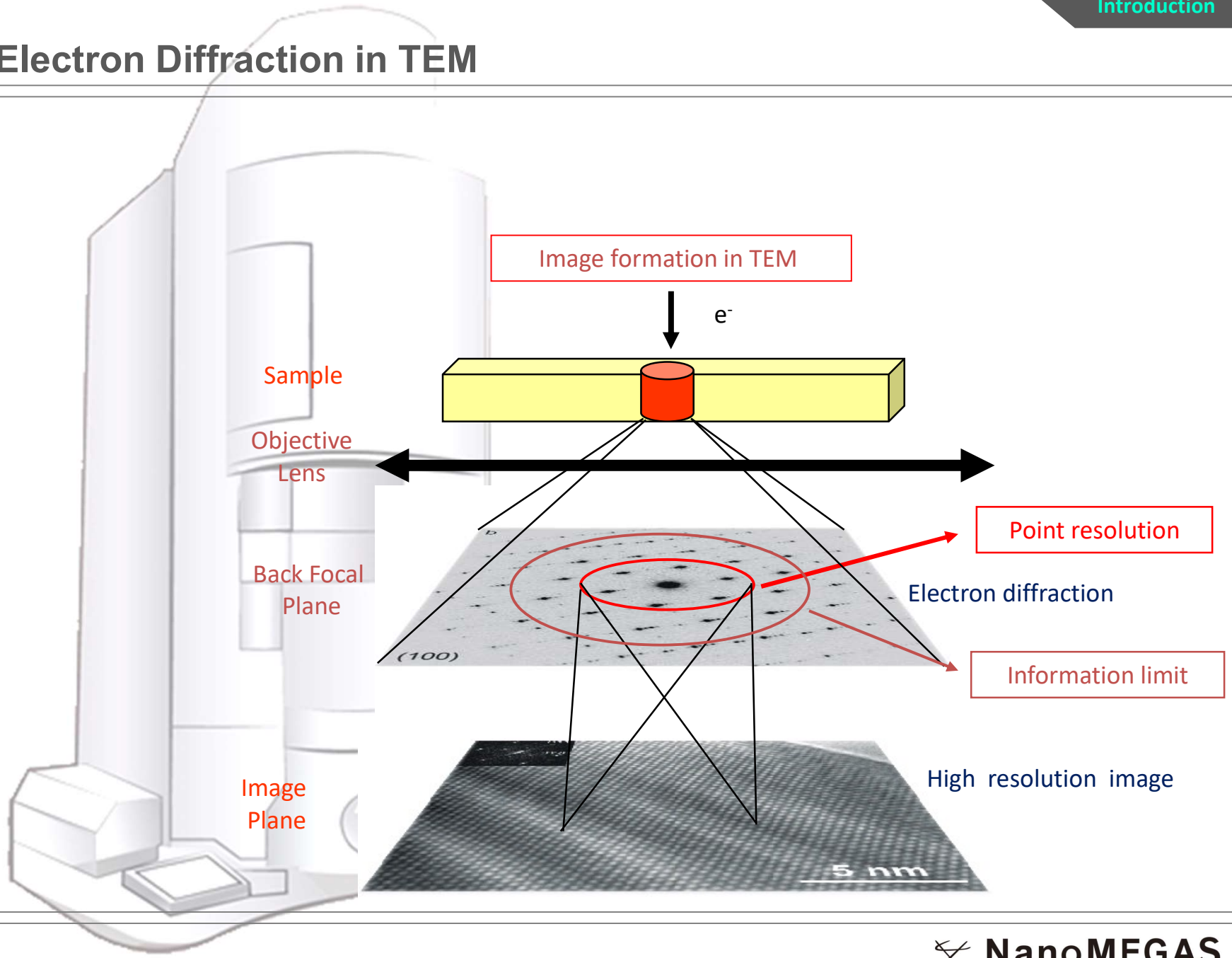
Advanced methods for the analysis of nanocrystals in nm-scale using Precession Electron Diffraction techniques in TEM

Thanos Galanis
Application Specialist

NanoMEGAS
Advanced Tools for electron diffraction

Electron Diffraction in TEM



Beam Precession Method (Vincent & Midgley 1994)

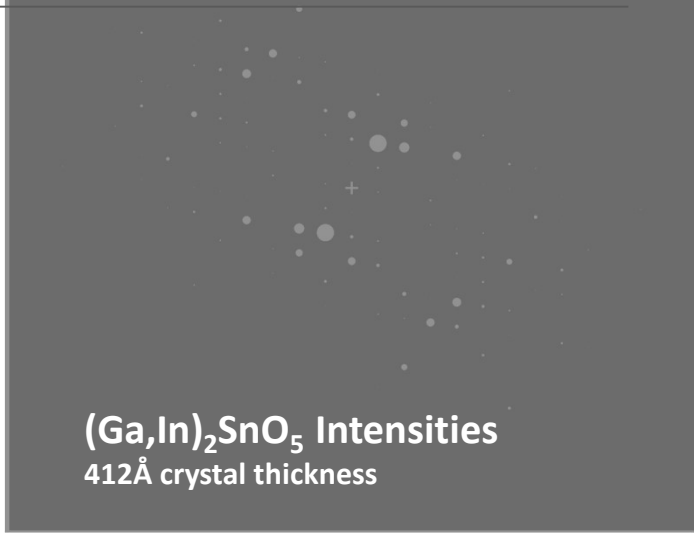
After C. Own PHD

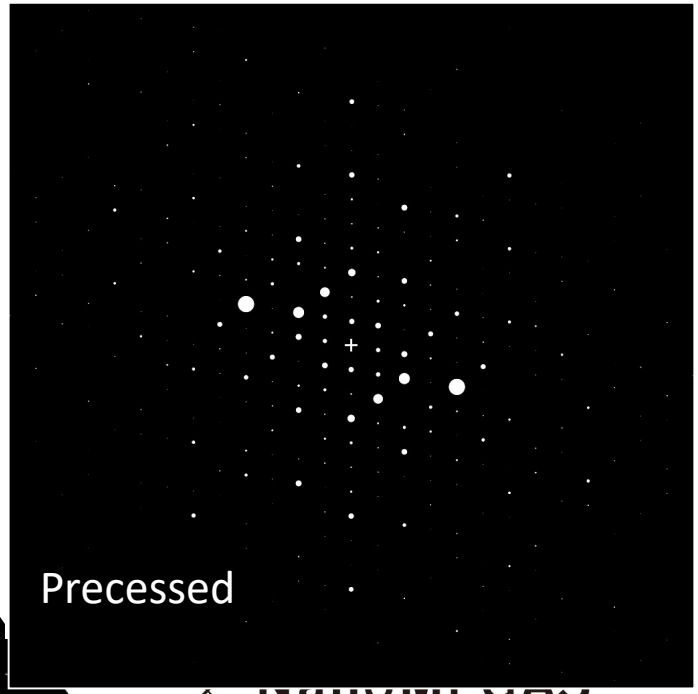
Scan

Sample

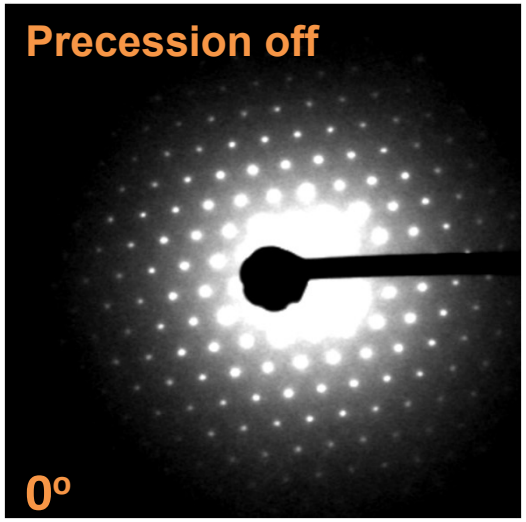
De-scan

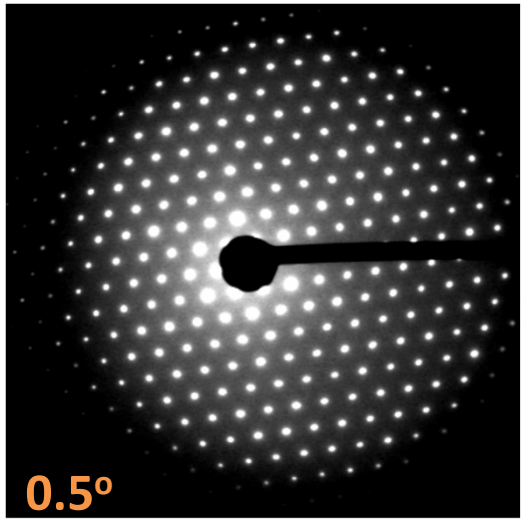
Precession Diffraction Pattern

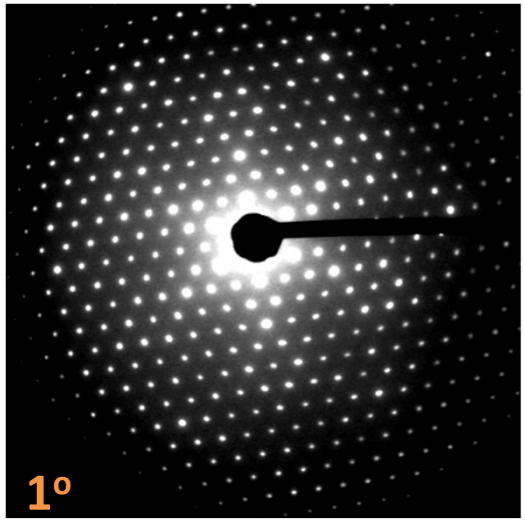


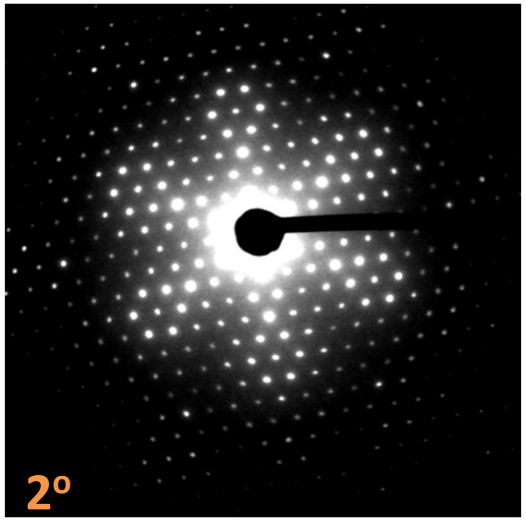


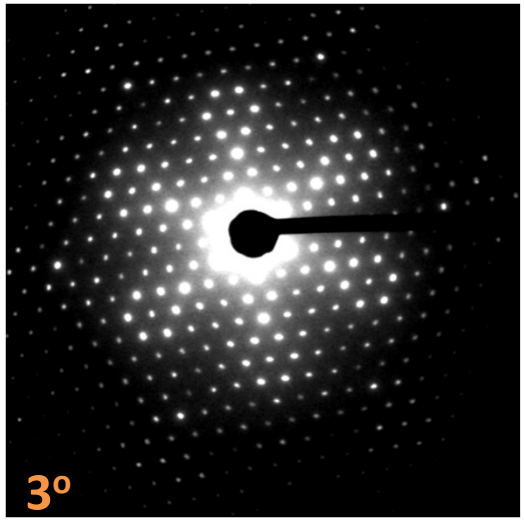
Precession Electron Diffraction









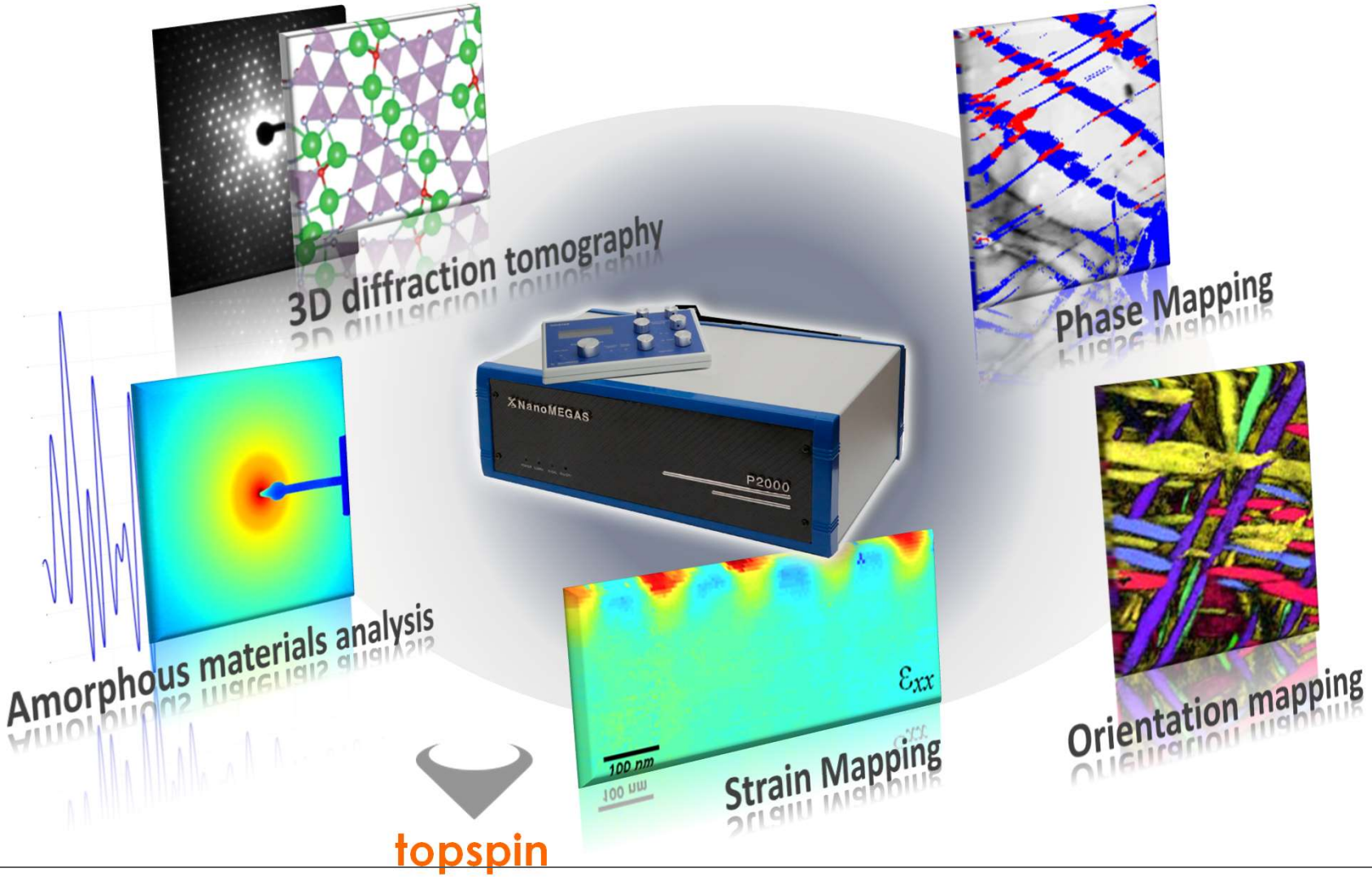


precession angle ↑

↑ higher resolution

(i.e. more reflections)

Precession Electron Diffraction Applications



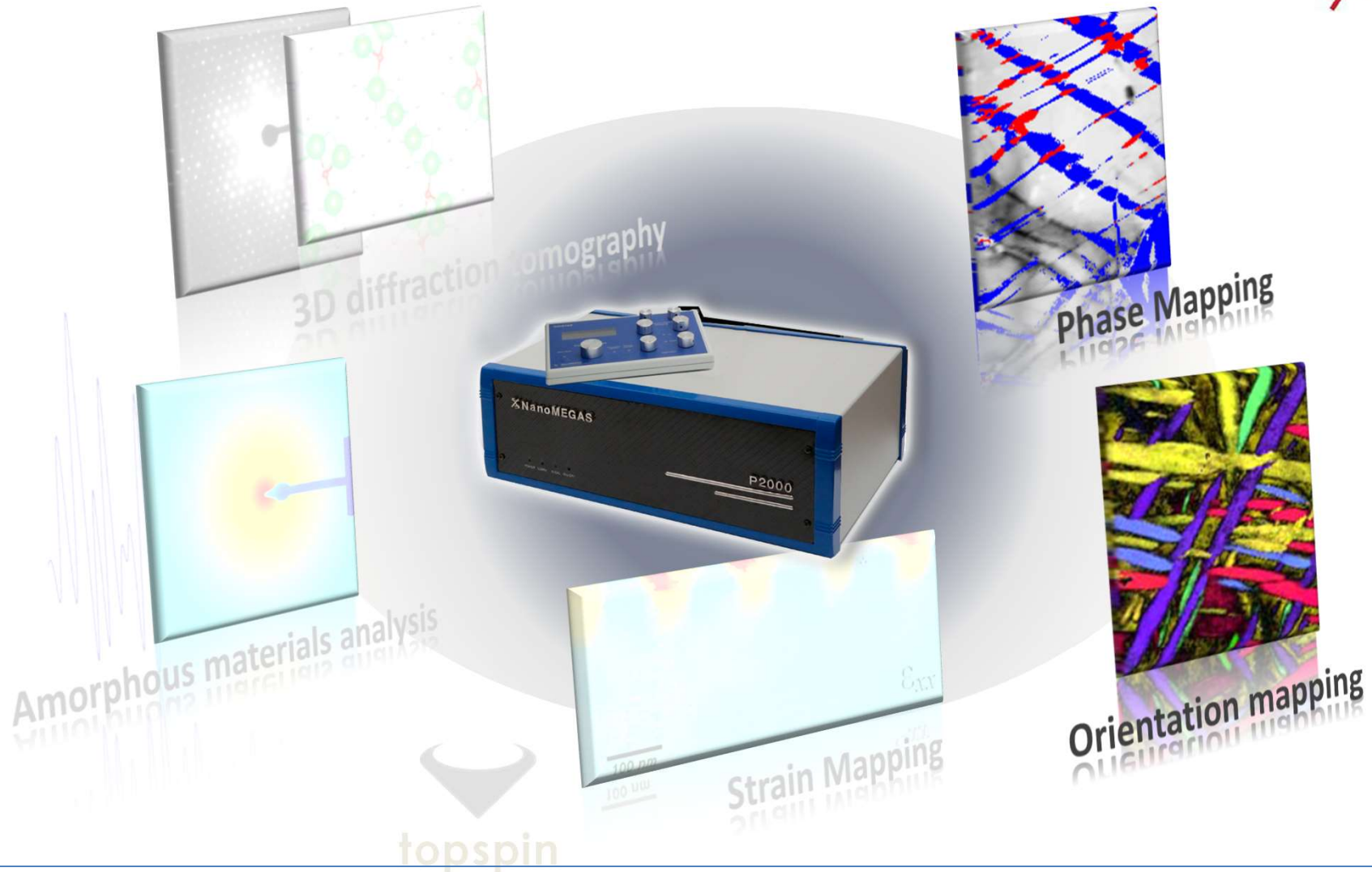
PED Applications available for every TEM

