The Discovery of the Smallest Metal Nanotube with a Square Cross-Section

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CAPES

FAPEMIG
Fundação de Amparo à Pesquisa do Estado de Minas Gerais

Metallic Nanowires

- New physical phenomena
- Quantized conductance
- Unusual structures
- Applications: nanocontacts, nanofilters, etc.

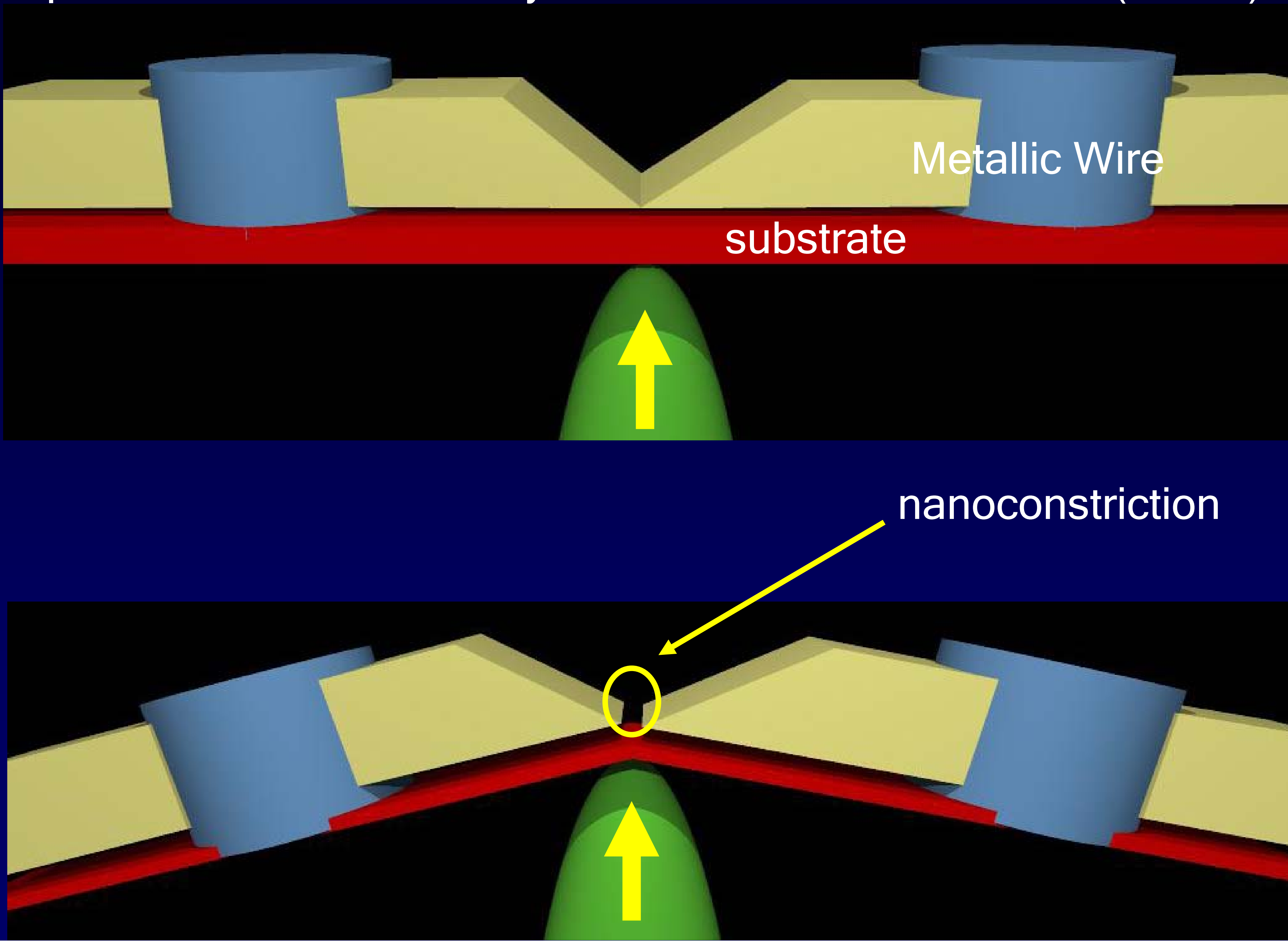
Metallic Nanowires (NWs)

U.Landman, W.D. Luedtke, N.A. Burnham, R.J. Colton, Atomistic Mechanisms and Dynamics of Adhesion, Nanoindentation, and Fracture, *Science* 248 (no. 4954), 454-461(1990).

Metallic Nanowires

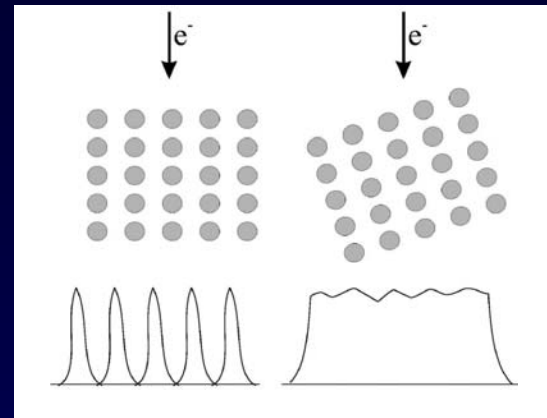
- Experimental setup
- Mechanically controllable break junctions
- High Resolution Transmission Electron Microscopy (HRTEM)

Experimental - Mechanically Controllable Break Junction (MCBJ)



High Resolution Transmission Electron Microscopy

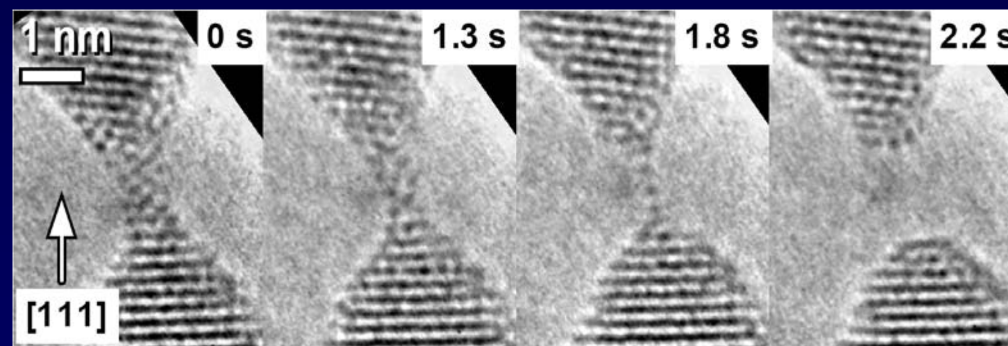
HRTEM JEM 3010 UHR,
300 kV, LaB_6, P ~ 10^{-7} mbar;
High sensitivity TV Camera
associated to a DVD



HRTEM

↓

2D Potential Projection



Atomic resolution: 1.7 Å
Image acquisition: 30 frames /s

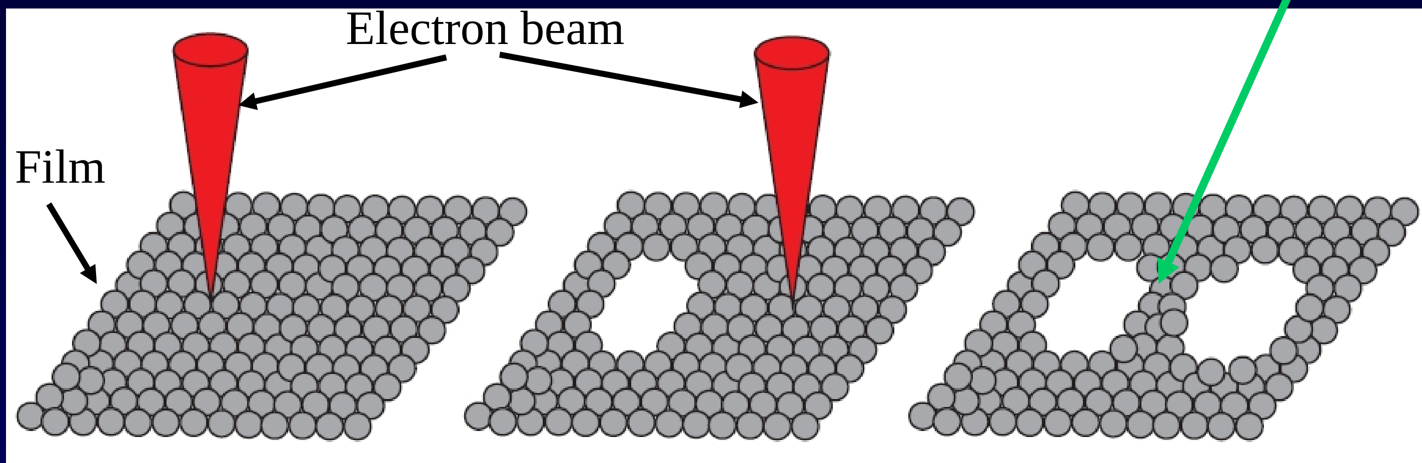
Combining atomic resolution with real-time image acquisition !!!!!

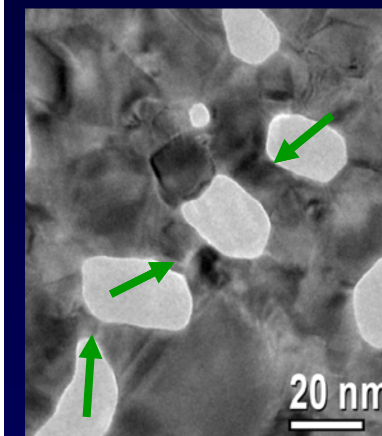
Structural Study: Time Resolved *In situ* HRTEM

1) Self-supported ~20 nm thick polycrystalline SILVER film.

2) Drill holes

3) nanobridge rupture is spontaneous and uncontrolled

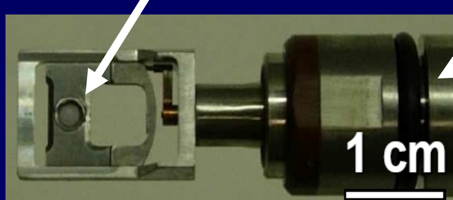




4) Cool the sample at ~150 K (Sample Holder Gatan 613-DH)

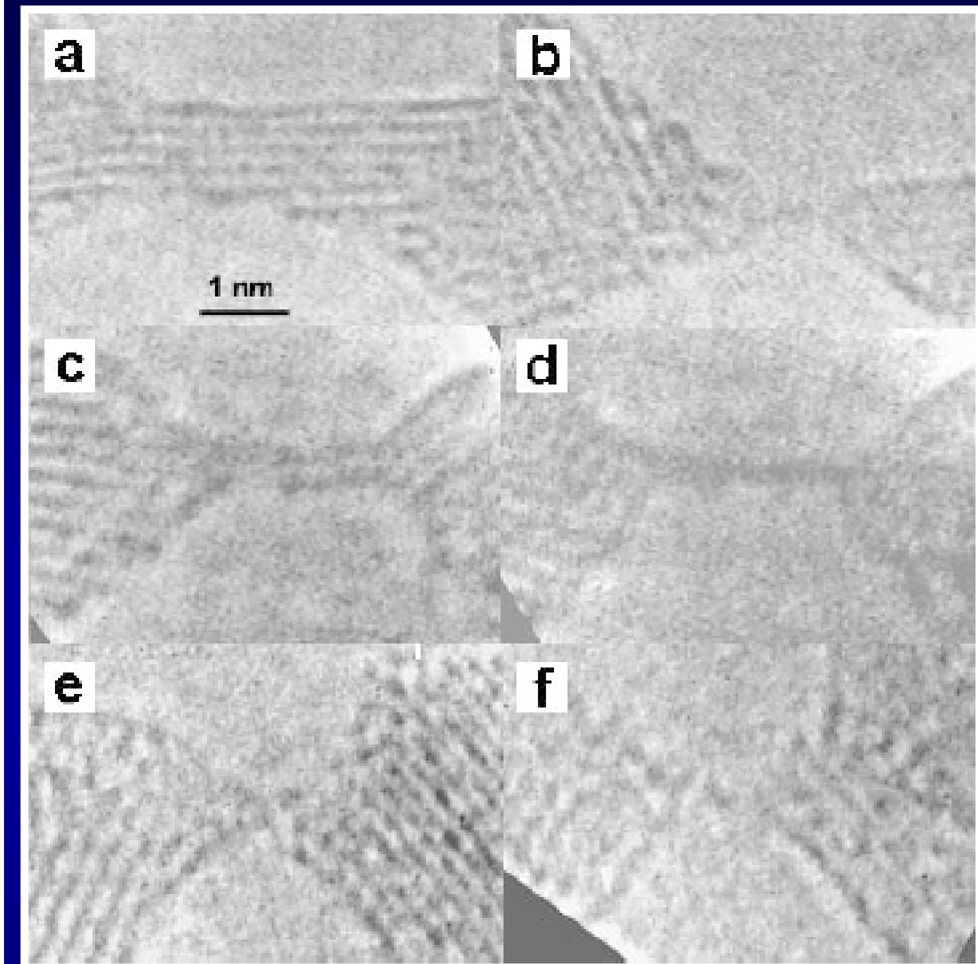
Time consuming !!

