Diffraction Pattern Indexing, Strain Mapping, 3D and Diffraction Tomography

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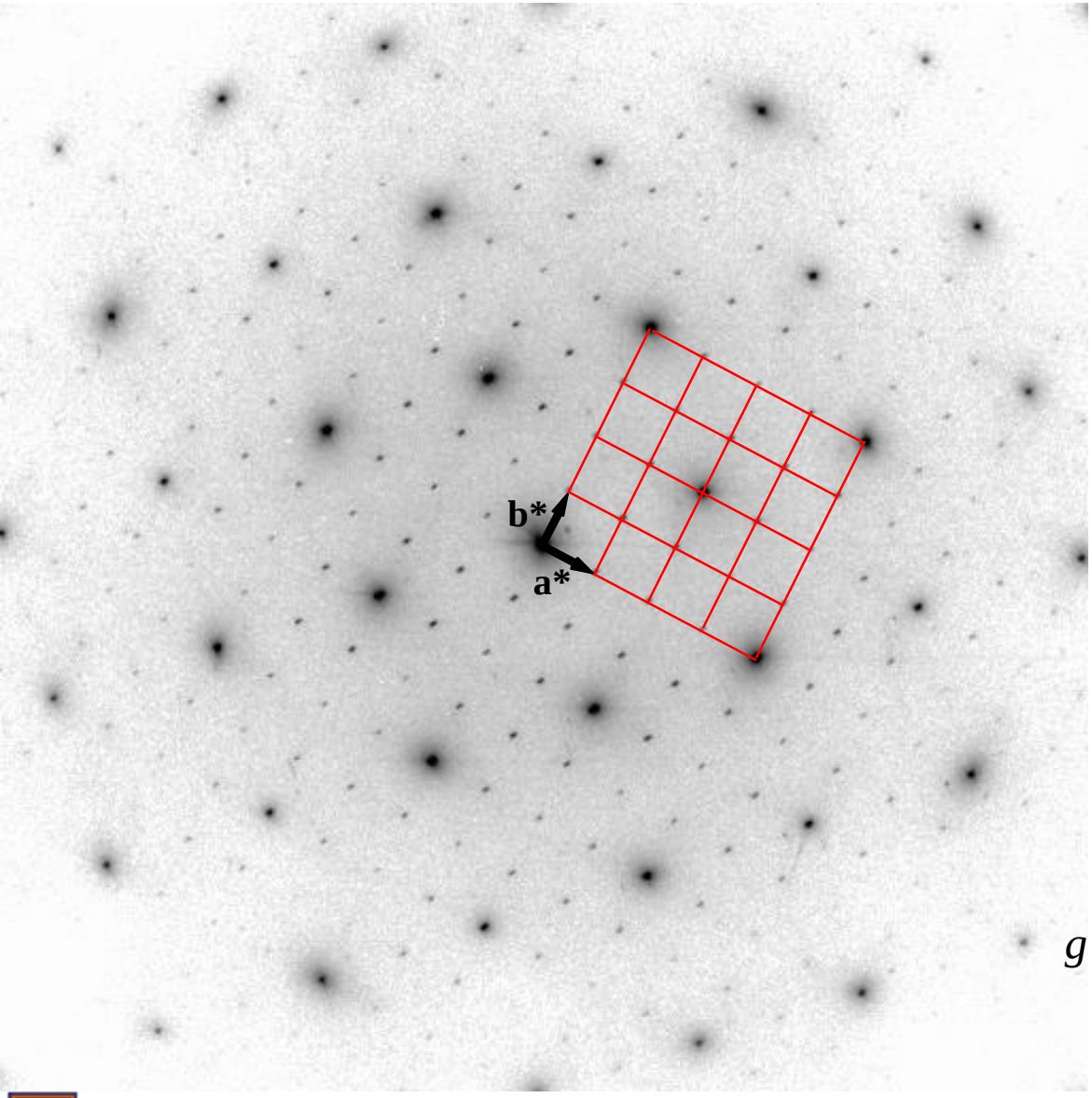
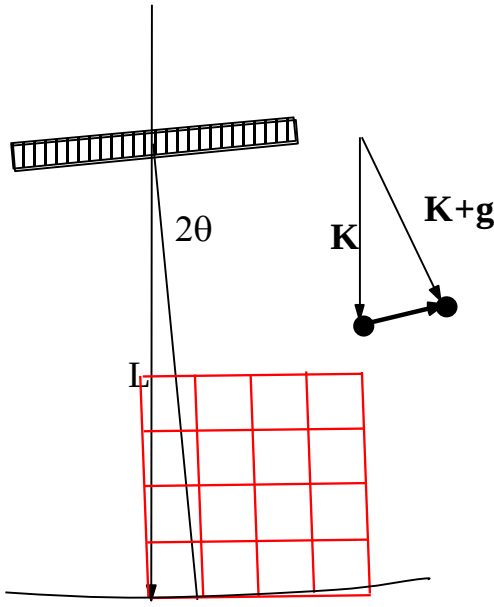
Covered Topics

- **Indexing electron diffraction patterns**
- **Analysis of SEND patterns**
- **HOLZ Lines**
- **Strain**
- **Electron diffraction tomography**
- **Nanostructure characterization**

Crystal Diffraction Pattern and The Reciprocal Lattice



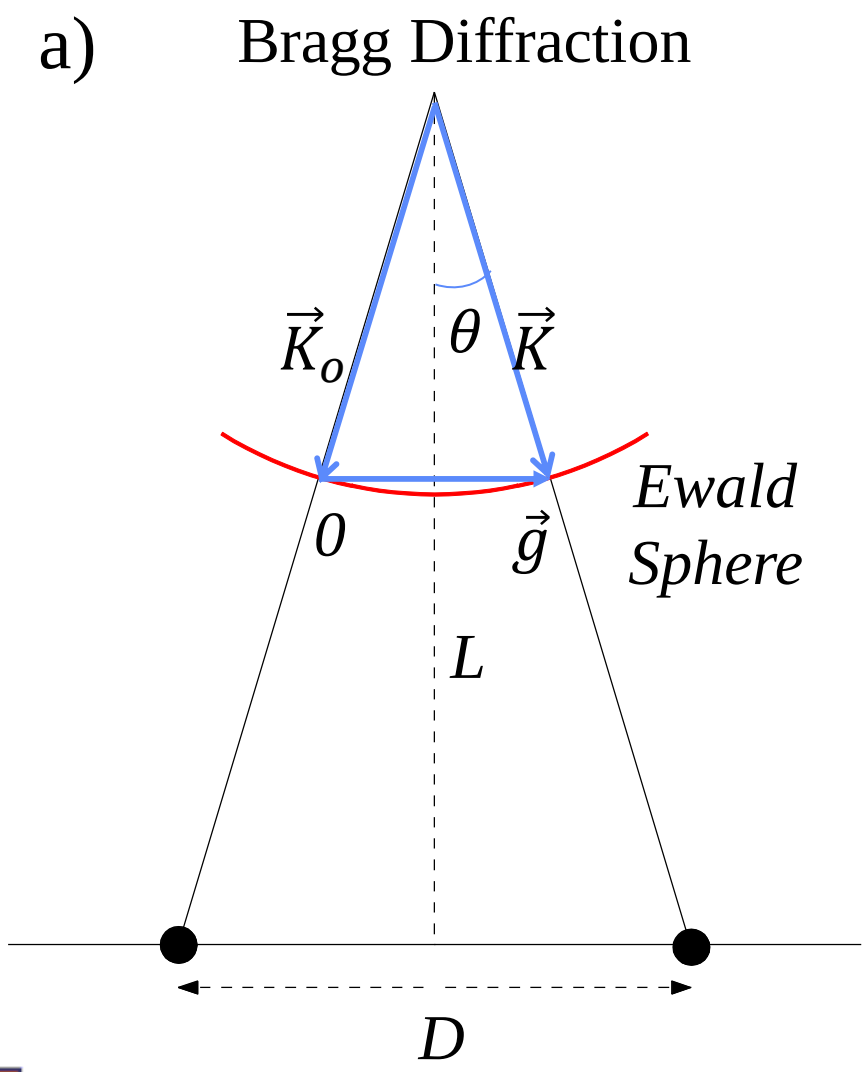


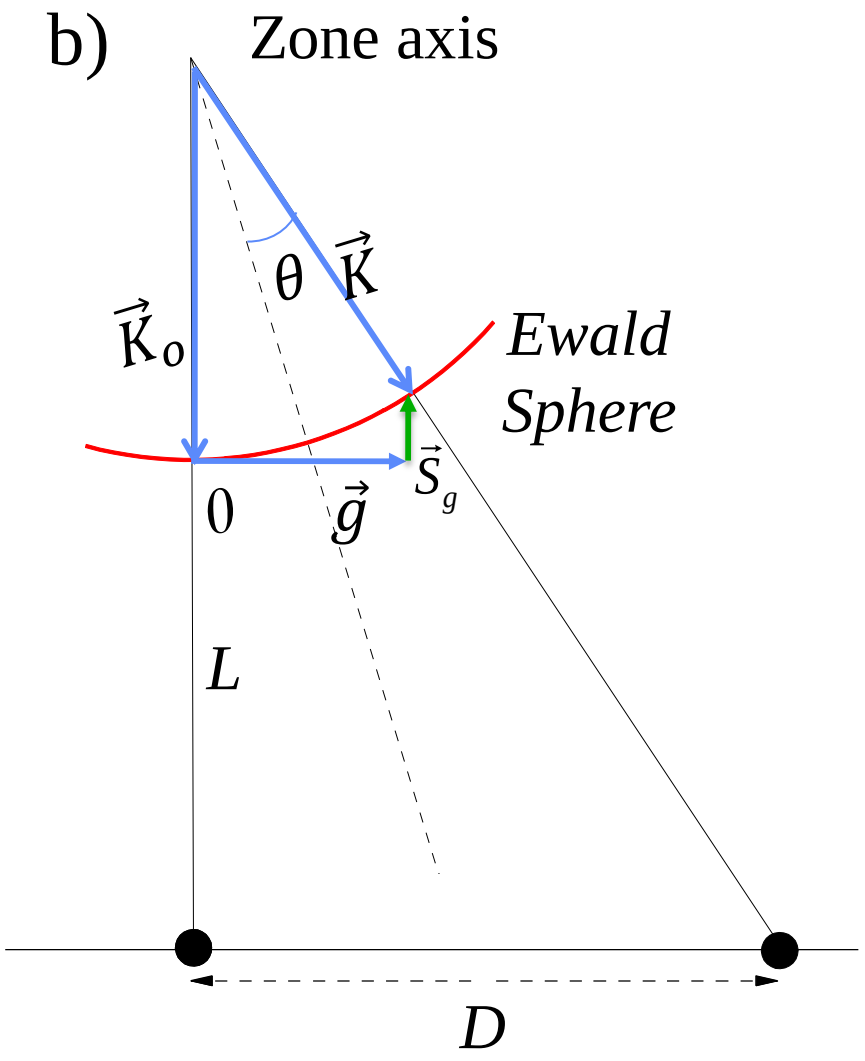
Bragg's Law

$$Sin\theta_B = \frac{g\lambda}{2}$$

$g \sim 1/\mathring{A}, \quad \lambda \sim 0.025\,\mathring{A}, \quad \theta \sim 12.5 mrad$

Diffraction Geometry





Indexing Diffraction Patterns

The basic equations:

$$\frac{D}{L} = \tan 2\theta \qquad 2d\sin\theta = \lambda \qquad d \approx \frac{L\lambda}{D}\left(1+\frac{1}{8}\left(\frac{D}{L}\right)^2\right)$$

For $D/L \ll 1$ $\quad g = 1/d = \boxed{D/L\lambda}$

For cubic crystals:

$$g = \sqrt{h^2+k^2+l^2}/a \qquad h,k,l \text{ integers}$$

$$uh+vk+lw = n$$

n = 0 for zero order *Laue* zone

$$\cos\phi = \frac{h_1h_2+k_1k_2+l_1l_2}{\sqrt{h_1^2+k_1^2+l_1^2}\sqrt{h_2^2+k_2^2+l_2^2}}$$

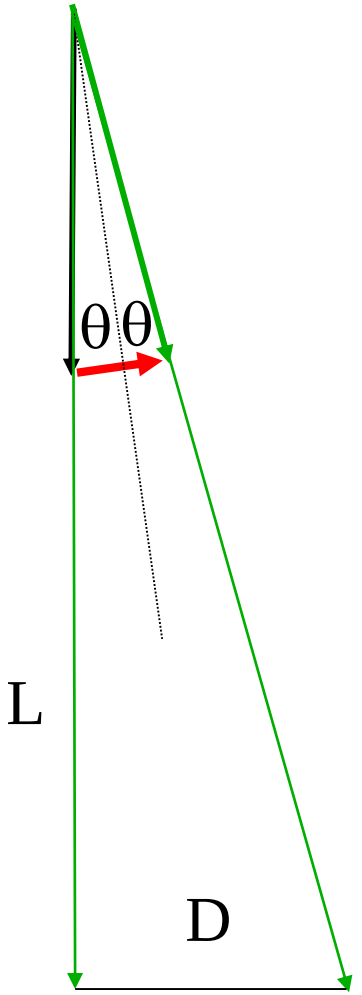


TABLE 2.4. Expressions for $d^*(hkl)$ and $d(hkl)$ in the Seven Crystal Systems[a]

System	$d^{*2}(hkl)$	$d^2(hkl)$
Triclinic	$h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2klb^*c^* \cos\alpha^* + 2lhc^*a^* \cos\beta^* + 2hka^*b^* \cos\gamma^*$	$K^2/d^{*2}(hkl)$
Monoclinic	$h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2hla^*c^* \cos\beta^*$	$\left\{\frac{1}{\sin^2\beta}\left[\frac{h^2}{a^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right] + \frac{k^2}{b^2}\right\}^{-1}$
Orthorhombic	$h^2a^{*2} + k^2b^{*2} + l^2c^{*2}$	$\left\{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}\right\}^{-1}$
Tetragonal	$(h^2 + k^2)a^{*2} + l^2c^{*2}$	$\left\{\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}\right\}^{-1}$
Hexagonal and trigonal (P)[b]	$(h^2 + k^2 + hk)a^{*2} + l^2c^{*2}$	$\left\{\frac{4(h^2 + k^2 + hk)}{3a^2} + \frac{l^2}{c^2}\right\}^{-1}$
Trigonal (R) (rhombohedral)	$[h^2 + k^2 + l^2 + 2(hk + kl + hl)(\cos\alpha^*)]a^{*2}$	$a^2(TR)^{-1}$, where $T = h^2 + k^2 + l^2 + 2(hk + kl + hl)[(\cos^2\alpha - \cos\alpha)/\sin^2\alpha]$ and $R = (\sin^2\alpha)/(1 - 3\cos^2\alpha + 2\cos^3\alpha)$
Cubic	$(h^2 + k^2 + l^2)a^{*2}$	$\left\{\frac{h^2 + k^2 + l^2}{a^2}\right\}^{-1} = \frac{a^2}{h^2 + k^2 + l^2}$

[a] In the monoclinic system, $d(100) = a \sin\beta$, $d(001) = c \sin\beta$, and hence $a = K/(a^* \sin\beta^*)$ and $c = K/(c^* \sin\beta^*)$.
[b] In the hexagonal system (and trigonal P), $a = b = K/(a^* \sin\gamma^*) = K/(a^*\sqrt{3}/2)$, since $\gamma^* = 60°$.
(In general, the expressions for d^{*2} are simpler in form than the corresponding expressions for d^2.)

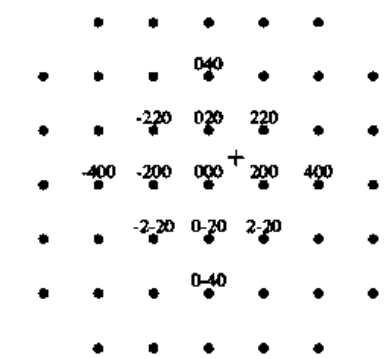
Find the Crystal Orientation
-The zone axis

- Find two shortest reflections, measure and index to obtain (h_1,k_1,l_1) and (h_2,k_2,l_2)

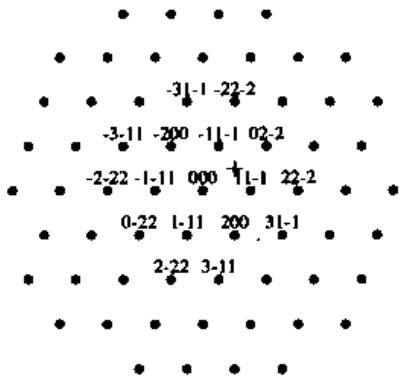
-Check the angle between these two and make sure hkl indexing is consistent with the lattice

-Calculate the zone axis using

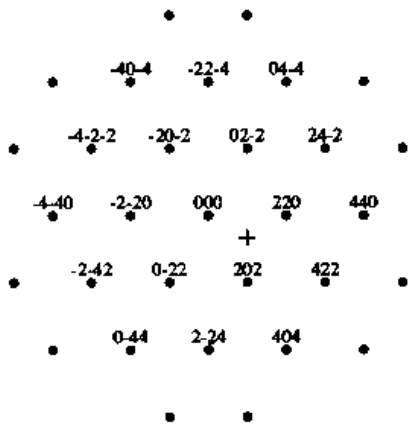
$$\vec{Z} = \vec{g}_1 \times \vec{g}_2 = \begin{vmatrix} \vec{a} & \vec{b} & \vec{c} \\ h_1 & k_1 & l_1 \\ h_2 & k_2 & l_2 \end{vmatrix} = \begin{matrix} \text{U} & \text{V} & \text{W} \\ [k_1 l_2 - l_1 k_2, & l_1 h_2 - h_1 l_2, & h_1 k_2 - k_1 h_2] \end{matrix}$$



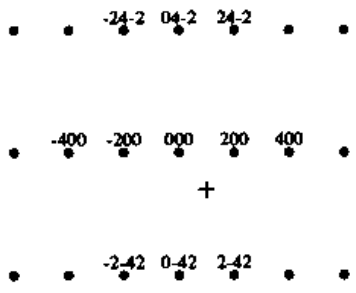
[001], + = (111)



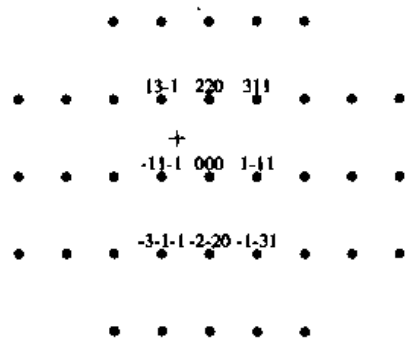
[011], + = (020)



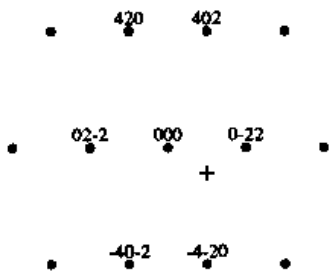
[-111], + = (111)



[012], + = (1-11)



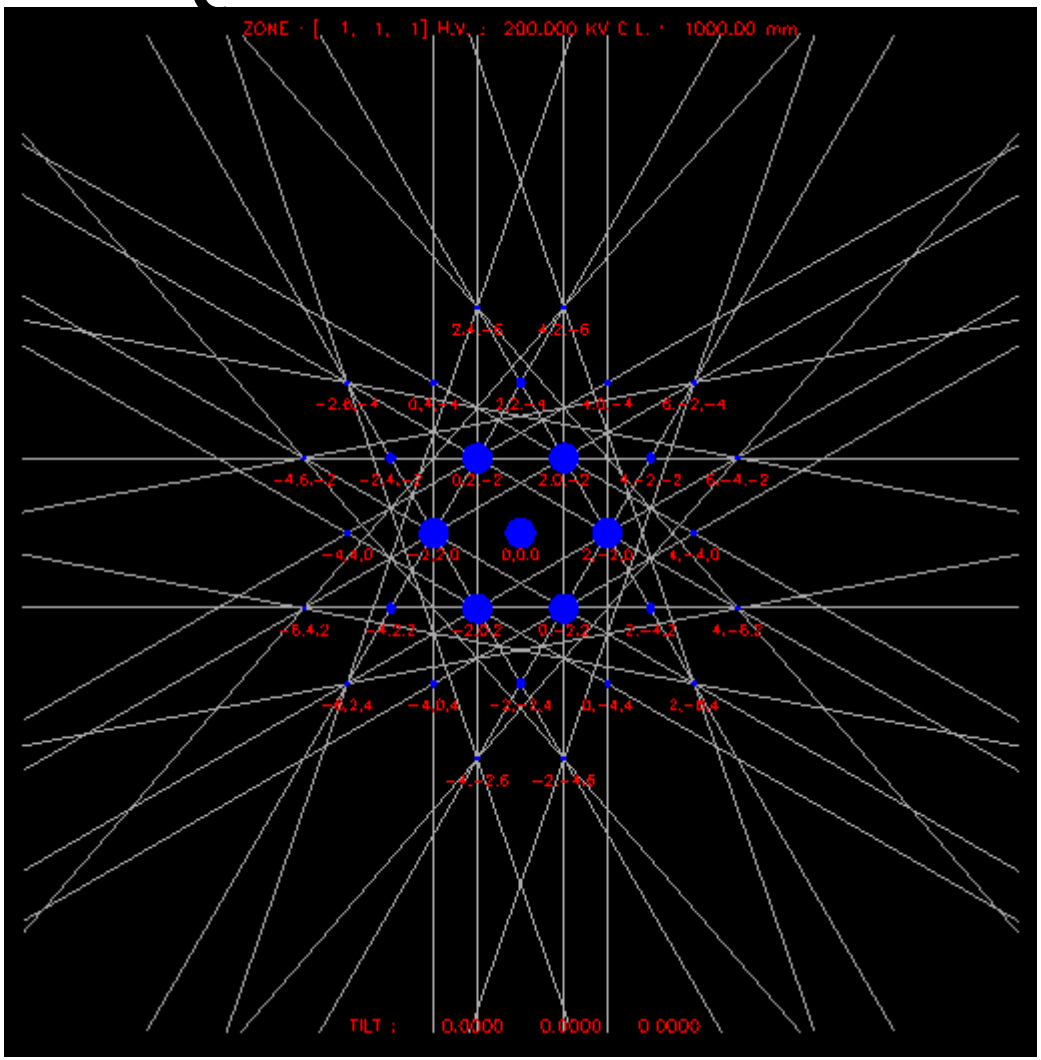
[-112], + = (020)



[-122], + = (-1-11)

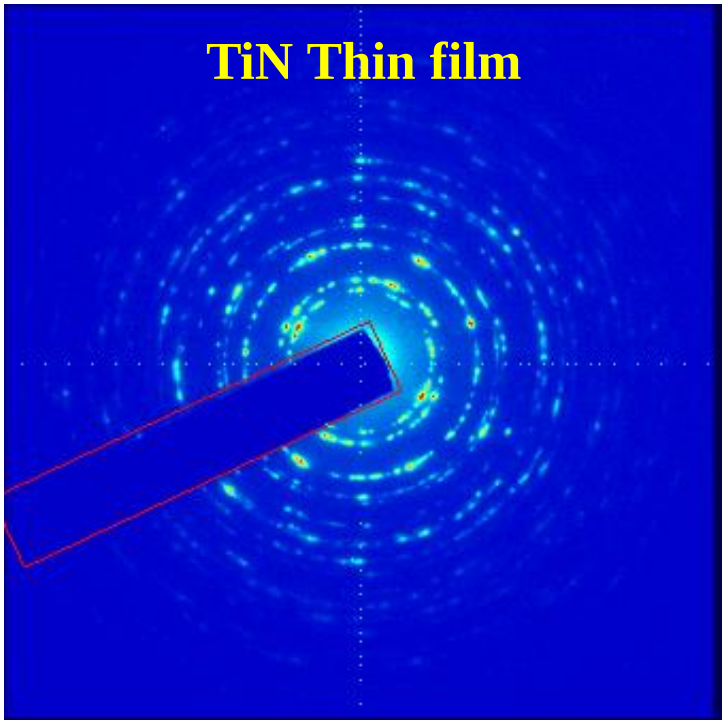
Figure A4.1. Twelve low-index zone-axis diffraction patterns for face-centered cubic crystals.

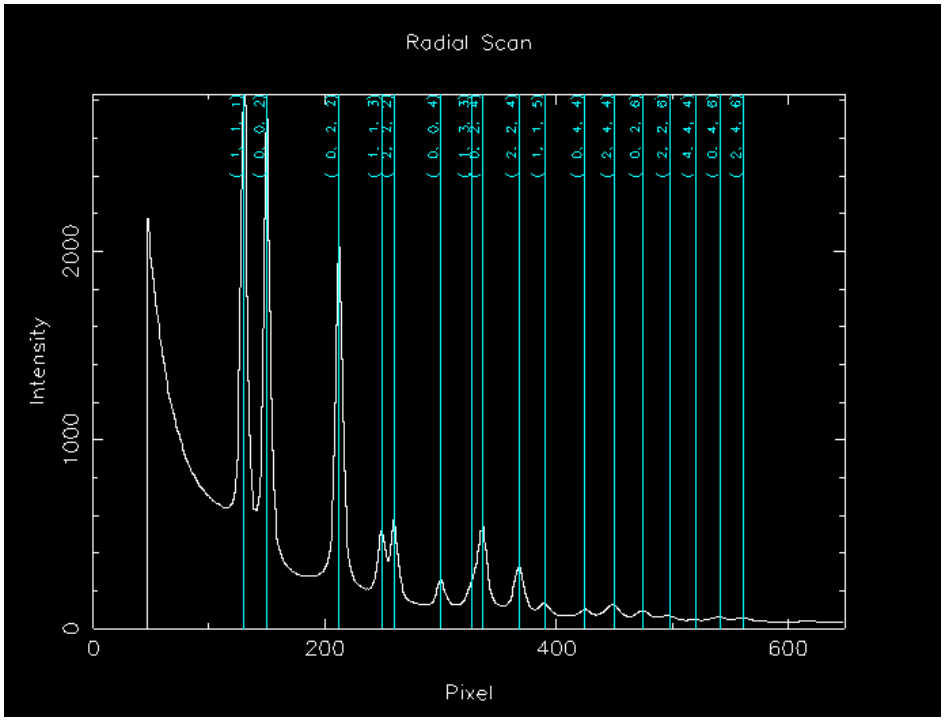
QED Software



Other resource: http://www.jems-saas.ch/Home/jemsWebSite/jems.html

Indexing Powder Diffraction Patterns





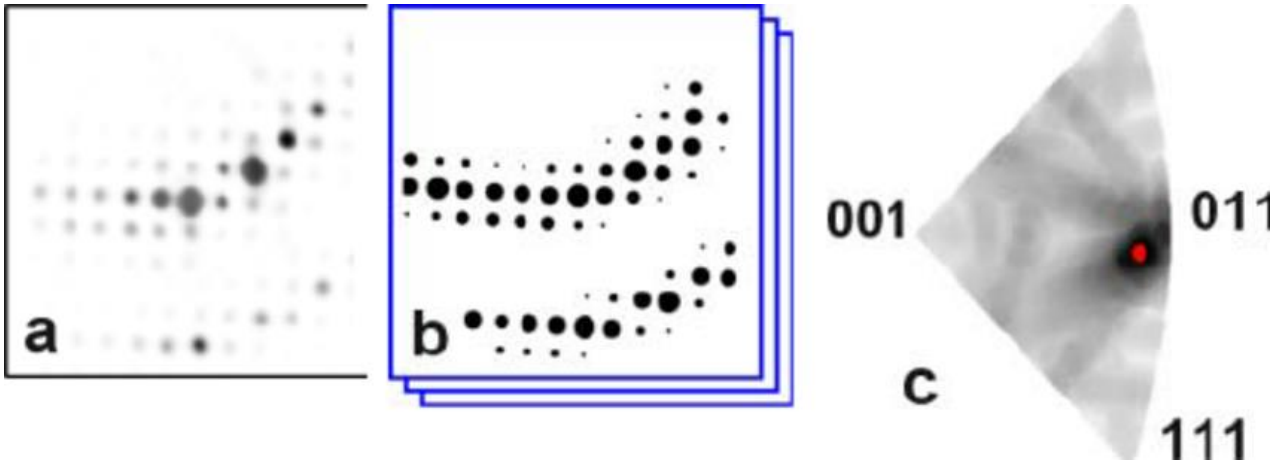
To do this:

1) Find diffraction center; 2) Radially averaging; 3) Generate g list; 4) Match with experimental pattern

Functions provided by QED

Indexing Spot Patterns by Computer

- Required for orientation and phase determination
- Mapping combined with SEND and SPED
- Diffraction pattern indexing is non-trivial
- Previous approaches include the use of 3D diffraction patterns, diffraction tomography, template matching



E. Rauch et al. Grenoble, Zeitschrift für Kristallographie 225(2) · March 2010

Electron Diffraction Indexing and Orientation Mapping (EDIOM)*

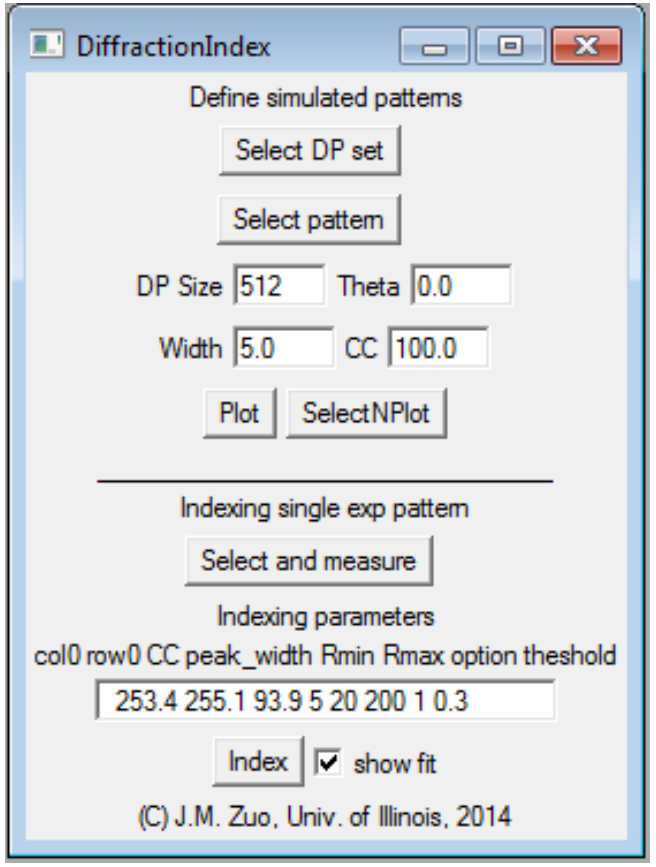
- **Principles**

A diffraction pattern can be predicted with reasonable accuracy for the peak positions and qualitatively for intensity. By fitting an experimental pattern with simulations, the orientation of crystal can be determined and diffraction peaks can be indexed based on matching.

