U. S. – India Workshop on Nanotechnology

Education and Research for Nanotechnology

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This is a particularly exciting time because:

Materials at the nanometer scale have exciting and novel properties. To understand and control them, we must have the ability to characterize materials at or below that scale.

A revolution in electron beam characterization of materials is now under way due to mastery (Dellby, Krivanek, Haider, Rose - 1997) of the design and construction of electron optical devices (CEOS, NION).

ACKNOWLEDGEMENTS

- Collaborators:
  - Z. Yu, K.A. Mkhoyan, S.Maccagnano, O.K. Krivanek (NION), P.E. Batson, D.A. Muller, T.Krauss (Chemistry, Rochester), D. Shashkov, R. Benedict, D.N. Seidman, L.H. Yang *(LLNL)*
- Financial Support:
  - NSF, DOE, DOD, NYSTAR

Example of Quantum Effect in CdSe--- Size Determines Color

Size dependent electronic and optical properties

Exciton Bohr Radius of CdSe
5.4 nm

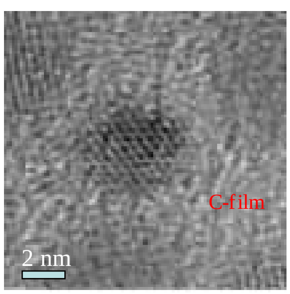
Strong quantum confinement – hence ‘quantum dots’

Krauss Group

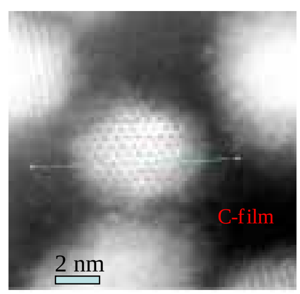
Diameter: 5.0 nm 3.5 nm 2.5 nm

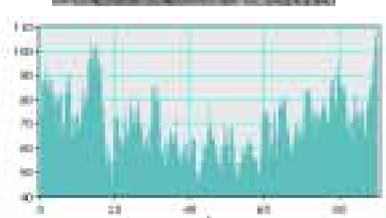
ADF-STEM - Z and thickness contrast

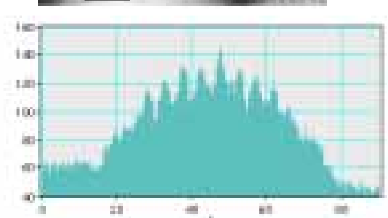
BF



ADF



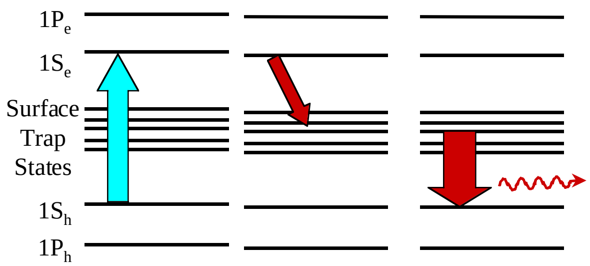


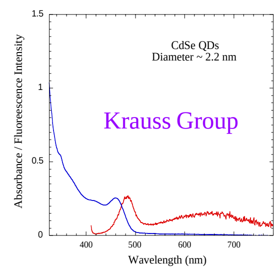


Core-shell CdSe/ZnS Quantum Dots

Surface Quality is Critical: 4-nm dot has ~ 1/3 atoms on the surface

Poor Quality Dot → Properties of dot determined by surface



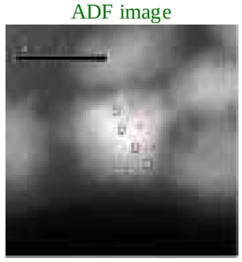


Surface passivation increases quantum yield (QY) by > 10 times to 55%. But it is still not perfect, only 50 % QY. Surface-related fluctuations in intensity and spectra were observed*.
*M. Nirmal et. al., *Nature*, **383**, 802 (1996).

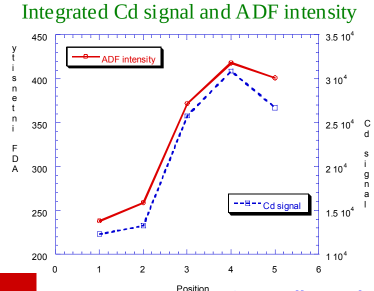
Incomplete or **ill-formed** shell?