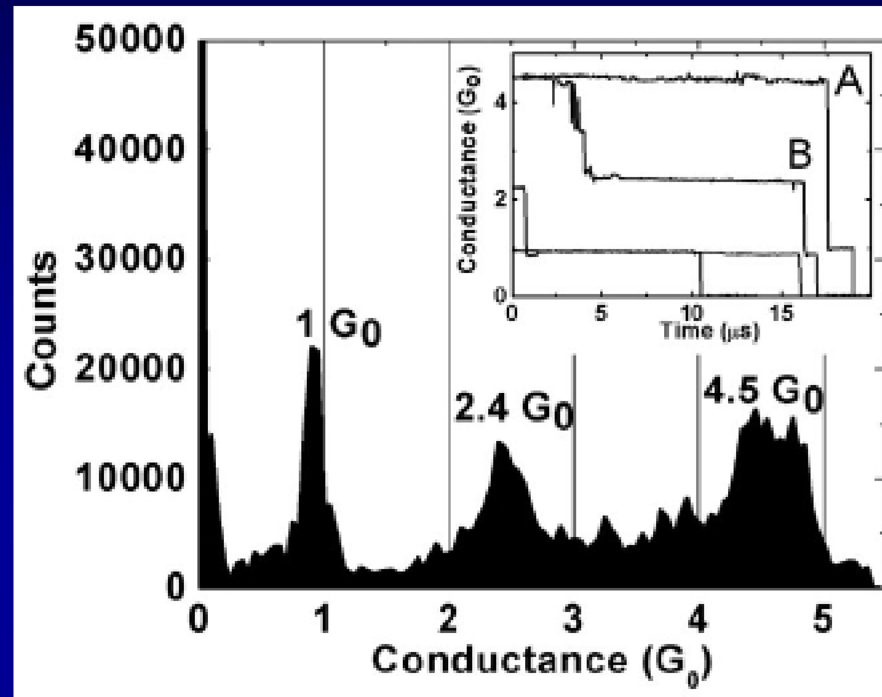
Self-suported SILVER film



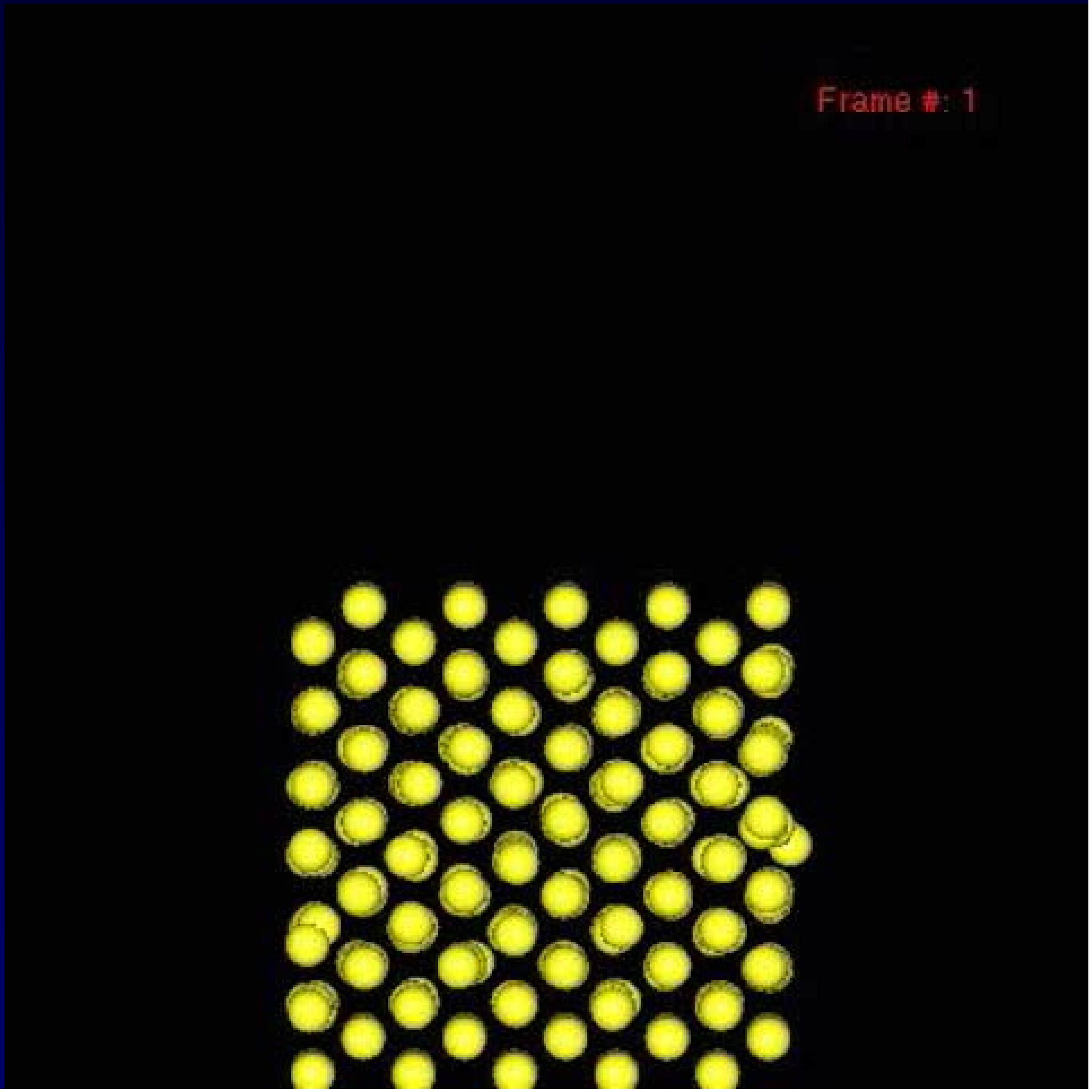
Kondo, Y. *et al*, **PRL 79, 3455 (1997)**
Lagos, M. *et al*, **Jour.Elec.Spec.Rel.Phen. 156, (2007)**

Cu



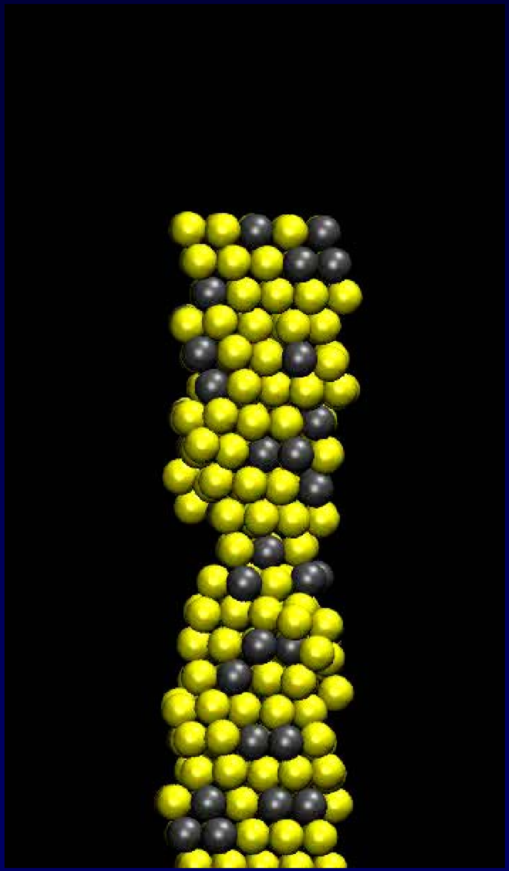


González et al., *Phys. Rev. Lett.*, 93, 126103 (2004).

