Chapter 4 Computational design of metal systems

- An overview on metals
- 0-Dimensional System: magic clusters
- **Growth of quantum-sized metallic films**
  - One Dimensional Metal System: Metal Atom Wires
  - Two Dimensional Metal System:
    - A brief overview of quantum growth
    - From precise structural control to property optimization
- Nano Plasmonics

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One Dimensional Metal System:
Metal Atom Wires

Quantum Size Effect and Electronic Stability of Free-standing Metal Atom Wires

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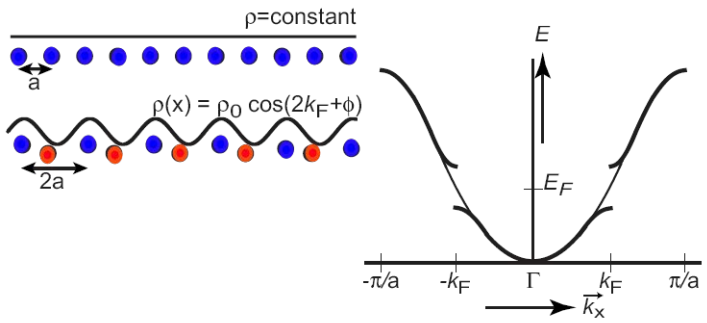
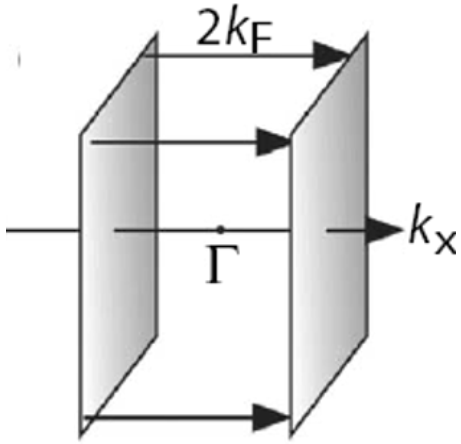
Exotic Properties of 1-D Systems

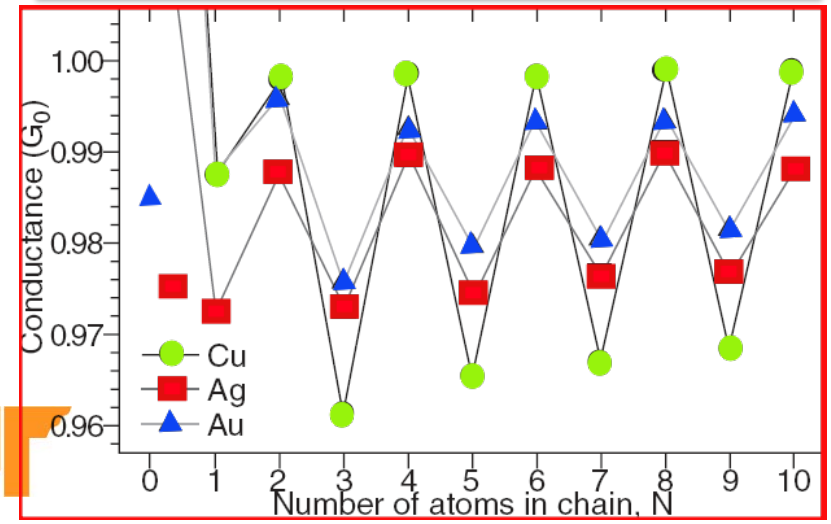
Peierls instability



Perfectly nested Fermi surface



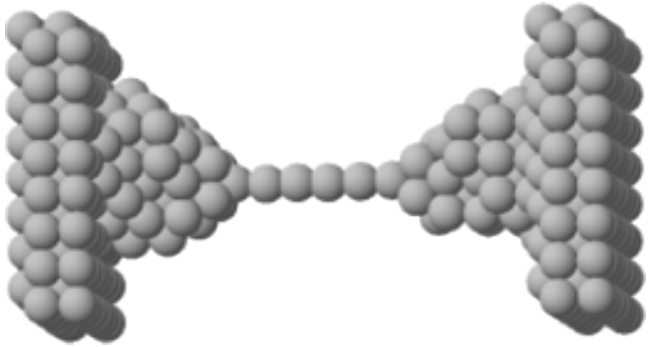
Conductance quantization



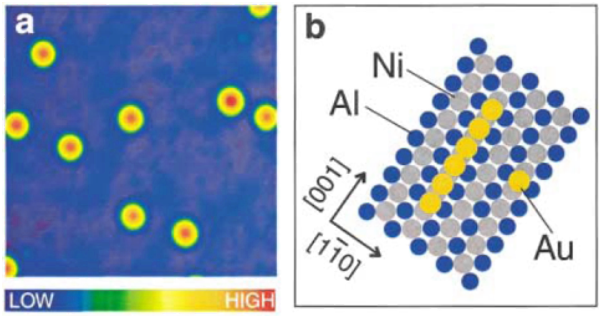
Non-Fermi liquid, Charge-spin decoupling

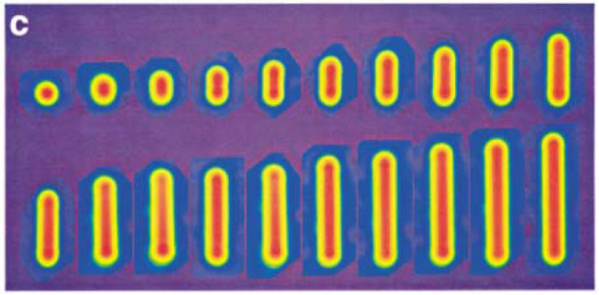
Fabrications of Metal Atom Wires

Mechanical break junctions

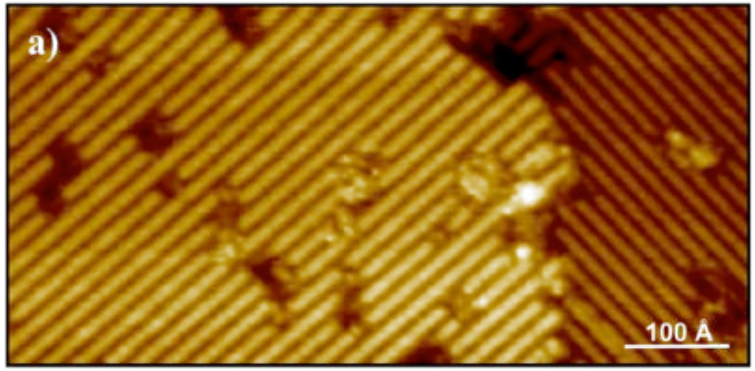


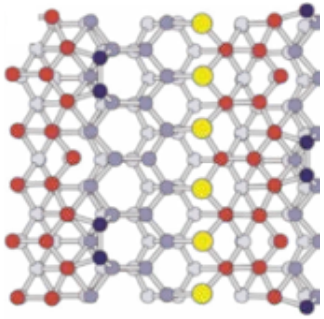
Manipulation by SPM





Self-assembly on substrates



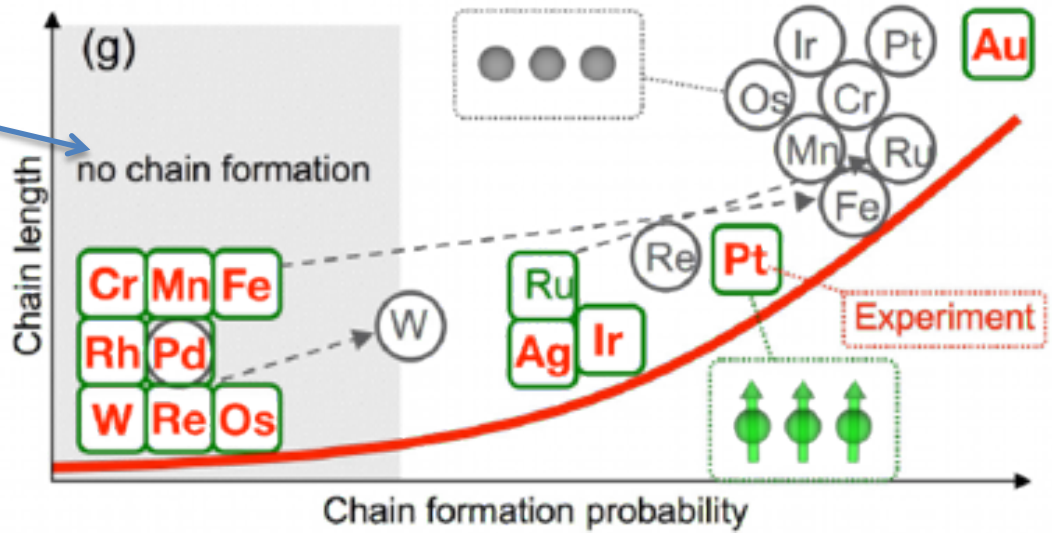


- Snijders, *et al*, RMP, **82**, 307(2010),
- Nilus, *et al*, Science, **297**,1853 (2002)

