2022 ATE accelerator school

Synchrotron X-ray Nanoscopy Studies of Nanoscale Materials

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2022.08.08~2022.08.12

Chosun University
조 선 대 학 교

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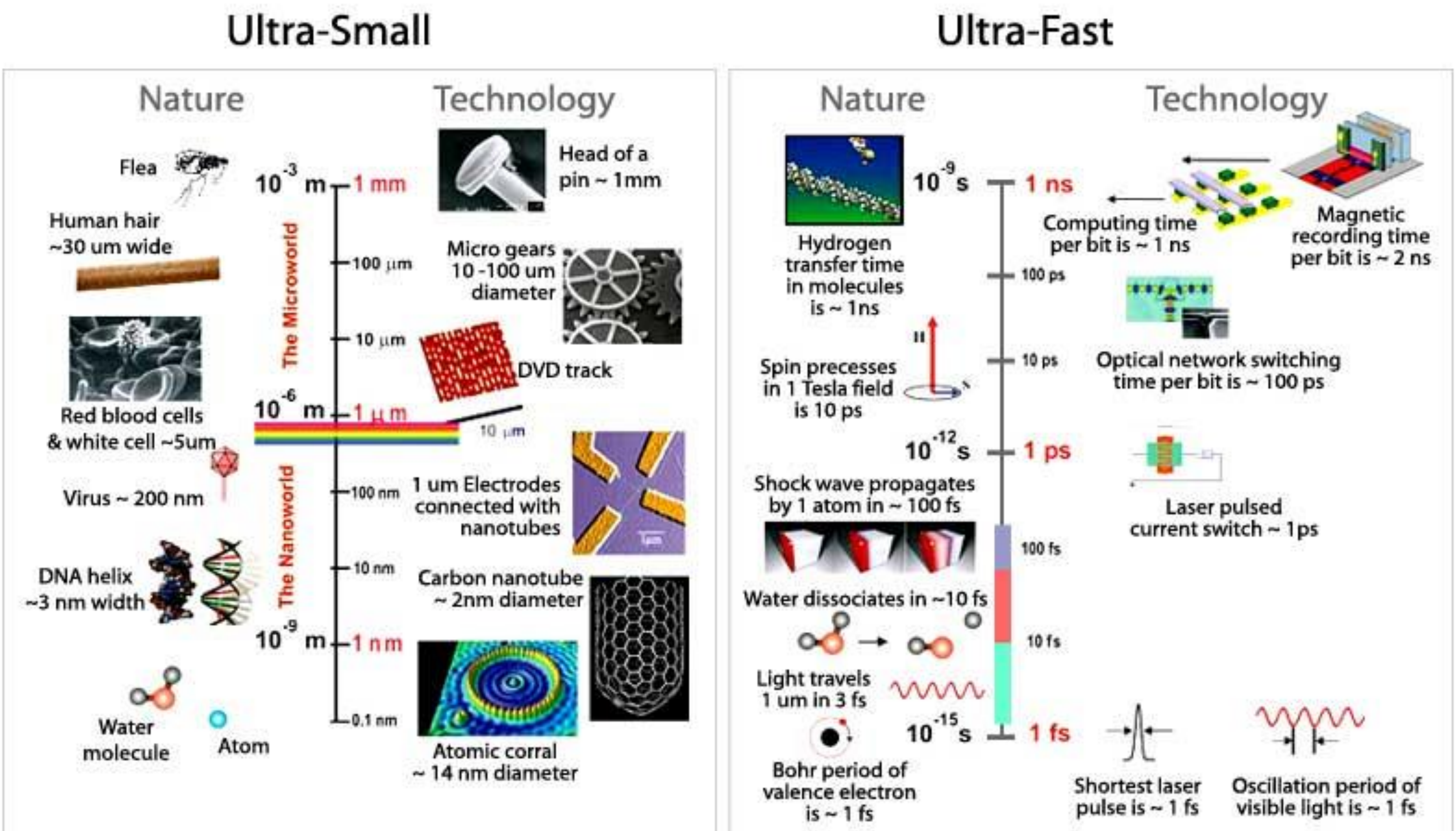
National Research Foundation (NRF)
through Science Research Center(SRC) program for
Center for Advanced X-ray Science (C-AXS)

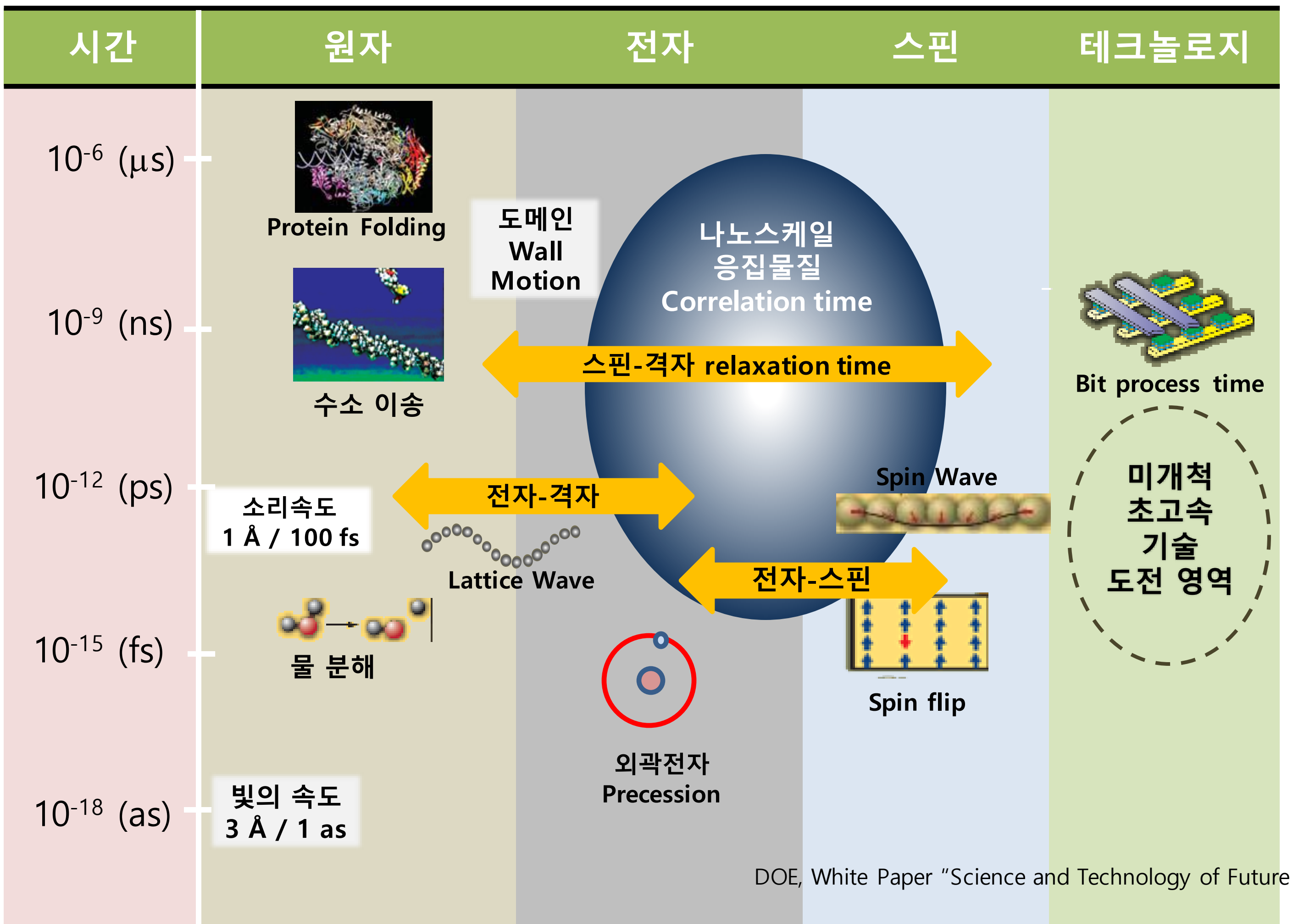
Chosun University
through Faculties Research Fund Program

Issues in Science



원자(분자)-전자-스핀 수준에서 물질의 이해

"정적/통계적" → "동역학적/개별적" 'Time Scale'



DOE, White Paper "Science and Technology of Future Light Sources" 참조

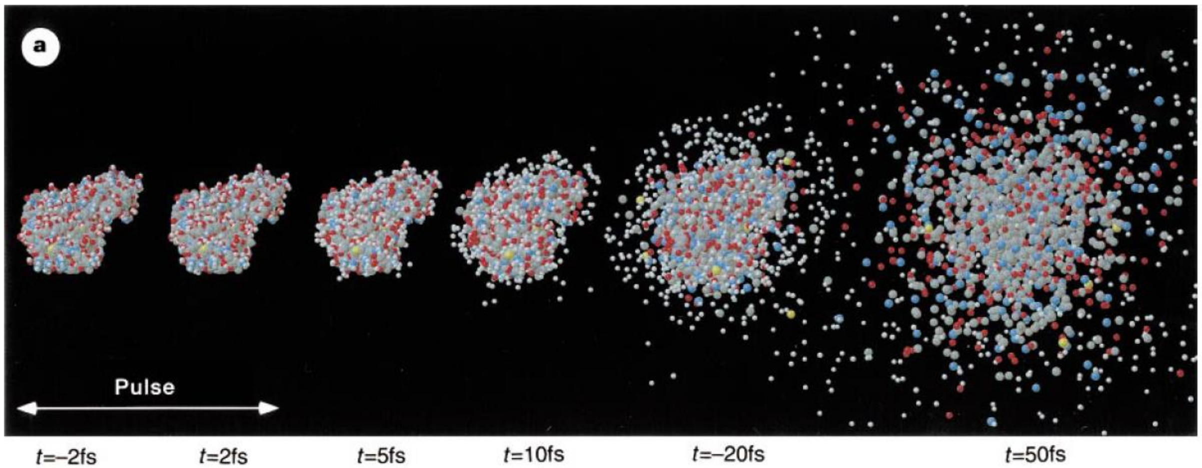
Molecular imaging with fs x-ray pulse

C-AXS

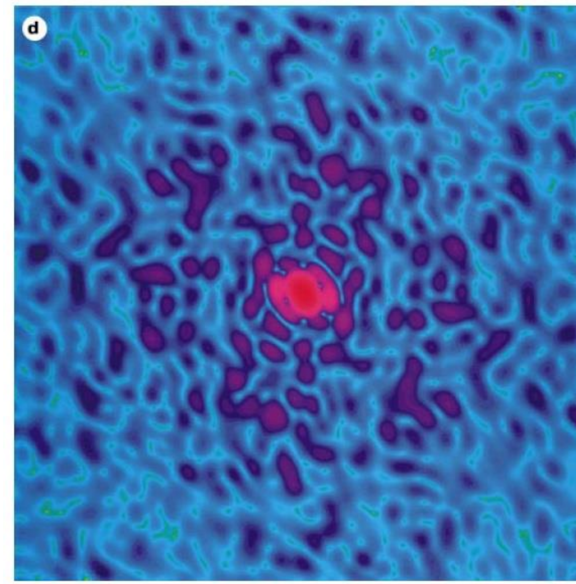
Potential for biomolecular imaging with femtosecond X-ray pulses

Richard Neutze*, Remco Wouts*, David van der Spoel*, Edgar Weckert†‡ & Janos Hajdu*

Nature **406**, 752 (2000)



Diffraction pattern



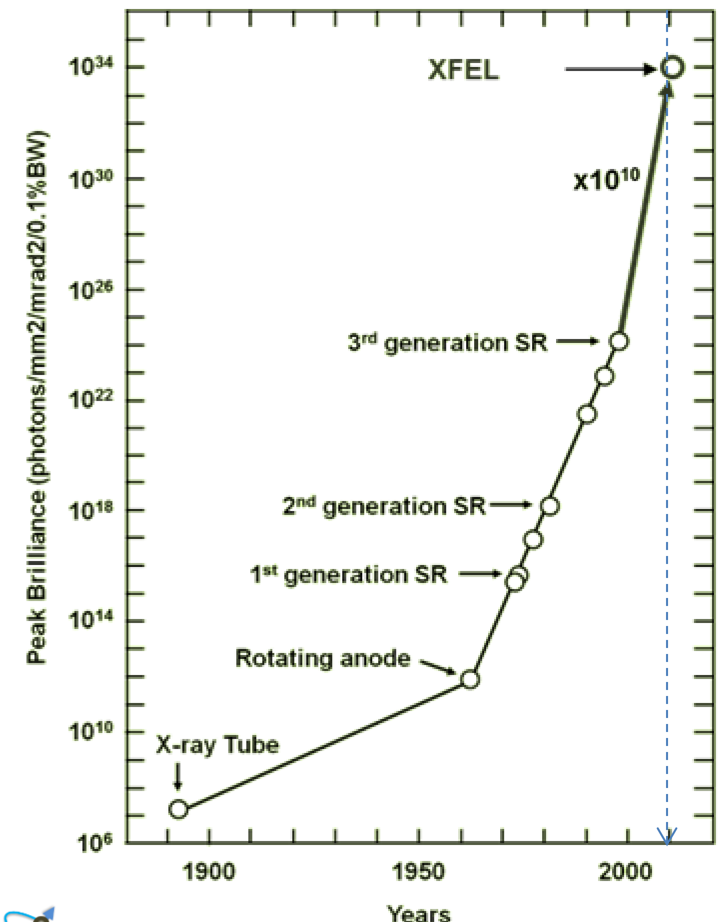
Ultra fast : Time of x-rays pulses → X-ray Free Electron Laser

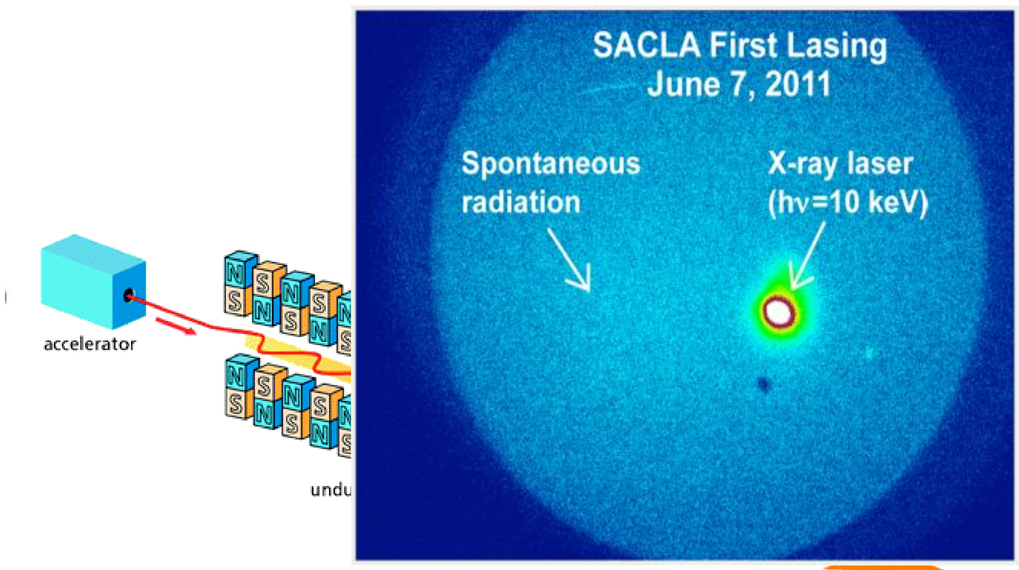
Ultra small : Spatial resolution of x-rays → X-ray focusing optics

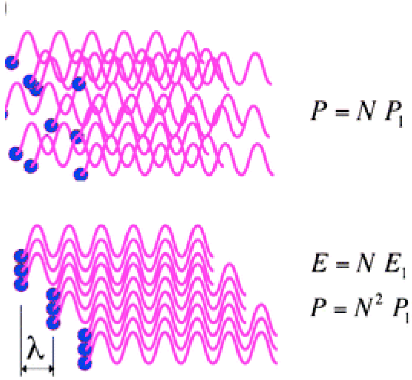
2010년대 : Ultimate X-선 광원

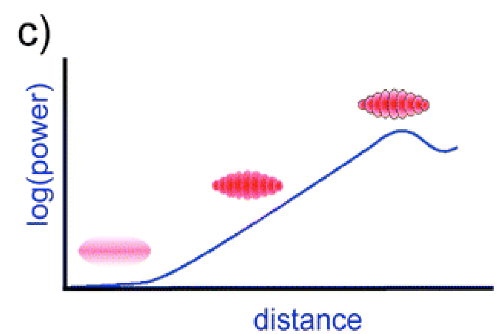
- X-ray Free Electron Lasers (XFEL)
- Ultimate Storage Ring (USR)

완벽한 Spatial Coherency (XFEL, USR)
극한의 Bright (FLUX) (XFEL, USR)
극도로 Short (PULSE) (XFEL)



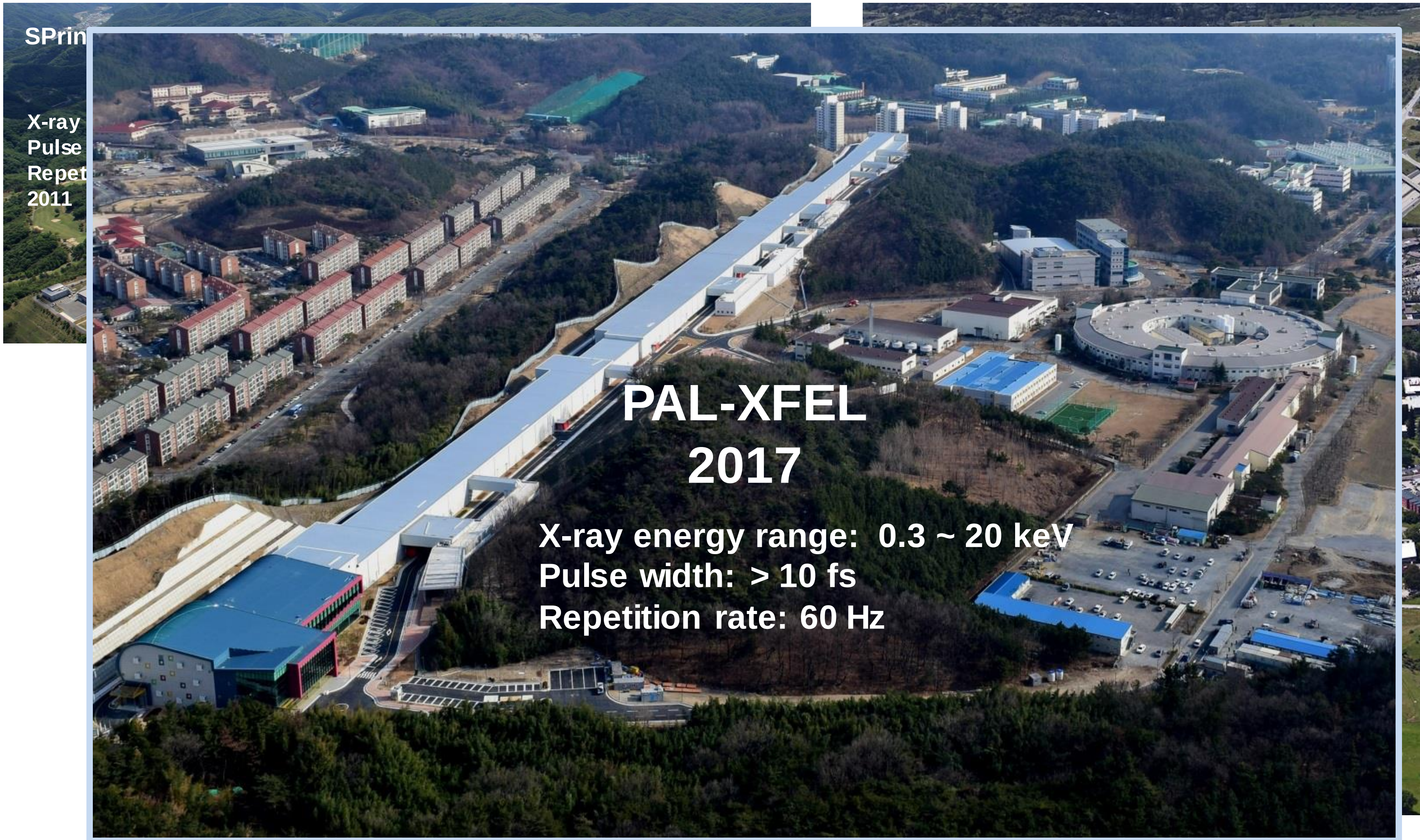






X-ray Free Electron Laser

C-AXS



X-ray probes

List of Nobel laureates (X-ray research)

When	What	Who	Why	Field of research	
1901	Physics	Wilhelm Conrad Röntgen	"in recognition of the extraordinary services he has rendered by the discovery of the remarkable rays subsequently named after him"	associated with crystallography	discovers X-rays
1905	Physics	Philipp Eduard Anton von Lenard	"for his work on cathode rays"		
1914	Physics	Max von Laue	"for his discovery of the diffraction of X-rays by crystals"	associated with crystallography	
1915	Physics	Sir William Henry Bragg and William Lawrence Bragg	"for their services in the analysis of crystal structure by means of X-rays"	associated with crystallography	extend the use of X-ray diffraction as a technique for determining crystal structure
1917	Physics	Charles Glover Barkla	"for his discovery of the characteristic Röntgen radiation of the elements"	associated with crystallography	
1924	Physics	Karl Manne Georg Siegbahn	"for his discoveries and research in the field of X-ray spectroscopy"		
1927	Physics	Arthur Holly Compton	"for his discovery of the effect named after him"		
1936	Chemistry	Petrus (Peter) Josephus Wilhelmus Debye	"for his contributions to our knowledge of molecular structure through his investigations on dipole moments and on the diffraction of X-rays and electrons in gases"	associated with crystallography	
1936	Physics	Victor Franz Hess	"for his discovery of cosmic radiation"		
1946	Physiology or Medicine	Hermann Joseph Muller	"for the discovery of the production of mutations by means of X-ray irradiation"		

List of Nobel laureates (X-ray research)

C-AXS

When	What	Who	Why	Field of research	
1958	Physics	Pavel Alekseyevich Cherenkov, Il′ja Mikhailovich Frank and Igor Yevgenyevich Tamm	“for the discovery and the interpretation of the Cherenkov effect”		
1961	Physics	Rudolf Ludwig Mössbauer	“for his researches concerning the resonance absorption of gamma radiation and his discovery in this connection of the effect which bears his name”		
1962	Chemistry	Max Ferdinand Perutz and John Cowdery Kendrew	“for their studies of the structures of globular proteins”	associated with crystallography	
1962	Physiology or Medicine	Francis Harry Compton Crick, James Dewey Watson and Maurice Hugh Frederick Wilkins	“for their discoveries concerning the molecular structure of nucleic acids and its significance for information transfer in living material”		
1964	Chemistry	Dorothy Crowfoot Hodgkin	“for her determinations by X-ray techniques of the structures of important biochemical substances” including Vitamin B12	associated with crystallography	
1972	Chemistry	Christian B. Anfinsen	“for his work on ribonuclease, especially concerning the connection between the amino acid sequence and the biologically active conformation”	associated with crystallography	
1972	Chemistry	Stanford Moore and William H. Stein	“for their contribution to the understanding of the connection between chemical structure and catalytic activity of the active centre of the ribonuclease molecule”		
1976	Chemistry	William N. Lipscomb	“for his studies on the structure of boranes illuminating problems of chemical bonding”	associated with crystallography	

List of Nobel laureates (X-ray research)