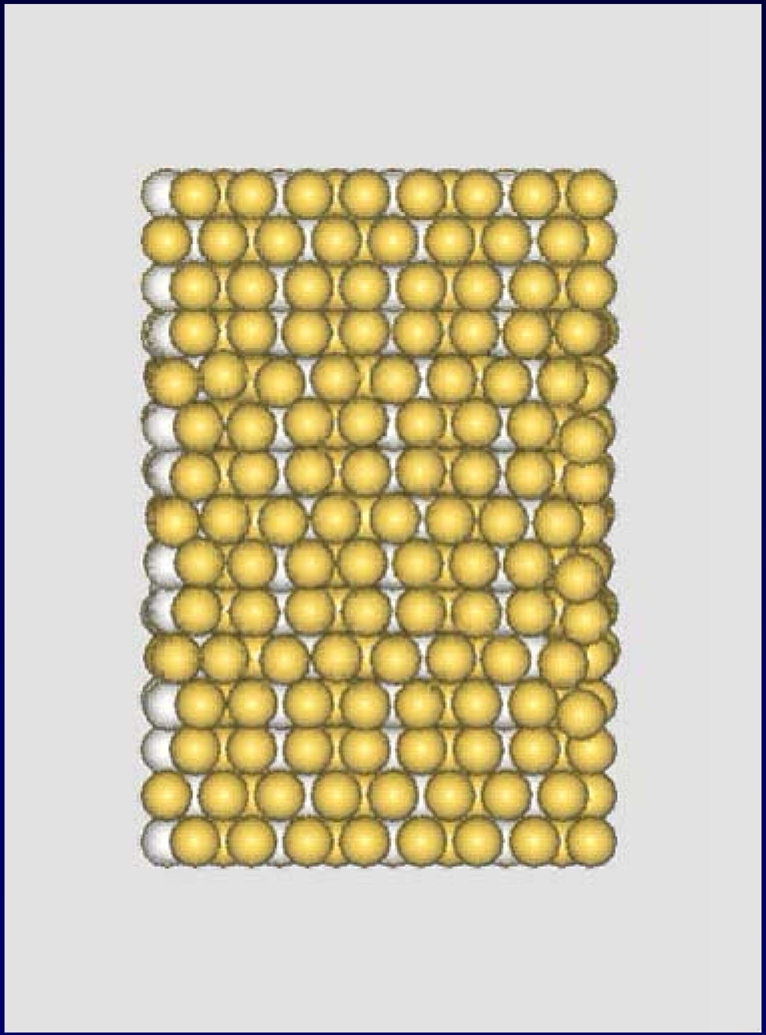


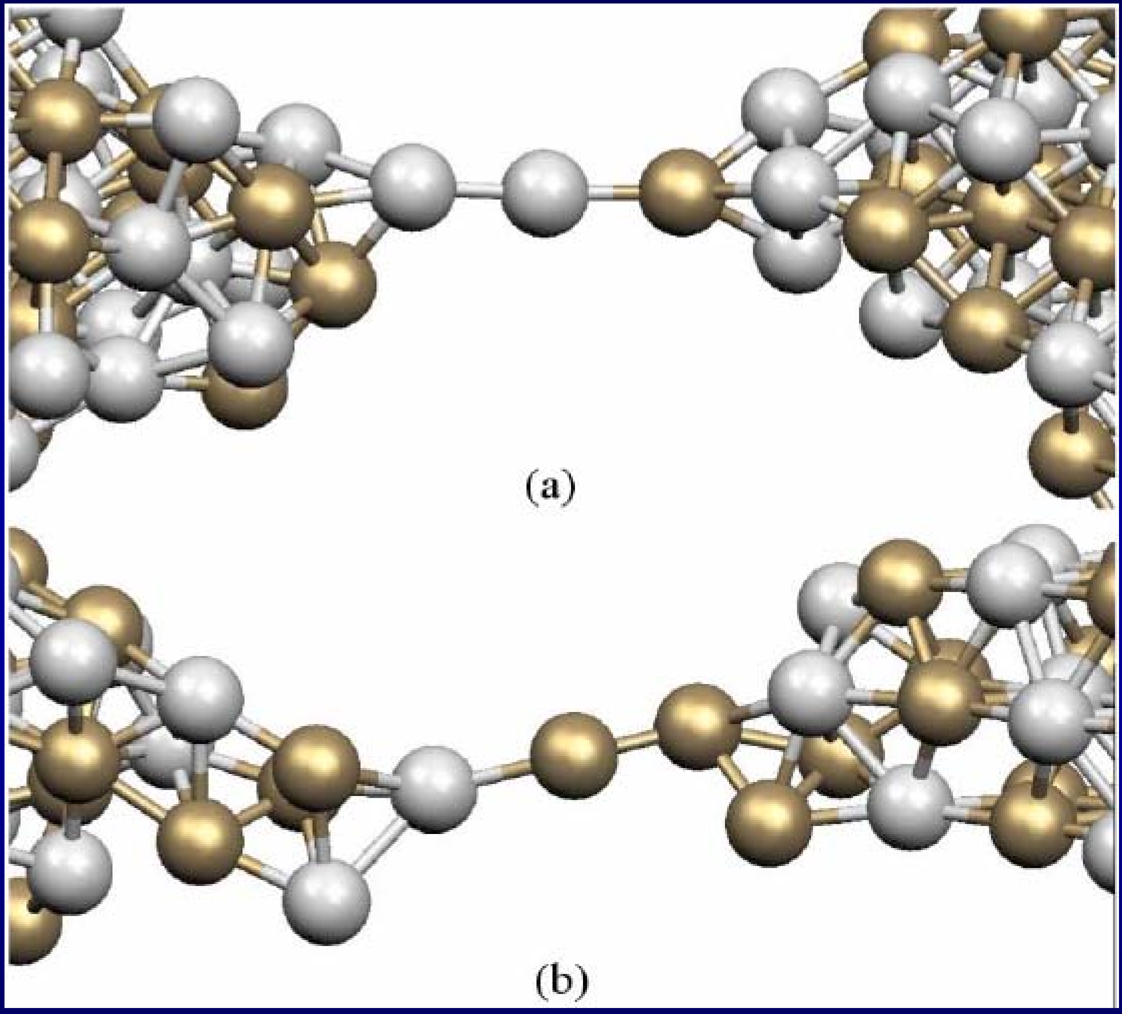
Rodrigues et al.
PRL (2008)

Au – Ag – Alloys



Bettini et al,
Nature Nano (2006)