Precession Electron Diffraction Applications

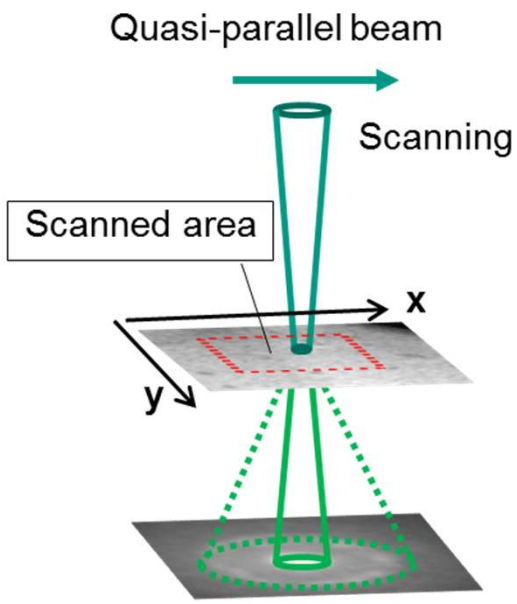
NEW structure analysis techinique for TEM

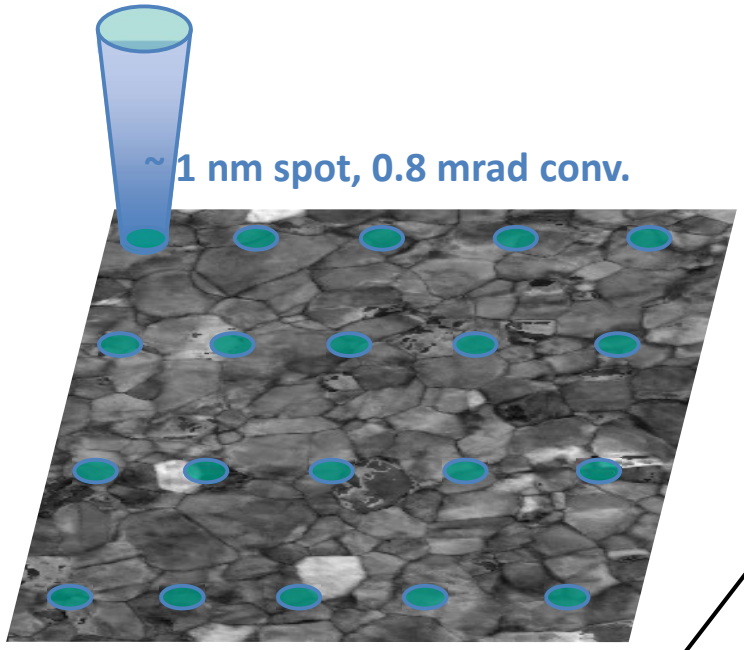
>150 installations world-wide in TEM (27 countries)

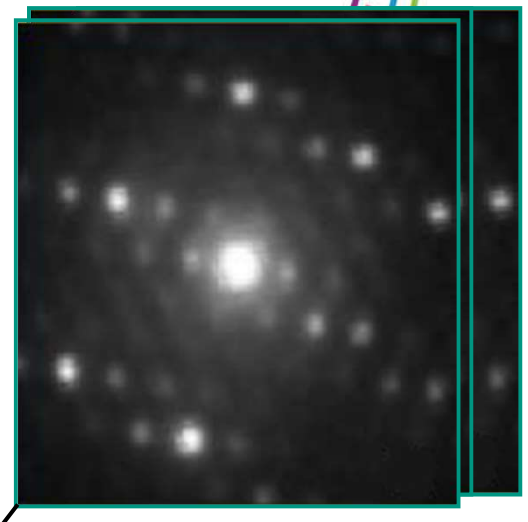
Precession Electron Diffraction Applications



ASTAR: Orientation & Phase Mapping

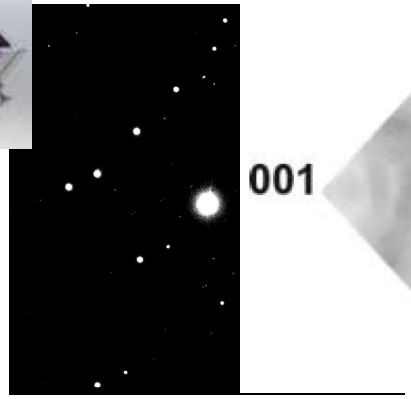


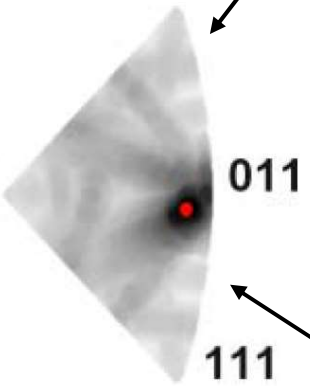


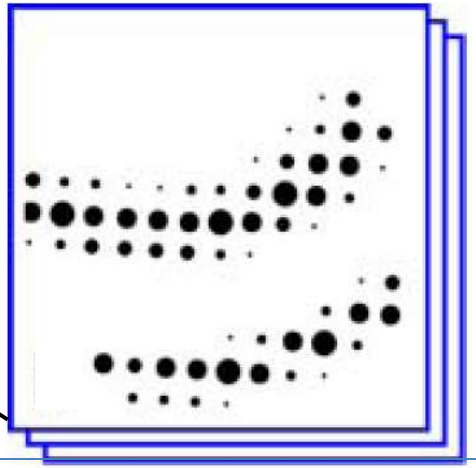


nanocrystal diffraction

simulated diffraction bank

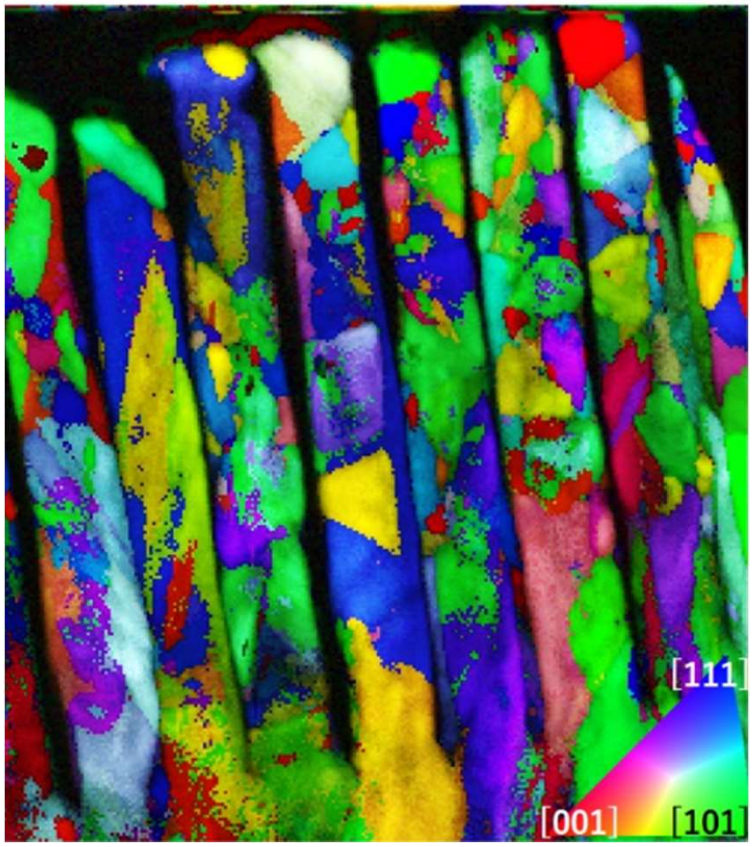






ASTAR: Diffraction Patterns Identification / Indexing

Orientation map



Sample : Ni Nanowires

Acquisition time:
(250 x 200 pixel)

5 min

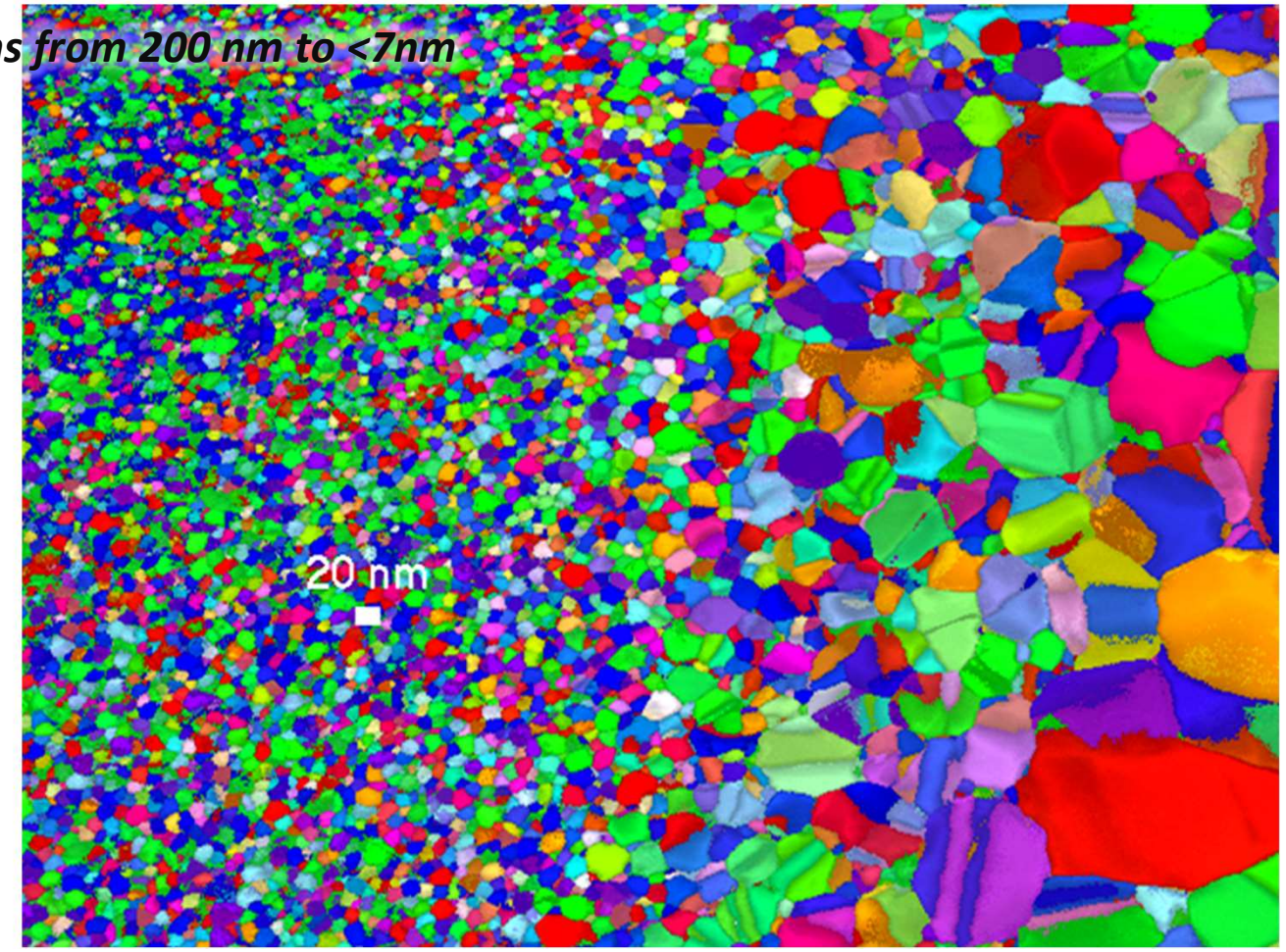
Processing time:
(for cubic)

5 -15 min

(hexagonal, tetragonal)
x 3- 4 more time

The power of ASTAR method

Cu grains from 200 nm to <7nm

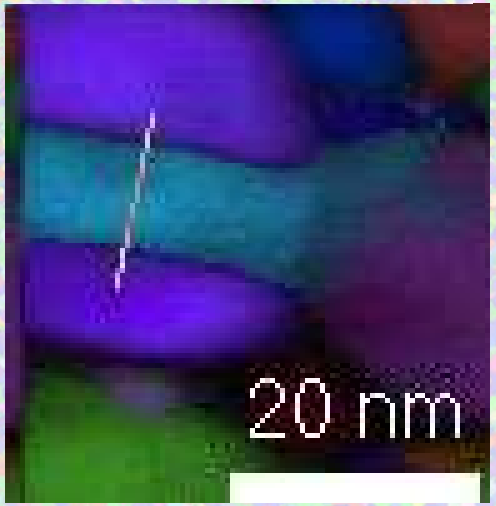


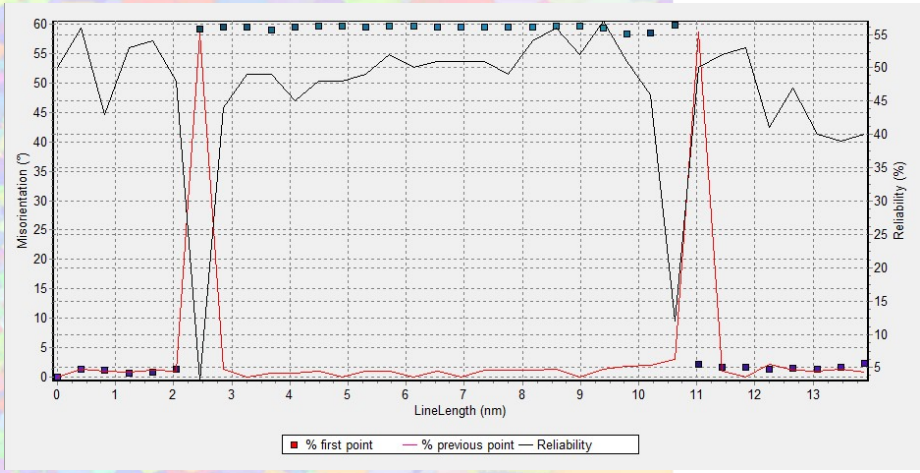
Courtesy to Muriel Veron; Jeol 2100 FEG

The power of ASTAR method

Cu grains from 200 nm to <7nm

Courtesy to M. Veron; **Jeol 2100 FEG**



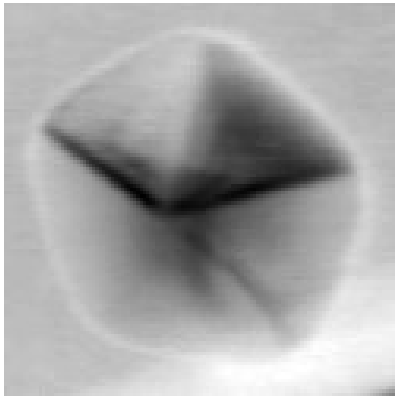


Crossing the twin boundaries, the reliability signal drops bellow 15 over a distance of less that 1 nm.