EELS spectra of Cd M-edge from a CdSe/ZnS QD

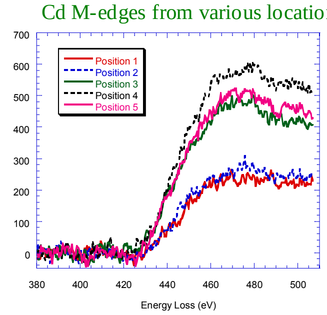
ADF image



Integrated Cd signal and ADF intensity



Cd M-edges from various locations

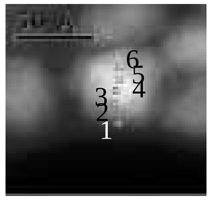


Localized EELS spectra from sub-nm area were taken from various locations of the QD. ADF intensities from these locations were recorded simultaneously with the EELS spectra.

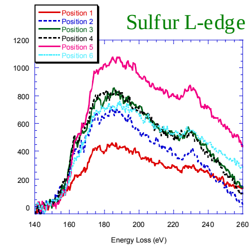
Cd signal follows the ADF intensities.

EELS spectra of sulfur L-edge from various positions

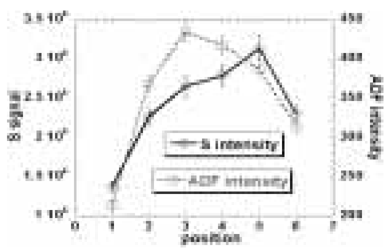
ADF image



Sulfur L-edge



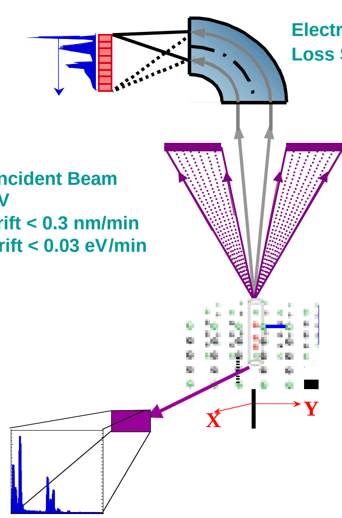
Integrated sulfur signal and ADF intensity



S signal does not follow the ADF intensities taken simultaneously with the EELS spectra.

S signal is higher close to the top edge (#5) than the center of the QD (# 3 and #4) but lower close to the bottom edge (# 2).

UHV-STEM: Operational Detail



(P)EELS and Bright Field Detectors

Electron Energy Loss Spectrometer

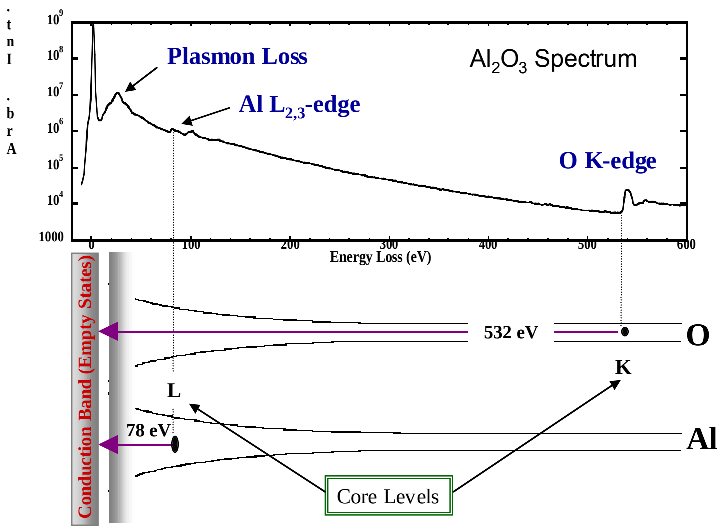
Annular Dark Field detector ~0.2 nm res.

100 keV Incident Beam
ΔE = 0.7eV
Spatial Drift < 0.3 nm/min
Energy Drift < 0.03 eV/min

1 atom wide (2.1 Å) beam is scanned across the sample in the x-y plane to form a 2-D image

Windowless EDX (X-ray) Detector

Electron Energy-Loss Spectrum (EELS)



Core-edge EELS can be used as fingerprints to check the chemical distribution of a sample.

The STEM probe provides localized EELS with sub-nm spatial resolution.