Formation Mechanisms of Metal Atom Wires

Mechanical break junctions

The creation of magnetic moments crucially reduces the probability of successful chain formation, and causes softening of the binding energy of atomic chains.



sd competition caused by the relativistic effects

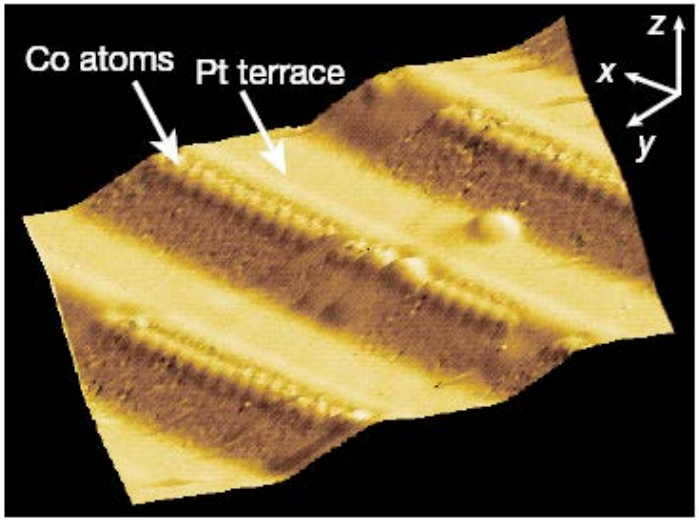
→ 5d metals prefer to form chains

- Bahn, *et al*, Phys. Rev. Lett, **87**, 266101 (2001)
- Smit, *et al*, Phys. Rev. Lett, **87**, 266102 (2001)
- Thiess, *et al,* Phys. Rev. Lett, **103**, 217201(2009)

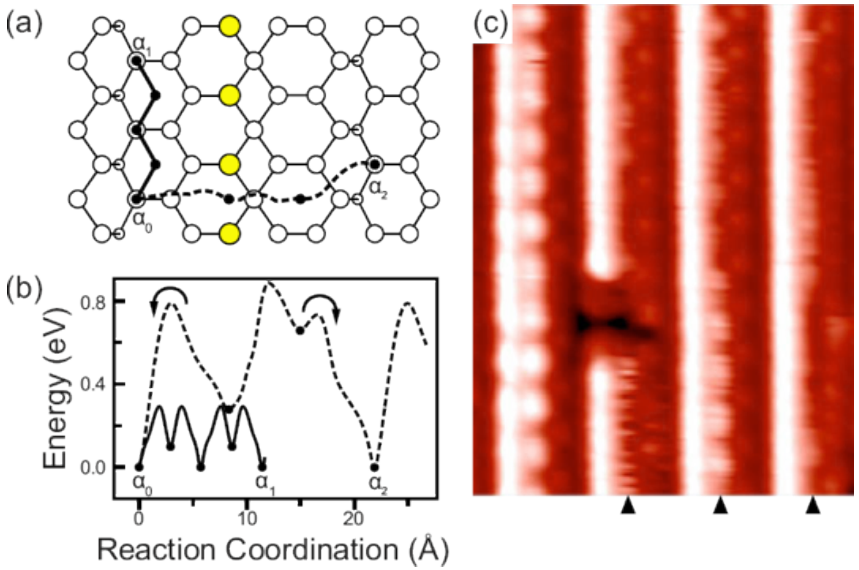
Formation Mechanisms of Metal Atom Wires

Self-Assembly

Co on Pt(111)



In on Si(553)-Au



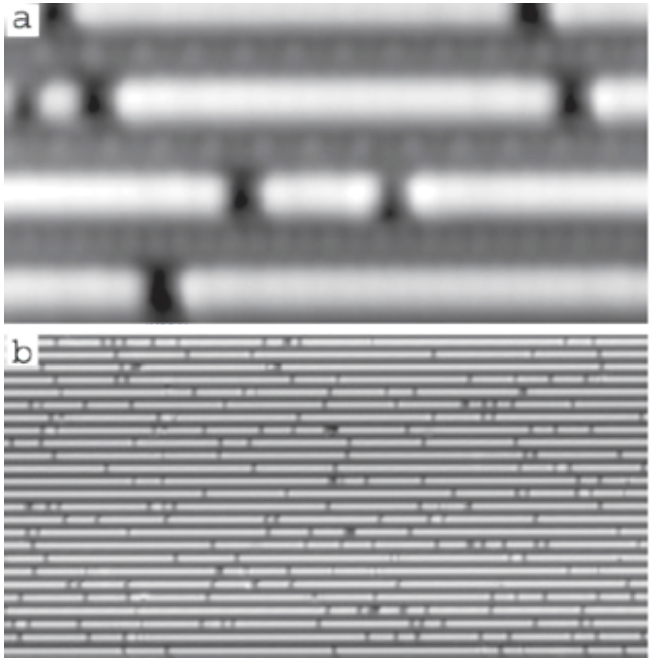
Anisotropic surfaces as growth templates: The microscopic mechanism of the templated self-assembly is due to well-aligned preferential adsorption sites and the strongly anisotropic surface diffusion.

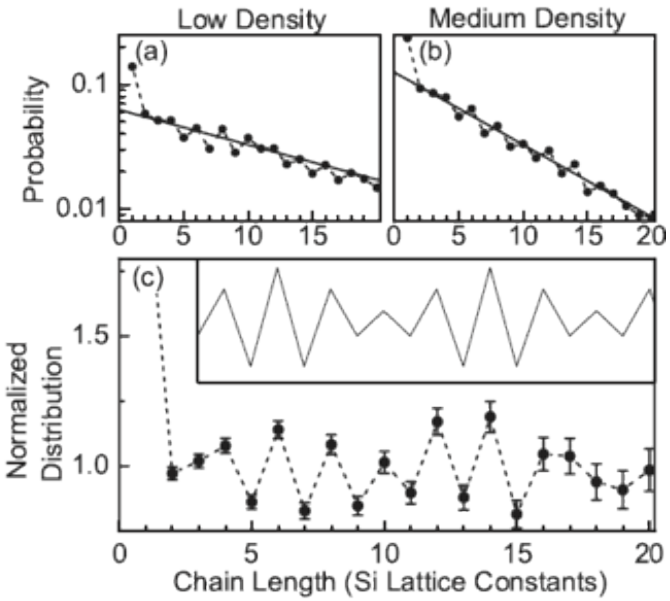
- Oncel, *et al*, J. Phys.: Condens.Matter, **20**, 393001 (2008)
- Kang, *et al*, Phys. Rev. B, **79**, 113403 (2009)
- Gambardella, *et al*, Nature, **416**, 301 (2002)

Size Distribution of Atom Wires

Au on Si(553)

- Crain, *et al*, Phys. Rev. Lett, **96**,156801(2006)