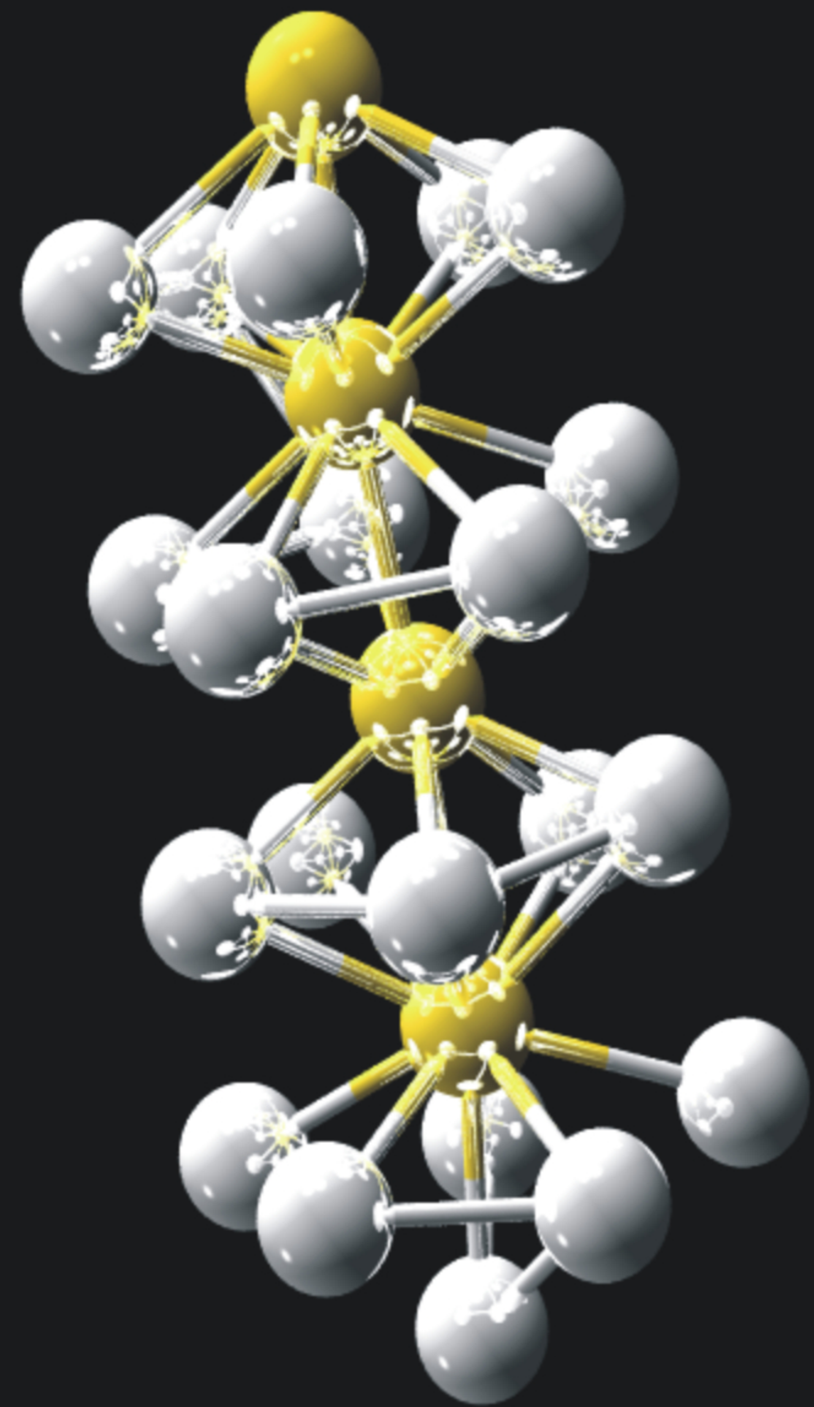
40% Au

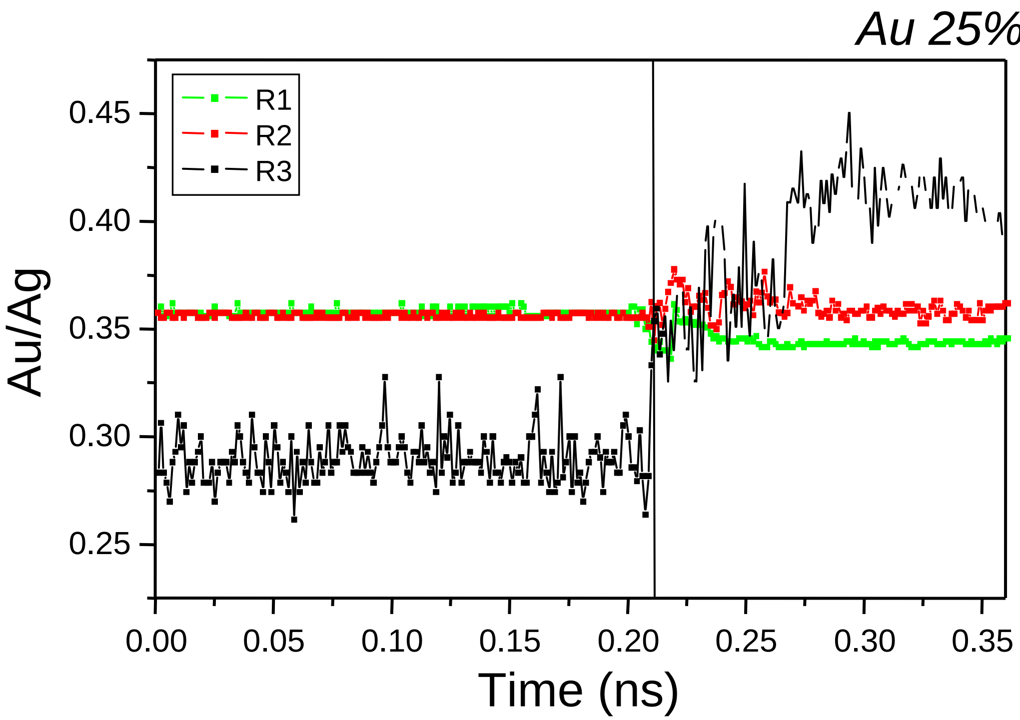
60% Au

NW - Alloy AuAg

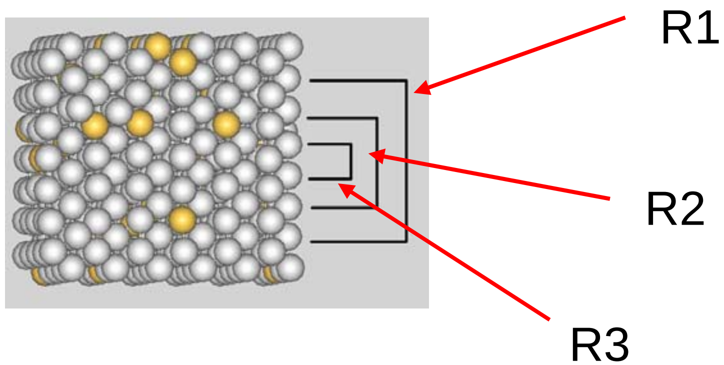
Encapsulated Au

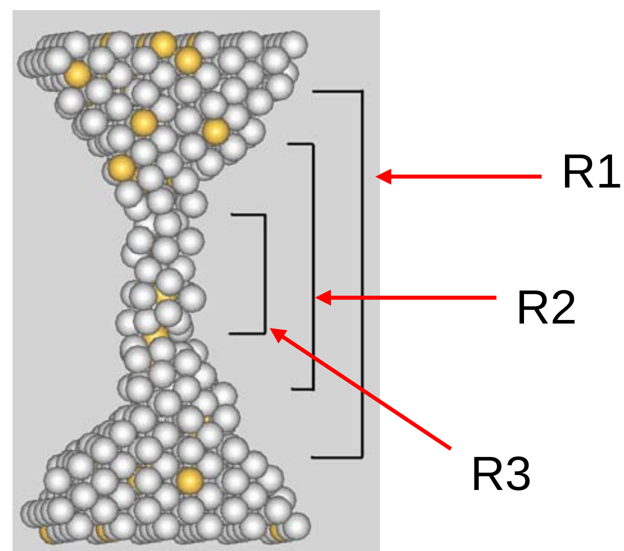
20% Au



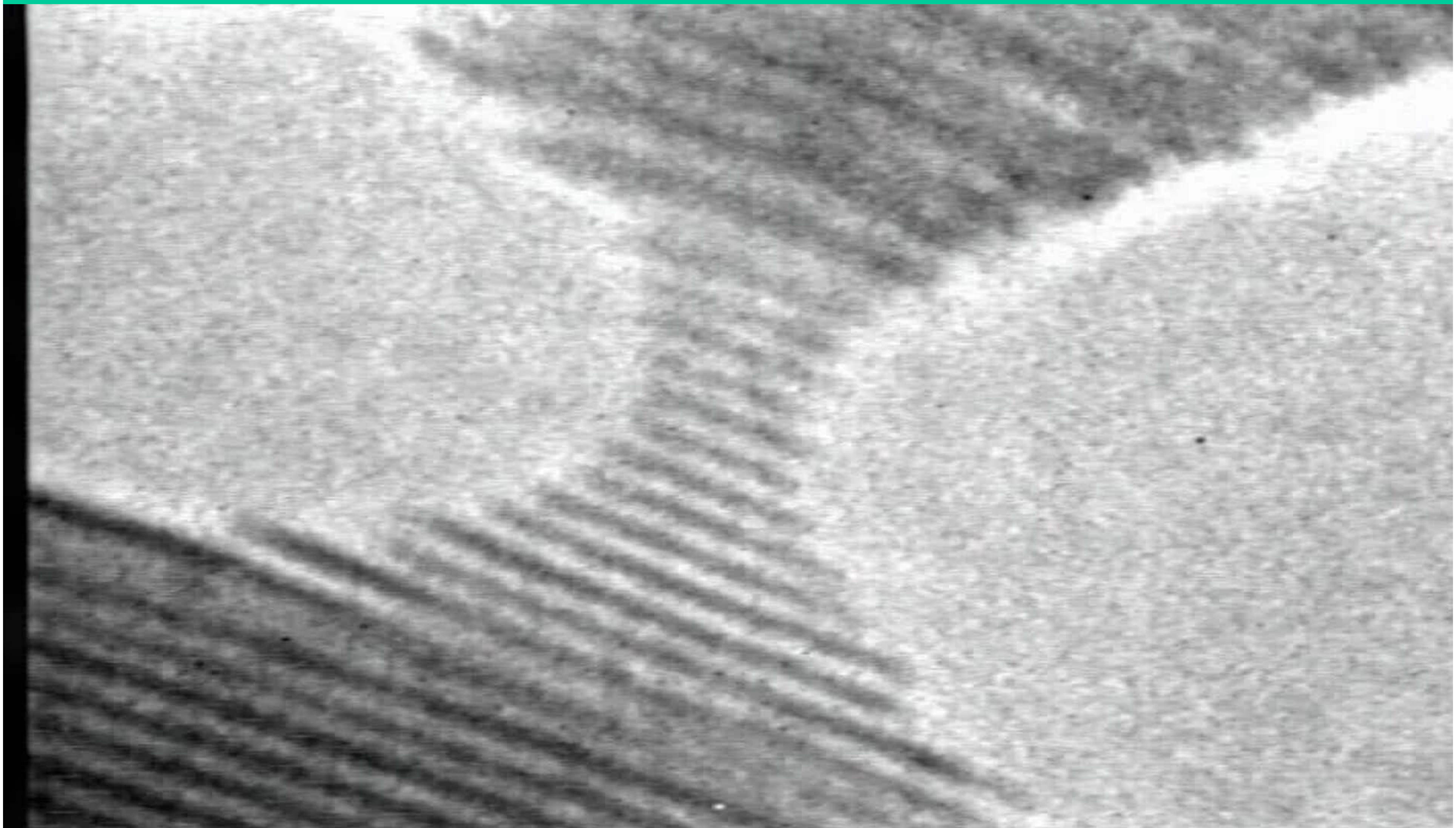


Clear Gold enrichment of junction





Gold-Silver Alloy Nanowires [100] and [111] Atomic Chains

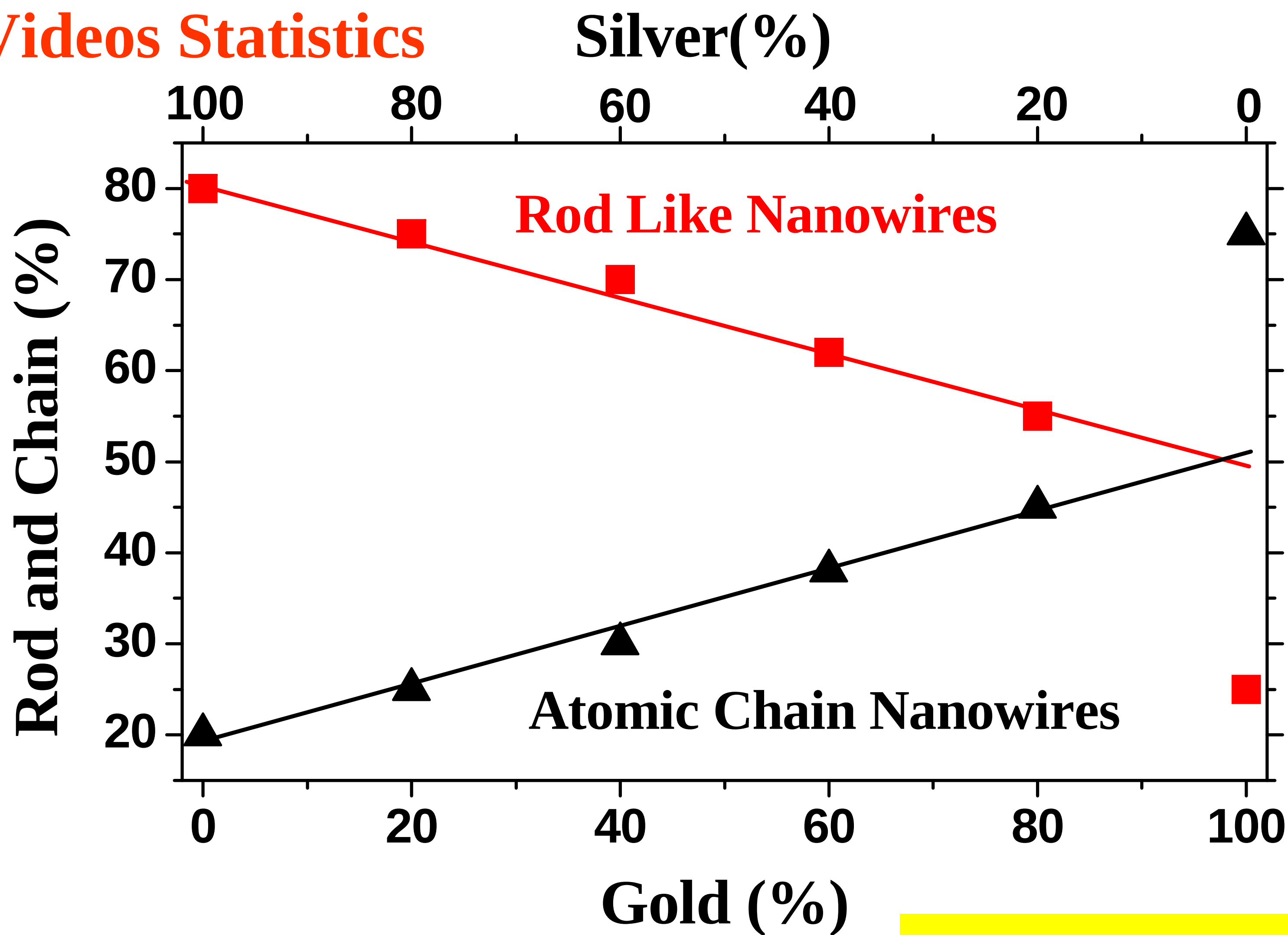


Bettini et al, Nature Nano (2006)

$Au_{60}Ag_{40}$ [110]