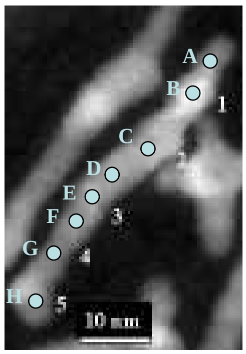
Core-Loss EELS

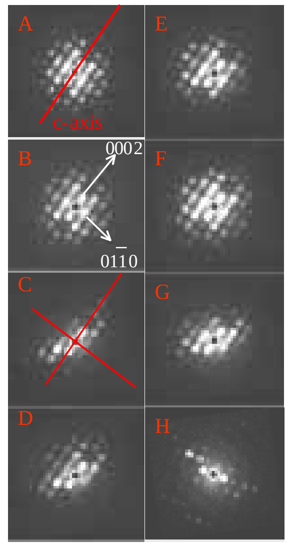
$$\frac{d^2\sigma(E,q)}{dEdq} = \frac{8\pi e^4}{\hbar^2 \upsilon^2}\frac{1}{q}\sum_{i,f}\left|\hat{\varepsilon}_q \cdot \langle f|\vec{r}|i\rangle\right|^2 \delta\left(E - E_f + E_i\right)$$

S $L_{2,3}$-edge in ZnS

• **Element Specific** ————	$\vert i\rangle$	$\vert 2p\rangle$
• **Dipole Selection Rules** ————	$\Delta l = \pm 1$	$\vert 3d\rangle$ ***for*** *l=1*
• **Site Specific** ————	$\{\vert i\rangle, \langle f\vert\}$	$\{\vert 2p\rangle, \langle 3d\vert\}$
• **Chemical Shift** ————	***Effect of Environment***	
• **Local** ————	***Defined by Probe Size***	

Nanodiffraction patterns from various positions on the QRs





All the nanodiffraction patterns suggest wurzite structure.

The intensity in the diffraction patterns changes suggesting the orientation of the QR relative to the electron beam changes along the rod.

The c-axis is roughly along the rod from “A” to “G”. At the foot a grain boundary exists.

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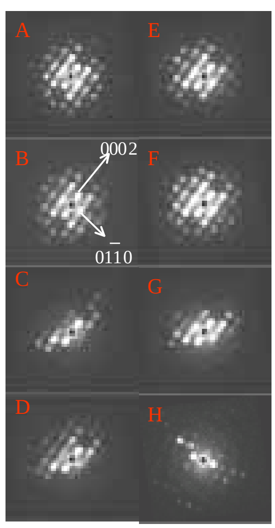
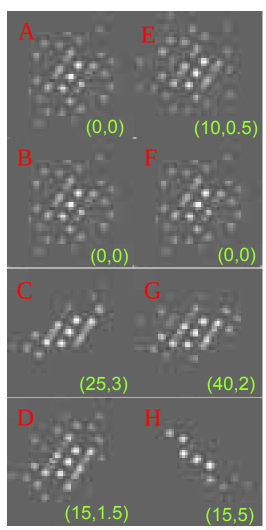
Matching nanodiffraction patterns

Experiment



Simulation



The simulated QR can be rotated about an arbitrary axis for an arbitrary angle and the resultant nanodiffraction pattern at each position can be simulated.

The index (x,y) on the lower right corner of each pattern means the QR is tilted y° off the zone axis about an axis x ° degrees away from the c-axis of the QR.

The error bar in x is 2° and the error bar in y is 0.2°.

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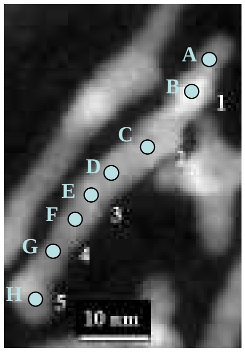
Topology of the QR

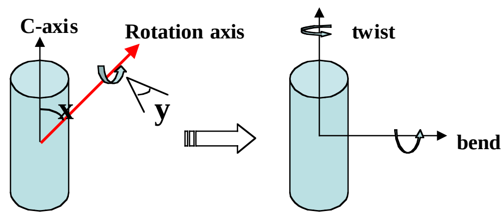


	A	B	C	D	E	F	G	H
Rotation angle y	0˚	0˚	3˚	1.5˚	0.5˚	0˚	2˚	5˚
Rotation axis x	0˚	0˚	25˚	15˚	10˚	0˚	40˚	15˚
Distance (nm)	4	9	19	26	30	33	40	50

Characteristics of rotation:

Small angle (2-3º)

Randomness



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What might we want to know?