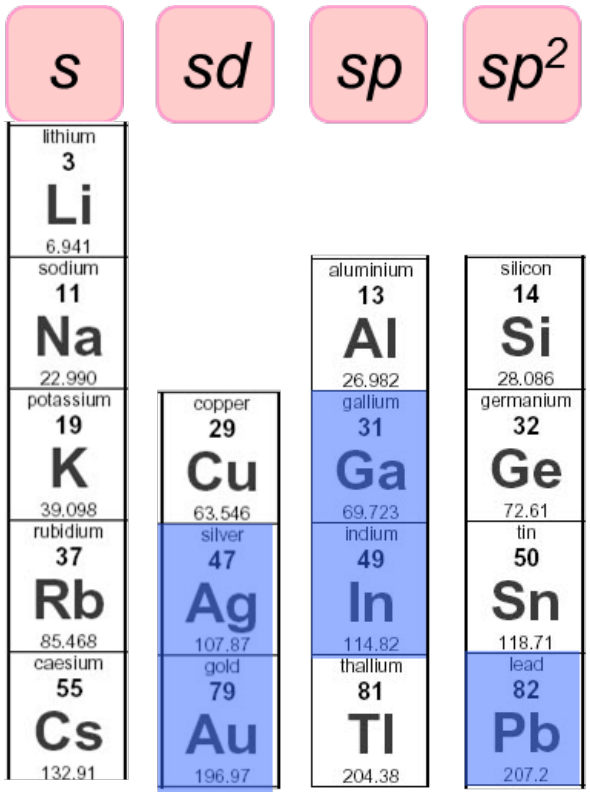


Gold deposited on Si(553) leads to self-assembly of atomic chains, which are broken into finite segments by defects.

STM study provides the distribution of chain lengths and the correlation between defects that separate the chains. The length distribution reveals oscillations, indicating changes in the cohesive energy as a function of chain length.

Even-odd oscillation up to 16 atoms

Representative Systems & Calculation Settings

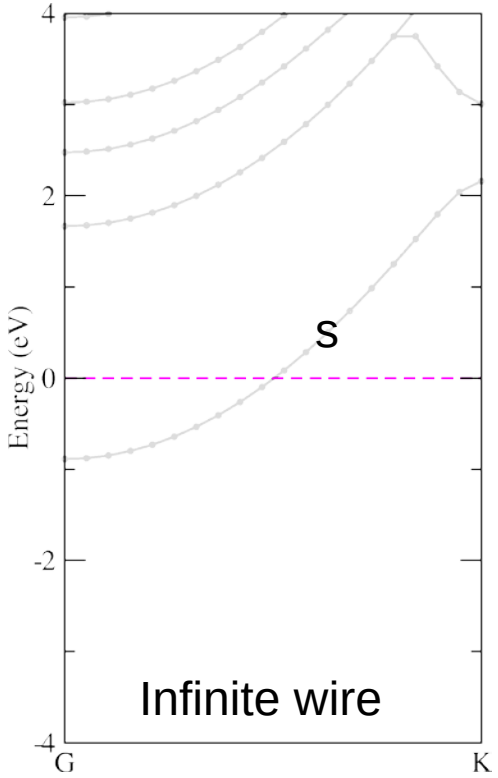


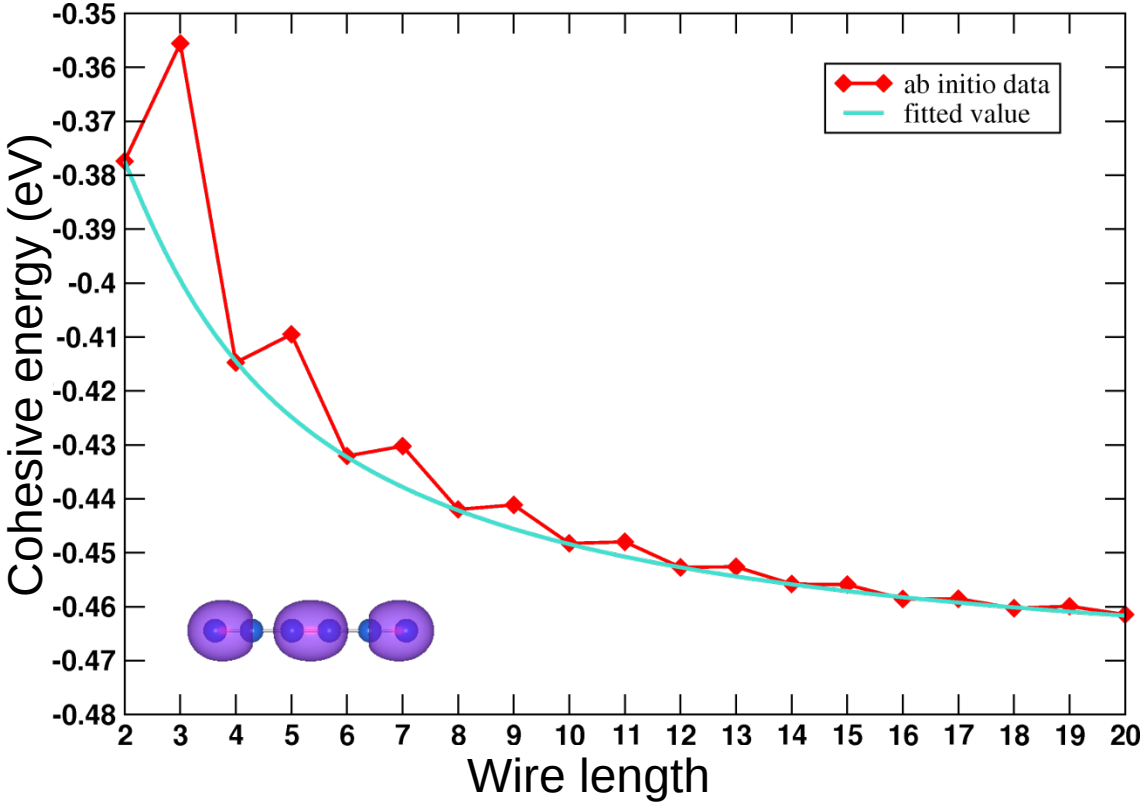
- Up to 20 atoms

- VASP (Vienna Ab-initio Simulation Package)
- DFT
- PAW
- PBE
- Images separation > 10.0 Å
- CG scheme for relaxation
- Residual force < 0.01 eV/Å
- Cohesive energy:

$$E_c(n)=(E_{wire}(n)-n\bullet E_{atom})/n$$

s electron system - Na ($3s^1$) atom wires

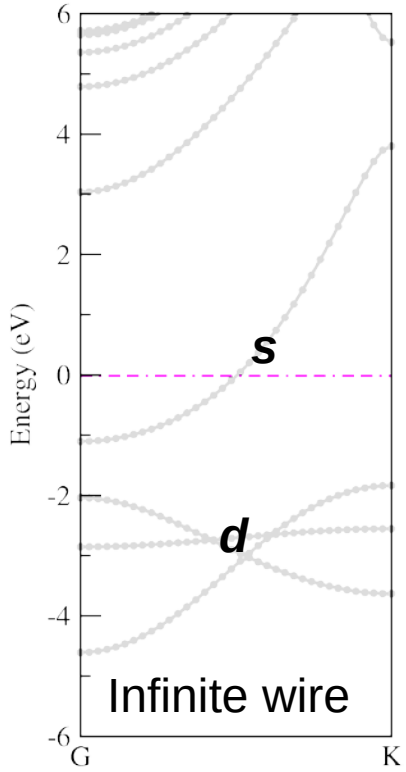


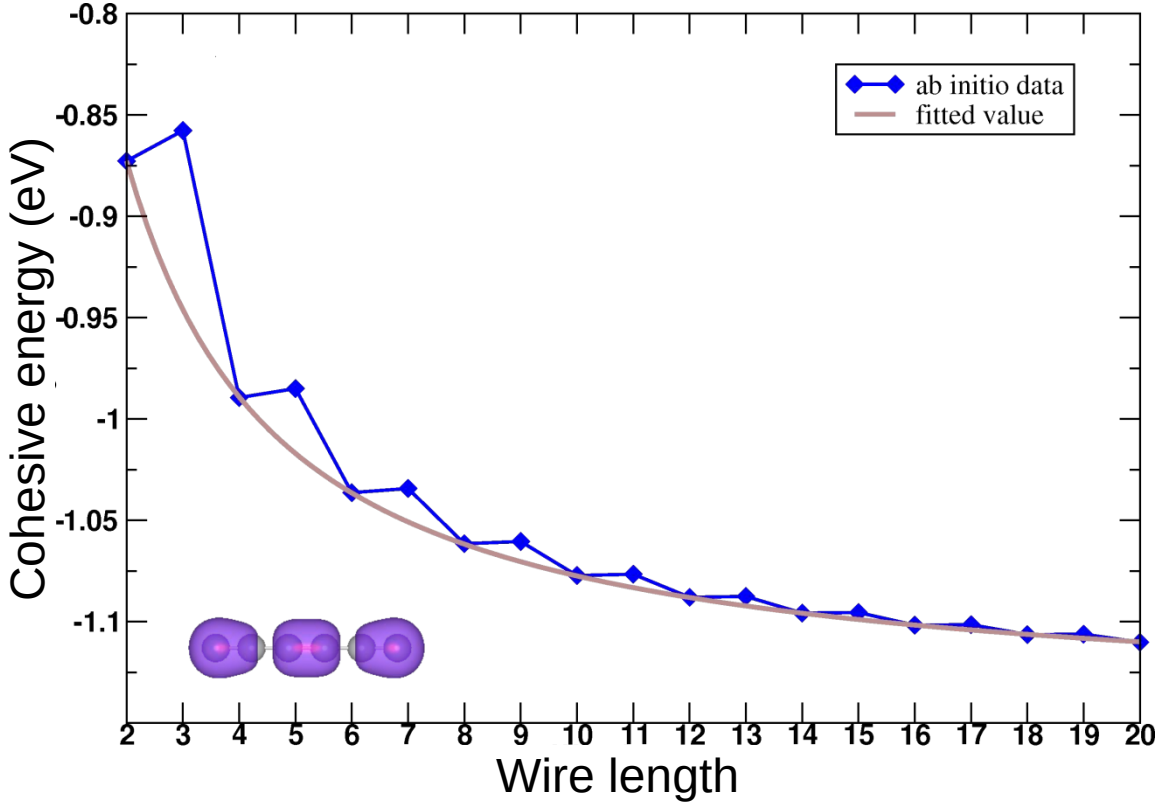


Electrons pairing up → Even-odd oscillation

1-D confinement → *1/r* nature

sd electron system – Ag ($4d^{10}.5s^{1}$) atom wires

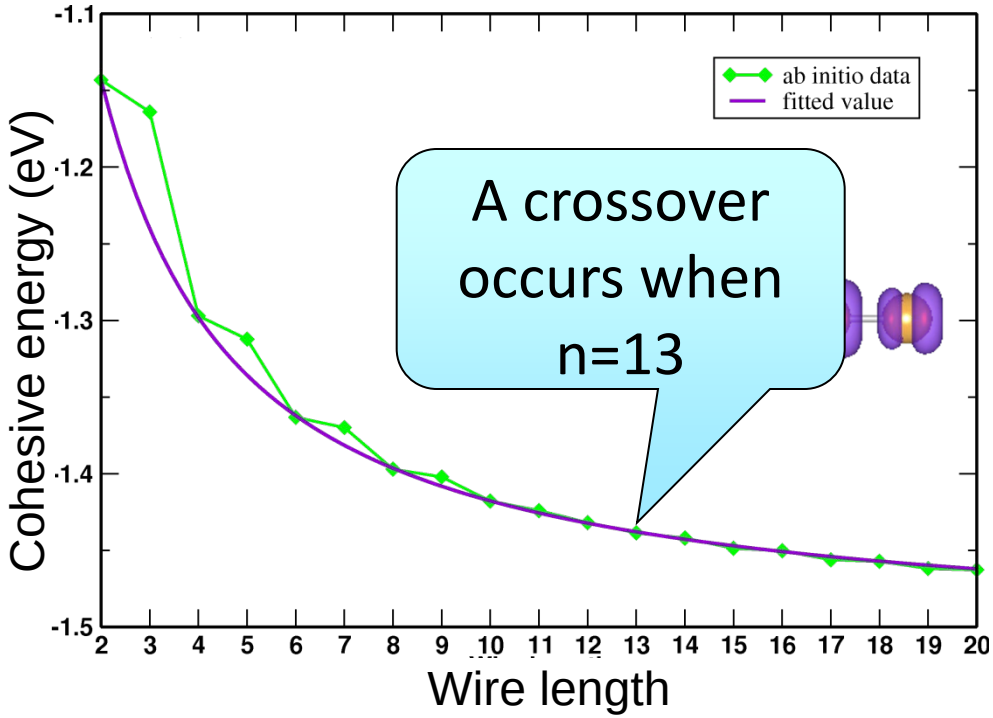




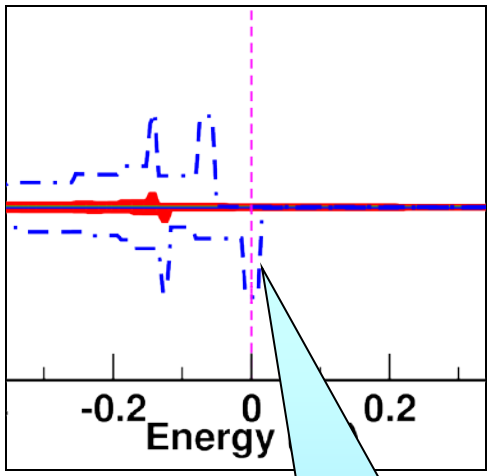
The same behavior as Na wires

sd hybridization → *Larger* cohesive energy