- **Implementation**

Procedures are programmed using C and Gatan script. A dialog called “DiffractionIndex” provides access to the custom functions (see Figure). Use pre-calculated Diffraction patterns by separate programs.

- Basic Procedures (step-by-step instructions given later)
  - Load pre-calculated diffraction data base using “select DP set”
  - Use “select and measure” to measure experimental pattern
  - Use “Index” to perform diffraction pattern fitting



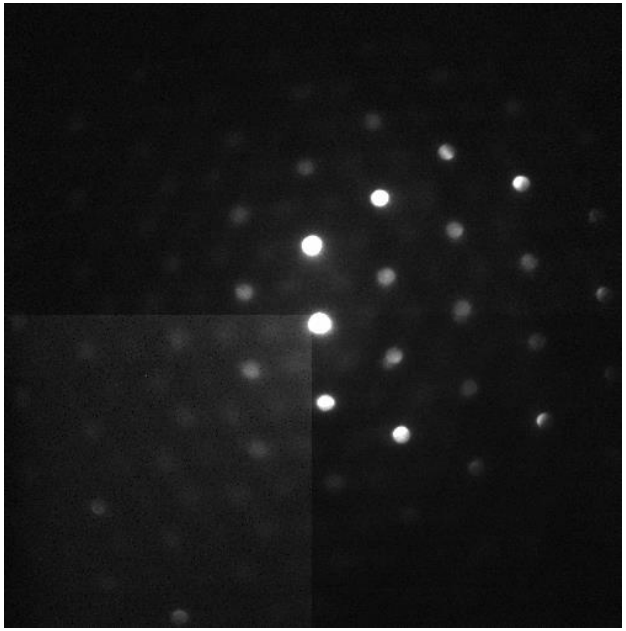
Diffraction Pattern Dataset

Dataset Format (Text f

```
#!dmap
# Diffraction map generated by QED, J.M. Zuo, Univ. Illir
input_Crystal_Data
#CIF FILE IMPORT
#LOCK=ON
#ICSD record,52700
#1|Au
#2|Gold,Au
#3|1|Cubic|225-1
#4|Fm-3m|225-1
crystal Gold: dw=iso
cell      4.0789     4.0789     4.0789    90.0000    90.0000
atom Au    0.000000  0.000000  0.000000  0.400000  1.00000
spg 225 1
np      3
0.0   0.0   1.0    0.00000    0.00000
1.0   1.0   1.0    0.36603    0.36603
0.0   1.0   1.0    0.00000    0.41421
AT
0.24516E+00     0.00000E+00     0.00000E+00
-0.15011E-16     0.24516E+00    -0.22459E-23
-0.15011E-16    -0.15011E-16     0.24516E+00
dx    0.007500
nsp     1518
#
DP       1
0      0    0.00000    0.00000    0.00000    0.00000    0.24516
   28
     0     2     0    0.490328    0.000000    0.490328 100.0000
     2     0     0    0.490328    0.490328    0.000000 100.0000
    -2     0     0    0.490328   -0.490328    0.000000 100.0000
     0    -2     0    0.490328    0.000000   -0.490328 100.0000
     2     2     0    0.693429    0.490328    0.490328
```

28						
0	2	0	0.490328	0.000000	0.490328	100.00000
2	0	0	0.490328	0.490328	0.000000	100.00000
-2	0	0	0.490328	-0.490328	0.000000	100.00000
0	-2	0	0.490328	0.000000	-0.490328	100.00000
2	2	0	0.693429	0.490328	0.490328	9.35473
-2	2	0	0.693429	-0.490328	0.490328	9.35473
2	-2	0	0.693429	0.490328	-0.490328	9.35473
-2	-2	0	0.693429	-0.490328	-0.490328	9.35473
0	4	0	0.980657	0.000000	0.980657	0.45754
4	0	0	0.980657	0.980657	0.000000	0.45754
-4	0	0	0.980657	-0.980657	0.000000	0.45754
0	-4	0	0.980657	0.000000	-0.980657	0.45754
4	2	0	1.096407	0.980657	0.490328	0.15504
-2	4	0	1.096407	-0.490328	0.980657	0.15504
2	4	0	1.096407	0.490328	0.980657	0.15504
-4	2	0	1.096407	-0.980657	0.490328	0.15504
4	-2	0	1.096407	0.980657	-0.490328	0.15504
-2	-4	0	1.096407	-0.490328	-0.980657	0.15504
2	-4	0	1.096407	0.490328	-0.980657	0.15504
-4	-2	0	1.096407	-0.980657	-0.490328	0.15504
4	4	0	1.386858	0.980657	0.980657	0.01333
-4	4	0	1.386858	-0.980657	0.980657	0.01333
4	-4	0	1.386858	0.980657	-0.980657	0.01333
-4	-4	0	1.386858	-0.980657	-0.980657	0.01333
6	0	0	1.470985	1.470985	0.000000	0.00695

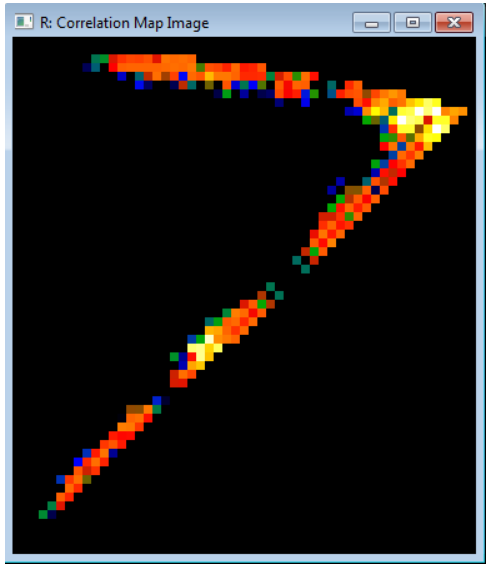
Pattern Matching using EDIOM



Original

Measured

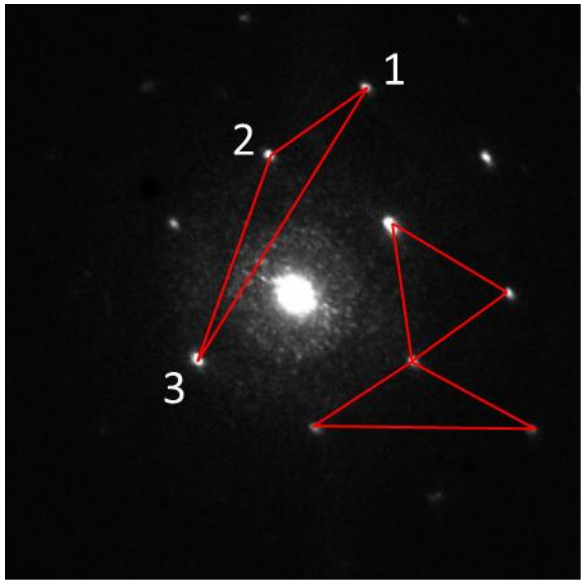
Fit

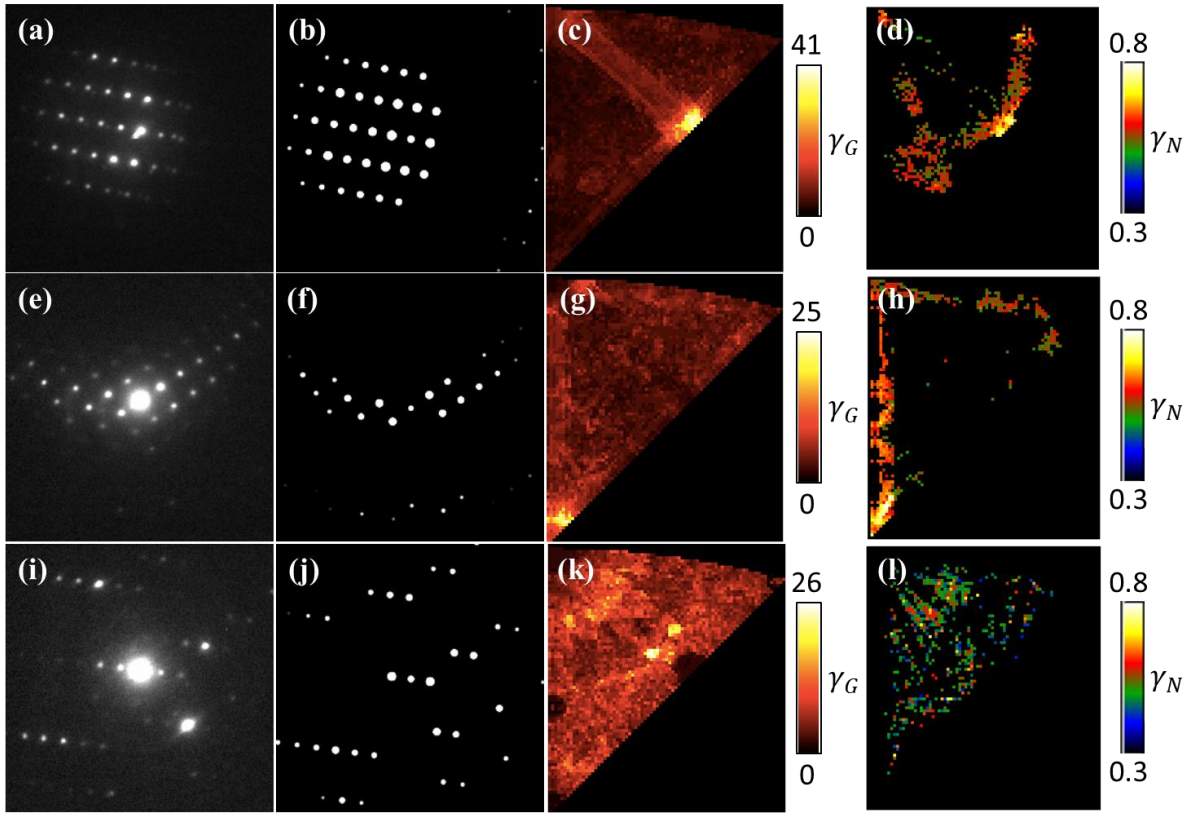


Fit index map

The Groth's Triangle algorithm

Pattern-matching algorithm for determining stellar positions from astronomical photographs



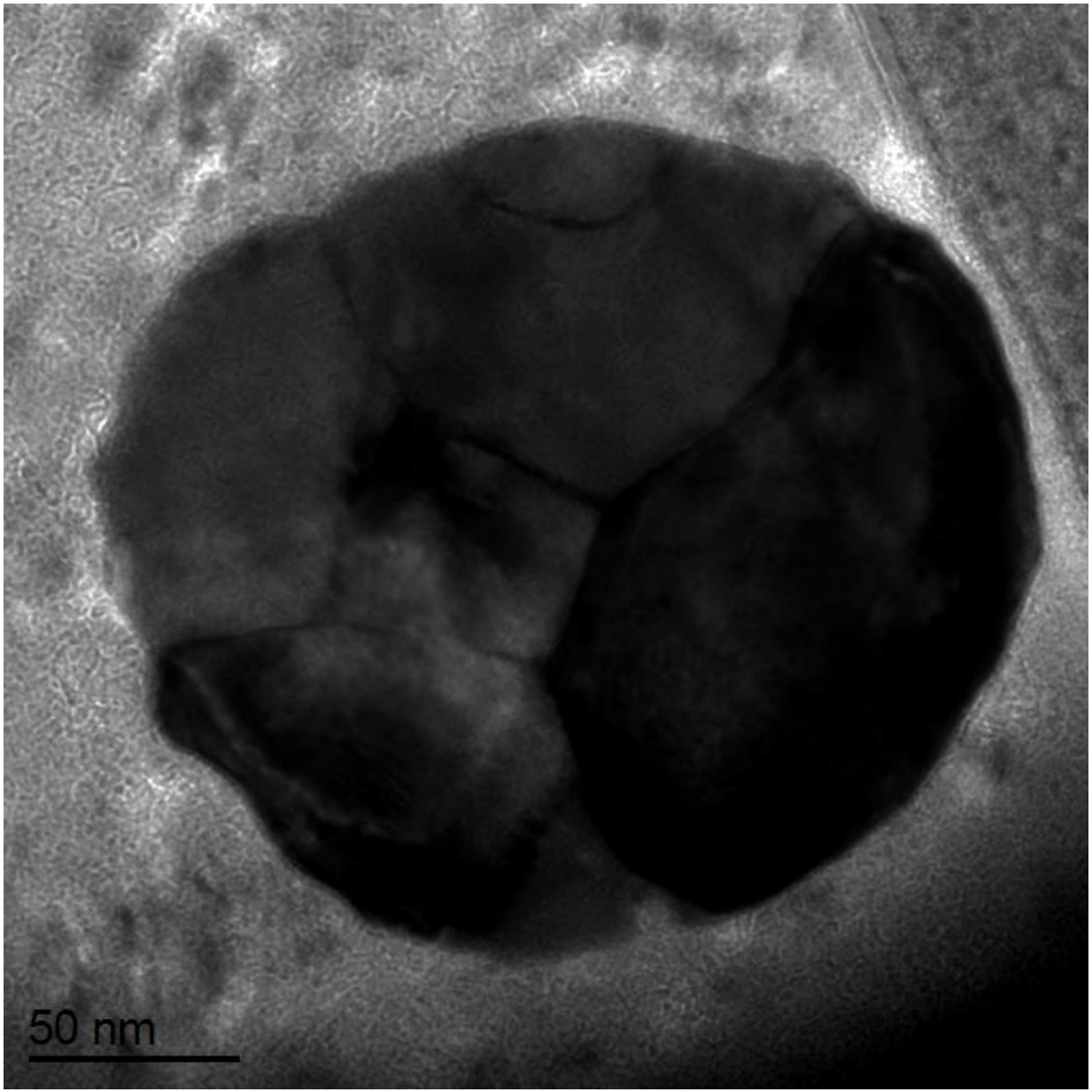


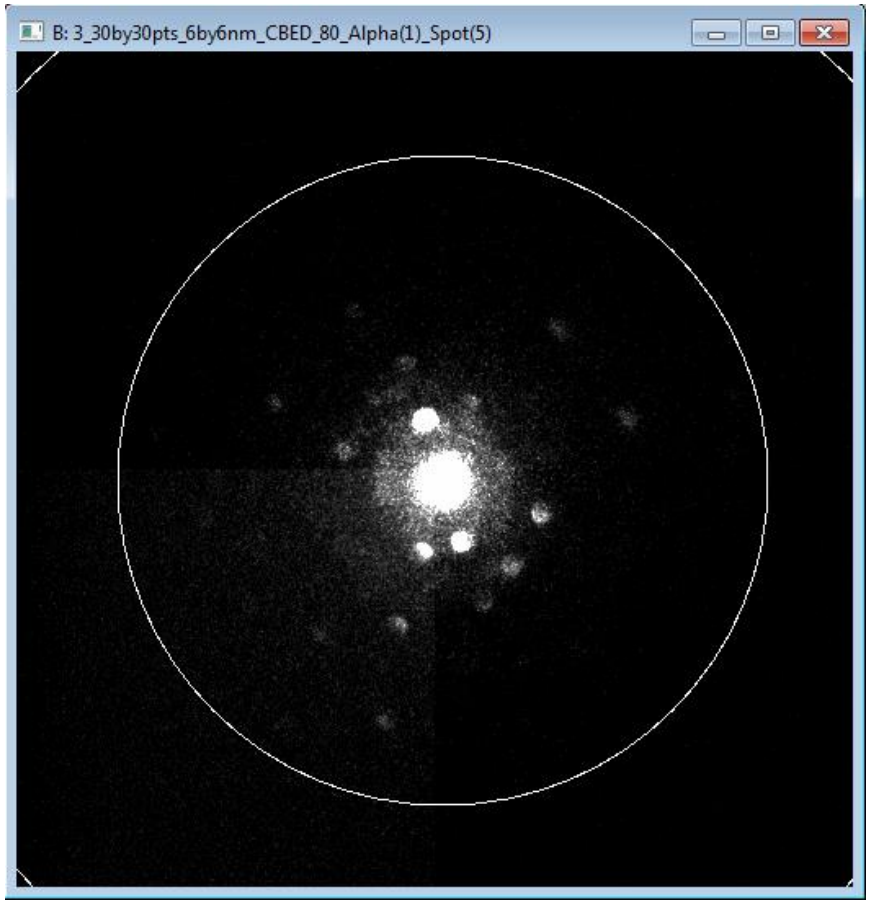
E.J. Groth, The Astronomical Journal. **91**, 1244 (1986)
Meng and Zuo, Submitted

Analysis of SEND Patterns

- Scanning Electron Nanodiffraction (SEND) generates a large dataset, we developed DigitalMicrograph scripts for the analysis of SEND patterns;
- The functions implemented include selected area diffraction, automated identification, correlation analysis, region identification, diffraction pattern indexing;
- The scripts run on Gatan GMS 2

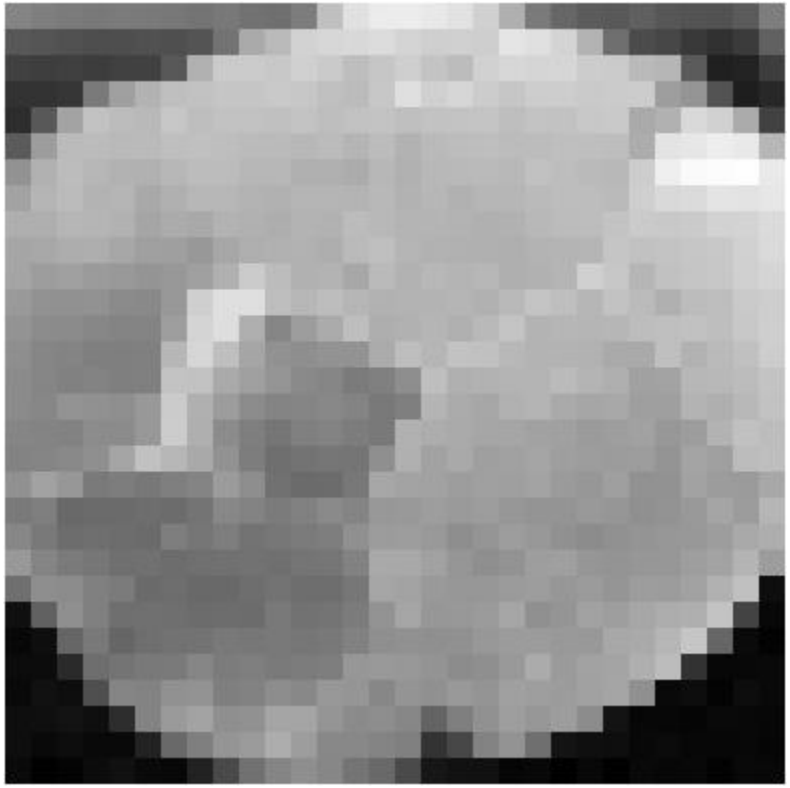
Au nanodisk will be used as an example for analysis