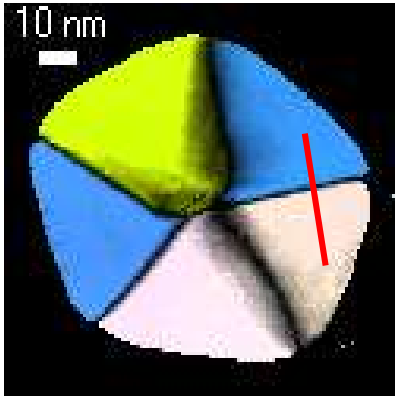
ASTAR spatial resolution <1nm

ASTAR: 1nm spatial resolution in Au particles sample

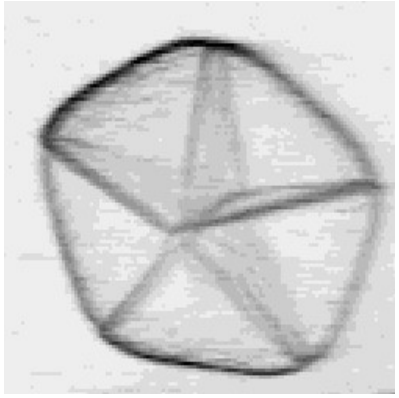
Multi-twinned Au particles (JEOL ARM 200)



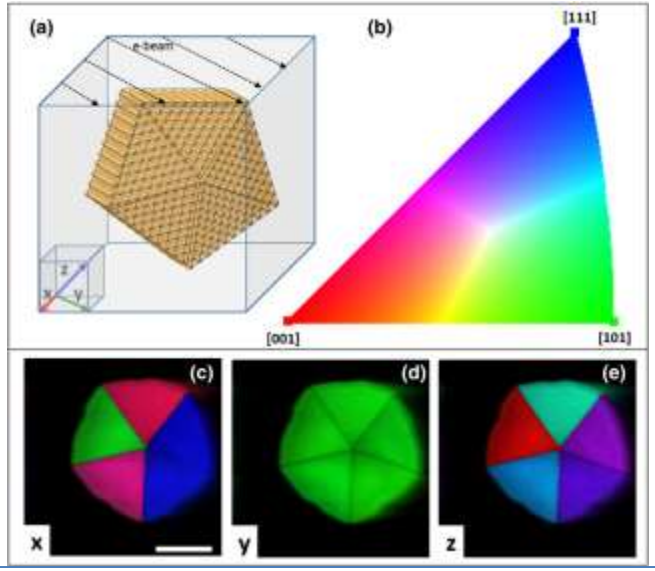
Virtual Bright-Field

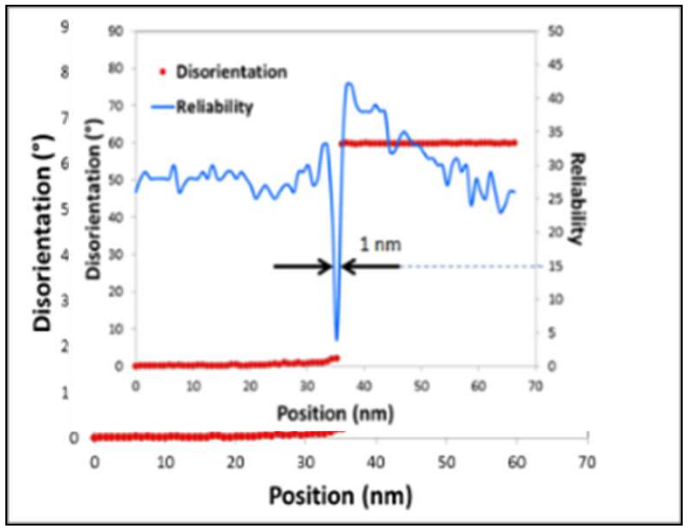


Orientation + Reliability



DP cross-correlation

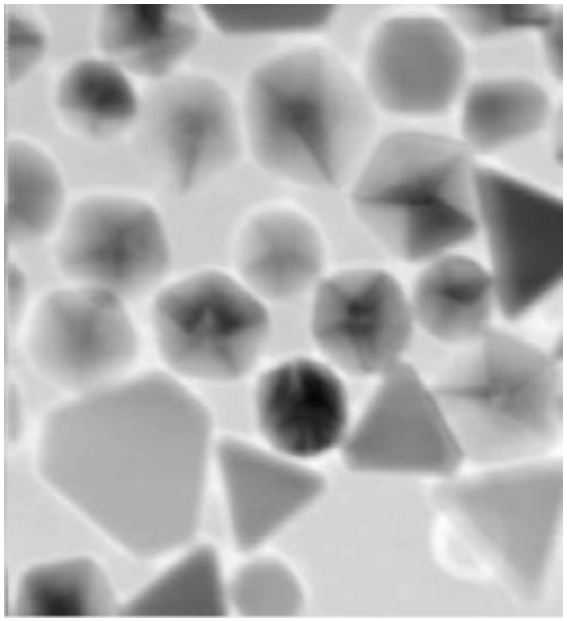




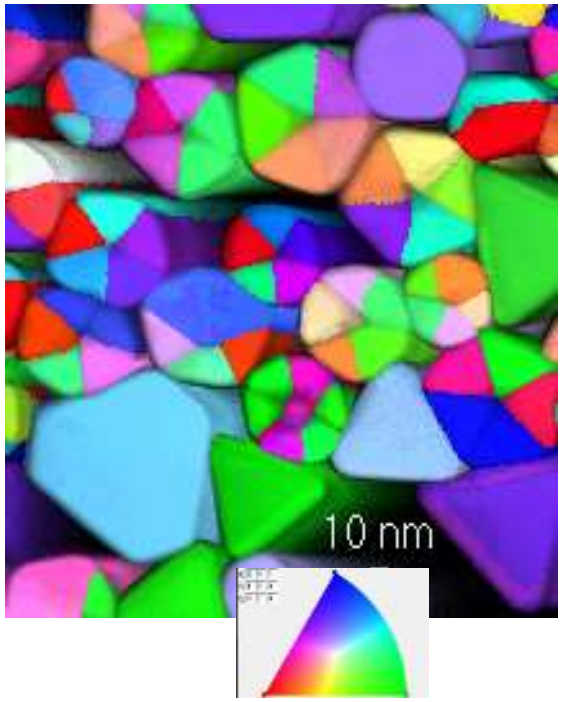
ASTAR: Diffraction pattern Cross-Correlation Map

Multi-twinned Au particles (JEOL ARM 200)

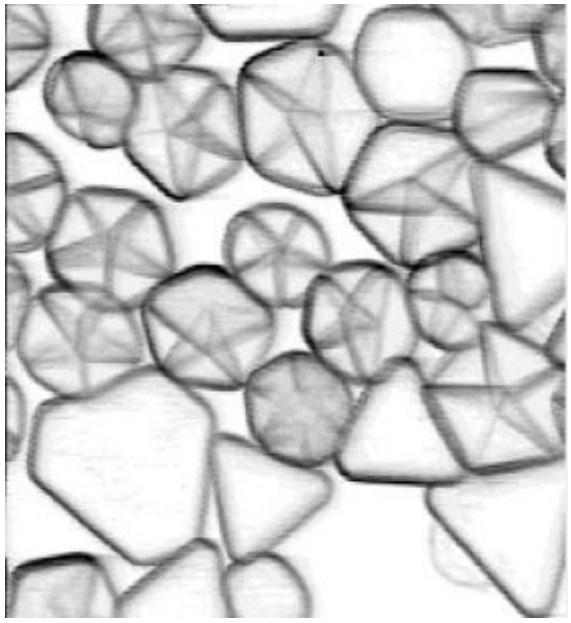
Virtual Bright-Field



Orientation map

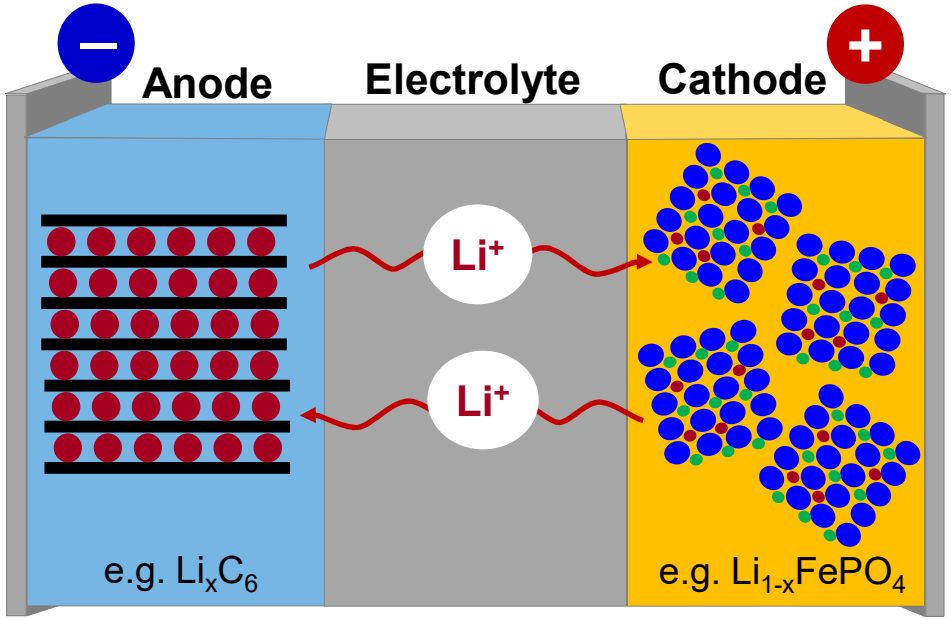


Diffraction Patterns cross-correlation

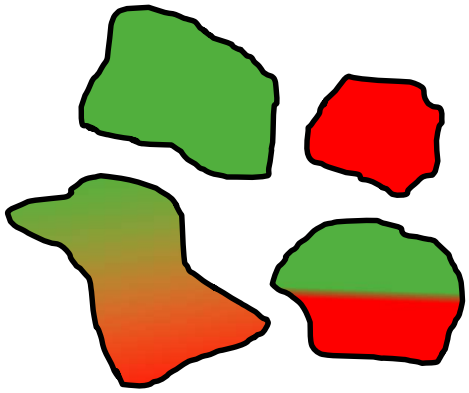


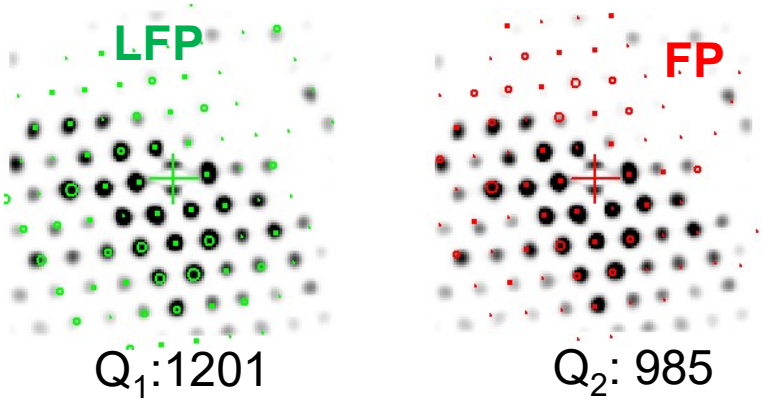
Cross-correlation weights the similarities between successive diffraction patterns and highlight through thickness structural features

ASTAR: Li-Ion Batteries / Phase Identification



$Li_{0.5}FePO_4$





Q_1:1201 Q_2: 985

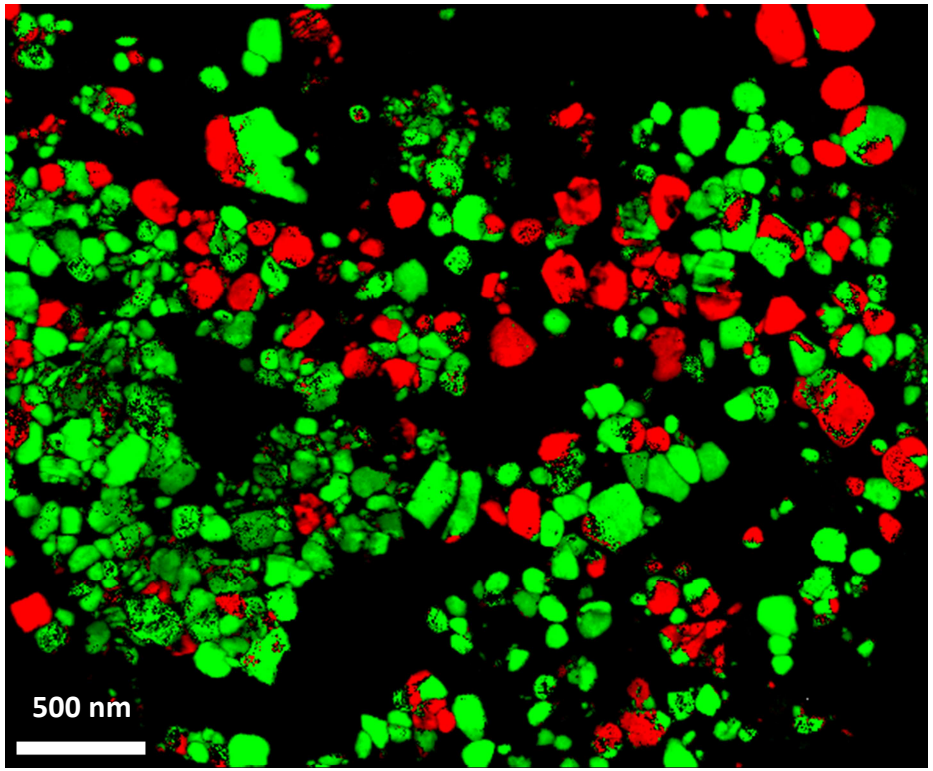
Lattice Spacings [Å]

hkl	$LiFePO_4$	$FePO_4$	Difference
100	10.33	9.81	5.0 %
010	6.01	5.79	3.8 %
001	4.69	4.78	1.8 %

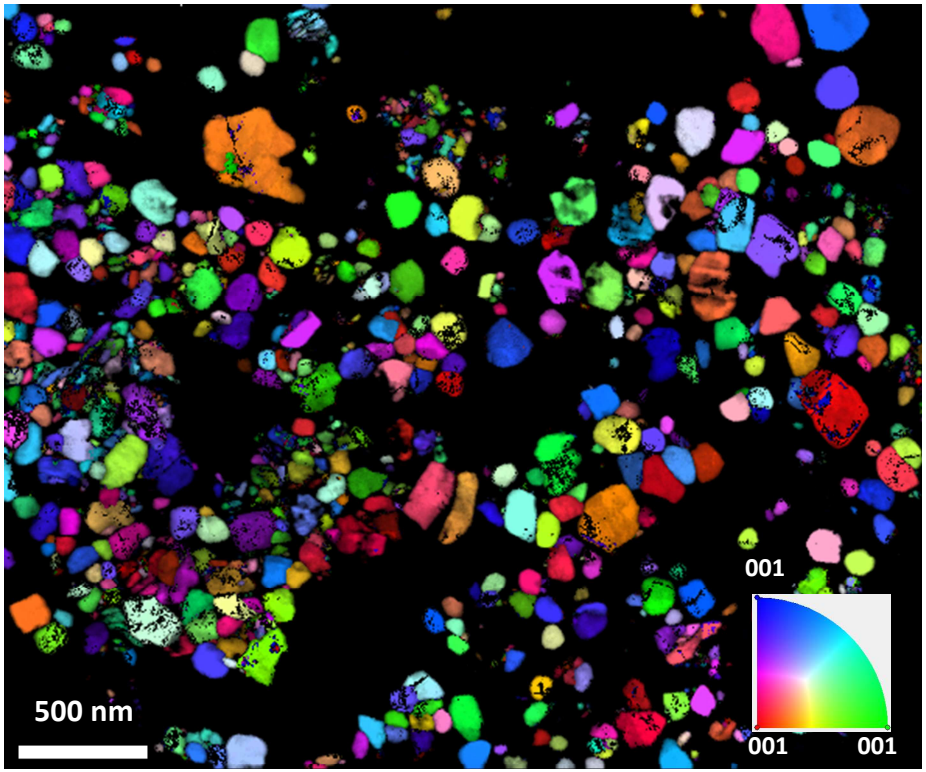
ASTAR: Li-Ion Batteries / Phase Identification

Green: $LiFePO_4$ Red: $FePO_4$

Phase Map



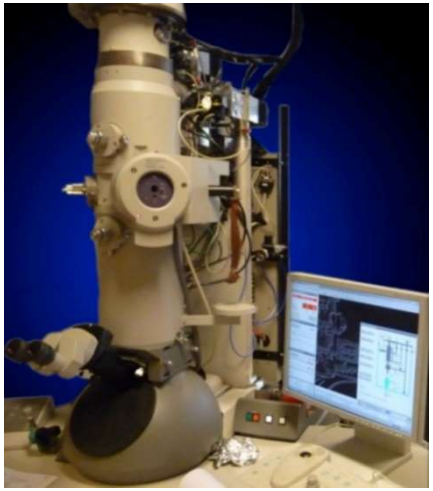
Orientation Map

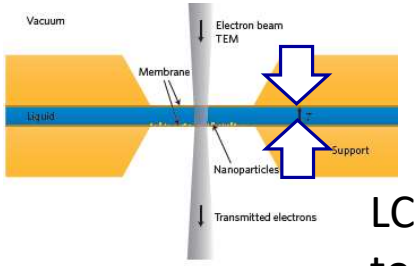


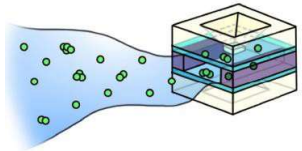
X. Mu et al., *Ultramicroscopy*, **2016**, *170*, 10-18

ASTAR: *In Situ* Orientation mapping in liquid

Liquid Cells (LC) in TEM allow to do image , electron diffraction and EDS analysis of samples in liquid