sd electron system - Au ($5d^{10}.6s^{1}$) atom wires



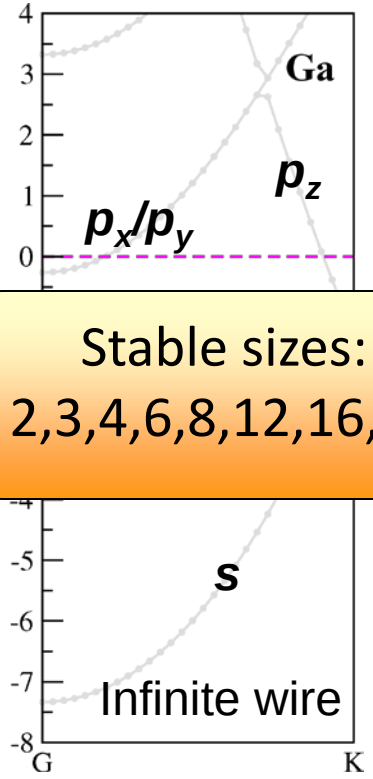
Infinite wire



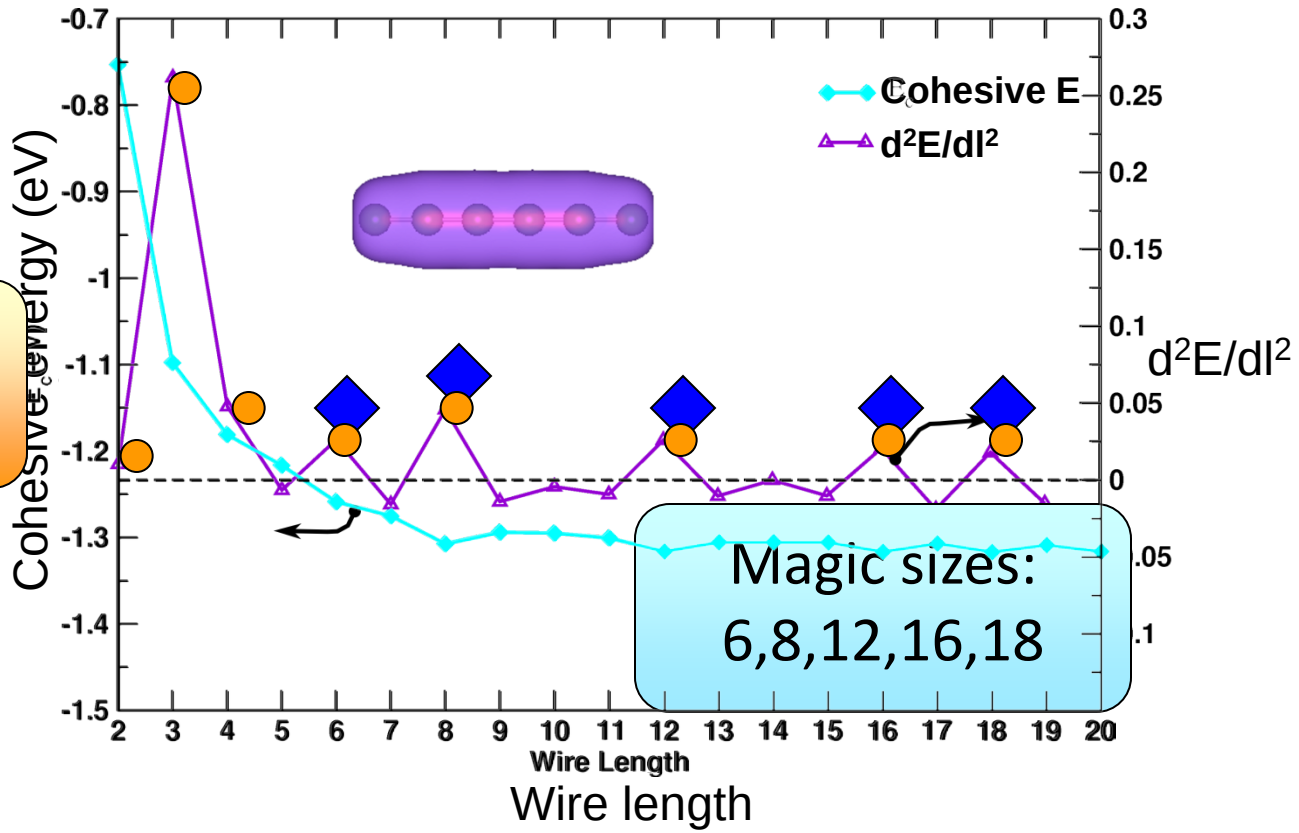
Stoner instability
Magnetic moment

Relativistic effect → A bit large oscillation

sp electron system - Ga ($4s^2.4p^1$) atom wires



Stable sizes:
2,3,4,6,8,12,16,18

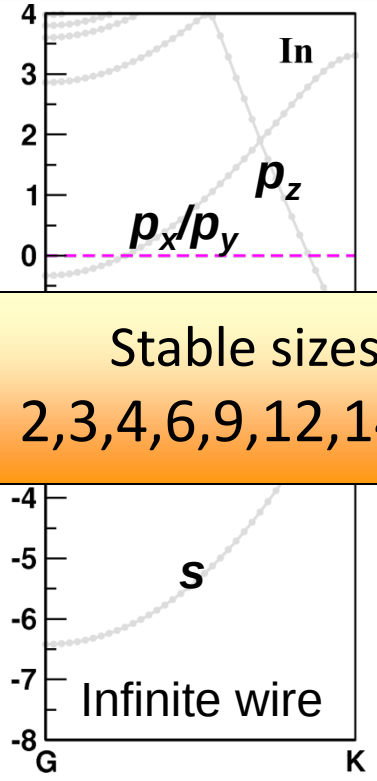


Magic sizes:
6,8,12,16,18

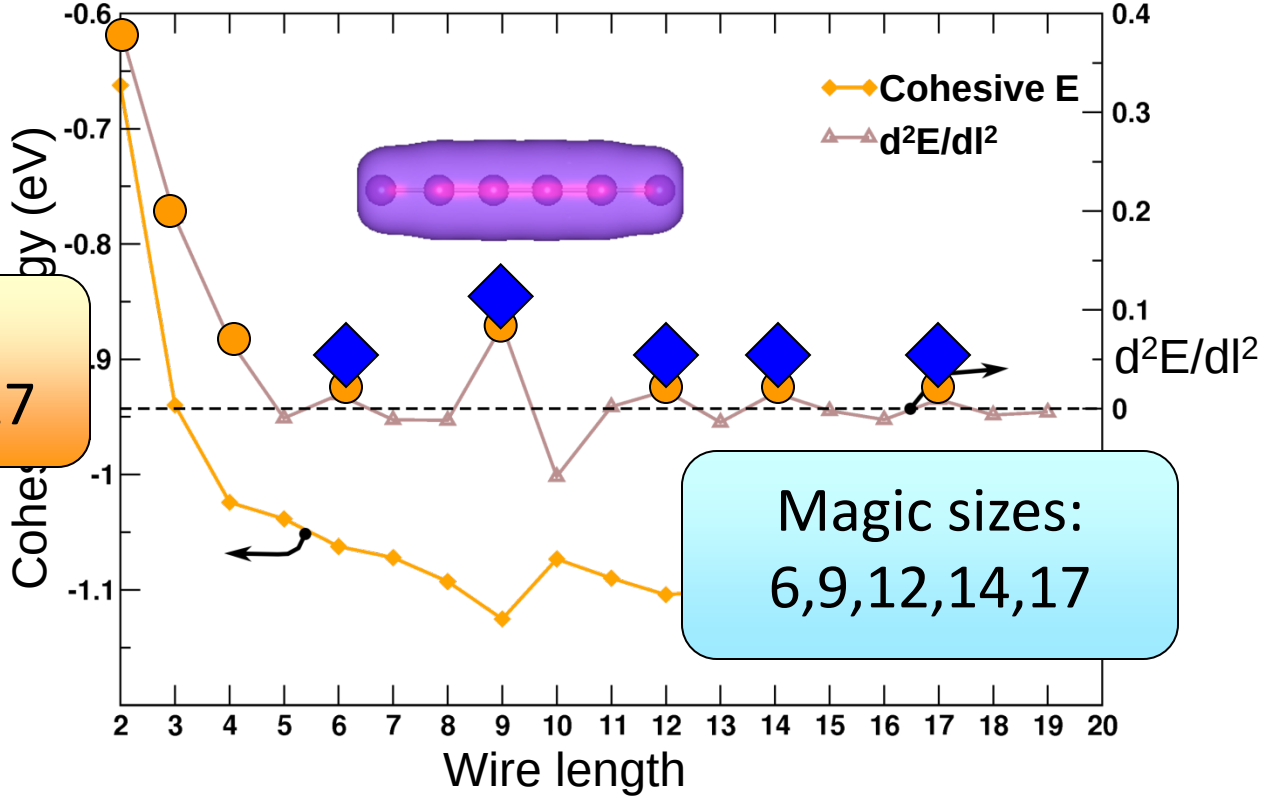
Little *sp* hybridization → Only *p* electron contributes binding