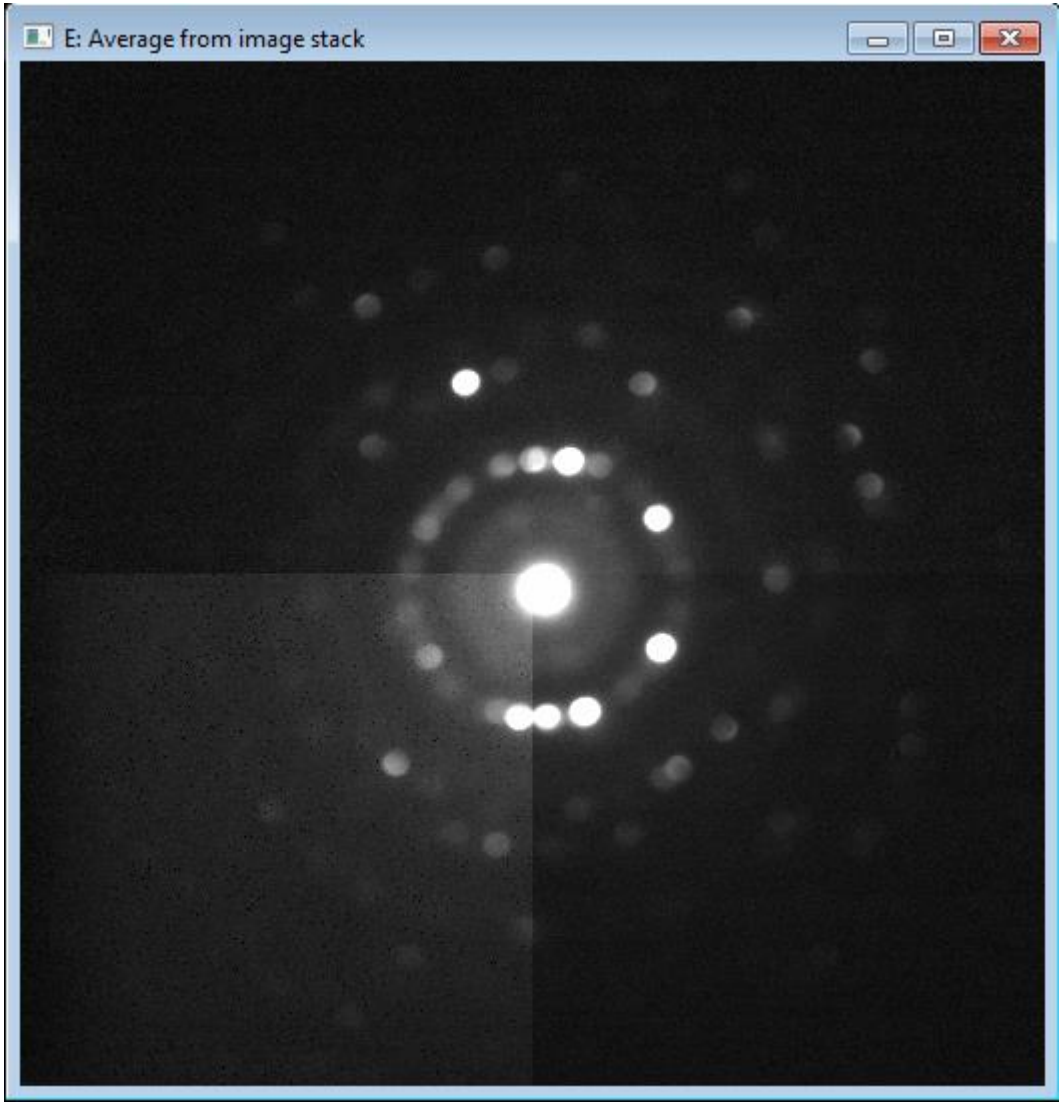


Scanning Electron Nanodiffraction
30x30 sampling, step size 6 nm

ADF Image-Integrated Intensity Map

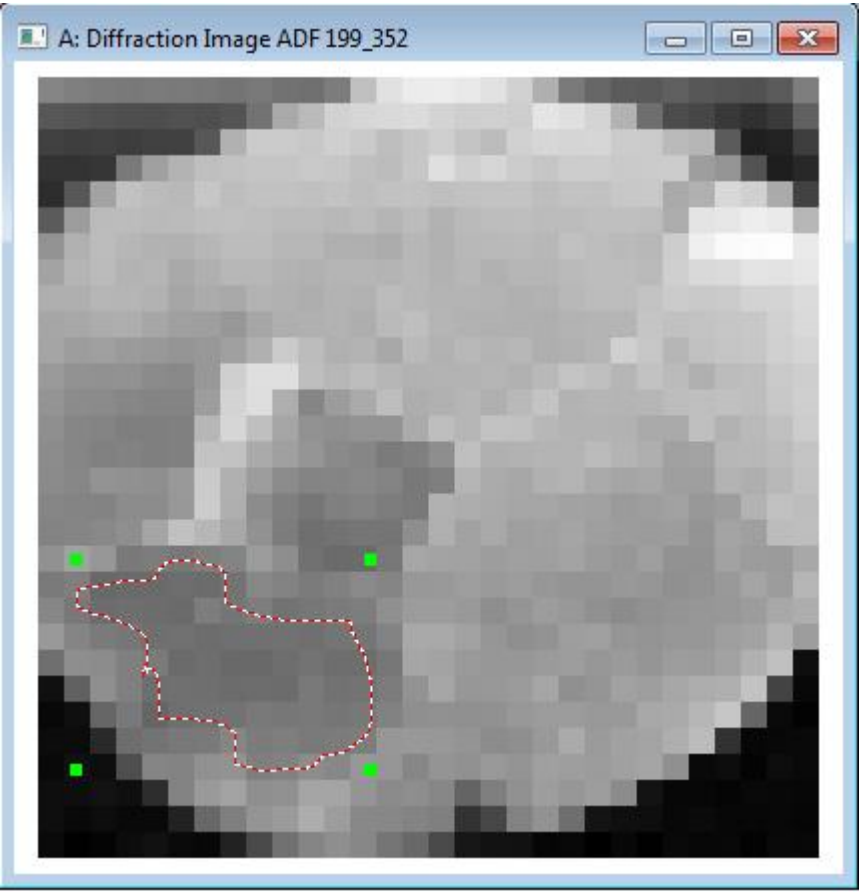


Average-Sum of All Diffraction Patterns



Script: StackAverage.s

Selected Area Diffraction

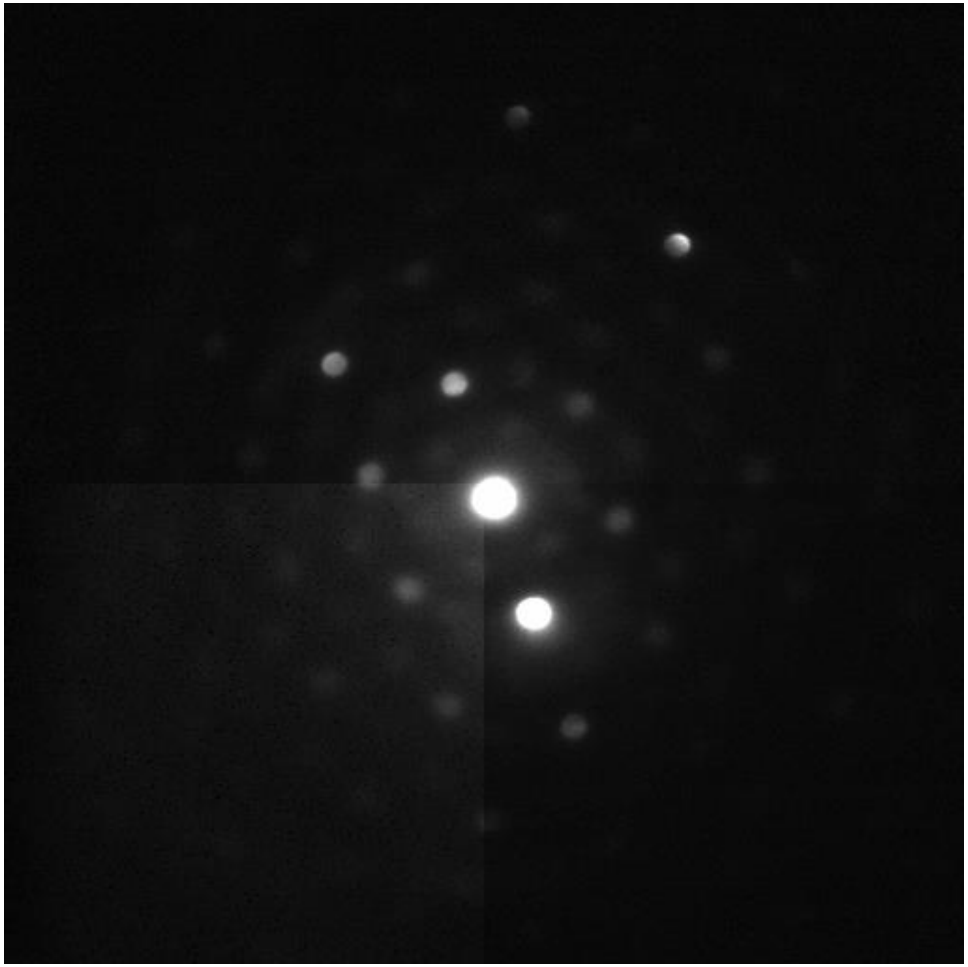


Script: Stack_MaskAverage.s

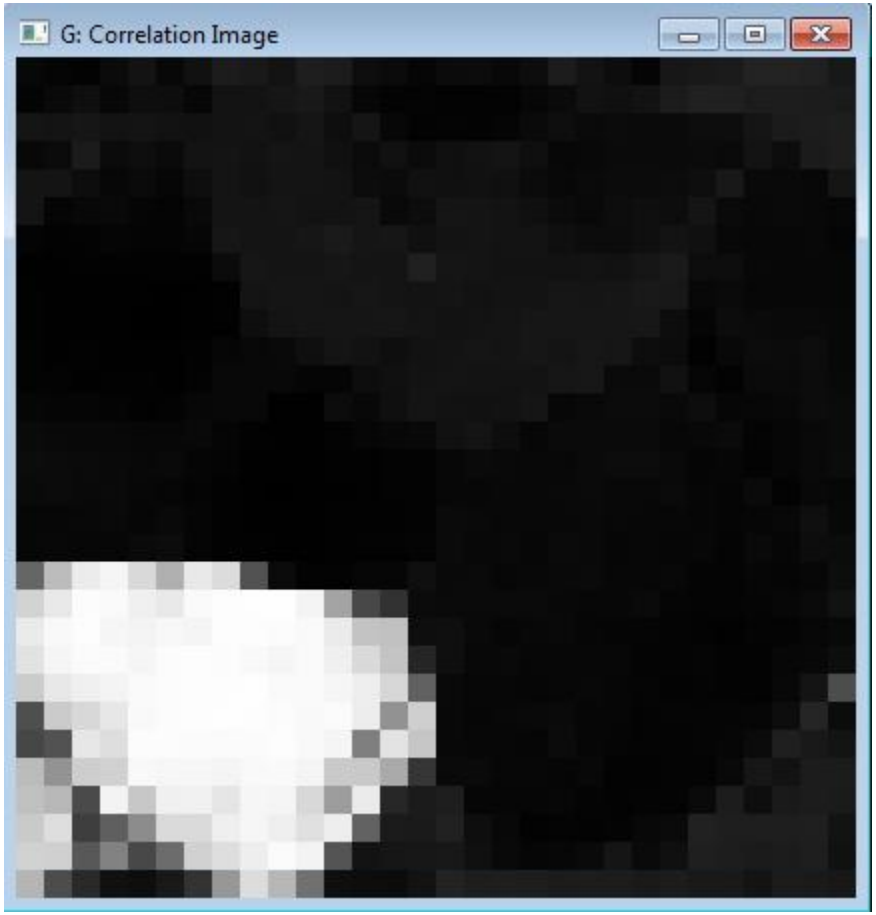
Correlation Analysis

- calculation the correlation coefficient for a specified template

Template



Correlation Image



Maximum correlation is 1

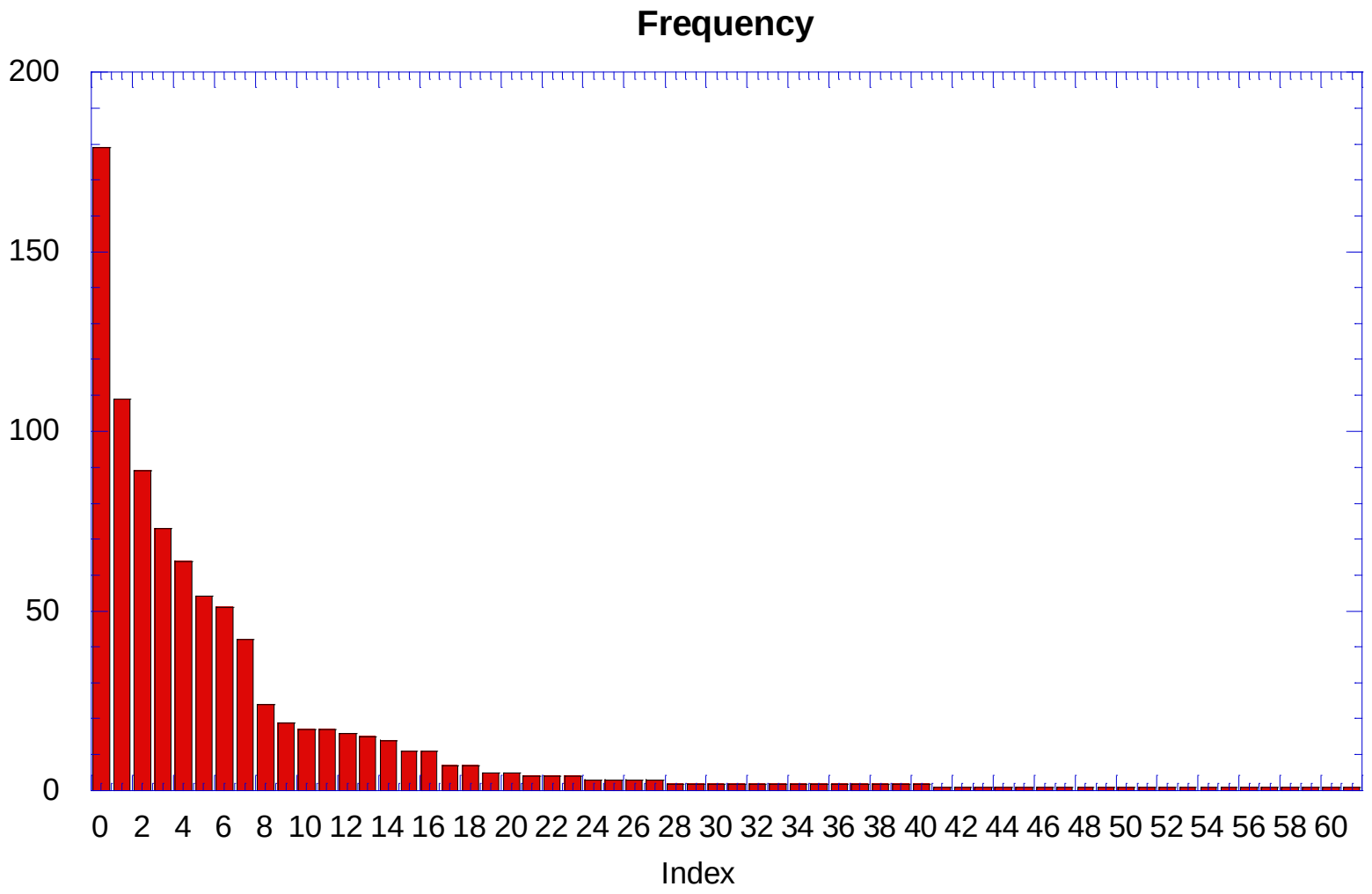
Script: Stack_XCFImage.s

Region Search

- Compare diffraction patterns for each pixels using correlation coefficient;
- Define a threshold for identical diffraction patterns;
- Regions having same diffraction pattern are shown in same color.

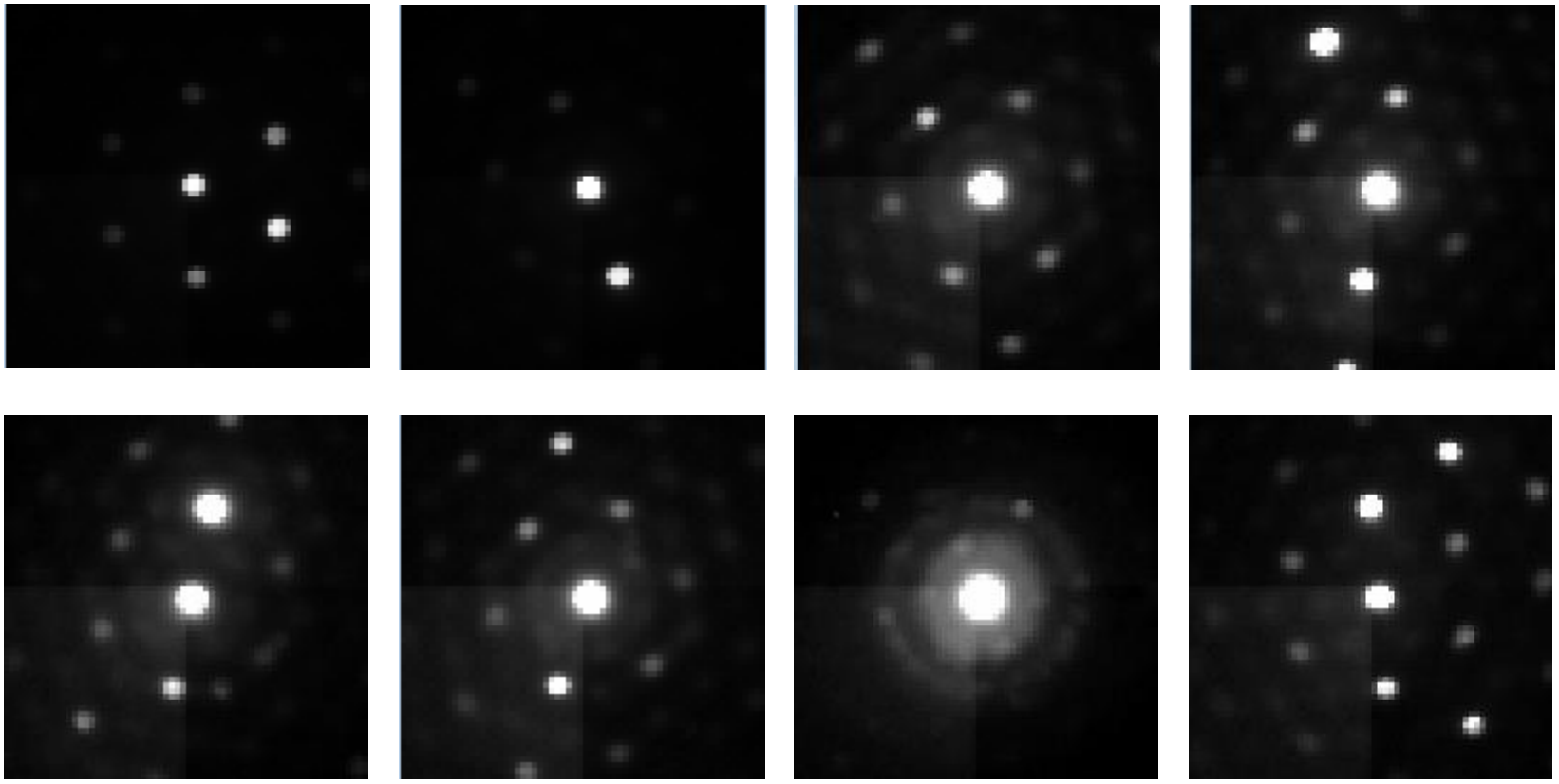
Script: Stack_XCFSearch.s

Results of Region Search



61 diffraction patterns found among 900 total using 0.65 threshold

Region Averaged Diffraction Patterns



0 most common, 1 next, etc

Covered Topics

- **Indexing electron diffraction patterns**
- **Analysis of SEND patterns**
- **HOLZ Lines**
- **Strain**
- **Electron diffraction tomography**
- **Nanostructure characterization**

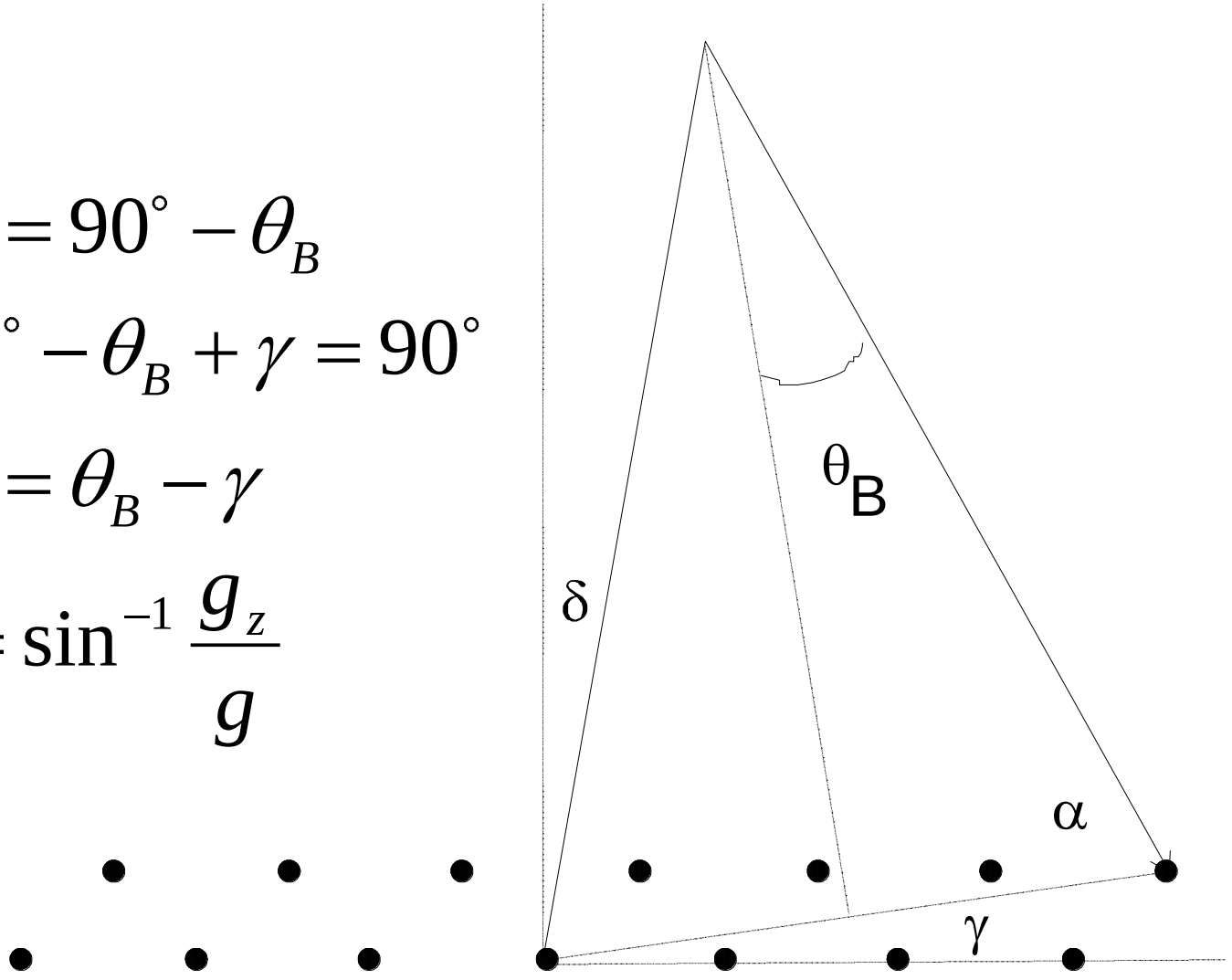
HOLZ Lines

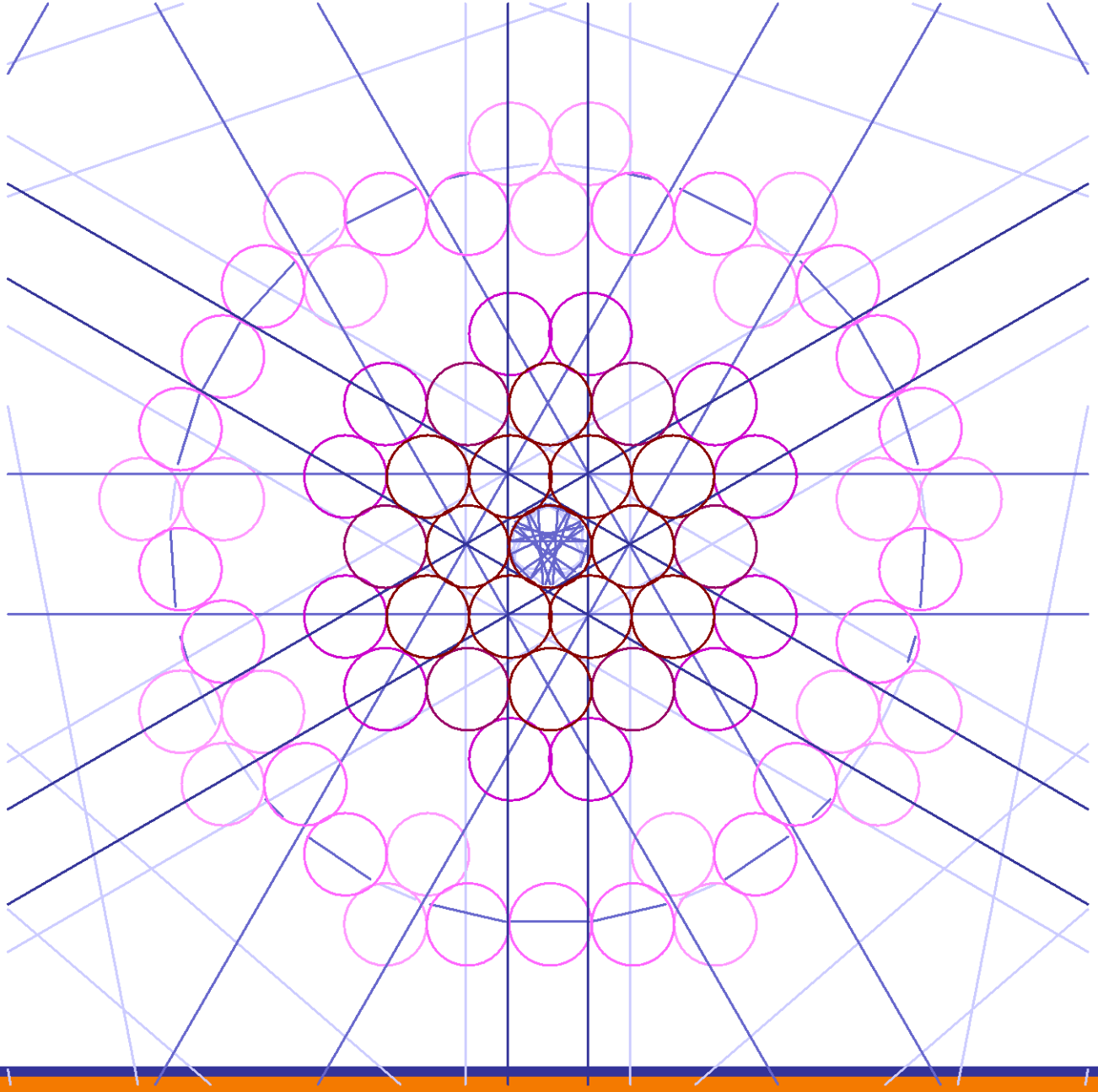
$$\alpha = 90^\circ - \theta_B$$

$$\delta + 90^\circ - \theta_B + \gamma = 90^\circ$$

$$\delta = \theta_B - \gamma$$

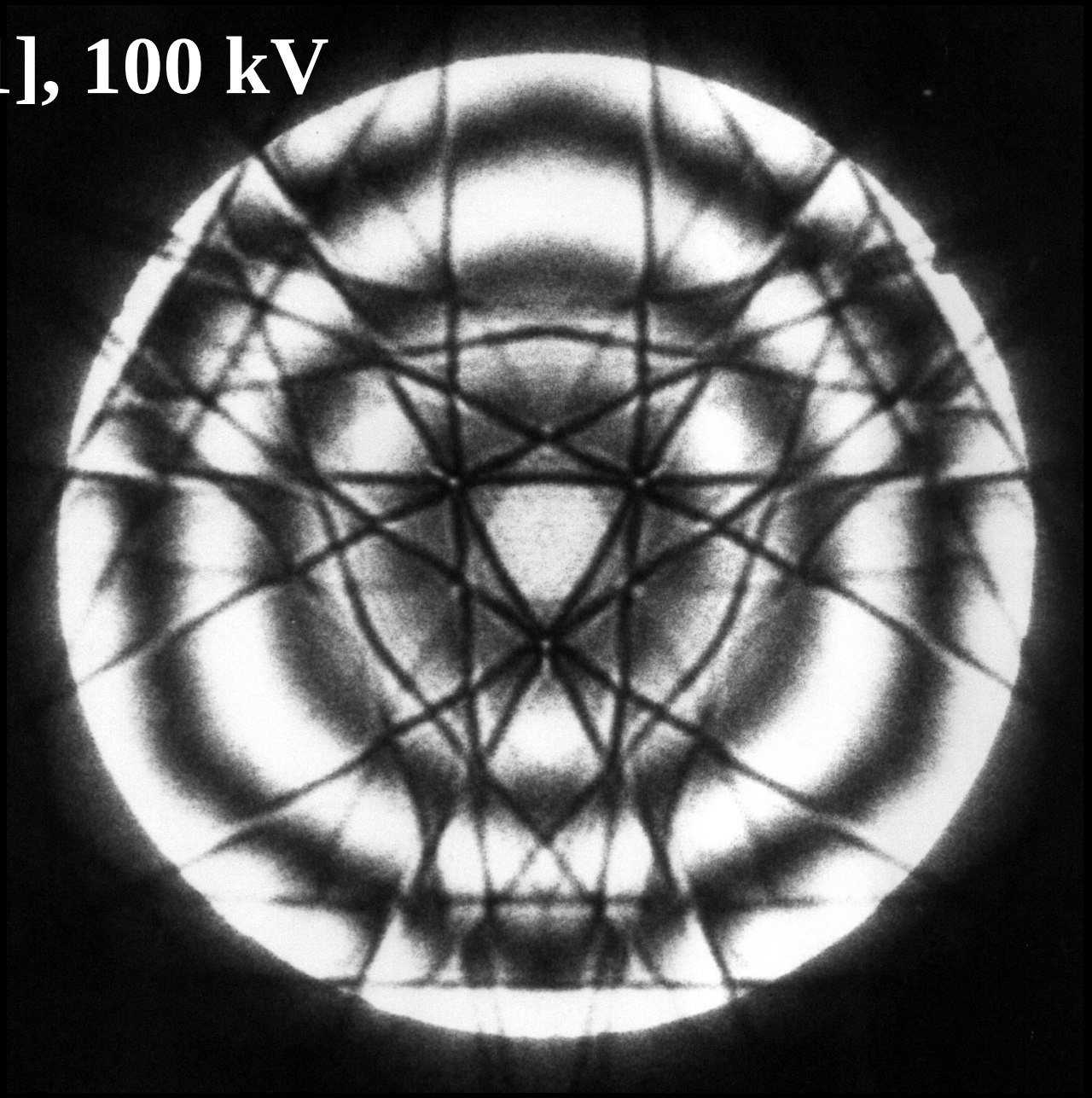
$$\gamma = \sin^{-1}\frac{g_z}{g}$$





Si[111]
100 kV

Si [111], 100 kV

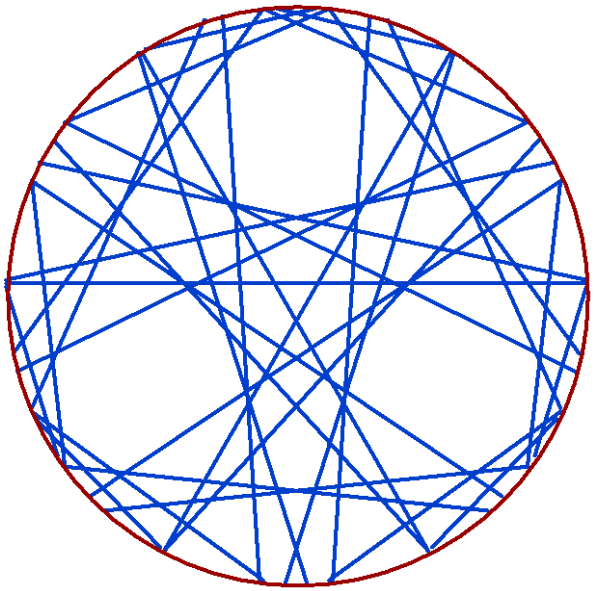


Kinematic versus Dynamic

Simulated, 100kV, Si[111], 160 beams

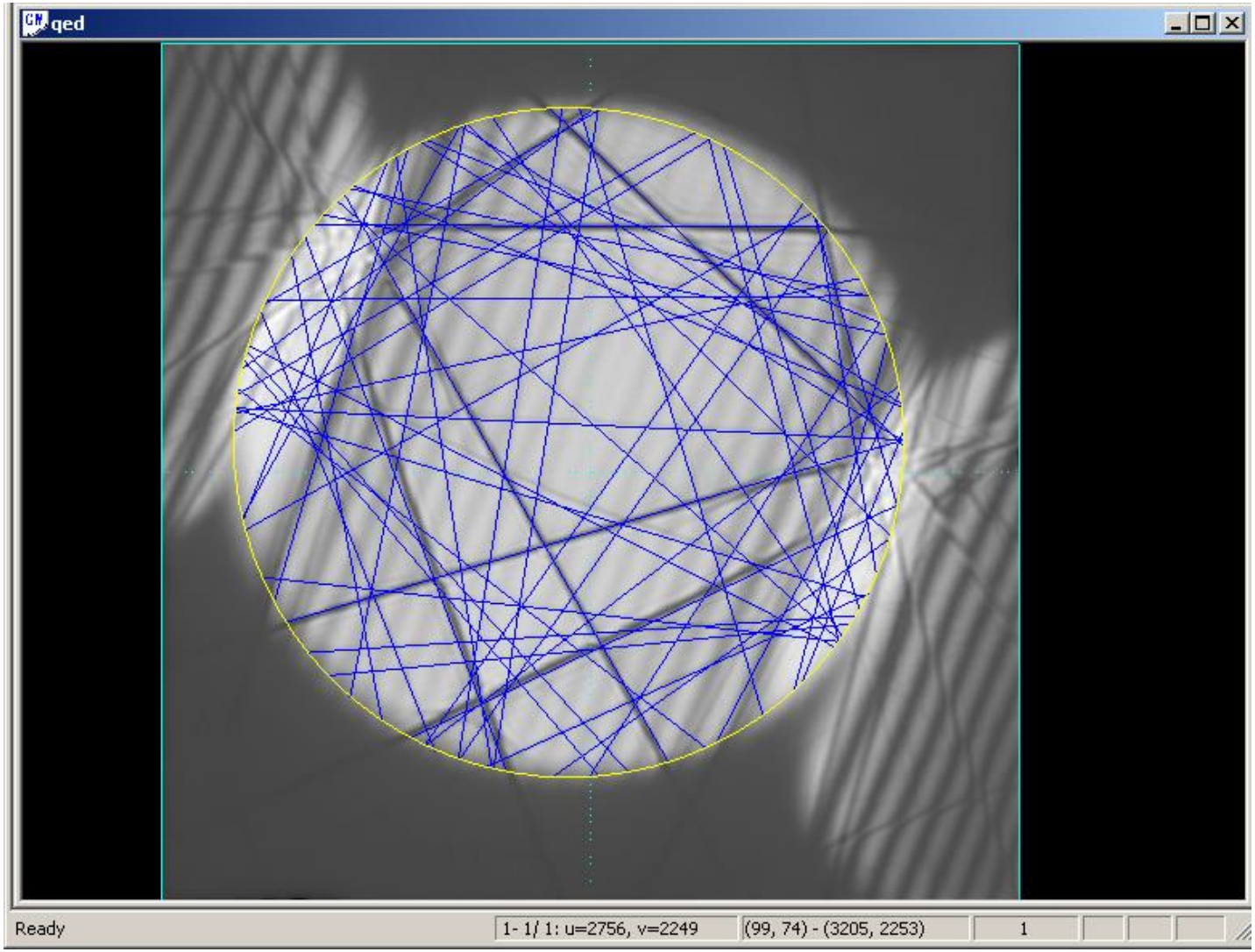
Kinematic Geometry:

$$K^2 - (\mathbf{K} + \mathbf{g})^2 = 0$$

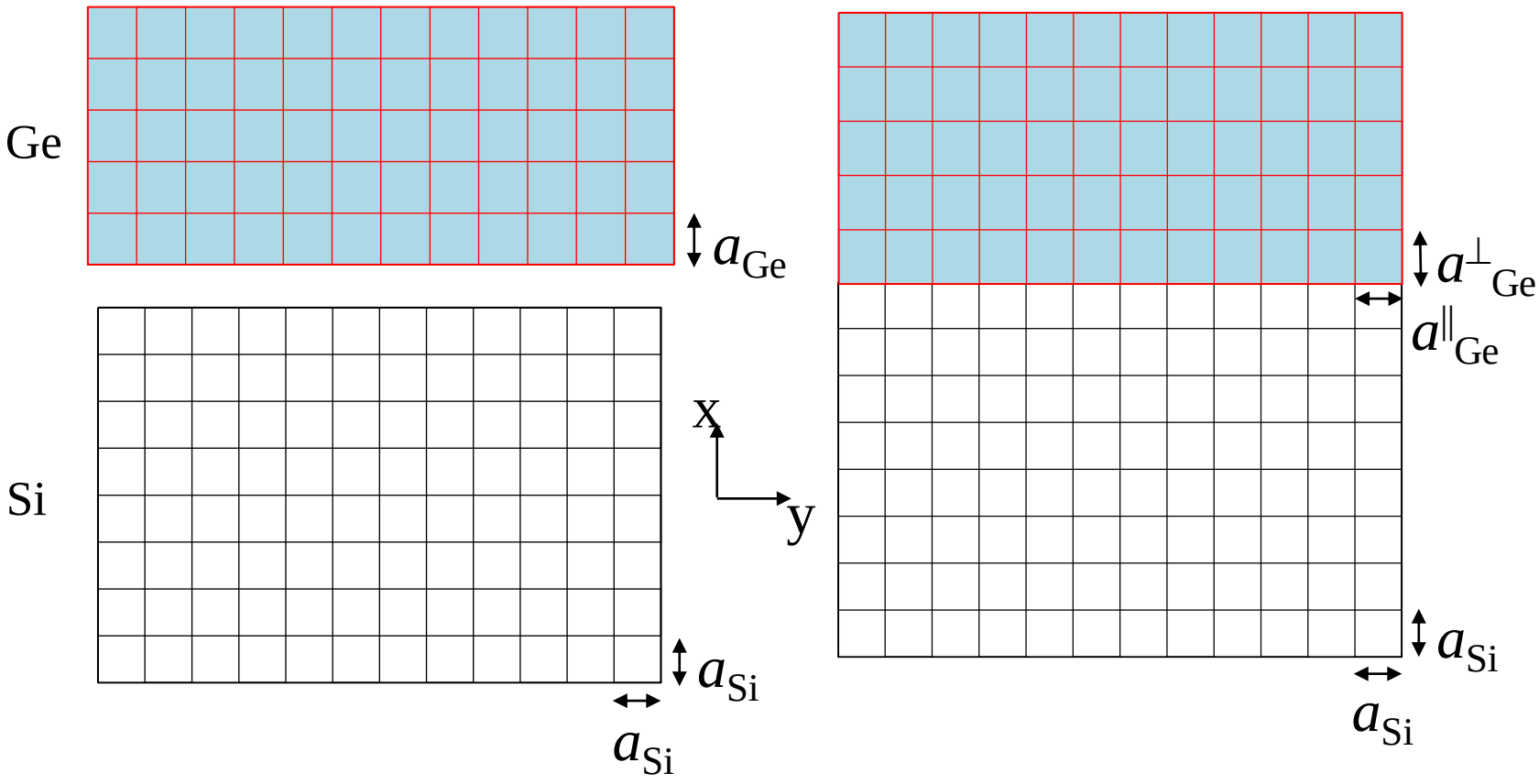


100 kV

Use of QED



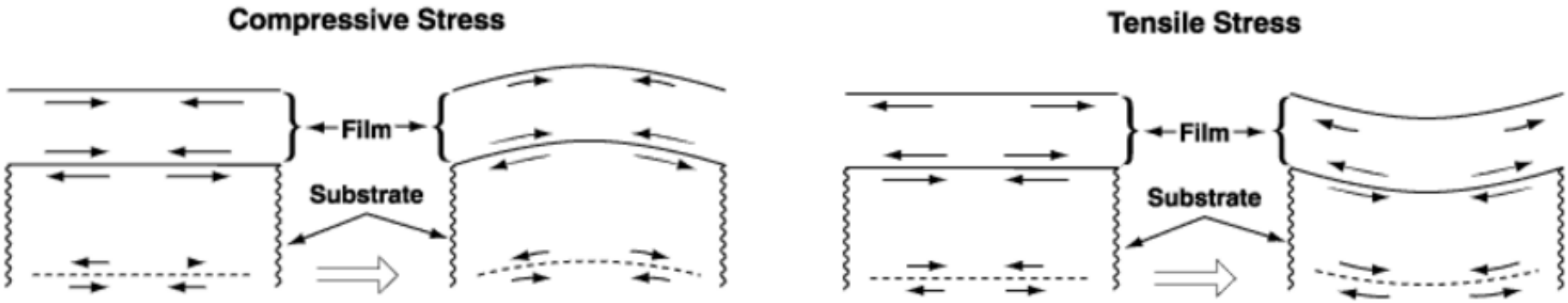
Strain



$$\varepsilon_{xx}^{mat} = (a - a_{Ge}) / a_{Ge} = a a_{Ge}^{-1} - 1$$

$$\varepsilon_{xx}^{La} = (a - a_{Si}) / a_{Si} = a a_{Si}^{-1} - 1$$

Thin film stress



$$\sigma = \sigma_{MECH} + \sigma_T + \sigma_I$$

Thermal stress: mismatch in thermal expansion coeff.