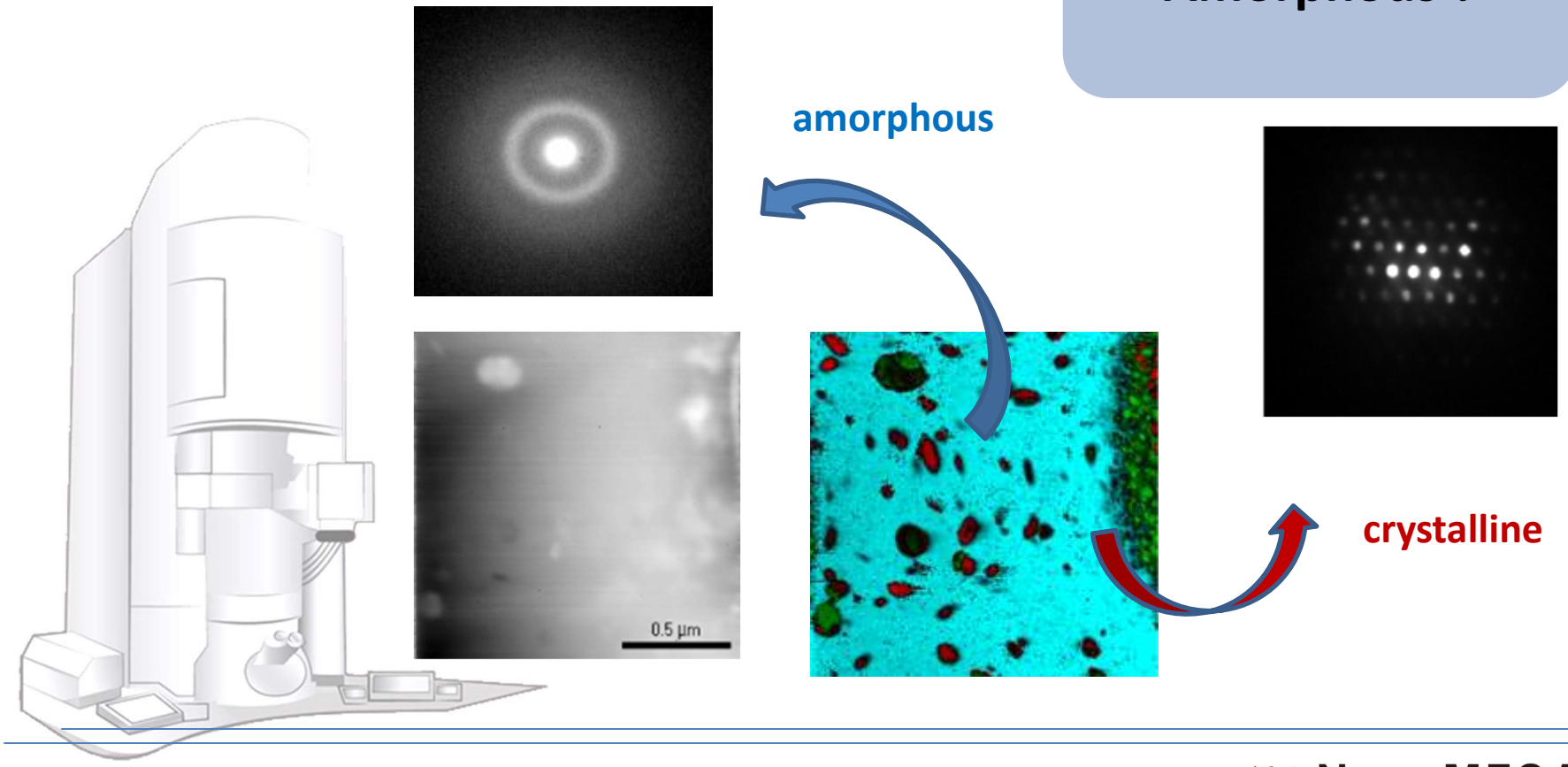
LC spacer 200 nm to 2 µm

(Top) **Poseidon Liquid cell holder** (image courtesy Protochips Inc) LC-TEM schematics (bottom) showing native liquid solution contained between two amorphous SiN thin layers (50 nm).Liquid can be sealed and imaged in TEM

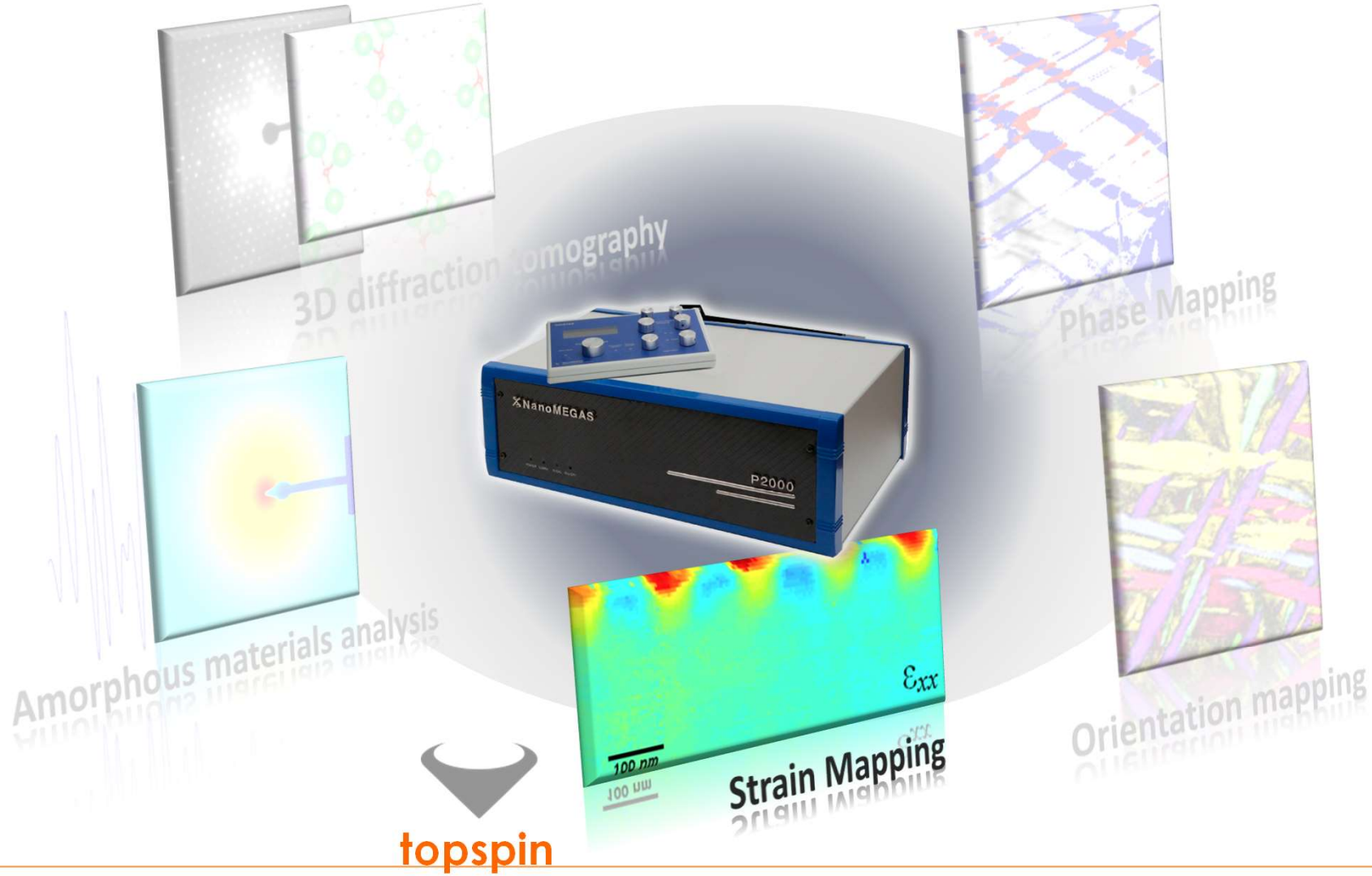
ASTAR: Amorphous – Crystalline Phase Distinguish

Example: Mg-Cu-Gd partly recrystallized metallic glass with Mg_2Cu and Cu_2Gd crystalline precipitates

Crystalline or Amorphous ?



Precession Electron Diffraction Applications

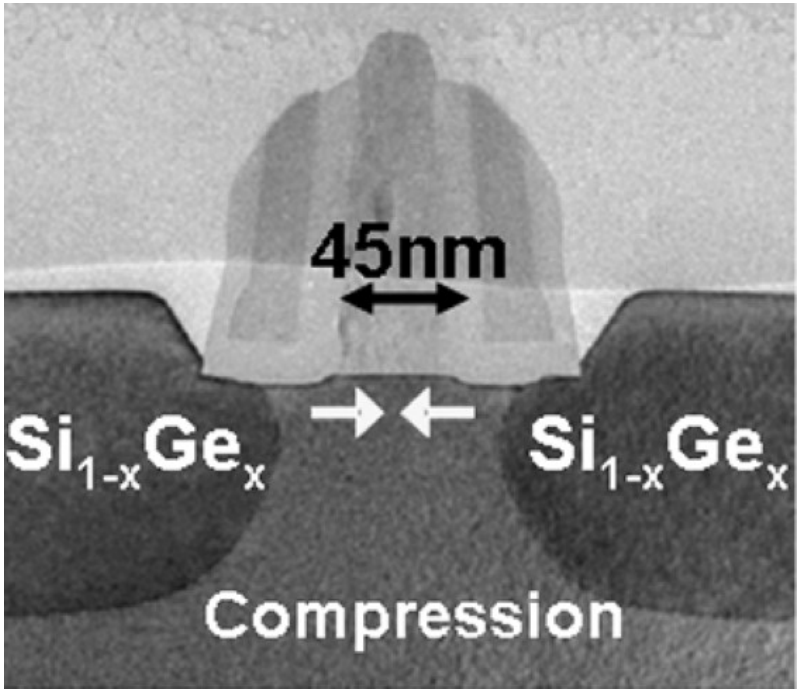


TopSPIN: Strain Mapping

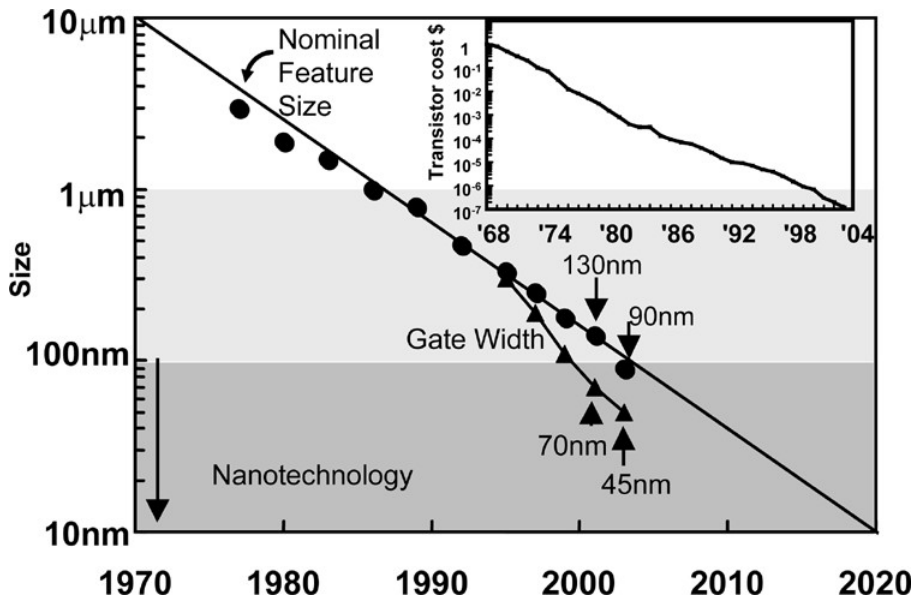
- Strain measurement is critical to monitor desired and unintended strain distributions
  - Desired: Strain introduced in Si to enhance electron mobility in the channel
  - Unintended: Stress concentration in devices leads to failure

- Strain measurement applications in semiconductor and materials science require high spatial resolution and high precision.

TopSPIN: Strain Mapping



pMOSFET

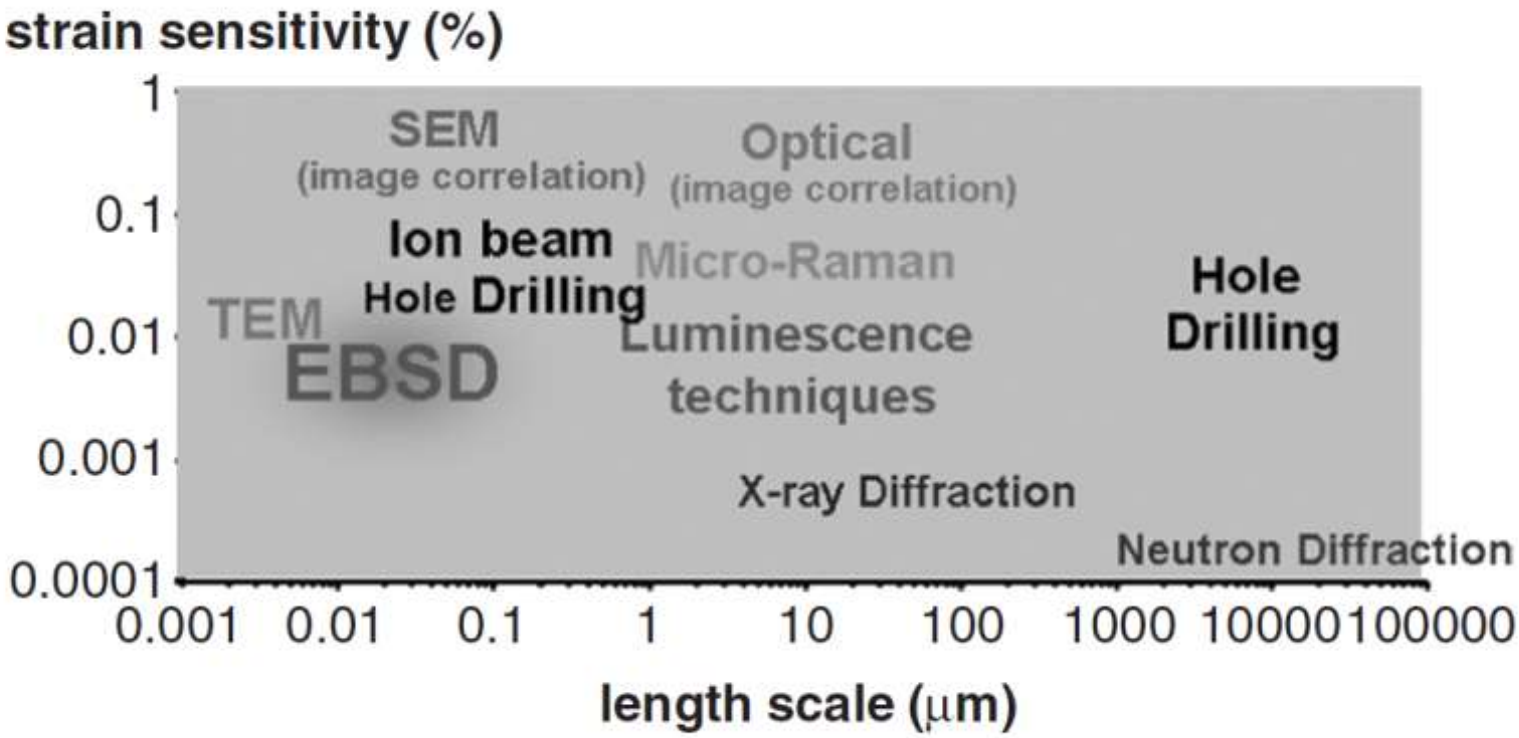


Requirements

- Desired spatial resolution ~ 1 nm
- Strain sensitivity << 0.1%
- Highly automated

Thompson et al., *IEEE Trans. On Electron Devices*, VOL. 51, NO. 11, 2004

TopSPIN: Strain Mapping



D. Dingley et al., *Journal of Electron Microscopy, 59,* S155-S163 (2010).

TopSPIN: Strain Mapping – Nanobeam Diffraction

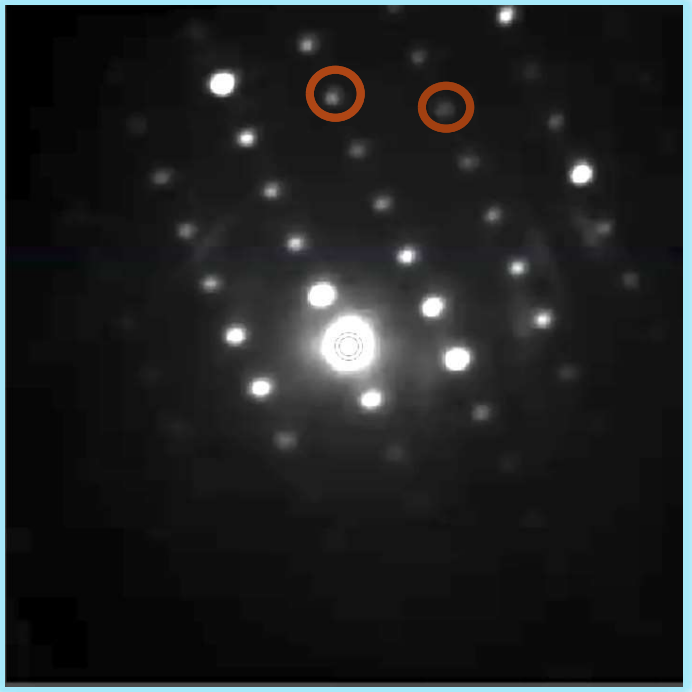
Strain determined by **measuring** shift in **spot positions**

