

Neutrons



Photons

The Complementarity of Real Space and Reciprocal Space

Lecture at Neutron and X-Ray School

J. Murray Gibson

June 12, 2009

Electrons?

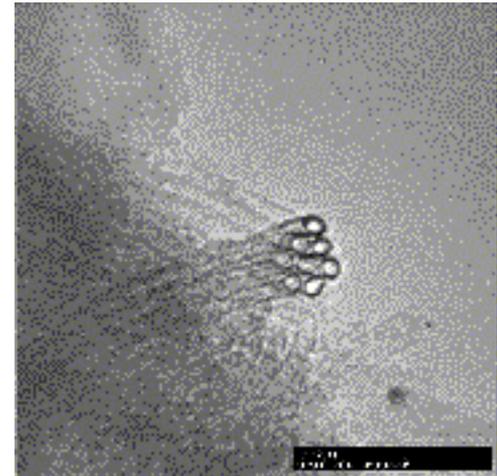
Outline

- Hour 1 – theory
 - Imaging/diffraction and Fourier optics
 - electrons, x-rays and neutrons....
- Hour 2 – examples
 - Picking the right tool for the problem

emphasize electron and x-ray microscopy as
complementary tools

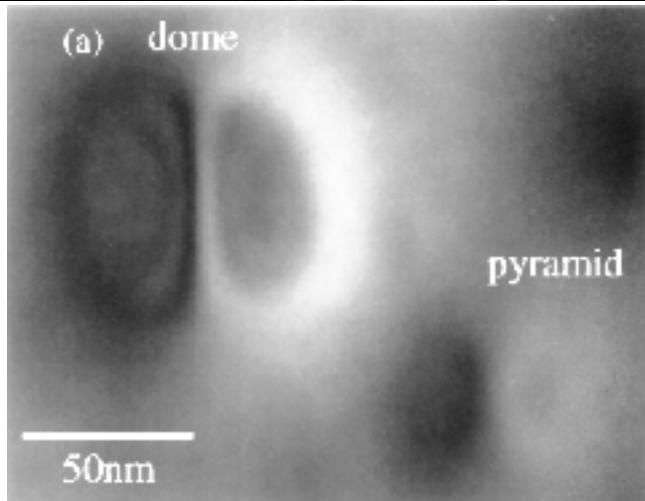
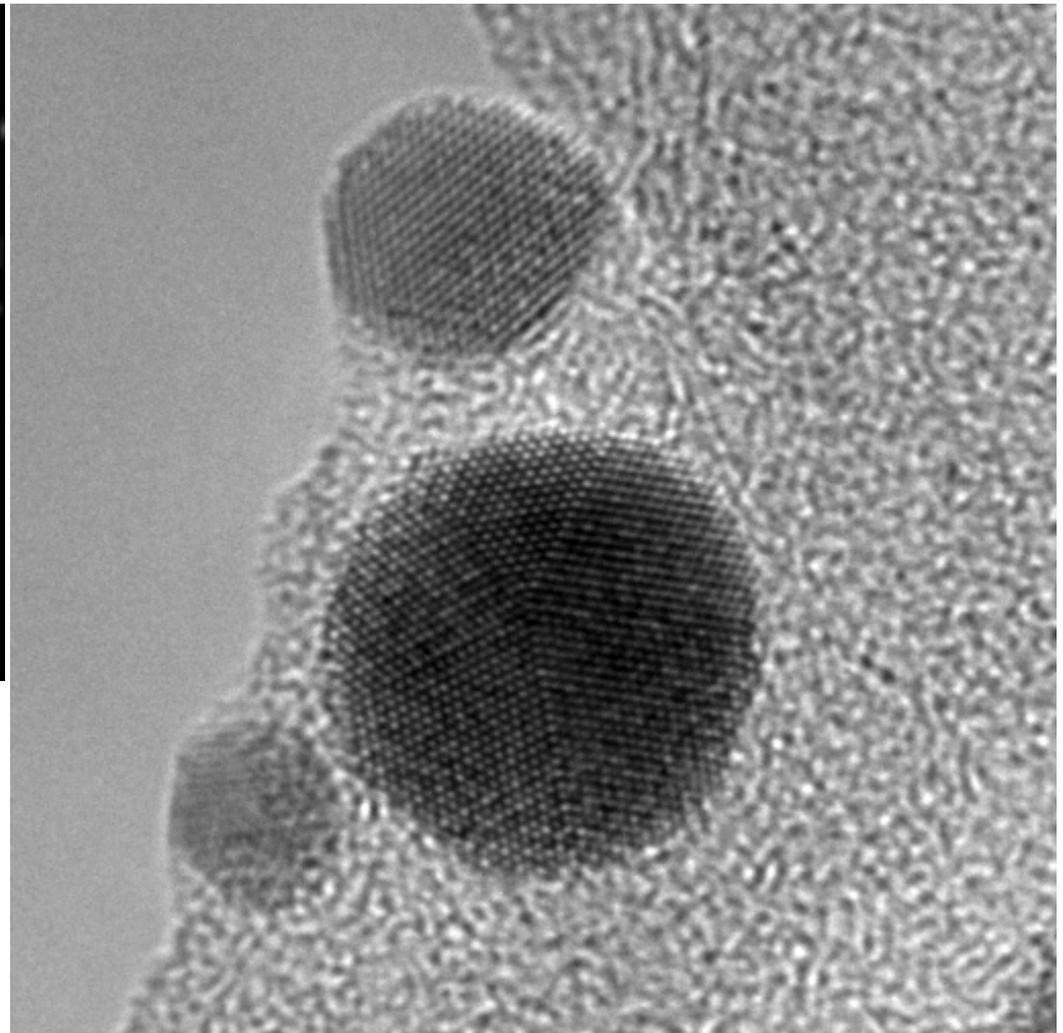
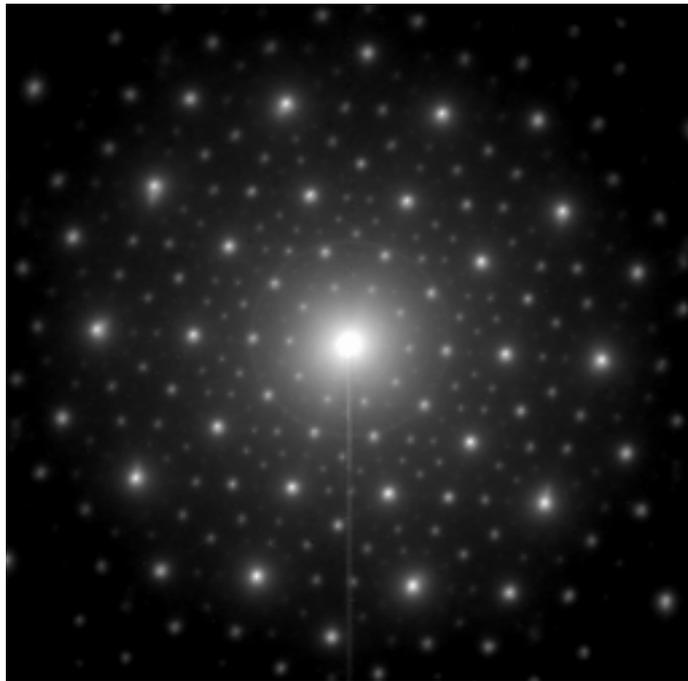
Why real-space?

- Yawn
 - I thought we were there already....
- Magnification
 - direct imaging of atoms..
- Diffraction Contrast
 - fourier optics



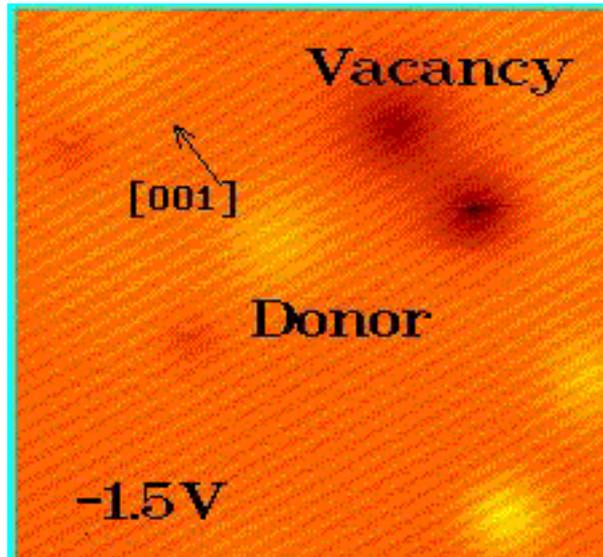
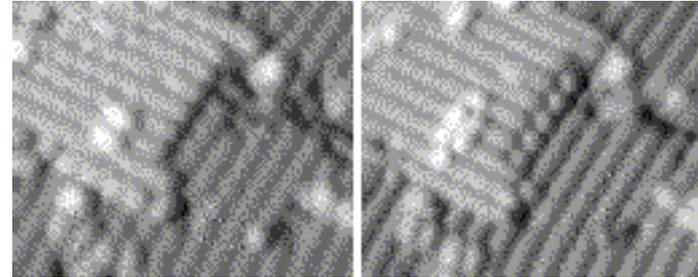
Smalley, Rice University

Microscopy with diffracting radiation



Scanning Probe Microscopy

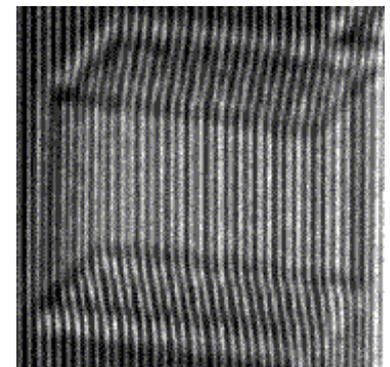
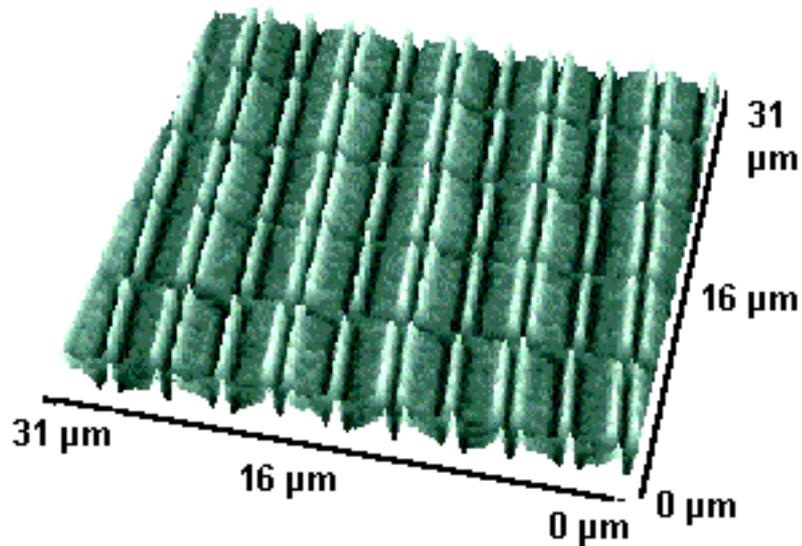
Atoms moving on a silicon surface



Imaging electronic states from
dopants and imperfections
in semiconductors

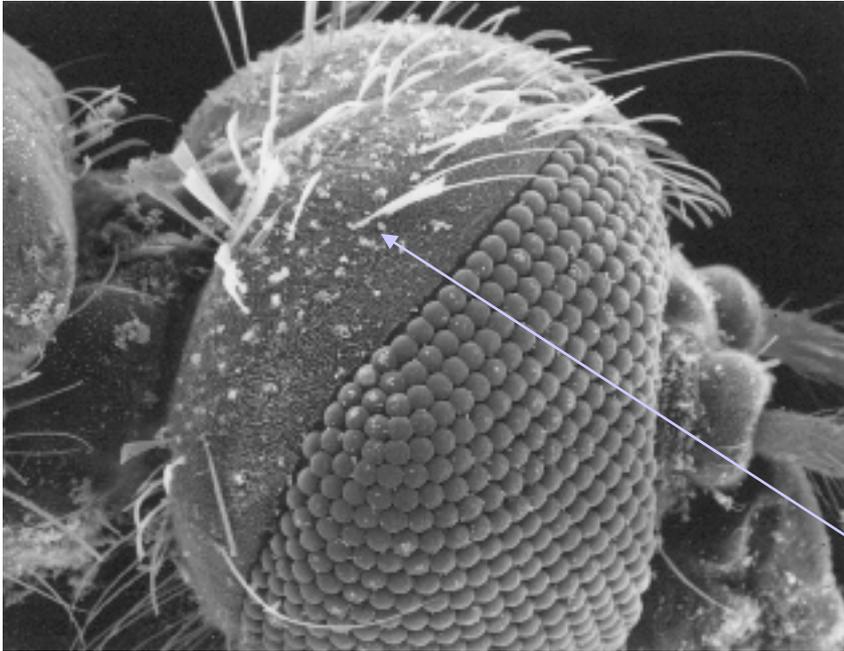
New Probes..

e.g. Magnetic Force Microscopy of a Hard Disk



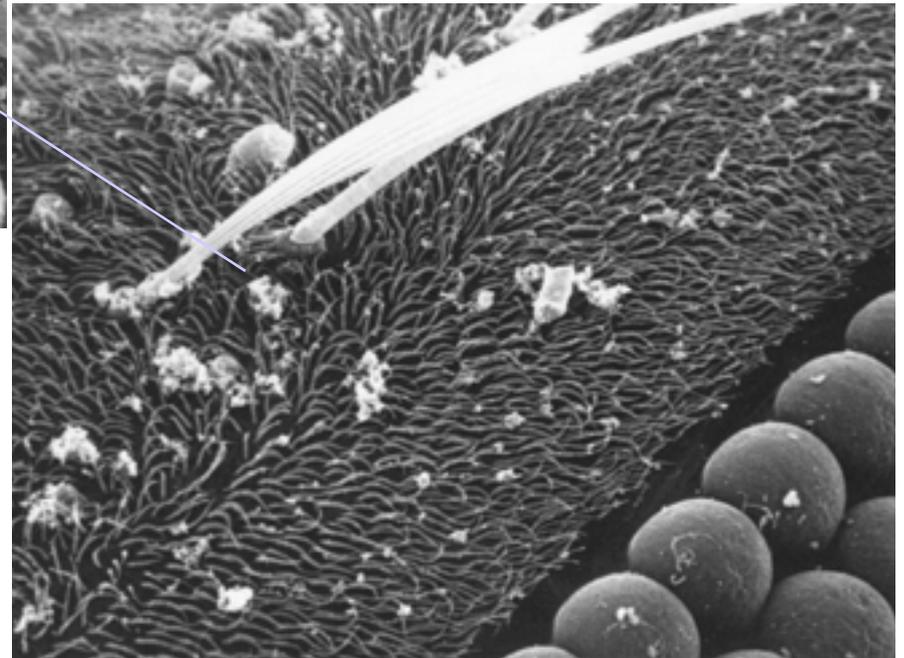
Related magnetic imaging - SEMPA, TEM Holography

Mosquito head and compound eye



Surface - “no” diffraction

1 μ m



note depth of field

Scanning
Electron
Microscopy

US Electron Beam Microcharacterization Facilities

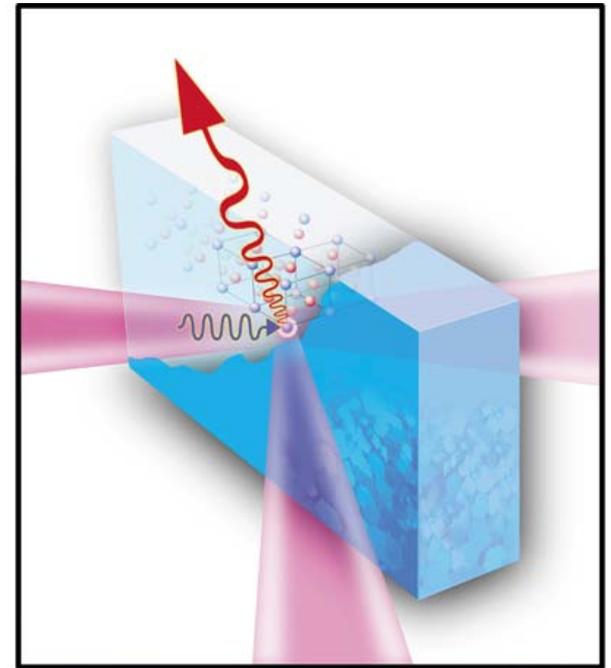


Argonne National Lab

- 4 DOE National Centers
 - specialized techniques
 - new aberration correction project - TEAM
- 26 NSF MRSEC Centers
 - broad central facilities
- ~100 other smaller centers
 - typically single instrument

X-Ray Microscopy

- **Hard x-rays focused to 30 nm (“Nanoprobe”)**
 - Nanoscale strain measurement
 - Imaging of domains, e.g., in ferroelectrics
 - Magnetism
 - Fluorescence spectro-microscopy
- **Aiming at sub 10nm resolution**
- **Now operating jointly with the Center for Nanoscale Materials at ANL**



Electron Scattering

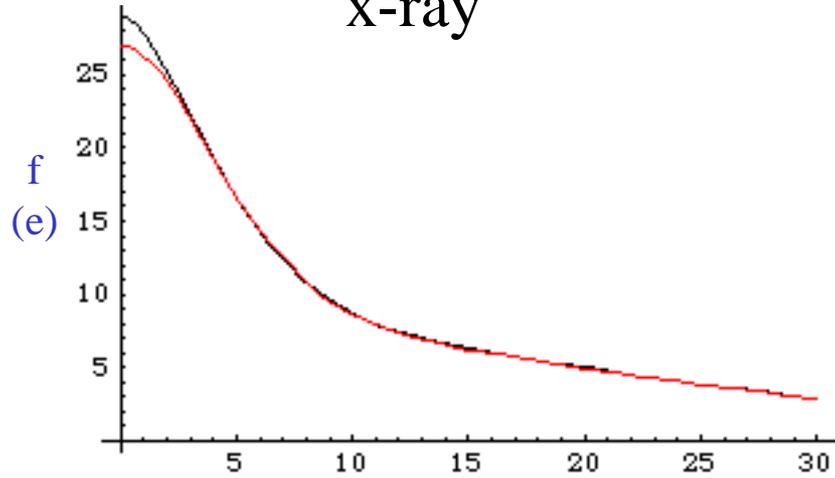
$$f_x(k) = \iint \rho(\underline{r}) e^{i\mathbf{k}\cdot\mathbf{r}} d^3 r \qquad f_{el}(k) = \iint V(\underline{r}) e^{i\mathbf{k}\cdot\mathbf{r}} d^3 r$$

$$\nabla^2 V(\underline{r}) = -\rho(\underline{r})/\epsilon_0$$

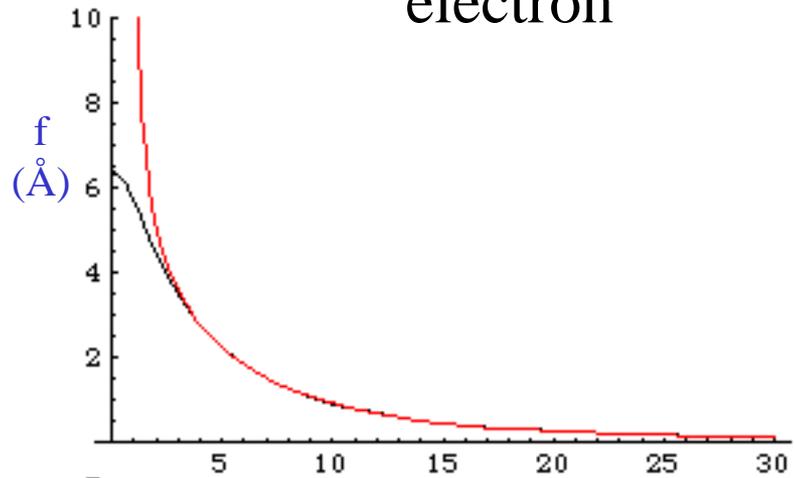
$$f_{el}(k) = a \frac{(Z - f_x)}{k^2} \qquad \text{Mott Formula}$$