Intrinsic stress: structure and deposition conditions

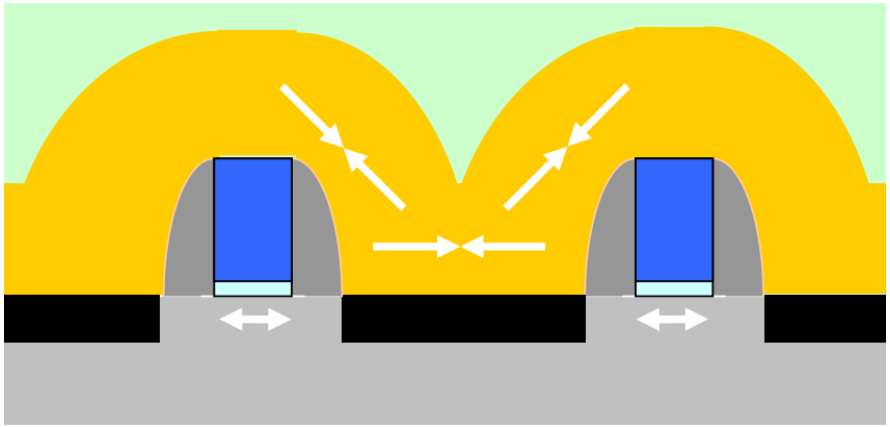
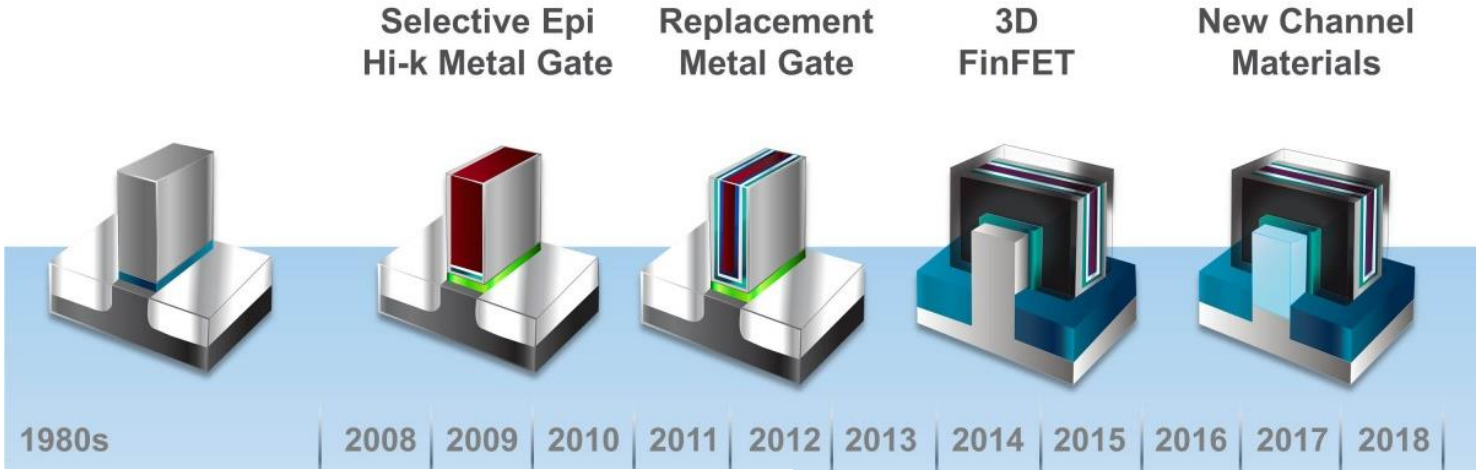
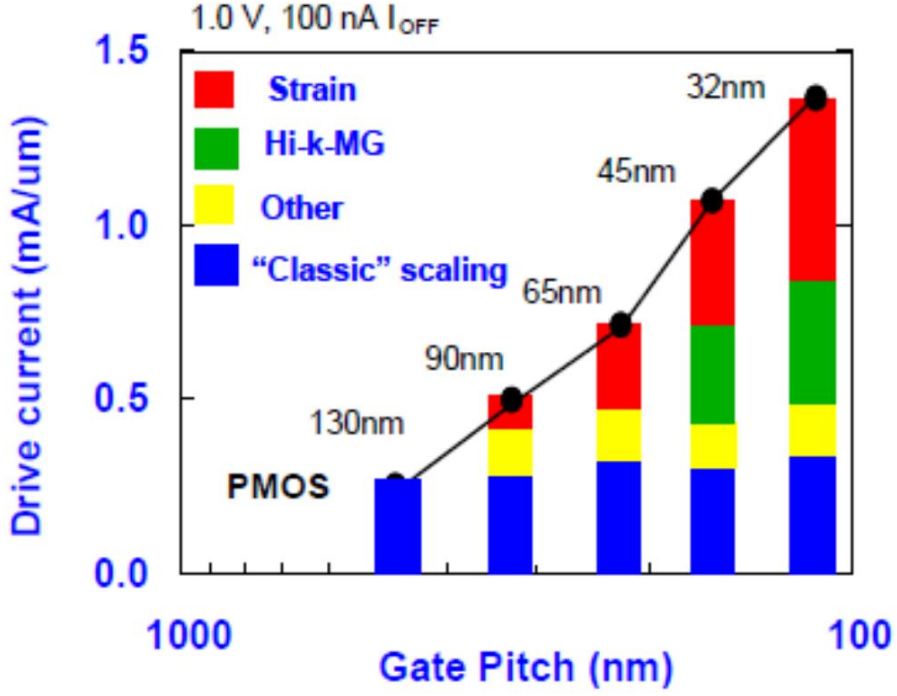


Figure source: Donald M. Mattox, WWW.SVC.ORG
Auth et al., Intel, Portland

Strain in transistor technology



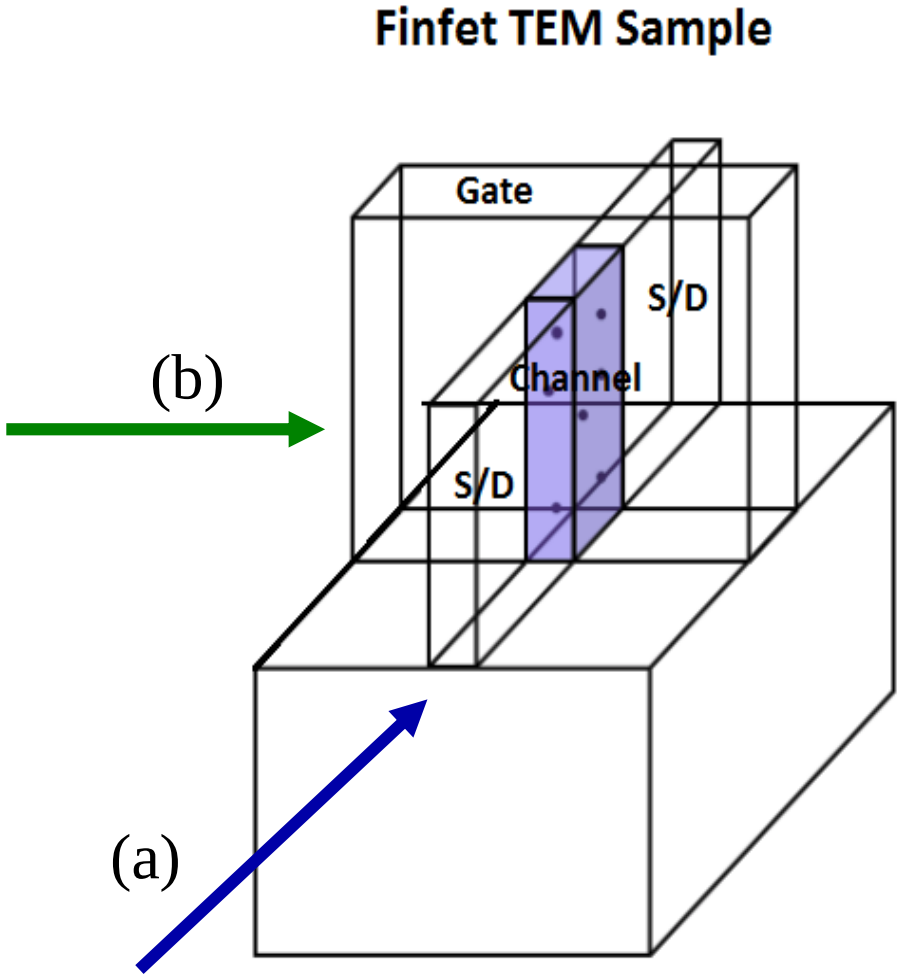


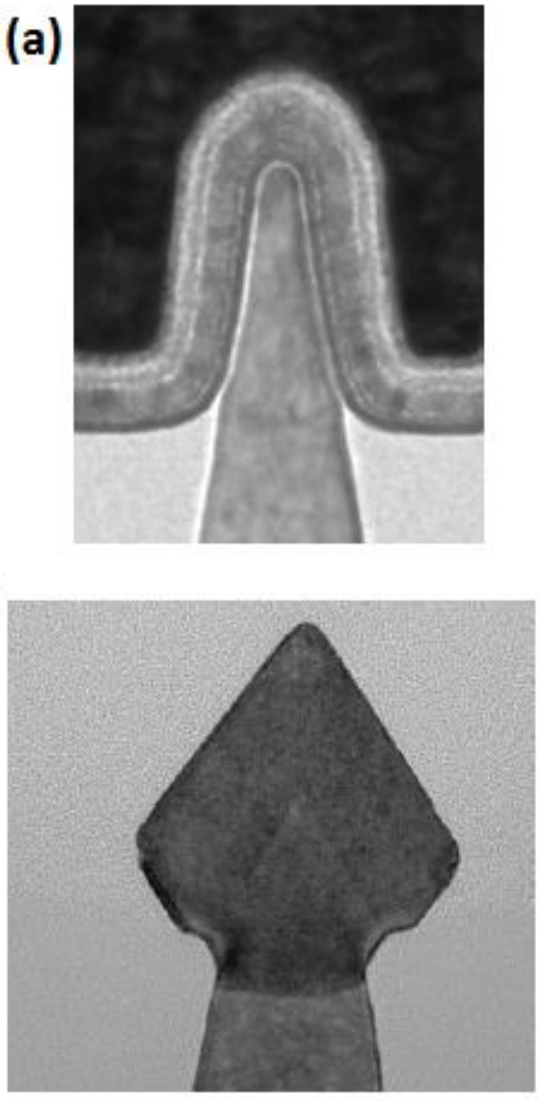
- At 32nm node, stress enhances hole mobility by 3.5x
- SiGe plays a key role in PMOS

http://semimd.com/applied/tag/applied-materials/

K. Kuhn et al, ECS 2010 (Intel)

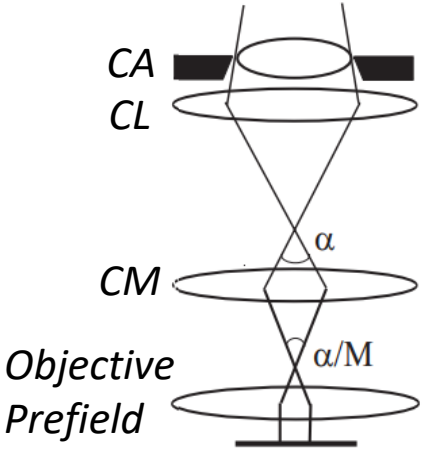
Three-dimensional finFET Devices



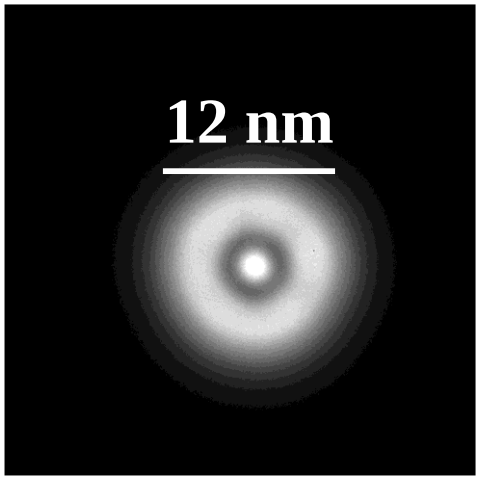


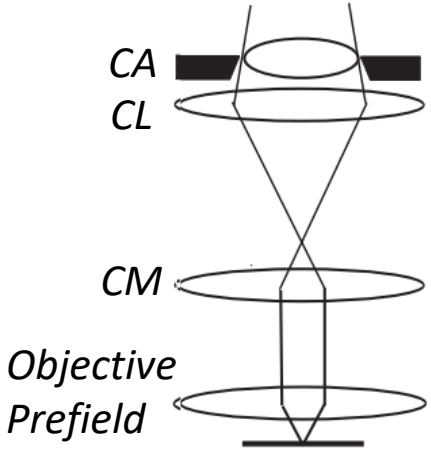
Channel structure embedded underneath the gate or S/D

Nanobeam Diffraction

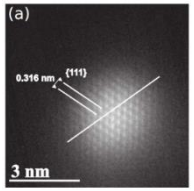


b) NAED

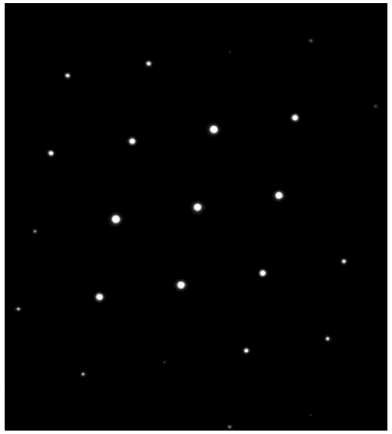


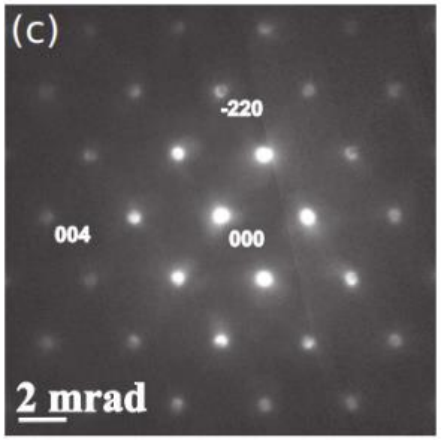


c) NBD



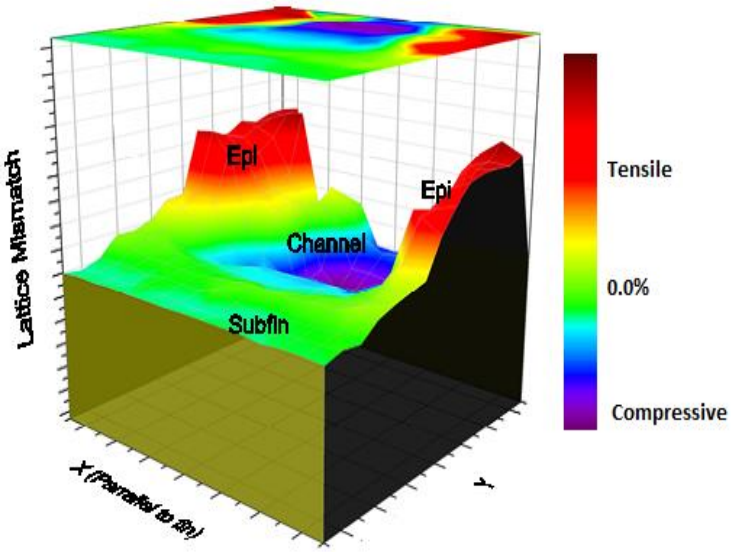
Diffraction pattern



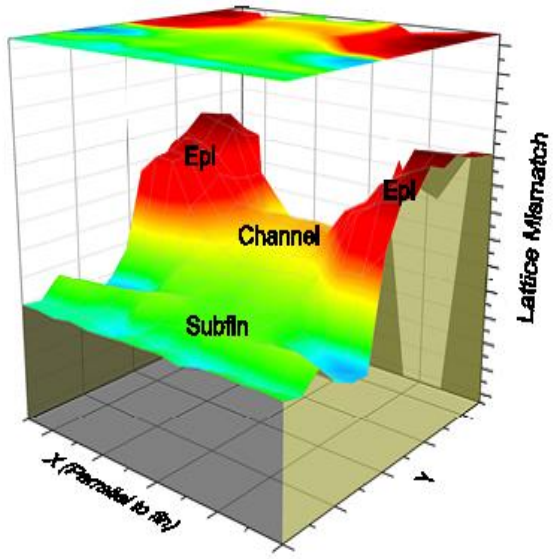


2D Device Strain Mapping using NBD

[110]

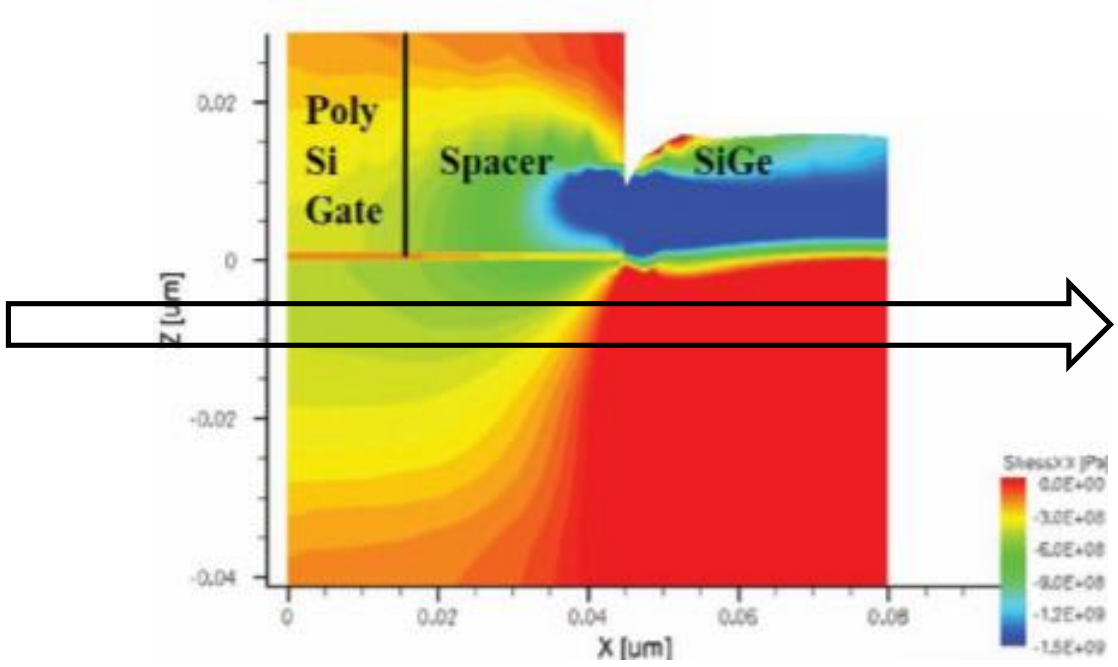


[001]



From a finFET transistor with a 4nm probe and a 20X20 pixels scan. The strain is displayed in term of lattice mismatch along the [001] and [110] channel directions.

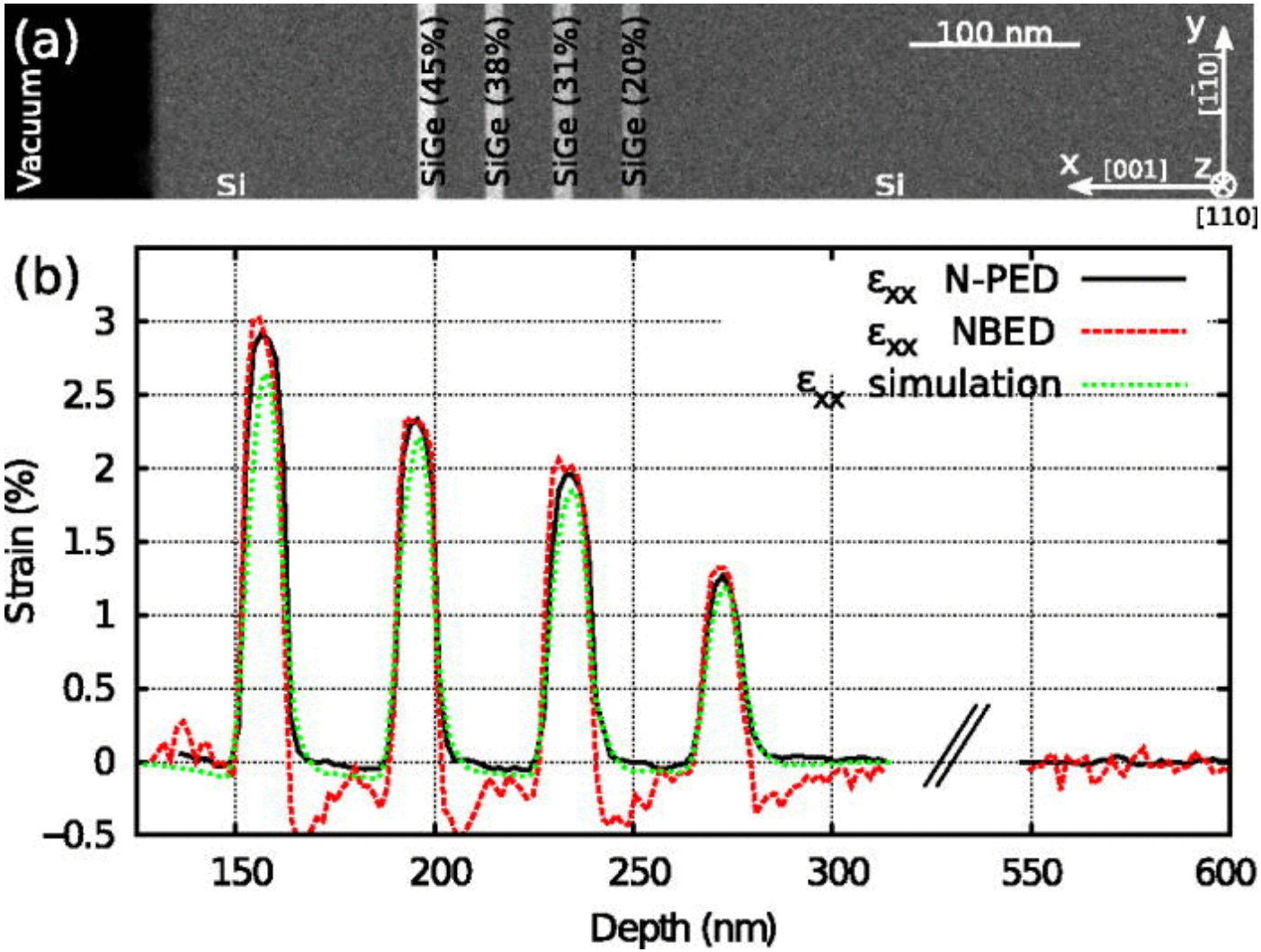
What's measured?



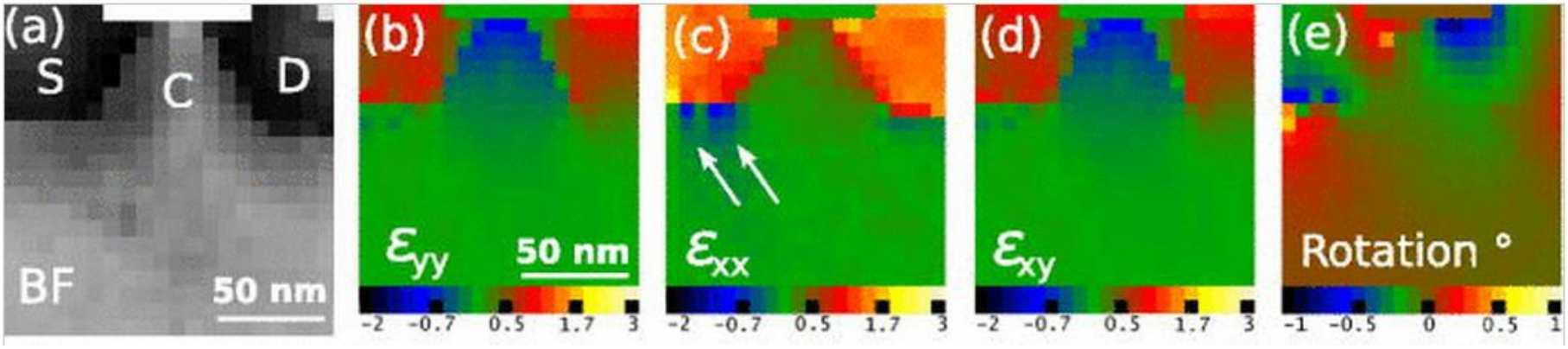
The problem with this picture:

- Electron multiple scattering, e.g. weak scattering is not a good approximation
- Electron diffraction is sensitive to thickness, orientation and composition

Improvements with Precession



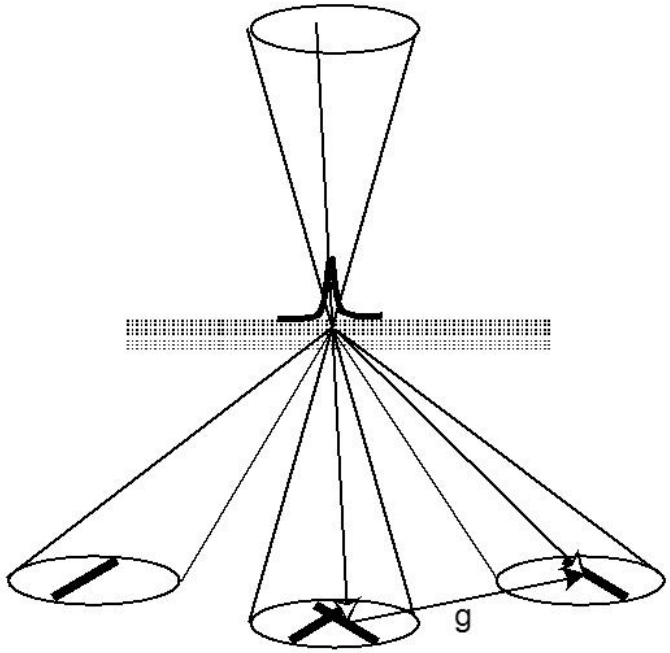
Improvements with Precession

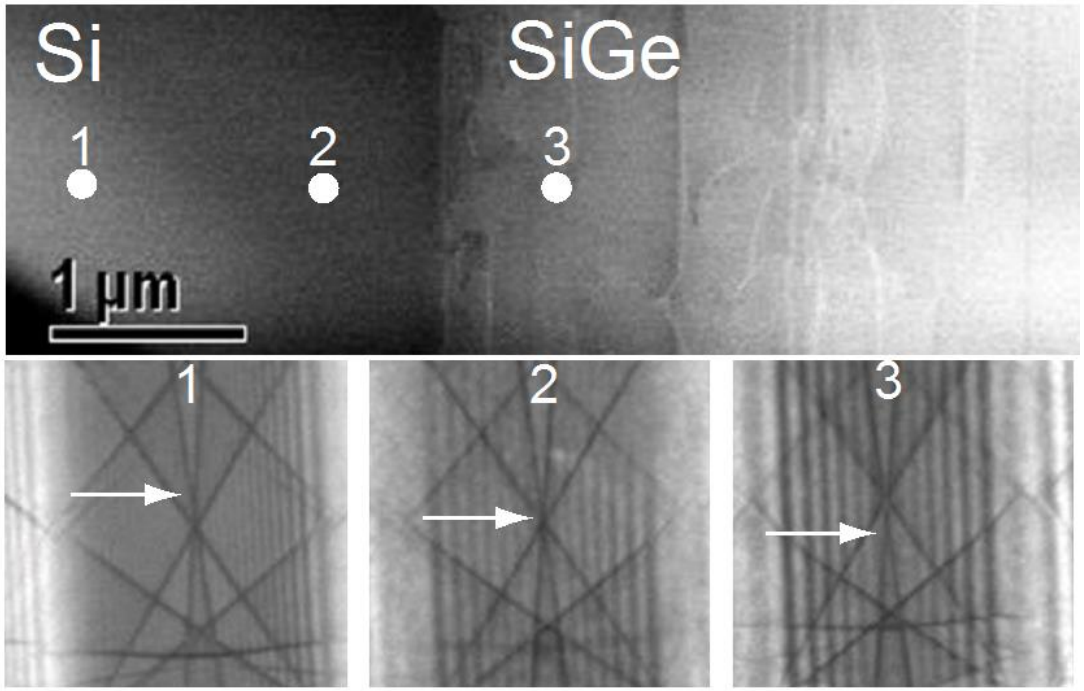


A transistor having recessed $Si_{0.65}Ge_{0.35}$ source and drain.