Advantage

- High spatial resolution - better than **1 nm**

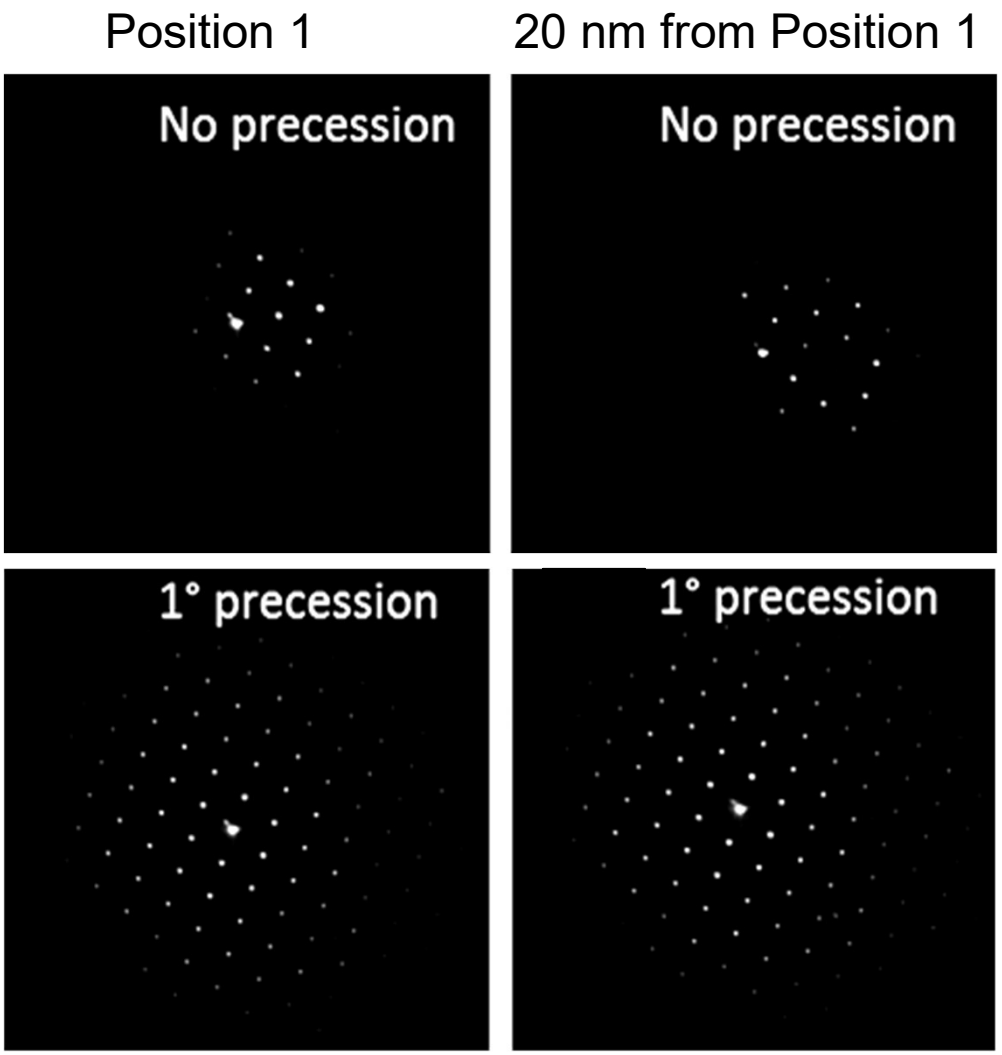
Disadvantage

- **Dynamical diffraction**



D. Cooper et al., Journal of Physics: Conference Series 326 012025 (2011).

TopSPIN: Dynamical Diffraction & Beam Precession



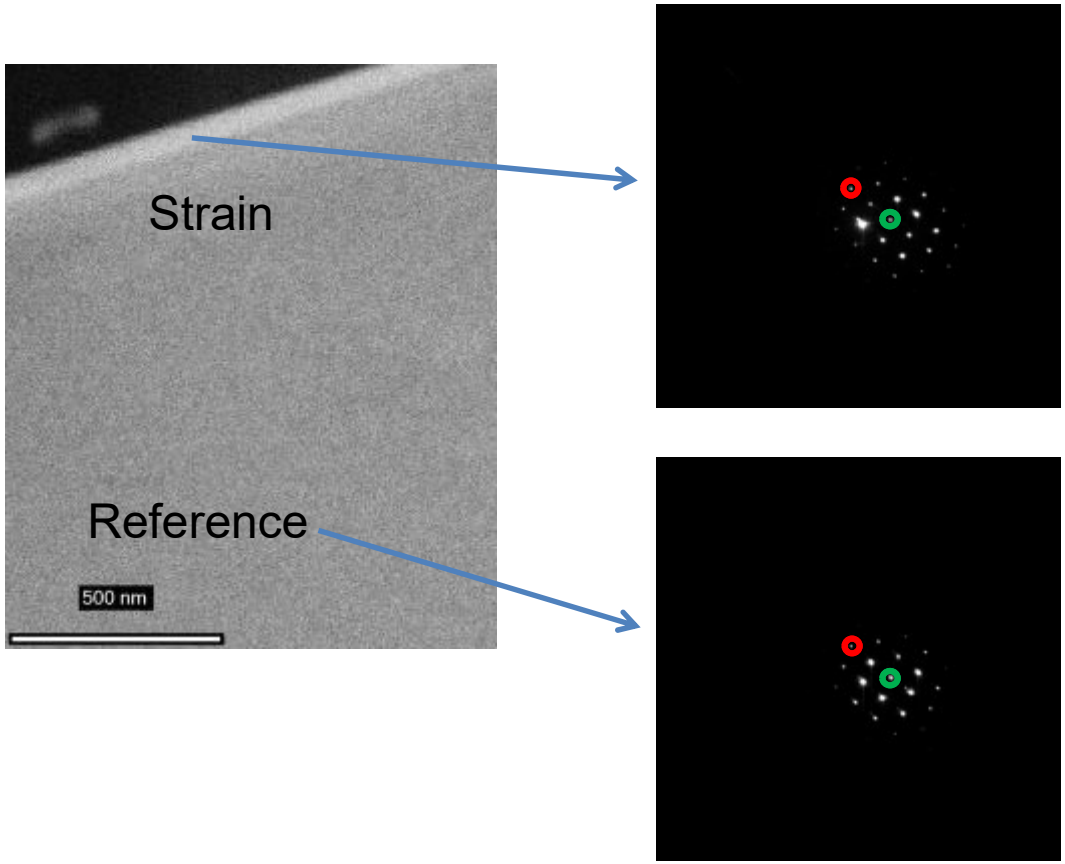
Precession improves patterns

- **Less sensitive to specimen thickness, bending**
- More **high-order spots** (higher sensitivity)

- Single crystal Si
- FIB prepared sample

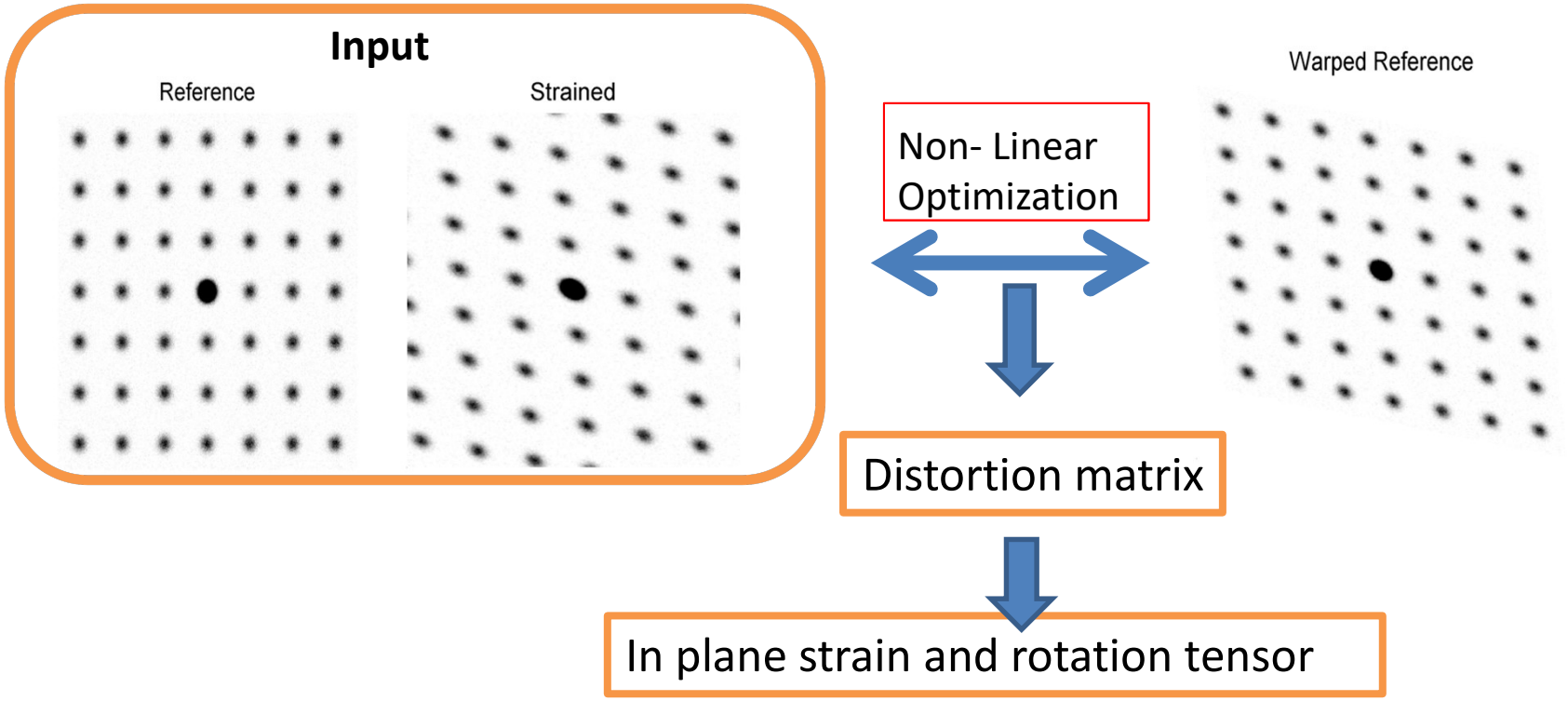
TopSPIN: Data acquisition – Optimum conditions

Typically use spot positions in nanobeam diffraction (NBD) patterns

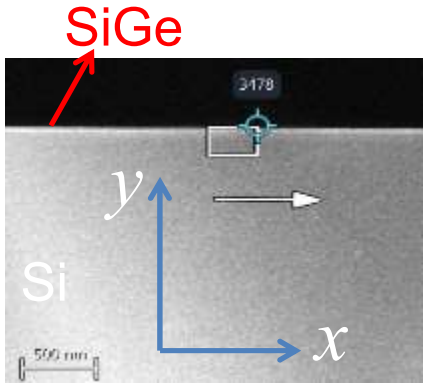


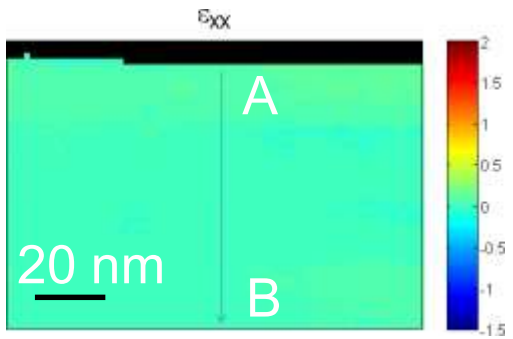
TopSPIN: Method Principles

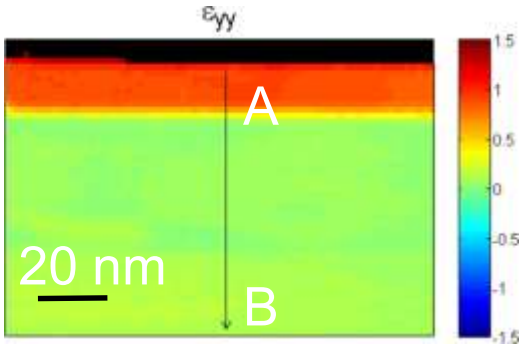
- Diffraction patterns from strained region are matched against a reference pattern.
- All pixels utilized, not just selected spot centers



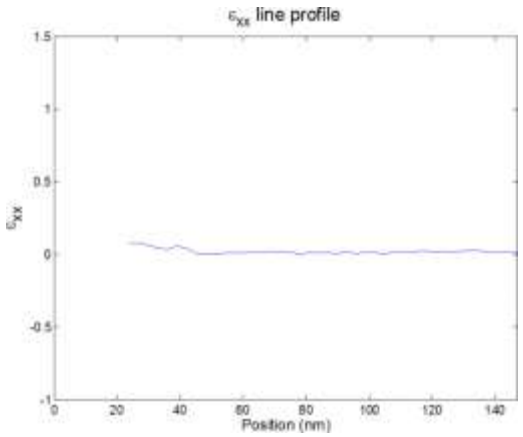
TopSPIN: Blanket Si – $Si_{1-x}Ge_x$

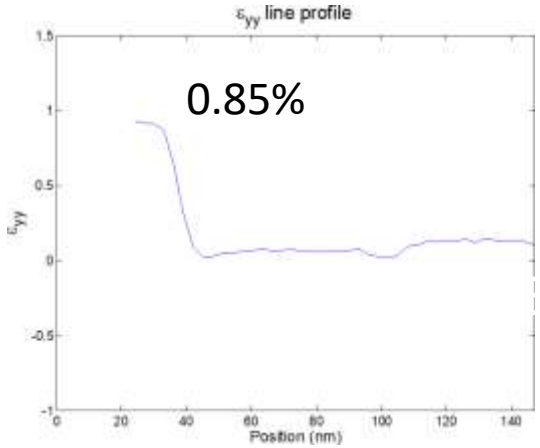






Step size: 3 nm
Precession angle 0.4 °





Si/SiGe multilayer:
Average strain : 1.2%
Precision: 0.02%
(from longitudinal profile)

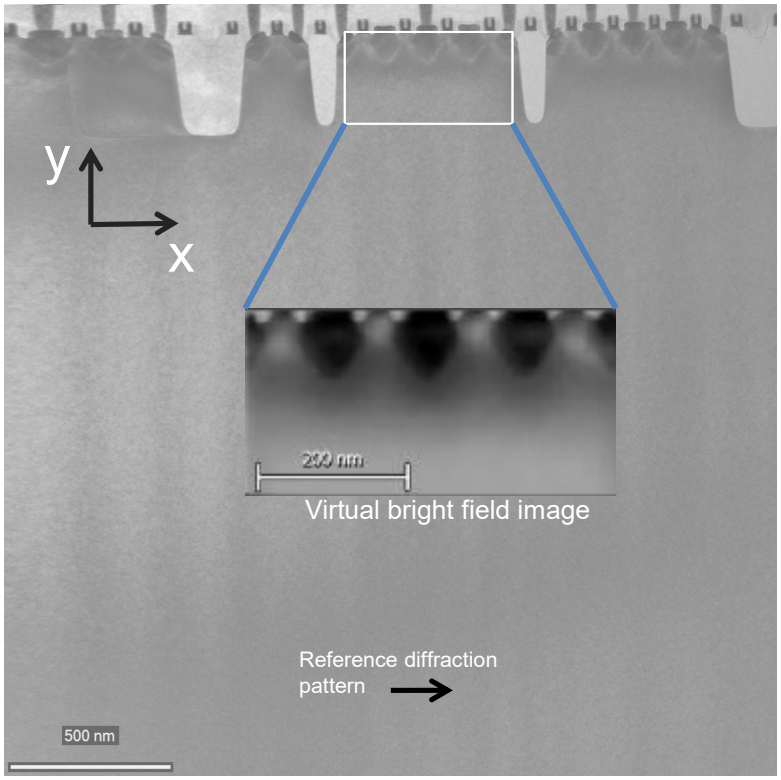
Sample Thickness: 37.7 nm
Ge composition: 14.2%

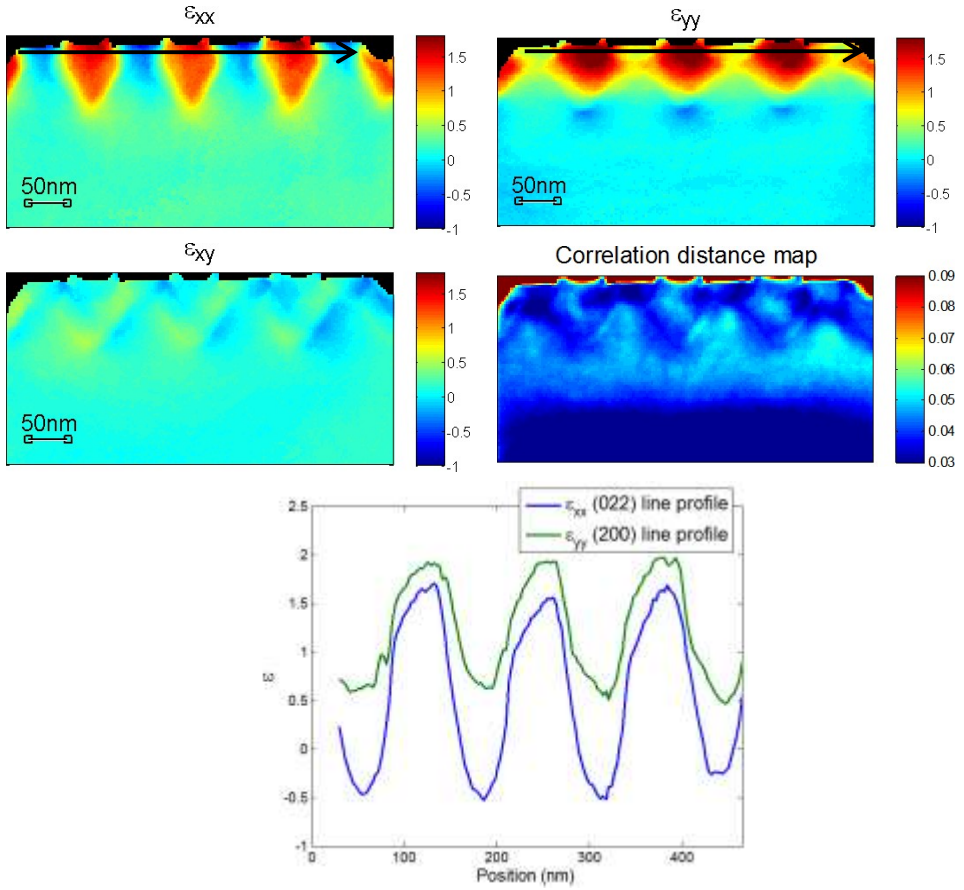
Microscope: 200 kV Zeiss Libra

TopSPIN: Typical Performance on Strain mapping

- **Practical spatial resolution @ 1 degree precession angle : 1 to 5 nm (FEG TEM)**
- **Sensitivity (precision) @ 1 degree precession angle: 0.1% to 0.01 %**
- Spatial resolution and sensitivity depents on model TEM, beam current, beam convergence and sample quality/thickness
- Fast and automated 1D & 2D Strain Mapping at the nanoscale