Atom Form Factors

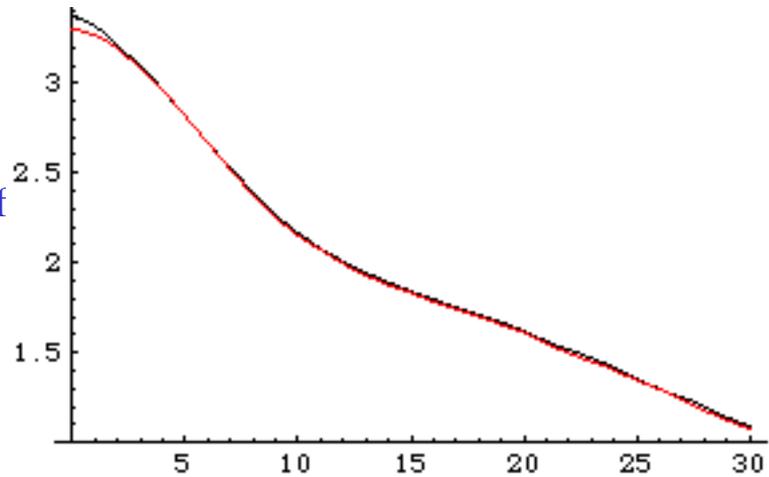
x-ray



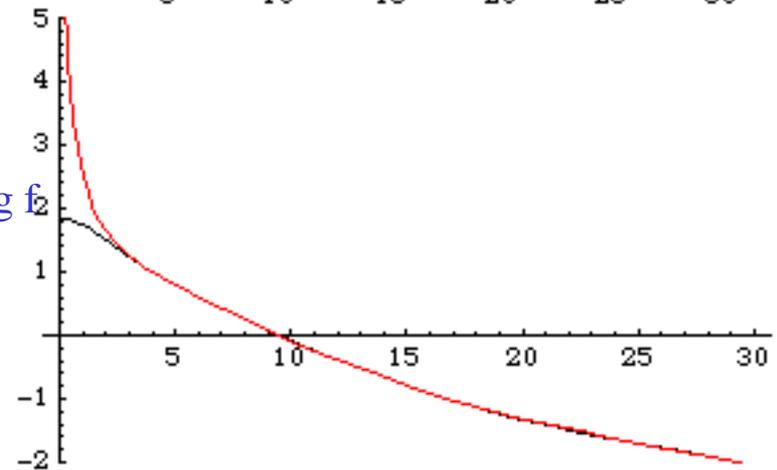
electron



$\log f$



$\log f$

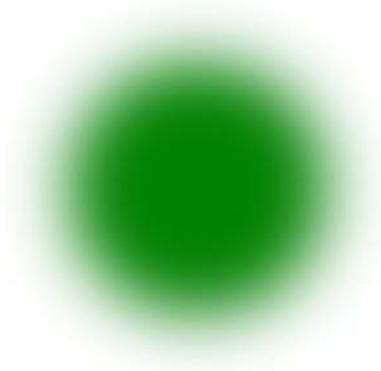


Sensitivity of form factors to charge

<i>d spacing (Å)</i>	<i>change in f_x (%)</i>	<i>change in f_{el} (%)</i>
2	-0.7	2.1
4	-3.4	32.3
8	-5.7	199.0

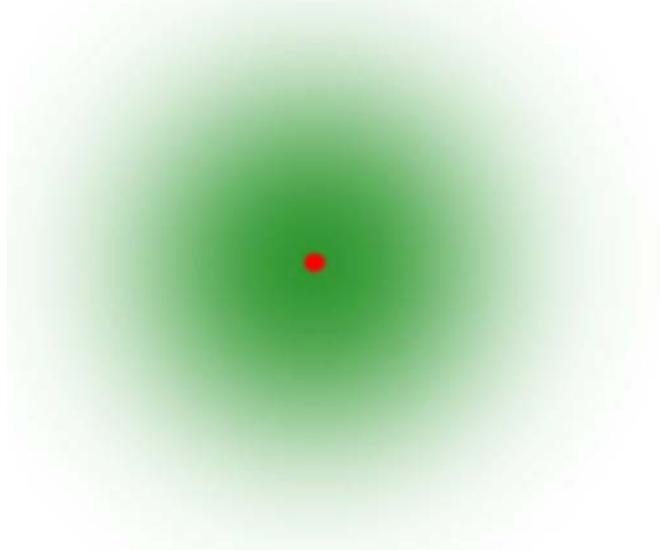
What the particle sees....

$\rho_e(\underline{r})$



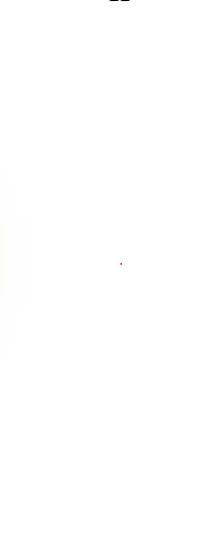
x-ray

$V(\underline{r})$



electron

m_n, \underline{J}



neutron

Electron Form Factors

- Similar dependence on Z
- At high angles - Rutherford-like

$$f_{el}(k) = a \frac{Z}{k^2}$$

Advantages/Disadvantages

Thermal Neutrons

$\lambda \sim d_{hkl}$
penetrates
strong contrast possible (e.g. H/D)
 $E \sim$ elementary excitations
strong magnetic scattering

low brilliance
some elements absorb strongly
restrictions on Q for large ΔE
excitations $< 100\text{meV}$

Synchrotron X-rays

$\lambda \sim d_{hkl}$
high brilliance
no kinematic restrictions
no ΔE restriction

strong absorption at low E
little contrast e.g. H-C
weak scattering
from light elements
radiation damage

Fast Electrons

$\lambda \ll d_{hkl}$
high brilliance, nanoprobe
no kinematic restrictions
no ΔE or ΔQ restriction
charge sensitive

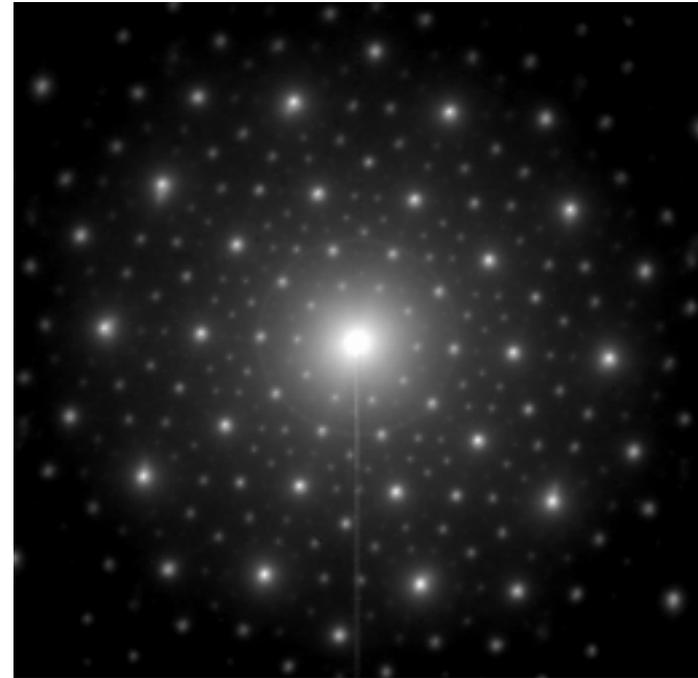
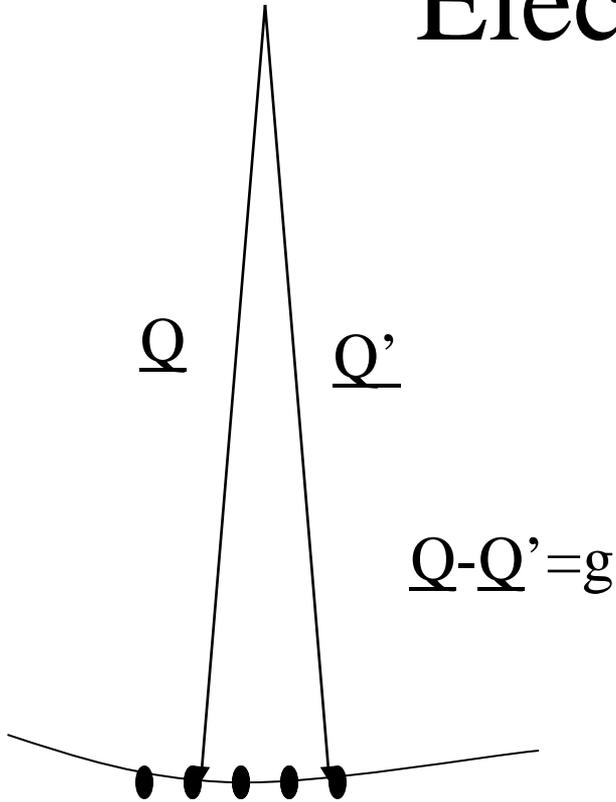
thin samples (or surfaces)
dynamical scattering
little contrast e.g. hydrocarbons
weak scattering from light elements
radiation damage

← courtesy Sunil Sinha →

Complementarity of techniques

<i>Radiation</i>	<i>Source Brightness (particles/cm²/ steradian/eV)</i>	<i>Elastic Mean- Free Path (Å)</i>	<i>Absor- ption Length (Å)</i>	<i>Minimum Probe Size (Å)</i>
<i>Neutrons</i>	10 ¹⁴	10 ⁸	10 ⁹	10 ⁷
<i>X-rays</i>	10 ²⁶	10 ⁴	10 ⁶	10 ³
<i>Electrons</i>	10 ²⁹	10 ²	10 ³	1

Electron Diffraction



Ewald sphere "flat"

Kinematic theory c.f. x-rays/neutrons

predicts diffraction pattern geometry, qualitative effects

Dynamical Theory of Diffraction

$$\frac{d\phi_0}{dz} = \frac{i\pi}{\xi_0} \phi_0 + \frac{i\pi}{\xi_g} \phi_g e^{2\pi isz}$$

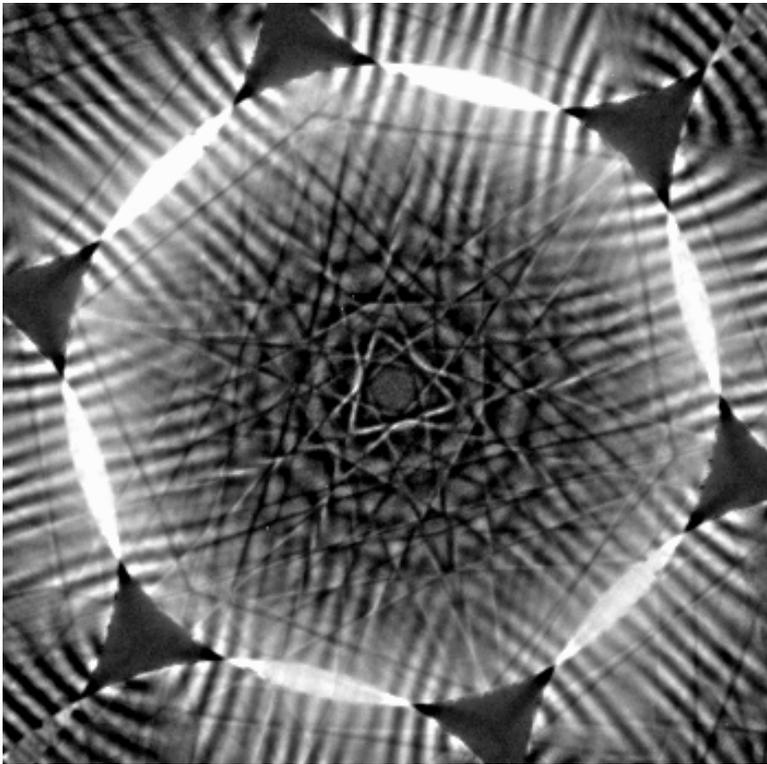
$$\frac{d\phi_g}{dz} = \frac{i\pi}{\xi_g} \phi_0 e^{-2\pi isz} + \frac{i\pi}{\xi_0} \phi_g$$

2-beam theory can
be extended to N beams
- BLOCH WAVES

Extinction distance: $\xi_g = \frac{\pi \Omega}{\lambda F}$ typically $\sim 1000 \text{ \AA}$
at 100kV

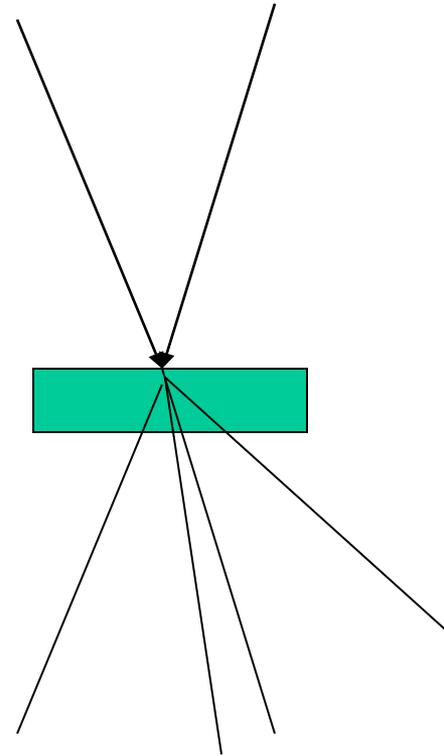
absorption is added as an imaginary extinction

Convergent Beam Electron Diffraction



reveals full symmetry

Si (111)



Imaging

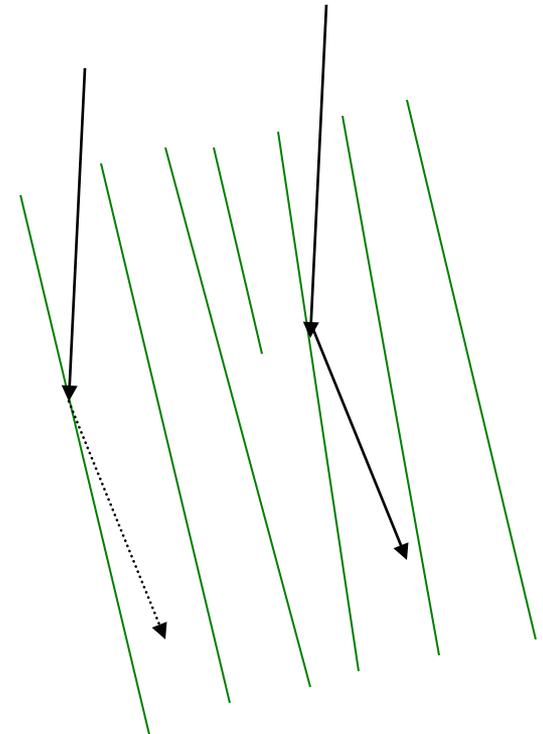
The column approximation:

$$\frac{d\phi_0}{dz} = \frac{i\pi}{\xi_0} \phi_0 + \frac{i\pi}{\xi_g} \phi_g e^{2\pi i(s z + \underline{g} \cdot d\underline{R} / dz)}$$

$$\frac{d\phi_g}{dz} = \frac{i\pi}{\xi_g} \phi_0 e^{-2\pi i s z} + \frac{i\pi}{\xi_0} \phi_g$$

Howie-Whelan Equations

predicts strain-contrast images well at $\sim 20\text{\AA}$ resolution

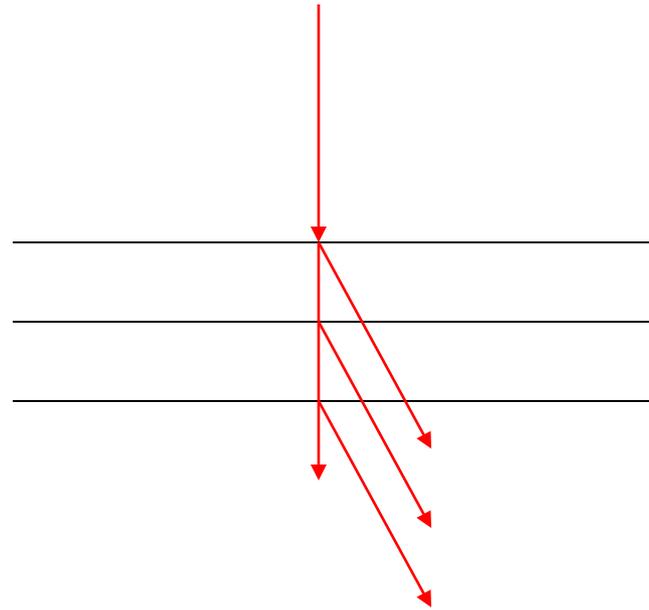


edge dislocation

displacement field \underline{R}

Multi-slice theory

More accurate but less-efficient approximation
propagates electrons between thin (kinematical) slices



includes many-beam
effects
and fresnel
propagation

appropriate for high-resolution ($<5\text{\AA}$) imaging

Fourier Optics

- Diffraction and Imaging

- Fraunhofer diffraction $F(\underline{Q}) = \iint \phi(\underline{r}) e^{i\underline{Q}\cdot\underline{r}}$

- one fourier transform

- Imaging (with a lens) $\varphi(\underline{r}) = \iint F(\underline{Q}) e^{-i\underline{Q}\cdot\underline{r}}$

- Second fourier transform



- It gets interesting when you filter in one space or the other

Simple Consequence

- Abbe's theory of the microscope **resolution**

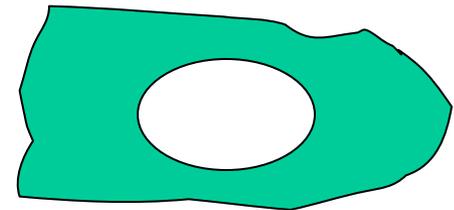
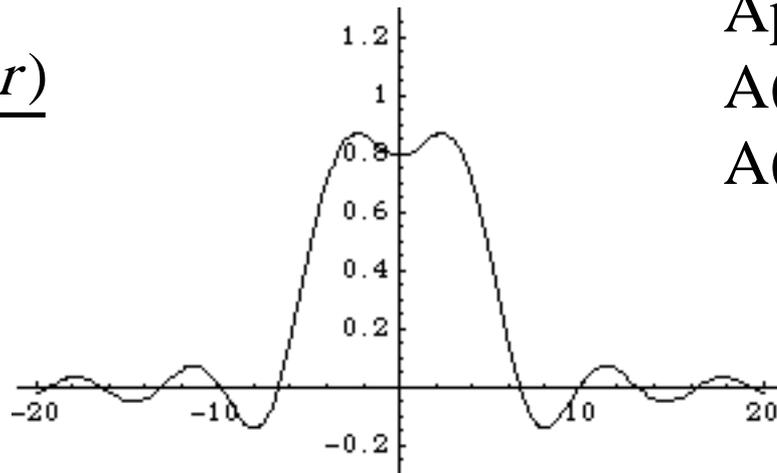
$$\varphi(\underline{r}) = \iint A(\underline{Q}) F(\underline{Q}) e^{-i\underline{Q} \cdot \underline{r}}$$

=convolution with F.T. (A)