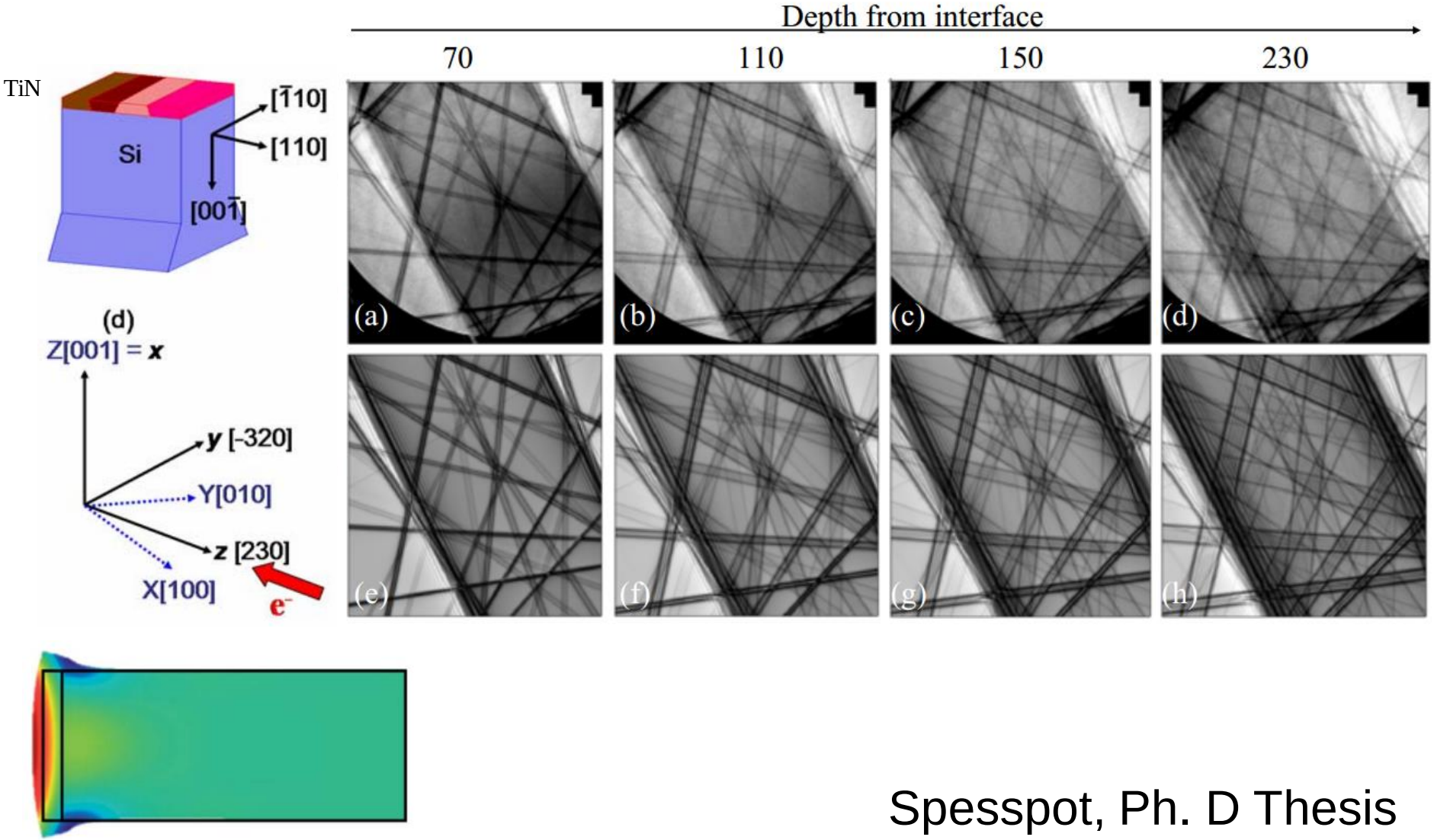
Beam semi-convergence angle of 1.8 mrad,
a precession angle of 0.5°, and a beam diameter of 2.5 nm.
The root mean square of strain in the Si substrate is $\sim 6 \times 10^{-4}$.

3D Strain Analysis



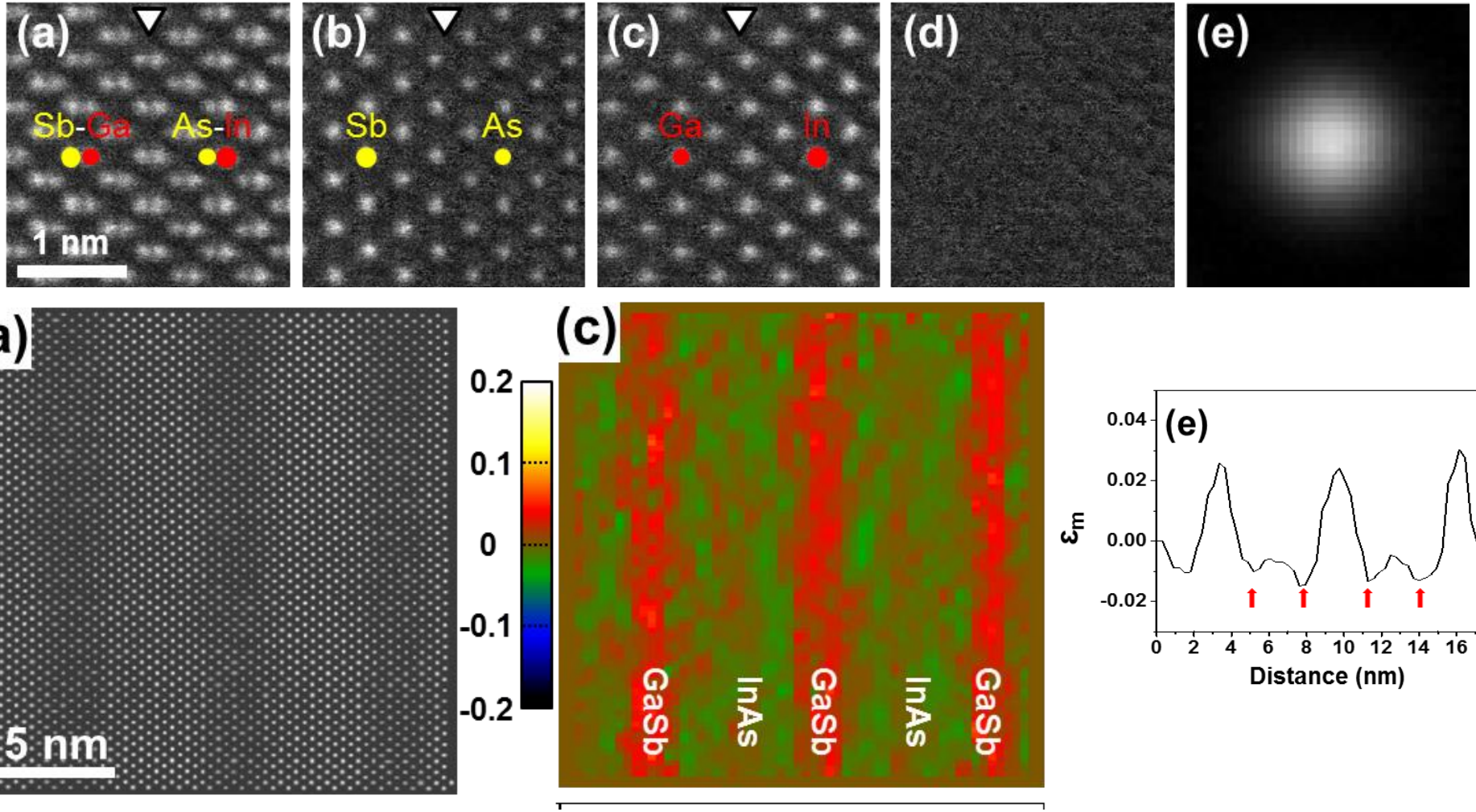


Martin, Y., Rouviere, J. L., Zuo, J. M., & Favre-Nicolin, V. (2016). Towards a full retrieval of the deformation tensor F using convergent beam electron diffraction. *Ultramicroscopy*, *160*, 64-73.



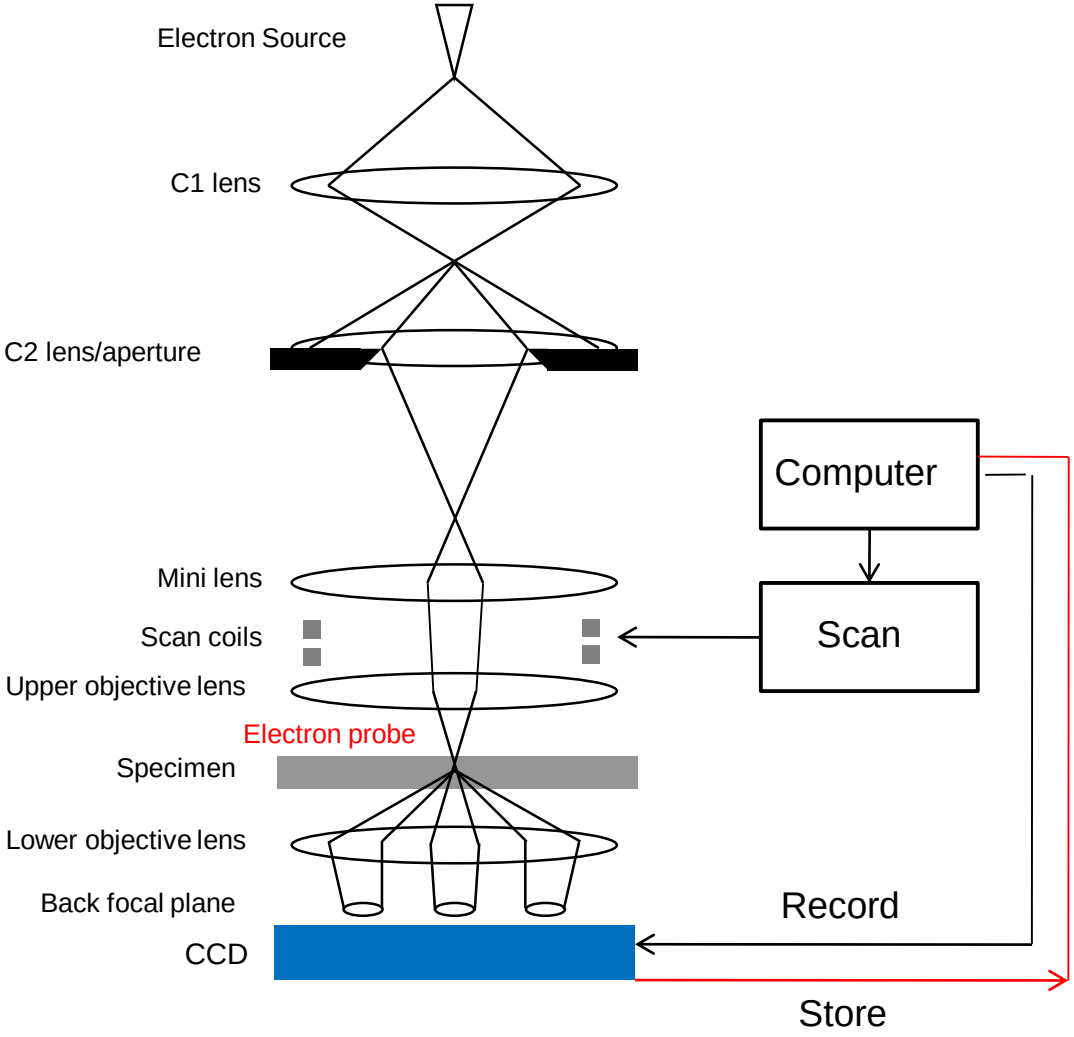
Spesspot, Ph. D Thesis

Use of STEM

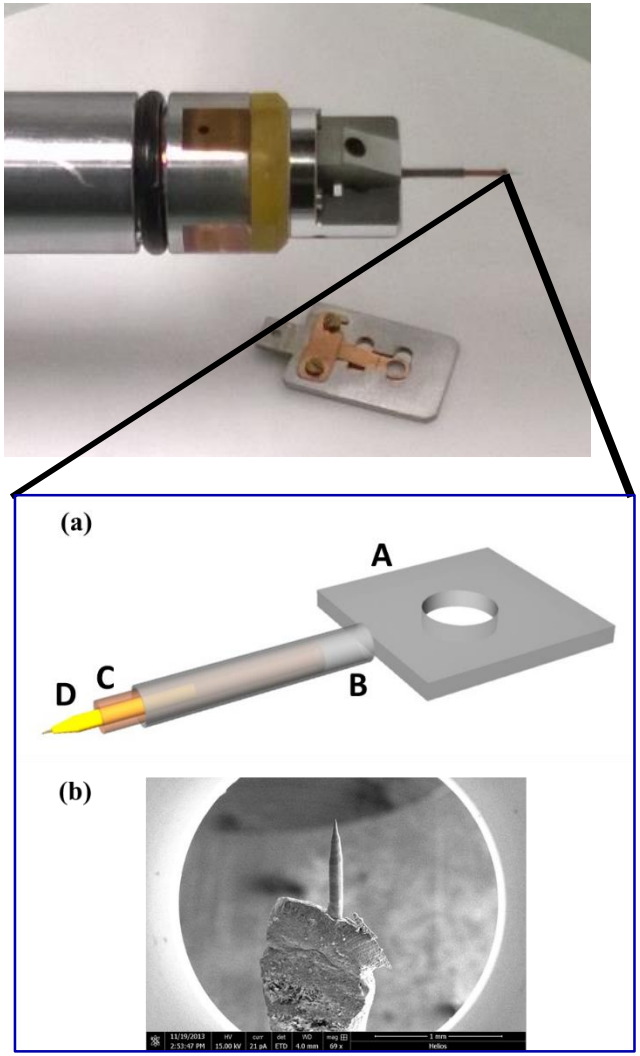


Micron, Volume 92, January 2017, Pages 6–12

Diffraction Tomography

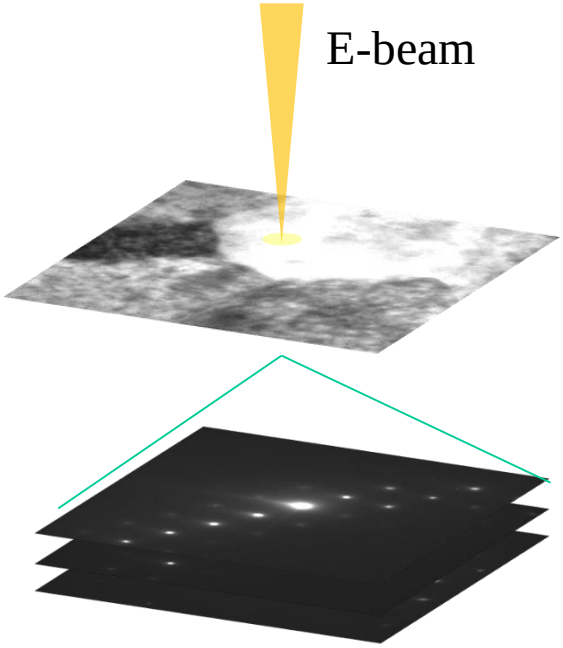


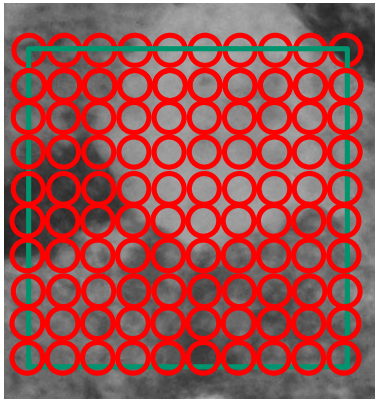
Zuo and Tao, in Scanning Transmission Electron Microscopy, Springer, 2011



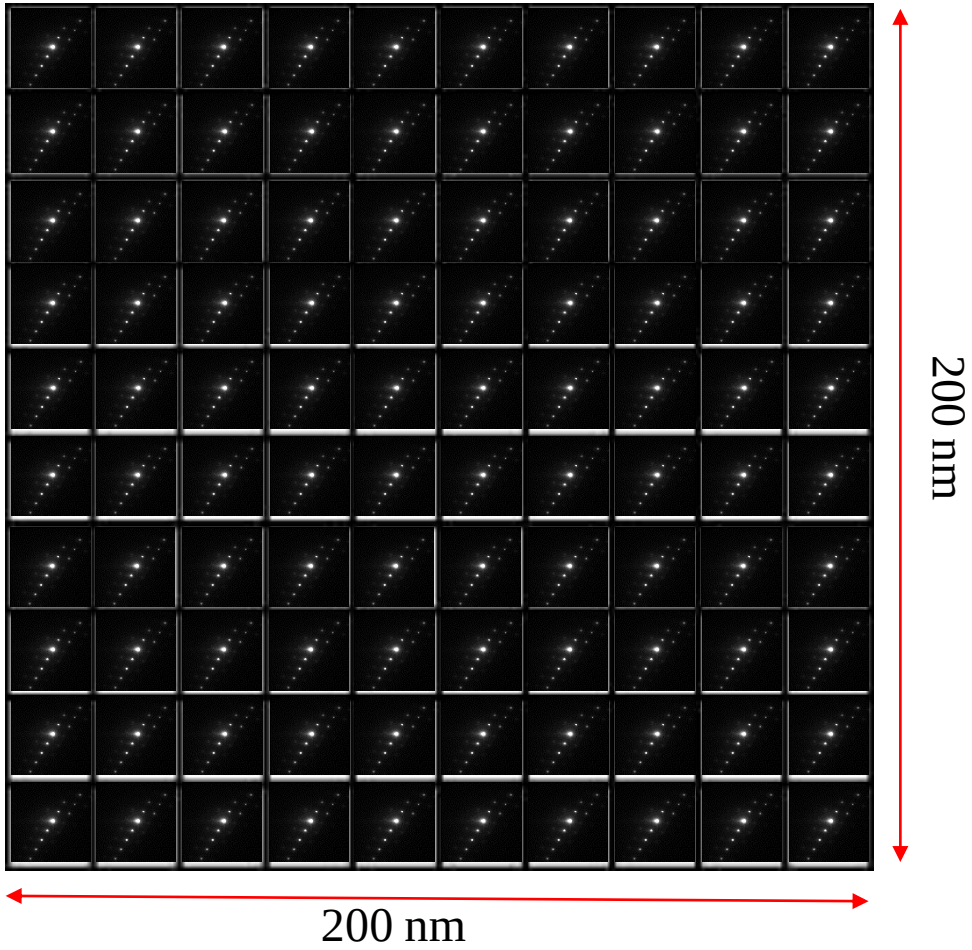
Modified JEOL single tilt holder
Meng and Zuo, IUCRJ, 2016

Scanning Electron Nanobeam Diffraction (SEND)



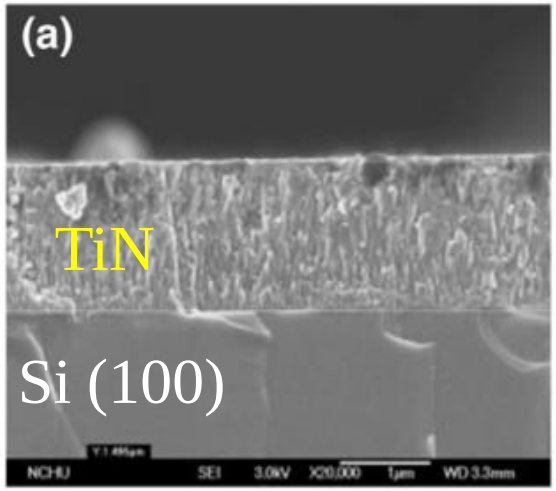


Nanocrystalline TiN film

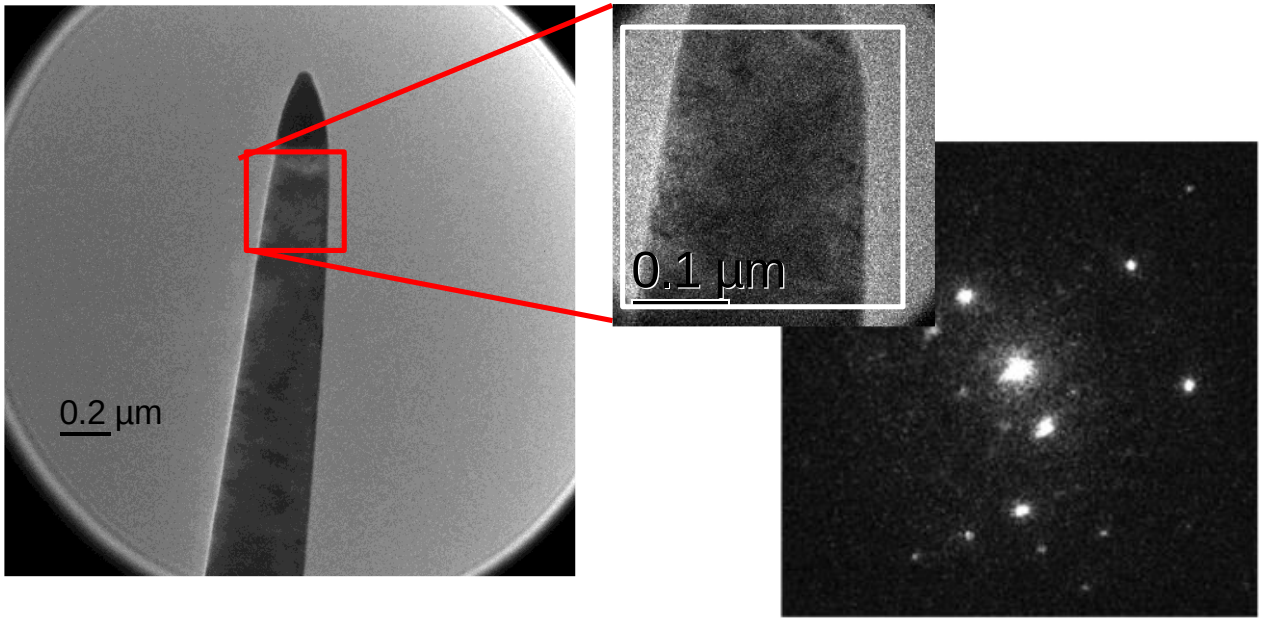


TiN sample

Sample	Pillar direction	Spot size	Scanning step	Scanning area	Exposure time	Angle covered	Rotation step	Scanning per angle
TiN	Perpendicular to the growth direction	7 nm	11 nm	26*26 (275*275 nm)	0.1 s	-85º to +85°	5°	~4 mins



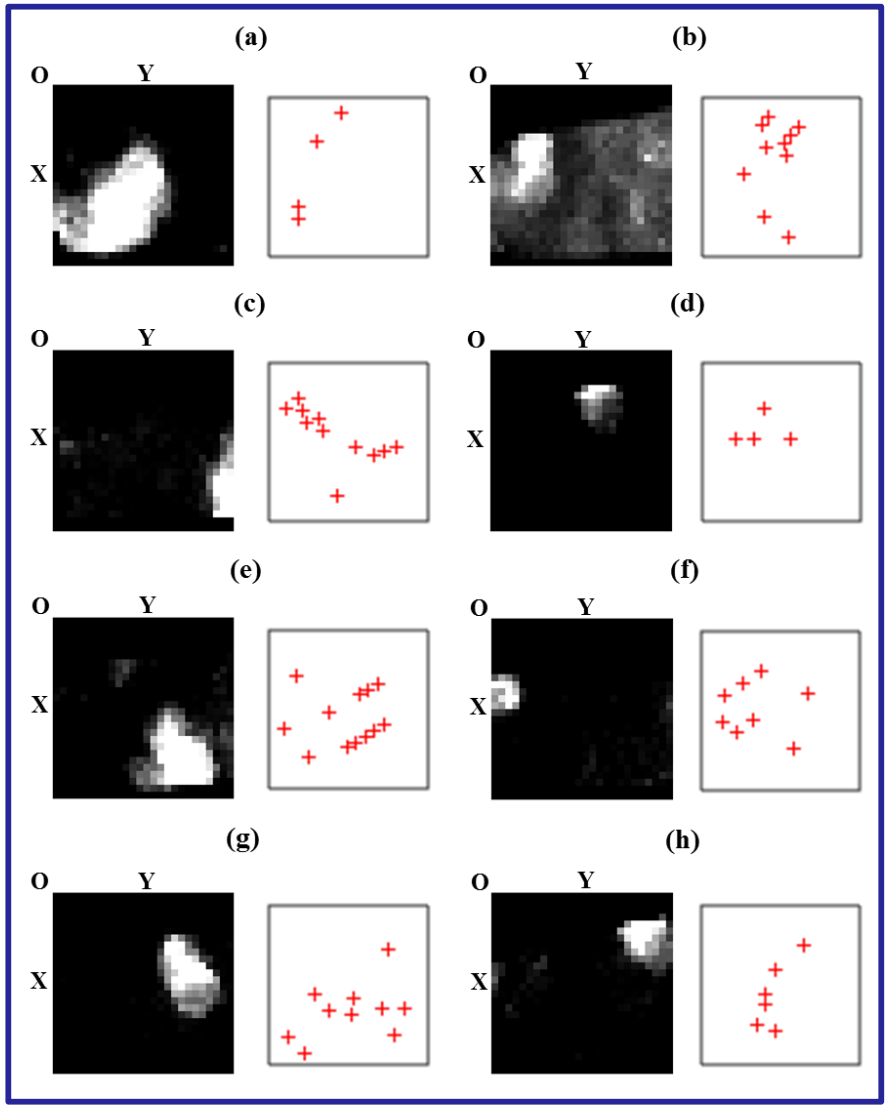
Jia-Hong Huang et al, *Surface & Coatings Technology* 239, 20-27 (2014)

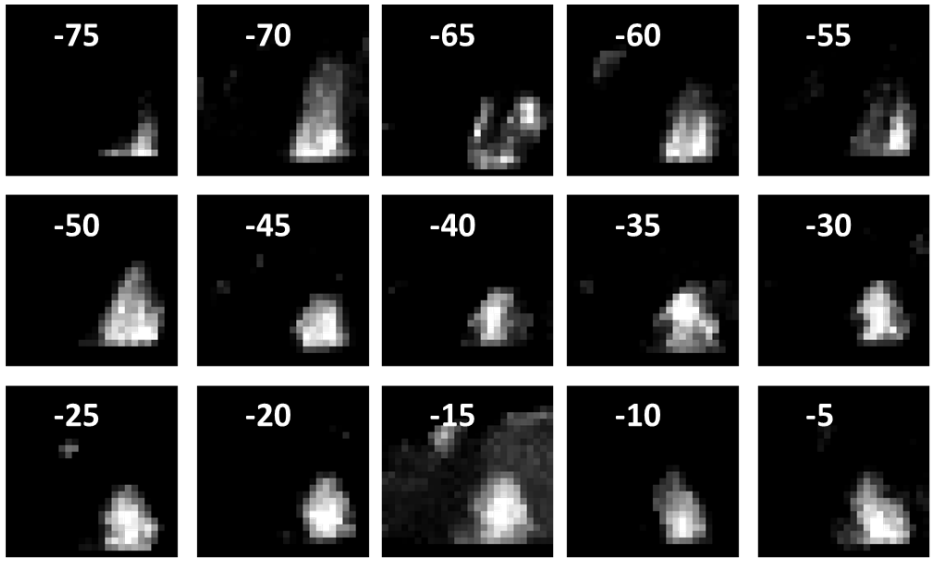


- 626 patterns are recorded for every sample rotation angle
- In total 23600 diffraction patterns are recorded
- Total experiment time: 6 ~ 8 hours