- Nature of the imperfections?
- Orientations
- Second phases
- Composition – and variation with position
- Strain distribution
- Electrical and mechanical properties
- Charge distributions – surface and bulk

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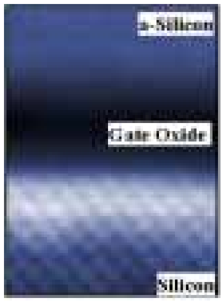
Si/SiO2 – a classic device problem



What is the electronic character of the thin gate oxide? And the interfaces?

What is the nature of the 'white line'? Strain, oxygen atoms in the silicon, rough interface?

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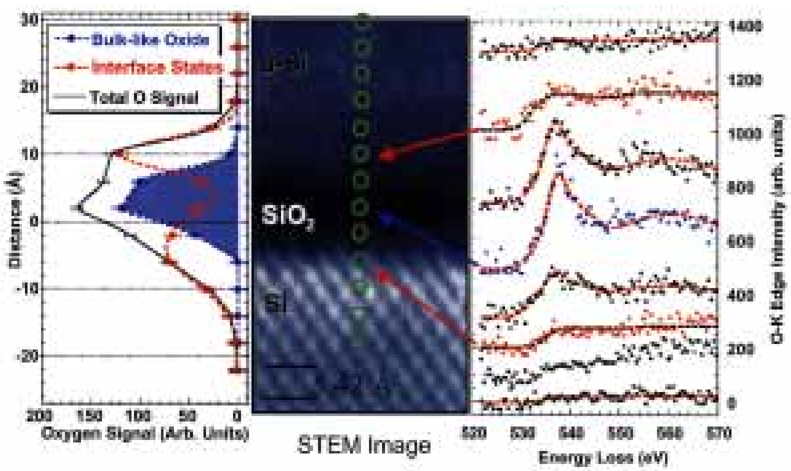
Bonding Information at Atomic Resolution



1.6 nm wide oxygen profile with 0.8 - 1 nm Bulk SiO_2

D. A. Muller *et al.*, Nature **399**, 759 (1999).

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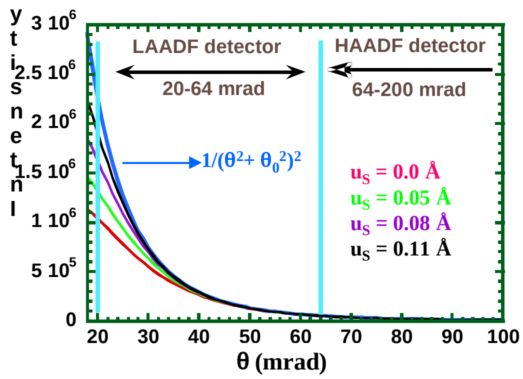
A simple model to study strain field

$$\sigma^S(\theta) = \frac{const}{(\theta^2 + \theta_0^2)^2}\left[1 - \exp(-2(M^T + M^S)\theta^2\right] \quad (1)$$

$M^T = 8\pi^2 u^{T^2} / \lambda^2$

$M^S = 8\pi^2 u^{S^2} / \lambda^2$

u^T= 0.078Å at T=300K
200 kV, λ =0.025Å, M^T=762.5



Strain-dependent scattering can be treated similarly to thermal diffuse scattering (TDS)[1,2,3].

Formula (1) for 200 kV electrons at various strain amplitude.

1 L. J. Allen and C. J. Rossouw, Physical Review B 42 (1990) 11644.
2 D. D. Perovic, C. J. Rossouw and A. Howie, Ultramicroscopy 52 (1993) 353.
3 G. Duscher et al., Characterization and Metrology for ULSI Technology(1998) 191.

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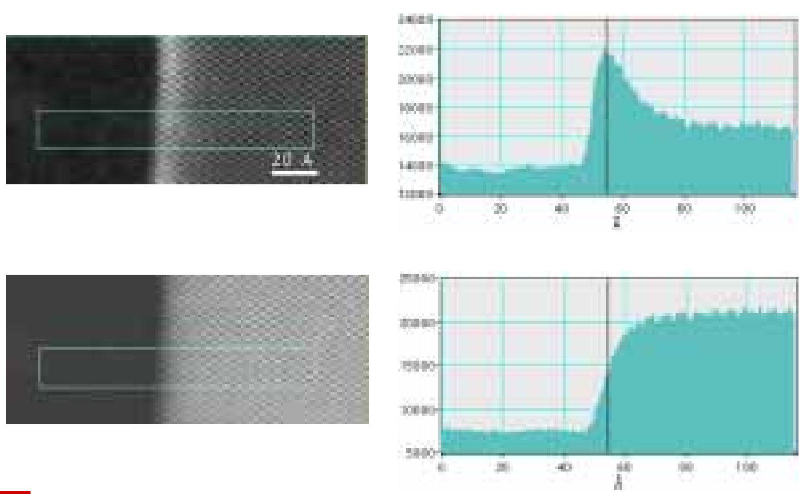
The strain contrast in LAADF

The strain contrast in LAADF is about +30% and –25% in HAADF.