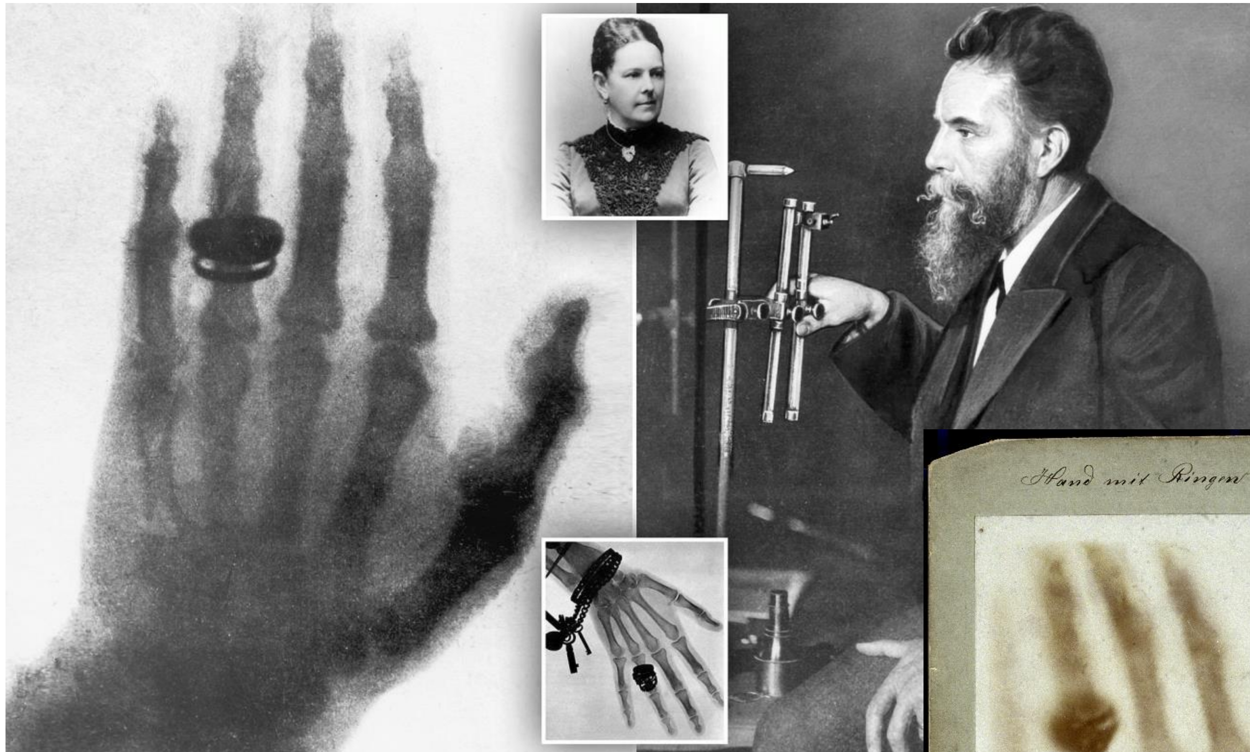
When	What	Who	Why	Field of research	
1979	Physiology or Medicine	Allan M. Cormack and Godfrey N. Hounsfield	"for the development of computer assisted tomography"		
1981	Physics	Kai M. Siegbahn	"for his contribution to the development of high-resolution electron spectroscopy"		
1985	Chemistry	Herbert A. Hauptman and Jerome Karle	"for their outstanding achievements in the development of direct methods for the determination of crystal structures"	associated with crystallography	
1988	Chemistry	Johann Deisenhofer, Robert Huber and Hartmut Michel	"for the determination of the three-dimensional structure of a photosynthetic reaction centre"	associated with crystallography	
1997	Chemistry	Paul D. Boyer and John E. Walker	"for their elucidation of the enzymatic mechanism underlying the synthesis of adenosine triphosphate (ATP)"		for his work on the structure of Bovine F1 ATP synthase
2003	Chemistry	Peter Agre and Roderick Mackinnon	"for discoveries concerning channels in cell membranes"	associated with crystallography	
2009	Chemistry	Venkatraman Ramakrishnan, Thomas A Steitz and Ada E Yonath	"for studies of the structure and function of the ribosome"	associated with crystallography	
2011	Chemistry	Dan Shechtman	"for the discovery of quasicrystals"	associated with crystallography	
2012	Chemistry	Robert J. Lefkowitz and Brian K. Kobilka	"for studies of G-protein-coupled receptors"	associated with crystallography	

The Fist Nobel laureate

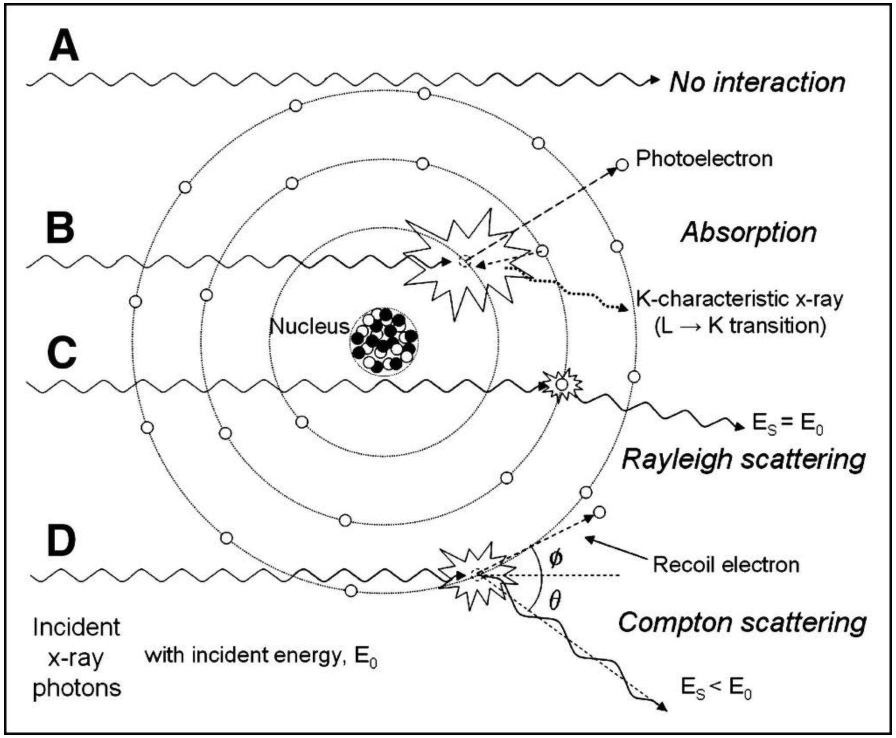
Photo from the Nobel Foundation archive.

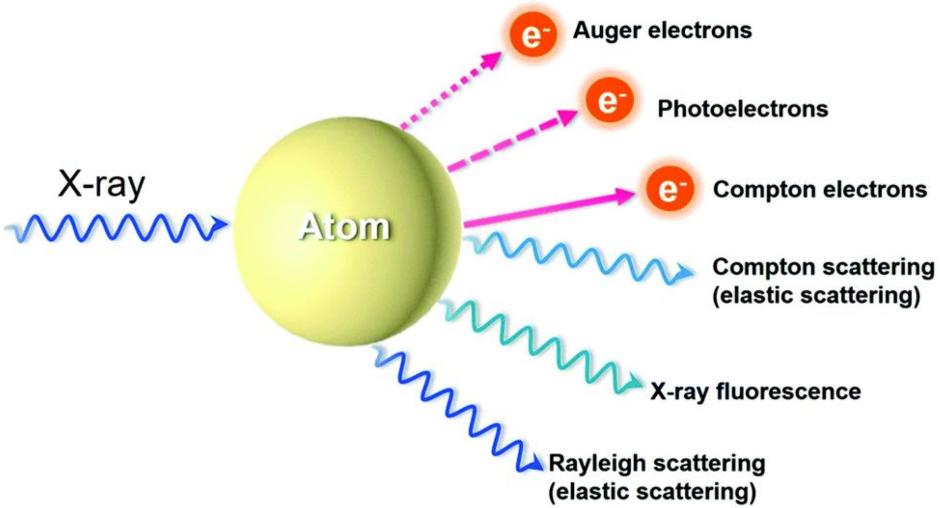
Wilhelm Conrad Röntgen

Prize share: 1/1



X-rays interact with matter





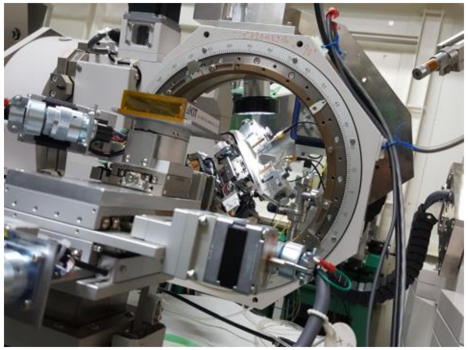
- ✓ **X-rays can probe the properties of matter (atoms).**
- ✓ **Varies probing techniques have been invented and utilized.**

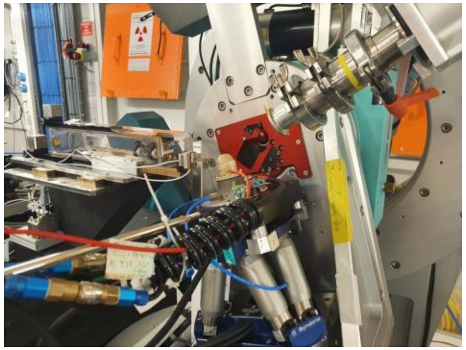
→ Absorption, Transmission, Diffraction, Scattering, Reflection, Refraction etc

Synchrotron facility

C-AXS

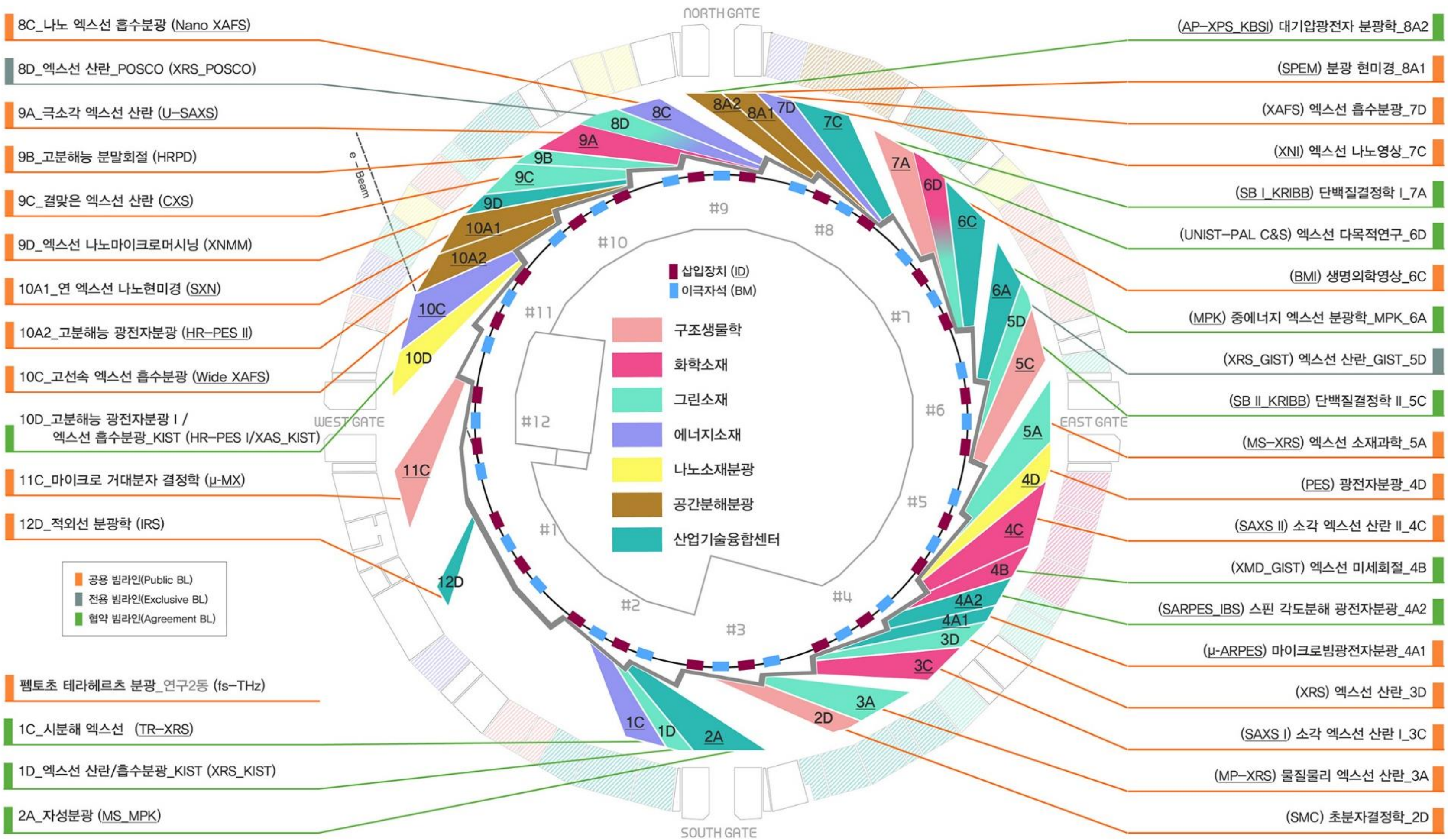
Synchrotron X-ray beamline : End-station





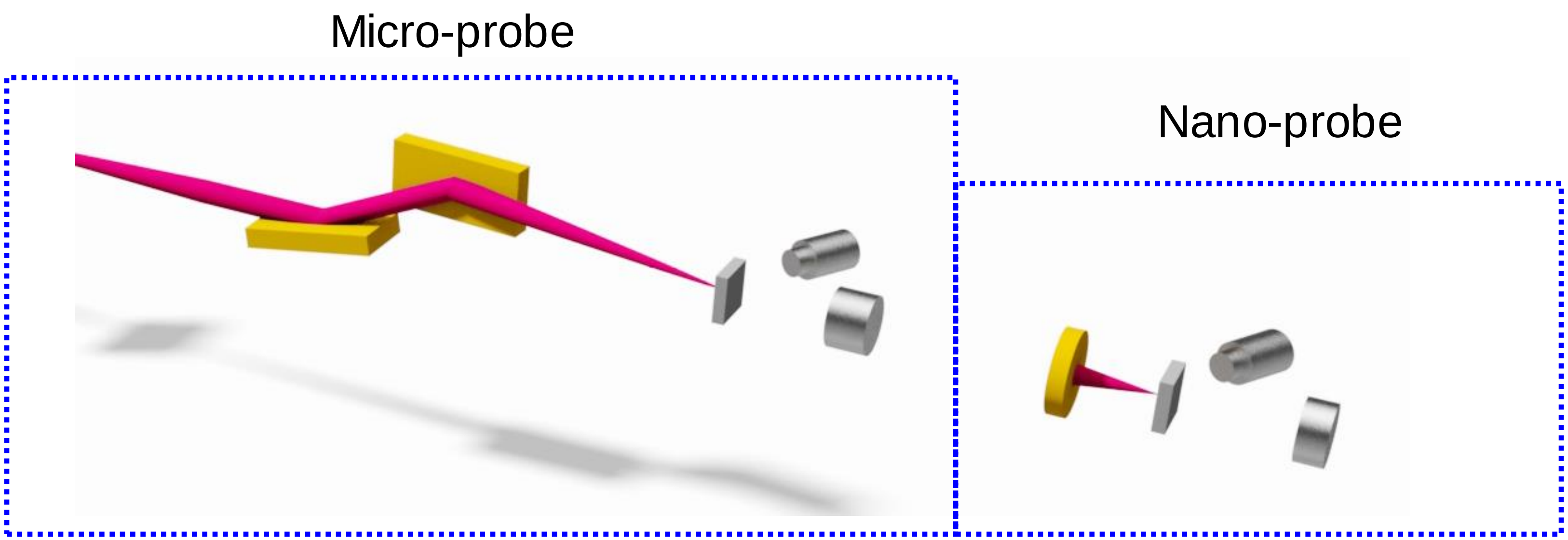
PLS-II : Beamline map

C-AXS



PAL 포항가속기연구소 과학기술정보통신부

Synchrotron X-ray beamline : End-station



Micro-probe for sub 1 μm (200 ~ 500 nm) : high-throughput setup

→ Optics : K-B mirror

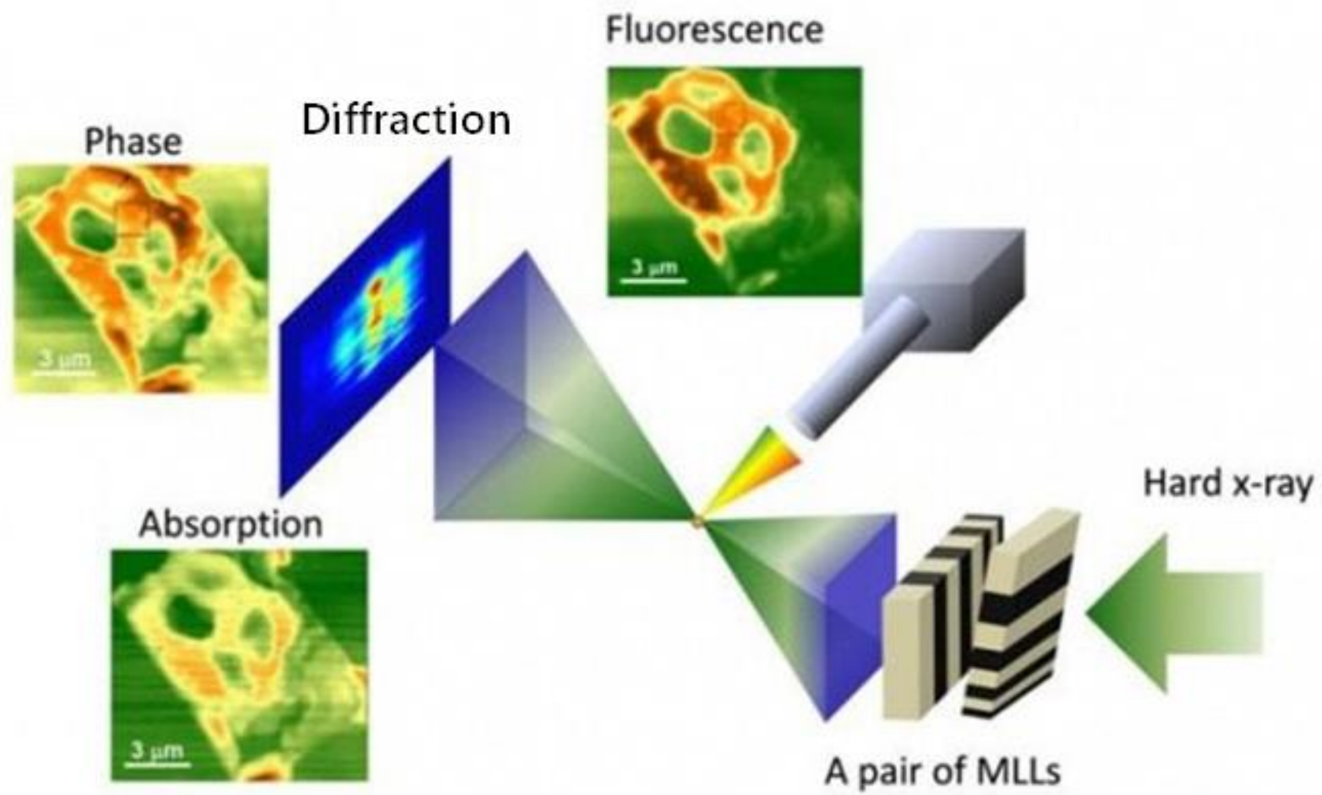
→ XRF, XES, Diffraction (6-circle diffractometer or scanner on optical table)

Nano-probe for sub 50 nm (push to resolution limit of sub 10 nm)

→ Optics : K-B mirror, FZP, (option : Multilayer Laue lens)

→ Ptychographic X-ray CT, 2D nano-XANES, 3D-XRF (all nano-stage on granite table)

X-rays interact with matter (atoms)

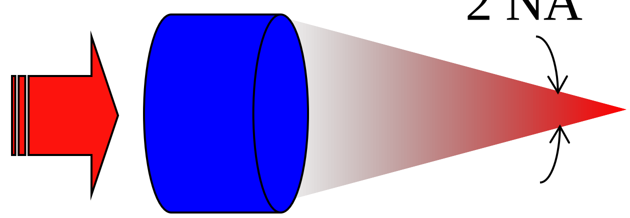


- ✓ **Multi-modal hard X-ray nano-probe** **(energy : ~8 keV, <25 keV)**
- ✓ ***Current Resolution : < 20 nm in 2D, 40 nm in 3D***
- ✓ ***In-situ capability : working distance, field-of-view, depth-of-focus***
- ✓ ***Optics : K-B mirror, CRL, Fresnel zone plate, Multilayer Laue Lens***

X-ray Nano-focusing Optics

X-ray Focusing Optics

Ultimate X-선 광원 개발 시작
: 2000년~



- *Rayleigh criterion* : Resolution = $\dfrac{\lambda}{2\,\mathrm{NA}}$

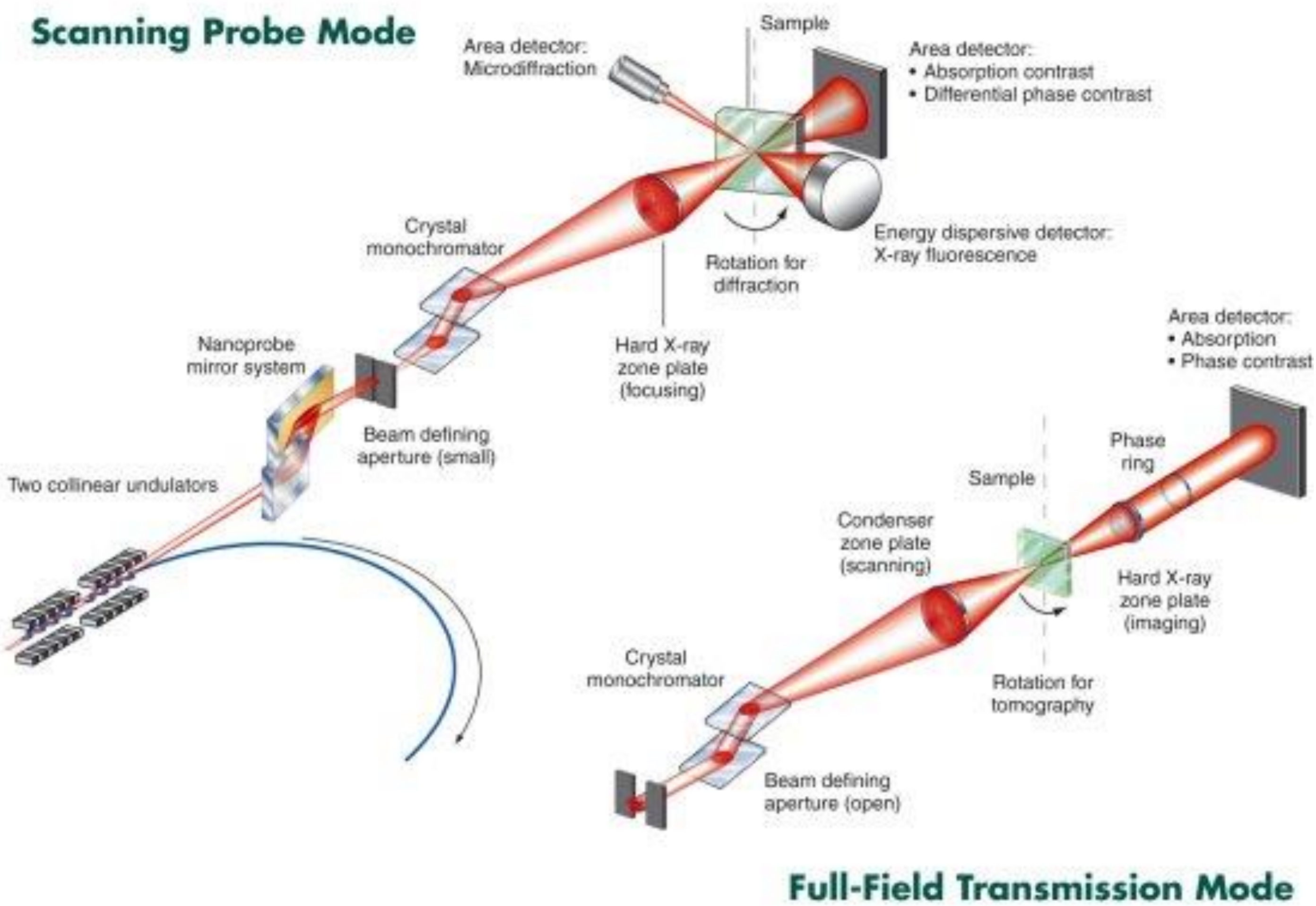
If optics with large NA and low aberrations can be produced
Can x-rays be focused down to the near atomic scale ?

Currently Resolution ~ $100 \times \lambda$

Questions :

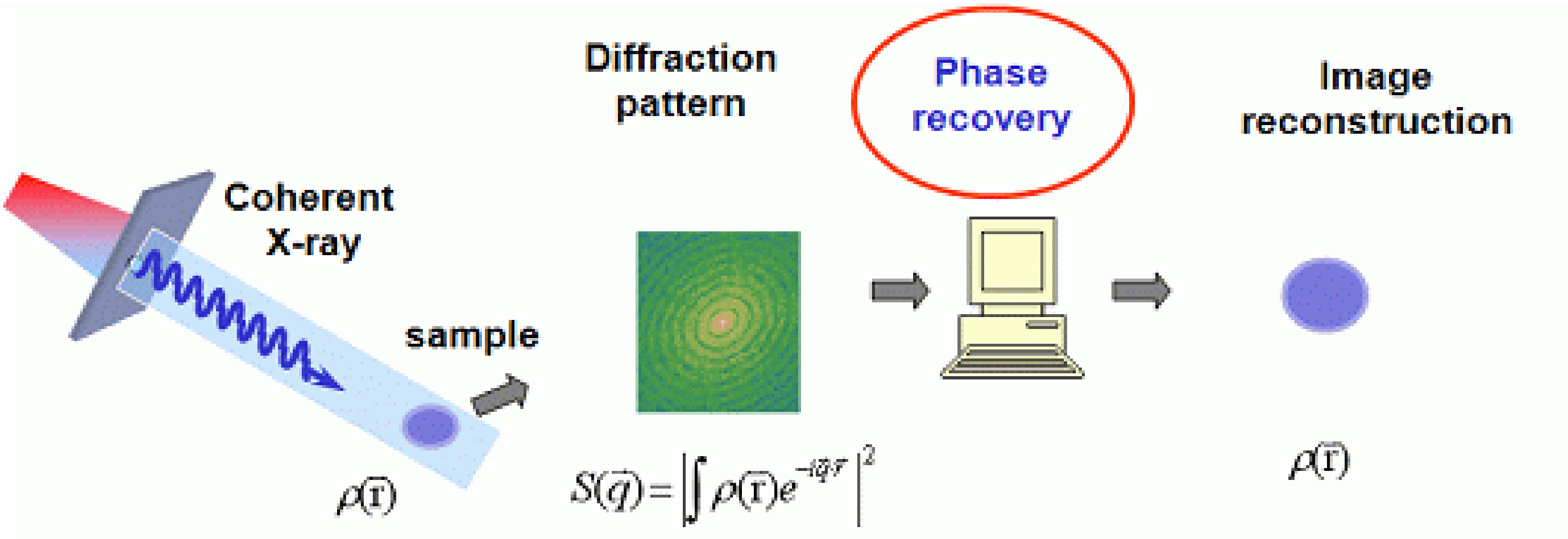
i) Where is the fundamental limit using real materials ?
ii) Can we fabricate optics that should reach the fundamental limit ?