Gold-Silver Alloy Nanowires Rod X Chain

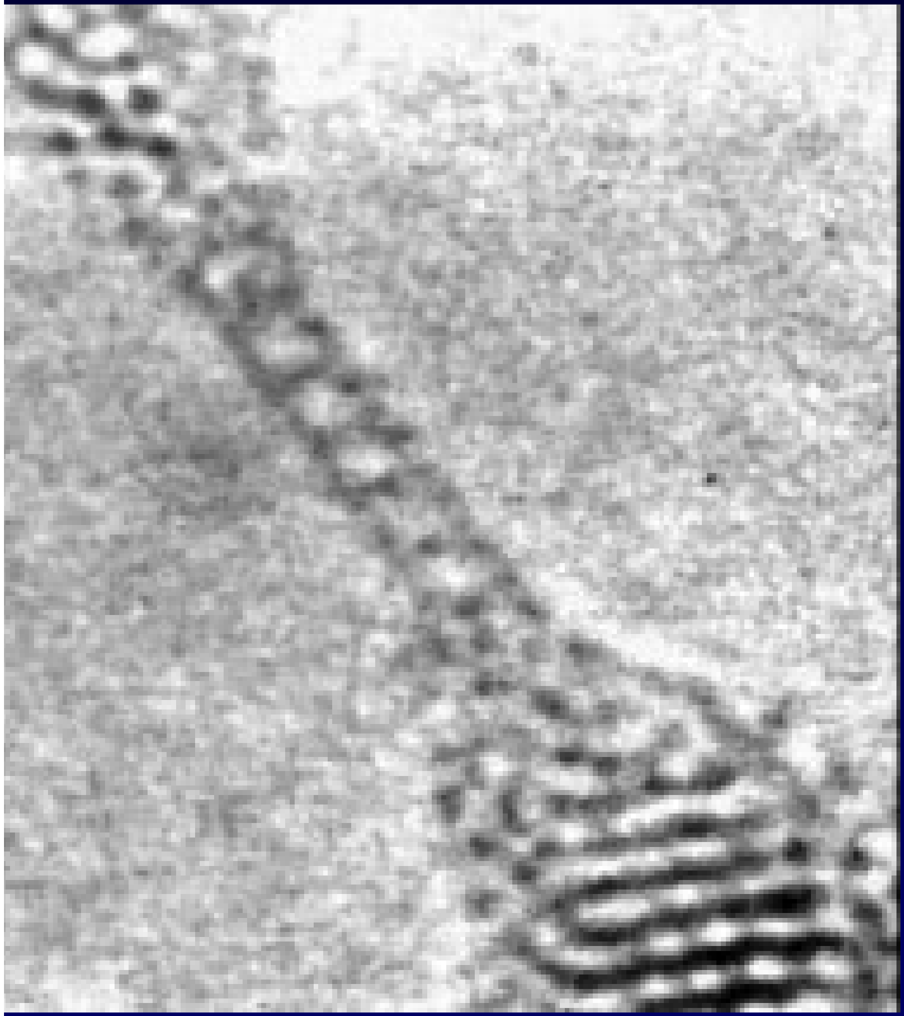
Videos Statistics

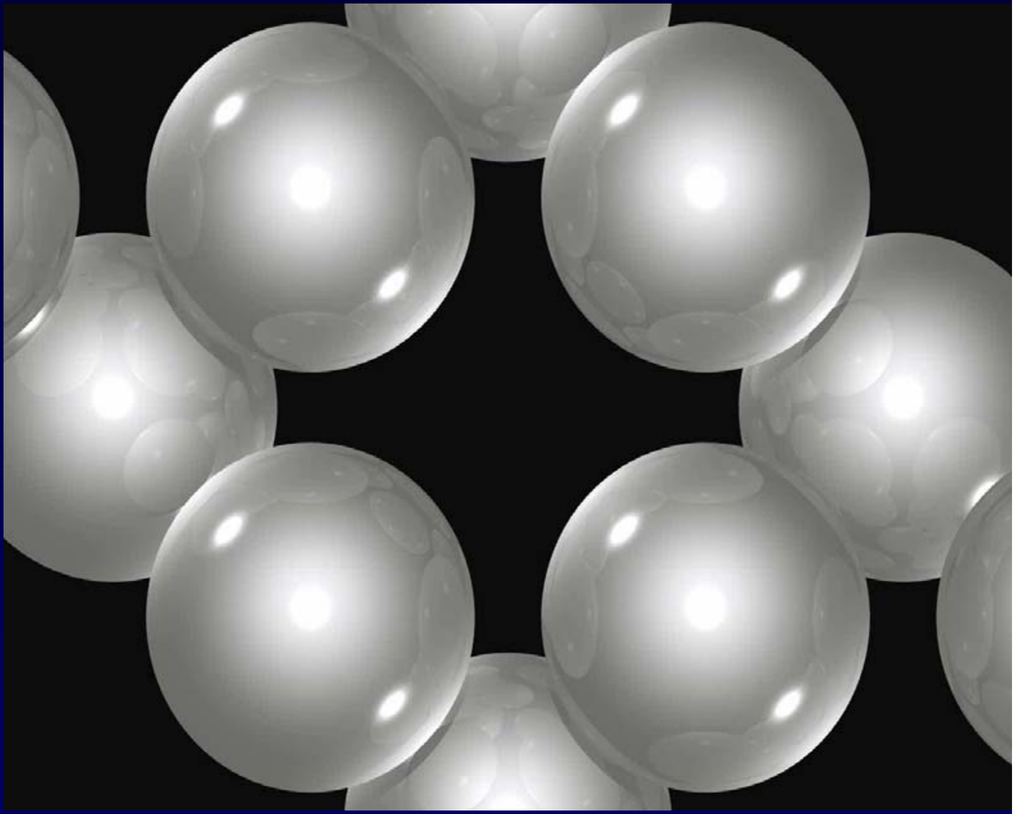


Mainly Gold Behavior

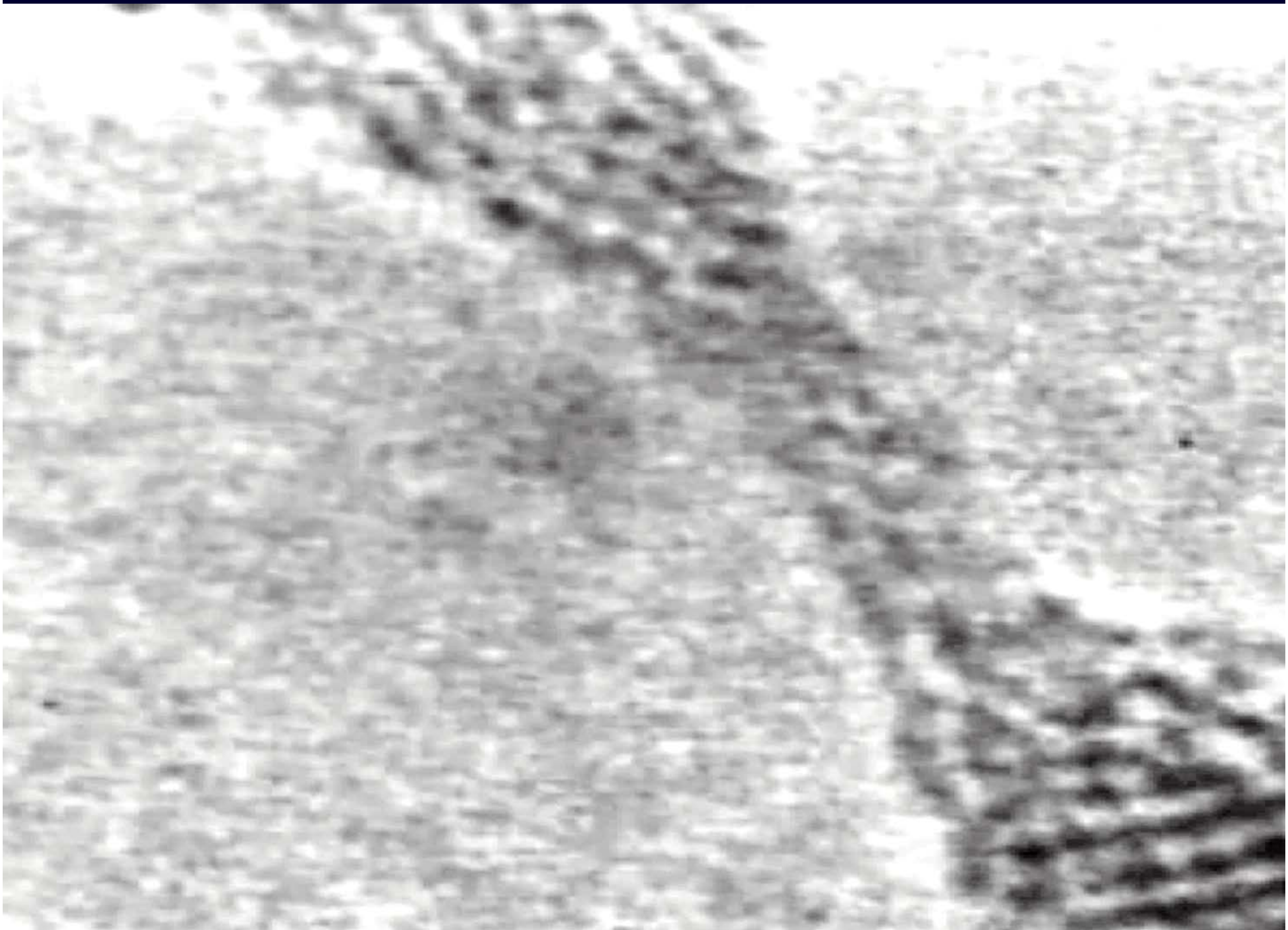

nature
nanotechnology
New directions for self-assembly
METAL NANOWIRES
When is an alloy not an alloy?
FLEXIBLE ELECTRONICS
Nanoribbons make waves
MOLECULAR JUNCTIONS
Nanoscale electron transport
METAL NANOWIRES
When is an alloy not an alloy?

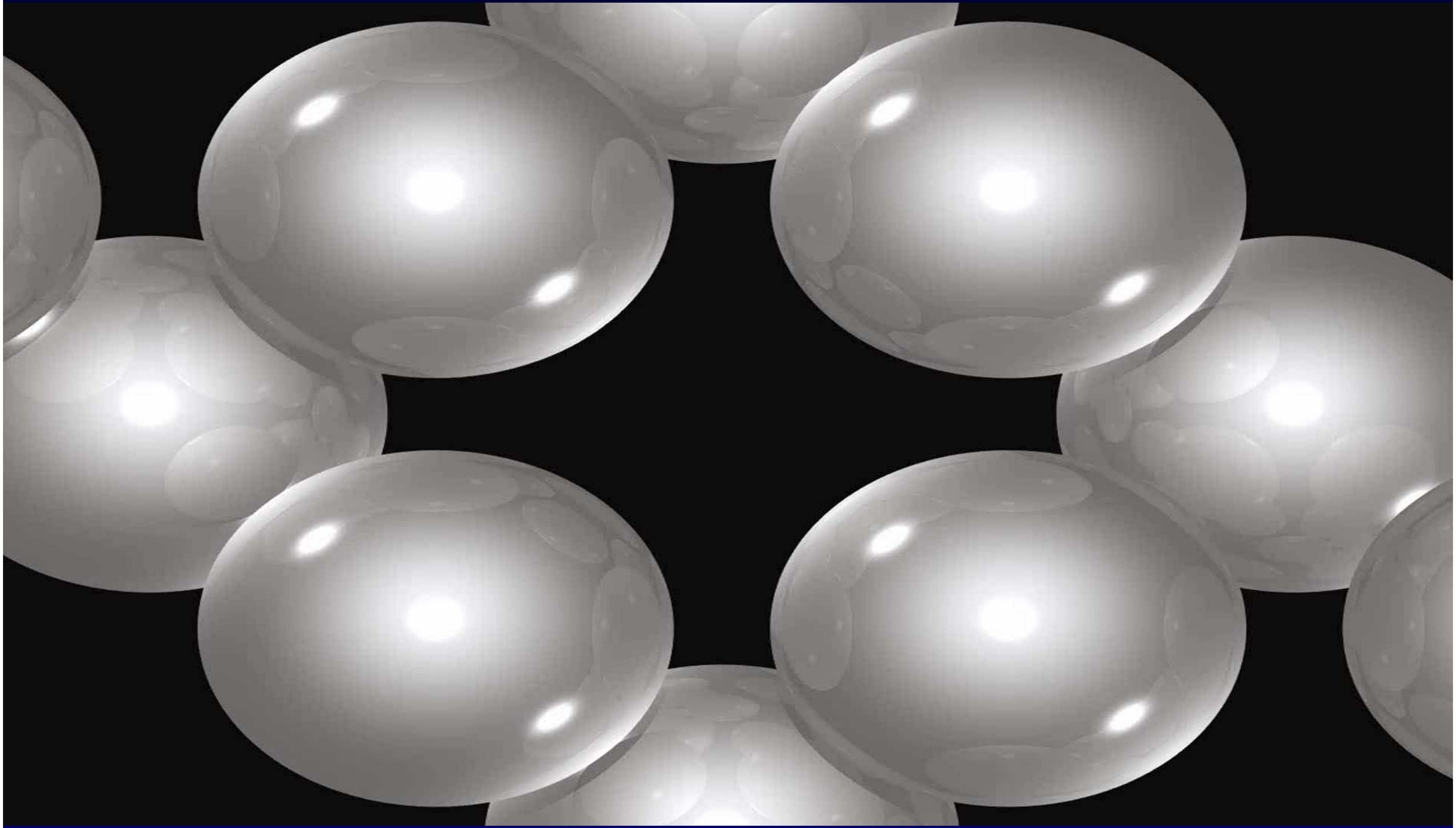
Smallest possible hollow Ag Nanotube!





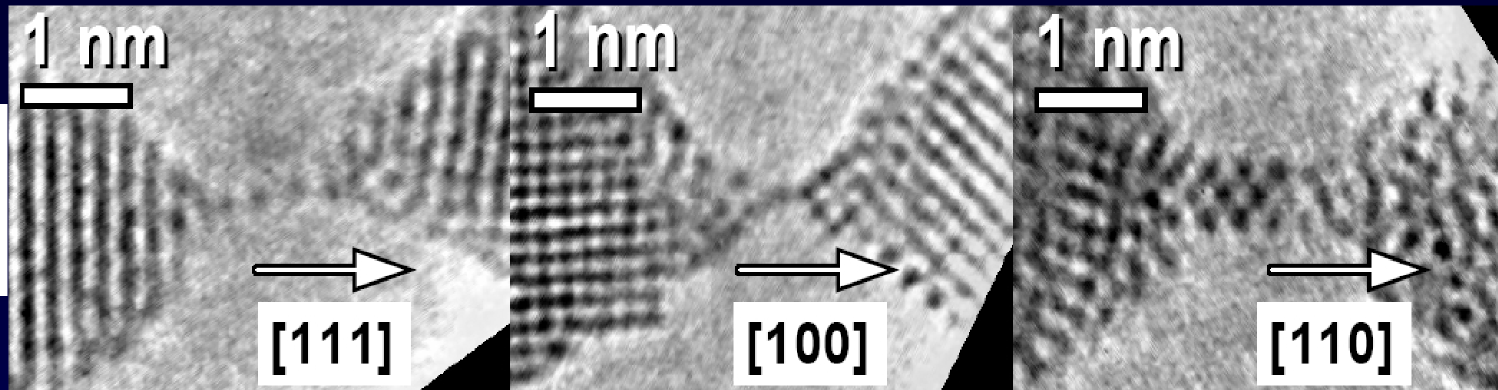
Lagos et al. – Nature Nanotechnology (2009)