Meng and Zuo, IUCRJ, 2016 in press

Principles of Reconstruction

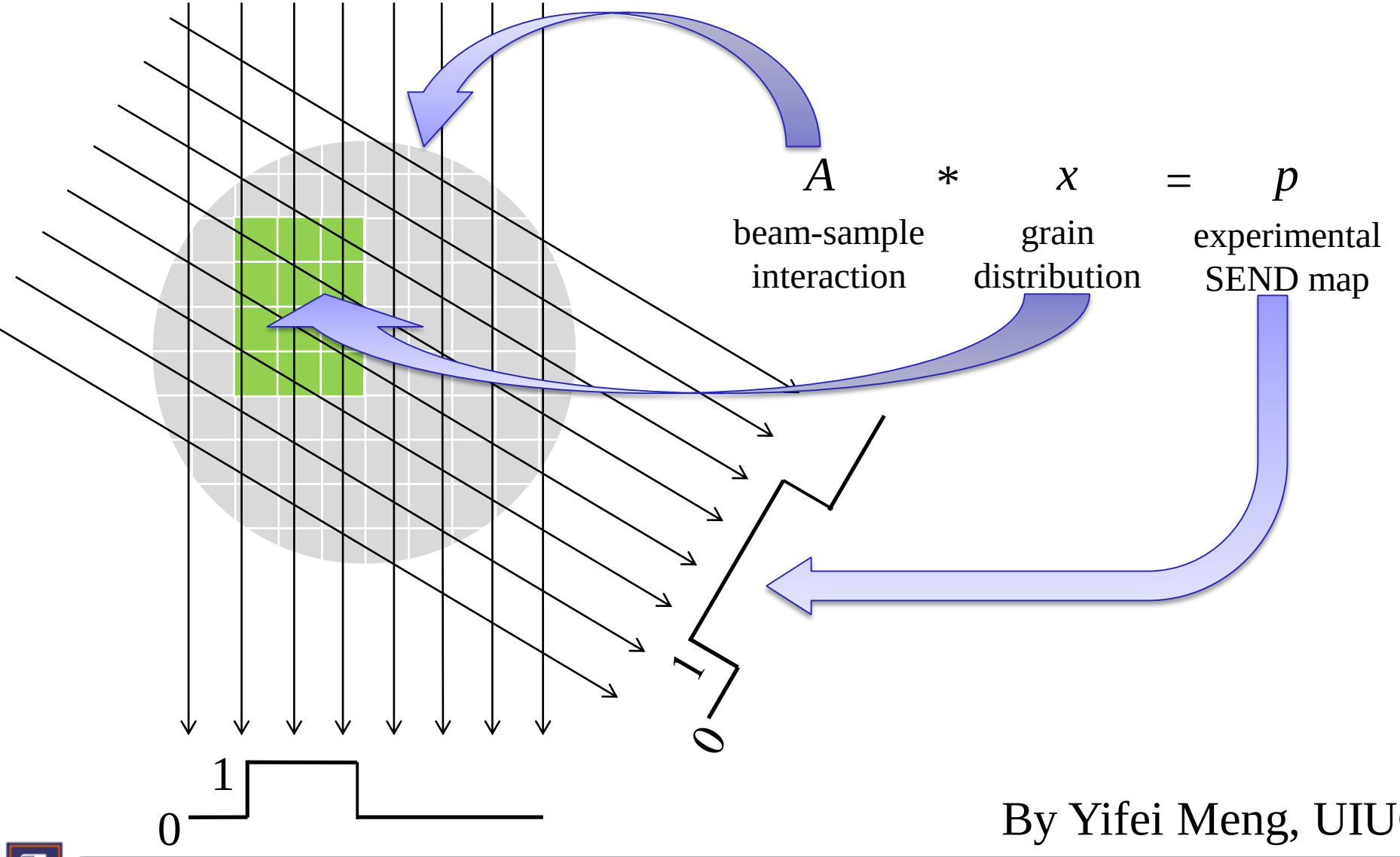




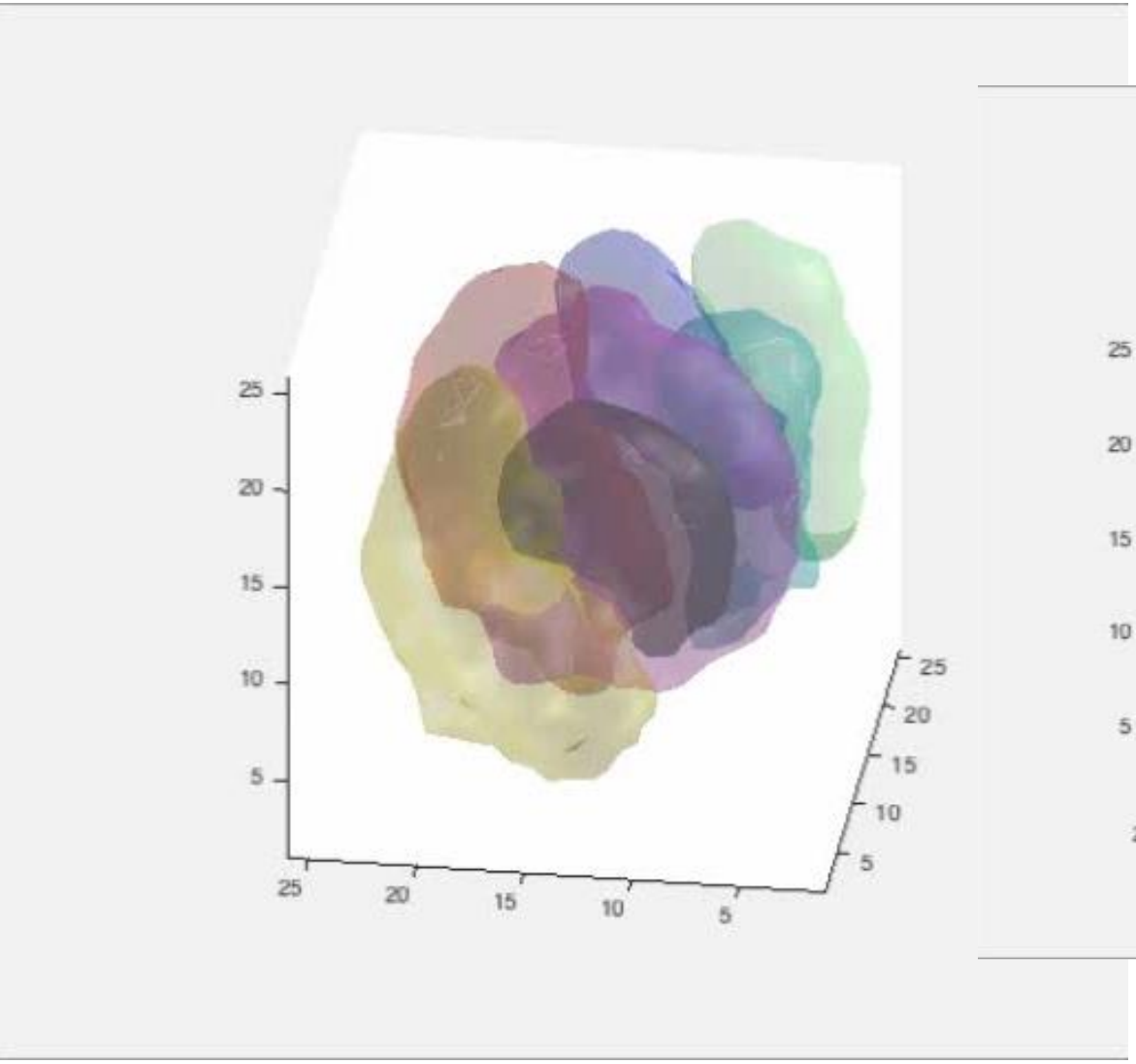
2 Projected grain image from filtered electron diffraction pattern

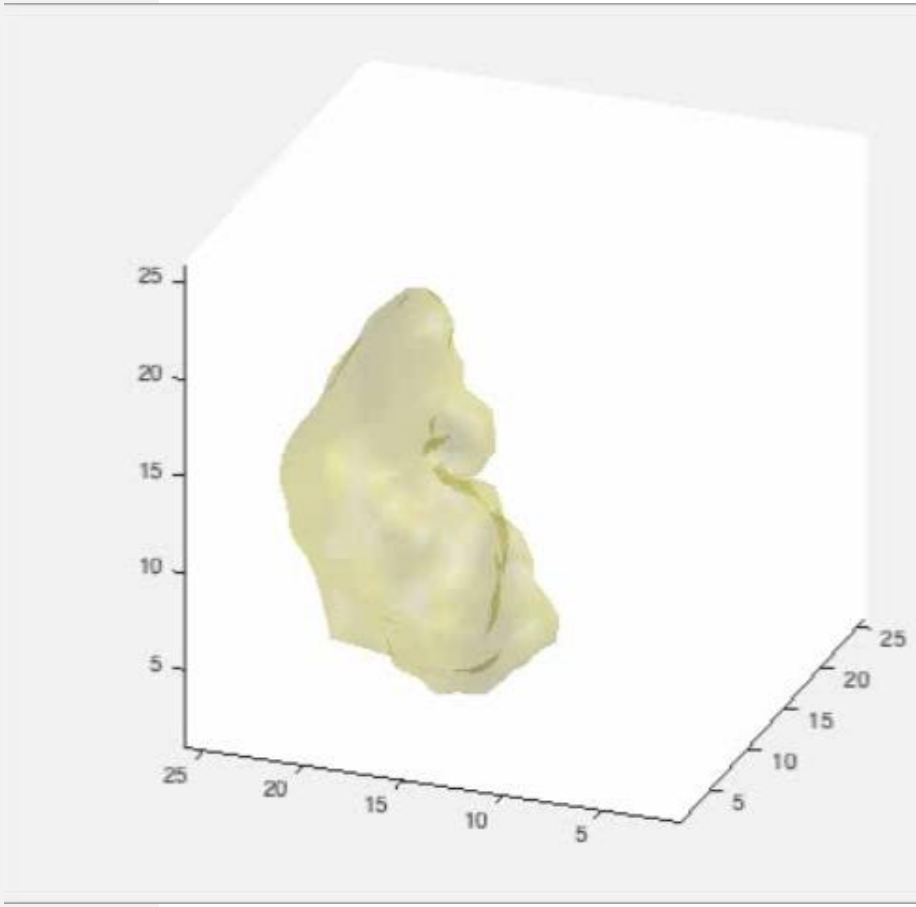
1 Spatially filtered electron diffraction patterns

Iterative reconstruction method

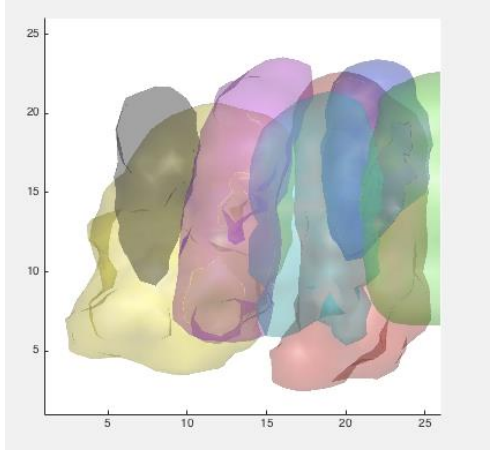


By Yifei Meng, UIUC





By Yifei Meng, UIUC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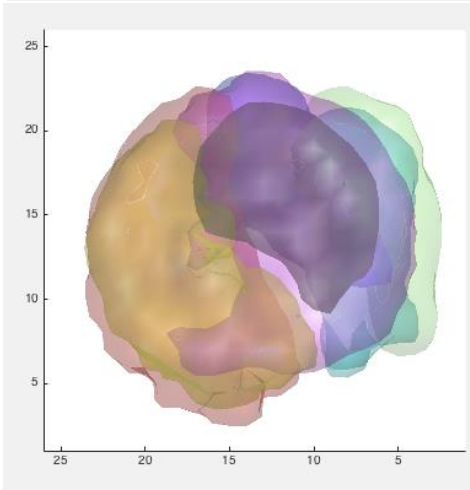
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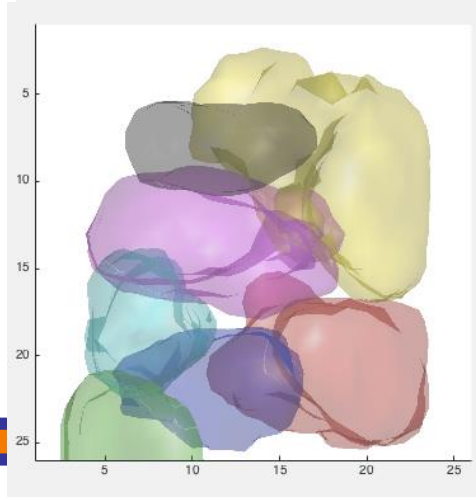
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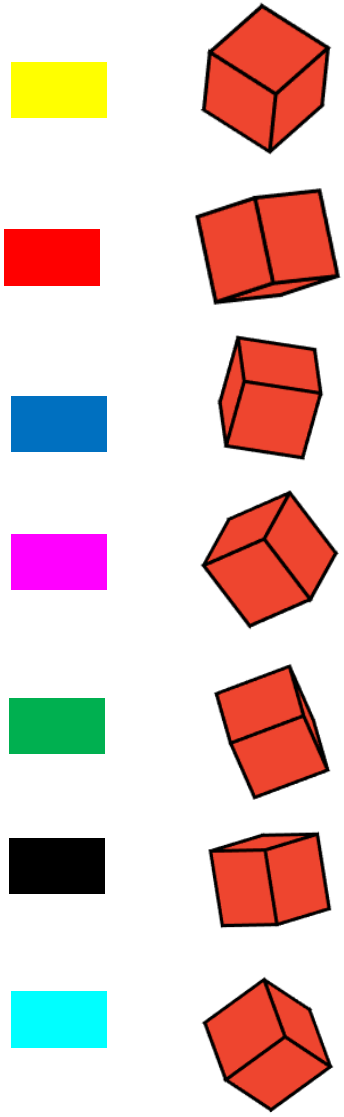
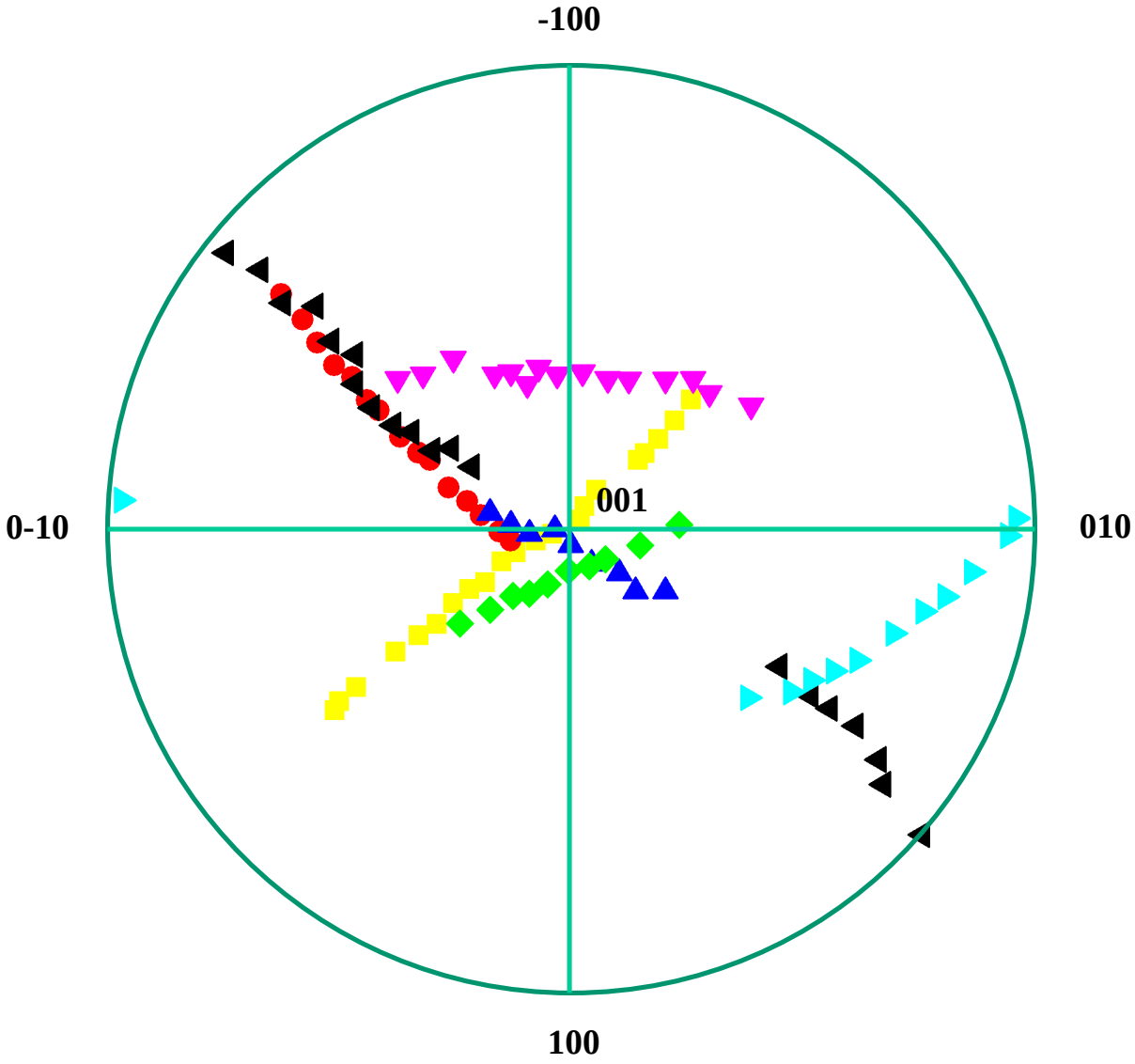
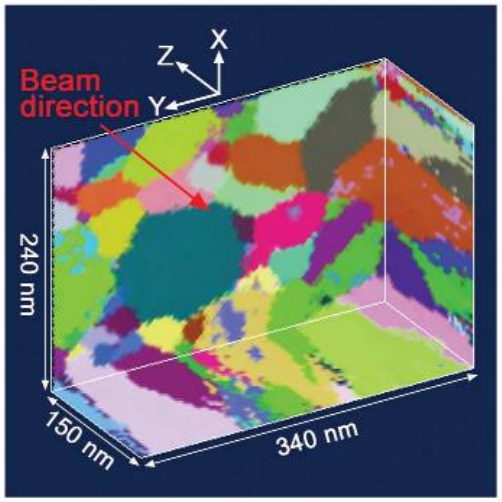




By Yifei Meng, UIUC

Conical Imaging versus 3D-SEND

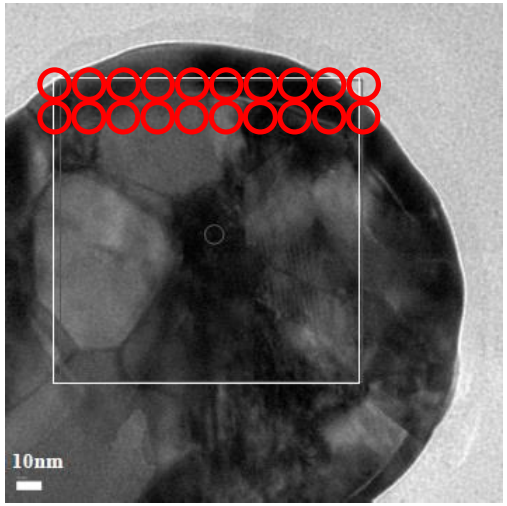


Liu, H.H., et al, Science, 2011. 332(6031): p. 833-834

- JEM-2100 TEM + Gatan CCD camera.
- ~100,000 dark-field images recorded over +/-30˚ , step of 1˚
- At tilt, the beam tilt angle was varied to cover up to 10 diffraction rings with the beam rotation angle varied 0 - 360˚ in steps of 2˚

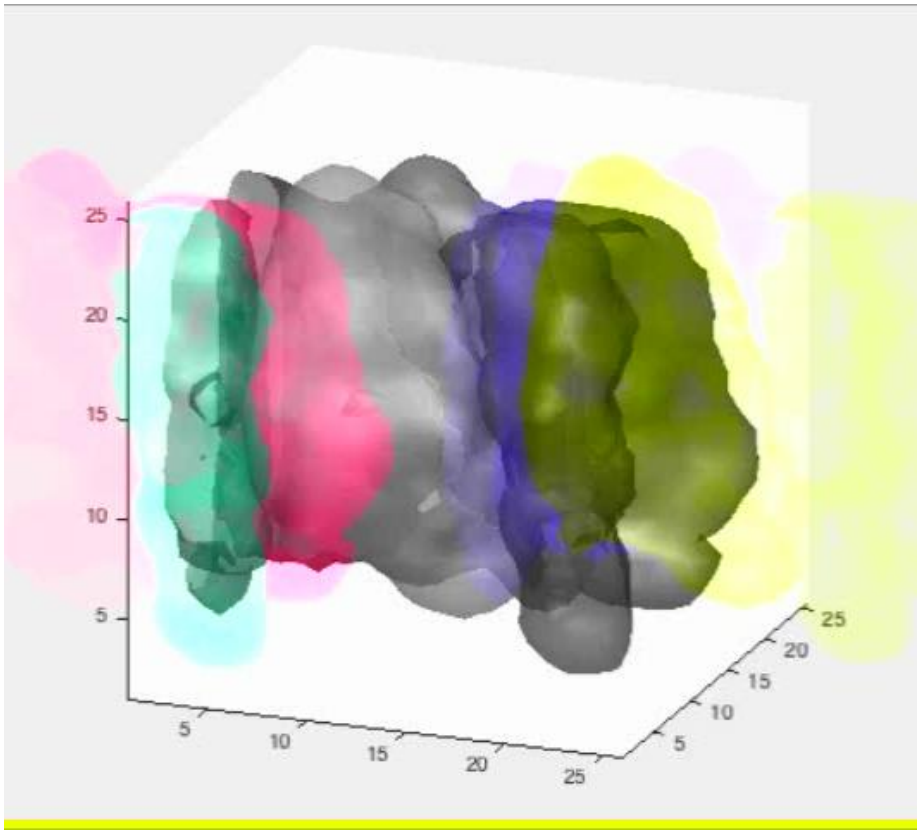
10x60x360/2 =108000 Dark-field images Sample illuminated 108000 times

30x30x170/5 =30600 Diffraction patterns Sample illuminated 34 times

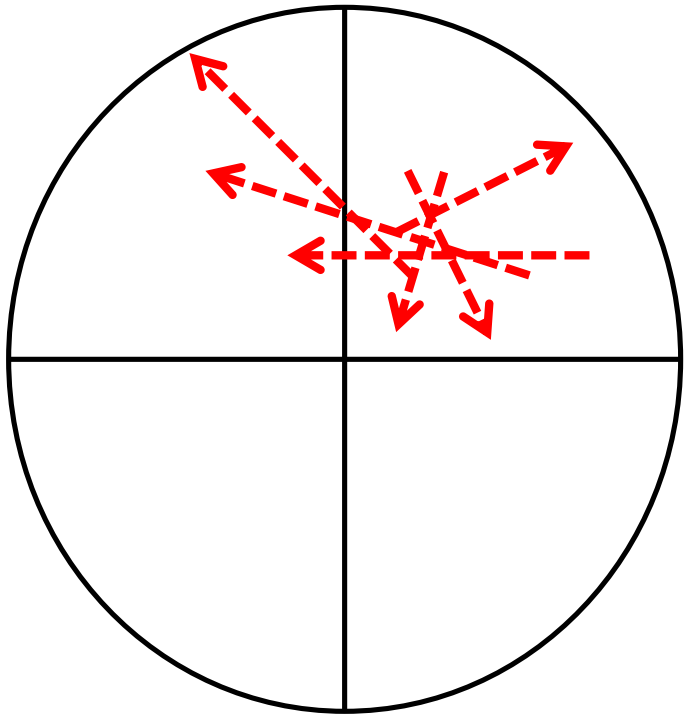


- JEOL2100
- Probe size: ~2 nm
- Step size: as needed
- Scanning area: limited by acquisition time
- Tilt range: -85 ˚ to +85 ˚
- Tilt step: 5˚