X-ray Microscopy



→ Resolution of microscopy can be determined by the performance of the focusing optics.

Coherent X-ray Diffractive Imaging (CDI)



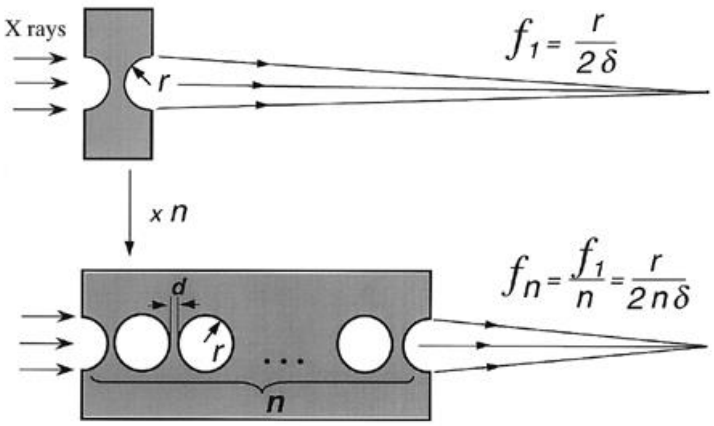
illumination

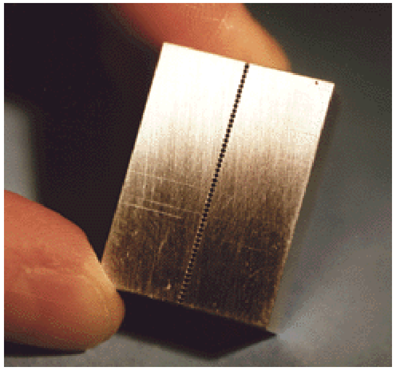
Intensity measurement

Algorithm

- Lessless Imaging technique by phase recovery
- Algorithm : Phase recovery → Coherent X-ray Diffractive Imaging (CDI)

Compound Refractive Lens (CRL)

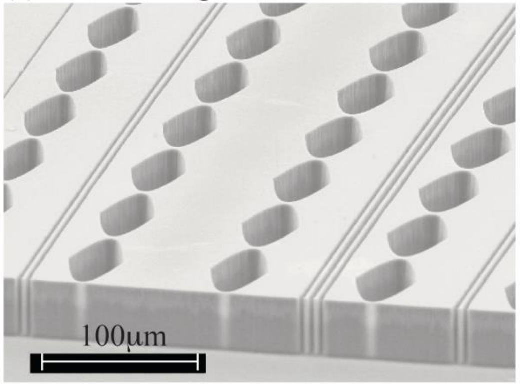




A. Snigirev et al. Nature (1996)

150 μm→ 8 μm

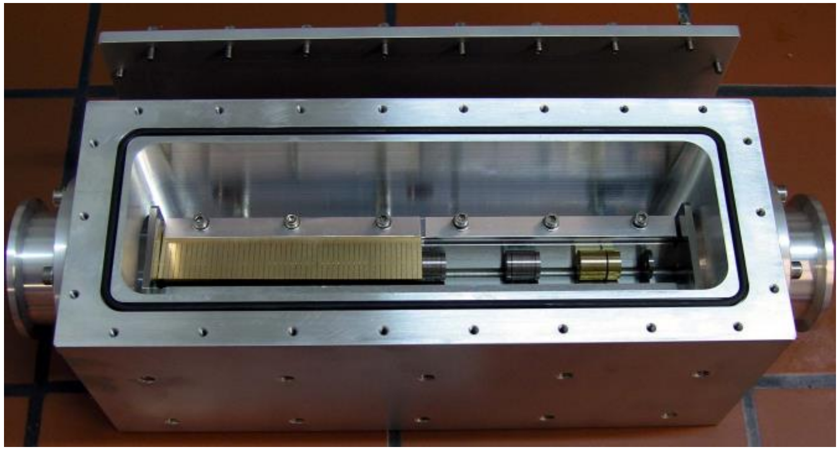
(a) nanofocusing refractive lenses



50 x 50 nm^2 @ 21 keV, ESRF

C. G. Schroer et al.

APL, ***87***, *124103 (2006)*

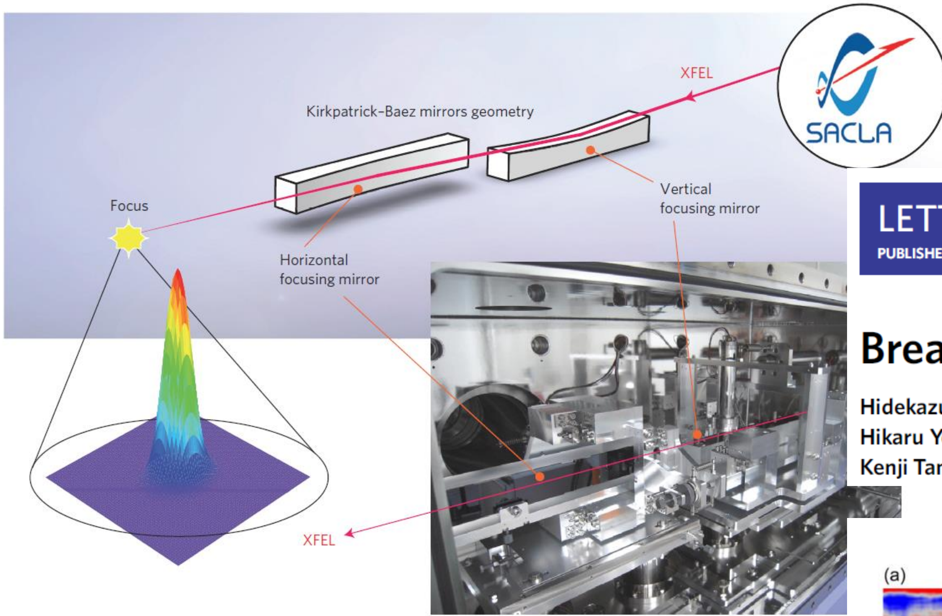


Materials : Be, Diamond, Si

Limited by weak refraction

→ Low efficiency

K-B mirror




LETTERS
PUBLISHED ONLINE: 22 NOVEMBER 2009 | DOI: 10.1038/NPHYS1457

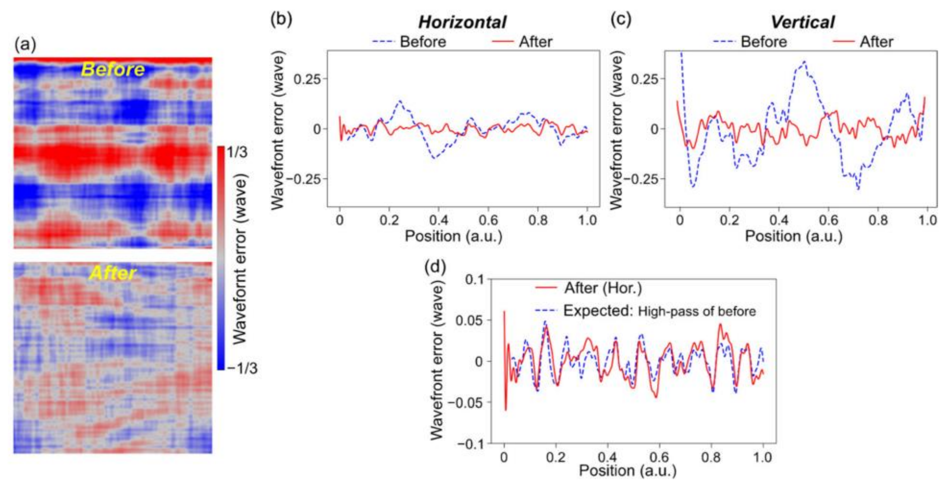
nature physics

Breaking the 10 nm barrier in hard-X-ray focusing

Hidekazu Mimura[1*], Soichiro Handa[1], Takashi Kimura[1], Hirokatsu Yumoto[2], Daisuke Yamakawa[1], Hikaru Yokoyama[1], Satoshi Matsuyama[1], Kouji Inagaki[1], Kazuya Yamamura[3], Yasuhisa Sano[1], Kenji Tamasaku[4], Yoshinori Nishino[4], Makina Yabashi[4], Tetsuya Ishikawa[4] and Kazuto Yamauchi[1,3]

Nature Physics, 6, 122 (2010) → *Spring-8*

Nature Photonics, 7, 43 (2013) → *SACLA*



Osaka University

7 nm (1D), 20 x 20 nm^2 (2D)

→ *Wave-front correction method*

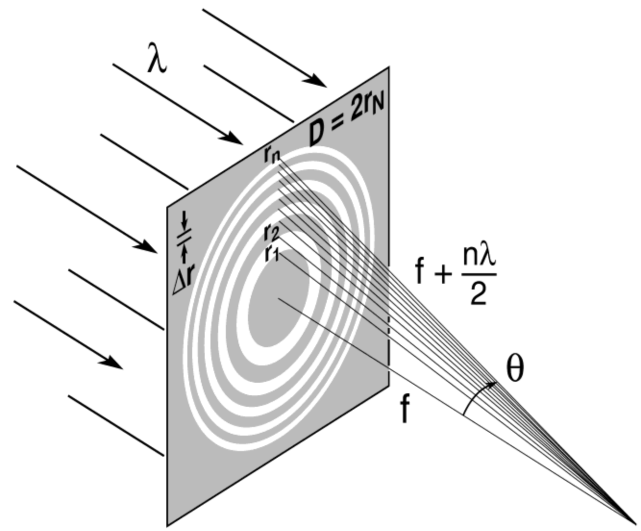
Diffractive optics with high NA

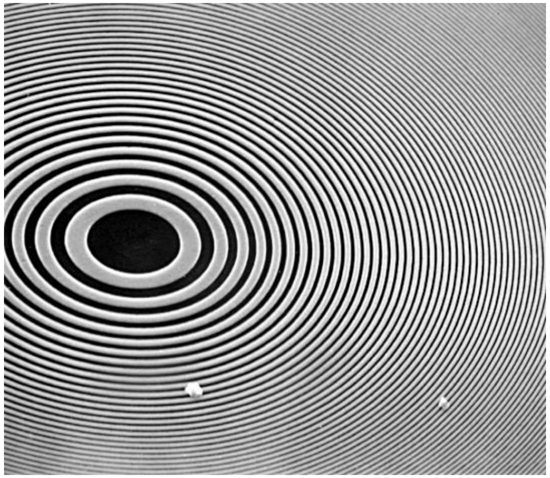
C-AXS

- Small focal spot sizes require small zone widths.
- Zone plate structures for hard x-rays must be several microns thick to achieve high efficiency, which implies high aspect ratios (>>100).
- It is difficult to produce such high aspect ratio structures using lithography.
- Sectioning of multilayers allows very high aspect ratios to be produced.

https://cxro.lbl.gov
https://zoneplate.lbl.gov

Fresnel Zone Plate

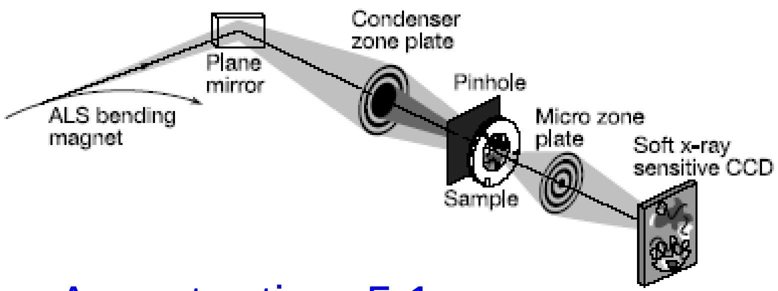




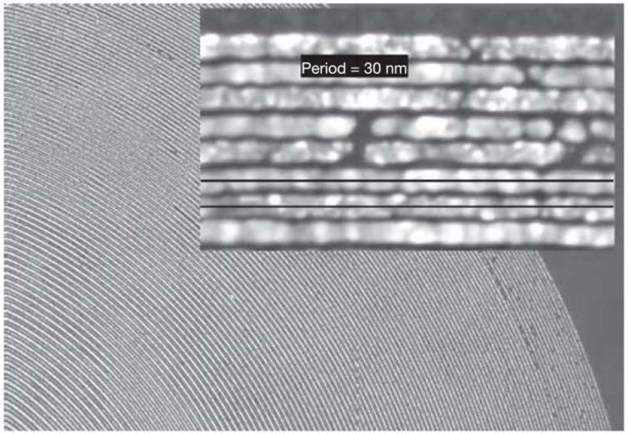
Soft X-ray microscopy at a spatial resolution better than 15 nm

Nature ***435***,*1210 (2005)*

Weilun Chao[1,2], Bruce D. Harteneck[1], J. Alexander Liddle[1], Erik H. Anderson[1] & David T. Attwood[1,2]

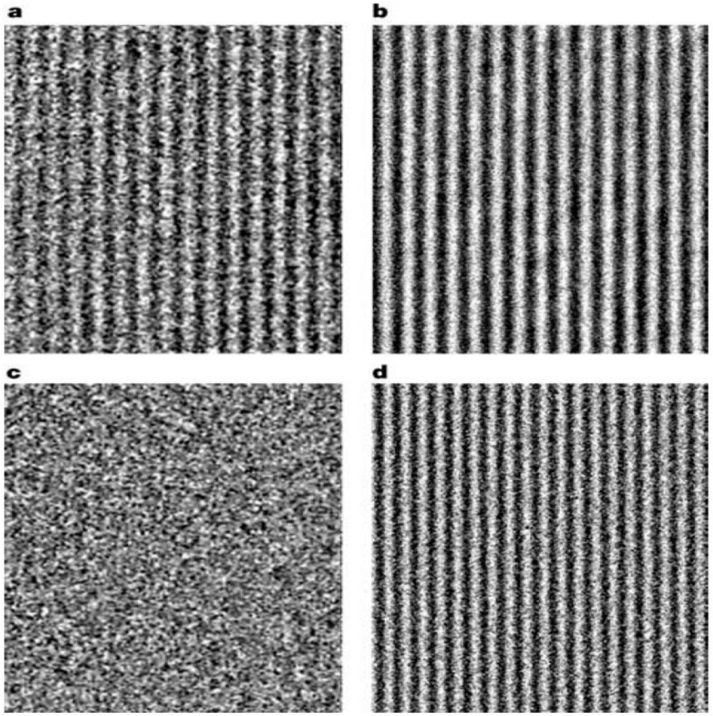


Aspect ratio ~ 5:1



Cr/Si Multilayer @ 0.8 keV

25 nm ZP   15 nm ZP



19.5 nm spacing

15.1 nm spacing

Multilayer Laue Lens

Multilayer Laue lens

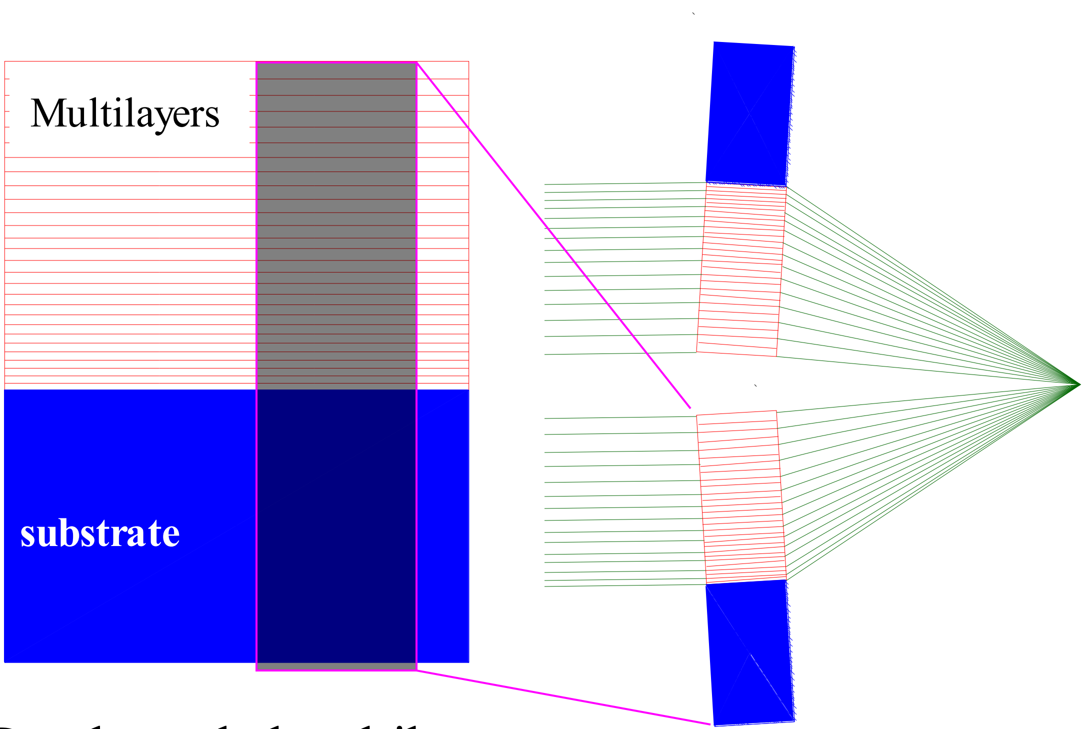
Deposition + Sectioning + Assembling

(1) Deposit multilayer with depth-graded spacing to form zones of linear zone plate (thinnest structures first!)

(2) Make cross-sections to allow use in Laue geometry (high aspect ratio structure)

(3) Assemble sections at right angles to form point focus (High efficiency)

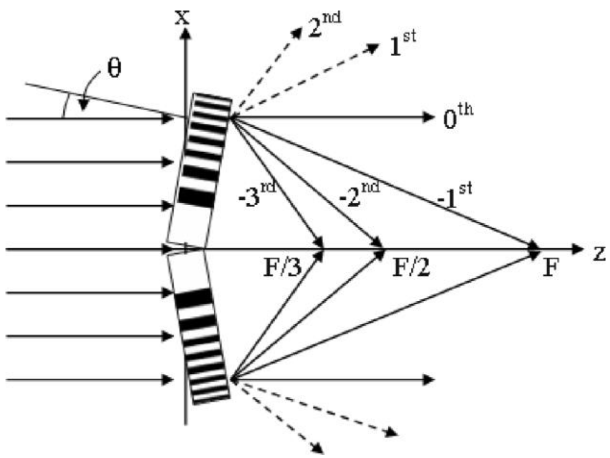
Multilayer Laue Lens

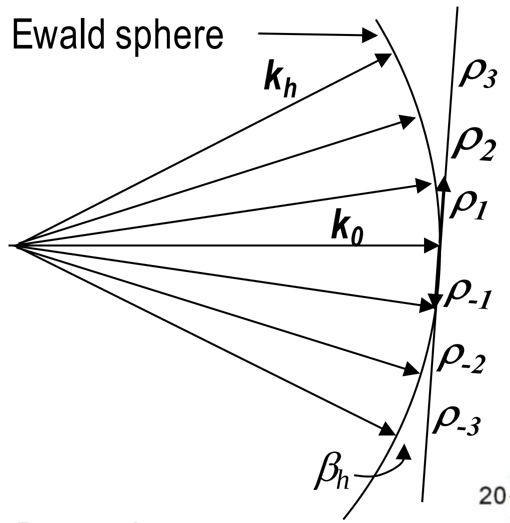


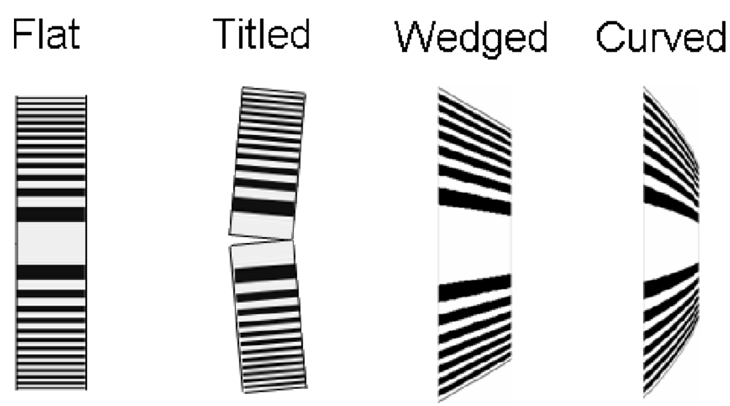
Depth-graded multilayers on flat Si substrate

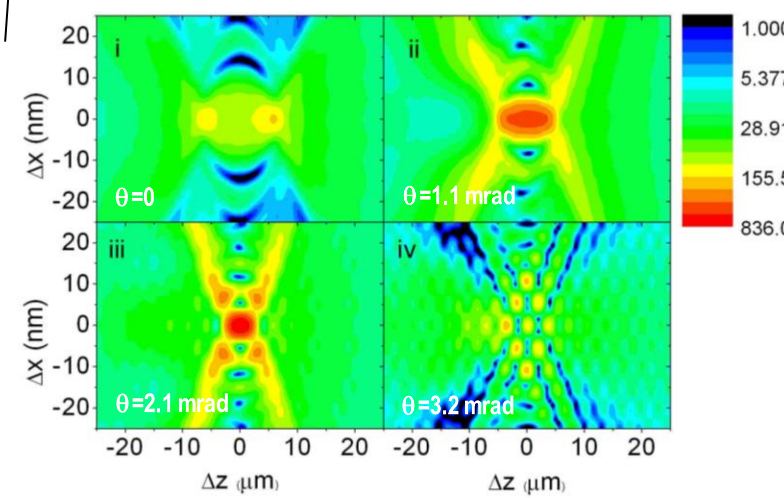
Dynamic diffraction effect (volume effect)

MLL is no longer optically “thin”, *i. e.*, geometrical theory fails.



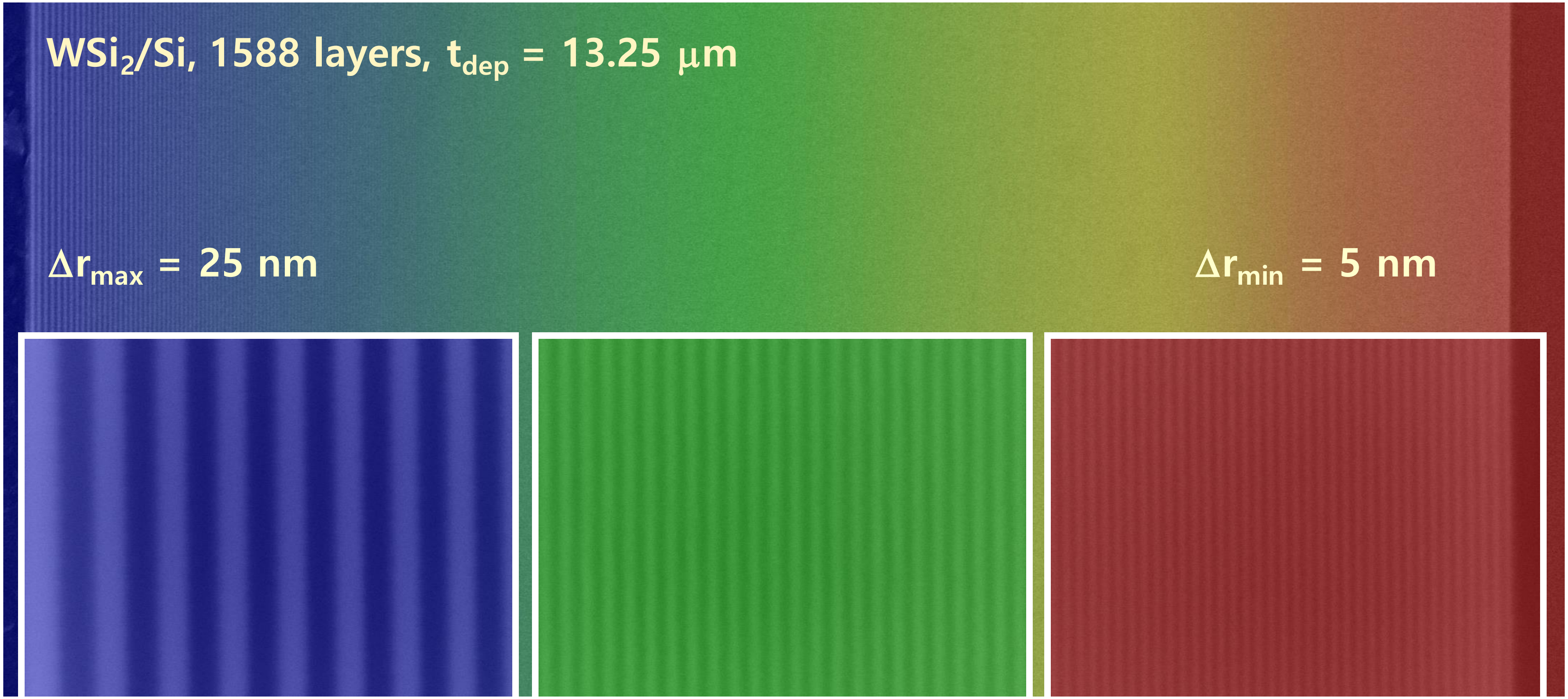






H. C. Kang et al., Phys. Rev. Lett. **96**, 127401 (2006).
H. F. Yan, H. C. Kang et al., Phys. Rev. B **76**, 115438 (2007).