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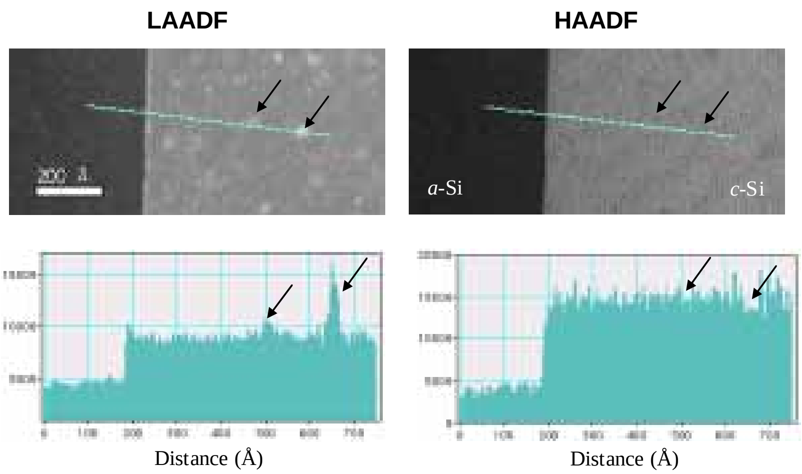
Ion Milling damage – evident as strain.



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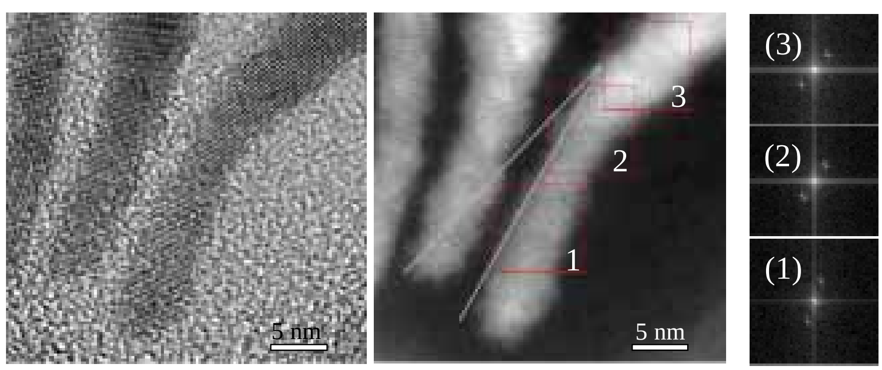
Mechanical Properties of CdSe



Shear force is $F_S = \mu_S \pi r^2 \tan\theta$

Given a 14 degree bend on a rod with radius 2.5 nm and the shear modulus as $5*10^{10}$ N/m^2, the shear force necessary for this bend is 2.5 * 10^{-7} Newton. This force is huge compared with the possible electrostatic force F = e2 / 4π__$_0$d^2 = 9 * 10^{-12} Newton for d = 5 nm and _ = 1.

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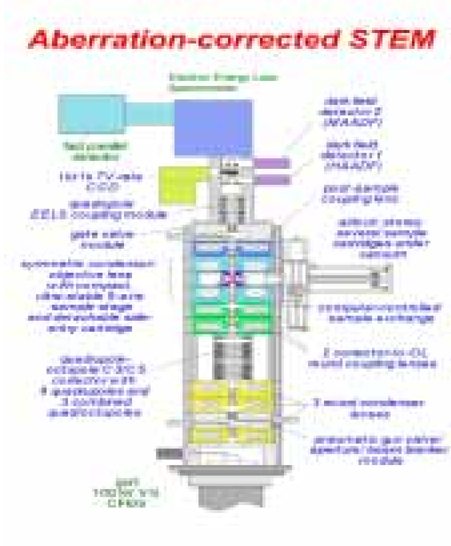
The New Breed: SuperSTEM



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Education for the Aberration-Free ERA

The new capability: Atomic scale composition, electronic structure, bonding and chemical details - **New imaging** modes, simpler but different.
Strain – vary the **nanodiffraction** detection conditions.
The third dimension – **electron tomography** – low and high resolution.
Charge and potential distributions - **electron holography**

Education Needs: Need expanded background, inelastic scattering with electronic structure background, elastic scattering with convergent beams, more precise numbers, specimen preparation, good instrumental background, good experimental technique, clean vacuum and specimen, stable environment, strong support, deep understanding (i.e., all of the above……).