An oscillation beyond the even-odd pattern

sp electron system - In ($5s^2.5p^1$) atom wires



Stable sizes:
2,3,4,6,9,12,14,17

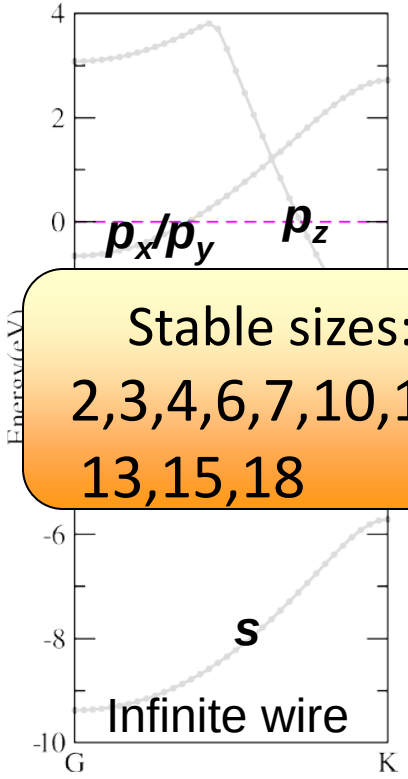


Magic sizes:
6,9,12,14,17

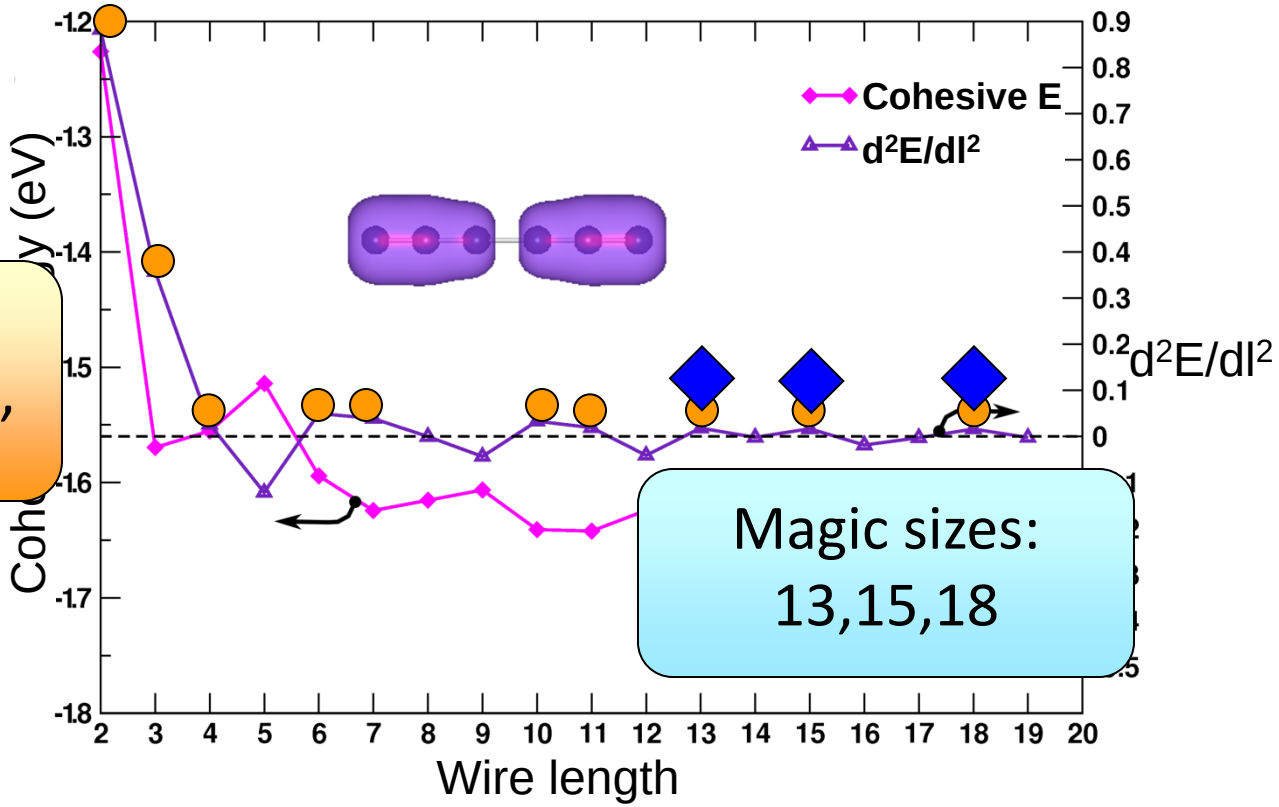
A similar behavior as Ga wires

Distinction between Ga and In ⟸ Nuclei radius

sp^2 electron system - Pb ($6s^2.6p^2$) atom wires



Stable sizes:
2,3,4,6,7,10,11,
13,15,18



Magic sizes:
13,15,18

Little *sp* hybridization → Only *p* electrons contribute to binding

Conclusions

Electronic nature of freestanding atom wires' stability

Cohesive energy versus wire length indicates the existence of preferred (or magic) lengths, but with different characteristics.

- ***s*-electron system – Na, K**: even-odd oscillation

  consecutive fillings of the ***s*** electrons in the quantum well states

- ***sd*-electron system – Ag, Au**: even-odd oscillation

  s states dominate due to the filled shells of the ***d*** states

- ***sp*-electron system – Ga, In**: complex oscillation

  minimal contributions of the filled ***s*** states and the dominance of the partially-filled ***p*** orbitals

Two Dimensional Metal System:

- A brief overview of quantum growth
- From precise structural control to property optimization

A Brief Review on

Quantum Stability of 2D Metal Overlayers

Zhenyu Zhang, Qian Niu, Chih-Kang Shih, PRL (1998)
Zhigang Suo and Zhenyu Zhang, PRB (1998)

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.

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Classical Growth Modes in Heteroepitaxy (A/B)

(Bauer, 1958)

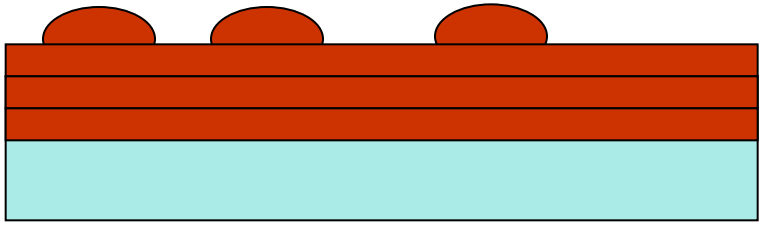
(a) 2D or layer-by-layer

(Frank - Van der Merwe)

$\Delta\gamma = \gamma_o + \gamma_i - \gamma_s < 0$

(b) 2D followed by 3D islanding

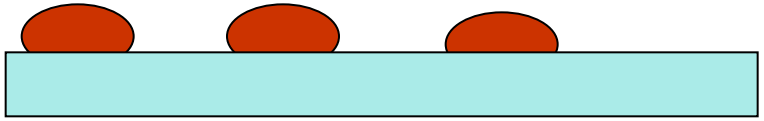
(Stranski - Krastanov)