16 nm hard X-ray nano beam



H. C. Kang et al. Physical Review Letters, 96 127401 (2006)

H. C. Kang et al. Applied Physics Letters, (2008)

Advanced Photon Source

Advanced Photon Source, Argonne National Laboratory

3rd generation synchrotron : undulator

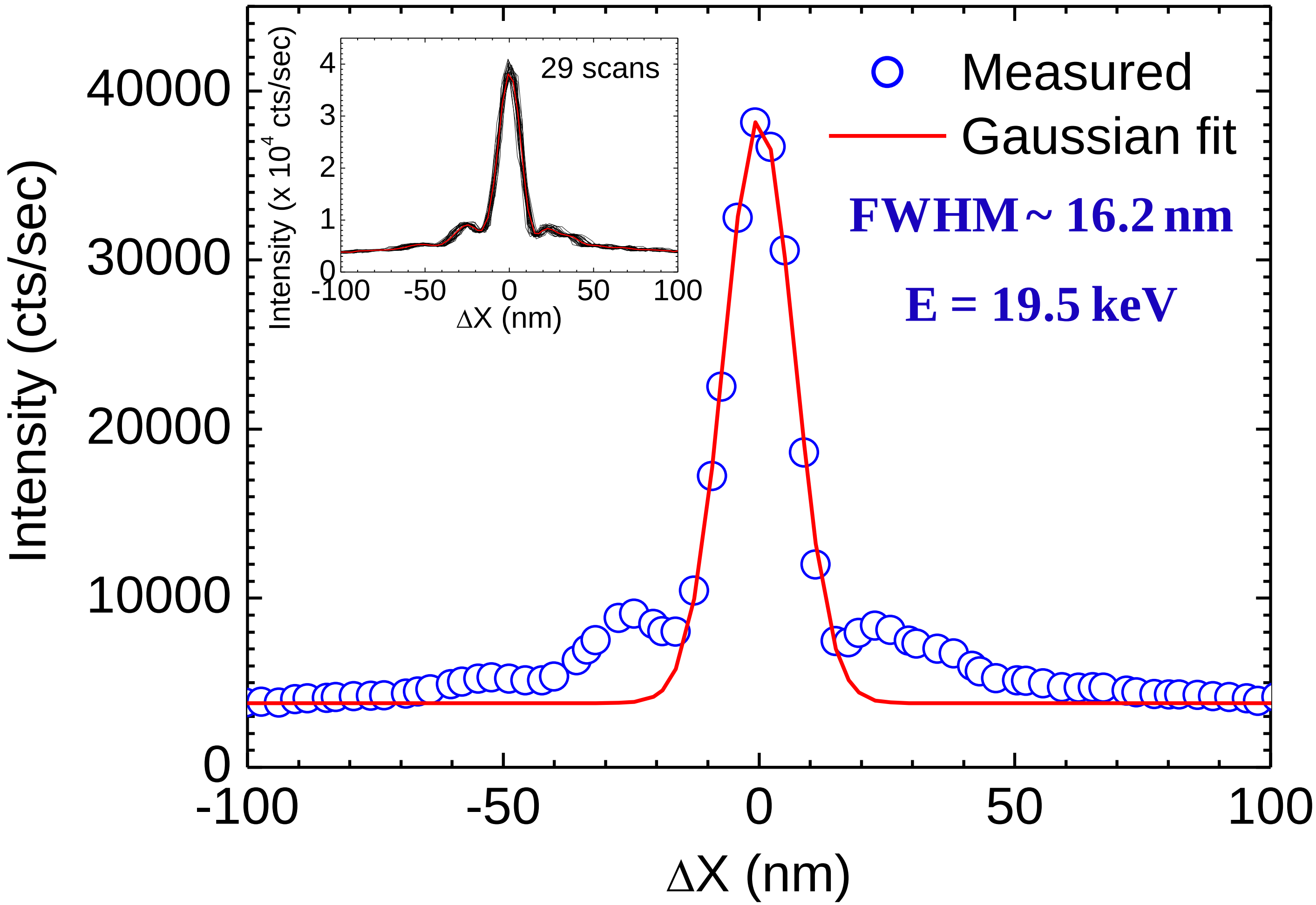
7 GeV

16 nm hard x-ray nano-beam

C-AXS

Section depth = 14.9 μm, Δr_{min} = 5 nm, f = 2.6 mm @ APS 26ID

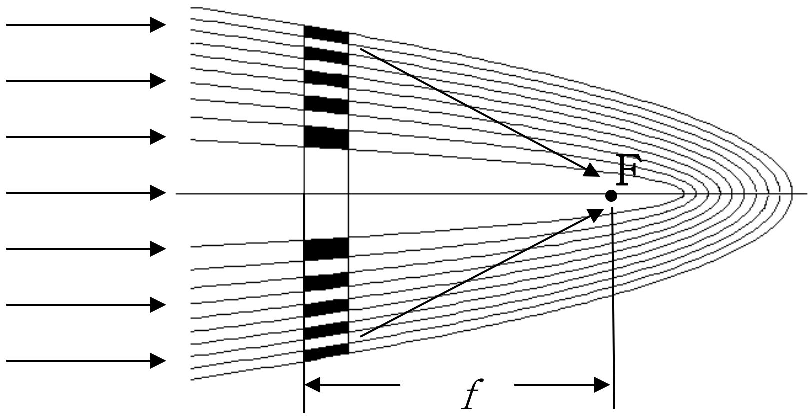
H. C. Kang *et al.* Appl. Phys. Lett. (2008)

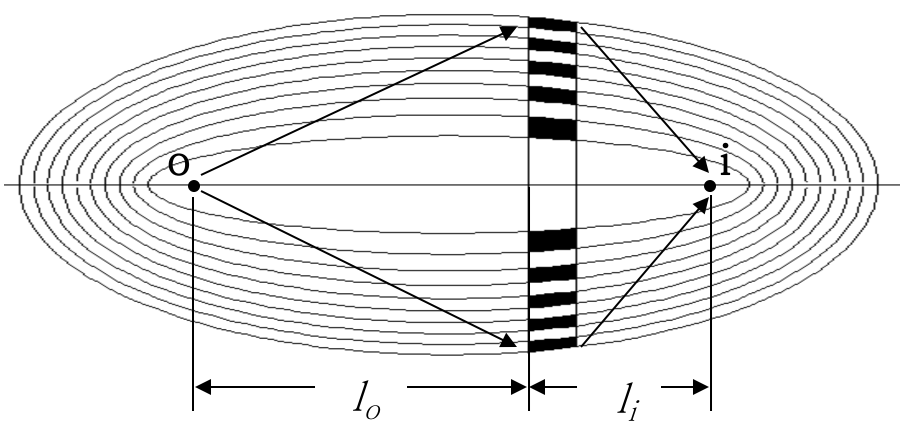


Future Direction : Ultimate Limit

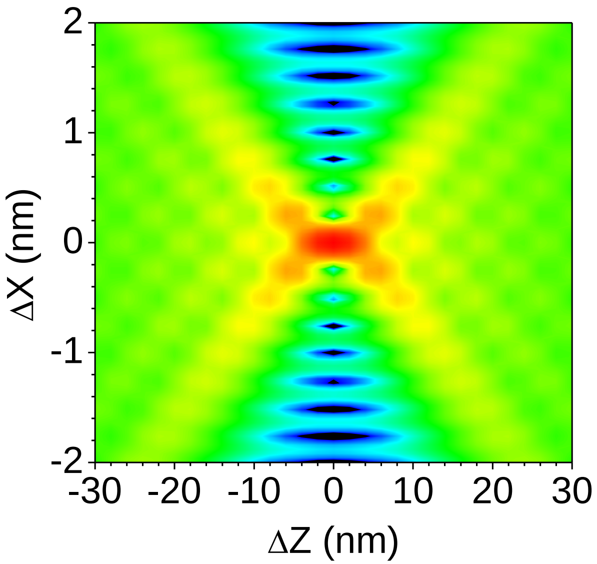
C-AXS

Curved Ideal MLL





Isophotes near the focus

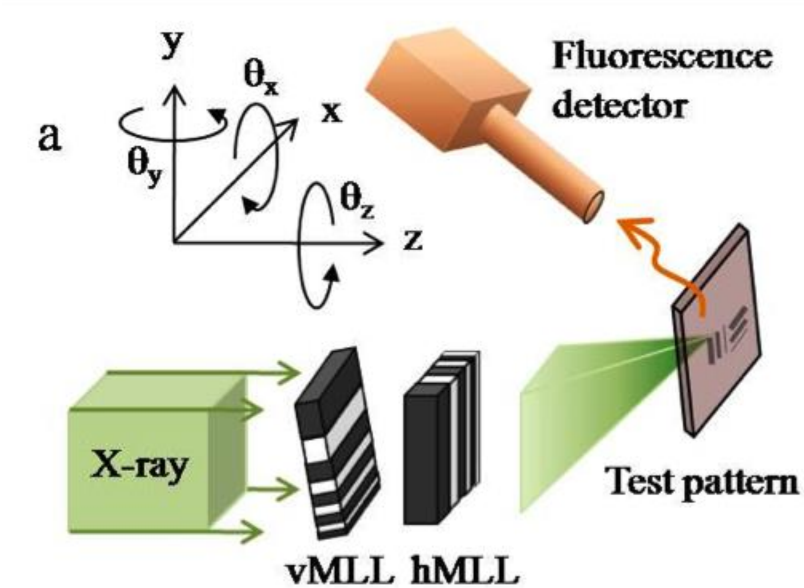


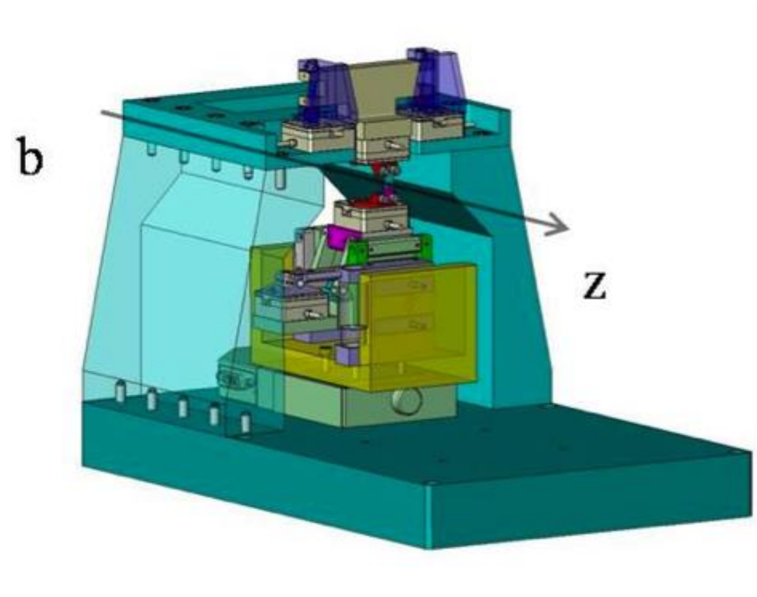
FWHM = 0.21 nm

It's ideal case !!!!!!

Scanning Fluorescence X-ray Microscopy with MLL (2-D focus)

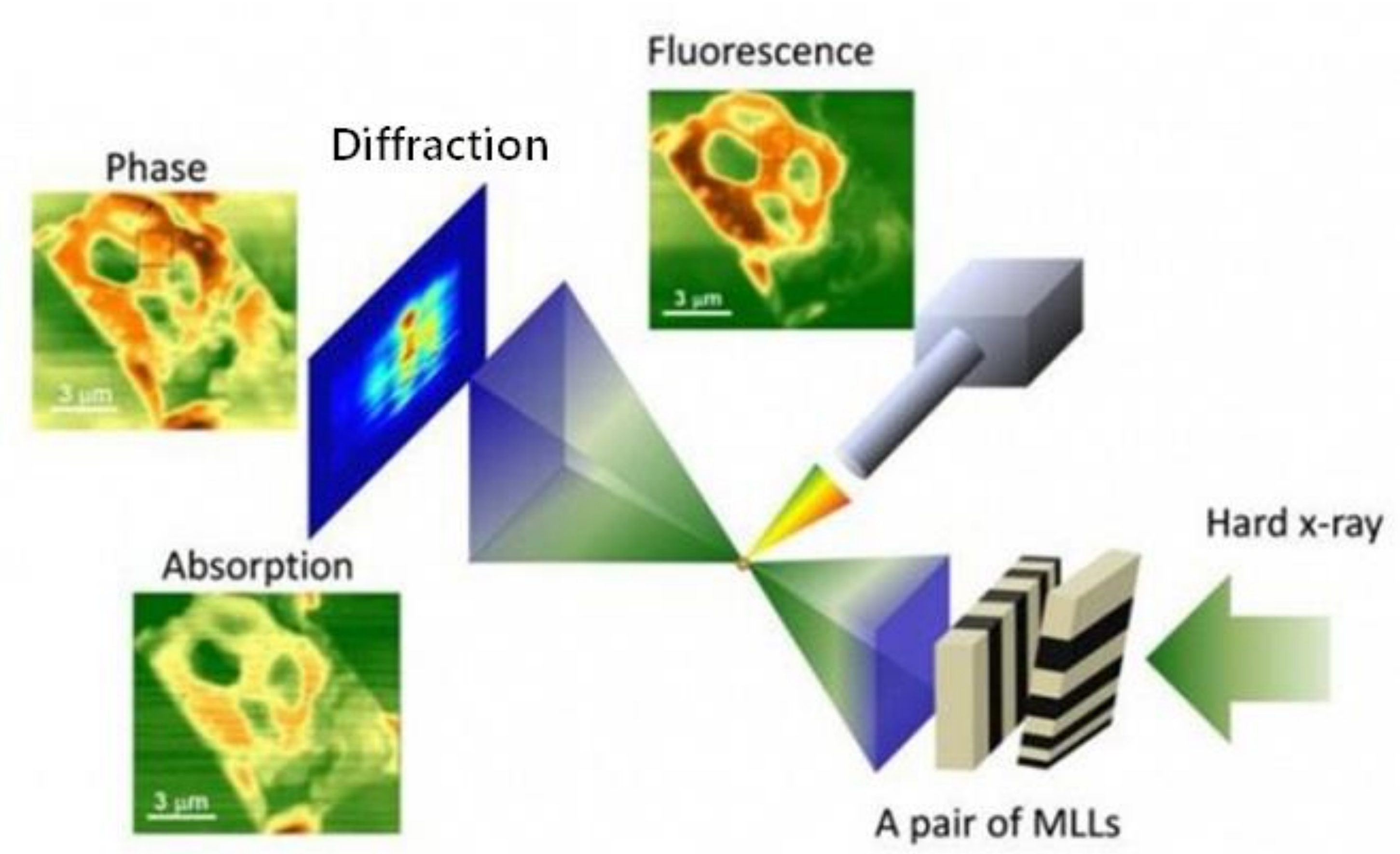
2-D MLL X-ray Microscope





- Two MLLs were crossed to make 2-D point focus.
- Special instrumentation is required to align MLLs accurately.
- (alignment of nano-beam and nano-sample)
- Utilization and user supporting program at NSLS-II

Multi-modal X-ray nano-probe

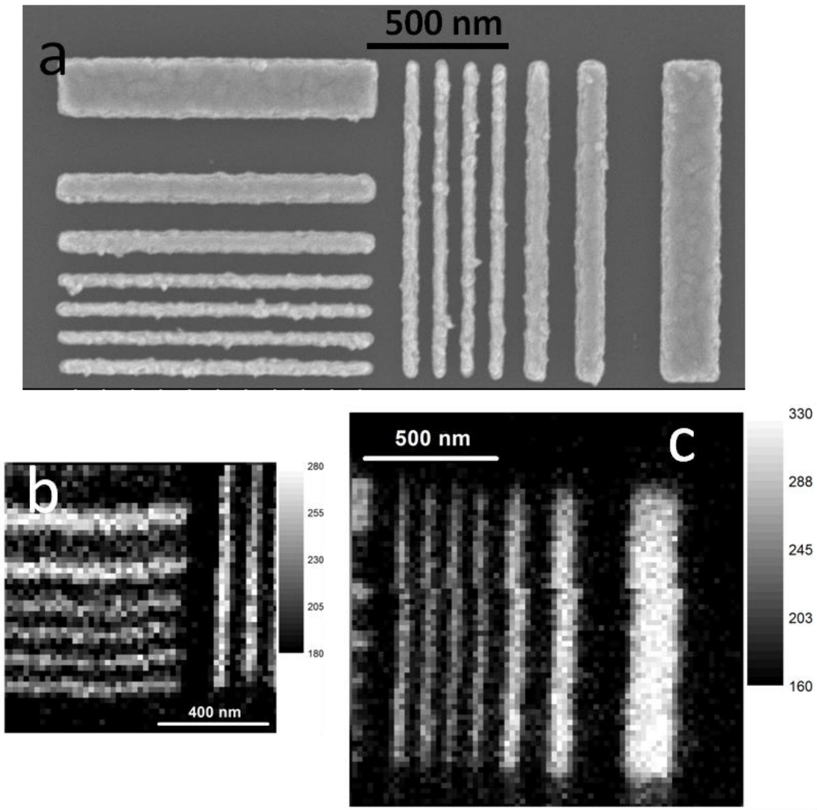


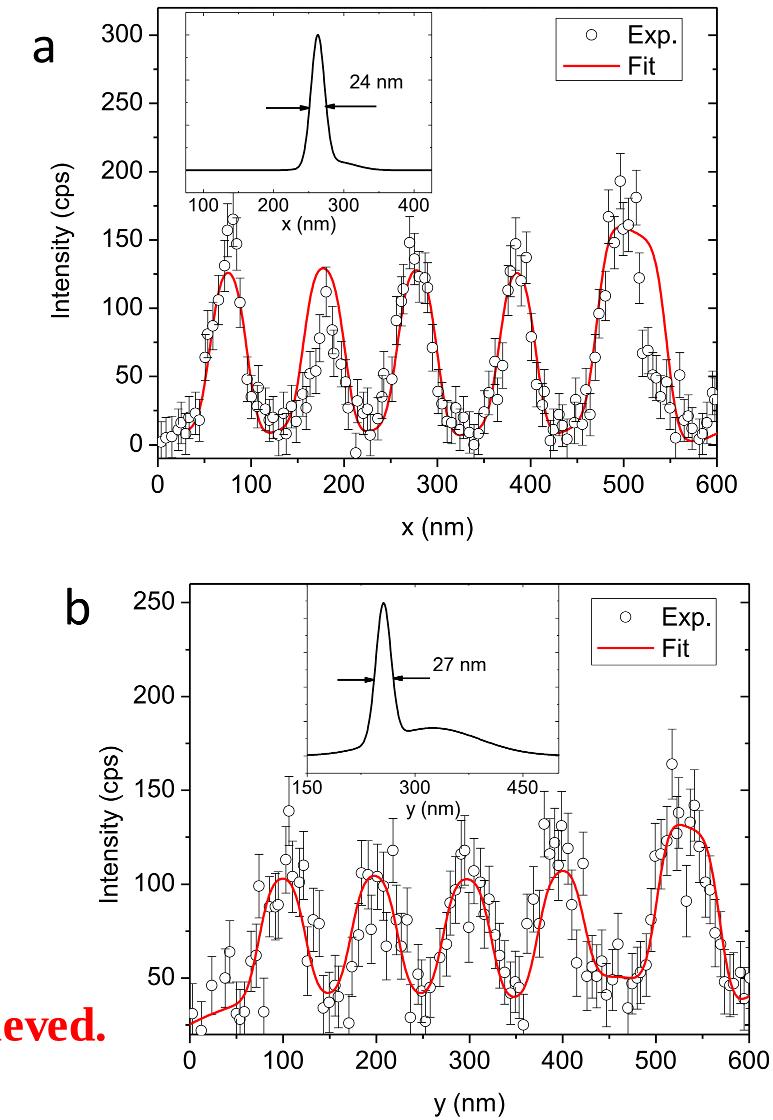
- ✓ **Multi-modal hard X-ray nano-probe (energy : ~8 keV, <25 keV)**
- ✓ ***Current Resolution : < 20 nm in 2D, 40 nm in 3D***
- ✓ ***In-situ capability : working distance, field-of-view, depth-of-focus***
- ✓ ***Optics : K-B mirror, Fresnel zone plate, Multilayer Laue Lens***

Fluorescence x-ray image of test patterns

C-AXS

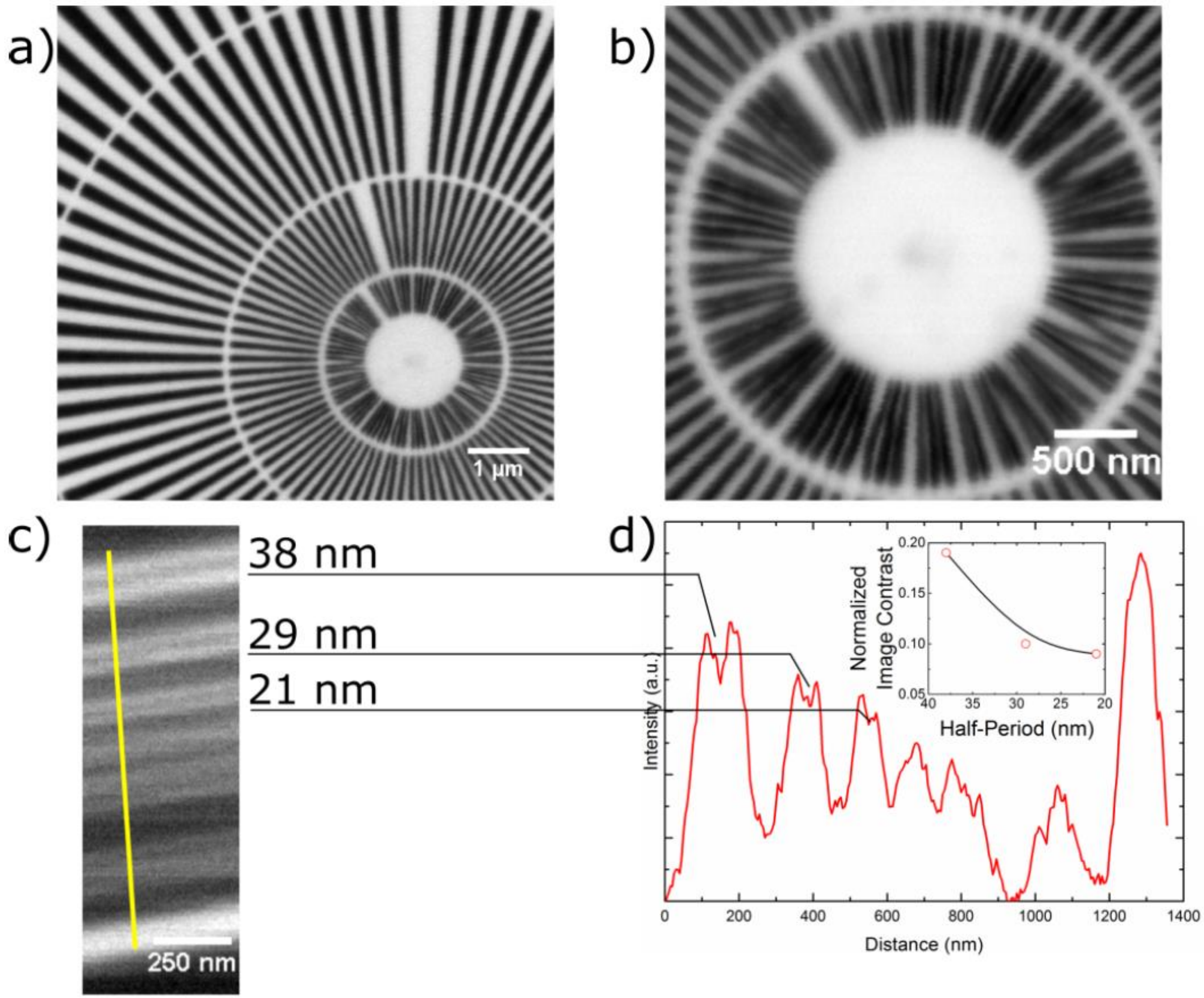
Optics Express 19, 15069 (2011)