TopSPIN: pMOS device Strain Mapping with Precession



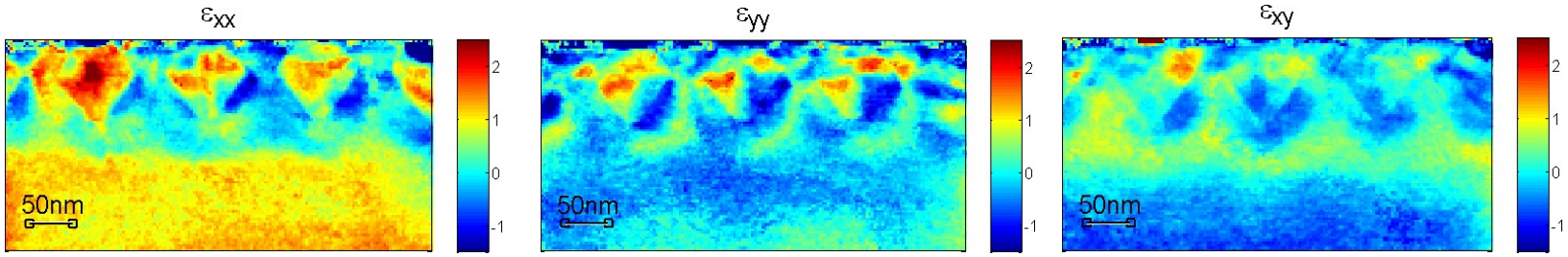


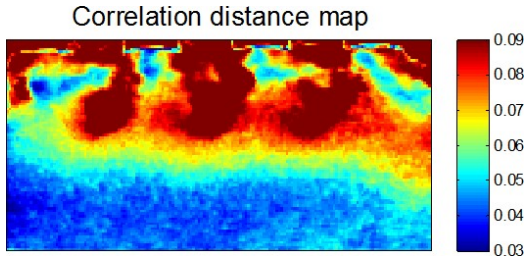
TEM: JEOL ARM200F
Step size: 3 nm
Precession angle: 0.7°

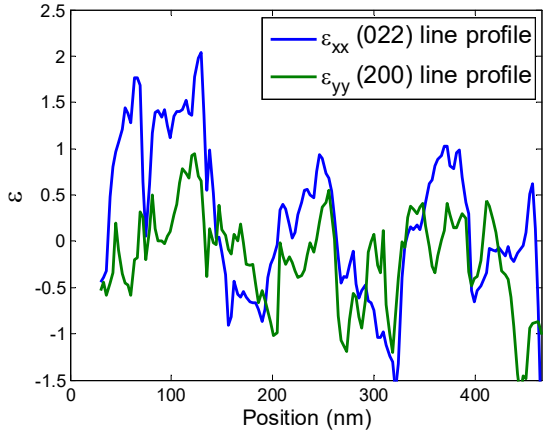
strain percentage

TopSPIN: pMOS device Strain Mapping without Precession

Same pMOS region without precession



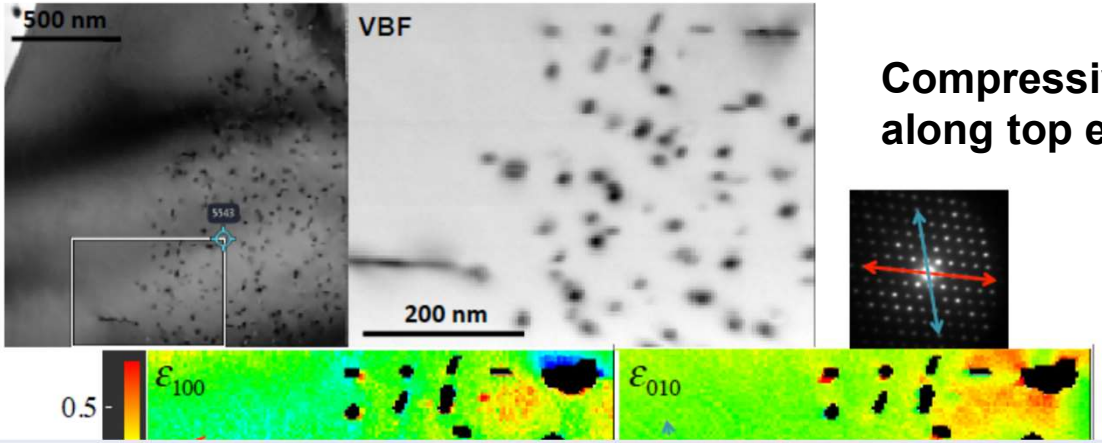




strain percentage

TEM: JEOL ARM200F
Step size: 3 nm
Precession angle: **NO**

TopSPIN: Strain mapping in Metals



Compressive strain up to 0.2%
along top edge of two large precipitate

IMPACT STATEMENT

This study demonstrates that nano precession electron diffraction can be extended from semiconductor devices to polycrystalline metals and ceramics to map nanoscale elastic strain fields with high strain resolution.

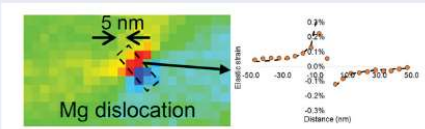
Strain analysis of Mg
close to AlN precipitates

ABSTRACT

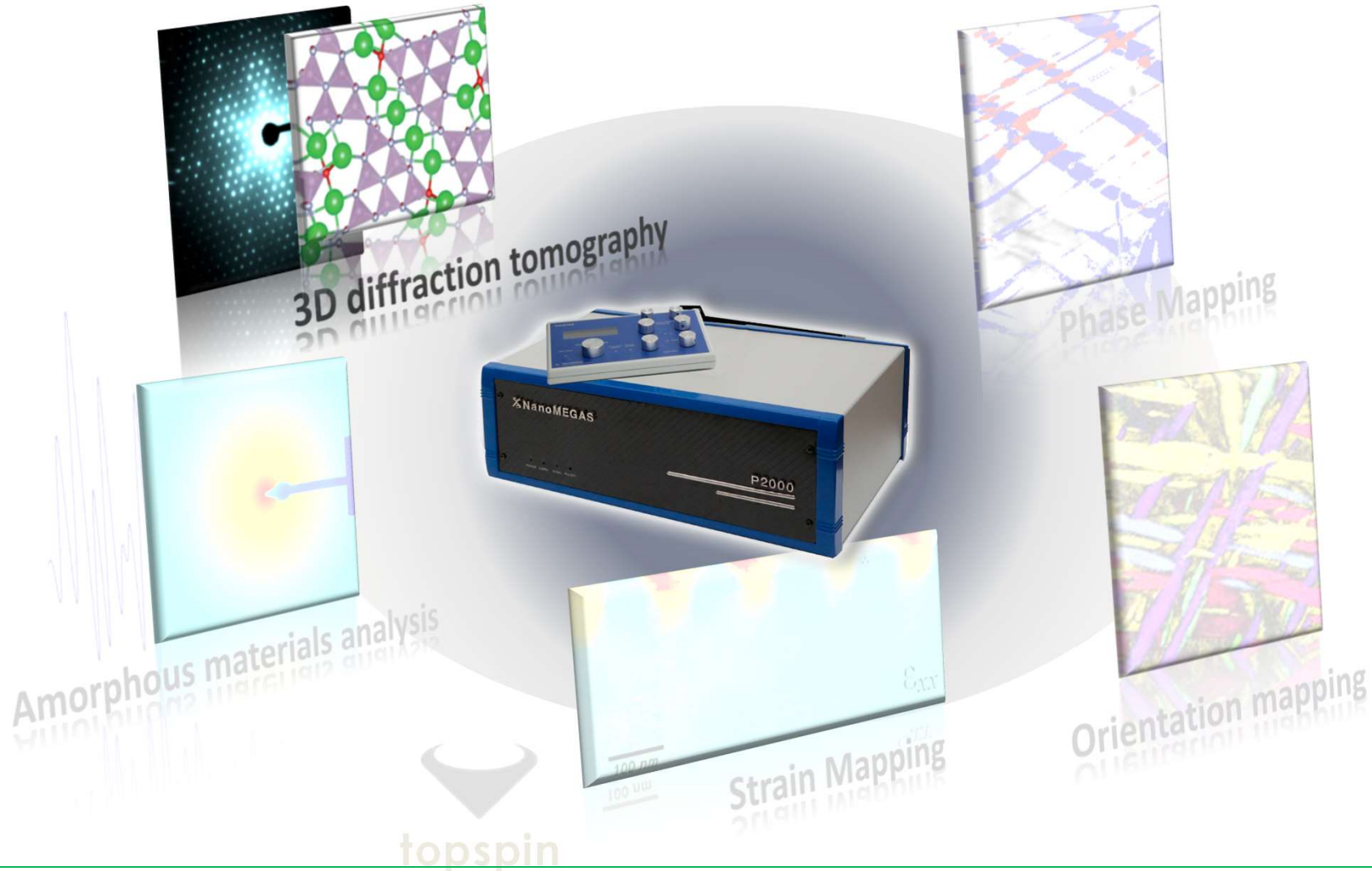
Measuring elastic strain with nanoscale resolution has historically been very difficult and required a marriage of simulations and experiments. Nano precession electron diffraction provides excellent strain and spatial resolution but has traditionally only been applied to single-crystalline semiconductors. The present study illustrates that the technique can also be applied to polycrystalline materials. The $\pm 2\sigma$ strain resolution was determined to be 0.15% and 0.10% for polycrystalline copper and boron carbide, respectively. Local strain maps were obtained near grain boundaries in boron carbide and dislocations in magnesium and shown to correlate with expected values, thus demonstrating the efficacy of this technique.

ARTICLE HISTORY
Received 30 October 2017

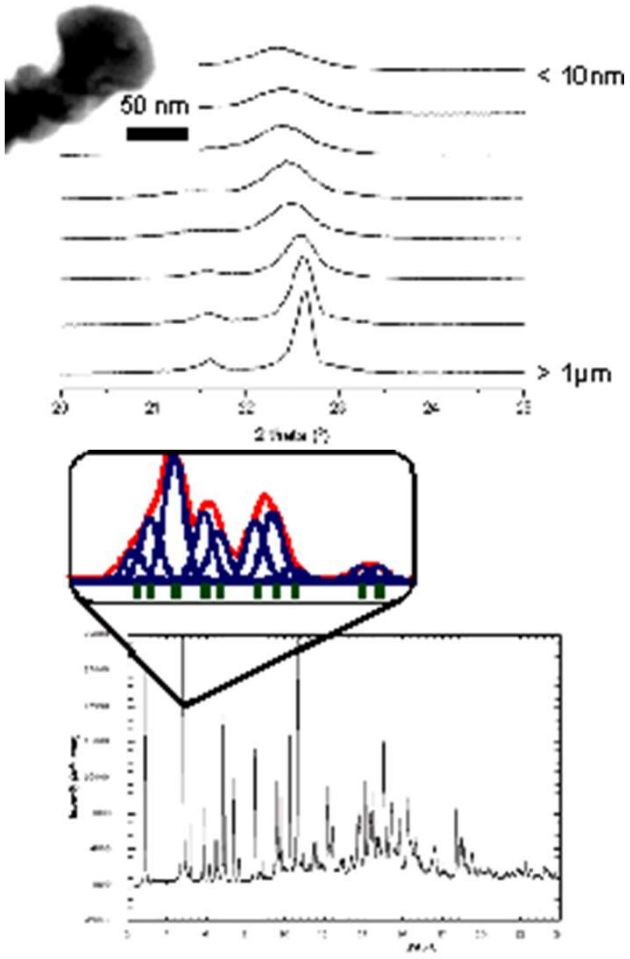
KEYWORDS
Nanobeam electron diffraction; strain measurement; transmission electron microscopy



Precession Electron Diffraction Applications



Why to Use Electron Crystallography?



X-Ray Crystallography Methods - Limits

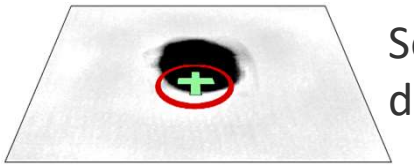
Small crystals

<0.5 micron in size, progressively broader X-Ray reflections peaks

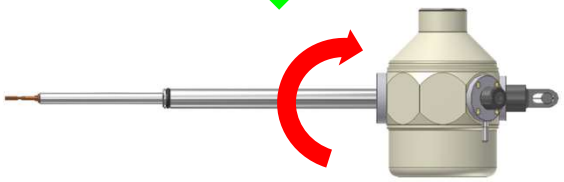
Overlapping Powder X-Ray peaks

poorly crystallized materials

PED tomography: Acquisition procedure principles

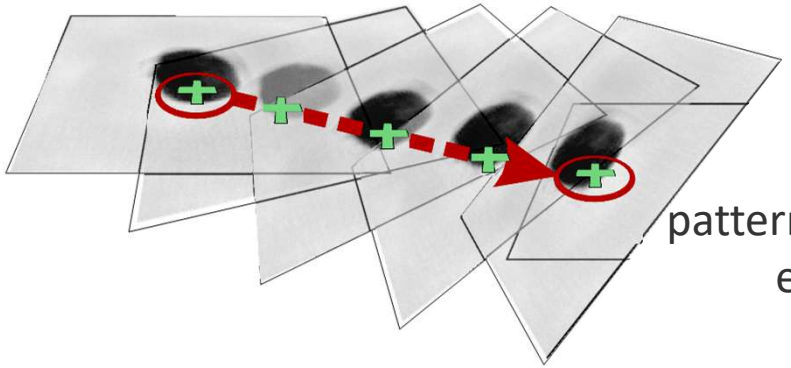


Select crystal & area for data acquisition

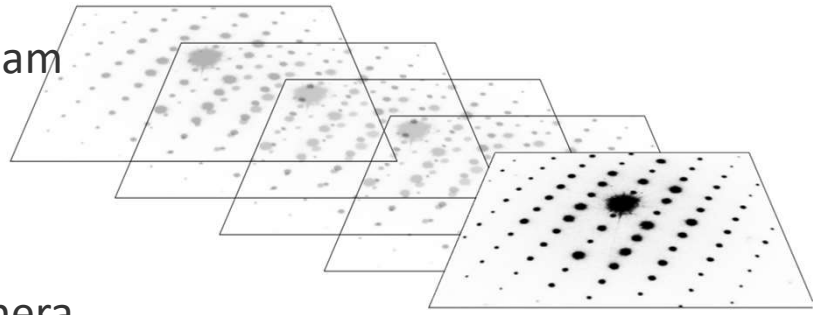


Tilt crystal every 1 degree

Track crystal back under the beam
OR follow the crystal by the beam



Acquire PED patterns with CCD camera every 1 degree



Merge sequential precession

MICRO ED method

Exposure time (0.5 to 2 sec)

PED tomography: Data Processing

1. Cell parameters determination
2. Indexing
3. Reciprocal S… reconstr…
4. In… …s measurement …rile creation)

ADT 3D software

Structure Determination

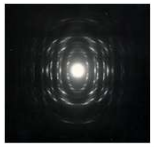
- Direct methods
- Charge Flipping
- Simulated Annealing
- More……

Structure Refinement

Electron Crystallography: From the early days….

ED studies of basic salts, metals, carbides, semiconductors, clay minerals, organics
Location of H atoms
Z.G. Pinsker, B.K.Vainshtein
B.B. Zvyagin

1937-1938

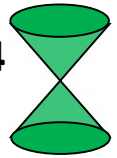


Direct Phasing Methods from ED of Organic and Inorganic compounds
D.L. Dorset , H. Hauptman

1976

Beam Precession ED
R. Vincent & P. A. Midgley

1994



Beam Precession Commercially available for every TEM

NanoMEGAS Advanced Tools for electron diffraction

2004

ED Organic Structure using Direct Detection Camera

J. P. Abrahams et al

2016

NanoMEGAS Advanced Tools for electron diffraction

> 300 structures solved with ED (2004 - 2019)

Continuous Rotation method
J. P. Abrahams et al; T. Gonen et al
2013-2015

Rotation ED
2010

U. Kolb et al
ED tomography (ADT)

2007

2016-2017
Lysozyme structure by ED tomography
1.8-Å resolution data
T. Gonen et al

PED & Dynamical refinement.
Detection of H atoms in organics
Palatinus et al

2017

Organic Structures solved using Direct Detection Camera
P. P. Das et al; T. Gruene et al
T. Gonen et al

NanoMEGAS Advanced Tools for electron diffraction

2018

Structural Solution from reactions in liquid cell
J. Haderman et al

2019

PED tomography: Data Processing

Zeolites:
ZSM-5, IM-5
ECS-3, Natrolite
ITQ-43

Minerals:
Barite, Mullite
Sarrabusite
Charoite-96
Charoite-90

Inorganic nanophases:
ZnSb, Zn_8Sb_7, NiTe, Ni_3Te_2,
Semiconductor 6H-SiC
$Li_2Ti_3NiO_8$

Metal Organic Frameworks (MOF):
MFU-4l, Bi-MOF
Basolite

Layered materials:
$Na_2Ti_6O_{13}$
$NaTi_3O_7OH{\cdot}2H_2O$
Hydrous silicate

Several materials have been studied by PED / 3D Diffraction Tomography

Organic:
NLO-active material
Pharmaceuticals
Oligo p-benzamides
Amides

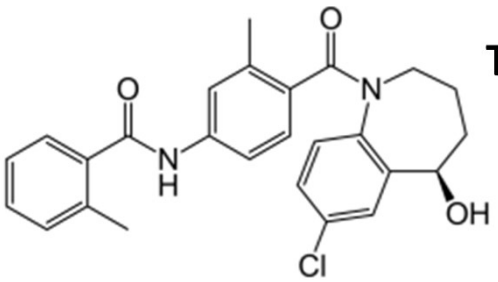
Phosphates:
SrP_3N_5O
$Ba_6P_{12}N_{17}O_9Br_3$

High pressure phases:
Hydrous Al-pyroxene

Tungstate:
$Na_2W_2O_7$, $Na_2W_4O_{13}$
$K_{20}Al_4W_{24}O_{88}$

Ca-compounds:
Calcite, Vaterite
Calcium silicate hydrate

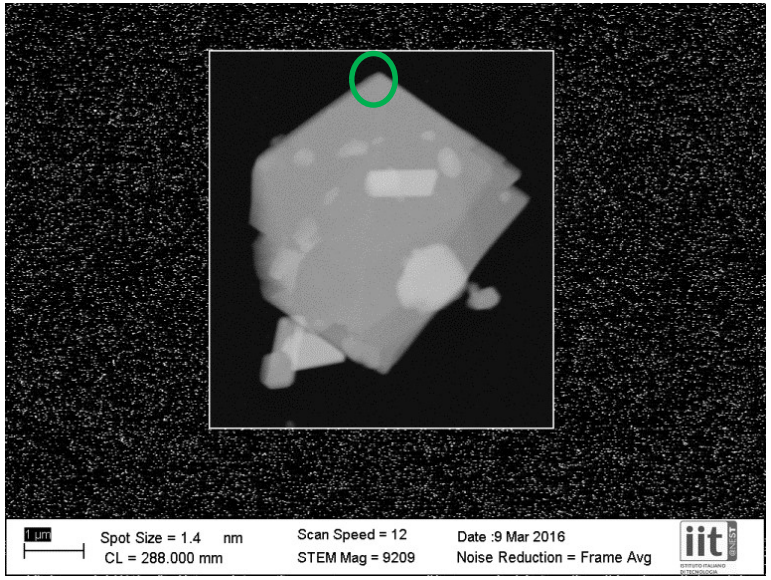
PED tomography: Structure Determination of Pharmaceuticals