$\Delta\gamma \sim 0$

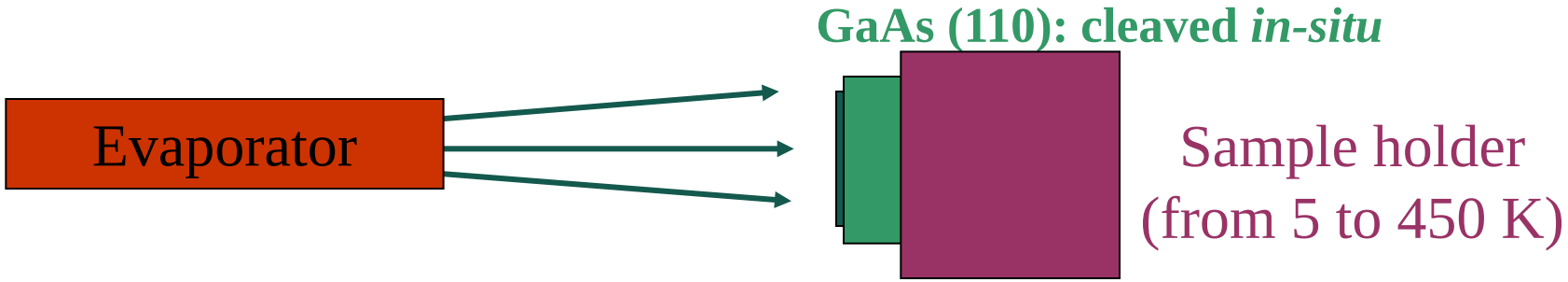
(c) 3D islanding

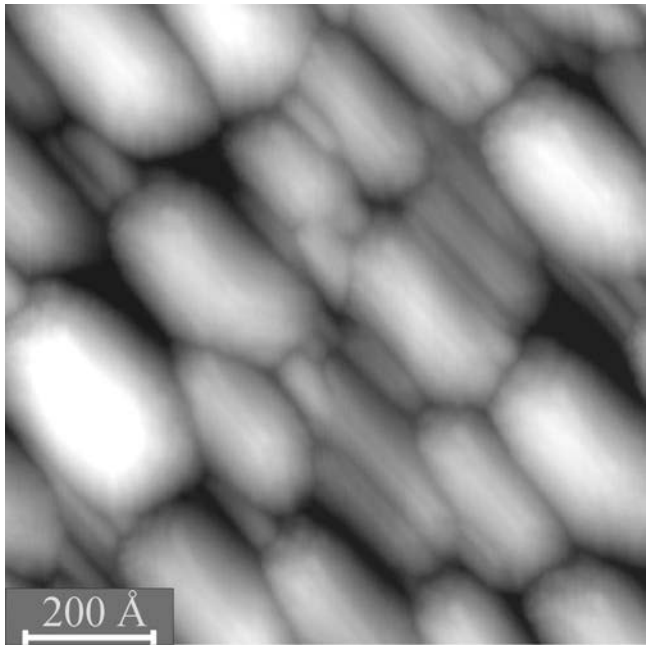
(Volmer - Weber)



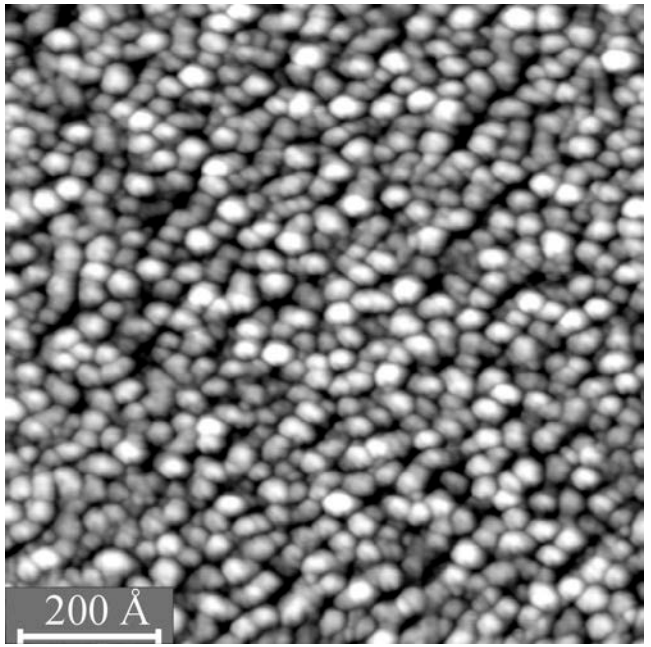
$\Delta\gamma > 0$

Ag/GaAs(110): A Prototype Nonwetting System





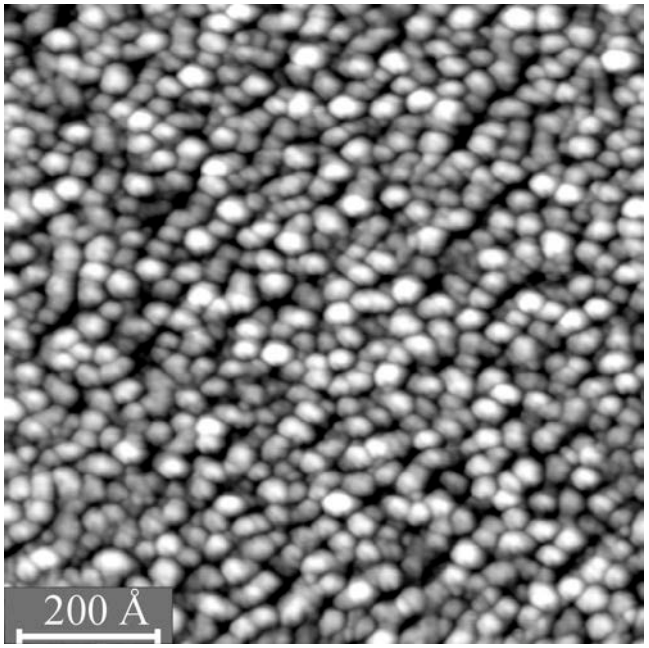
(1.5 nm deposition at 300 K)

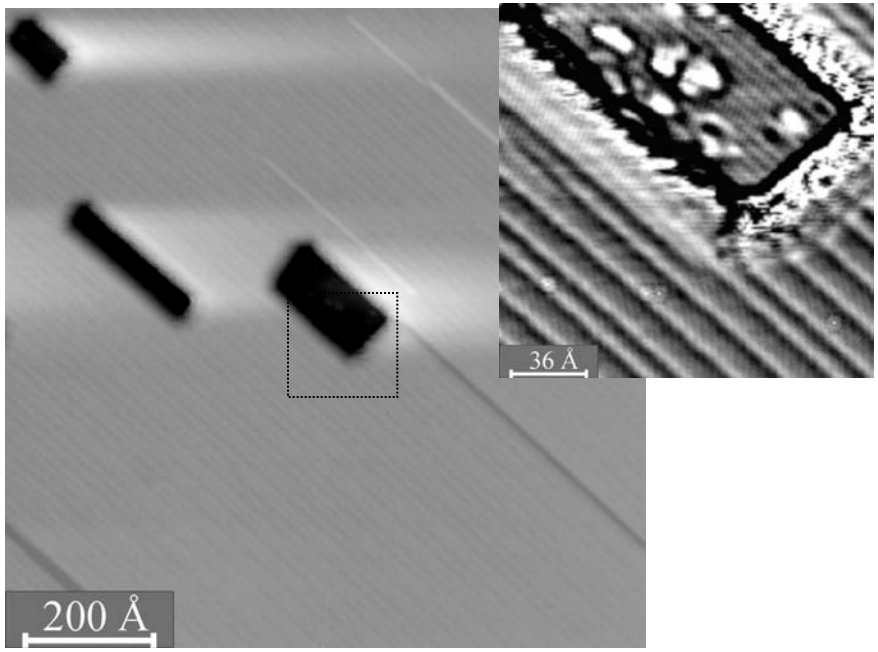


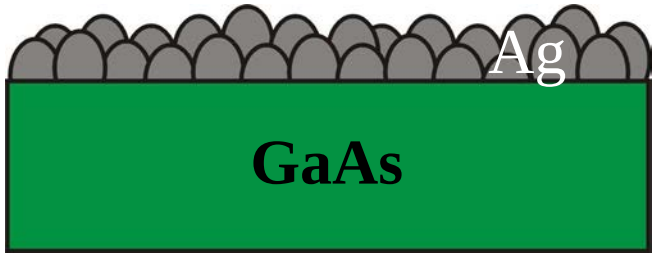
(1.5 nm deposition at 135 K)

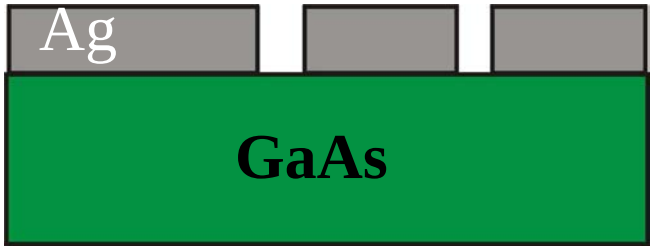
Formation of Atomically Flat Ag films Above h_c

(Smith, Chao, Niu, Shih, Science 273, 226 (1996))