- ➢Smallest line width : 50 nm
- ➢**24 nm x 27 nm image resolution was achieved.**
- ➢**Photon flux : 5x10^7 photons/sec**

Imaging resolution : Siemens star pattern

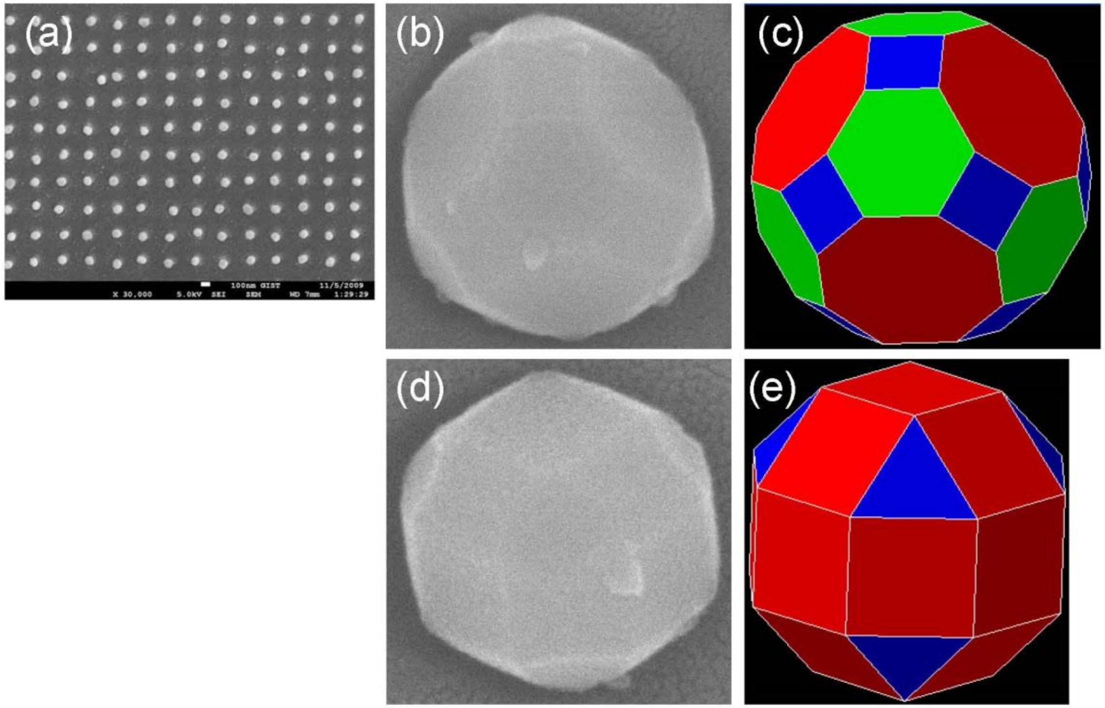


Scientific Applications

- Fluorescence x-ray microscopy of PtNi nano-crystal catalyst

- Element mapping of Solid Oxide Fuel Cell

Pt-Ni nano-crystal catalysts

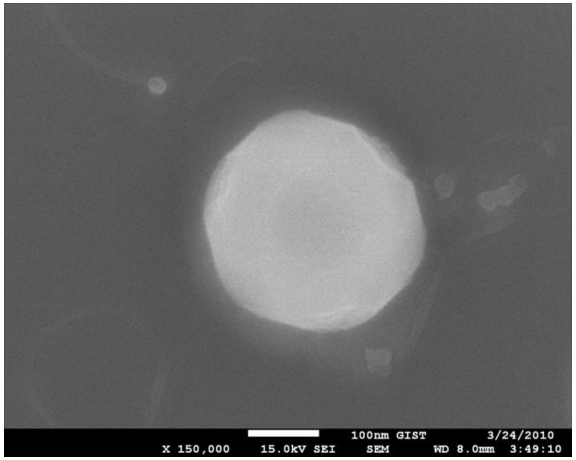


(a) SEM image of array of Pt-Ni nano-crystals. (b),(c) SEM image and model of great rhombicubooctahedron. (d),(e) SEM image and model of small rhombicubooctahedron.

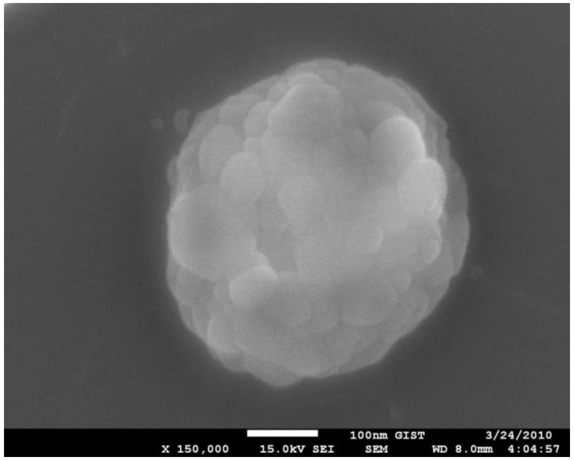
Pt-Ni nano-crystal catalyst is an emerging material for the energy related applications.
100 times higher chemical reaction activity than Pt nano-crystal catalyst.

→ High temperature stability & oxidation

Pt-Ni nano-crystal catalysts



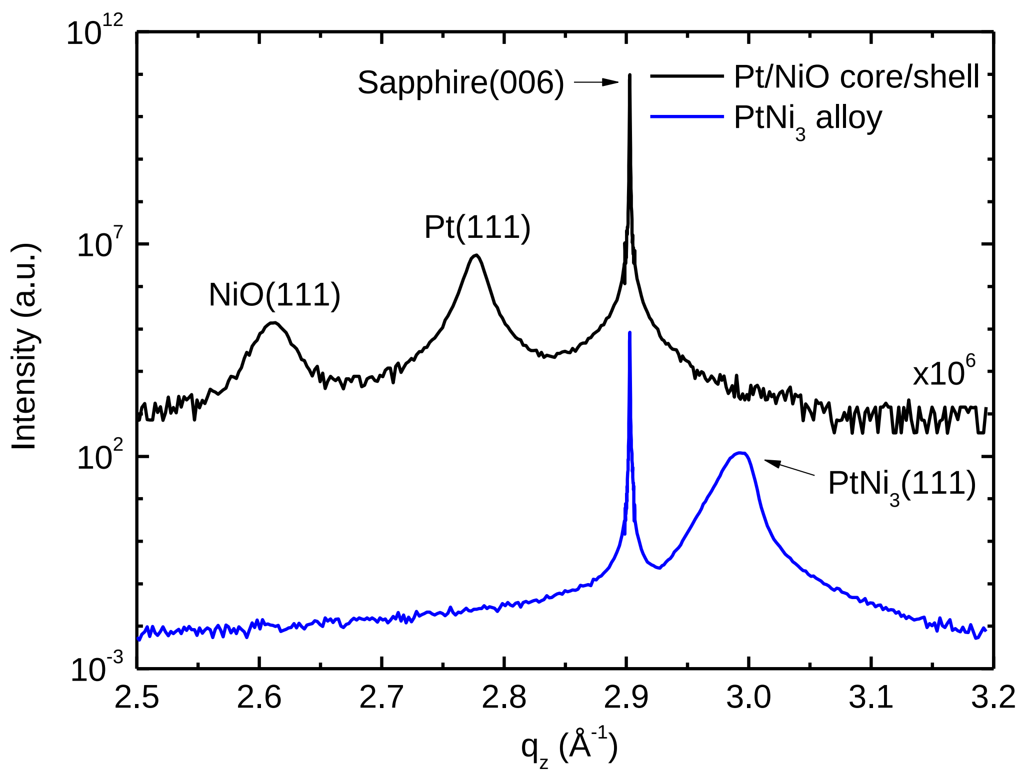
Oxidation

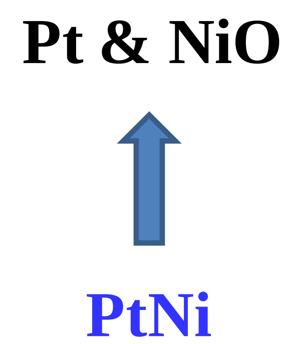


By thermal oxidation, the Pt-Ni alloy nano- crystal is oxidized.

→What is the chemical distribution in the skin ?
→ What kind of elements is prefer to react with oxygen ?

X-ray Diffraction Patterns

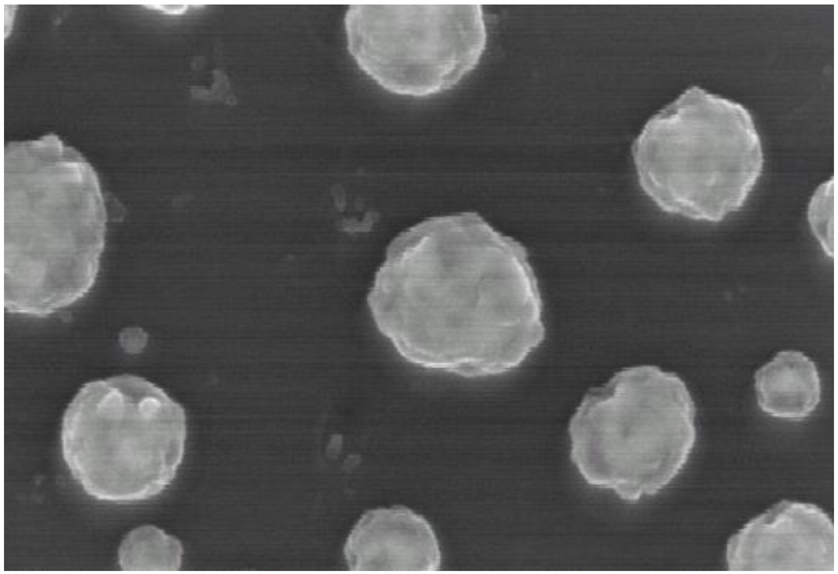


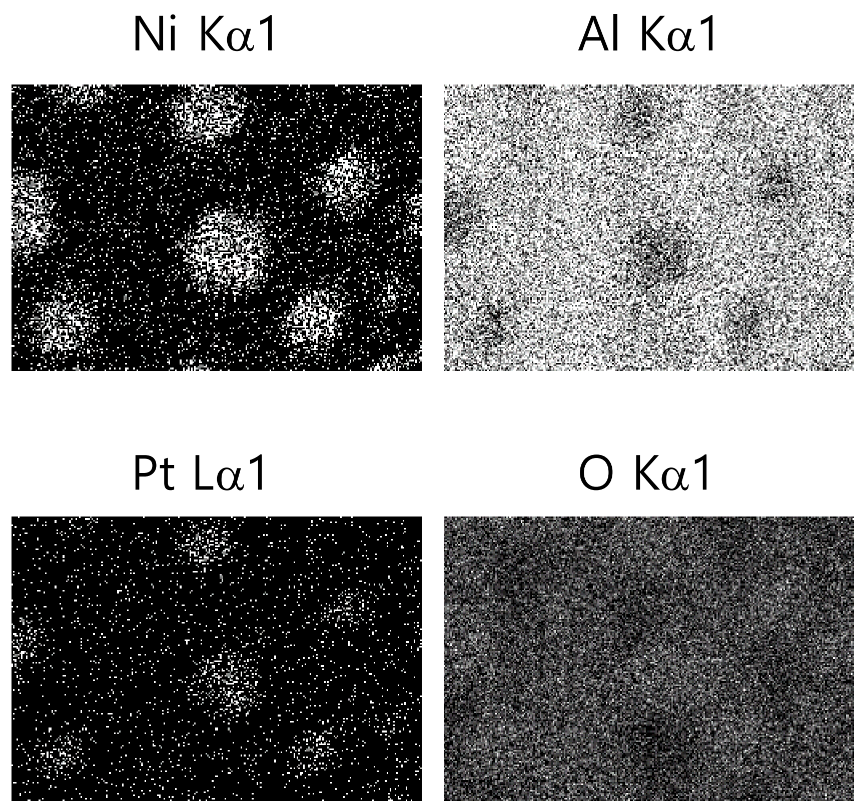


By oxidation, Pt(111) and NiO(111) Bragg peaks appeared, while $PtNi_3$(111) peak disappeared completely.

Pt-Ni nano-crystal catalysts

EDX by SEM



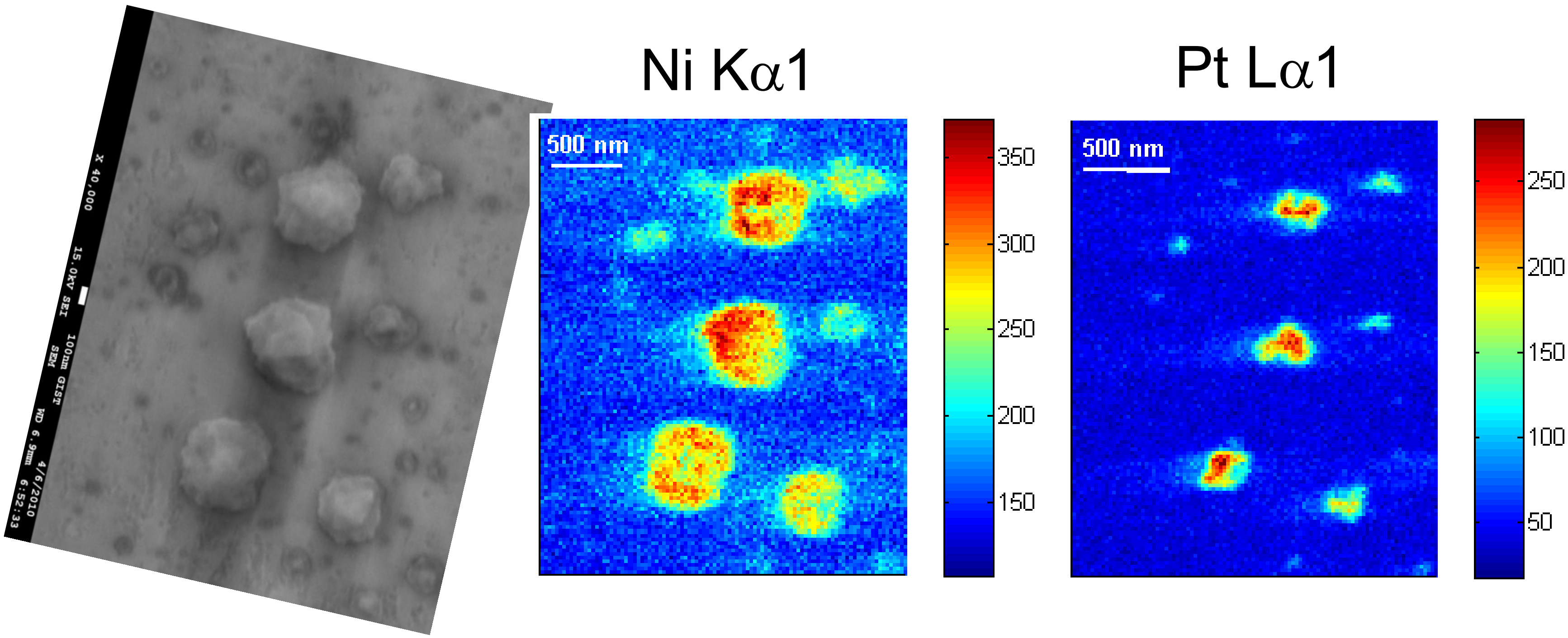


Not sensitive for nano-scale materials

Limitation by drifting and charging during the measurement

Pt-Ni nano-crystal catalysts

Fluorescence x-ray microscopy by MLL

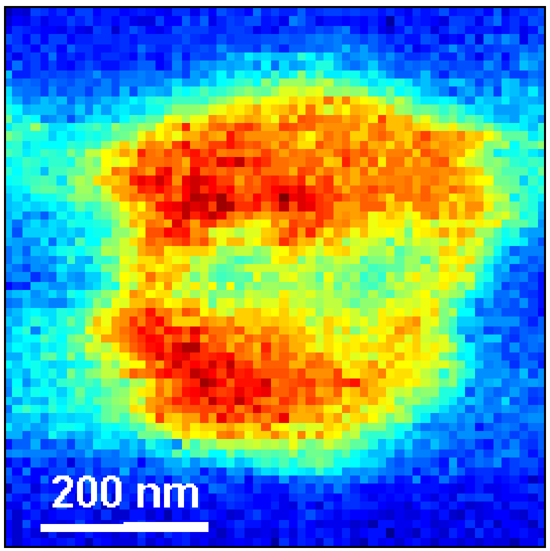


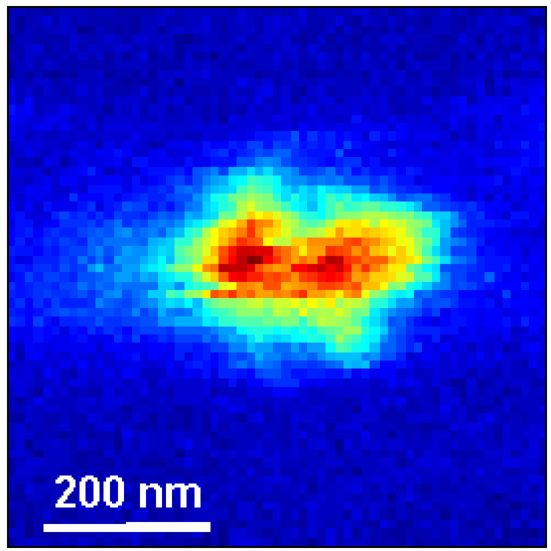
H. C. Kang *et al.* Nanoscale, 2013, 5, 7184–7187

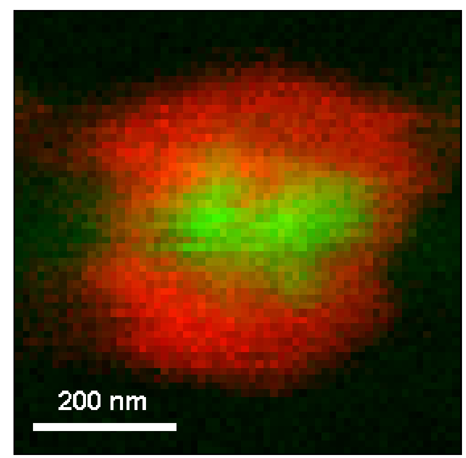
Pt-Ni nano-crystal catalysts

Fluorescence x-ray microscopy by MLL

Ni Kα1 | Pt Lα1





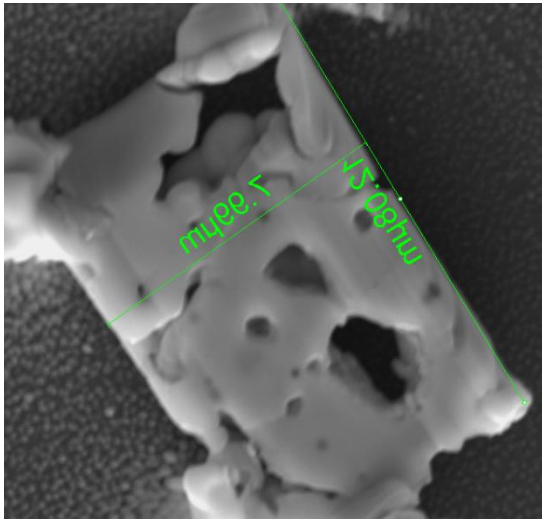


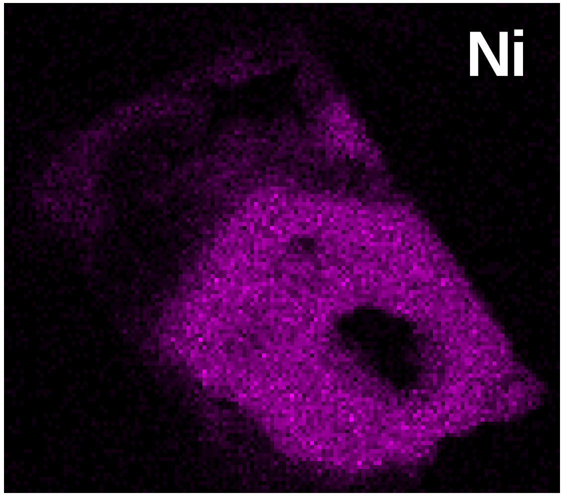
Pt-NiO Core/Shell Structure !!!!!!!

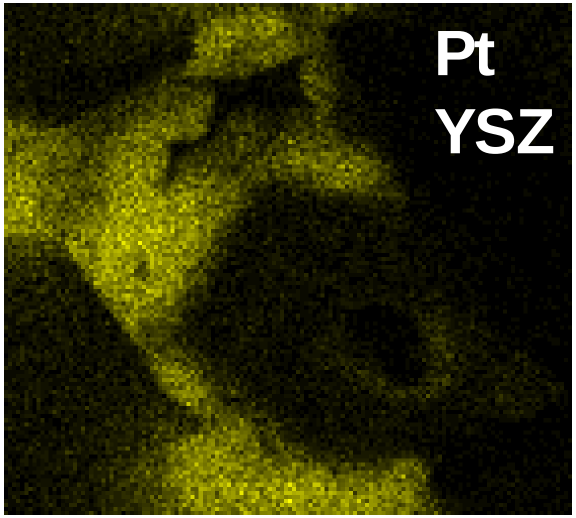
Distribution of Ni in YSZ:Ni Solid Oxide Fuel Cell

EDX by SEM

SEM/EDS images





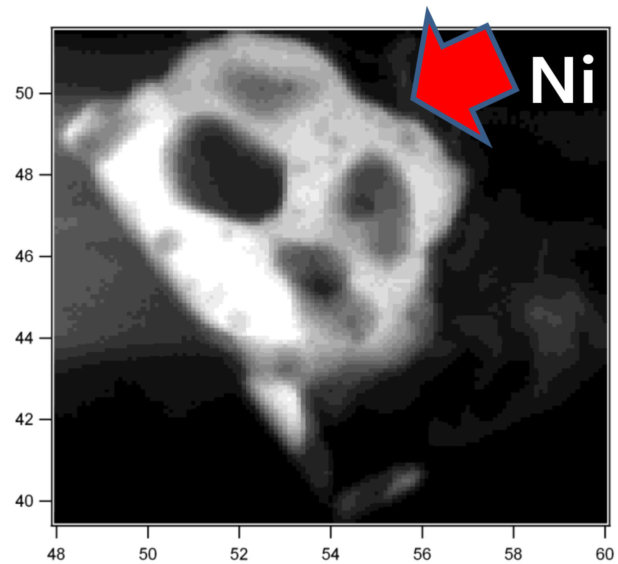


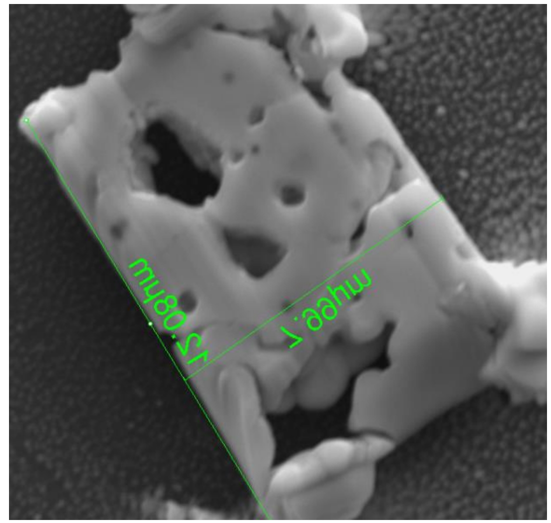
Sample is made by FIB process, and mounted on the SiN membrane.

