector results

Atomic-resolution chemical mapping using energy-dispersive x-ray spectroscopy

A. J. D’Alfonso,1 B. Freitag,2 D. Klenov,2 and L. J. Allen1
1School of Physics, University of Melbourne, Parkville, Victoria 3010, Australia
2FEI Company, Building AAE, Achterweg Noord 5, Eindhoven, The Netherlands
(Received 16 July 2009; revised manuscript received 19 September 2009; published 8 March 2010)

We demonstrate atomic-resolution chemical mapping using energy-dispersive x-ray spectroscopy in scanning transmission electron microscopy. Theoretical simulations of the imaging process demonstrate that these images are directly interpretable. This is due to the fact that the effective ionization interaction is local and this is an incoherent mode of imaging.
Super-X on Titan G2 60-300

- 4 Silicon Drift Detectors (SDD) symmetrically around sample : 120 mm² detector area
- 0.7 srad collection angle with symmetric design allowing for tilt flexibility in EDS
- Enhanced sensitivity for light elements
- 200,000 cps (output) were measured
- Dwell times per pixel down to 10 µs, i.e. 100,000 spectra/sec
- Patent pending

- Super-X on Titan has high sensitivity like Osiris, but additionally
- high spatial resolution for atomic EDS (due to Cs-correction)
- atomic resolution at low voltage (less knock-on damage)
- Tecnai speed -> Osiris from hours to minutes
  Titan speed -> Probe Cs-corrected/XFEG from minutes to seconds
Electron Diffraction on TITAN

TITAN 3-condenser lens system provides wide range of possibilities for diffraction experiments:

- Nano size parallel beam.
- Variable beam convergence for fixed aperture size

Nano size coherent parallel electron beam formation:

- Nanoprobe mode or Microprobe Mode

- Choice of small C2 apertures 20um to 5um.

- High Spot numbers and Strong Gun lens settings
what is new: Precession Electron Diffraction

Available with TITAN SW 1.2 (release mid 2011)

Controlled from TITAN user interface
In TITAN SW Dynamical Conical Dark Field Alignments:

- Adjust Pivot Points and corrects distortions in Diffraction mode

TITAN SW 1.2 (will be released end of 2010) Activation of De-scan:

- Beam movement is made stationary Diffraction Mode

E Yücelen Ph.D. Thesis (FEI)
Experimental methods to acquire data for electron crystallography

\((\text{Ba,Na})_3\text{Nb}_5\text{O}_{15}\) Crystal seen along c direction

- \(a=1.759\text{nm}\)
- \(b=1.762\text{nm}\)
- \(c=0.3995\text{nm}\)
- Space group \(\text{Cmm2}\)
(Ba,Na)$_3$Nb$_5$O$_{15}$ Kinematical Diffraction pattern seen along [001] direction
Recording Images on FLUCAM
Beam Profile

Microprobe mode

Beam size at FWHM is 4.5nm

E Yücelen Ph.D. Thesis (FEI)
Nano Beam Diffraction with 4.5nm focused electron beam

Nano Beam Diffraction with 35nm parallel electron beam
Nano Beam Diffraction with 4.5nm focused electron beam

Help by activating Dark Field Mode and accessing beam tilt to achieve near Zone axis

Convergence semi angle lower than 1mrad
Nano Beam Diffraction Pattern

Precession Diffraction Pattern

Precession Angle is 50 mrad

E Yücelen Ph.D. Thesis (FEI)
EFTEM Thickness Maps
Thickness Maps: Profiles

Thickness change drastically within 20 nm!
Structure Imaging Using HRTEM

Where are atoms?
Phase of the exit wave

Exit wave Reconstruction
After processing 20 HRTEM 2k x 2k images

Nb, O, Ba columns and Na/Ba columns can be identified

In Phase image of Electron Exit wave

E. Yücelen Ph.D. Thesis (FEI)
Amplitude of the exit wave
Acknowledgements

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- Prof. Henny Zandbergen (TU Delft)