Tolvaptan: autosomal dominant polycystic kidney disease

NO CRYO USED

STEM image of the crystal



Three (3) data sets acquired

-40 º to +23 º

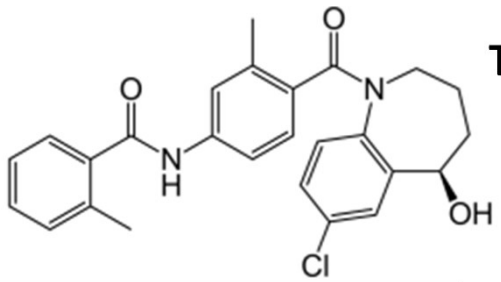
-40 º to +35 º

-20 º to +38 º

Tilt step: 1 degree

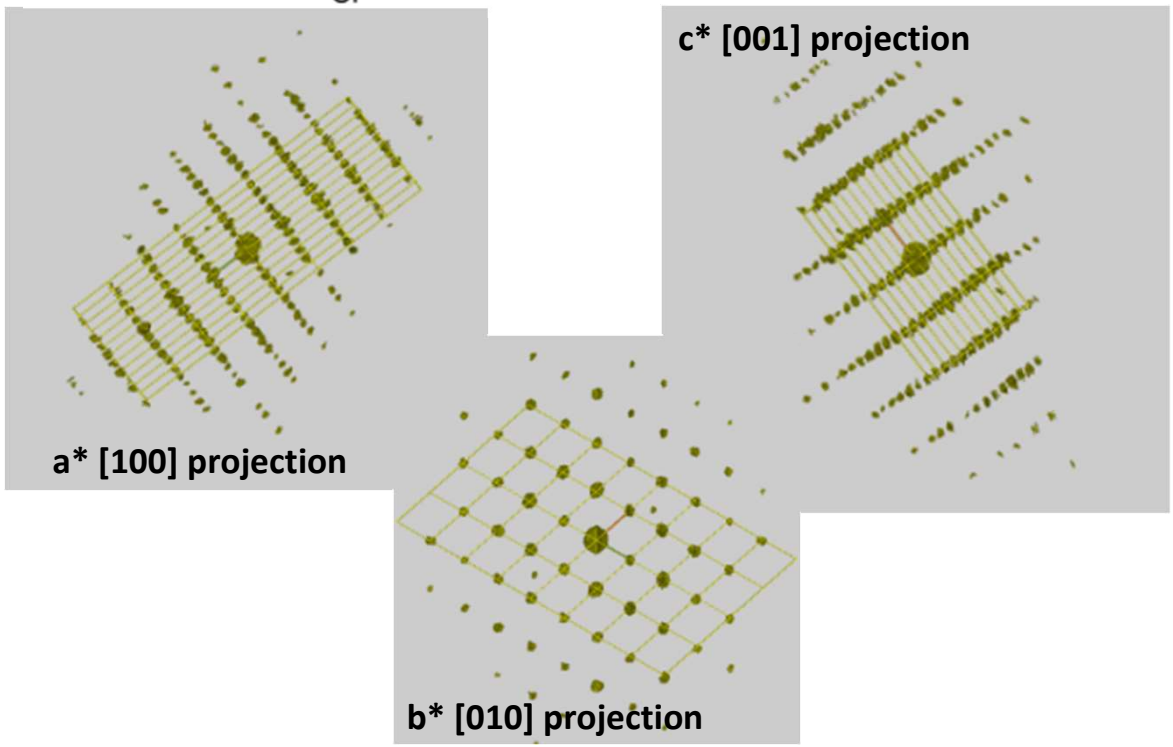
The crystals were not suitable for single crystal X-ray diffraction

PED tomography: Structure Determination of Pharmaceuticals



Tolvaptan: autosomal dominant polycystic kidney disease

NO CRYO USED



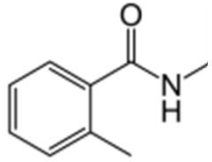
Electron Diffraction

a = 7.52 Å
b = 38.53 Å
c = 8.44 Å
β = 107,82
SPG: $P2_1/n$

Single Crystal X-ray (literature)

a = 7.63 Å
b = 38.01 Å
c = 8.56 Å
β = 108,12
SPG: $P2_1/n$

PED tomography: Structure Determination of Pharmaceuticals



Tolvaptan: autosomal dominant

Elec

ease

from

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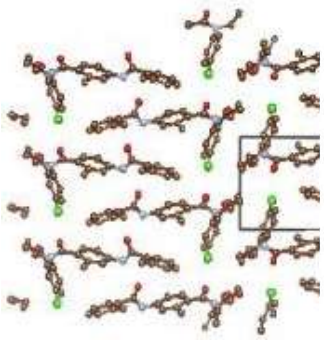

ORGANIC PROCESS RESEARCH & DEVELOPMENT
OPR&D
Article
pubs.acs.org/OPRD

Crystal Structures of Two Important Pharmaceuticals Solved by 3D Precession Electron Diffraction Tomography

Partha P. Das,[†] Enrico Mugnaioli,[‡] Stavros Nicolopoulos,[†] Camilla Tossi,[‡,∥] Mauro Gemmi,[‡] Athanasios Galanis,[†] Gheorghe Borodi,[§] and Mihaela M. Pop[*,⊥]

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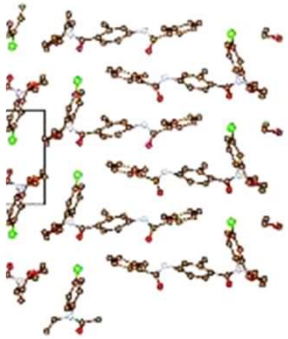
[‡]Center for Nanotechnology Innovation@NEST, Istituto Italiano di Tecnologia, Piazza San Silvestro 12, 56127 Pisa, Italy
[§]Molecular and Biomolecular Physics Department, National Institute for R&D of Isotopic and Molecular Technologies, 67-103 Donat, Cluj-Napoca 400293, Romania
[∥]Department of Electronics and Nanoengineering, School of Electrical Engineering, Aalto University, 00076 Aalto, Finland
[⊥]TeraCrystal, 67-103 Donat, Cluj-Napoca 400293, Romania

Supporting Information

ABSTRACT: The crystal structures of two important marketed pharmaceuticals, namely, ramelteon (RAM) and tolvaptan (TOL), were determined for the first time using 3D precession electron diffraction tomography (PEDT) on 500 nm-sized crystals. The results were compared with the same structures determined by single-crystal X-ray diffraction on subsequently grown 50−200 μm single crystals, indicating a good match of molecular conformation, crystal packing, and unit cell parameters. The X-ray crystal structures were used to validate the developed workflow of data acquisition and structure solution with electron diffraction. This study highlights that 3D PEDT alone is able to provide accurate crystal structures from pharmaceutical nanocrystals that will suffice for most practical applications when no larger crystals can be grown.

KEYWORDS: *precession electron diffraction, electron diffraction tomography, crystal structure, ramelteon, tolvaptan*



PED tomography: Structure Determination of Pharmaceuticals

Article published in January 2017

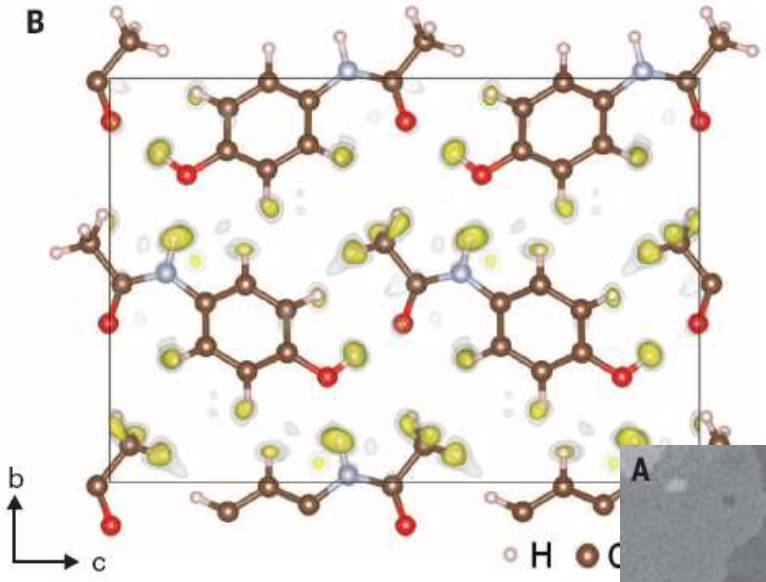
REPORT

MATERIALS SCIENCE

Hydrogen positions in single nanocrystals revealed by electron diffraction

L. Palatinus,[1*] P. Brázda,[1] P. Boullay,[2*] O. Perez,[2] M. Klementová,[1] S. Petit,[2] V. Eigner,[1] M. Zaarour,[3] S. Mintova[3]

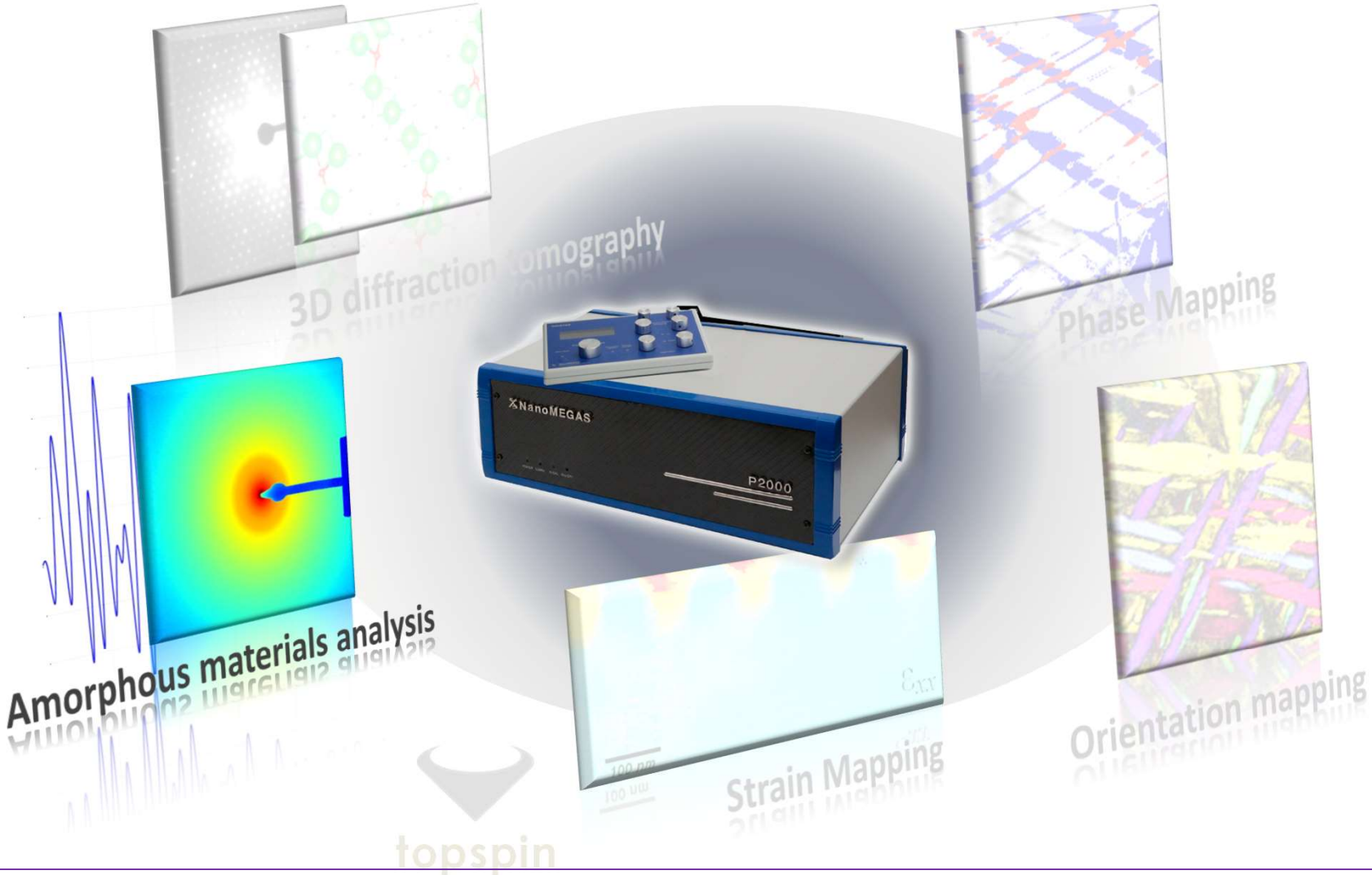
The localization of hydrogen atoms is an essential part of crystal structure analysis, but it is difficult because of their small scattering power. We report the direct localization of hydrogen atoms in nanocrystalline materials, achieved using the recently developed approach of dynamical refinement of precession electron diffraction tomography data. We used this method to locate hydrogen atoms in both an organic (paracetamol) and an inorganic (framework cobalt aluminophosphate) material. The results demonstrate that the technique can reliably reveal fine structural details, including the positions of hydrogen atoms in single crystals with micro- to nanosized dimensions.



Dynamical refinement

Palatinus et al, Science, 355, 166 - 169

Precession Electron Diffraction Applications

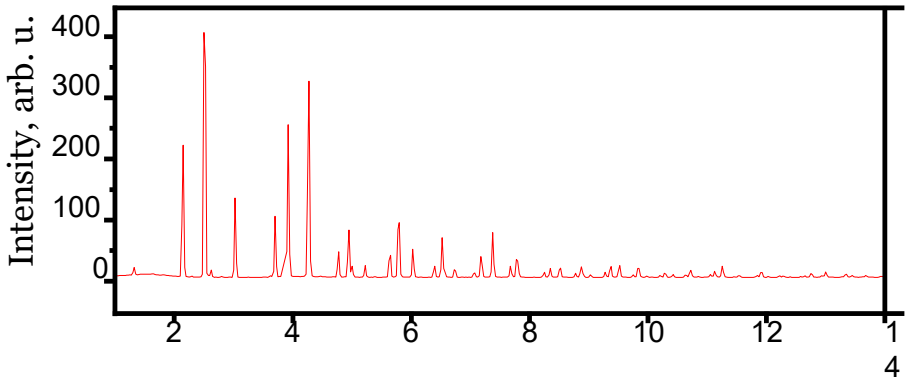


Amorphous Materials – Pair Distribution Function

How X-ray diffraction sees different materials

Crystalline materials

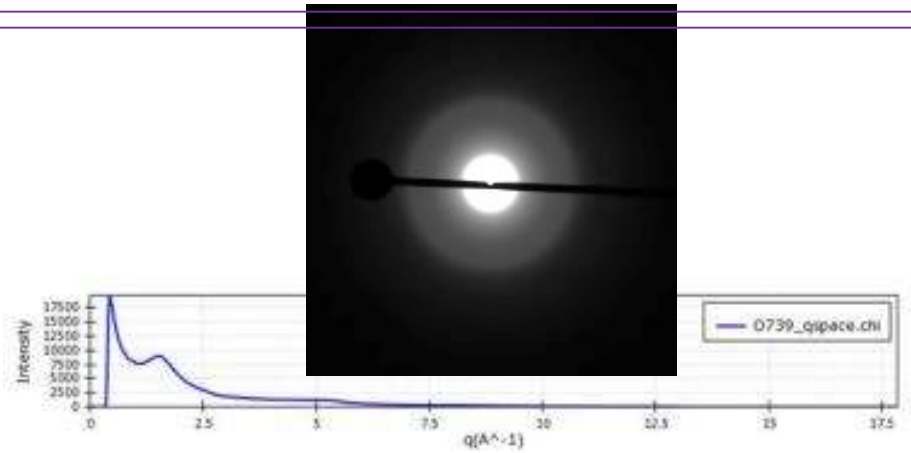
- Traditional crystallography
  - "Large" crystallites
  - Intense and sharp Bragg peaks visible
  - Structure refinement



Scattering vector Q, Å^{-1}

Amorphous Materials – Pair Distribution Function

- Amorphous
  - Glasses, Liquids
  - Structural coherence length < 1 nm
  - Broad diffuse scattering features