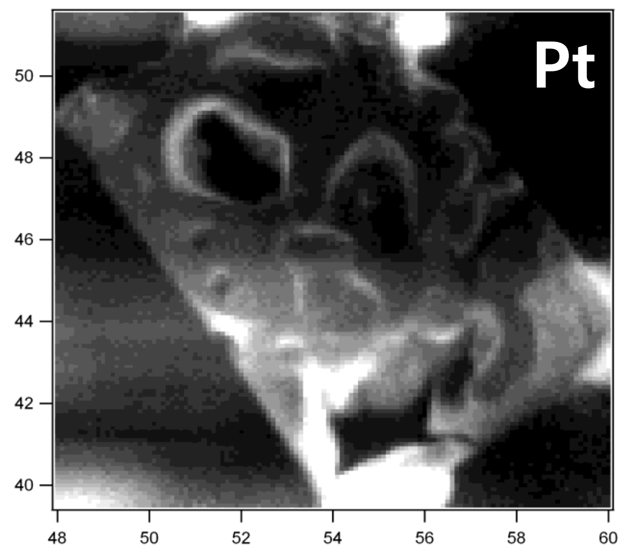
Probing depth is limited to few ten nm.(skin sensitive)

X-ray fluorescence microscopy

C-AXS

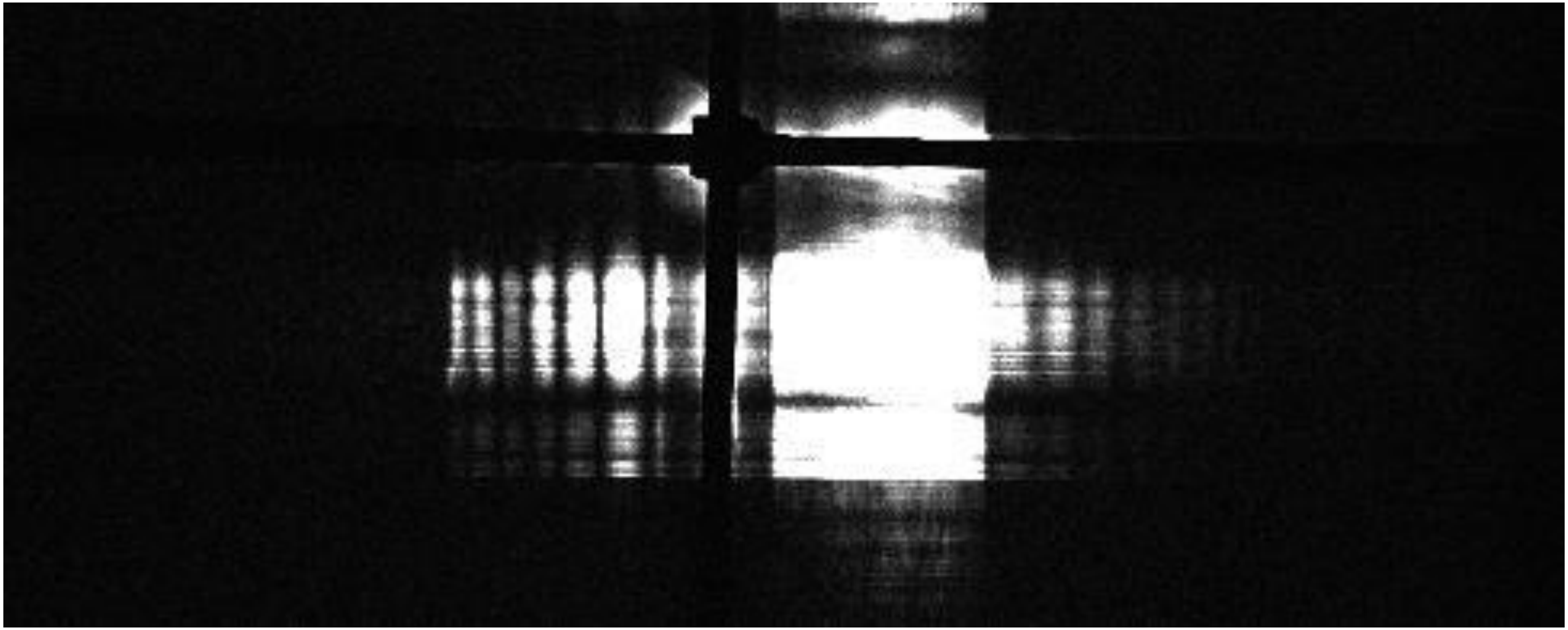






Small feature is observed.
→ Nanometer scale pores

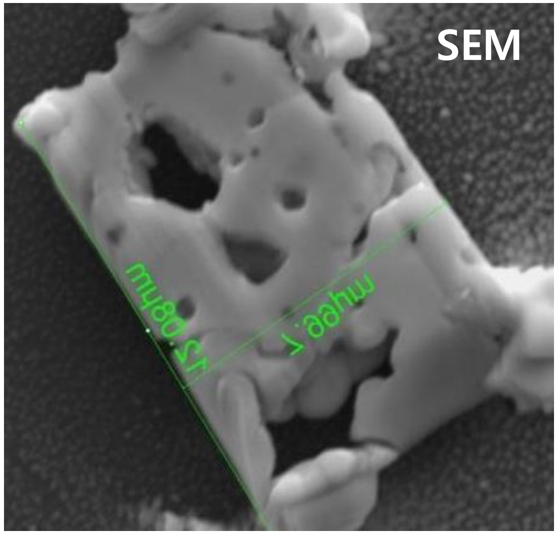
Differential Phase Contrast Imaging

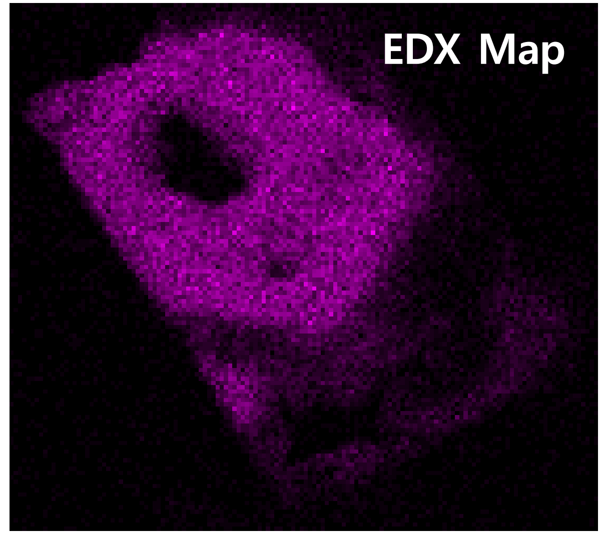


- Far-field diffraction pattern is measured during scanning the sample across the x-ray nano-focus.
- Intensity variation can be used to reconstruct the DPC imaging

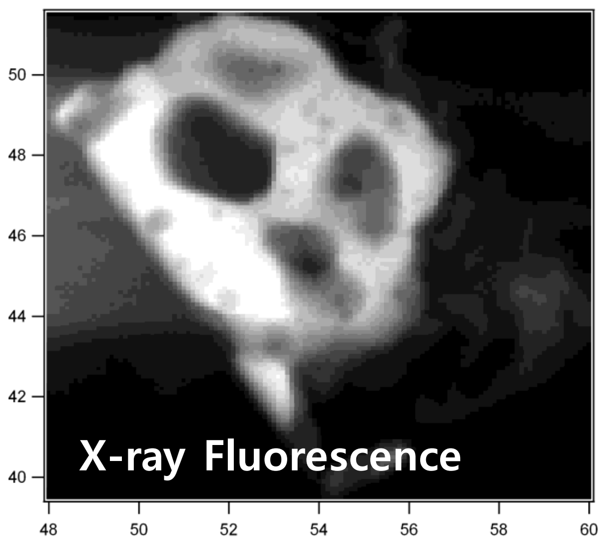
Differential Phase Contrast Imaging

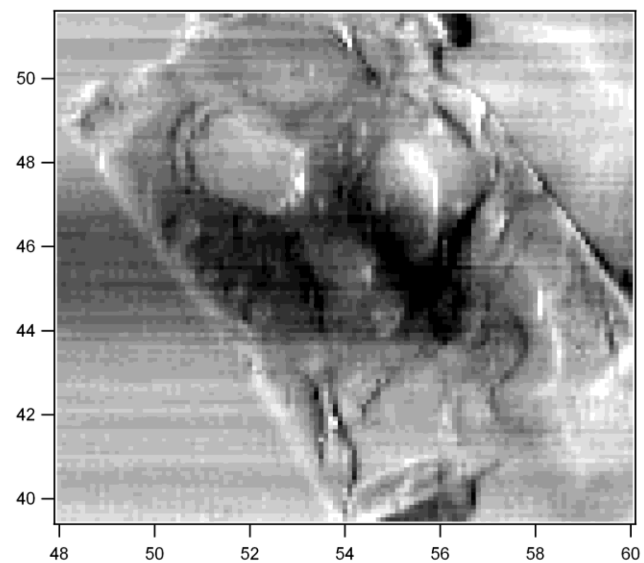
C-AXS





Scientific Reports
3 : 1307 (2013)

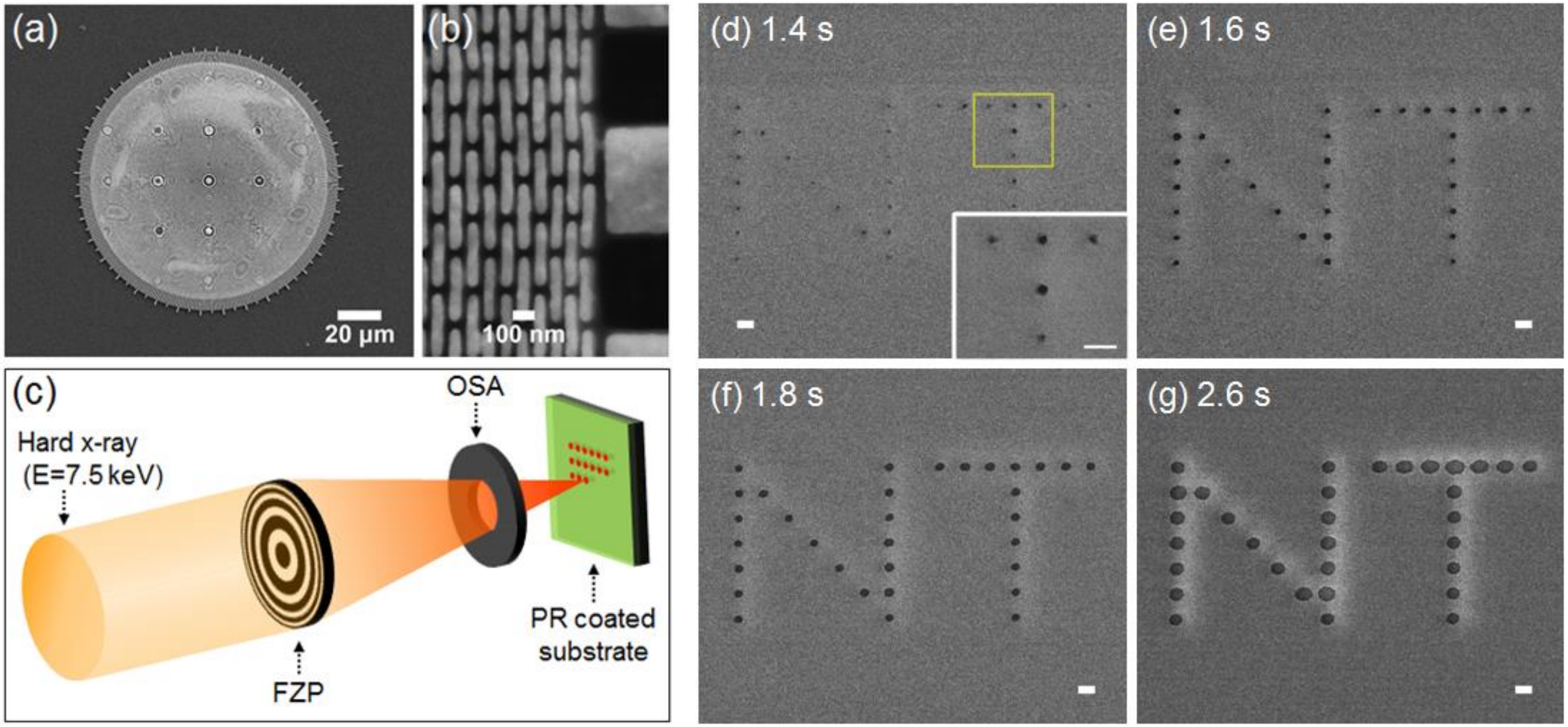




(20 nm focus &
20 nm step)

X-ray Microscope at Pohang Light Source

X-ray Nano-Writer

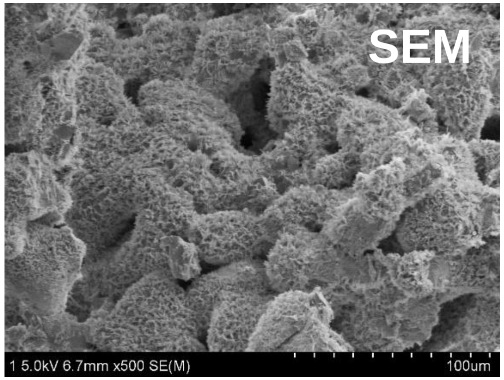


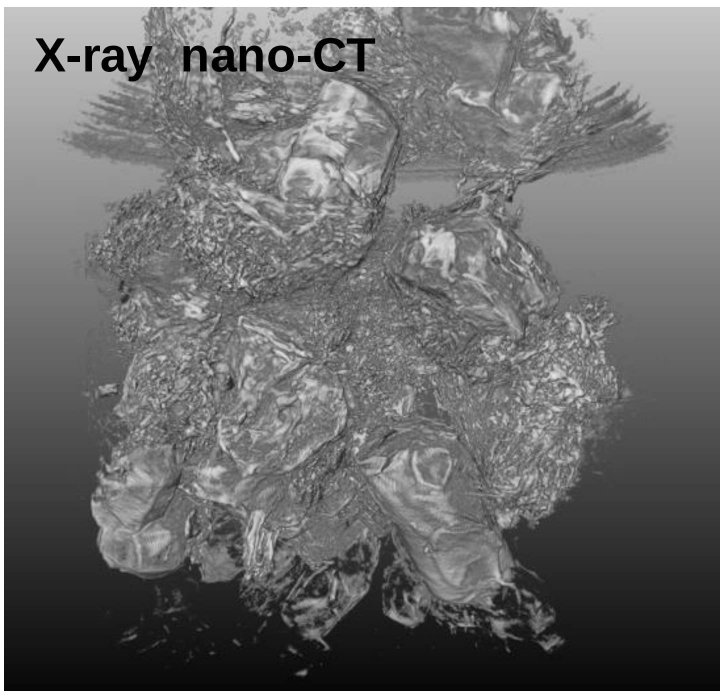
- 20 nm X-ray nano-beam @ 9C beamline
- X-ray nano-beam diffraction can be utilized.
- Mechanical stability is very important.

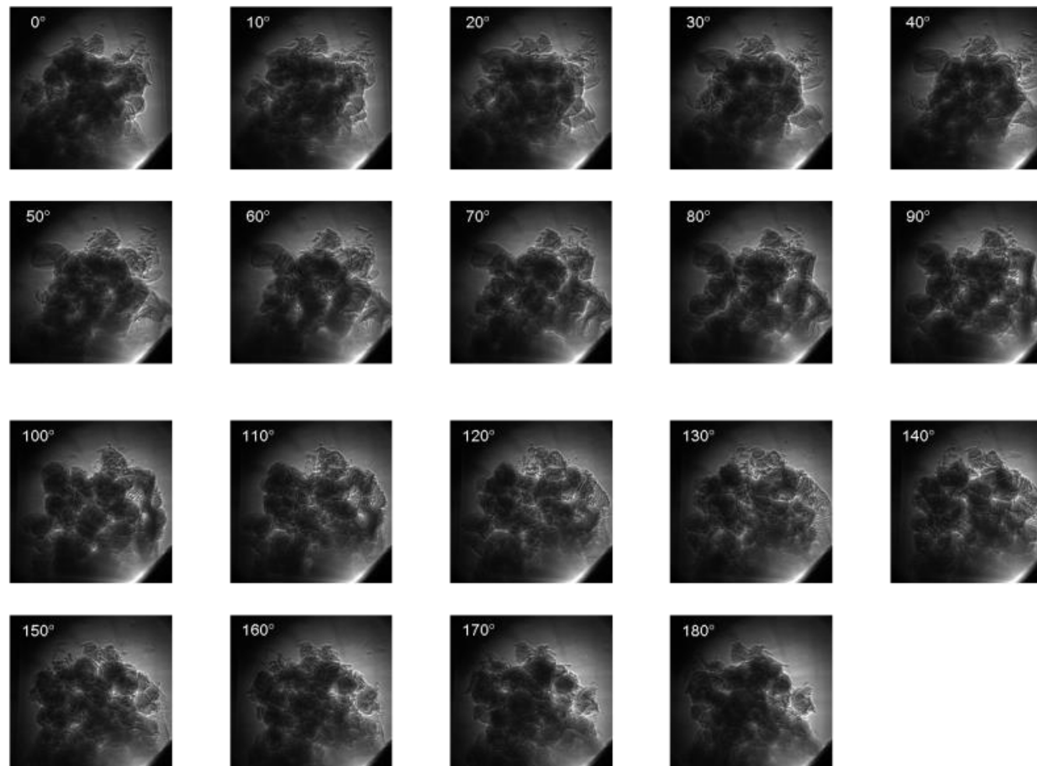
Optic Express 18, 24975 (2010)
J. Appl. Phys. 109, 044307 (2011)
J. Synchrotron Rad. 18, 143 (2011)
J. Synchrotron Rad. 22, 156 (2015)
J. Synchrotron Rad. 22, 781 (2015)

X-ray Nano-CT at the PLS-II

X-ray nano-CT image of synthetic bone graft

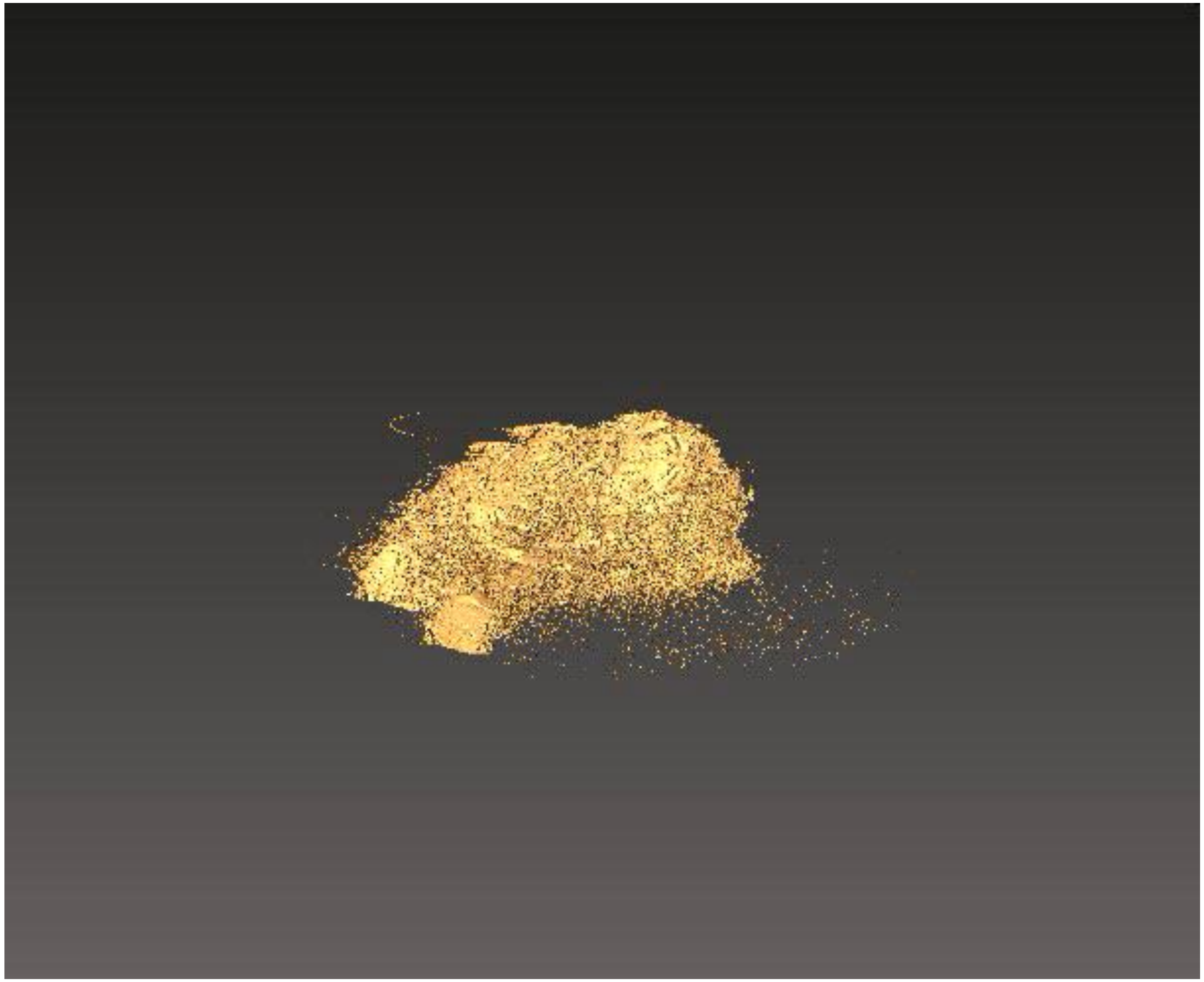






FOV ~ 20 μm, R ~ 100 nm

X-ray nano-CT image of synthetic bone graft

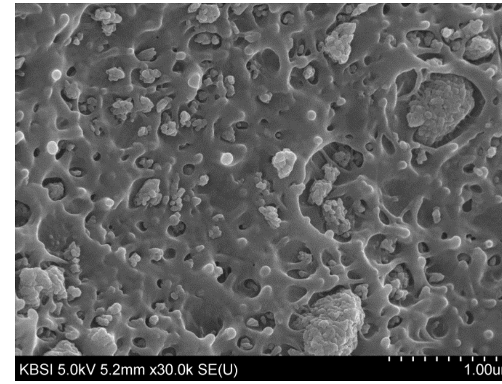


X-ray nano-CT image of bone screw

PLA powder **HA powder** **PLA+HA bone-screw**

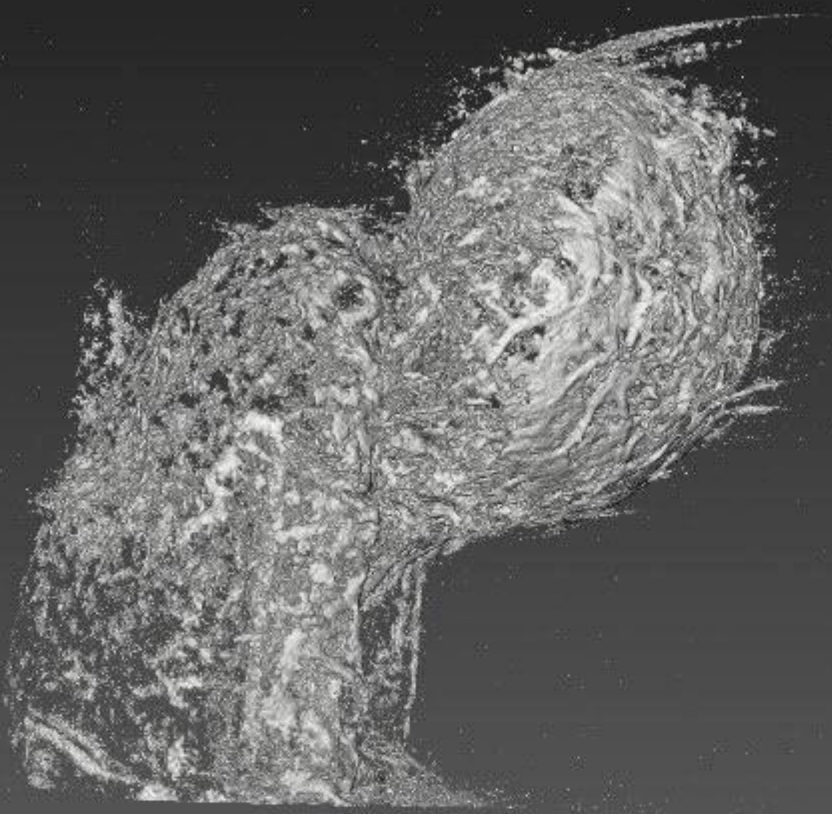
+

→



PLA : polymer matrix
HA : ceramic particles

- Cryo-system is required !!!