– and the Rayleigh Criterion

$$PSF = \frac{2J_1(Q_0 r)}{Q_0 r}$$

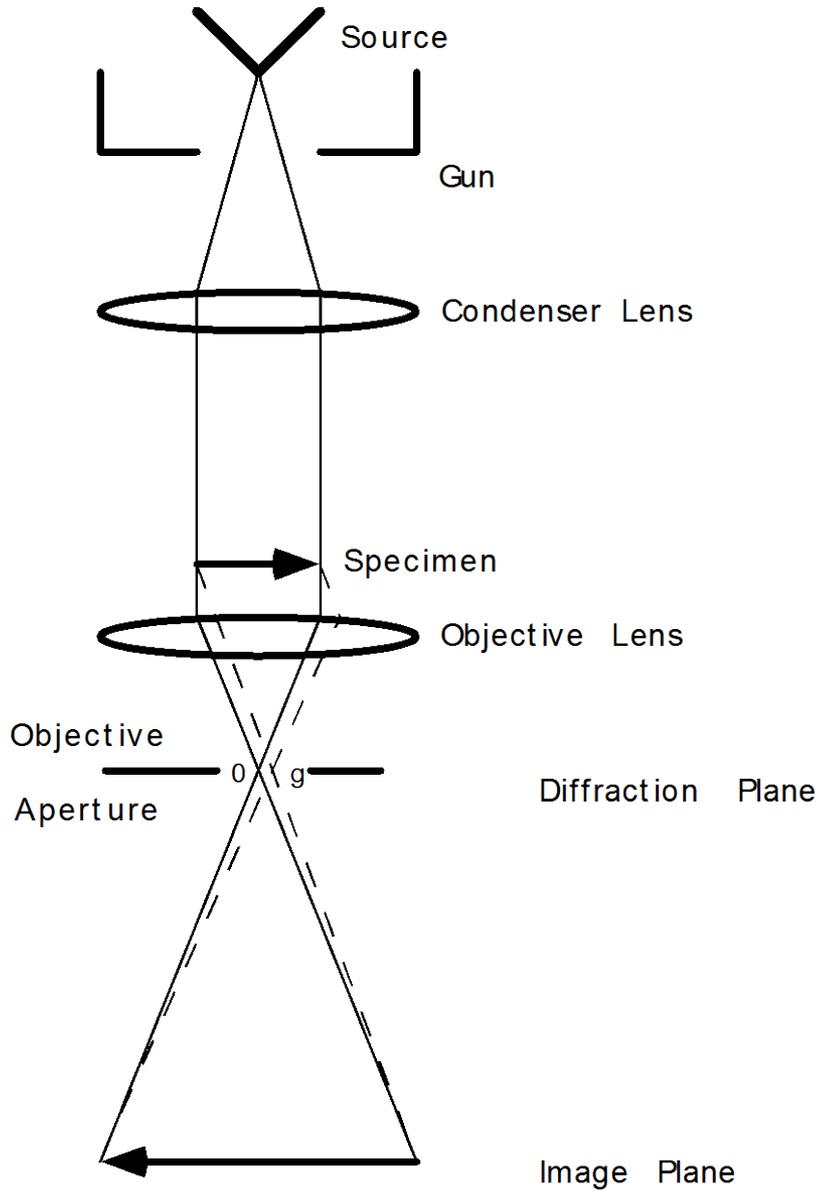
$$\Delta = \frac{1.22}{Q_0}$$



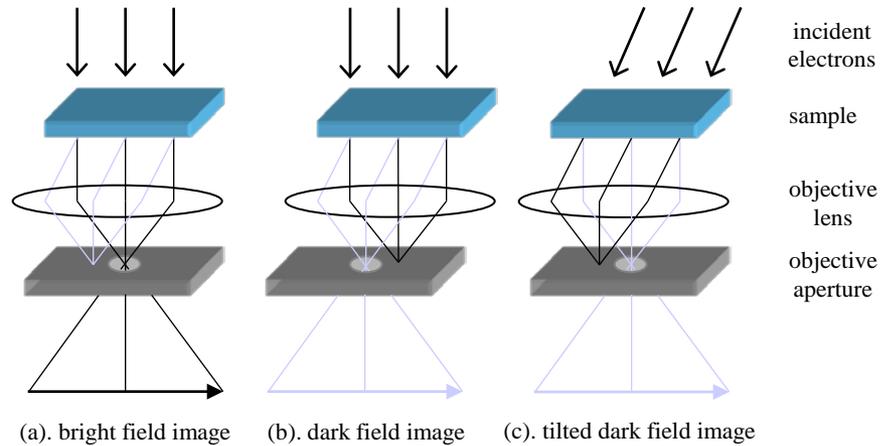
Aperture in focal plane

$$A(Q) = 1; Q < Q_0$$

$$A(Q) = 0; Q > Q_0$$



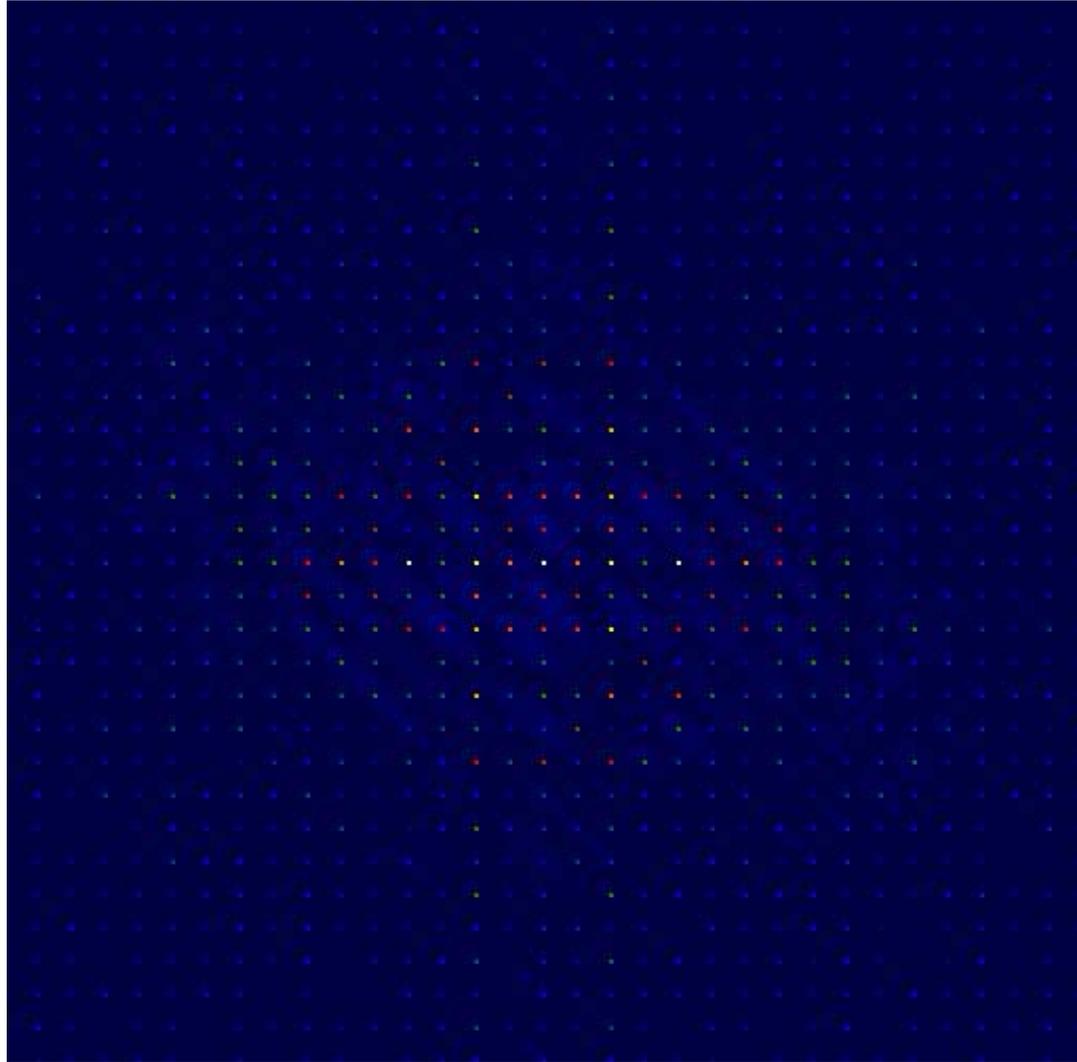
Bright and Dark Field Imaging



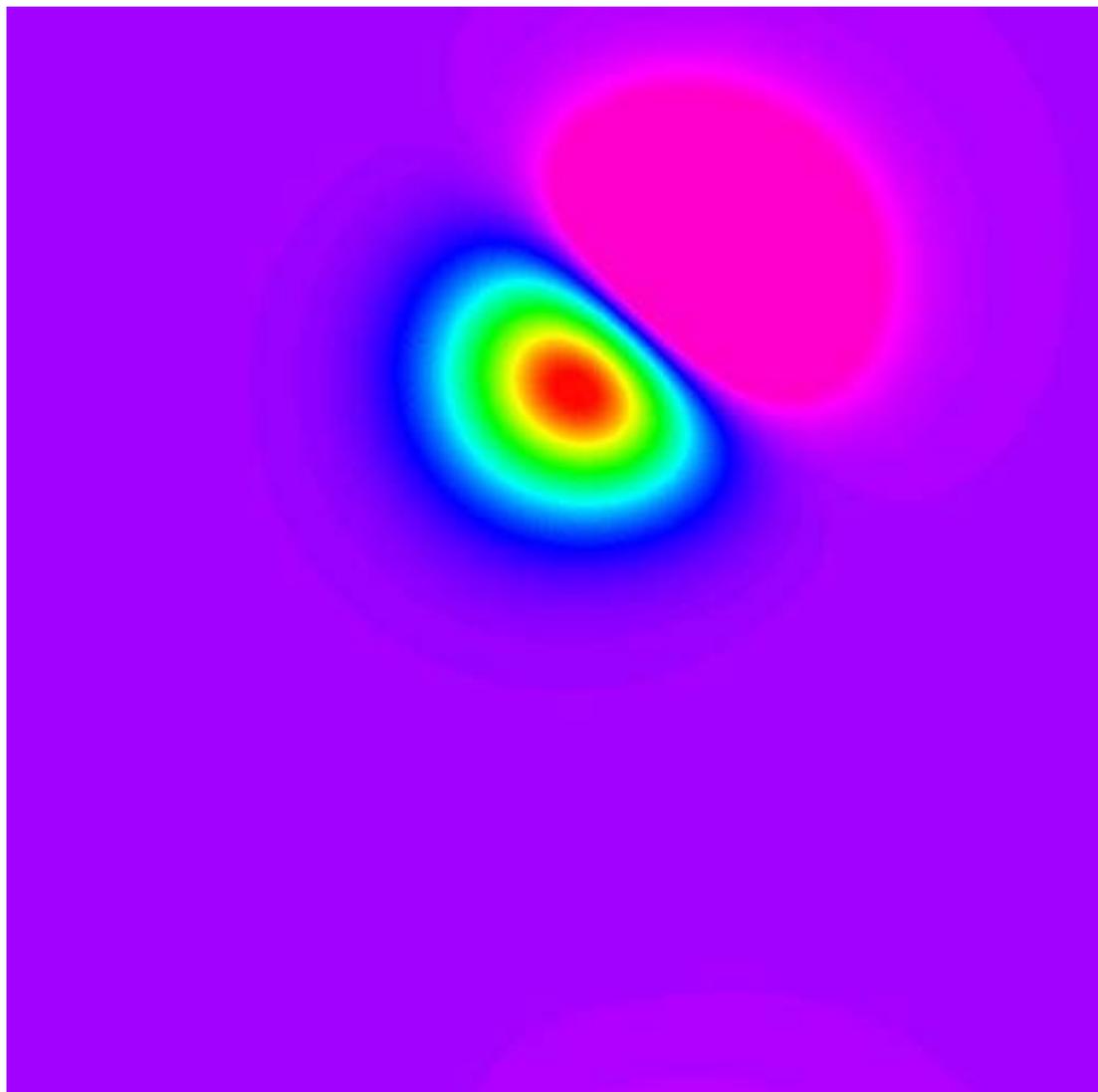
A 2-D Perfect Crystal?



and it's diffraction pattern



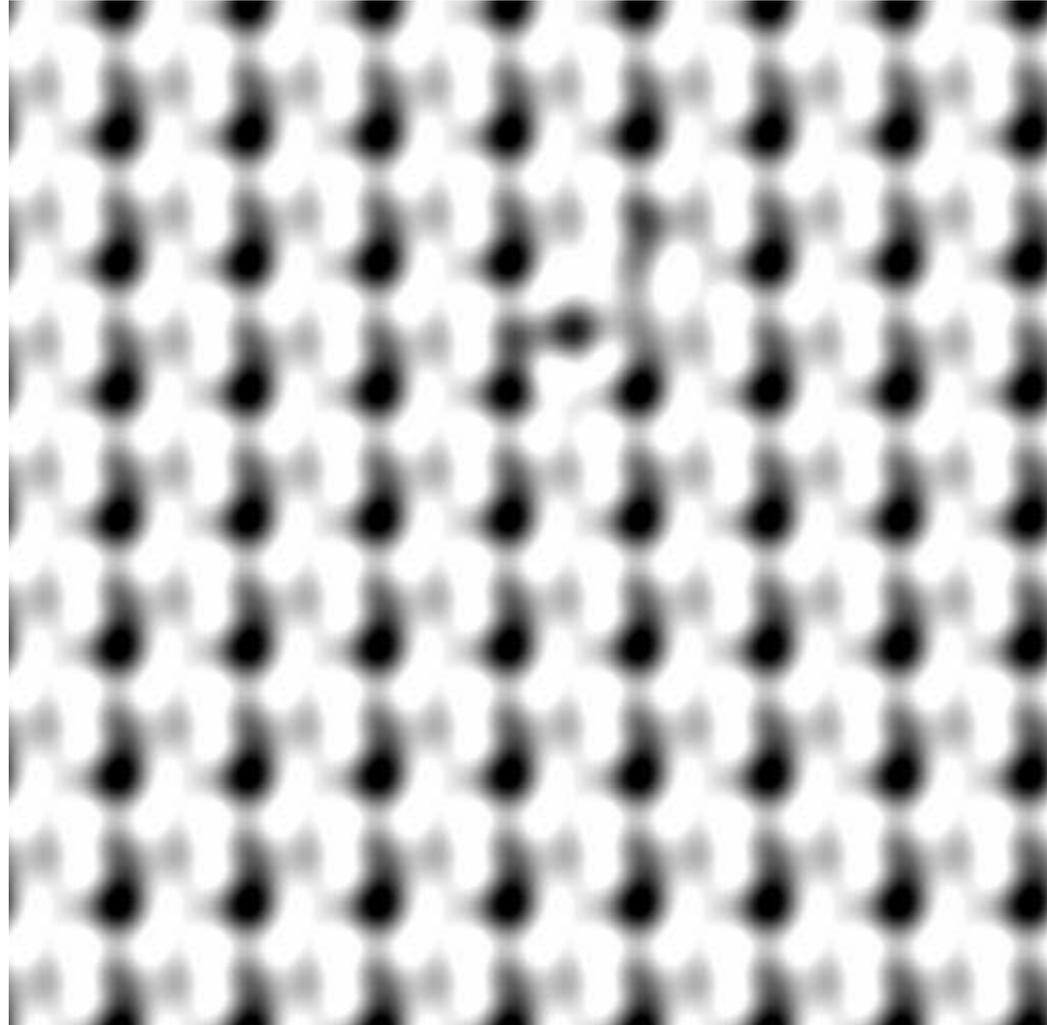
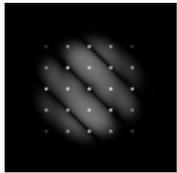
Dark-field image



The point defect...

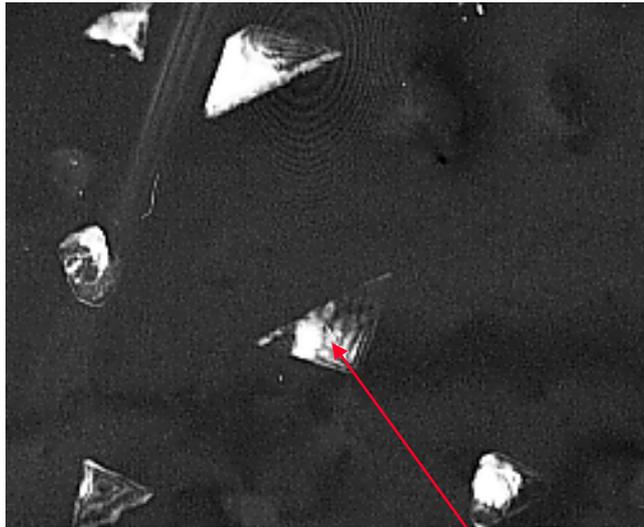


“High-resolution image”

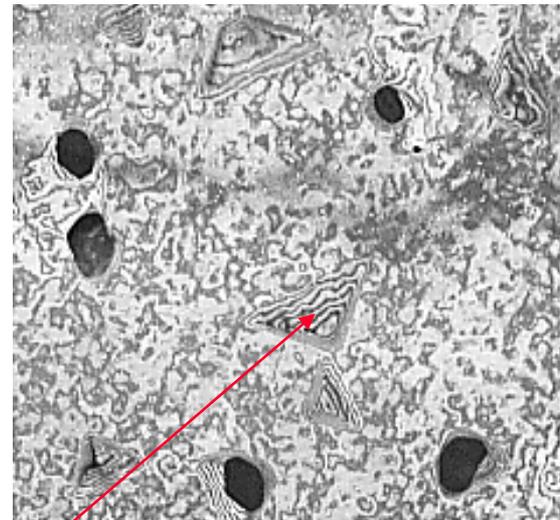


Amplitude Contrast Imaging

Cu₂O Reflection

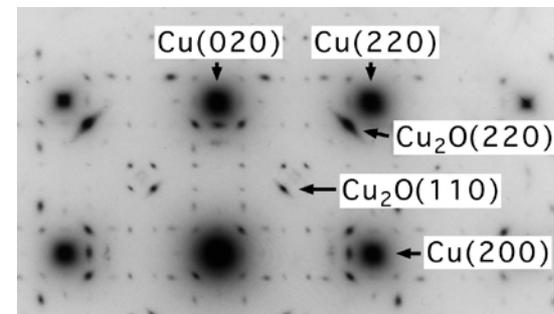


Cu Reflection



Mixed phase system..

same island

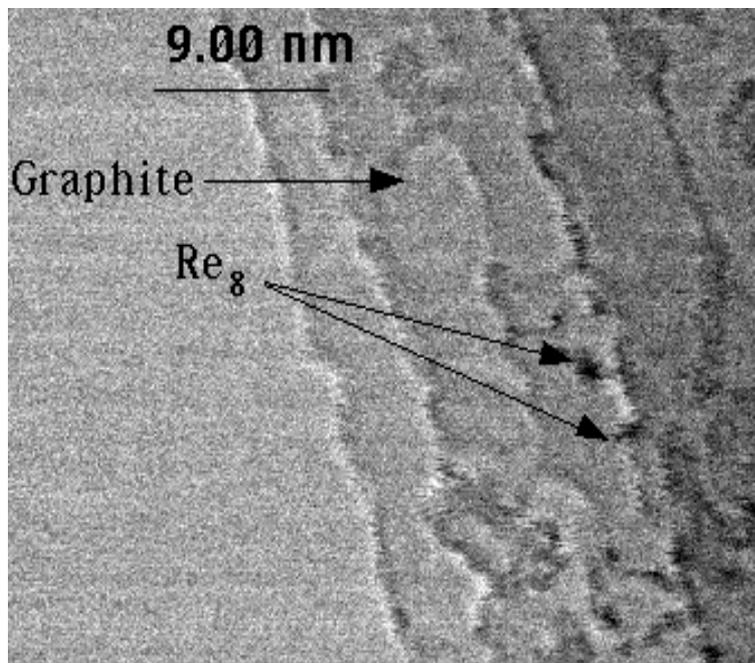


[Self-limiting oxidation of copper](#)

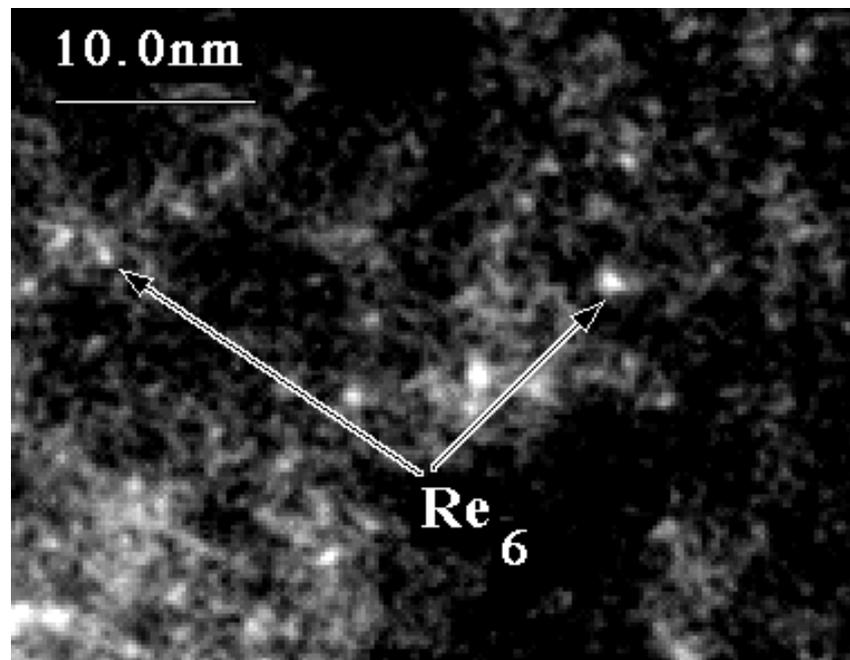
Yang, JC; Kolasa, B; Gibson, JM,
APPLIED PHYSICS LETTS,
73, 2841 (1998)

Scanning Transmission Electron Microscopy

“Z-Contrast” STEM



Bright-field STEM Image



High-angle ADF dark-field image

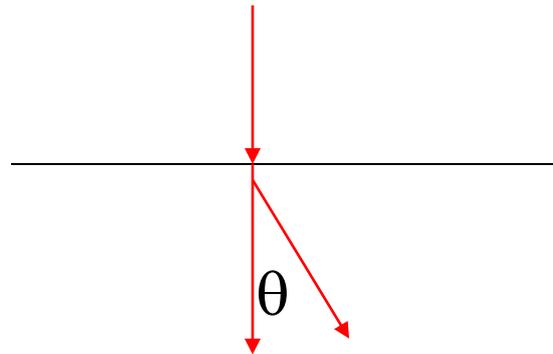
The principle of reciprocity..