Possible cures: broader dissemination of these techniques within the community, need capable groups that can train the scientists of the future (graduate students), write textbooks, etc. Make the specialist valuable again! Need research into new ideas for exploiting the new capabilities. U.S. system does not allow this!

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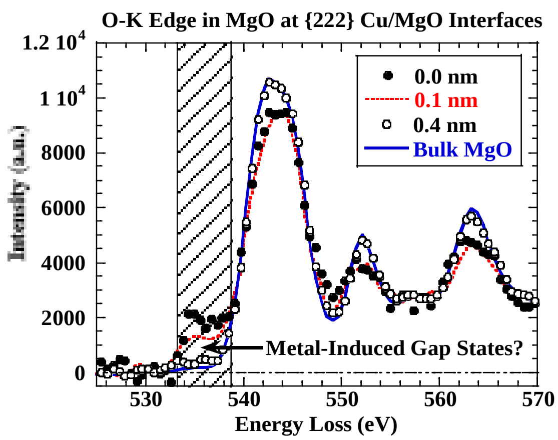
Atomic Scale EELS

Dr. D. Muller (Cornell Univ, *Lucent Technologies)*
J. Silcox *(Appl. & Eng. Phys.)*
D. Shashkov, R. Benedict, D.N. Seidman *(Mat. Sci. & Eng, Northwestern Univ.)*
L.H. Yang *(Cond. Mat. Phys. Div, LLNL)*



O-K edges at various distances from a <222>MgO/Cu heterointerface. The "bulk" spectrum is taken from the center of the MgO precipitate (thick solid line). Spectra are scaled to match the post-edge background. The cross-hatching marks the appropriate position of the unoccupied portion of the band gap in MgO.

Atomic Scale Observations of Metal-Induced Gap States at <222> MgO/Cu Interfaces. Physical Review Letters, 80, 21, 1998

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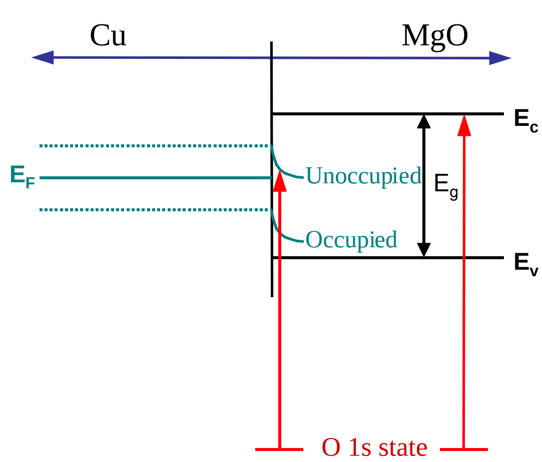
Metal Induced Gap States



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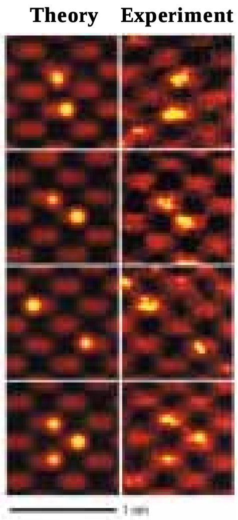
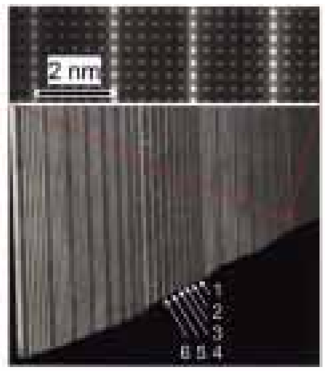
Atomic-Scale Imaging





A. Ohtomo, D.A. Muller, J.L. Grazul and H.Y Hwang, Nature **419**, 378 (2002)

P. Voyles, D.A. Muller, J.L. Grazul, P.H. Citrin and H.-J. L. Gossmann *et al*., Nature **416**, 826 (2002)