Multimodal X-ray Nano-probe

Hard X-ray Nano-probe 빔라인 구축 현황

→ MAX-IV의 NanoMax (스웨덴)

→ APS의 26-ID-C (미국)

→ NSLS-II의 3-ID (미국)

→ PETRA-III의 P06 (독일)

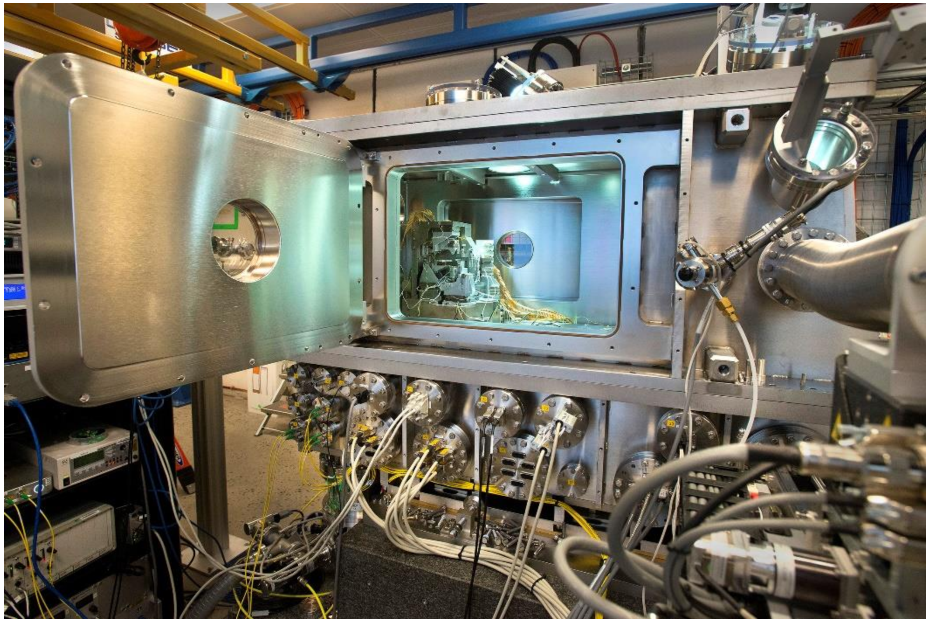
→ ESRF의 ID01 (프랑스)

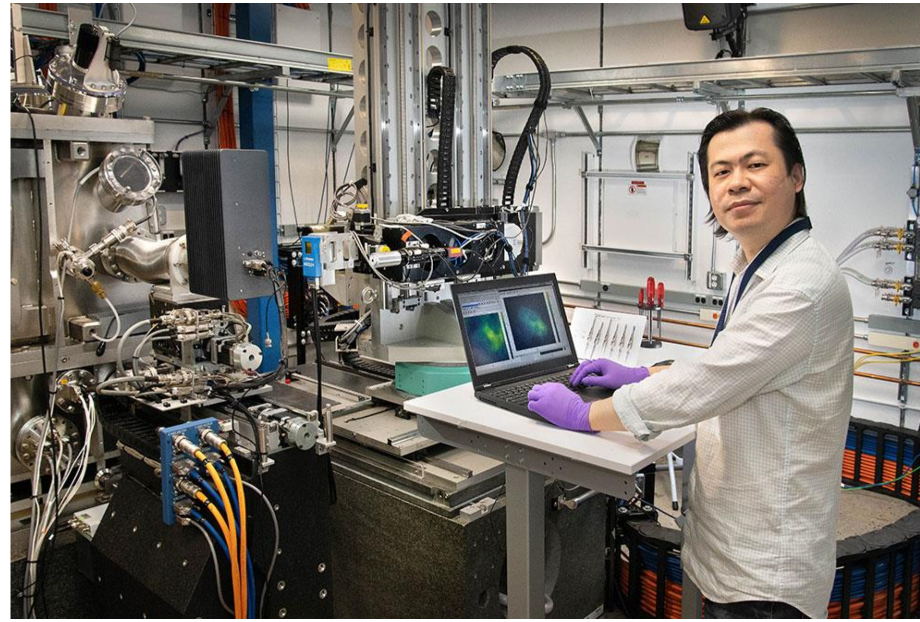
→ DLS의 I14 (영국)

→ PETRA-III의 P23 (독일)

모든 방사광가속기에서 설치 운영 중 혹은 계획 중

NSLS-II, 3ID Nanoprobe beamline





FZP setup : 2D & 3D XRF and ptychography imaging, 2D nano-XANES imaging

→ Beam size : ~ 40 nm

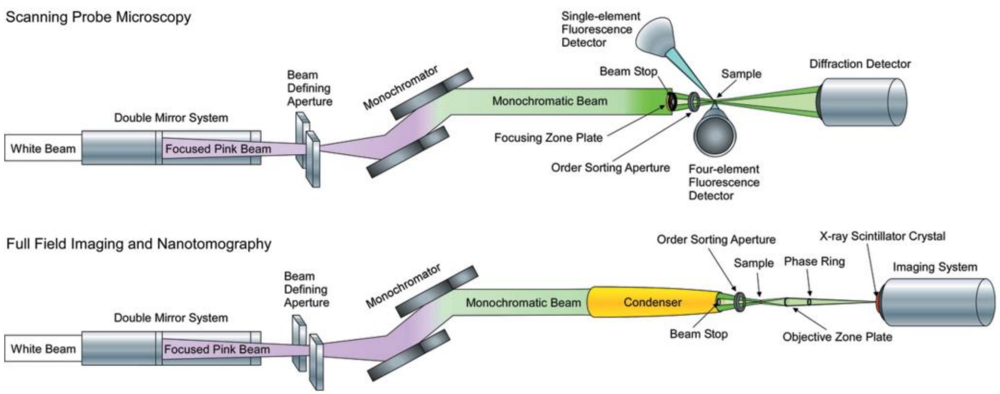
→ Energy : 6~13 keV

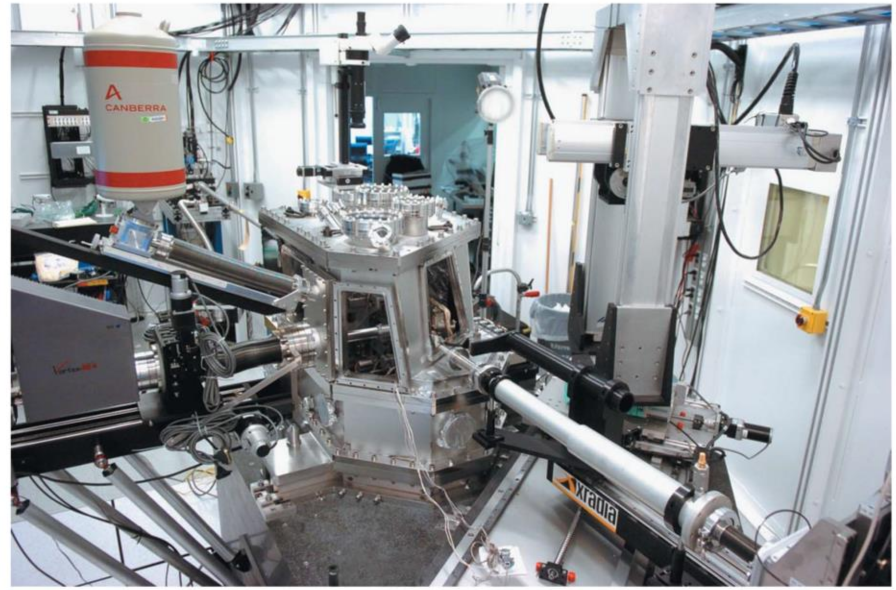
Multilayer Laue lens setup : 2D & 3D XRF and ptychography imaging

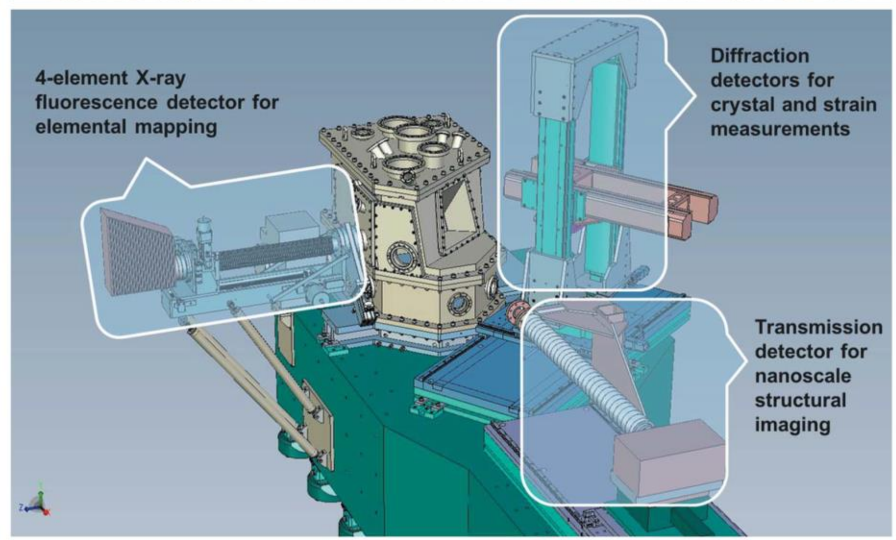
→ Beam size : < 20 nm

→ Energy : 12~17 keV

APS, 26ID Nanoprobe beamline







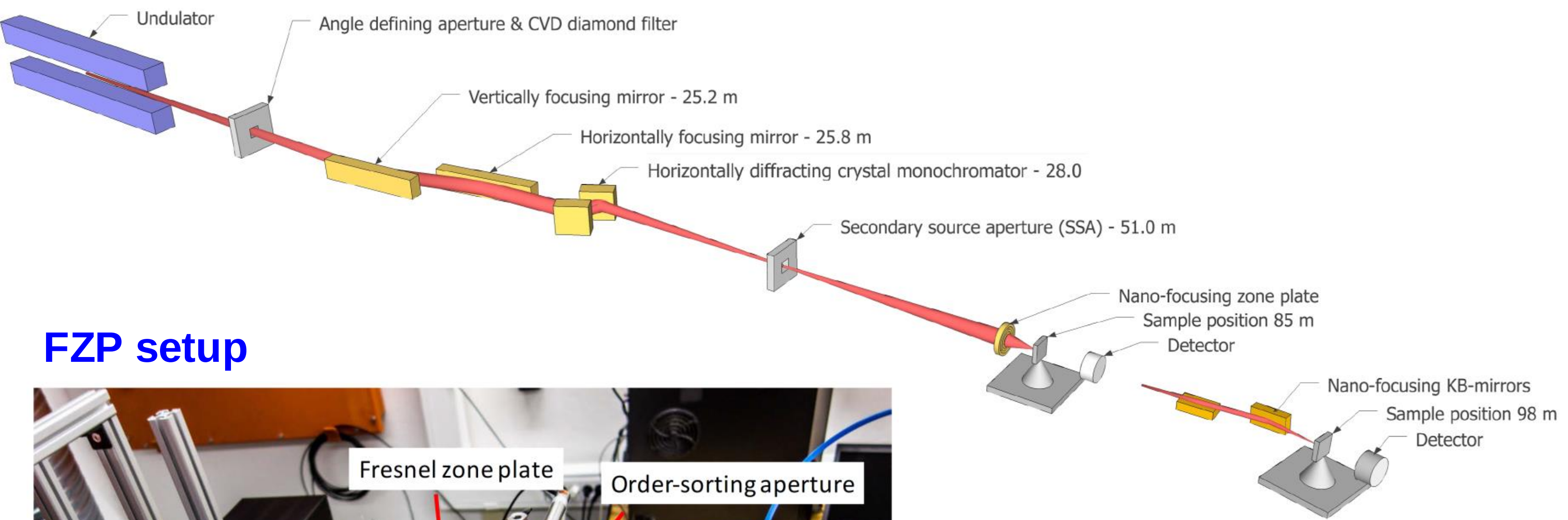
→ A single end-station

→ Scanning probe + STXM

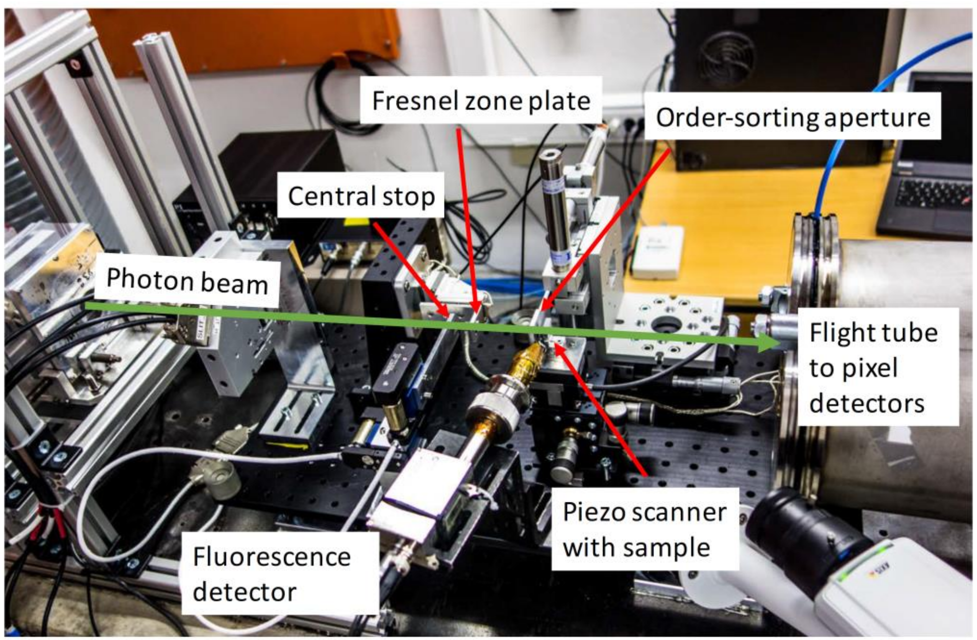
→ Optics : Capillary condenser, only FZP

→ Push to resolution limit

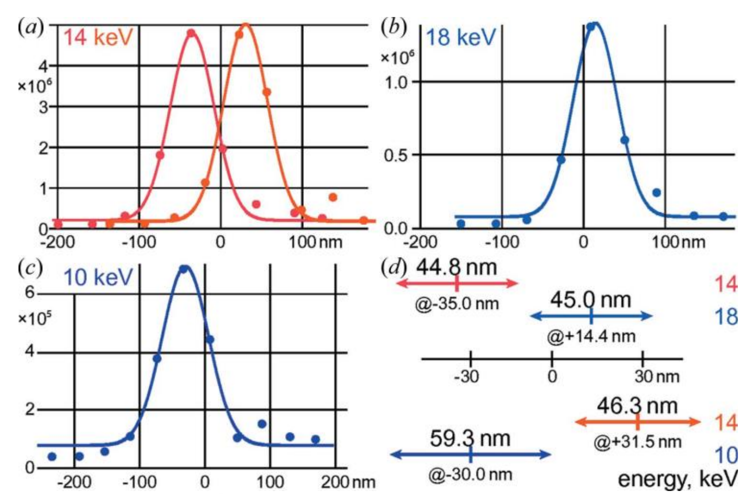
MAX IV, NanoMAX beamline



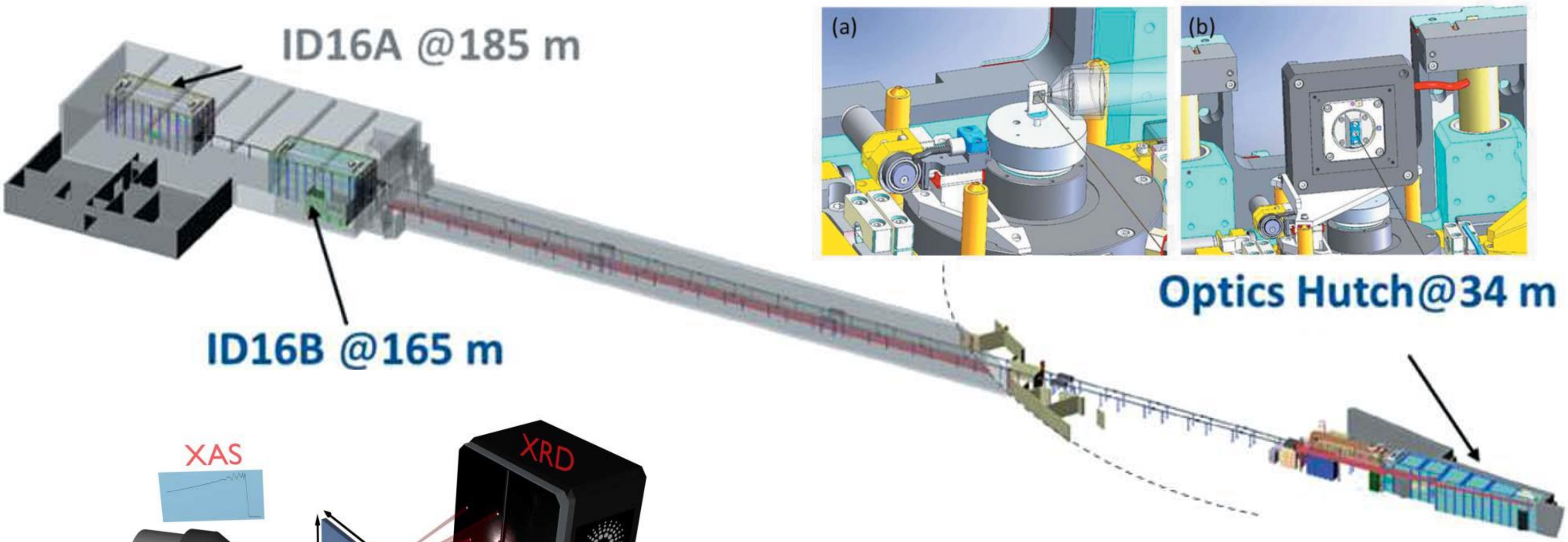
FZP setup

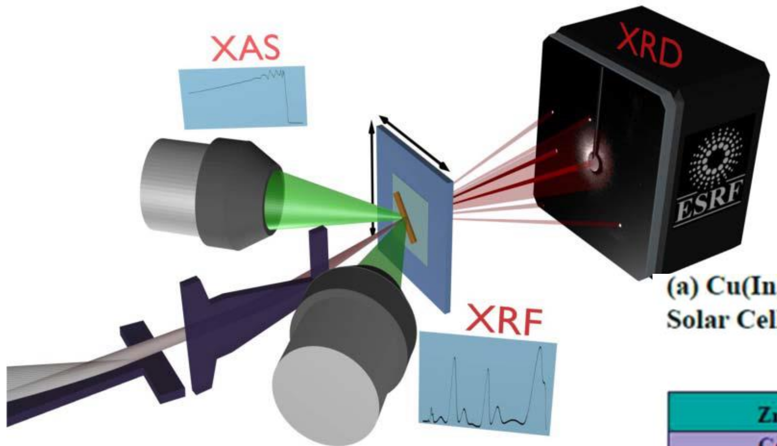


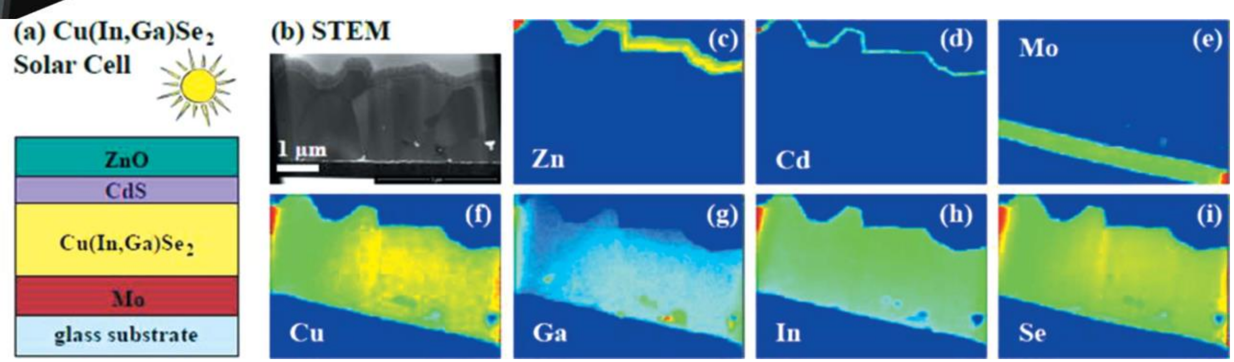
KB mirror setup



ESRF, ID16B Nanoprobe beamline



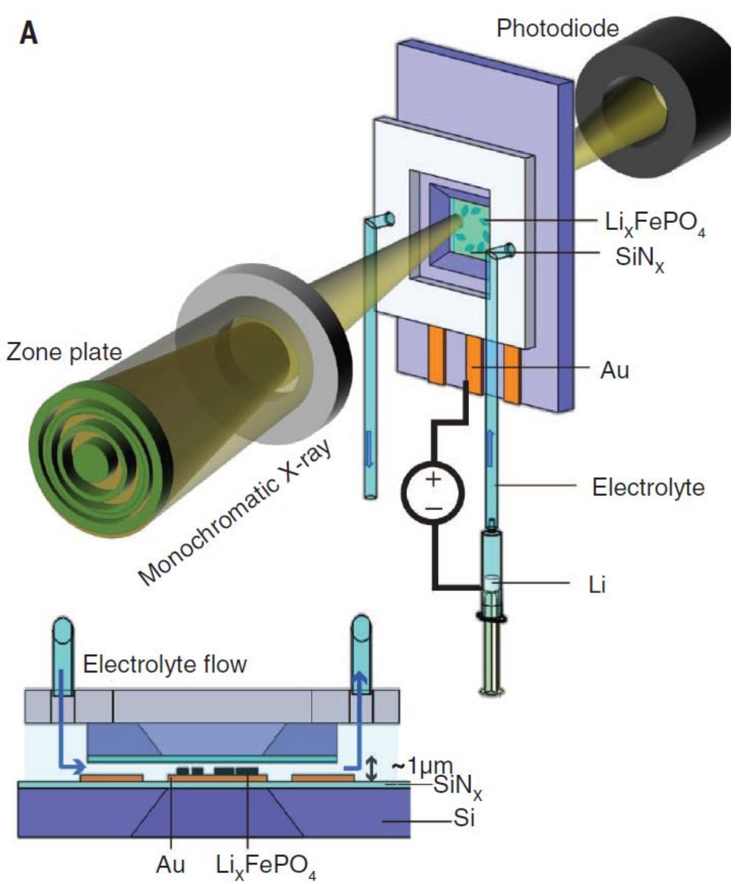


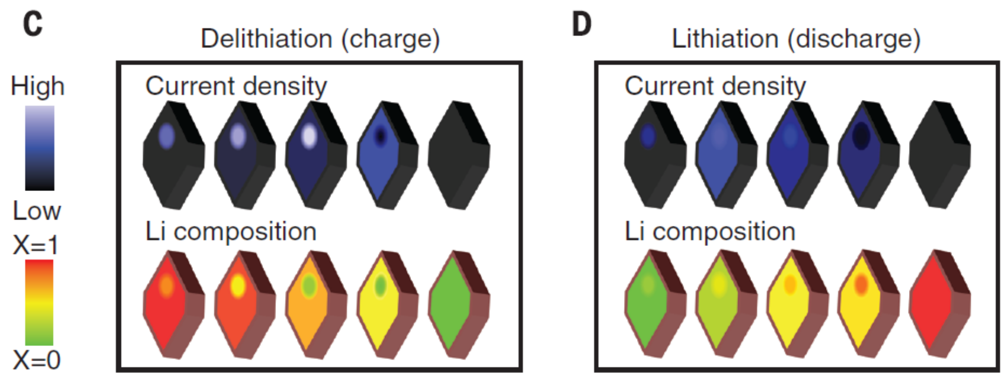


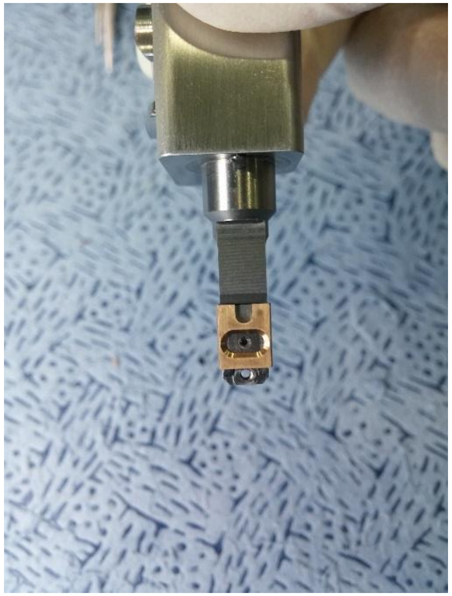
Scientific Issues studied by multimodal X-ray nanoprobe

In-operando Electrochemical Cell

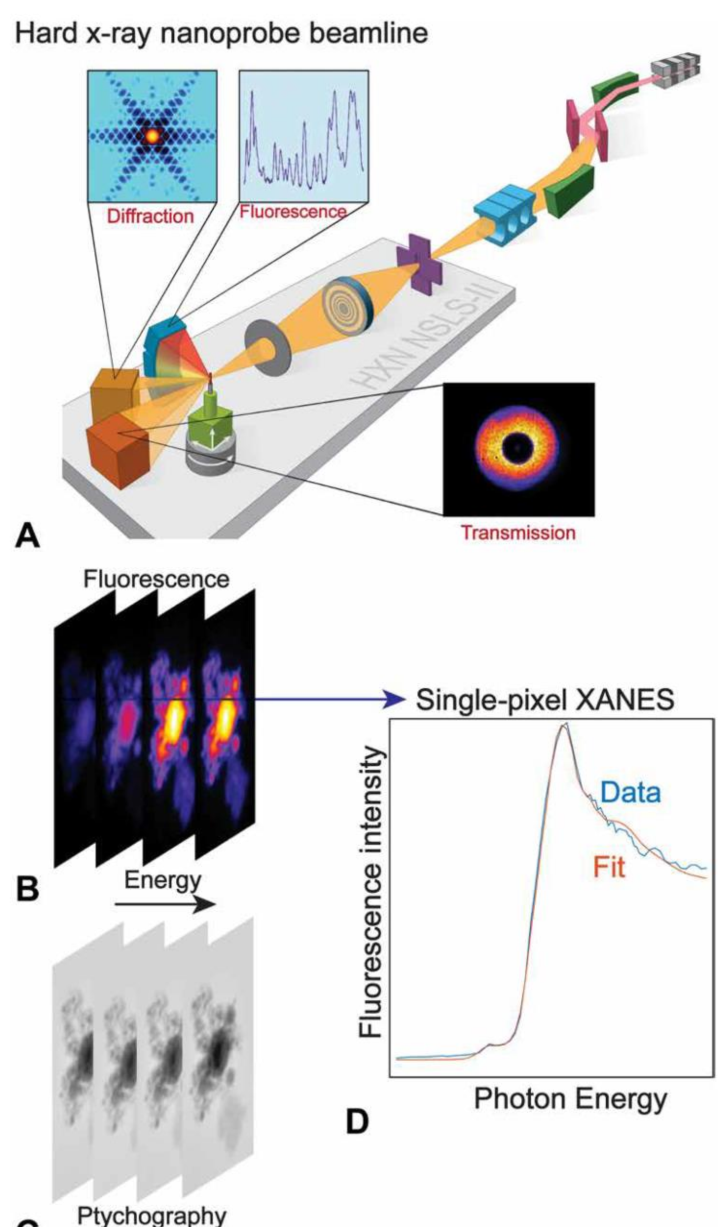
Science, 353, 566 (2016)