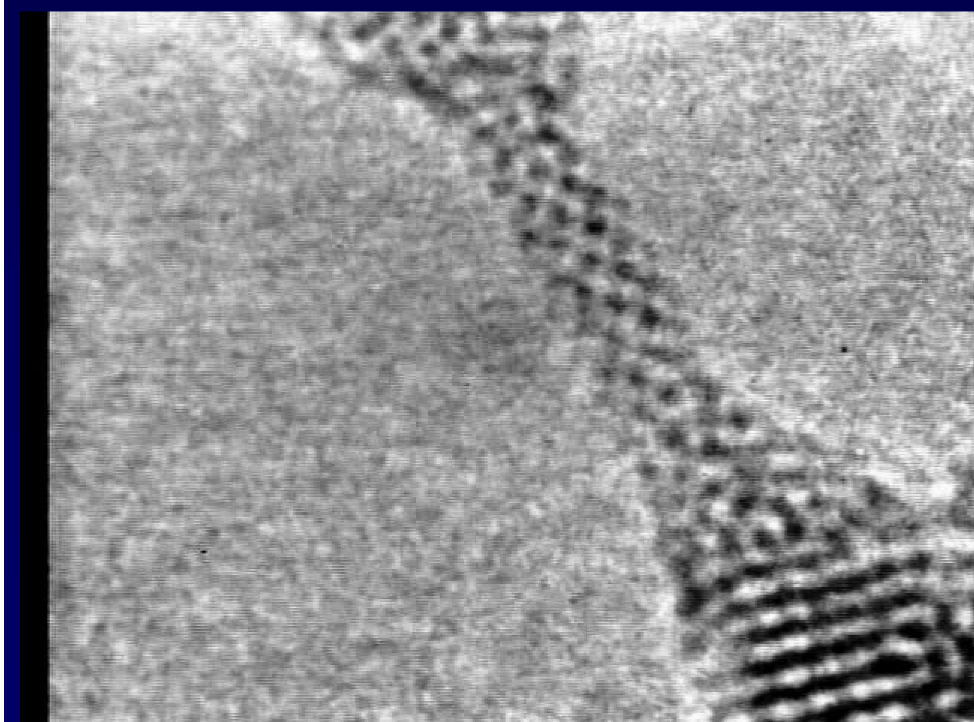


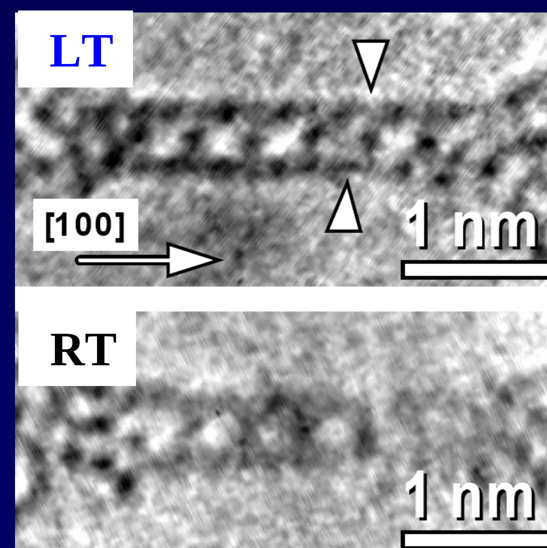
Structural Observation: Silver Nanowires

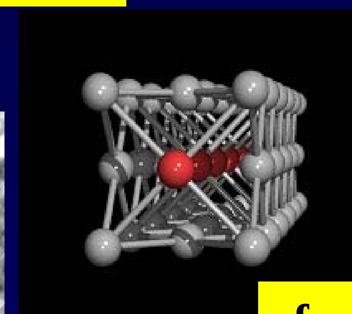
NW´s along
[111]/[100]/[110]
axis



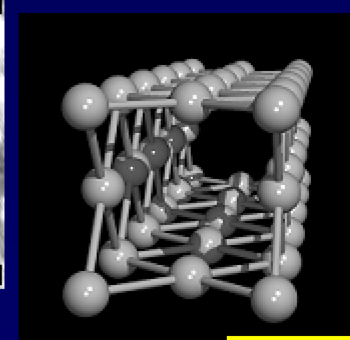
A <u>New</u> Tubular Structure of [100] NW is observed at **RT** and **LT**