[Stability of supported organometallic clusters probed by a mass-sensitive TEM technique](#)

Singhal, A; Gibson, JM; Treacy, MMJ, JOURNAL OF PHYSICAL CHEMISTRY 100 6385 (1996)

Phase Contrast and High Resolution

- To image lattice resolution $< d$
 - $\Rightarrow Q_0 > g$ so no amplitude contrast



fresnel phase shift $\sim \pi/\lambda z\theta^2$

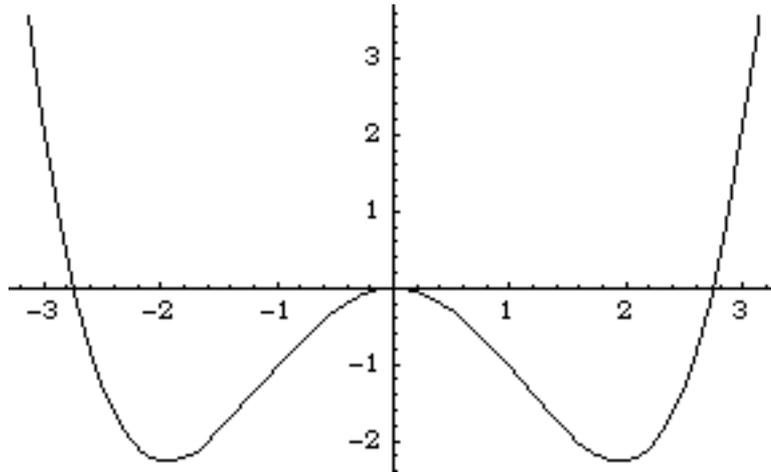
assume object is weak phase shift
(kinematical theory)

$$\psi = e^{i\sigma V(\underline{r})} \approx 1 + i\sigma V(\underline{r})$$

You want a phase shift near $-\pi/2$ (Zernicke phase contrast)

Phase shift with aberrations

Phase shifting function (should be near $-\pi/2$)



$$\gamma = \pi \lambda (zk^2 + C_s k^4 / 2)$$

$$k = \frac{q}{2\pi}$$

C_s is the spherical aberration coefficient

Ideal defocus (Scherzer) $z = -1.2\sqrt{C_s\lambda} \Rightarrow r = 0.67(C_s\lambda^3)^{1/4}$

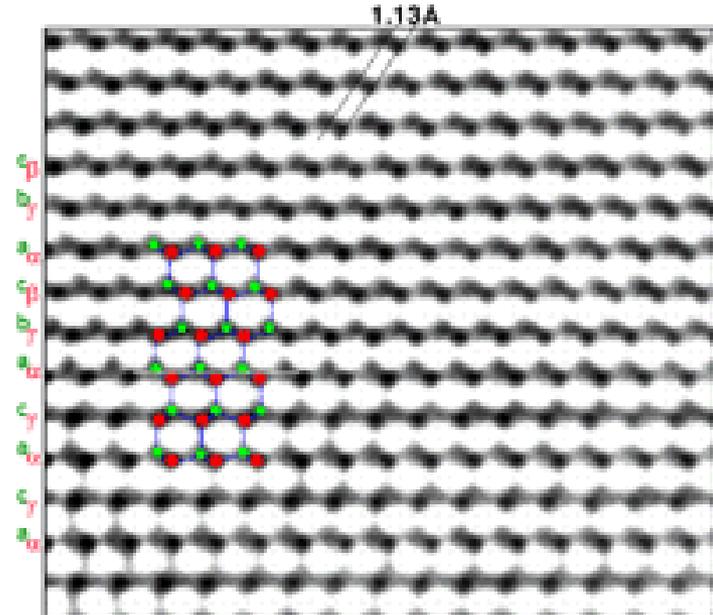
point-to-point resolution

State of the art high-resolution

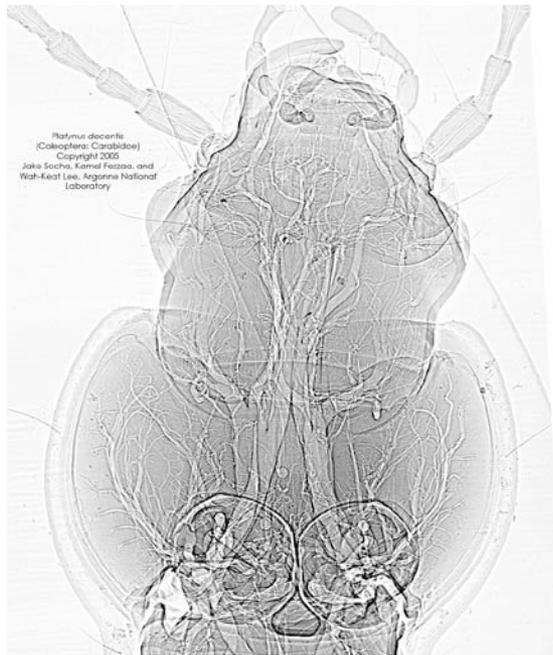
GaN (LBL)

this picture shows
reconstructed electron
wavefunction revealing
split Ga/N atoms

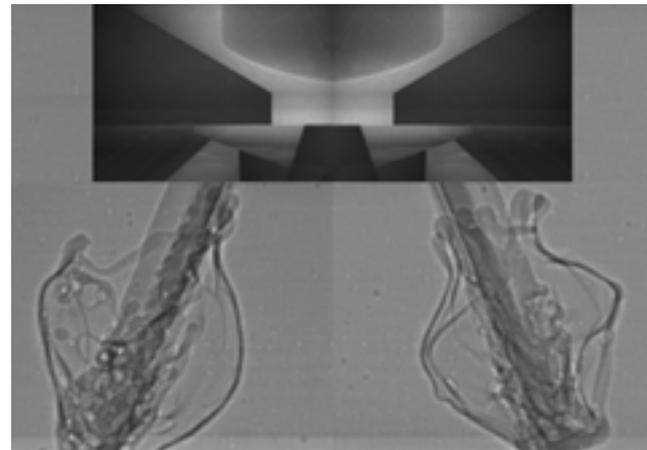
removing the microscope
aberrations - wavefront reconstruction,
aberration correction



Phase Contrast X-Ray Imaging



Big bugs, Socha et al.,
PNAS **104**, 13198, (2007)



Fuel Sprays: Wang, YJ et al.
NATURE PHYSICS,
4 305 (2008)

Examples

Quantitative determination of local structure and charge distribution in copper oxide

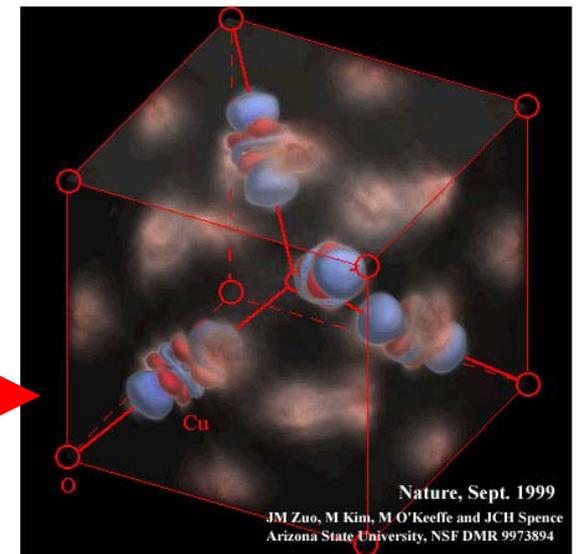
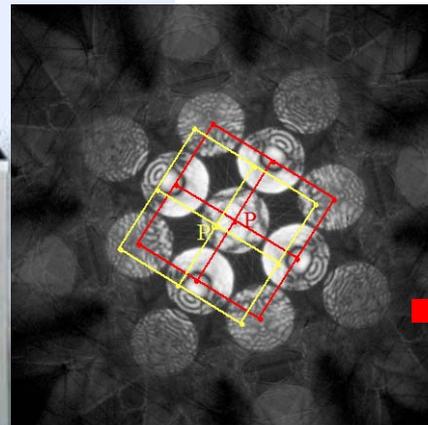
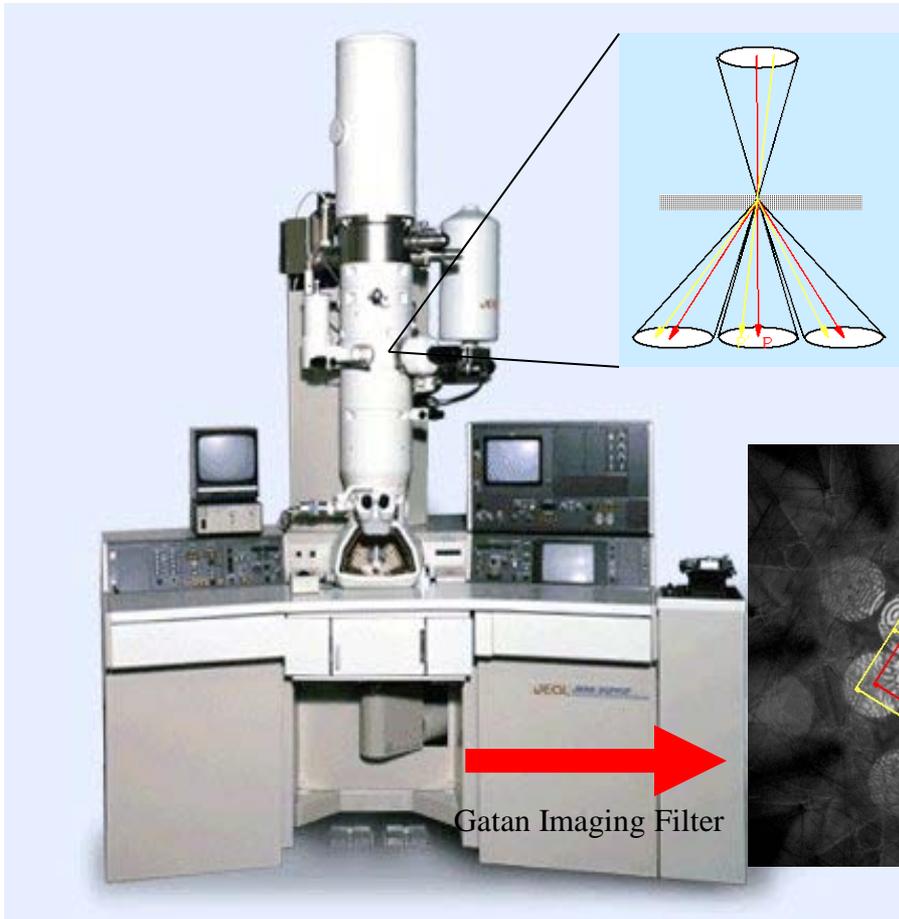
To study :

- Charge and charge states in complex oxides

Using Electron sensitivity to crystal bonding

- combined with x-ray higher order SF accuracy

- Probe formation allows local study



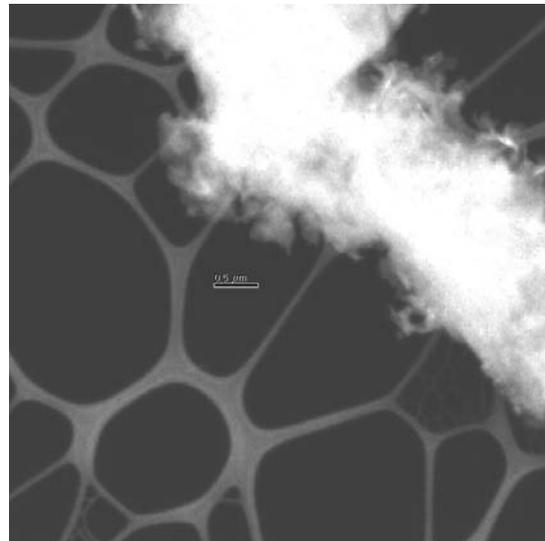
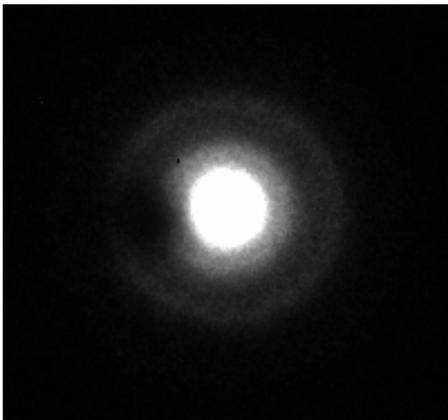
J.M. Zuo and Spence

d-orbitals visualized

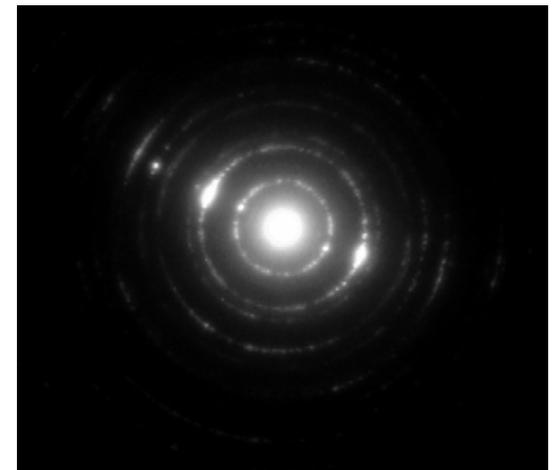
Crystallites in glass

- Recent experience with IPNS experiment
- Thermal poling of SiO_2 induced optical nonlinearity
 - Initial IPNS data suggested structural change in amorphous material
(Cabrillo, Gibson, Johnson, Bermejo et. al.)
- TEM shows ~5% small crystallites (cristobalite)

unpoled



poled



Role of microscopy in confirming homogeneity

Self-limiting oxidation of copper

J. C. Yang,^{a)} B. Kolasa, and J. M. Gibson

Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

M. Yeadon

Institute of Materials Research and Engineering, National University of Singapore, 119260, Singapore

assumes cation drift in uniform film

$$1/h = A - B \ln(t)$$

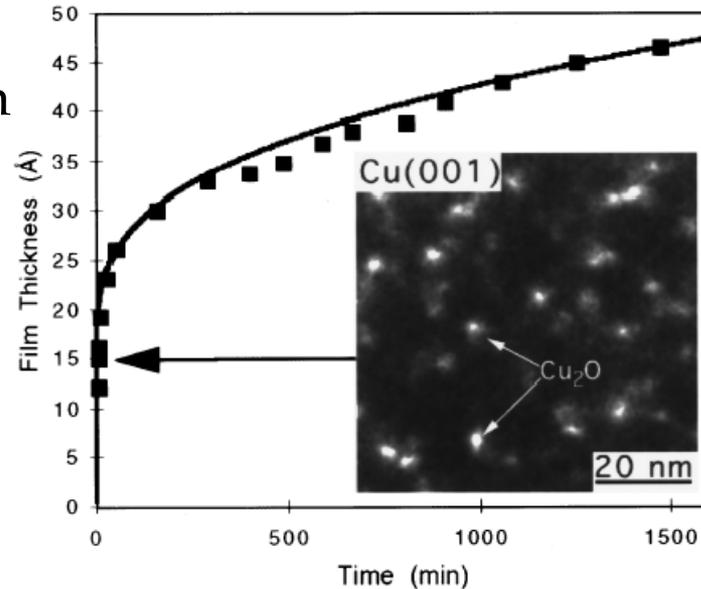
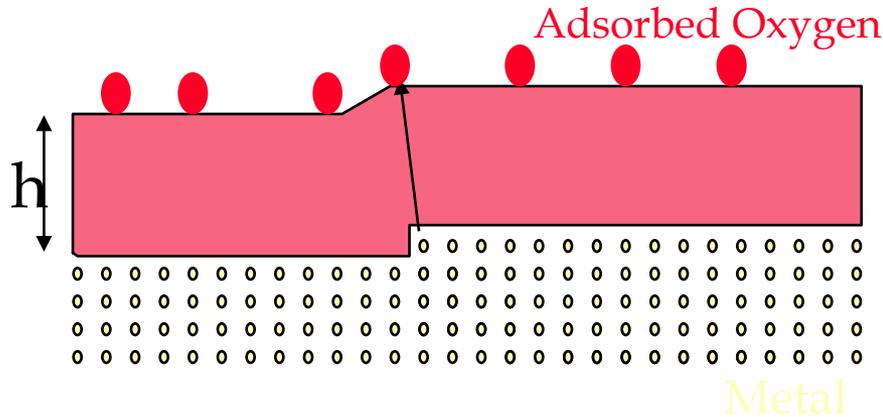
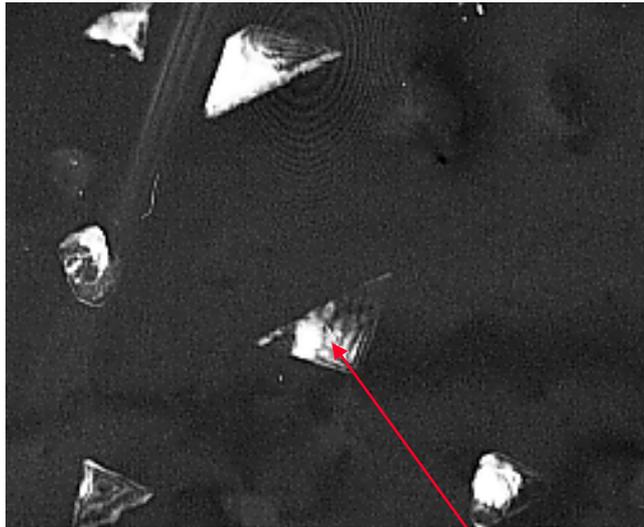


FIG. 1. Oxide thickness Cu_2O of vs time from Young *et al.* (see Ref. 2) of the thickness of the Cu_2O as function of time, when single crystal (001) Cu was oxidized in 760 Torr O_2 at 70°C . The arrow points to the experimental condition we used. (Inset) Dark field image from the Cu_2O reflection, where the bright specks are Cu_2O islands.

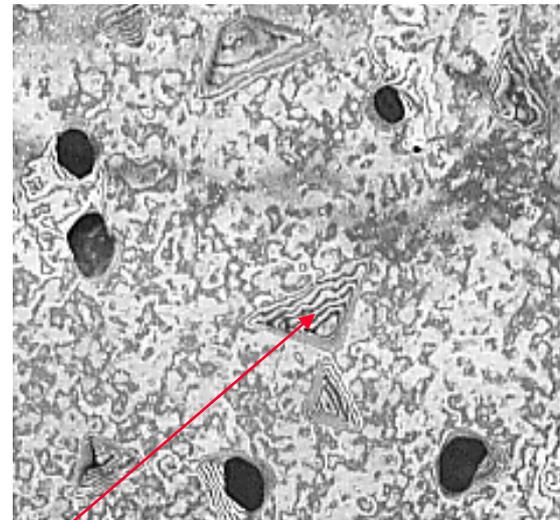
N.Cabrera, N.F. Mott, Rept. Progr. Phys. **12**, 163 (1948)

Dark-field imaging of phases

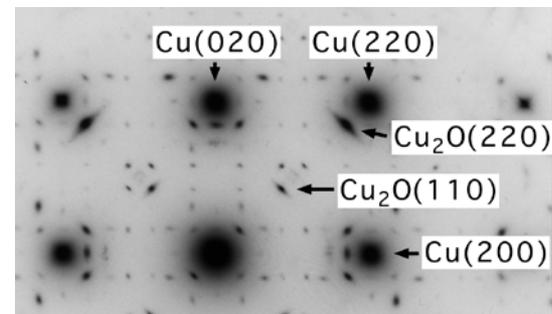
Cu₂O Reflection



Cu Reflection



same island



Strain Evolution in Coherent Ge/Si Islands

Chuan-Pu Liu,^{1,*} J. Murray Gibson,¹ David G. Cahill,¹ Theodore I. Kamins,² David P. Basile,² and R. Stanley Williams²

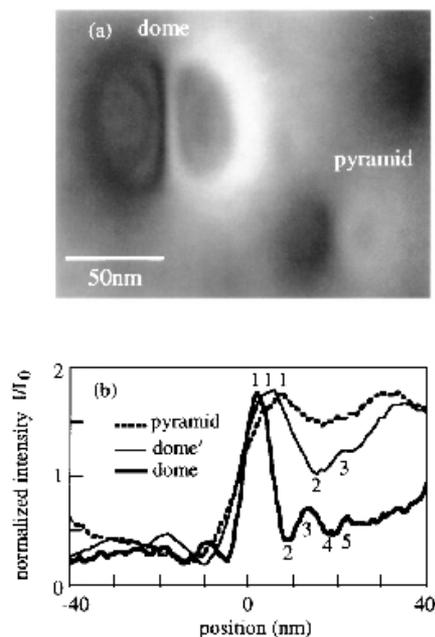


FIG. 1. Dark-field images of a pyramid and a dome using $g = 400$. (b) Line traces across three typical islands found in the experiment, where the fringes on one side of the images are numbered.