SEND data acquired from JEOL 2200FS



TiN Horizontal cut

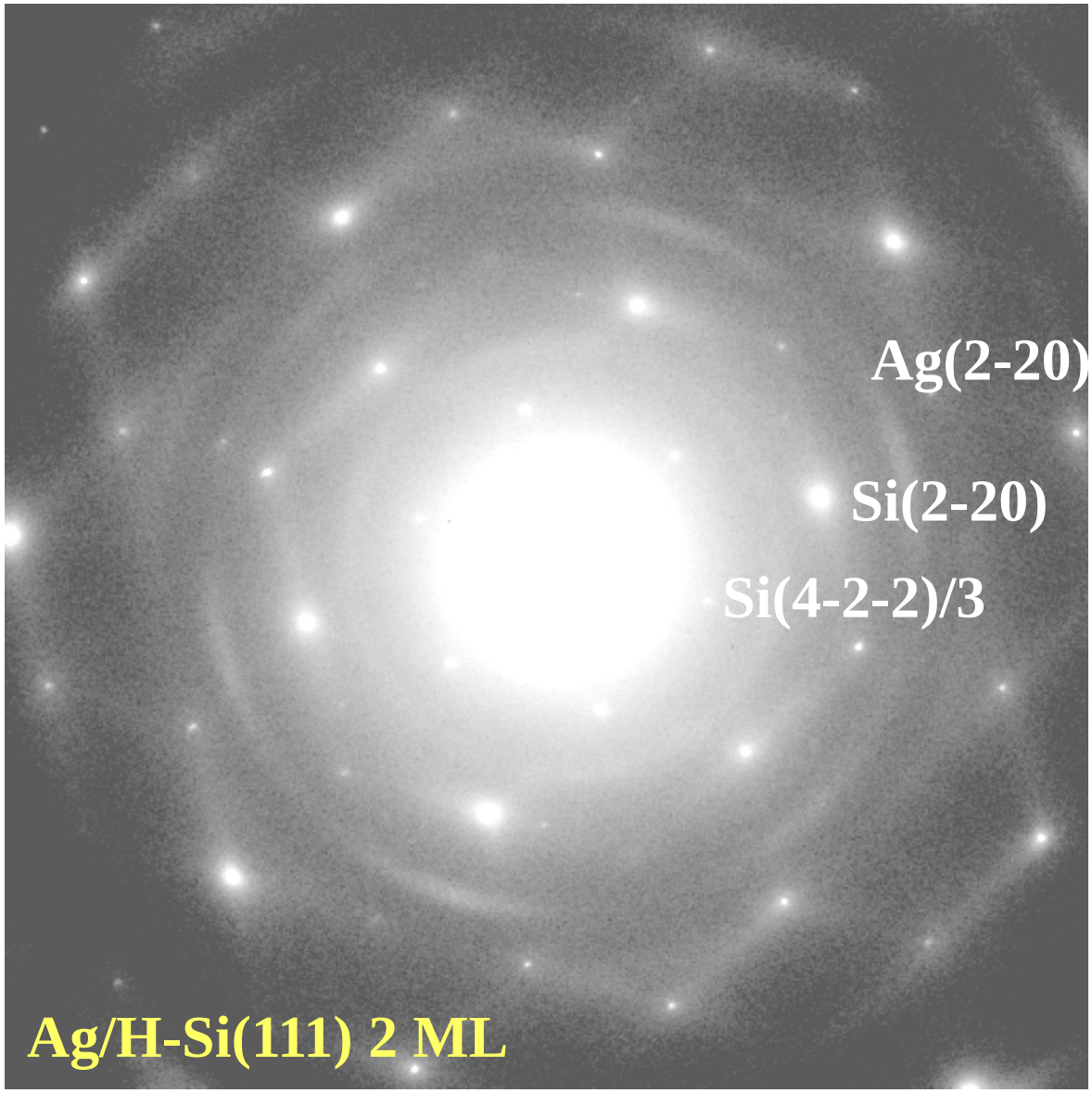


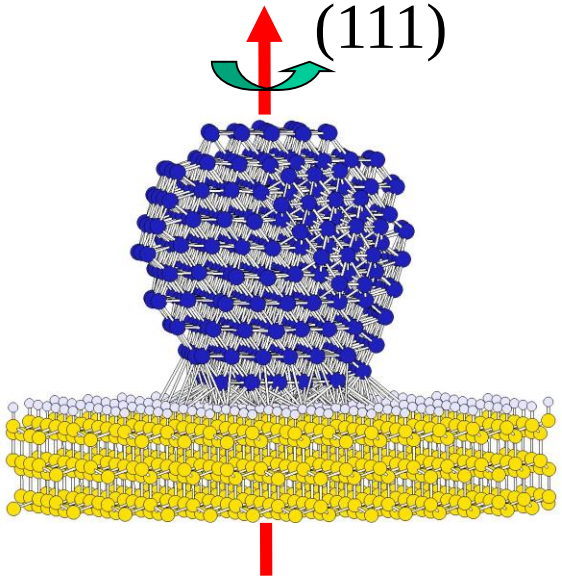
Benefits of FEG

- Smaller beam
- More intensity

Covered Topics

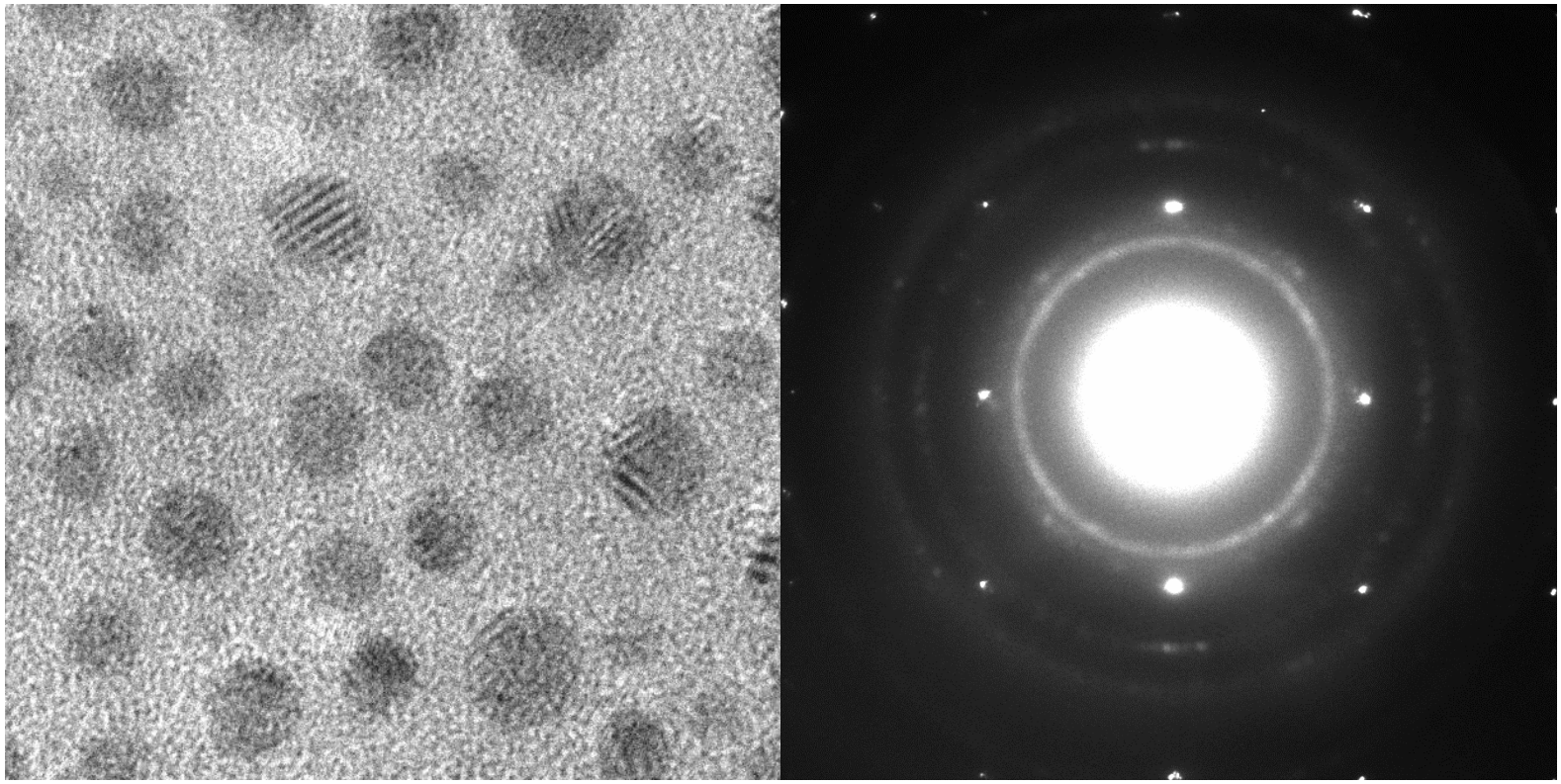
- **Indexing electron diffraction patterns**
- **Analysis of SEND patterns**
- **HOLZ Lines**
- **Strain**
- **Electron diffraction tomography**
- **Nanostructure characterization**





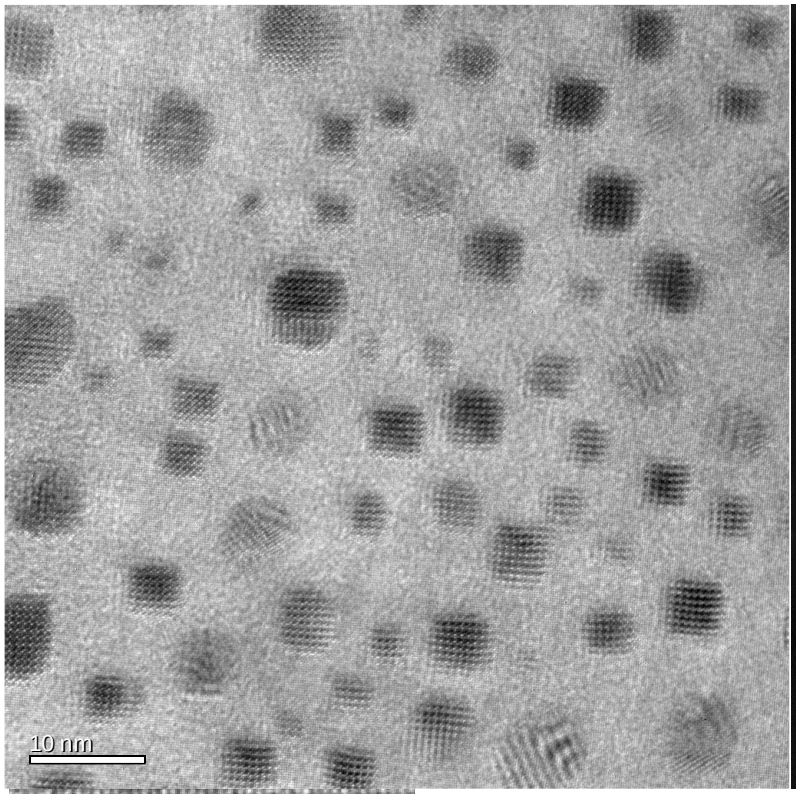
As deposited

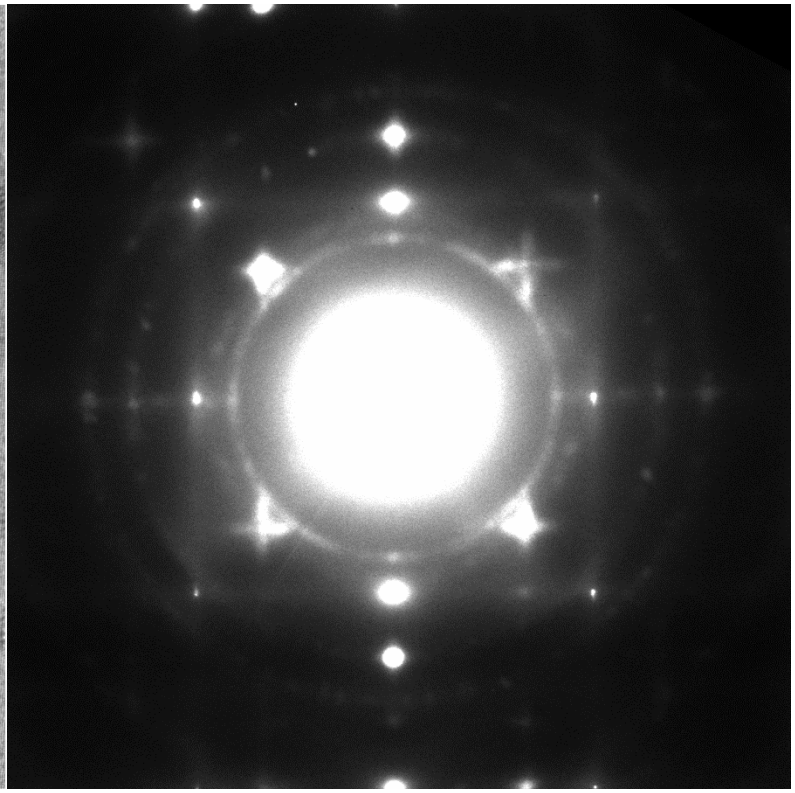
Ag on H-Si(100)

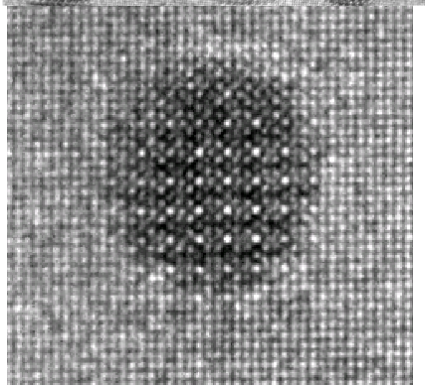


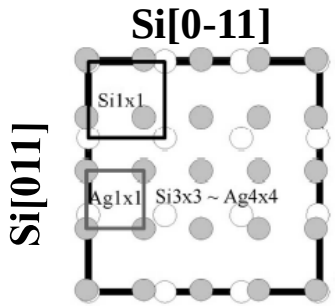
8 ML, RT as deposited

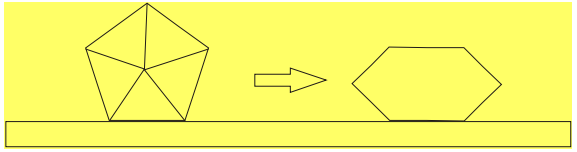
8 ML, Annealed for 2 hrs at 450ºC





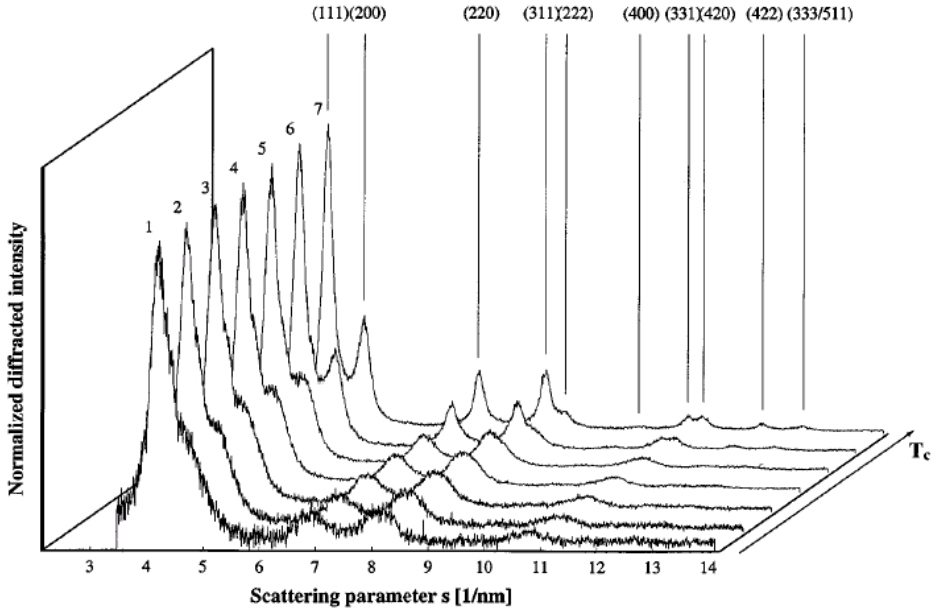




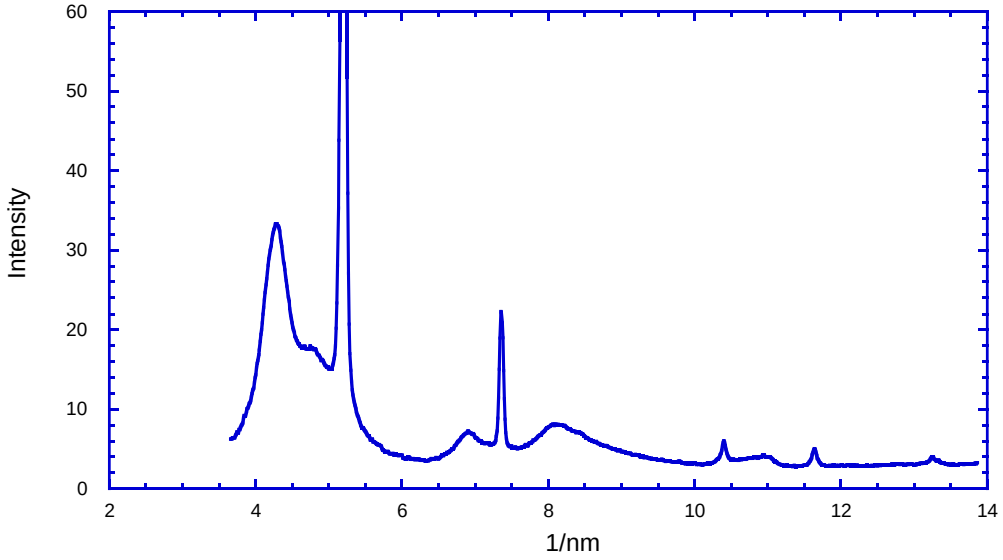


The structure of RT-deposited Ag clusters

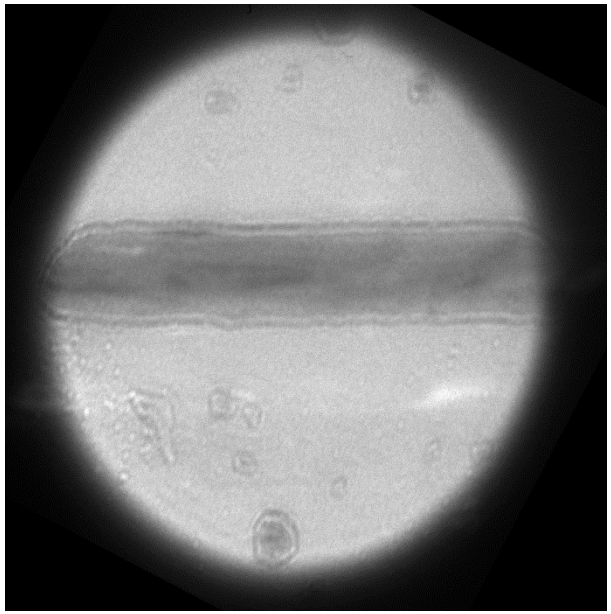
Diffraction patterns of Ag clusters in a molecular He Gas (D. Reinhard et al, PRB, 55, 7868, 1997)

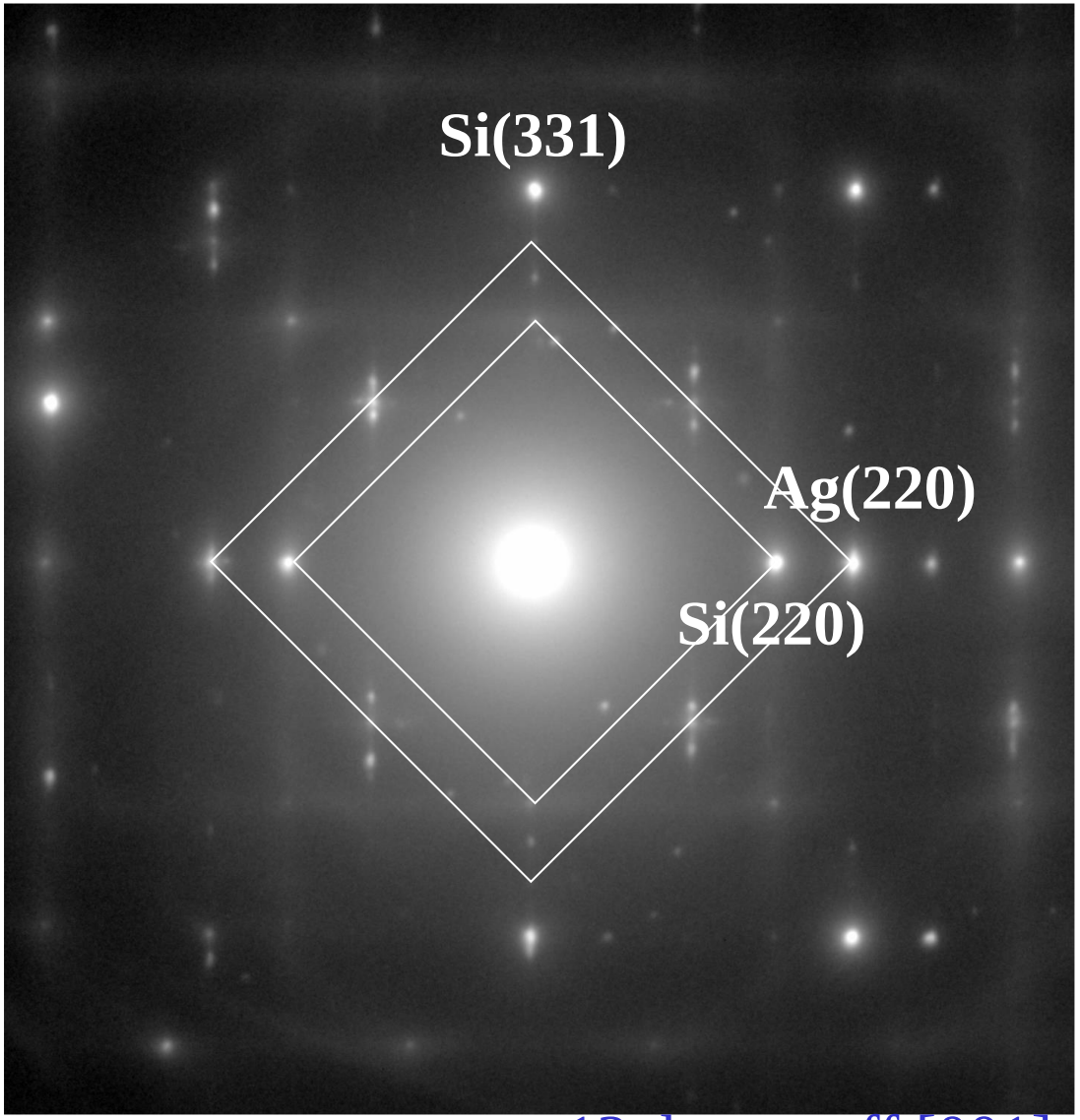


Diffraction patterns of Ag clusters on H-Si(100) deposited at RT



Where is the strain? Epitaxial Relationship





$a_{Si}/a_{Ag} \approx 4/3$

Ag(001)||Si(001)
Ag[220]||Si[220]
Or
Ag[2-20]||Si[2-20]

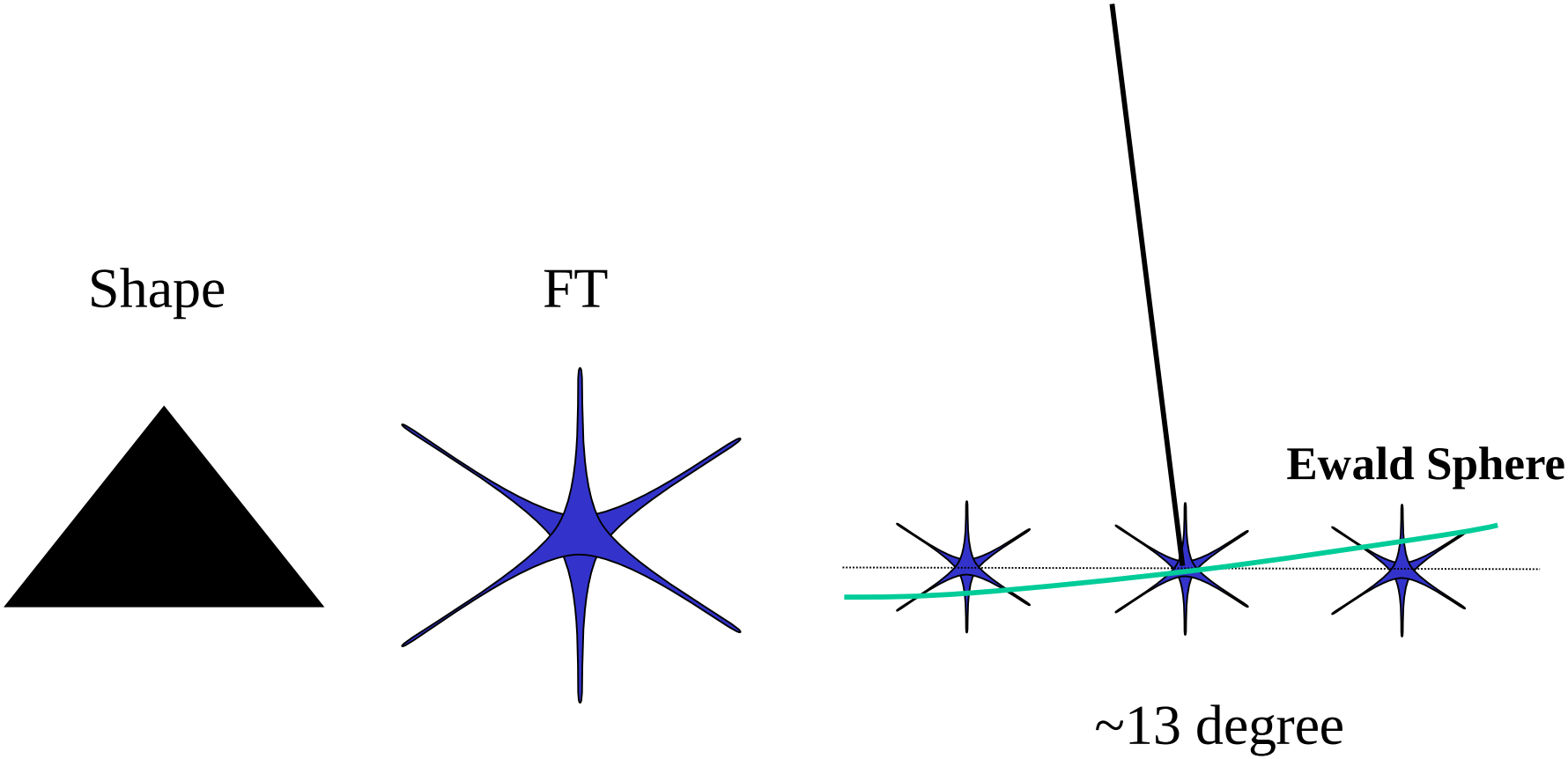
At RT: $\Delta a/a = -0.3\%$

At 450˚C: $\Delta a/a = -1\%$

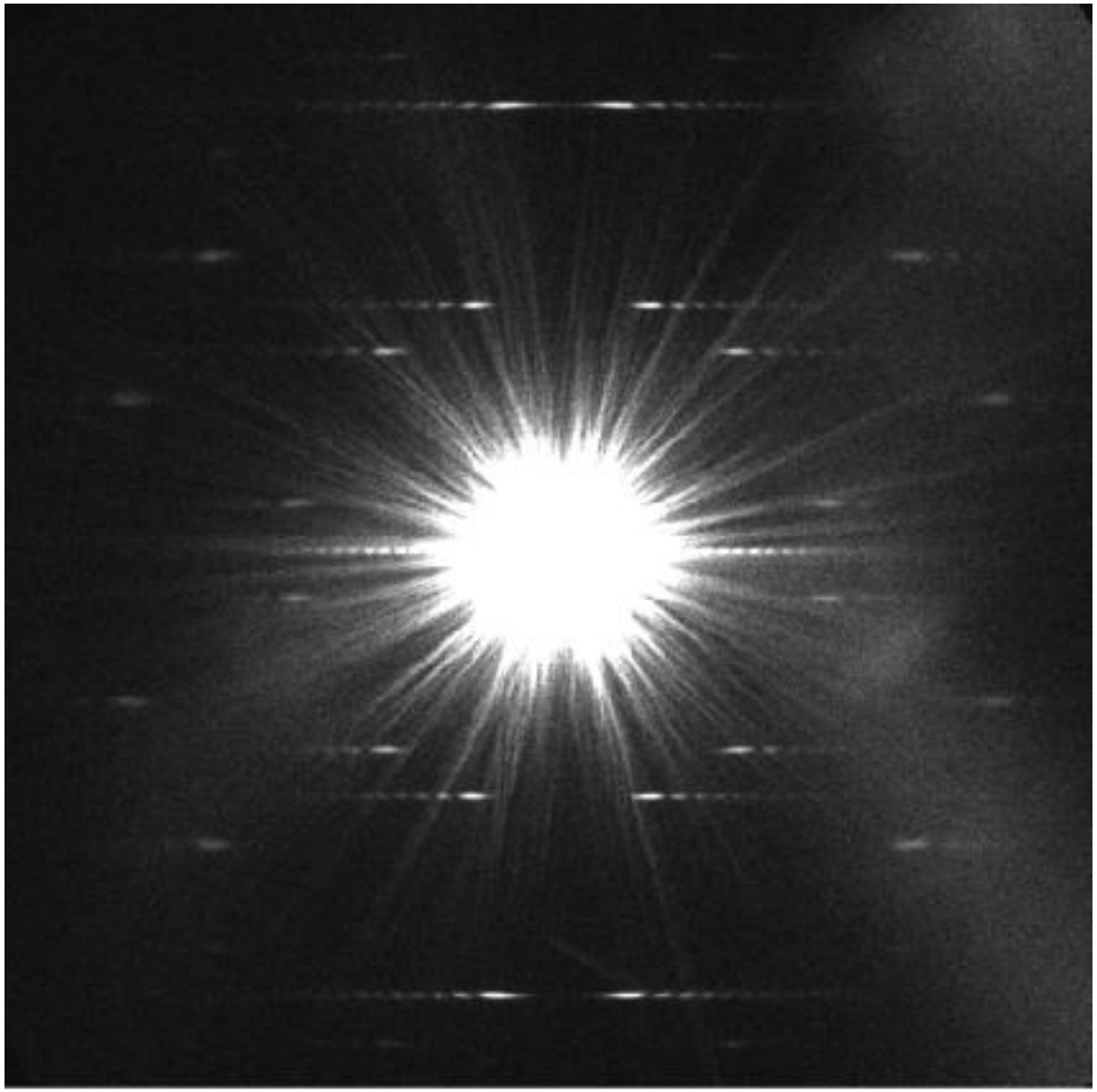
~13 degree off [001]

Shape

FT

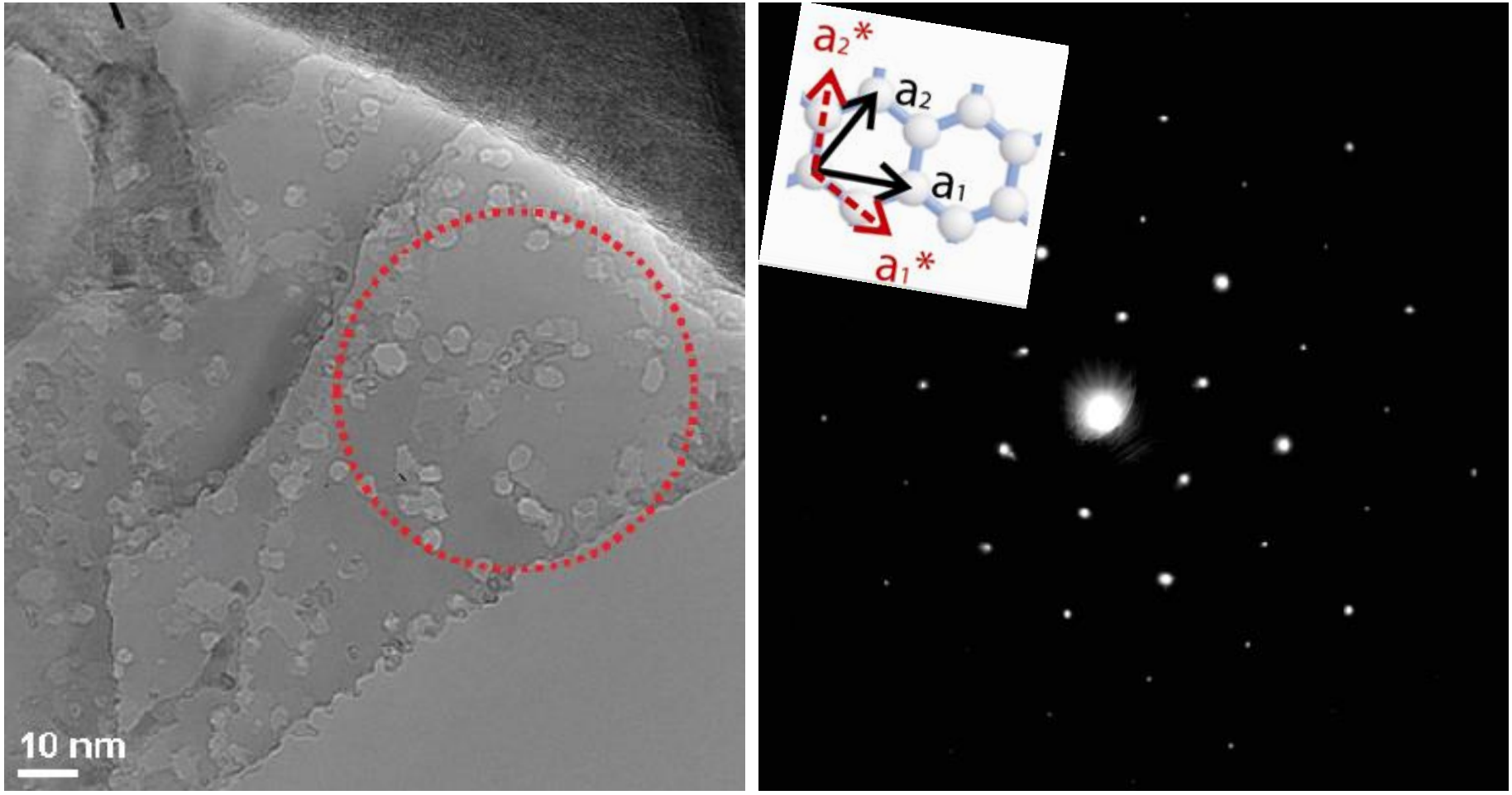


Single Wall CNT Diffraction Pattern



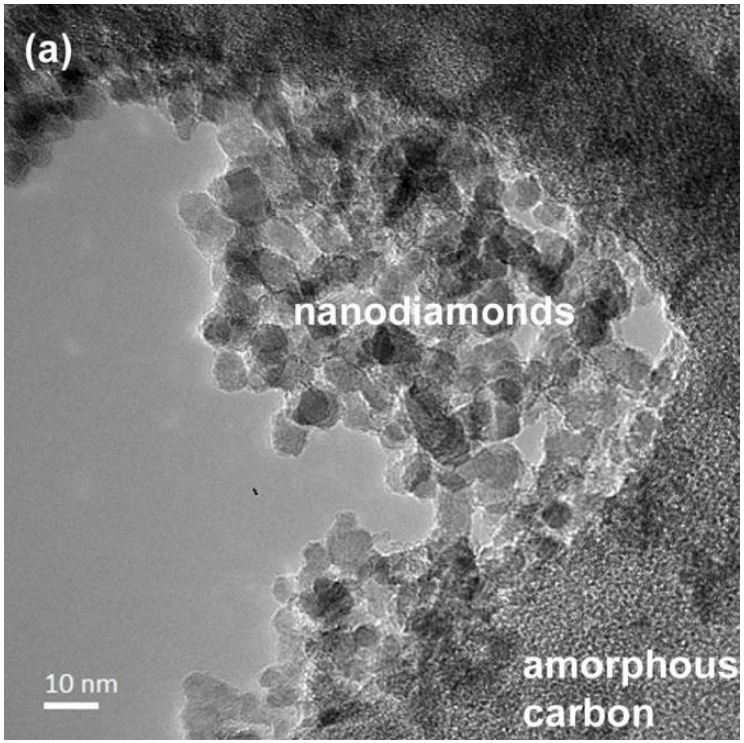
Zeitschrift fur Kristallographie 222, 625-633 (2007)