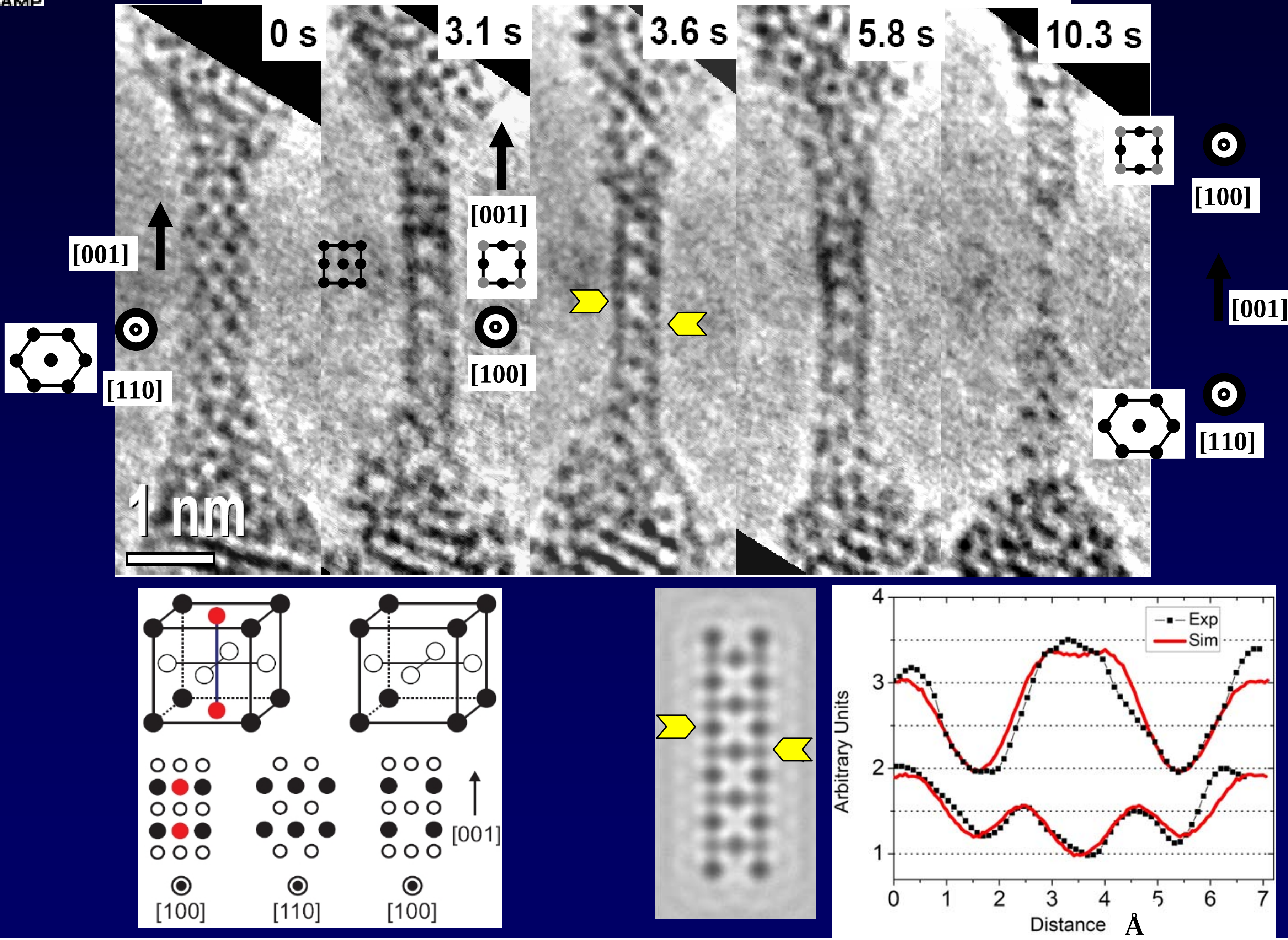


fcc

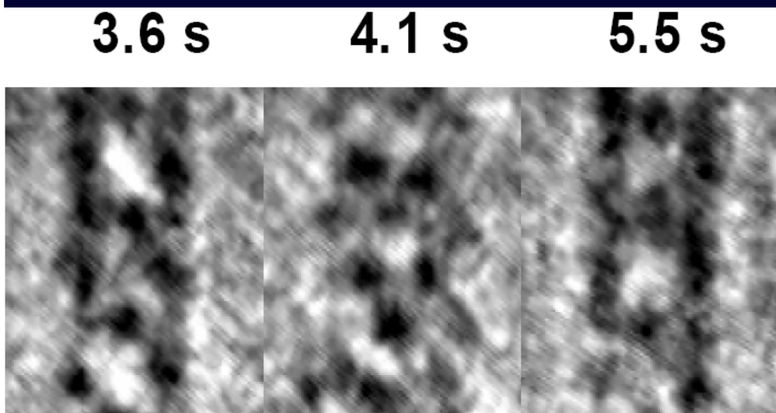


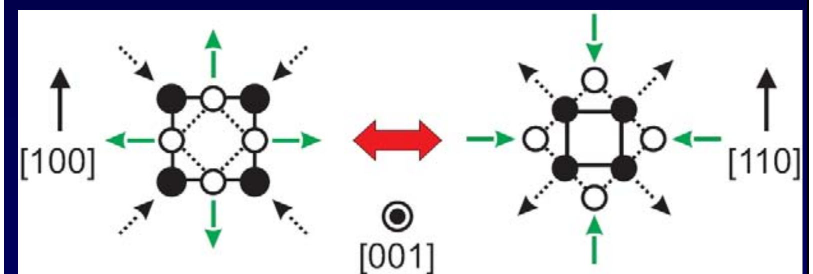
tube

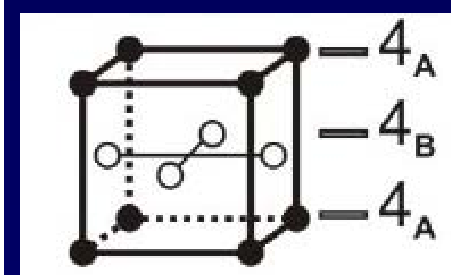
Dynamic Structural Evolution

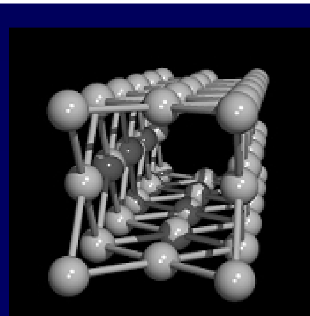


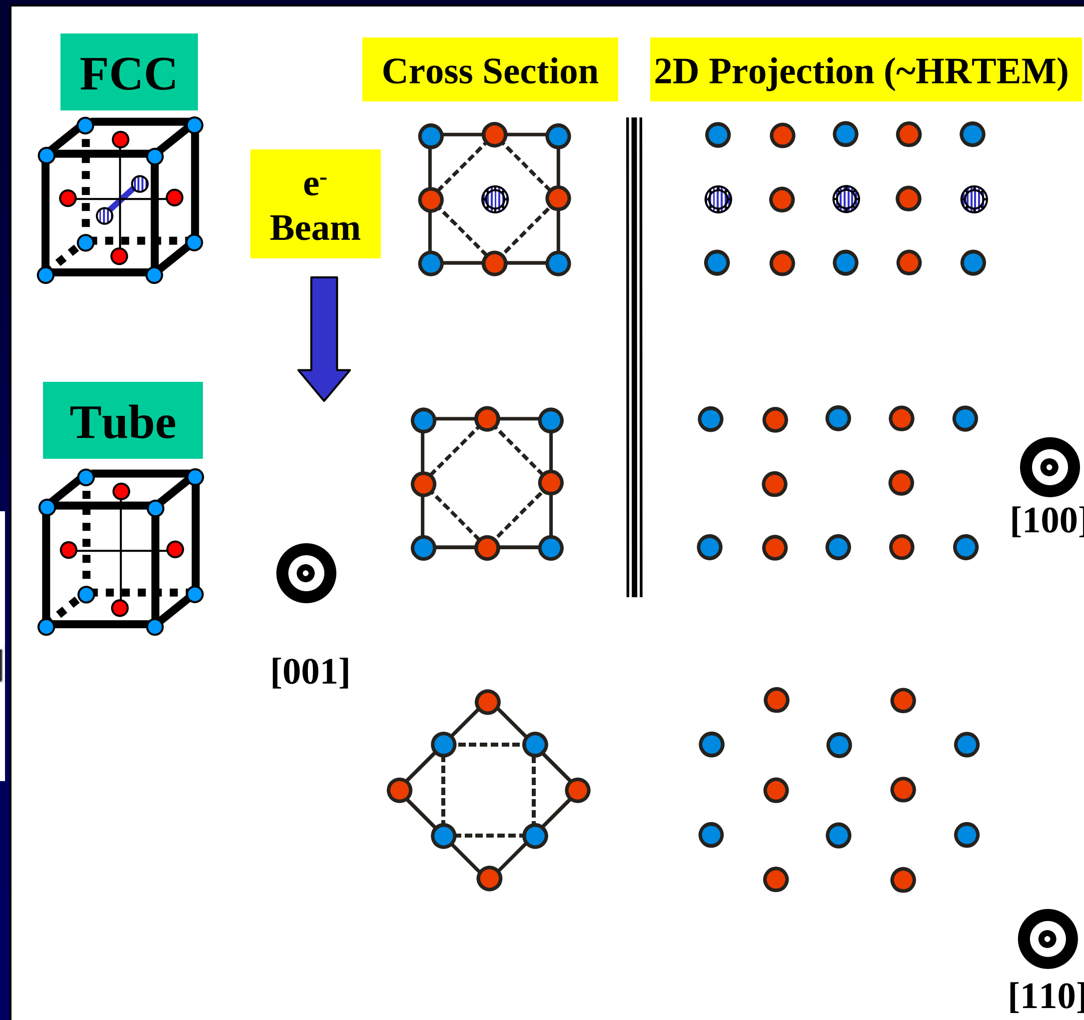
Breathing Mode











Fluctuations between two configurations

Apparent axial rotation!!!!

Evidence of HOLLOW structure!!

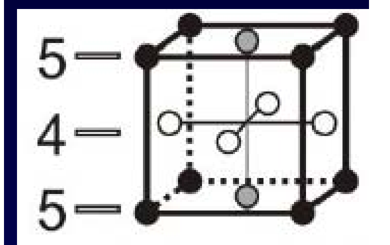
Formation of the Tubular Nanostructure

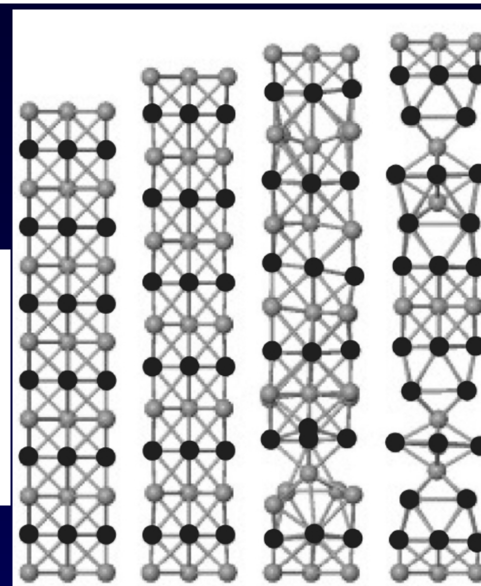
Molecular Simulations (Different Stress Conditions)

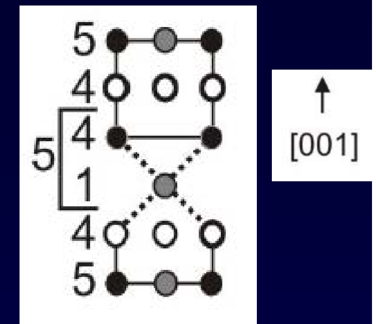
FCC 5/4 stacking

59 atoms,
Relaxed structures

Elongation (**0.1 Å step** between buffer layers)

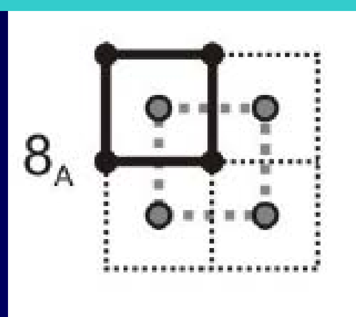


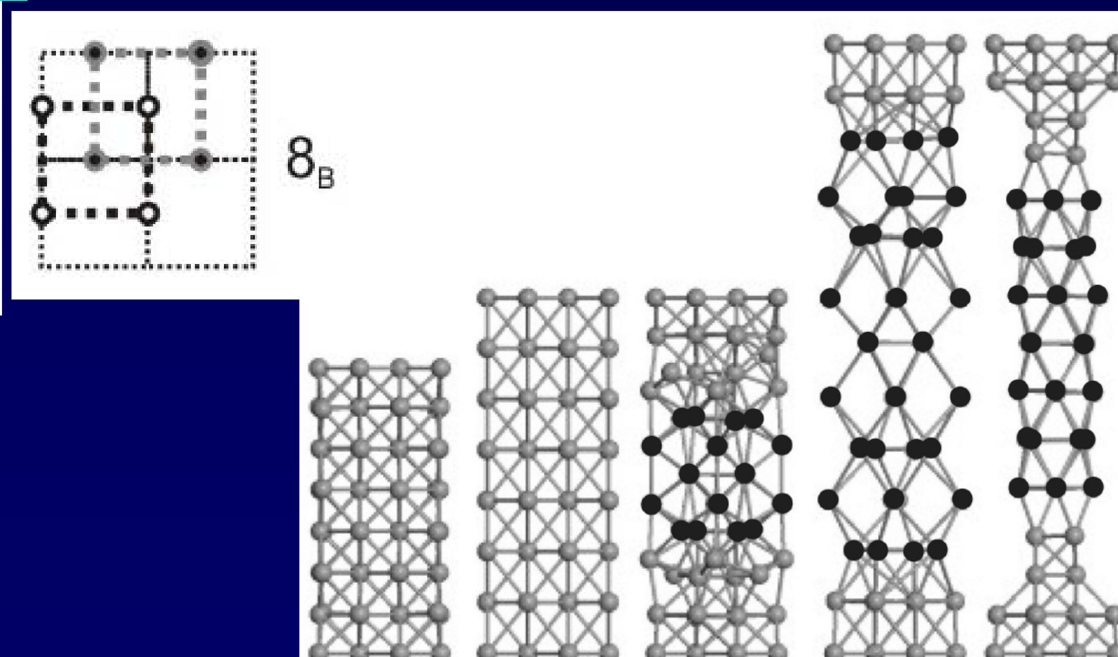




Split plane 5 → 4+1 (**Removal** of the central atom)

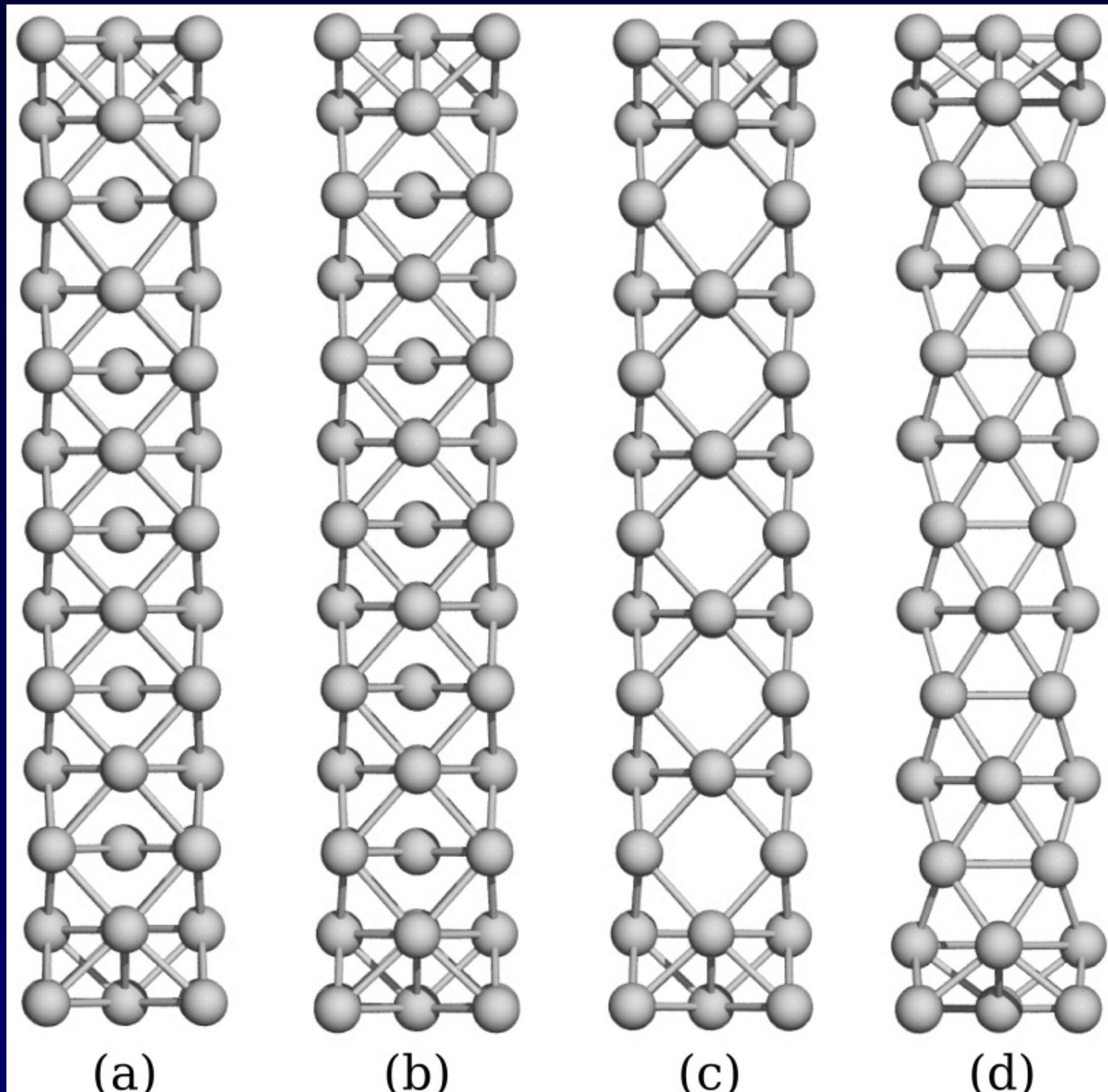
FCC $8_A/8_B$ stacking





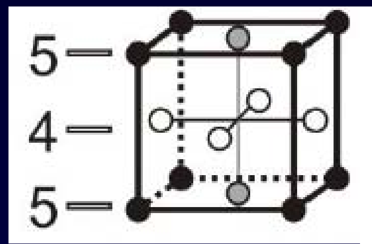
64 atoms,
Relaxed structures

Elongation (**0.5 Å step** between layers)

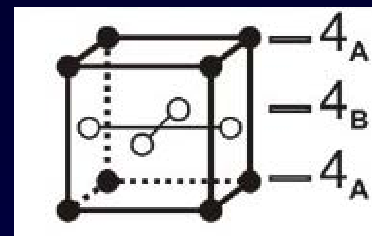

(a)
(b)
(c)
(d)

Structural Stability

FCC
5/4 stacking

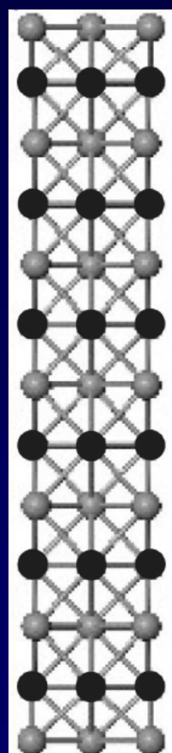


↑ [001]