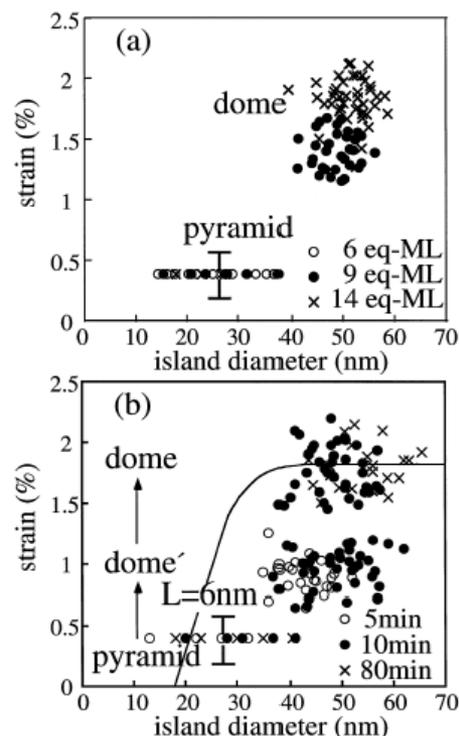
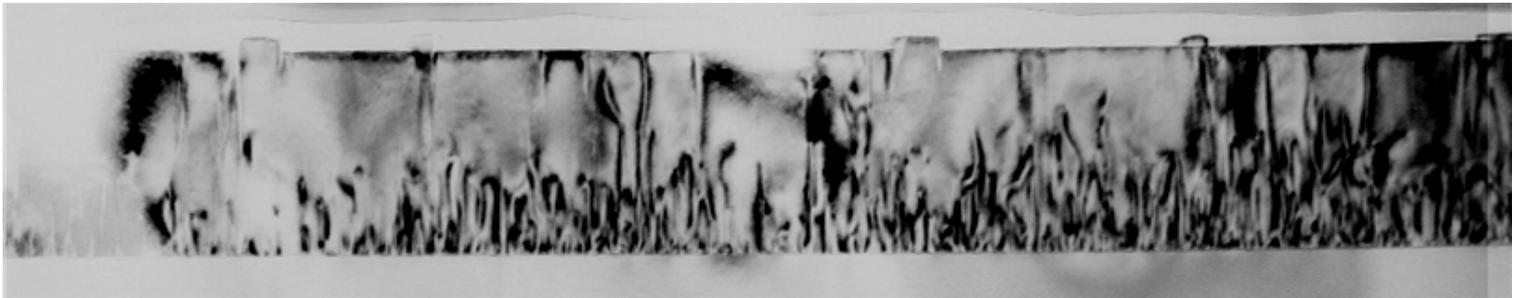


FIG. 2. Strain in Ge islands vs island diameter. (a) For as-deposited samples 6, 9, and 14 eq-ML thick grown at 600 °C and (b) for 8 eq-ML thick samples deposited at 550 °C and annealed at 550 °C for 5, 10, and 80 min. The error ranges both in diameter and strain are 10%. The solid curve in (b) represents the dependence of the island diameter on the strain of equilibrium islands with isotropic surface energies, derived from the work of Kukta and Freund [17] using $L = 6$ nm (see text for details). The island populations in a sample annealed for 40 min are similar to that for 80 min (data not shown).

Defect Imaging



Threading dislocations in GaN

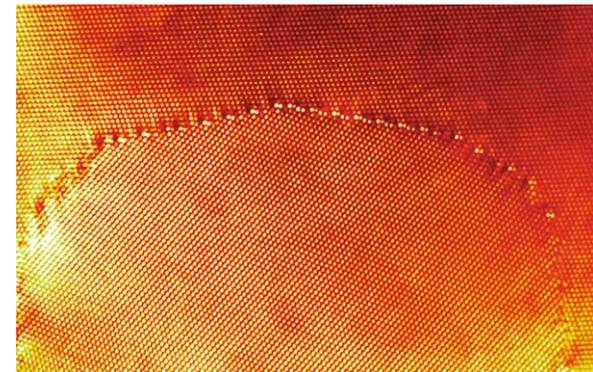
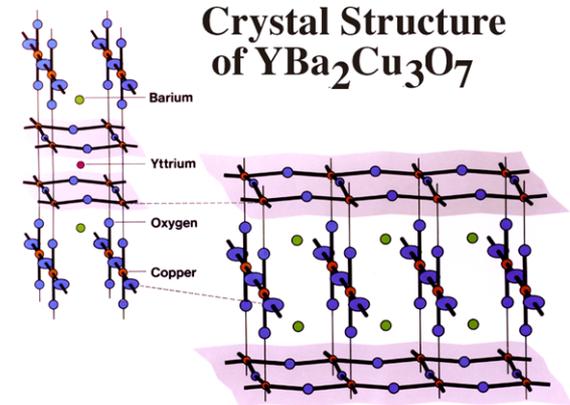
Strain contrast imaging of defects
- allows determination of burger's vector

Density (/cm ²)	10 ¹⁴	10 ¹²	10 ⁴
Technique	XRD rocking curve	TEM	X-ray Tomography

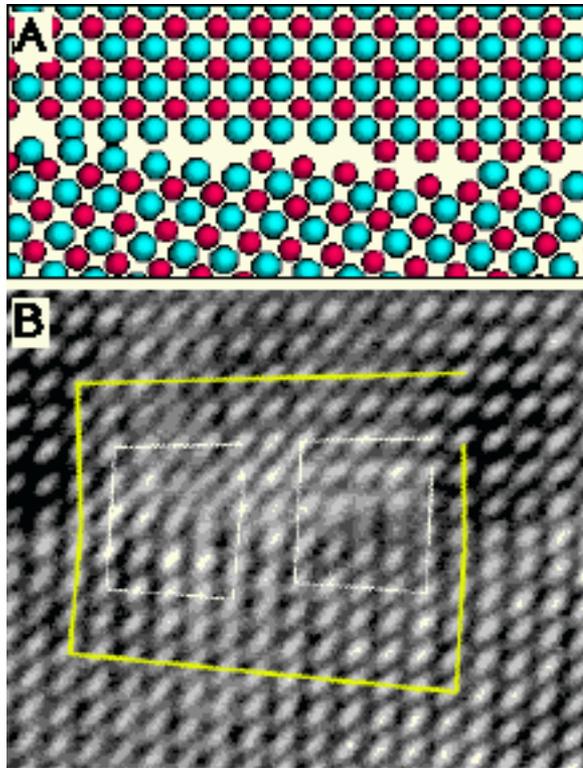
Pop. density in Chicago?

High T_c Superconductors

- Neutron Diffraction -
 - crystal structure
- X-Ray Photoemission
 - understand pairing mechanism?
- Transmission Electron Microscopy
 - Thin film structure and defects
 - Grain Boundaries
 - Understand J_c



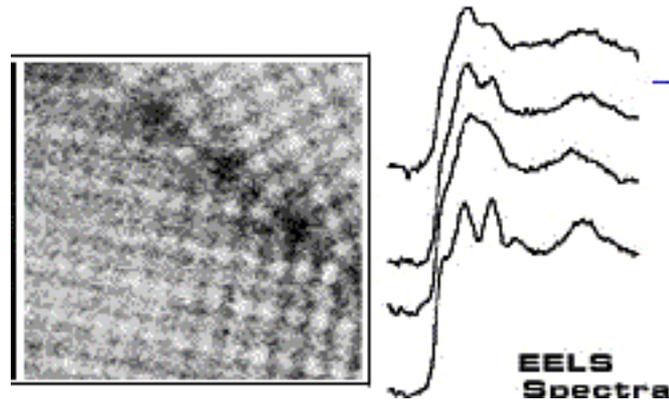
Interface Science



Atomic structure
of grain boundary in zirconia

Merkle ANL

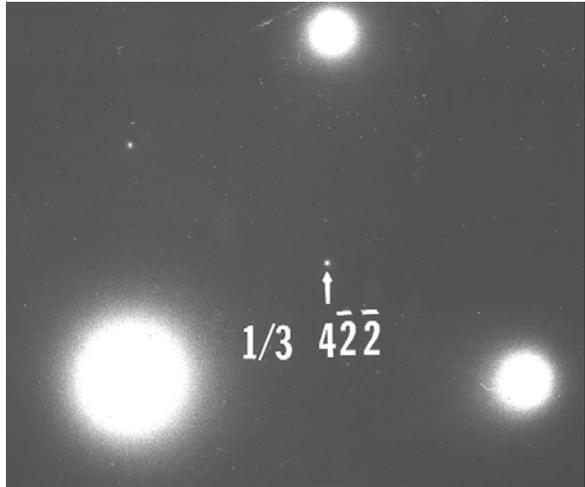
“Atomic Scale” Spectroscopy



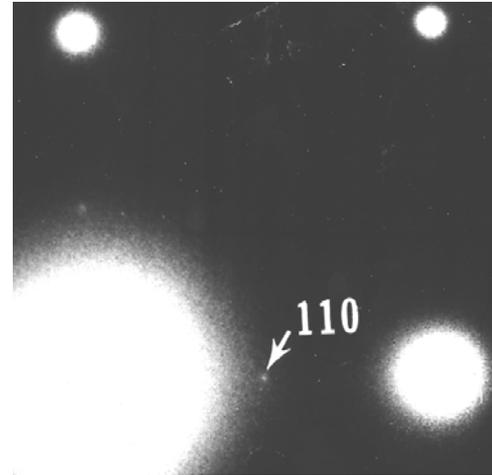
Browning, U. Illinois Chicago

near-edge structure of oxygen near a zirconia boundary

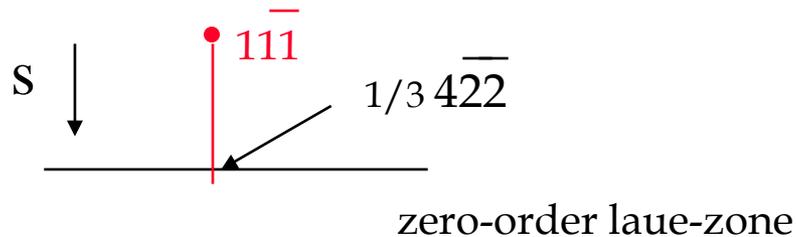
Surface/Interface Roughness



Silicon (111)



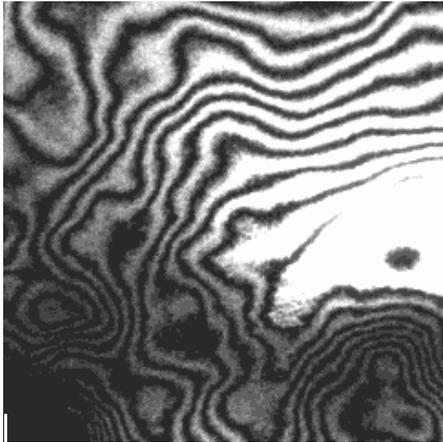
Silicon (100)



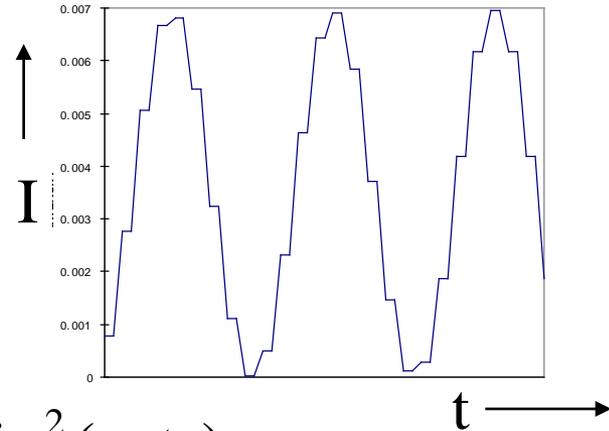
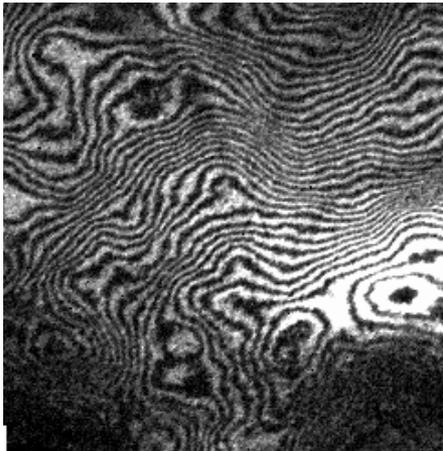
Crystal Truncation Rods

Imaging Roughness

$s=0.02\text{\AA}^{-1}$

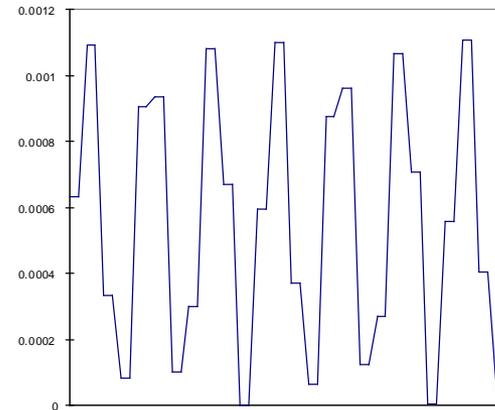


$s=0.05\text{\AA}^{-1}$



$$I = \frac{1}{s^2 \xi_g^2} \sin^2(\pi t s)$$

x10

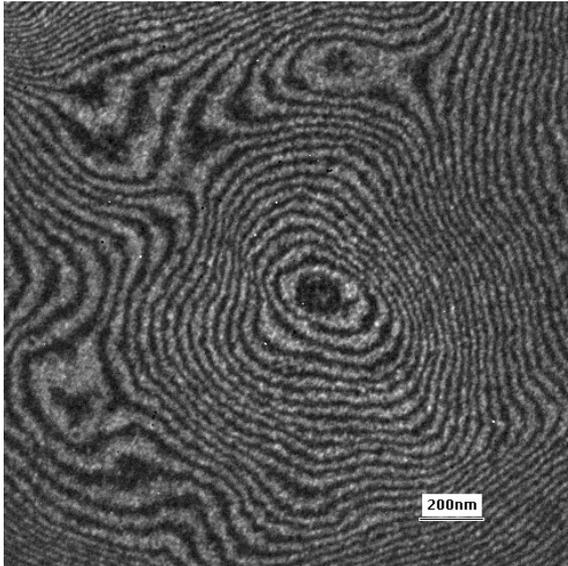
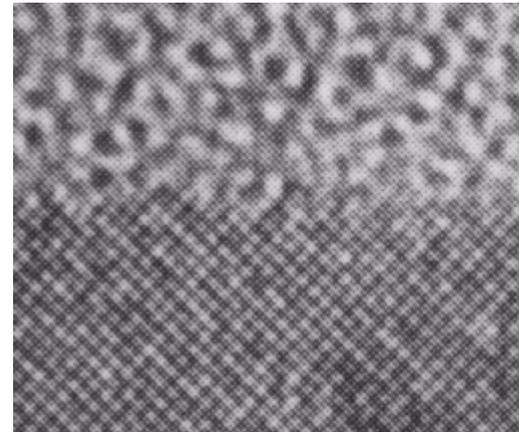


“diffraction contrast” dark field imaging

Transmission Electron Microscopy and Roughness

- familiar in cross-section

but limited by projection,
and sampling

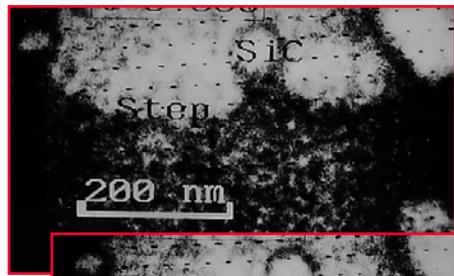


Our method uses plan-view imaging
limited to specially prepared
samples

Earlier work on dynamics of UHV oxidation/etching

SiO formation = etching

SiO₂ formation = oxide growth

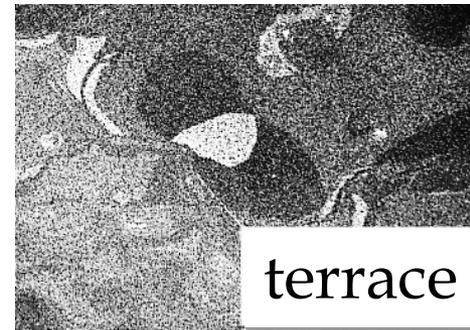


10 mins

time

0.26s

step flow



terrace attack

Ross, Gibson and Twisten, Surf. Sci. **310**, 243 (1994)

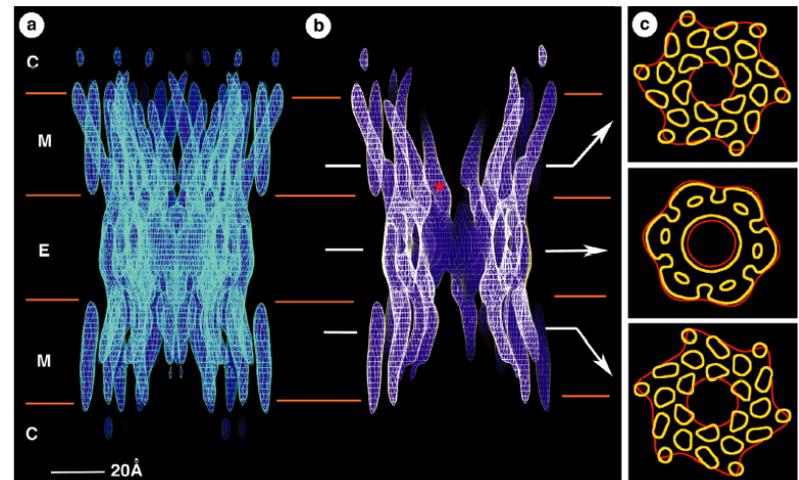
Structural Biology

Phasing reflections for large structures

Three-Dimensional Structure of a Recombinant Gap Junction Membrane Channel

Vinzenz M. Unger,^{1*} Nalin M. Kumar,¹ Norton B. Gilula,¹
Mark Yeager^{1,2,†}

Gap junction membrane channels mediate electrical and metabolic coupling between adjacent cells. The structure of a recombinant cardiac gap junction channel was determined by electron crystallography at resolutions of 7.5 angstroms in the membrane plane and 21 angstroms in the vertical direction. The dodecameric channel was formed by the end-to-end docking of two hexamers, each of which displayed 24 rods of density in the membrane interior, which is consistent with an α -helical conformation for the four transmembrane domains of each connexin subunit. The transmembrane α -helical rods contrasted with the double-layered appearance of the extracellular domains. Although not indicative for a particular type of secondary structure, the protein density that formed the extracellular vestibule provided a tight seal to exclude the exchange of substances with the extracellular milieu.

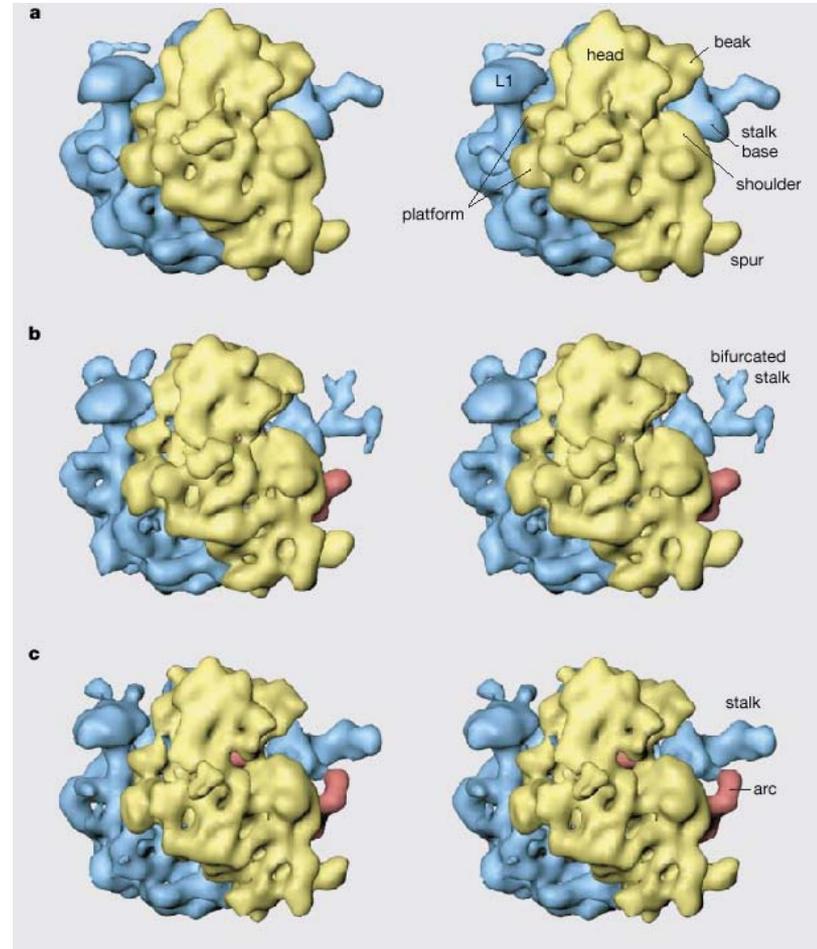


A ratchet-like inter-subunit reorganization of the ribosome during translocation

Joachim Frank^{*†‡} & Rajendra Kumar Agrawal^{†‡}

^{*} Howard Hughes Medical Institute, [†] Health Research Incorporated at the Wadsworth Center, and [‡] Department of Biomedical Sciences, State University of New York at Albany, Empire State Plaza, PO Box 509, Albany, New York 12201-0509, USA

The ribosome is a macromolecular assembly that is responsible for protein biosynthesis following genetic instructions in all organisms. It is composed of two unequal subunits: the smaller subunit binds messenger RNA and the anticodon end of transfer RNAs, and helps to decode the mRNA; and the larger subunit interacts with the amino-acid-carrying end of tRNAs and catalyses the formation of the peptide bonds. After peptide-bond formation, elongation factor G (EF-G) binds to the ribosome, triggering the translocation of peptidyl-tRNA from its aminoacyl site to the peptidyl site, and movement of mRNA by one codon¹. Here we analyse three-dimensional cryo-electron microscopy maps of the *Escherichia coli* 70S ribosome in various functional states, and show that both EF-G binding and subsequent GTP



x-ray structure this year depended on 7.5 Å e-structure

Nanoscience

Nanomechanics of Individual Carbon Nanotubes from Pyrolytically Grown Arrays

Ruiping Gao,^{1,4} Zhong L. Wang,^{1,*} Zhigang Bai,¹ Walter A. de Heer,² Liming Dai,³ and Mei Gao³

¹School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0245

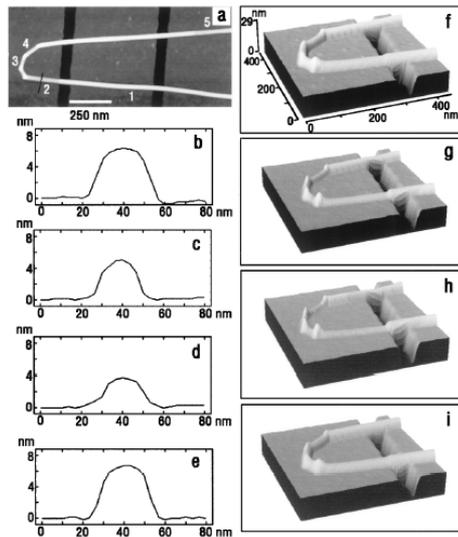


FIG. 1. Deformability of a MWCNT deposited on a patterned silicon wafer as visualized with tapping-mode AFM operated far below mechanical resonance of a cantilever at different set points. The height in this and all subsequent images was coded in gray scale, with darker tones corresponding to lower features.