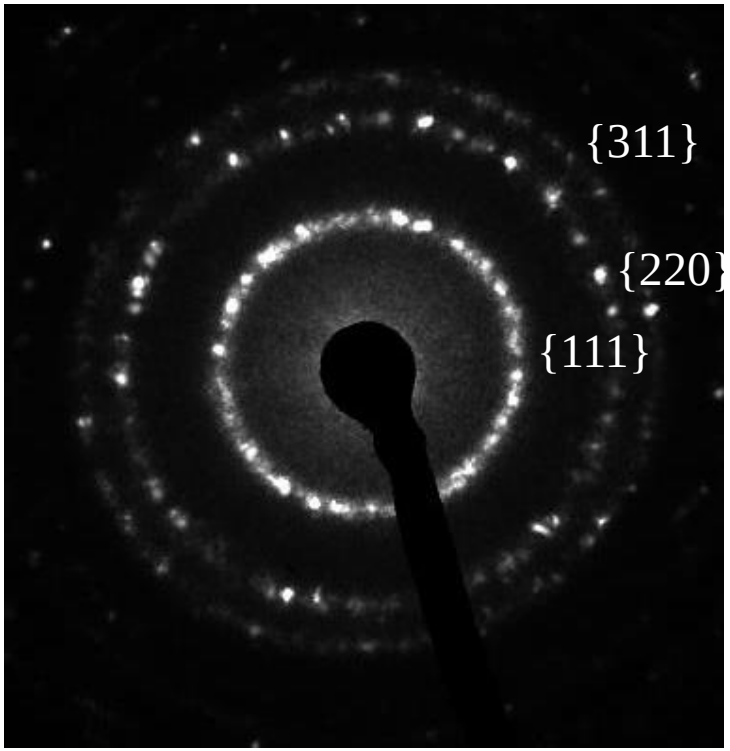
Diffraction from Graphene



From Ke Ran, UIUC

Nano-diamond

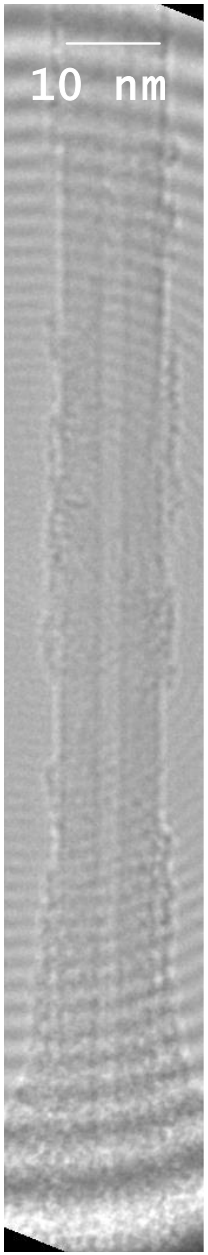


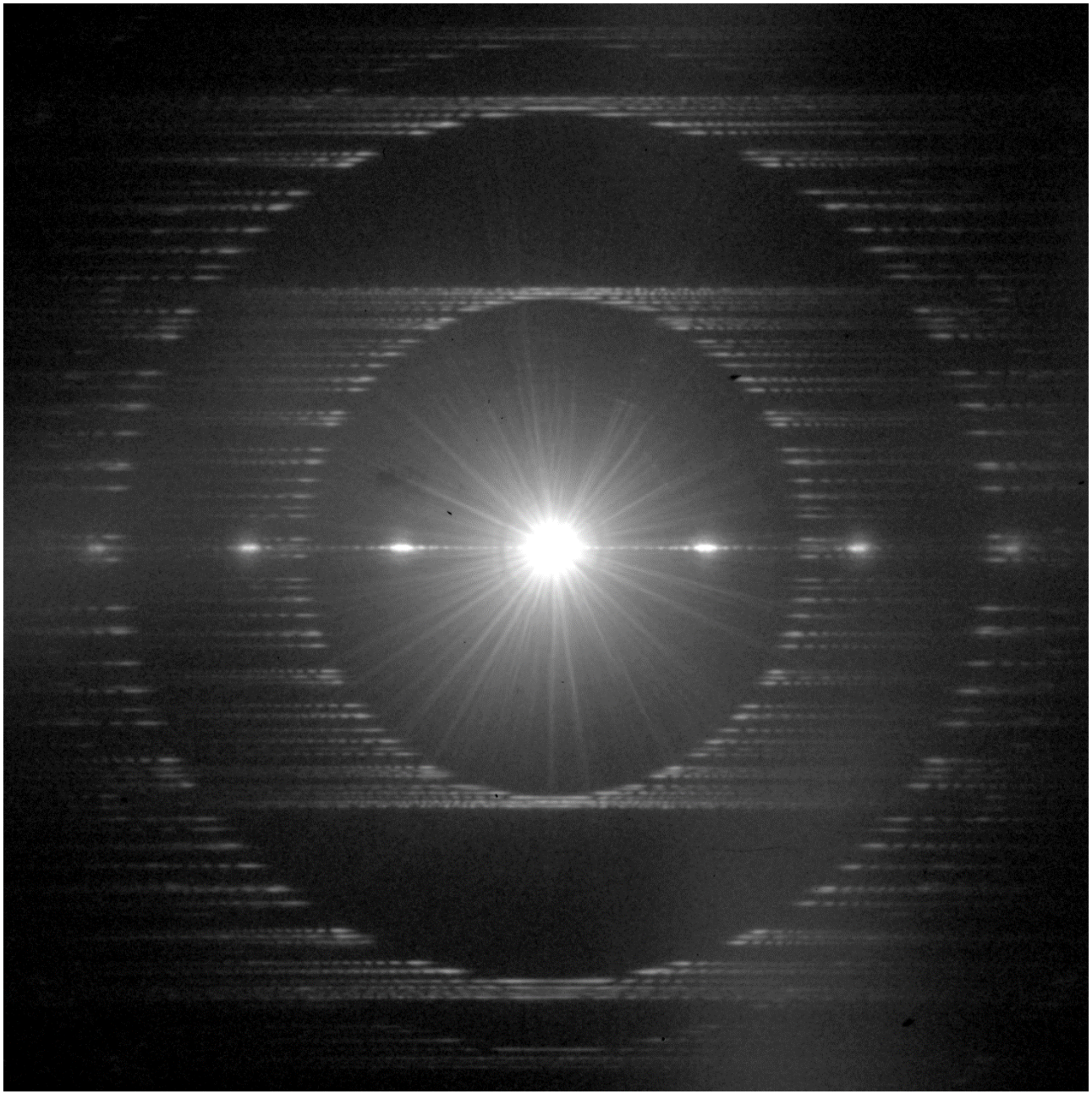


No {002} spots observed
No graphite reflections

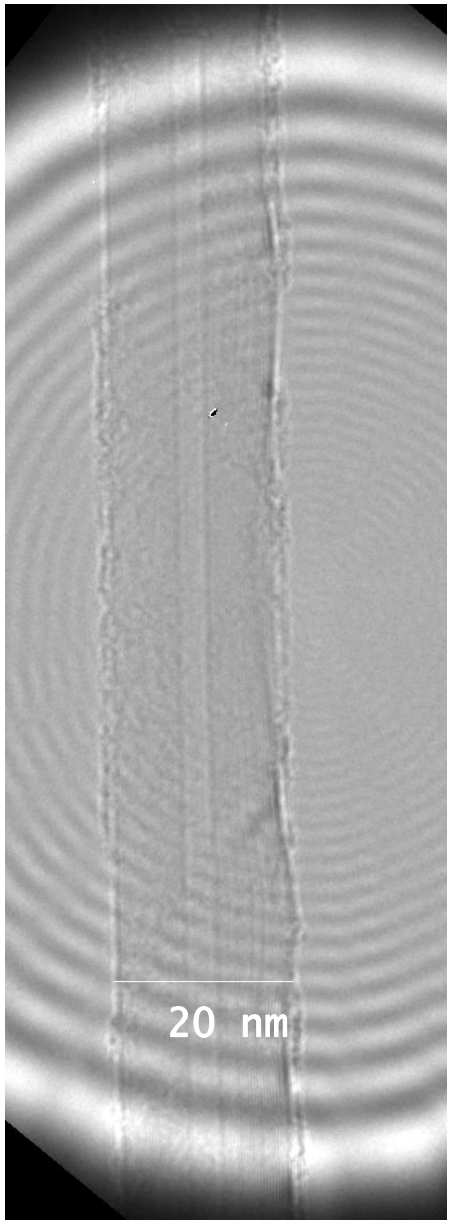
Jiong Zhang, Thesis, UIUC

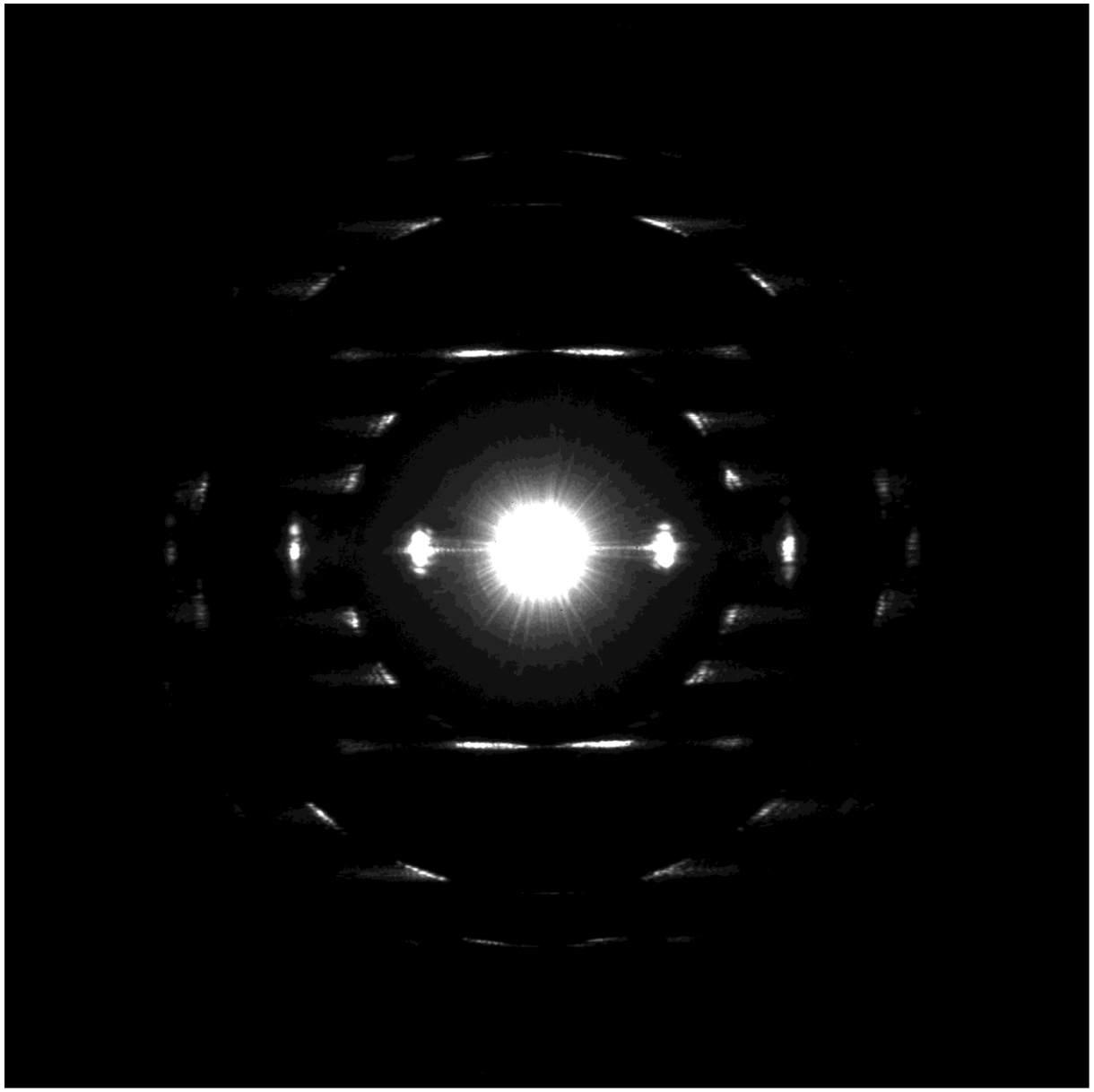
Multiwall Carbon Nanotubes (Arc Discharge)



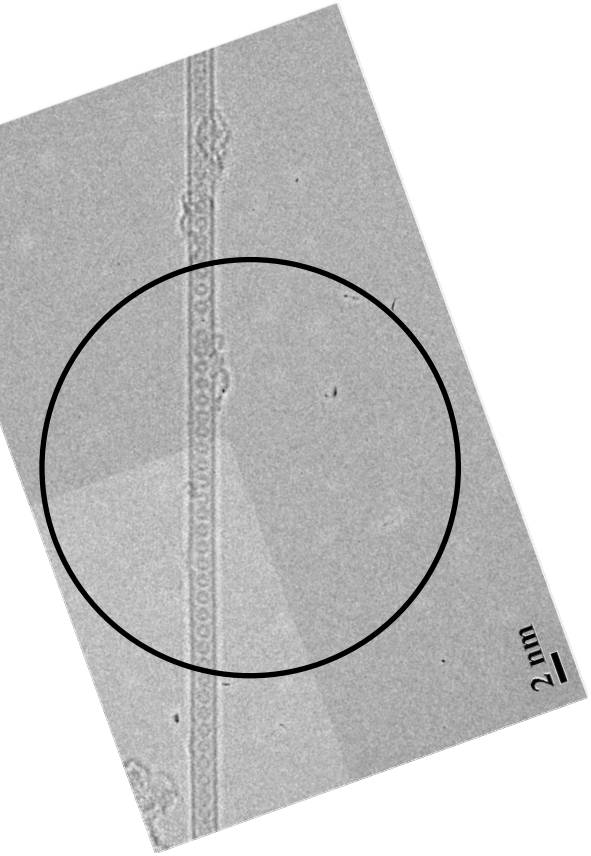


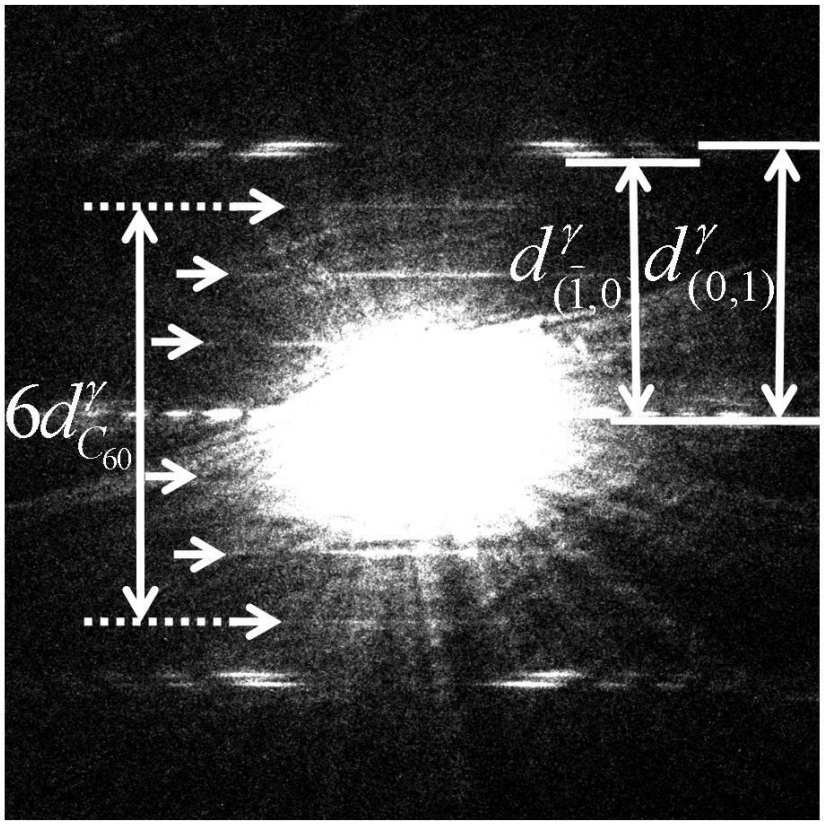
Multiwall Carbon Nanotubes

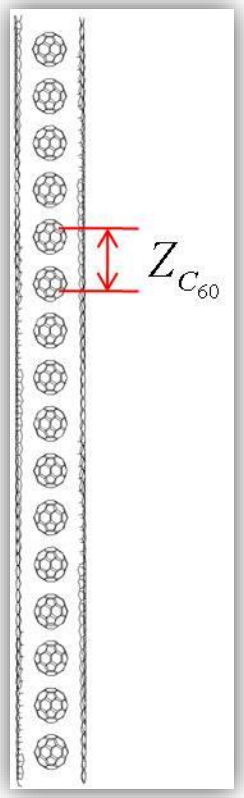




Single Peapod Electron Diffraction Pattern

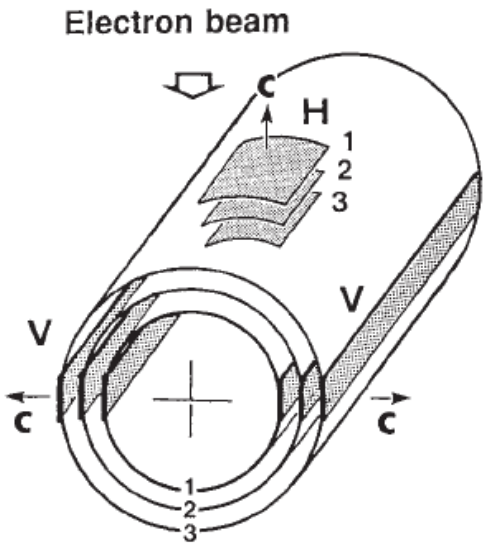


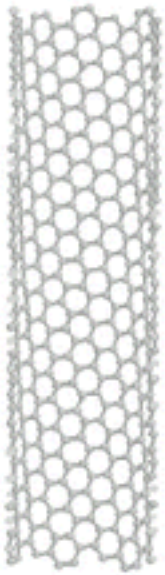


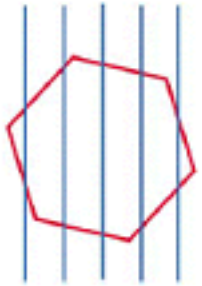


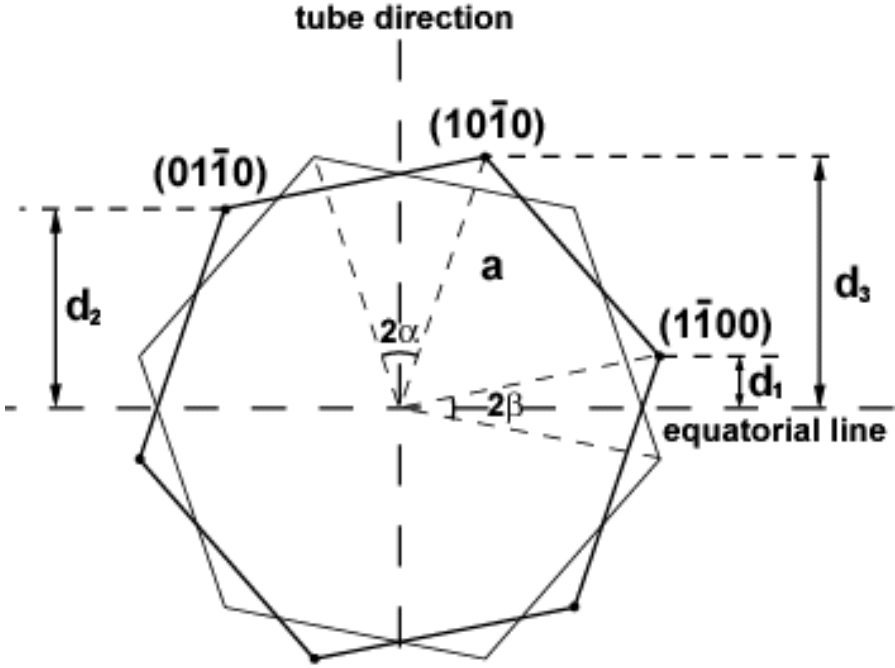
K. Ran, X. Mi, Z. J. Shi, Q. Chen, Y. F. Shi, and J. M. Zuo, Carbon 50 (15), 5450-5457 (2012)

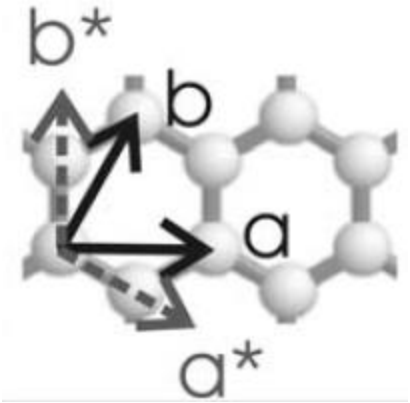
Understanding Nanotube Diffraction









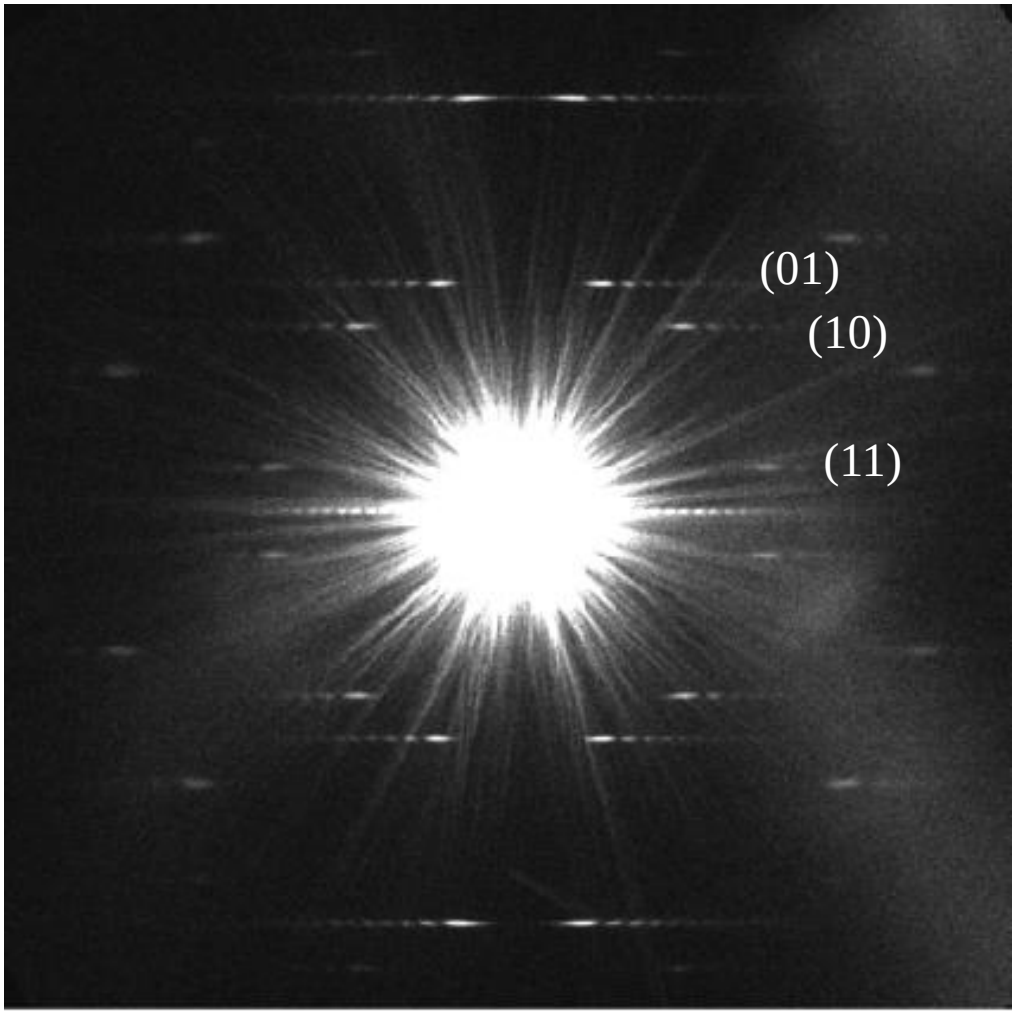


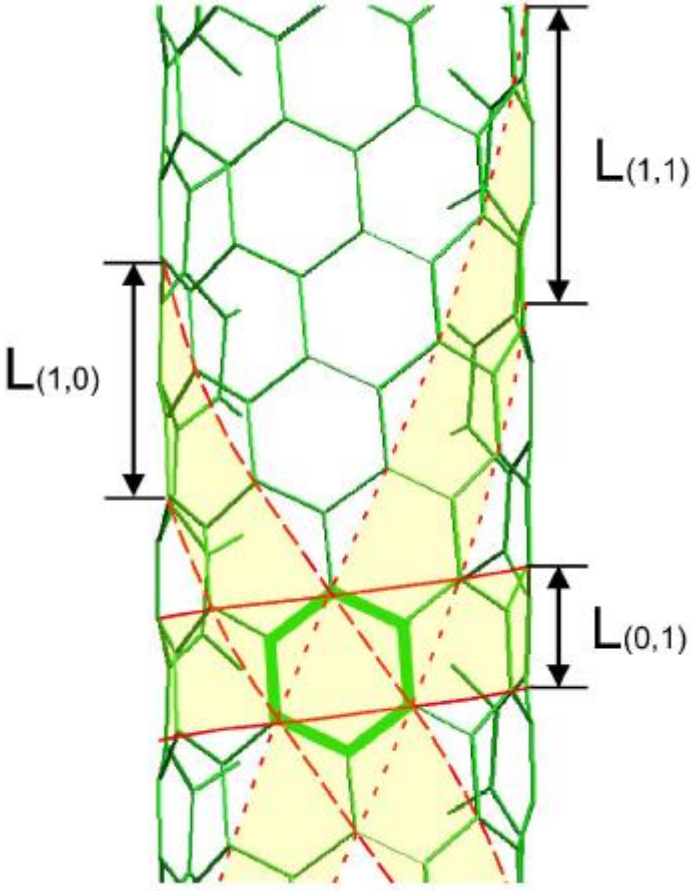
$$\alpha = \text{atan}\left(\frac{1}{\sqrt{3}} \bullet \frac{d_2 - d_1}{d_3}\right)$$

$$= \text{atan}\left(\frac{1}{\sqrt{3}} \bullet \frac{2d_2 - d_3}{d_3}\right)$$

M. Gao et al., "Structure determination of single wall carbon nanotubes", Appl. Phys. Lett. 82, 2703-2705 (2003)

Understanding Nanotube Diffraction





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- **J.M. Zuo and J.C.H. Spence, Advanced Transmission Electron Microscopy, Imaging and Diffraction in Nanoscience, Springer, 2017**