Amorphous material 1

$d_1 > d_2$

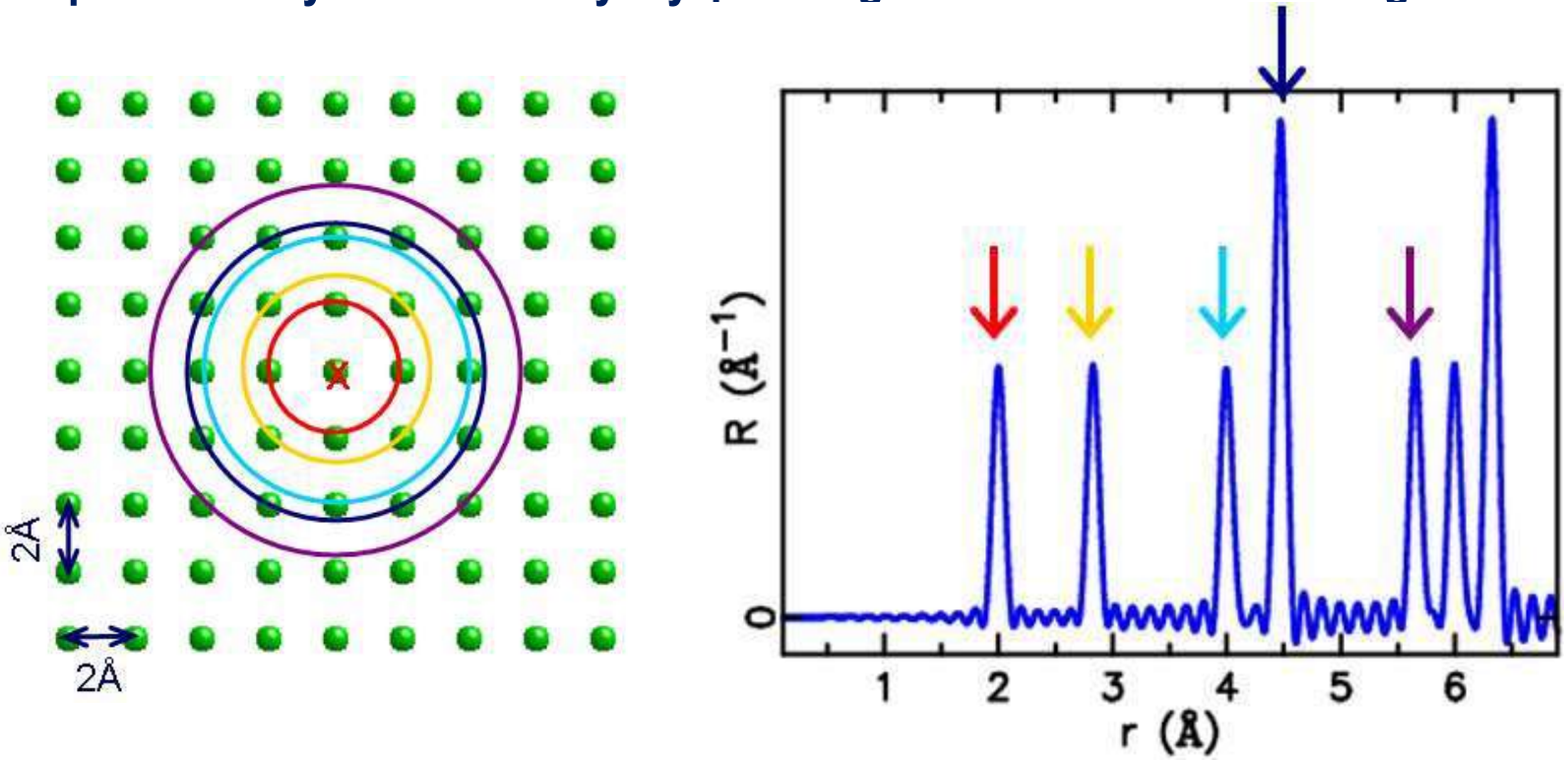
Amorphous material 2

Average distance between the atoms: d_1

Average distance between the atoms: d_2

Amorphous Materials – Pair Distribution Function

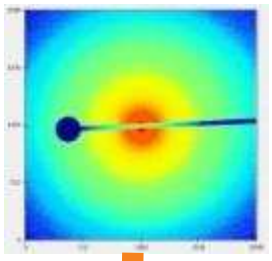
A total pair-distribution function (PDF) is obtained by repeating this process systematically by placing each atom in the origin.



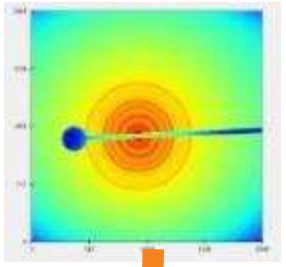
Pair Distribution Function G(r) is probability of finding an atom in a distance r

Amorphous Materials – Pair Distribution Function

amorphous

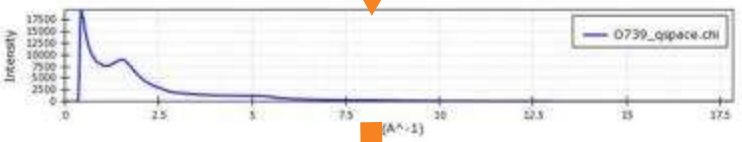


X-Ray diffraction data I(q)

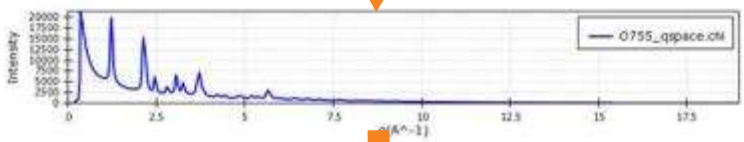


Nanomaterial

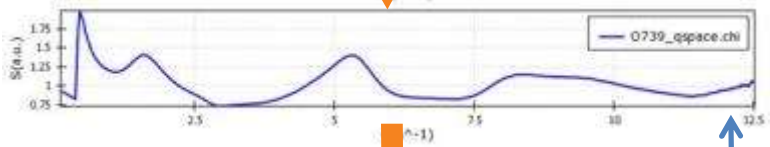
Corrected and Integrated data I(q)



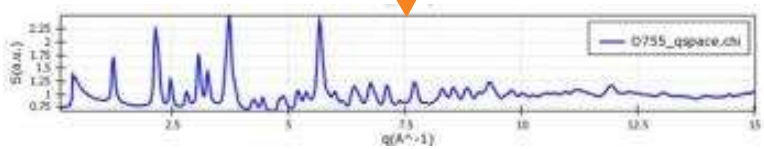
Corrected and Integrated data I(q)



Normalization to calculate S(q)



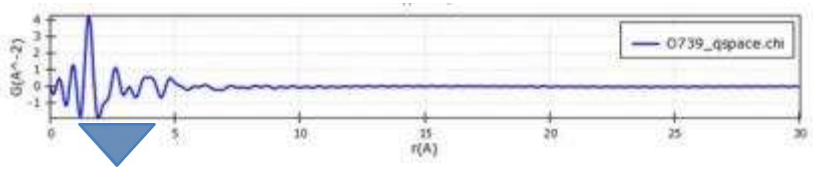
Normalization to calculate S(q)



Fourier transformation

Qmax for FT

PDF

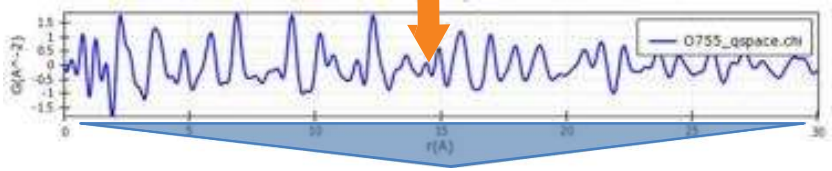


Short range order

Fourier transformation

Qmax for FT

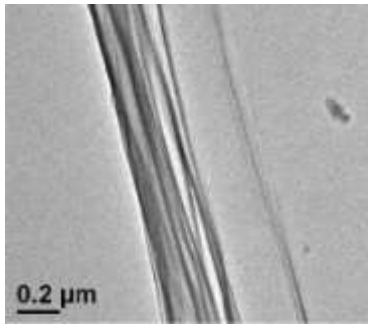
PDF

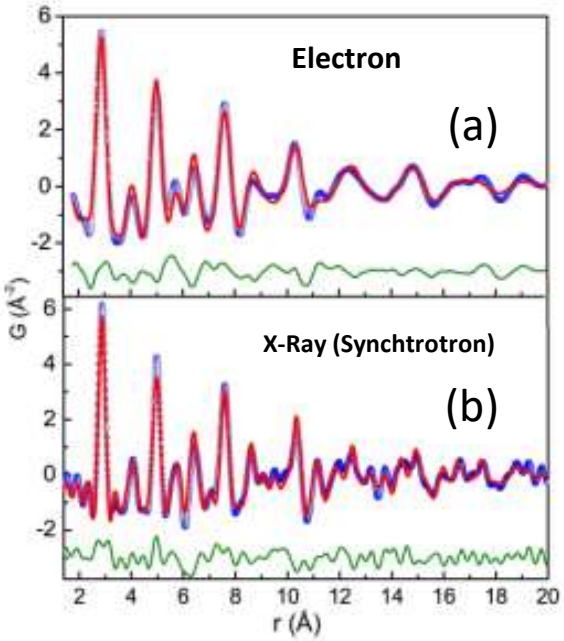


Long range order

Amorphous Materials – Pair Distribution Function

Comparison e- PDF vs X-Ray PDF - Au nanoparticles





Fitting of Au structure model with PDF

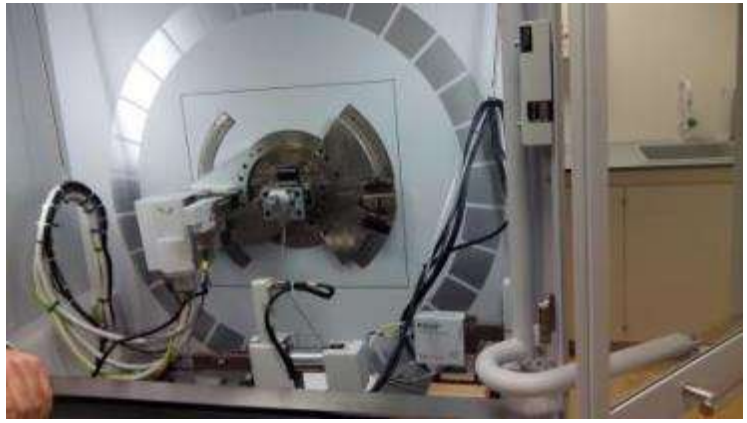
(a) e- PDF calculated from ED Data
(b) PDF calculated from X-Ray data

PDF obtained from election diffraction data and PDF obtained from X-ray are fully comparable , using e-PDF very small amorphous areas can be studied

Billinge et al. *Condensed Material* 2012

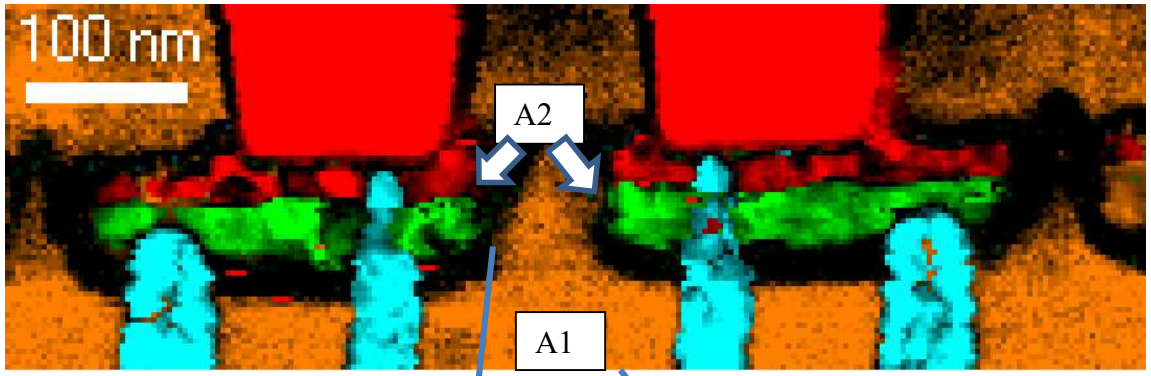
Amorphous Materials – Pair Distribution Function

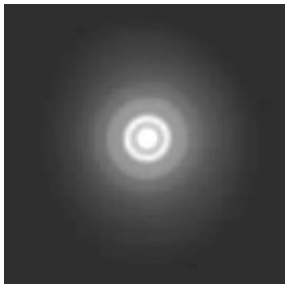
X-Ray PDF Diffraction : 24 h for single sample data collection (Ag/Mo radiation)



TEM – e PDF : 1 ms-1 sec data collection

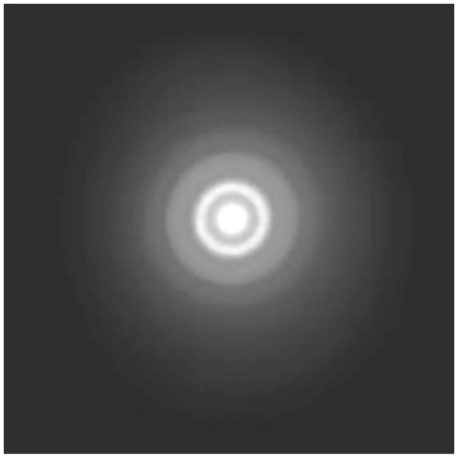
ePDF: Analysis of amorphous Semiconductor material



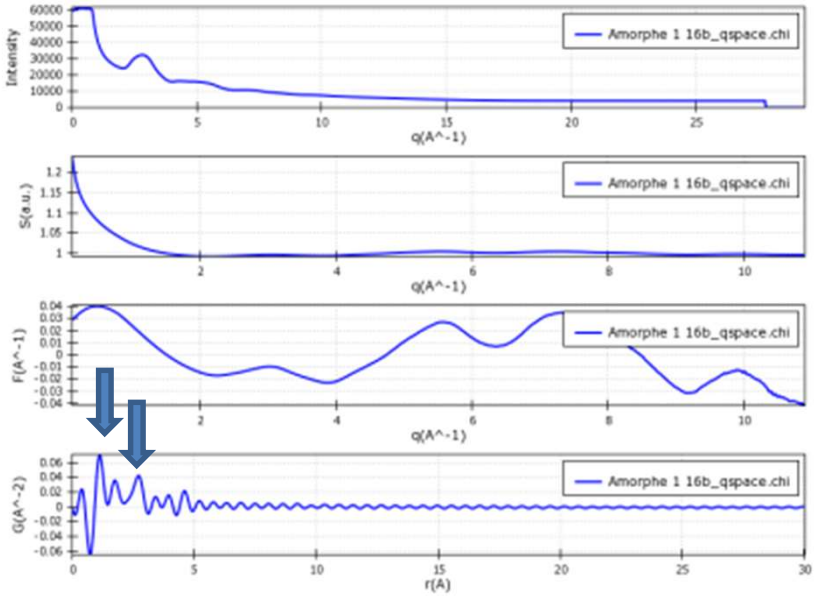


A1 region SiO2 amorphous
A2 (black) region Si3N4 amorphous

ePDF: Analysis of amorphous Semiconductor material

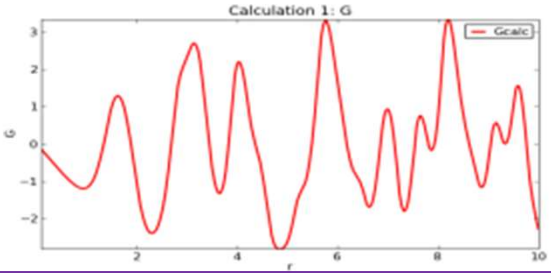


Gatan CCD 2kx 2k Qmax 10 Å-1



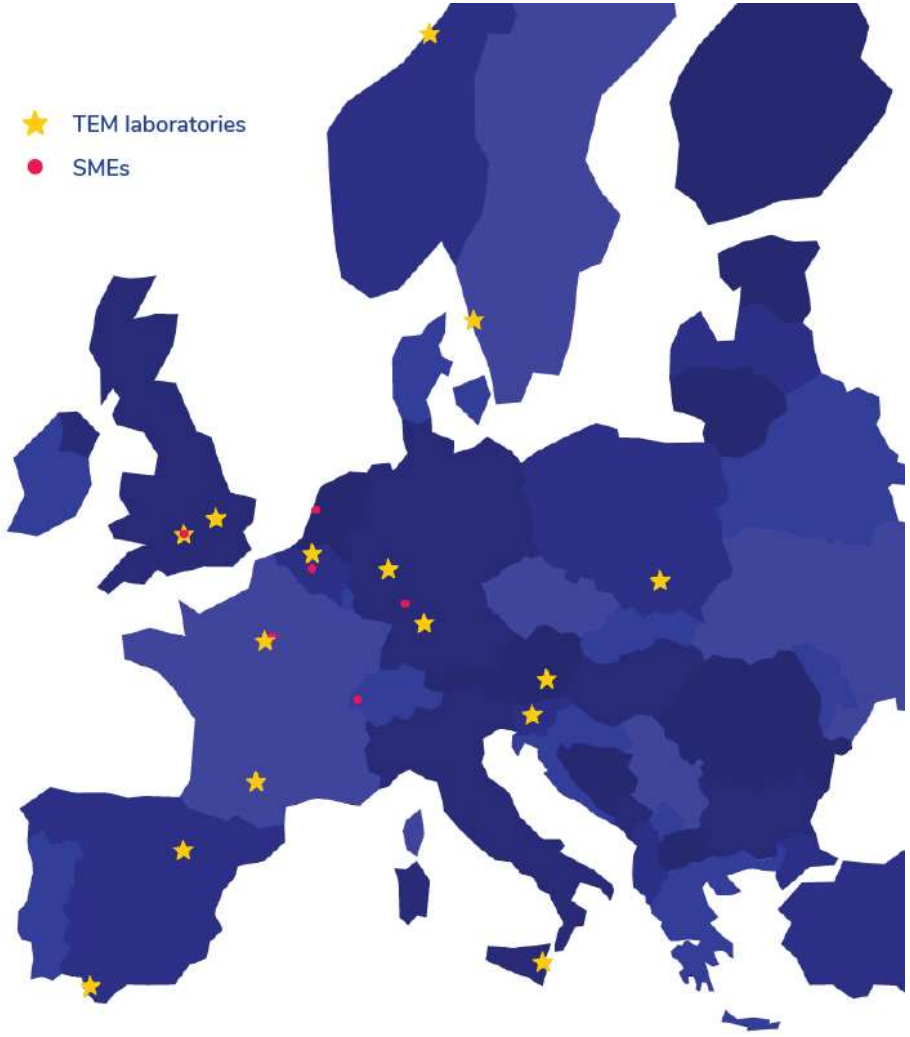
Distances found from PDF analysis match Si3N4 amorphous

1.10 Å
1.747 Å
2.75 Å



Si3N4

ESTEEM 3 in a nutshell



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