AFM - *Yu et al.*
PRL 85, 1456, (2000)

shear modulus

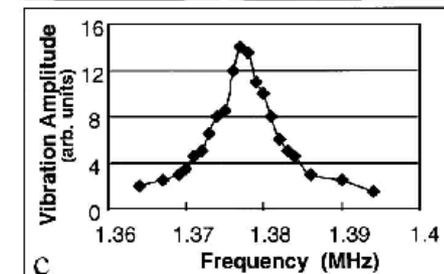
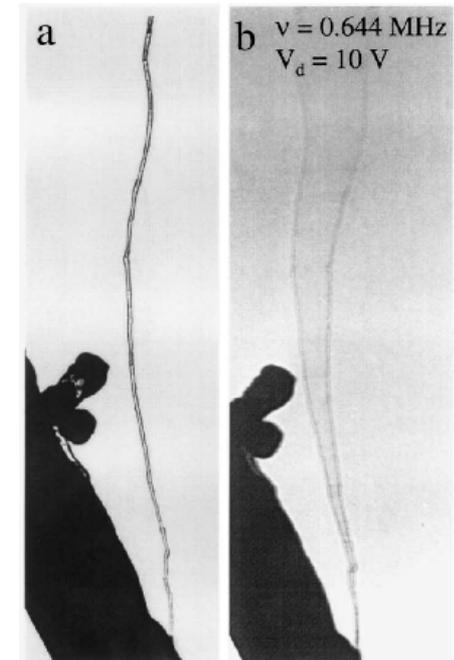
$$\nu_i = \frac{\beta_i^2}{8\pi} \frac{1}{L^2} \sqrt{\frac{(D^2 + D_1^2)E_b}{\rho}},$$

$E \sim 30 \text{ GPa}$

without defects

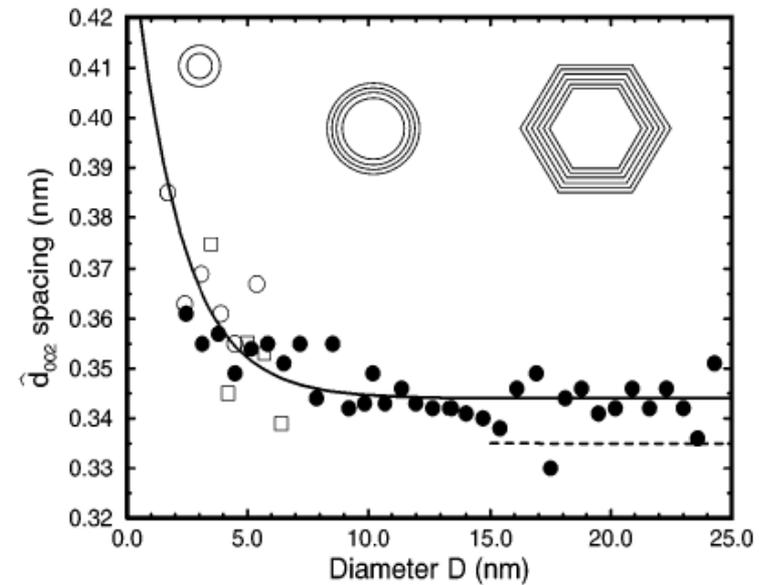
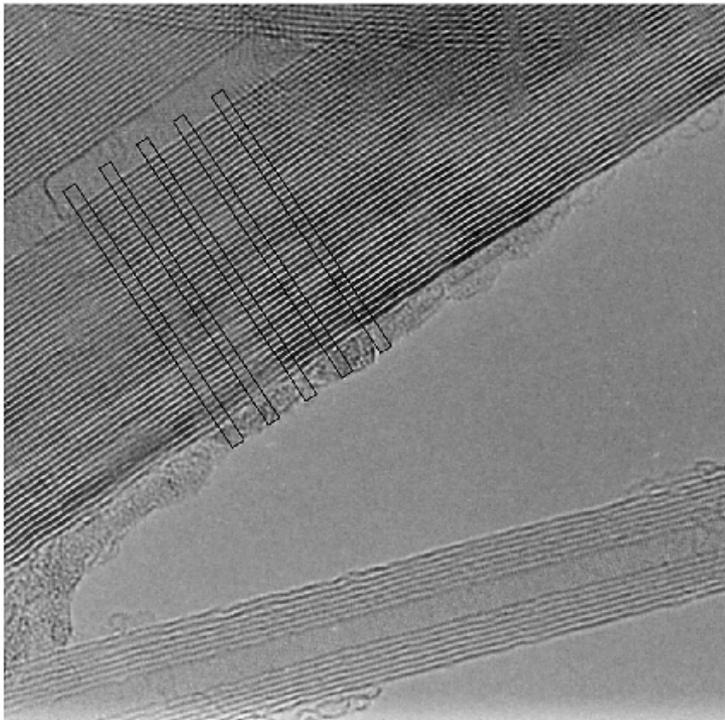
$E \sim 3 \text{ GPa}$

with defects



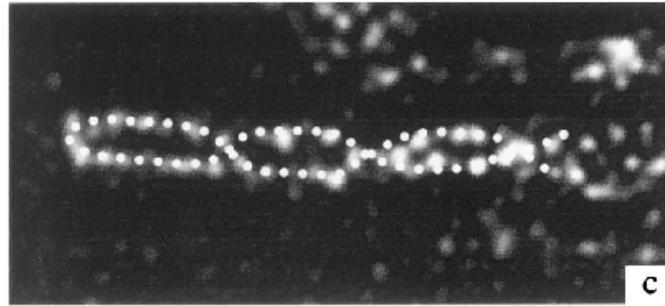
Size Effects in Carbon Nanotubes

C.-H. Kiang,¹ M. Endo,² P. M. Ajayan,³ G. Dresselhaus,⁴ and M. S. Dresselhaus⁵



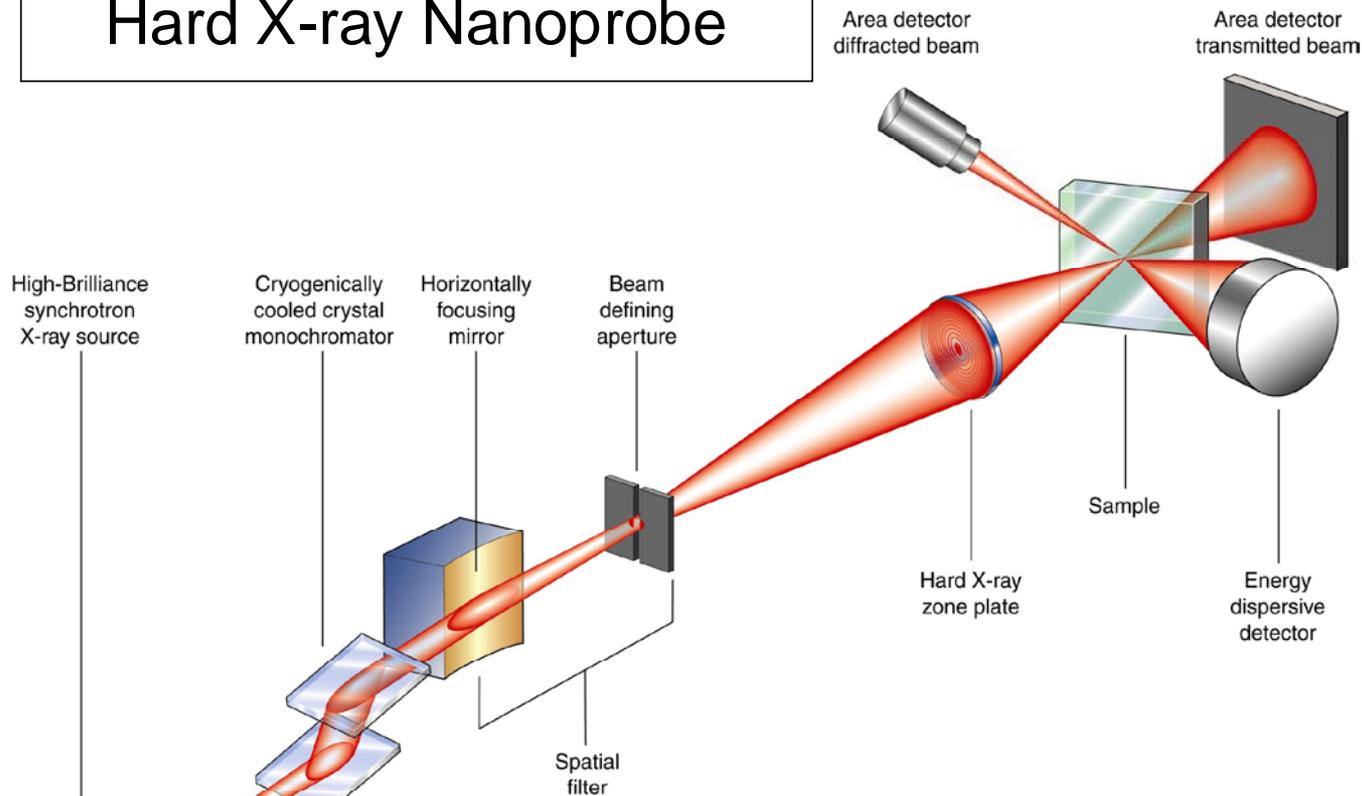
helicity plays a role in properties/structure

Applications of Z Contrast



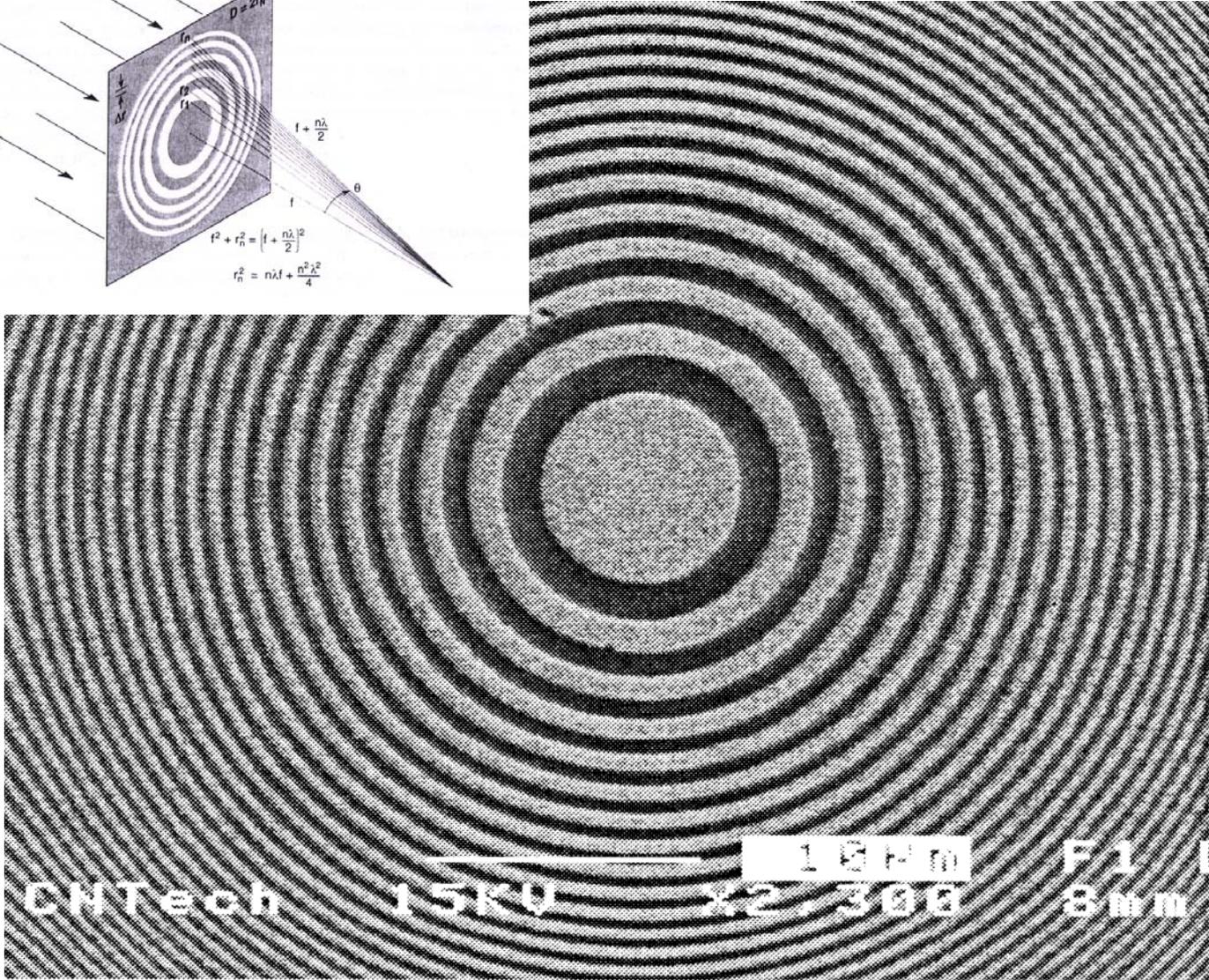
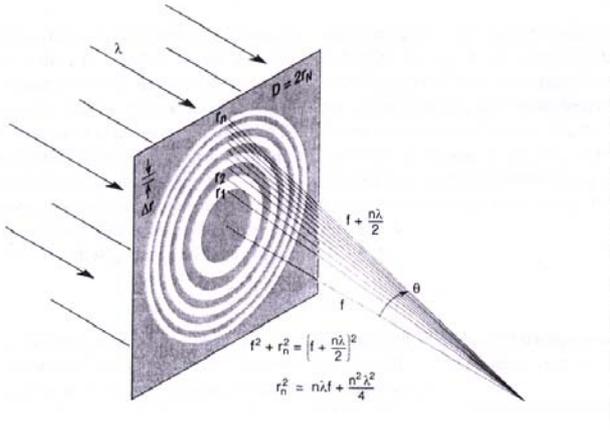
Iodine atoms in 1nm diameter C-SWNT
Fan. et al. PRL 84, 4621 (2000)

Hard X-ray Nanoprobe



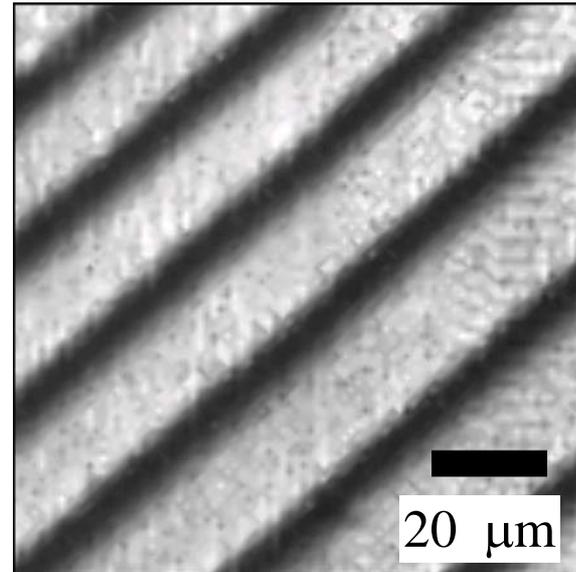
- ❖ **Unique, versatile instrument to study individual nanostructures (30 nm spatial resolution)**
- ❖ **Quantitative atomic-scale structure, strain, orientation imaging**
- ❖ **Sensitive trace element and chemical state analysis**
- ❖ **Ability to penetrate overlayers, environments, fields**

Zone Plate

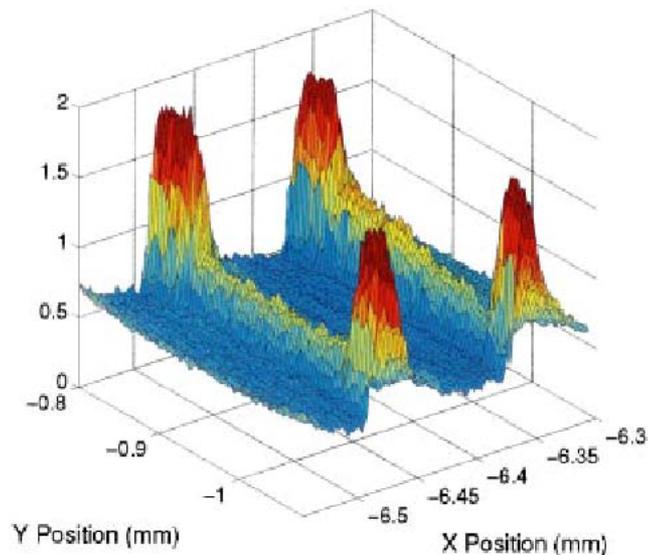


X-ray Microprobe Experiments

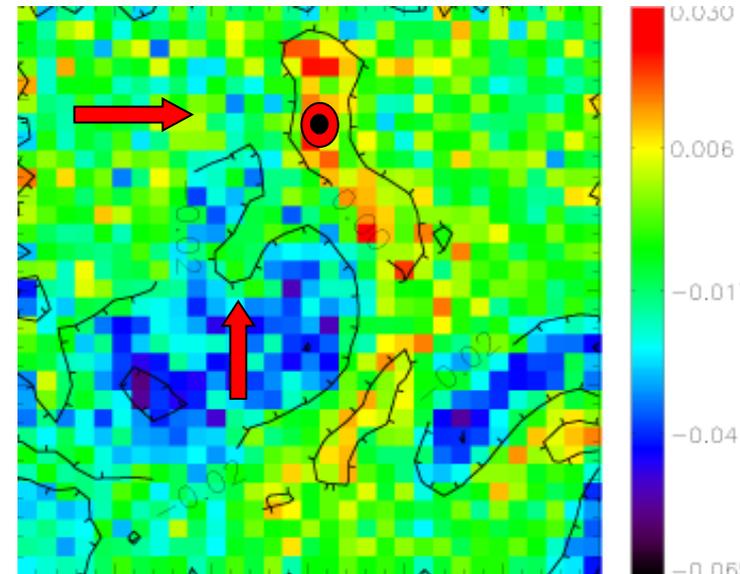
Nanometer-scale
physics in ferroelectrics
(P. Evans, Lucent)



Magnetization in
 HoFe_2
J. Pollmann, *et al.*,
Rev. Sci. Instrum. 71
2386 (2000).