TUBE
$4_A/4_B$ stacking

Total Energy Calculations
***ab initio* DFT**



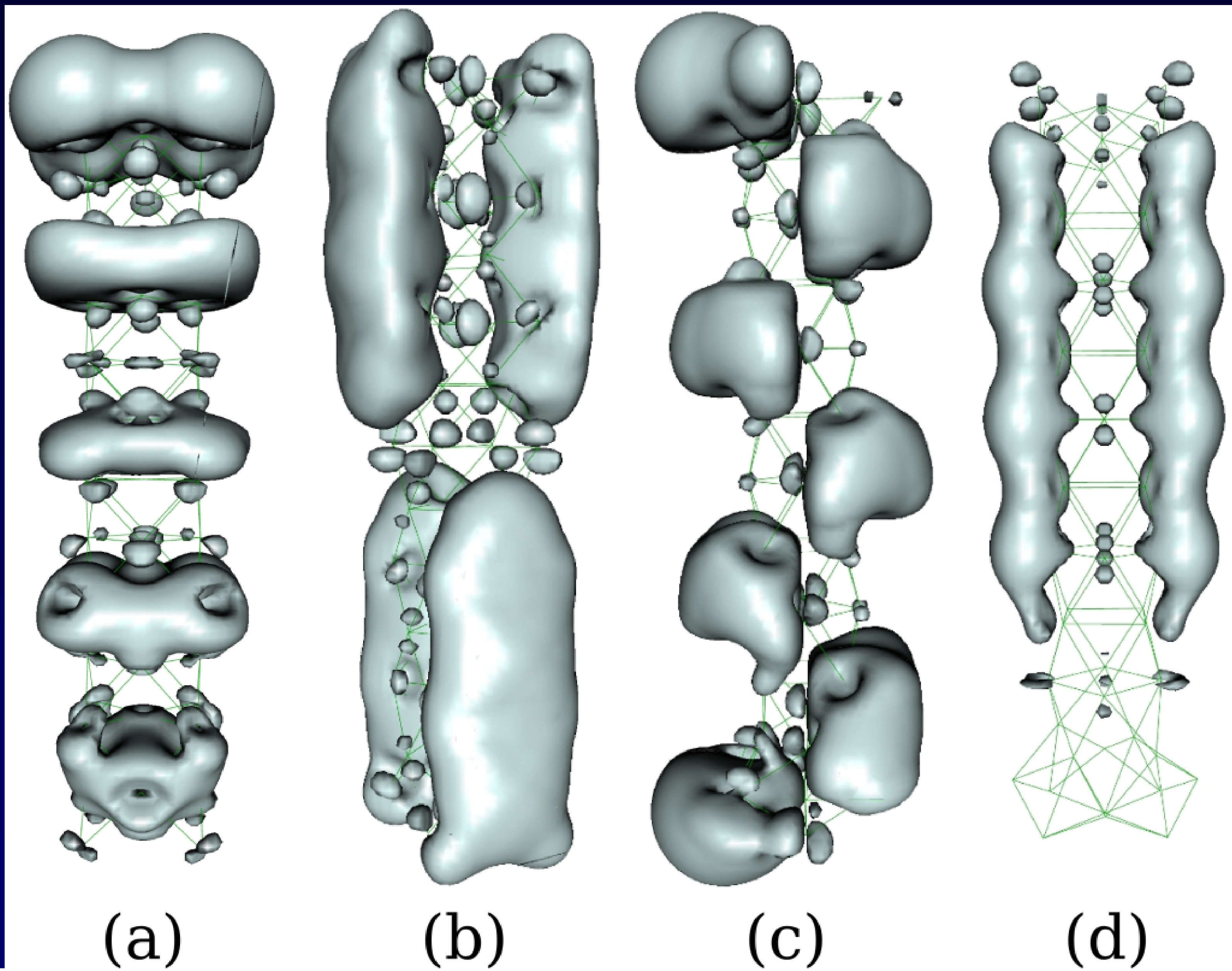
↑ [001]

Stacked Atomic Layers	FCC Energy (eV)	TUBE $E_{TUBE}-E_{FCC}$ (eV)
5	-4.035299	0.078759
7	-4.195817	0.098302
9	-4.278174	0.139482
11	-4.337848	0.163282
13	-4.344577	0.143624

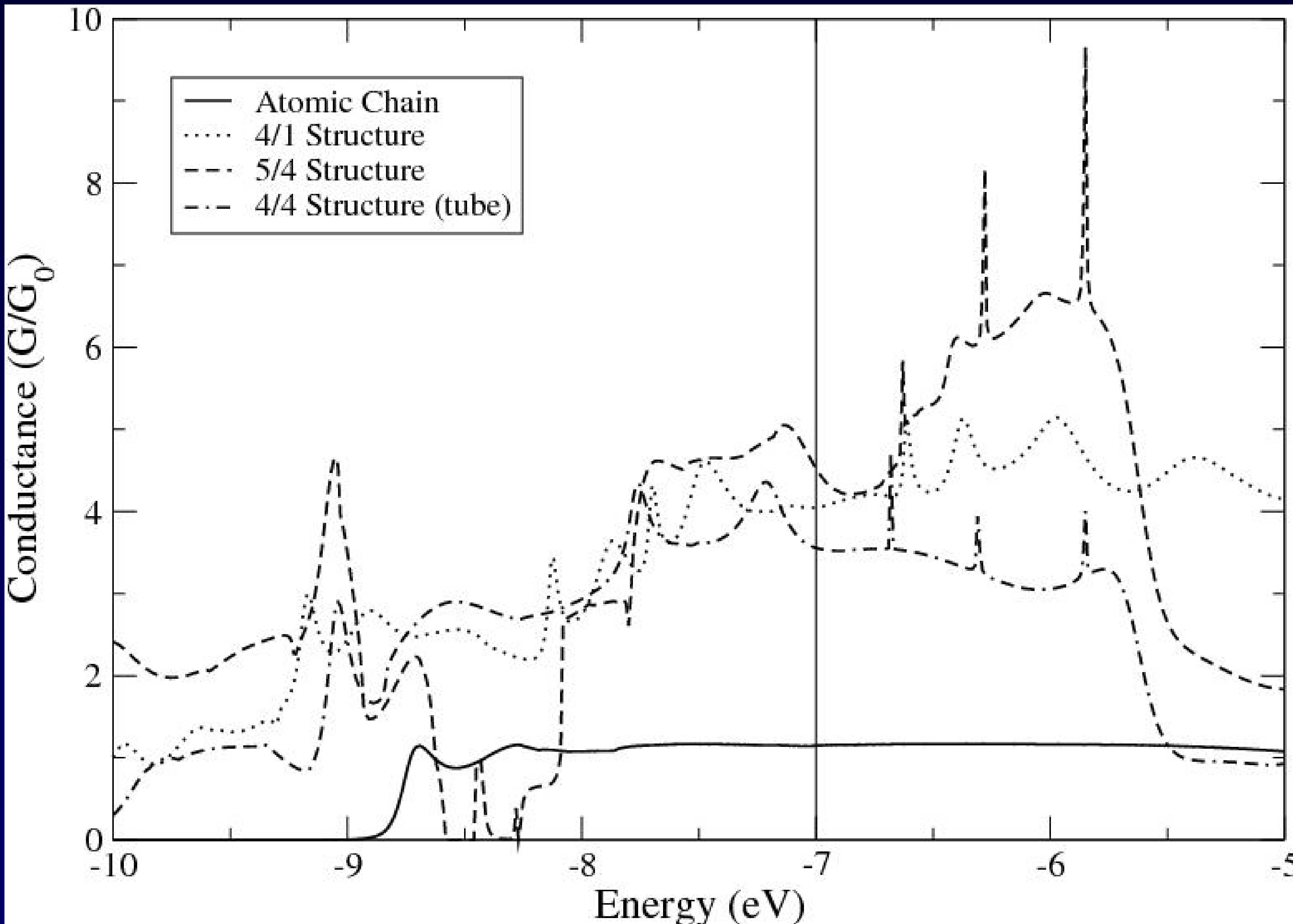
Tube is sligthly less stable than FCC one!!

Elastic energy (elongation) → **Tube formation and stabilization**

Frontier Orbitals – ab initio calculations – Still metallic!
Galvão et al. - unpublished

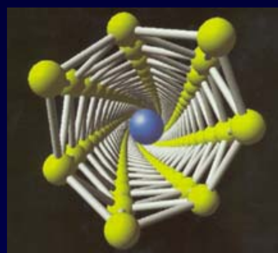


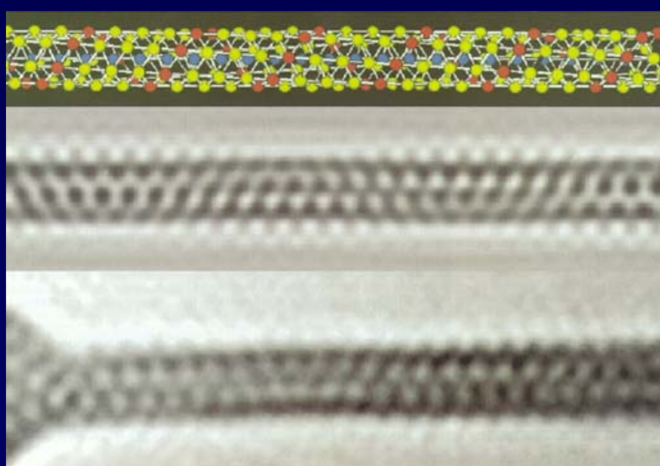
Transport Simulations



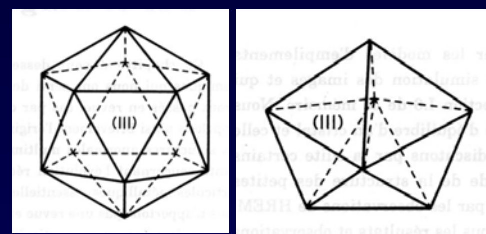
Club of non-crystallographic structures

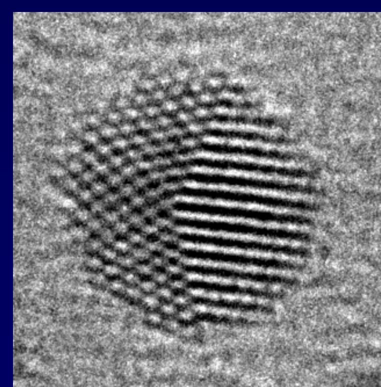
Helical Au Nanowires



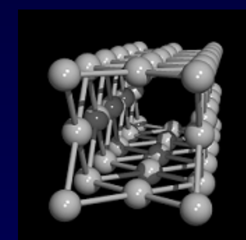


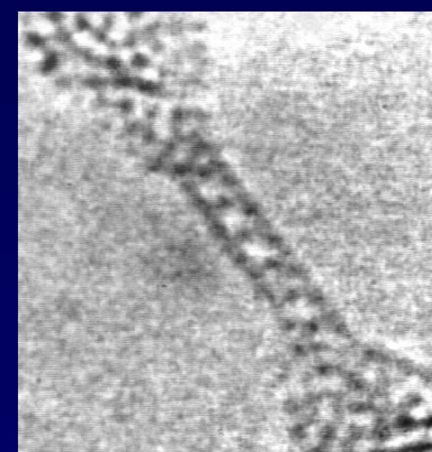
Metallic Nanoparticles





Silver Nanotube





Conclusions

- Experimental observation of the smallest square cross-section silver tube.

- The square cross-section tube structure is formed by the stacking ($4_A/4_B$) of two different squares containing 4 atoms arranged on the corners.

- Apparent axial rotation of the silver nanotube is explained by fluctuations between two stable atomic configurations (breathing mode).

- Total energy *ab initio* calculations (DFT) indicate that nanotube configuration is slightly less stable than FCC one.

- A process of structural evolution from FCC to tube configuration is proposed ($8_A/8_B \rightarrow 4_A/4_B$).

- Nature Nanotechnology v4, 149 (2009).