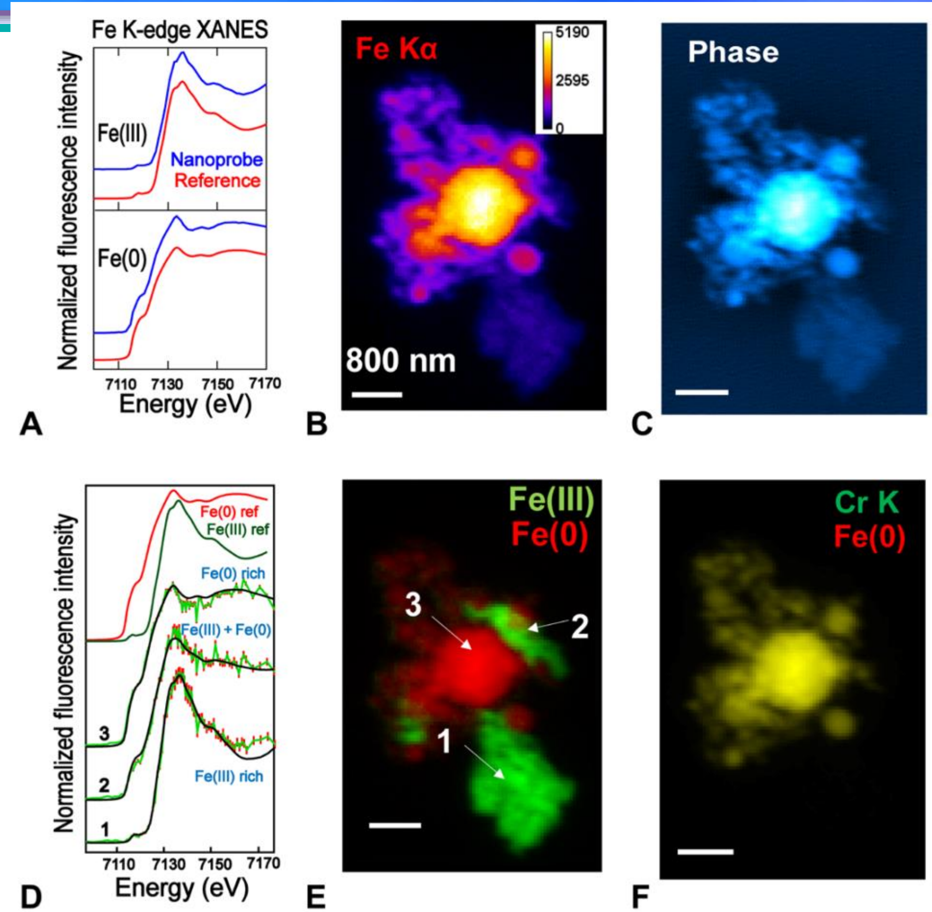






Nano-XANES





Scale bars, 800 nm.
Data collection details: 120 × 80 points, 50-nm steps, 40-ms dwell time, 77 energy points, and ~8.2 hours total acquisition time.
Science Adv. 2020.

In-operando Semiconductor device

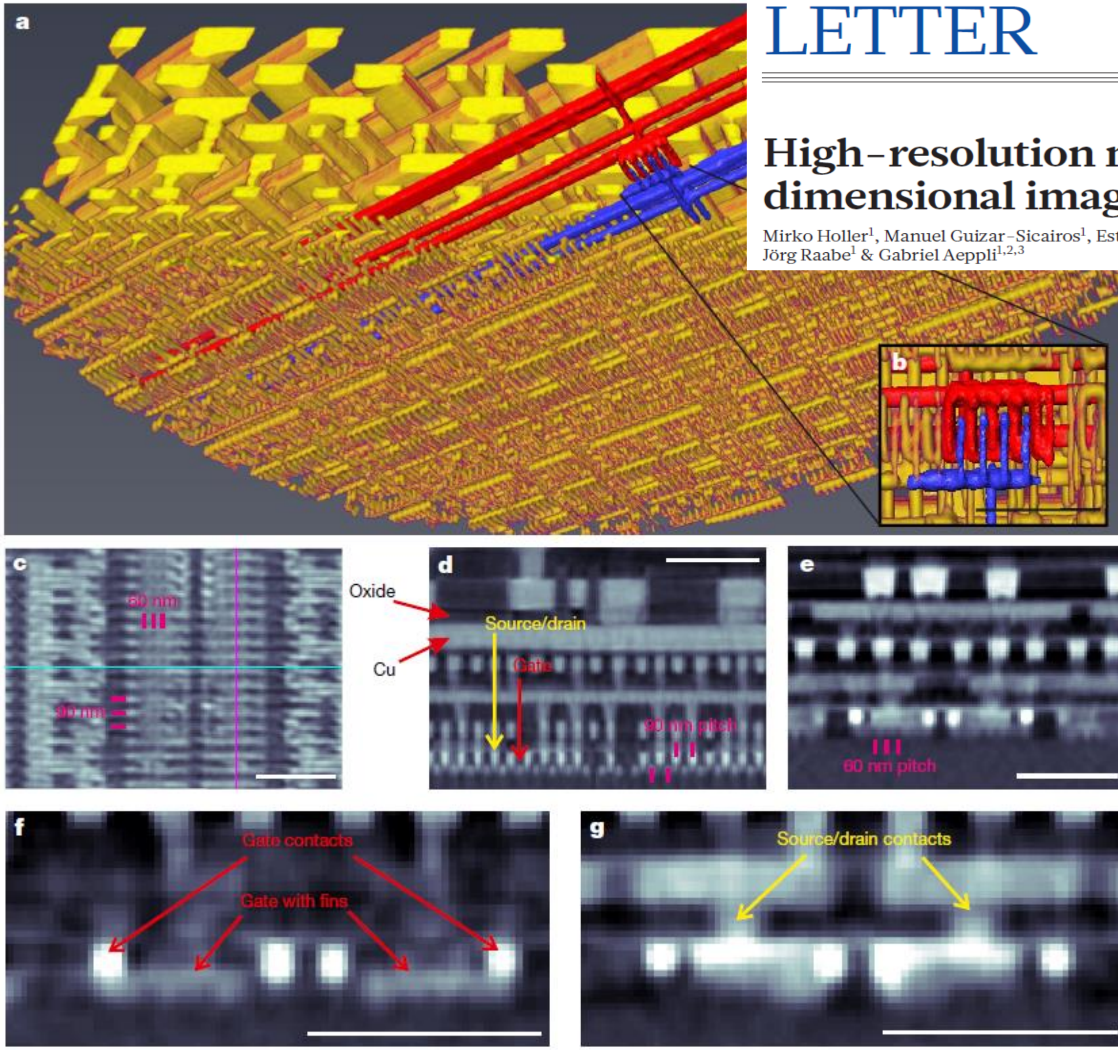
Nature 543, 402 (2017)

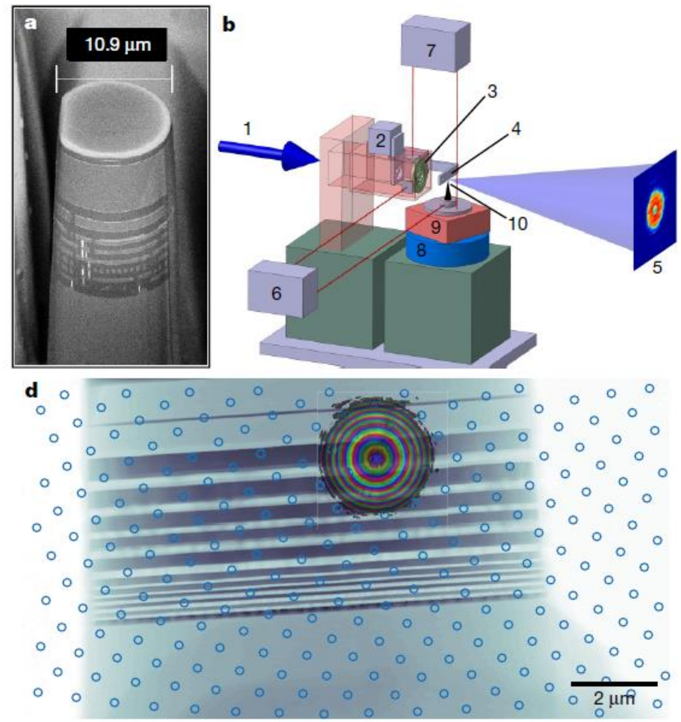
LETTER

doi:10.1038/nature21698

High-resolution non-destructive three-dimensional imaging of integrated circuits

Mirko Holler[1], Manuel Guizar-Sicairos[1], Esther H. R. Tsai[1], Roberto Dinapoli[1], Elisabeth Müller[1], Oliver Bunk[1], Jörg Raabe[1] & Gabriel Aeppli[1,2,3]

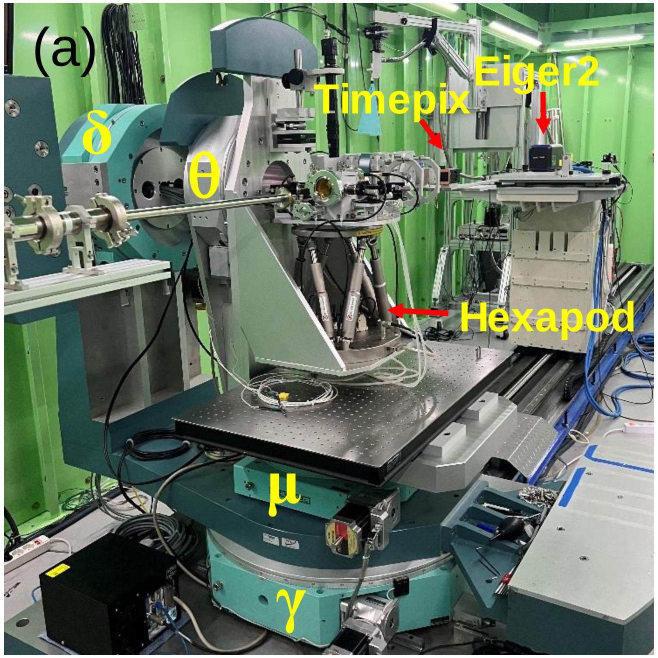


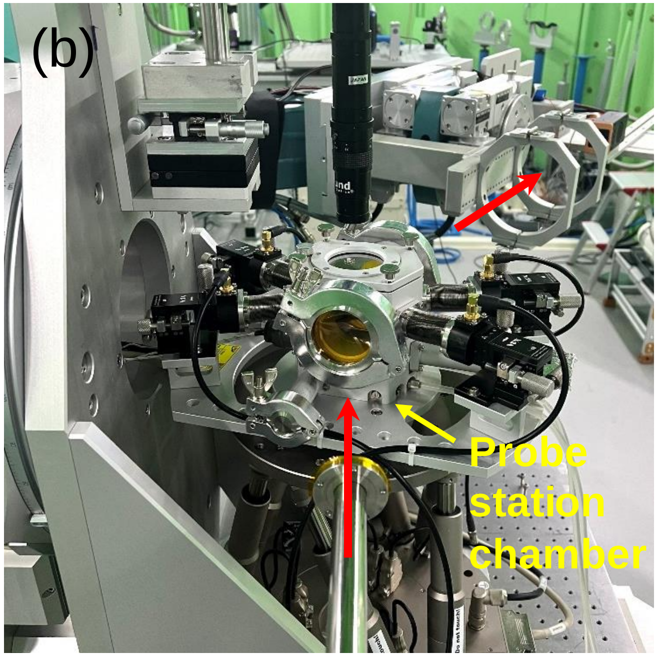


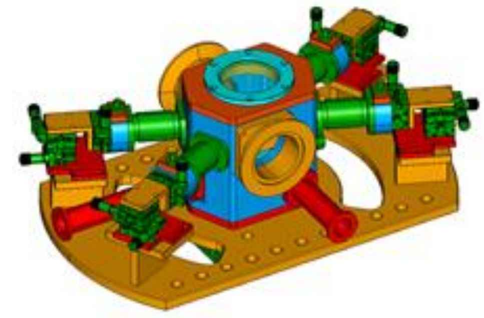
Multimodal X-ray probe at PLS-II

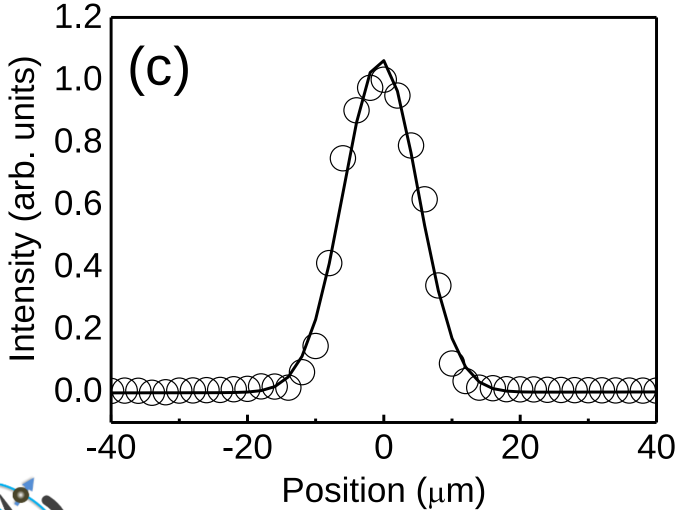
Multimodal X-ray probe station at 9C

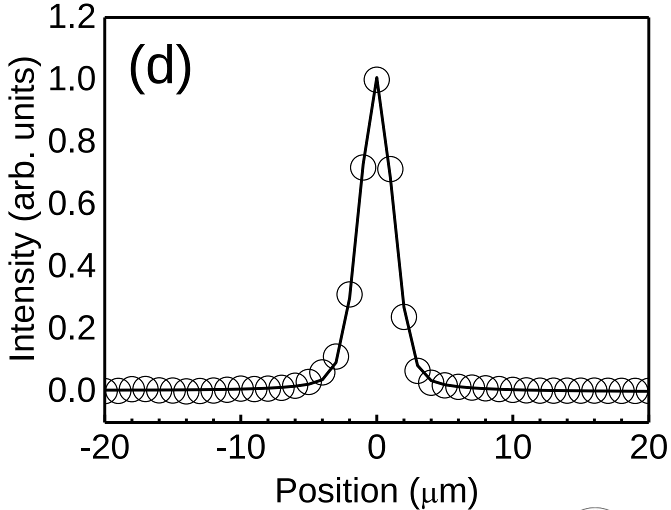
C-AXS







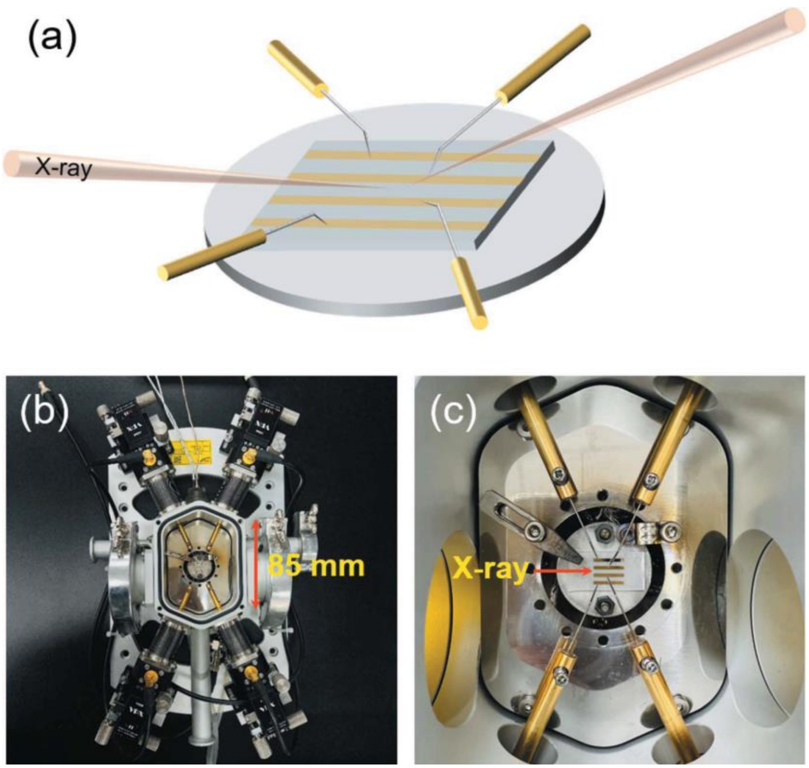


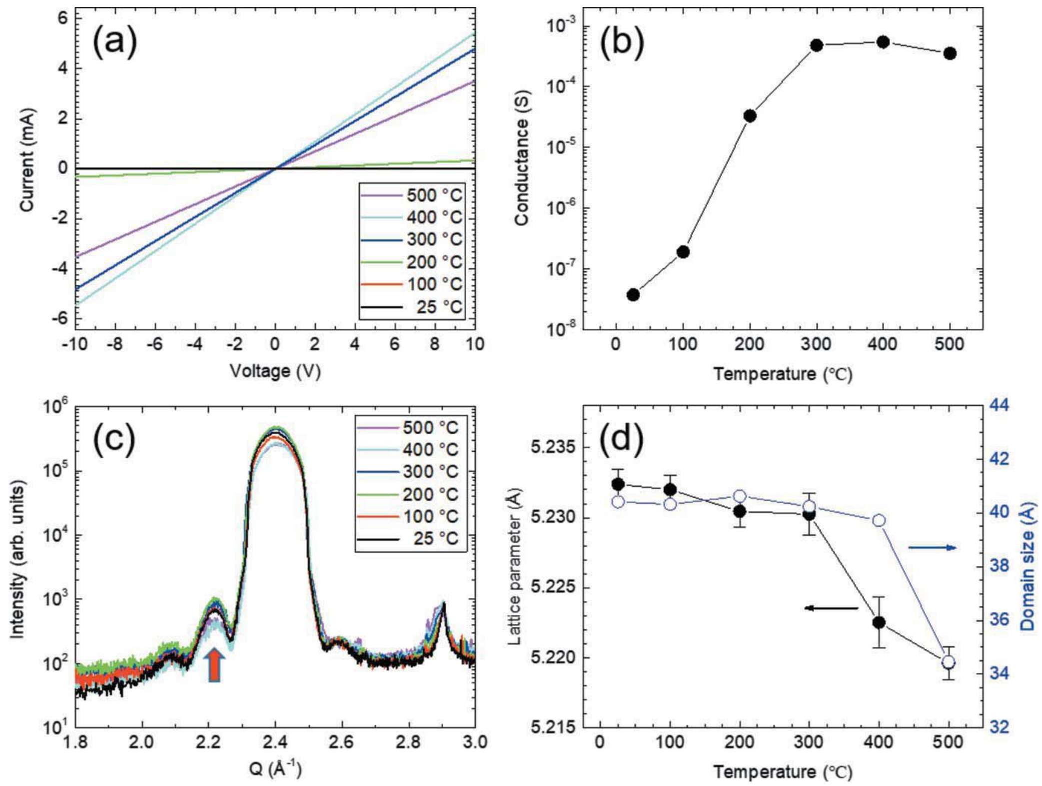


J. Synchrotron Rad. 29,1114-1121 (2022)

The purpose of this apparatus is to measure coherent X-ray diffraction, X-ray fluorescence and electrical properties simultaneously.

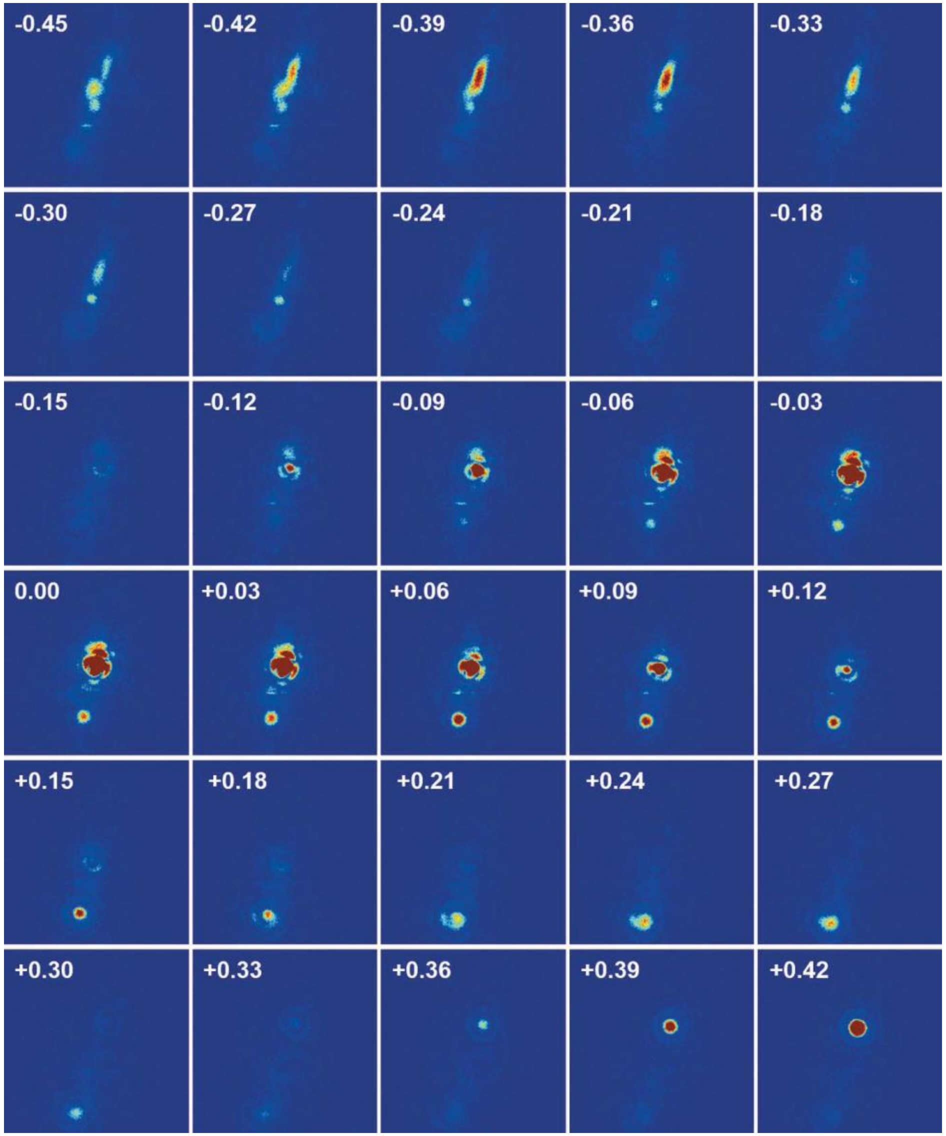
Multimodal X-ray probe station at 9C

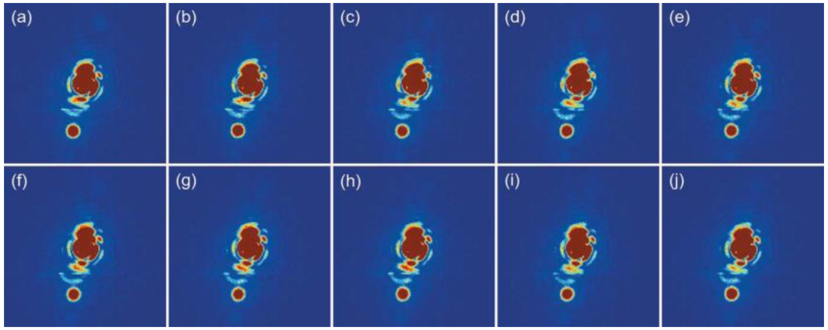




In-situ annealing process of epitaxial ZnO/Sapphire(0001) thin films for studying the variation of electrical transport properties associated with strain relaxation.

Bragg Coherent Diffractive Imaging





Summary

❖ We have developing the X-ray nanoprobe for studying the properties of materials comprehensively.

❖ X-ray nano-focusing optics is a key component to improve the imaging resolution.

❖ X-ray nanoprobe provides the great opportunities in nano-science.

❖ X-ray nano-CT is now feasible at the PLS-II.

❖ The impact of Imaging that resolve nanometer scale objects is expected to be large on many areas of science.


감사합니다 !!!