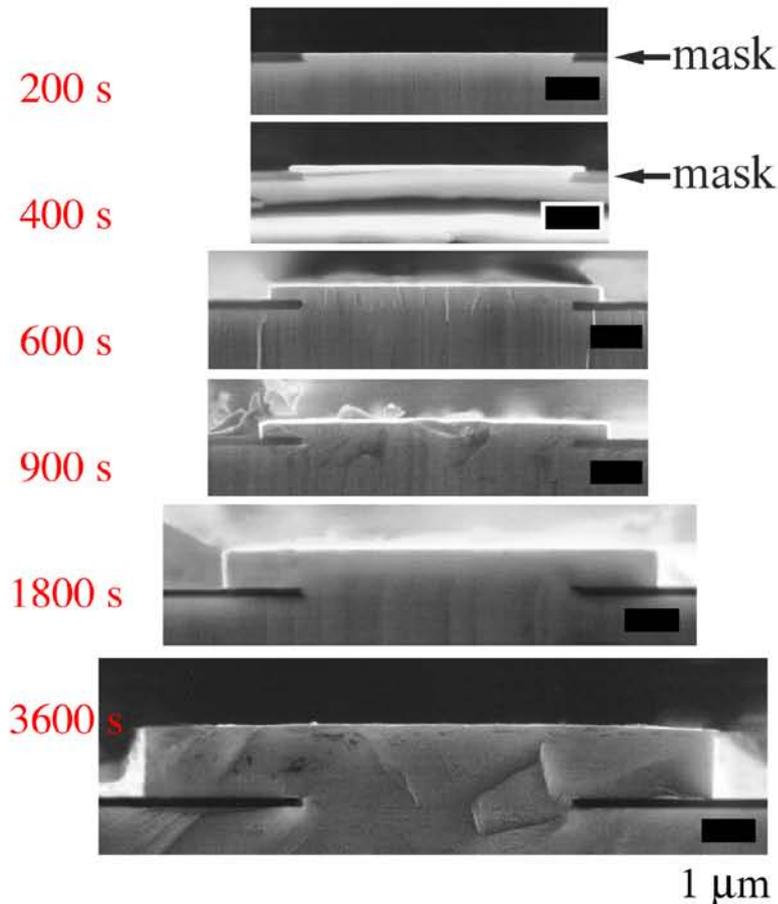
Stress under
metallization on Si
(100)
P.-C. Wang, *et al.*,
Appl. Phys. Lett. 76
3726 (2000).



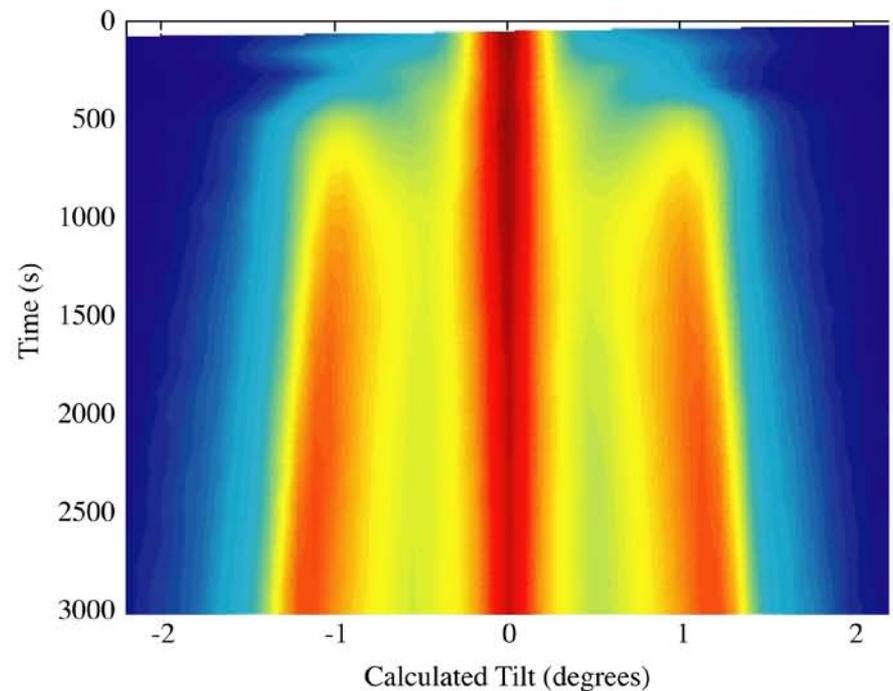
Real-Time X-ray Characterization of Patterned Growth

P. Fini *et al.*, *APL* **76**, 3893 (2000)

Growth morphology (ex-situ SEM):



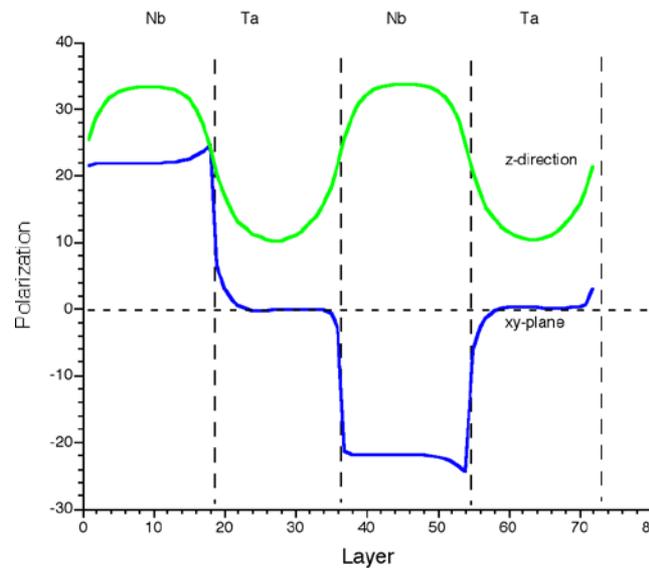
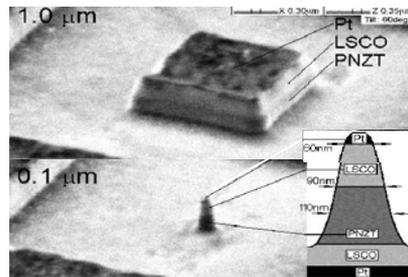
In-situ X-ray measurement of wing tilt during growth:



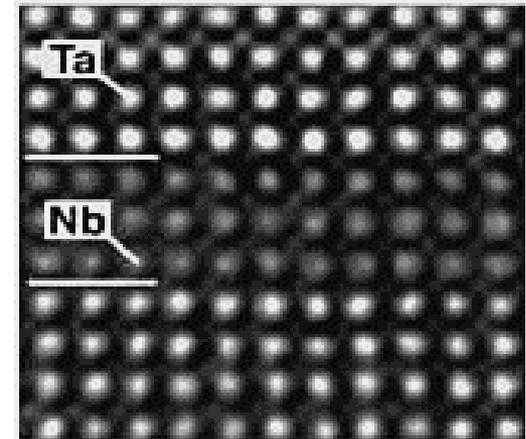
Wing tilt occurs at outset of overgrowth,
not during cooling

Nanoprobe diffraction studies of Nanopatterning - ETCHING

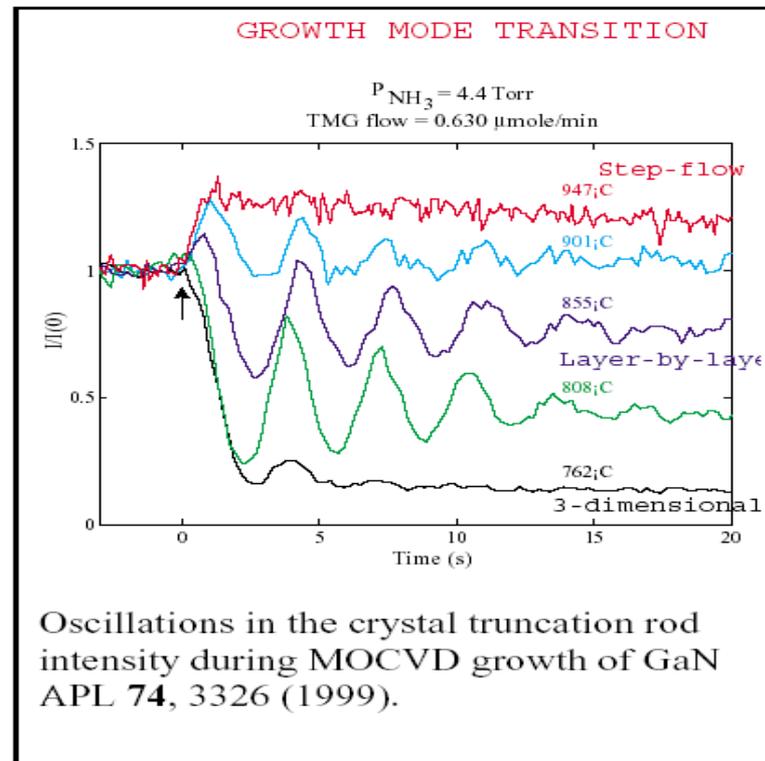
- Microfocused beam will allow illumination of individual nanostructures.
- Need to understand subtractive processes as well as additive (growth)
- Novel materials will be investigated (e.g., multicomponent oxides).



hybrid
structures

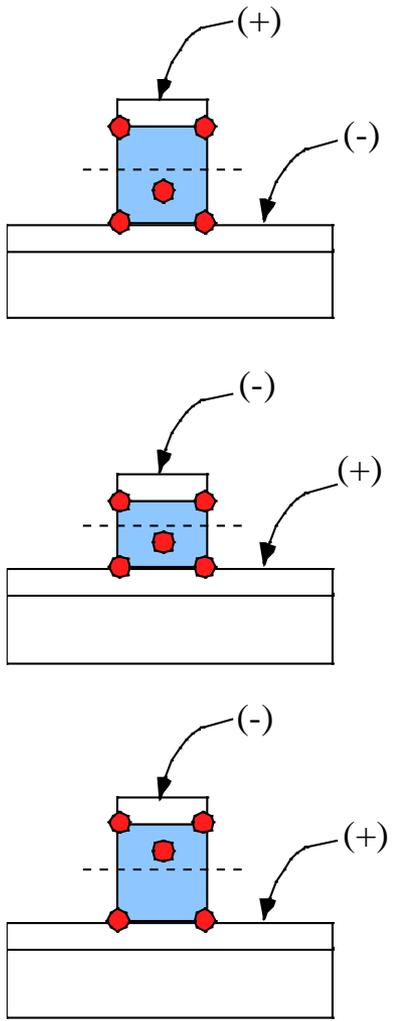
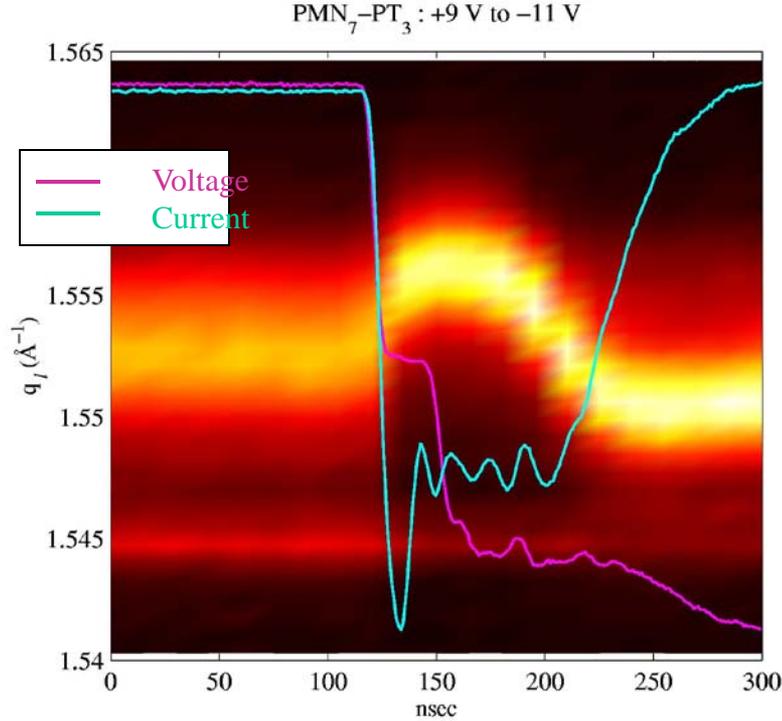


Studies of Growth and Etching



Time-Resolved Studies of Ferroelectric Switching

- Lattice parameter during switching has been measured with 17 nsec time resolution.
- Two-step response to voltage: prompt piezoresponse followed by switching on ~ 100 nsec time scale.

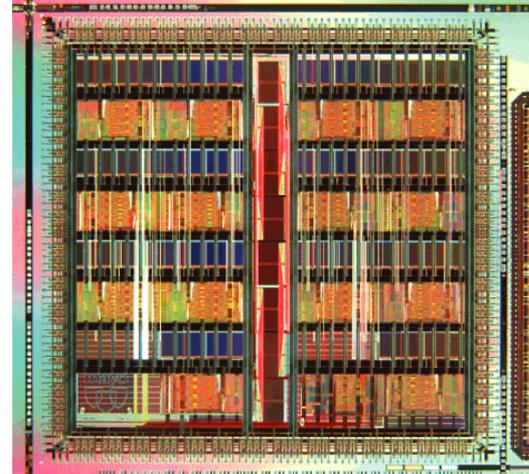


Measurement of Strain in Al-Cu Interconnect Lines

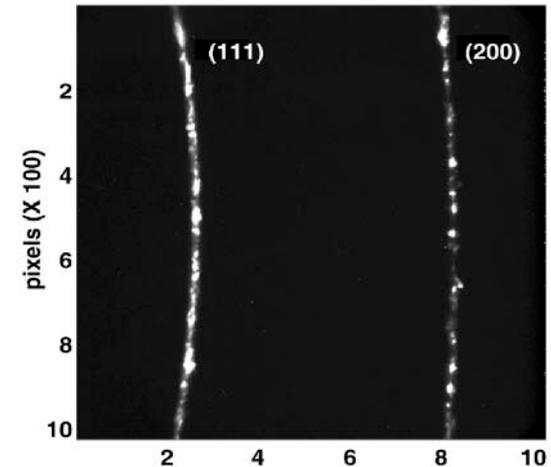
Using X-ray Microdiffraction

- Reliability of integrated circuit Al-Cu interconnects in electronics impacted by electromigration and mechanical stress.
- X-ray microdiffraction from interconnects reveals origin and details of microscopic stress.
- Can lead to increasingly reliable devices (computers, etc.) even as they become more complex.

H. Solak et al., J. Appl. Phys 86, 884 (1999).

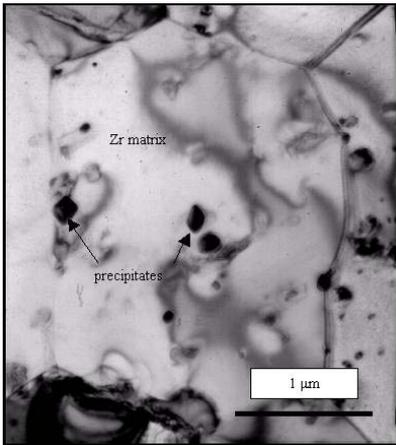


Fast Fourier transform integrated circuit (Special Purpose Processor Development Group, Mayo Clinic)



Microdiffraction pattern from a thick-blanket Al-Cu film.

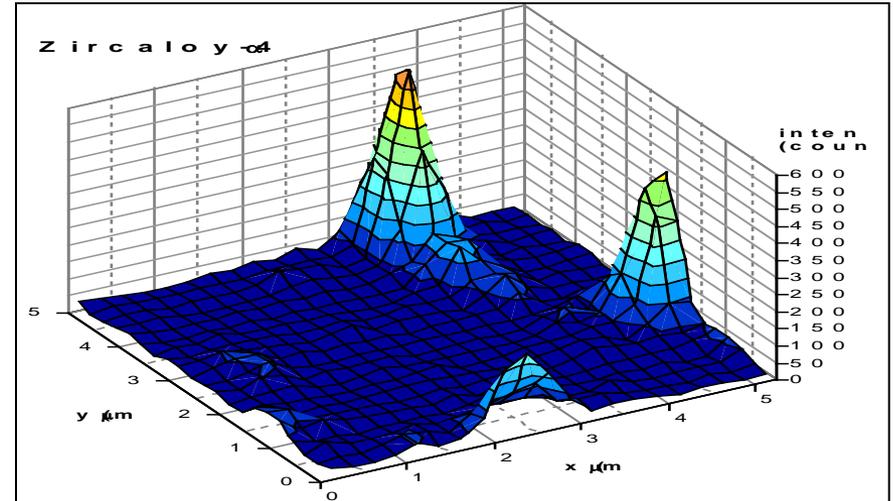
X-Ray Fluorescence Microscopy - complementary to Transmission Electron Microscopy



Transmission
Electron
Microscopy of
Zircalloy grain

	Zircaloy-4 (weight %)	ZRLO (weight %)
Fe	0.24	0.11
Cr	0.11	0.001
Sn	1.64	1.08
Ni	0.0034	<0.001
Nb	-	1.23
O	0.112	0.145
Cu	0.002	0.002
Hf	<0.004	<0.004

Measured
overall
compositions



Examining compositions in metal alloy precipitates

X-Ray fluorescence imaging of single bacterial cells

Kemner et al.

Science 306, 686 (2004).

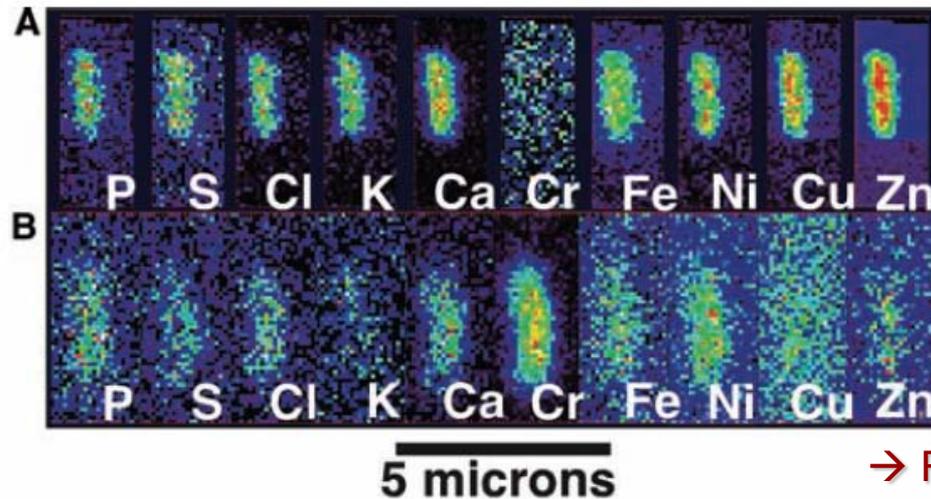
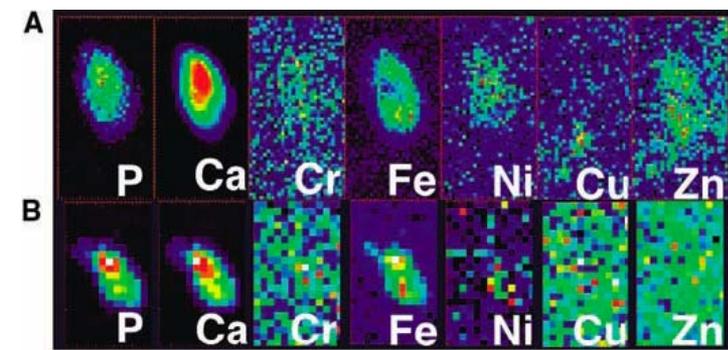
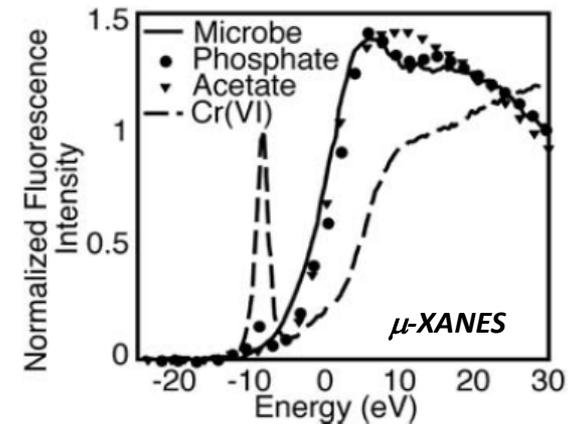


Fig. 1. False-color micro-XRF maps of qualitative spatial distributions and concentration gradients of elements in and around planktonic *P. fluorescens* microbes harvested before (A) and after (B) exposure to potassium dichromate [Cr(VI)] solution (1000 ppm) for 6 hours.

→ Redox states Cr(III)



A: planktonic bacterium cell before exposure to Cr

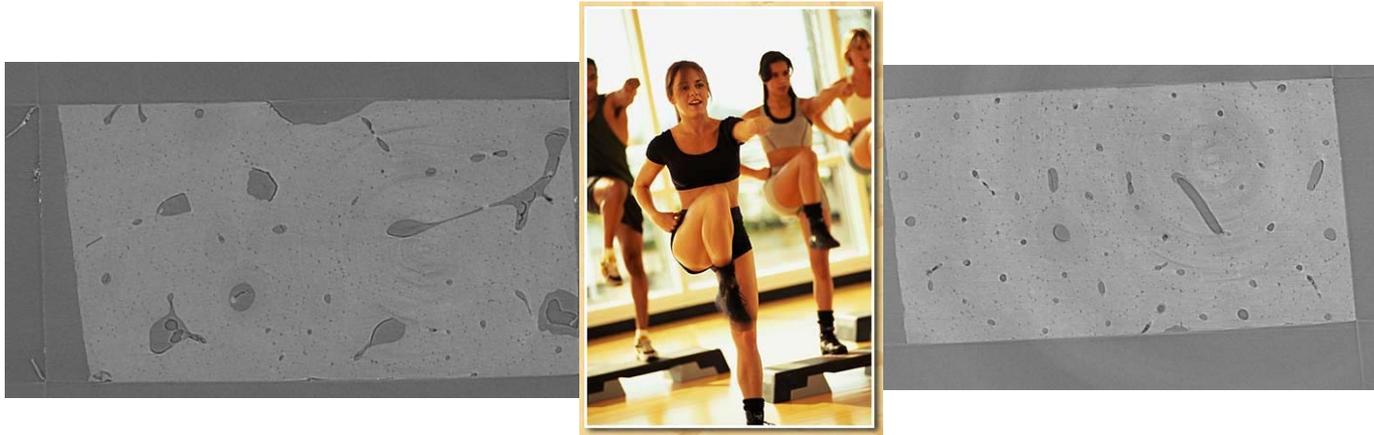
B: planktonic cell after exposure to 1000 ppm Cr(VI)

Isolated planktonic cell accumulates Cr, loses 'typical' cellular elements, and stains 'dead'

Surface adhered cell does not take up Cr, shows no change in elemental content, and remains alive

Attachment of prokaryotic cells to surfaces modulates elemental content and response to environmental challenges

Advanced X-ray imaging reveals hierarchical structure

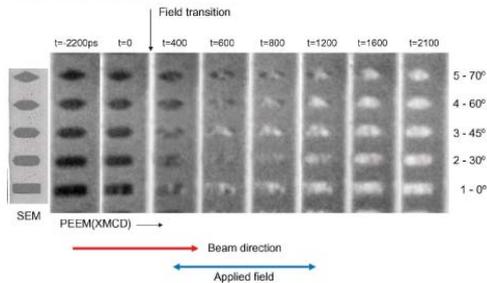


The effect of different exercise regimens on bone – S. Stock, NWU 2-BM

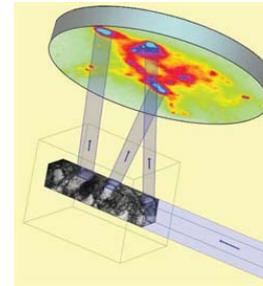


Big bugs, Socha et al., PNAS **104**, 13198, (2007)

Magnetization Reversal

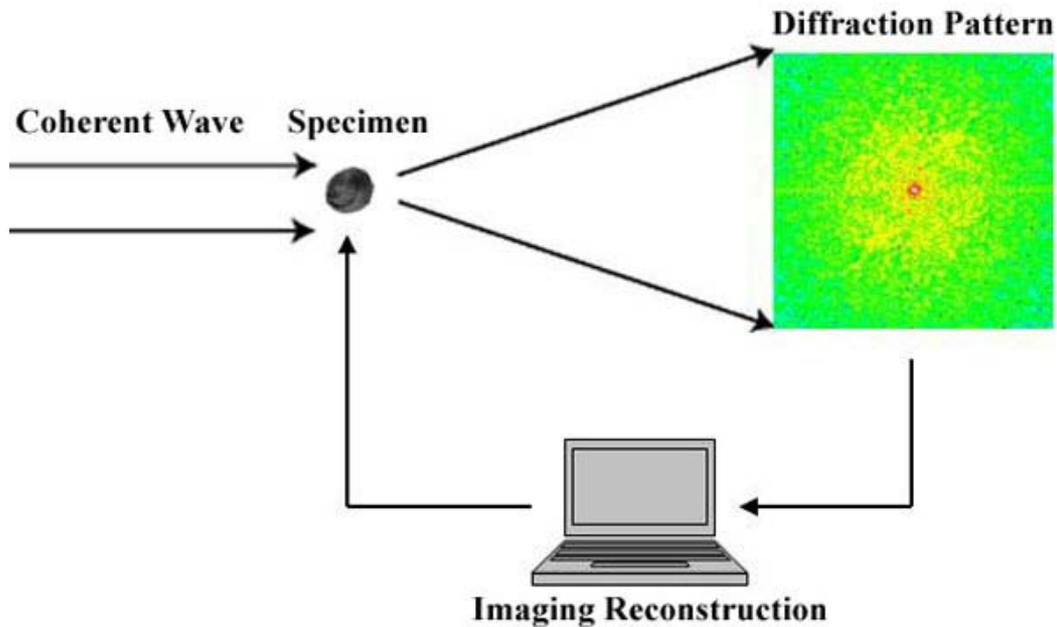


Magnetic instability regions in patterned structures
Han et al., Phys. Rev. Lett. **98**, 147202 (2007)



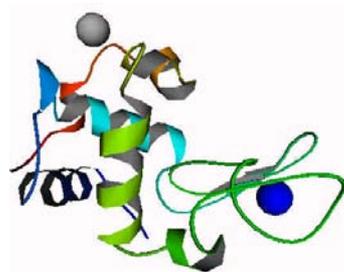
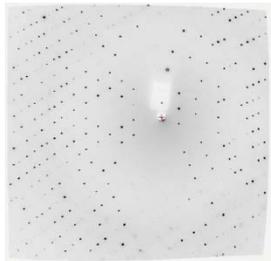
Dislocation walls are lumpy,
Levine et al., Nat. Mater. **5**, 619 (2006)

Coherent X-Ray Diffraction

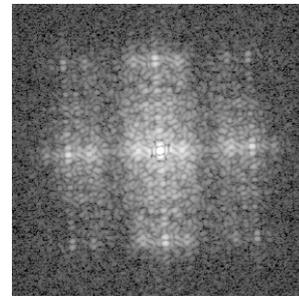


- Coherent diffraction imaging is much like crystallography but applied to **noncrystalline** materials
- First proposed by David Sayre in 1980, and first experimental demonstration by John Miao et al in 1999 using soft x-rays
- Requires a **fully coherent** x-ray beam

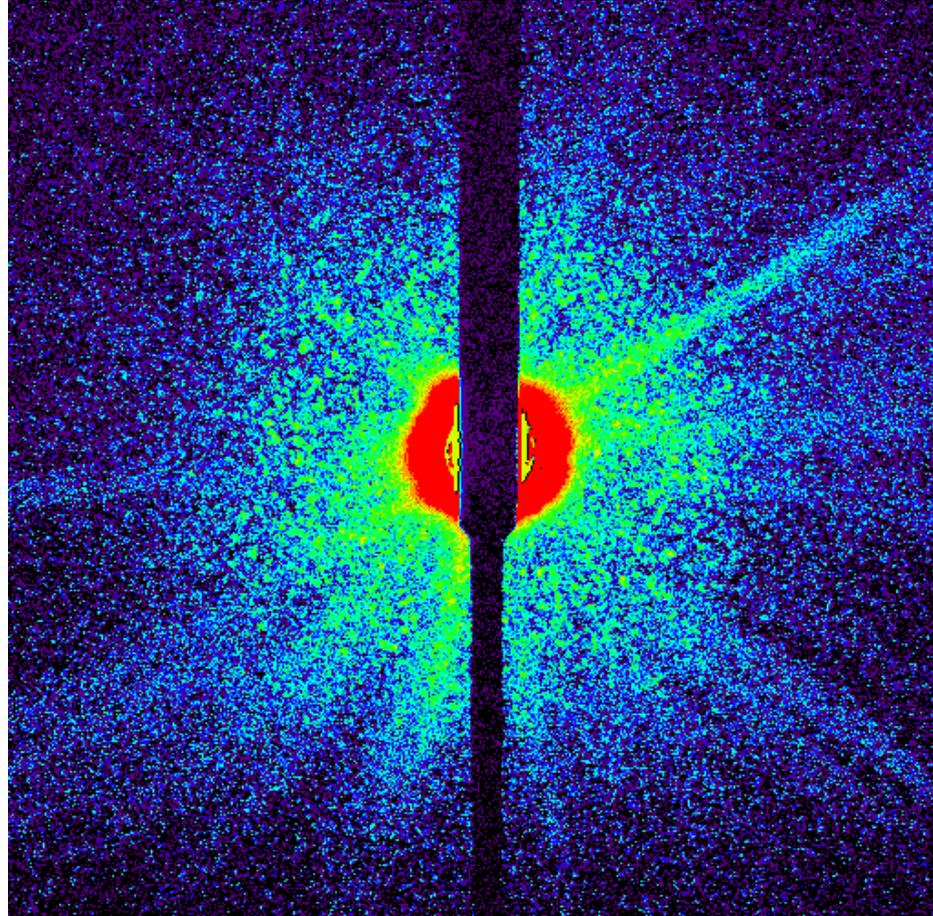
Analogous to crystallography



Miao et al. (1999)



Soft x-ray speckle of static aerogels

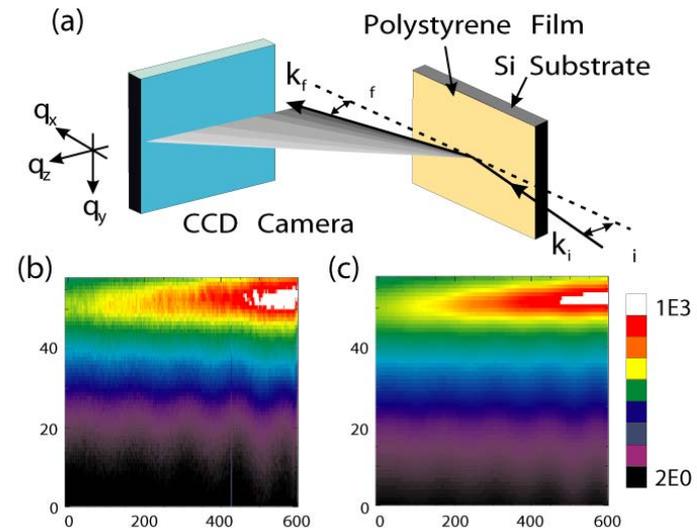


Speckle pattern produced by aerogel sample (0.014 g/cm^3). Pattern was recorded with 1.83 keV x-rays using a 5- μm pinhole source and monochromatic ($E/\Delta E \sim 1000$) beam.

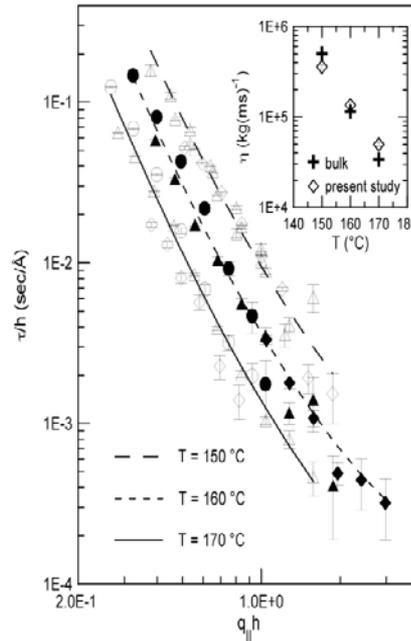
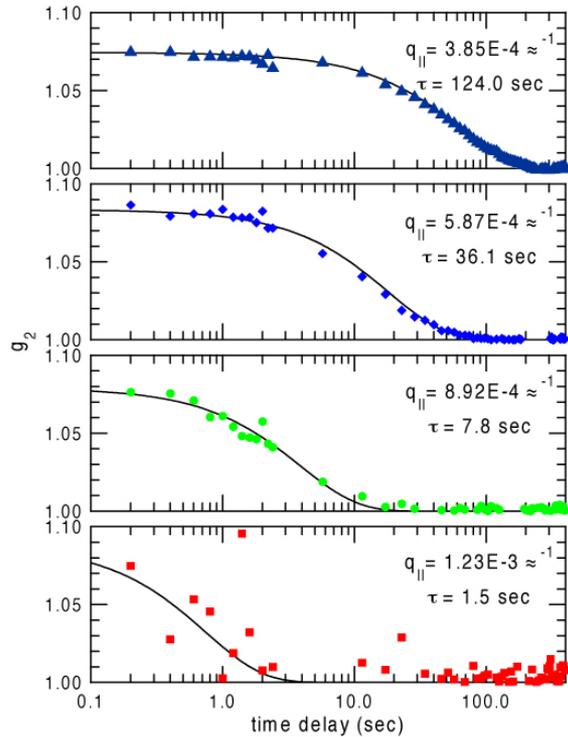
Ian McNulty, APS

Surface dynamics of polymer films

- Motivated by reports that T_g at the surface of polymer films is reduced Kim, Ruehm, Lurio, Basu, Lal, Mochrie, and Sinha used XPCS at 8-ID to characterize the relaxation of thermally excited height fluctuations on the surface of polystyrene(PS) films to investigate how the near-surface viscosity might differ from that of the bulk PS.



Surface Dynamics of Polymer Films

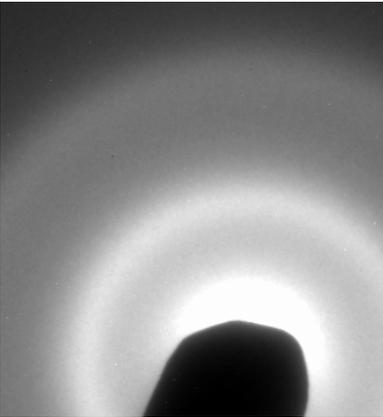
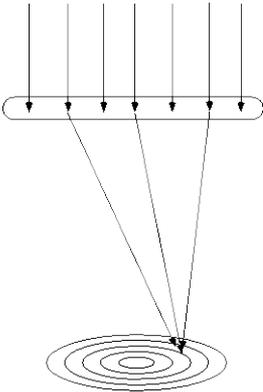


Intensity correlation of the reveals the characteristic relaxation times for capillary waves

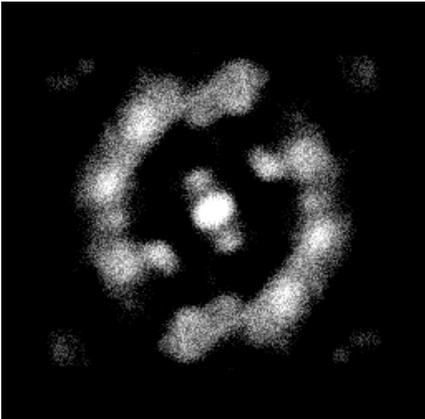
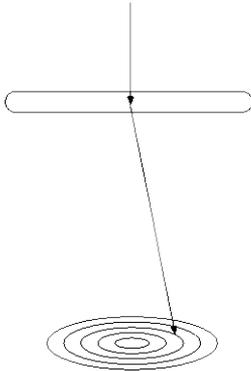
Shows no change in T_g near surface

Fluctuation (Electron) Microscopy

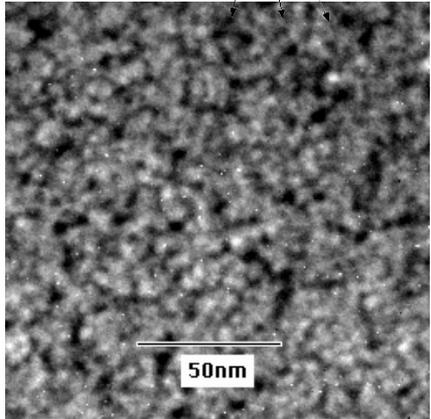
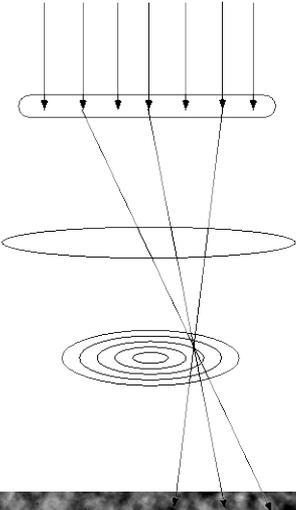
Diffraction



Microdiffraction
"Speckle Diffraction"

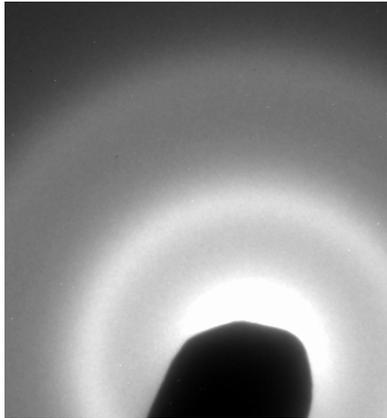


Speckle Imaging



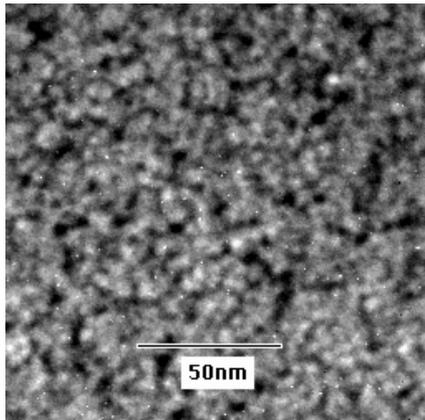
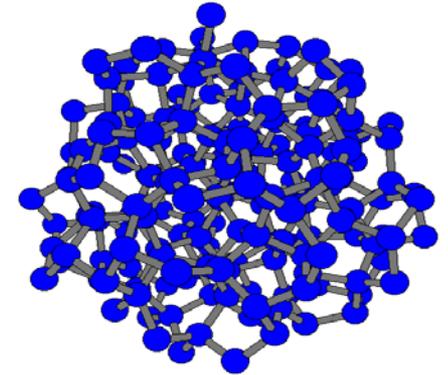
“coherent diffraction”

New structural information from glasses - Fluctuation Microscopy



Diffraction \Rightarrow Pair Correlation Function

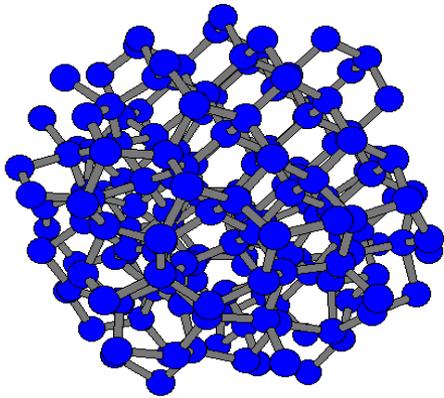
\Rightarrow short-range order



Imaging (speckle) \Rightarrow Pair-Pair Correlation
Function

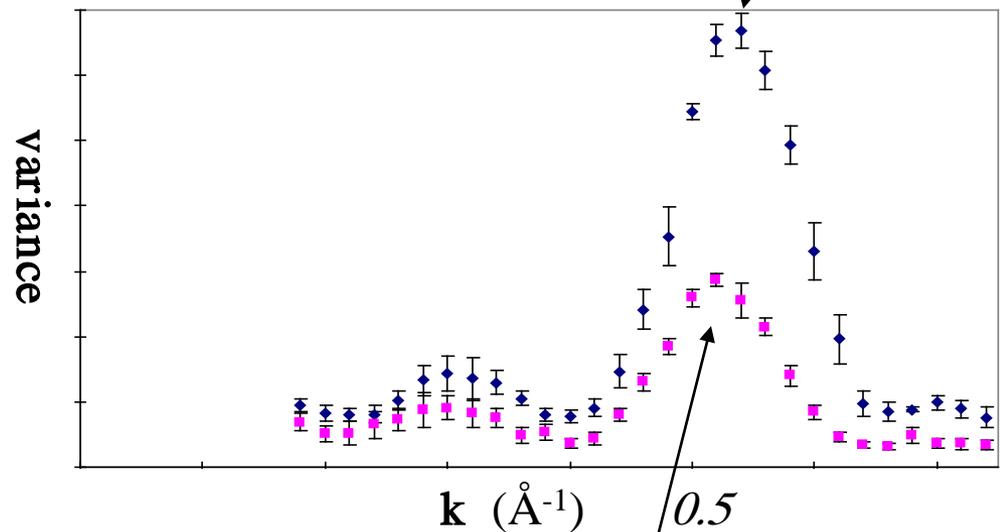
\Rightarrow medium-range order

Paracrystallinity in a-Si/Ge



Important effects on thermodynamic and physical properties - electrical stability, impurity diffusion

Medium-range order ($\sim 15\text{\AA}$) found in deposited amorphous semiconductors
- not seen by diffraction



Become more like random networks on annealing
or light soaking in a-Si(H)

Further Reading

- **“Electron Microscopy of Thin Crystals”**, Hirsch et. al. (Kreiger, New York 1977)
- **“Diffraction Physics”**, J.M. Cowley, (North Holland, Amsterdam 1981)
- **“Transmission Electron Microscopy”**, L. Reimer, (Springer-Verlag, Berlin 1984)
- **“Transmission Electron Microscopy: A Textbook for Materials Science”**, D.B. Williams and C.B. Carter, (Plenum, New York 1996)