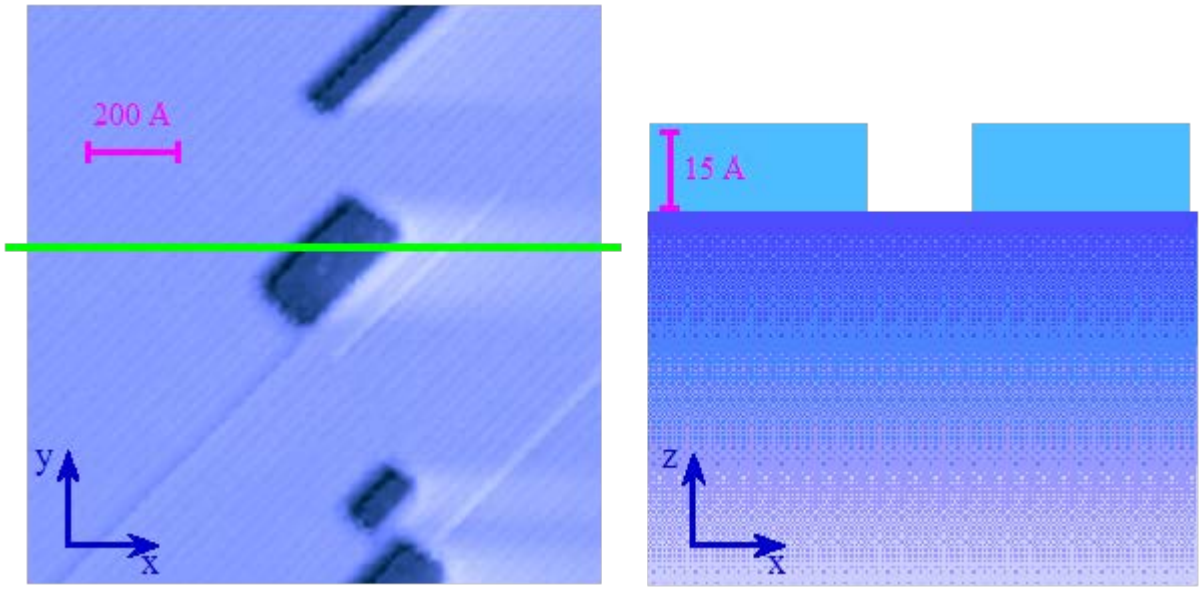




h_c = 6 ML

LT deposition ⟶ Annealing to RT

What Defines the Critical Thickness for Ag Growth on GaAs(110)?

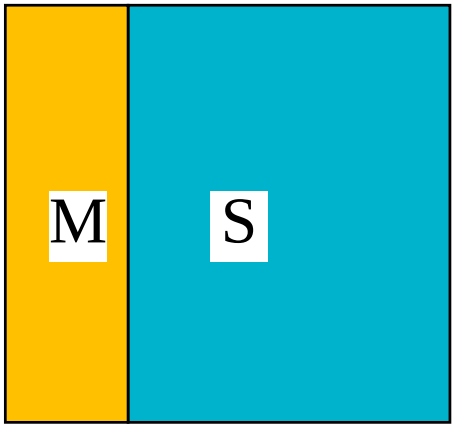


♦ Individual atomistic mechanisms are insufficient to explain this phenomenon.

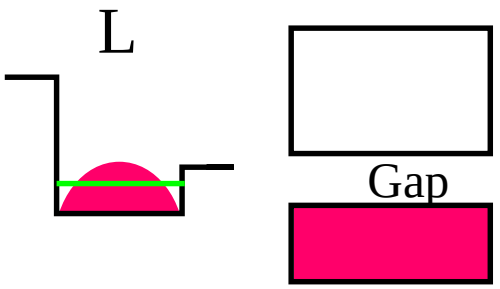
♦ Neither due to strain.

First Conjecture:

The critical thickness is defined by the confined motion of the conduction electrons in the metallic overlayer.



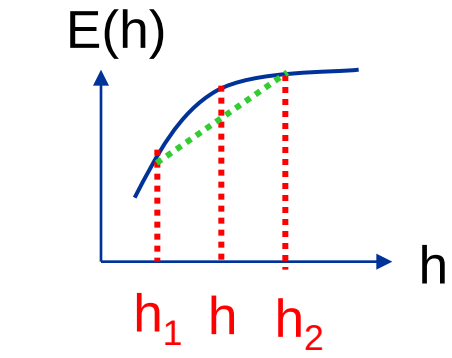
From any Q.M. textbook:

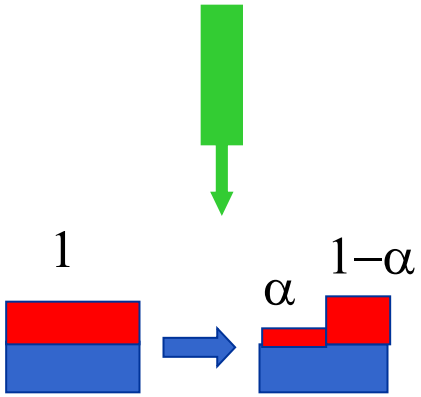


Exist the 1st bound state if $L > L_c$

Generic Guideline (Mechanics 101)

Stability analysis of flat films with increasing thickness





$E(h) > \alpha E(h_1) + (1-\alpha) E(h_2)$
ALWAYS!

Unstable at any h
{E”(h) < 0}

Stable at any h
{E”(h) > 0}

Critical thickness

h_c

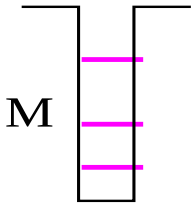
Magic thickness

h_m

Electronic Stability of Ultrathin Ag/GaAs(110)

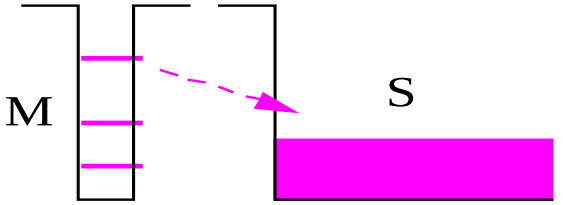
(Zhang, Niu, Shih, PRL 80, 1026 (1998))

Quantum-Size Effects

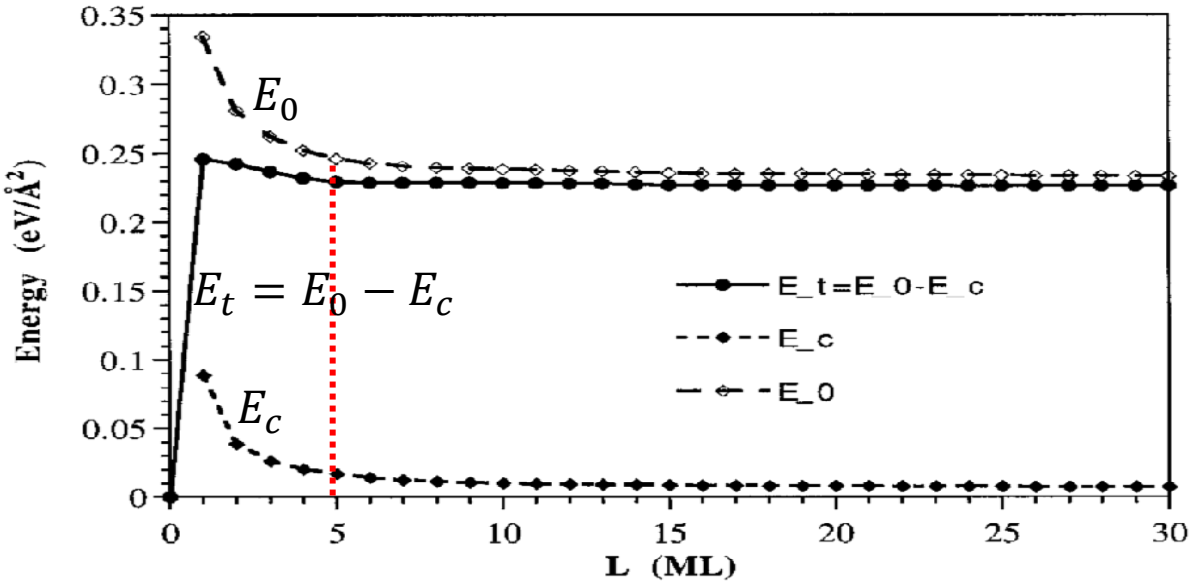


energy increase
due to confinement

Substrate Effects

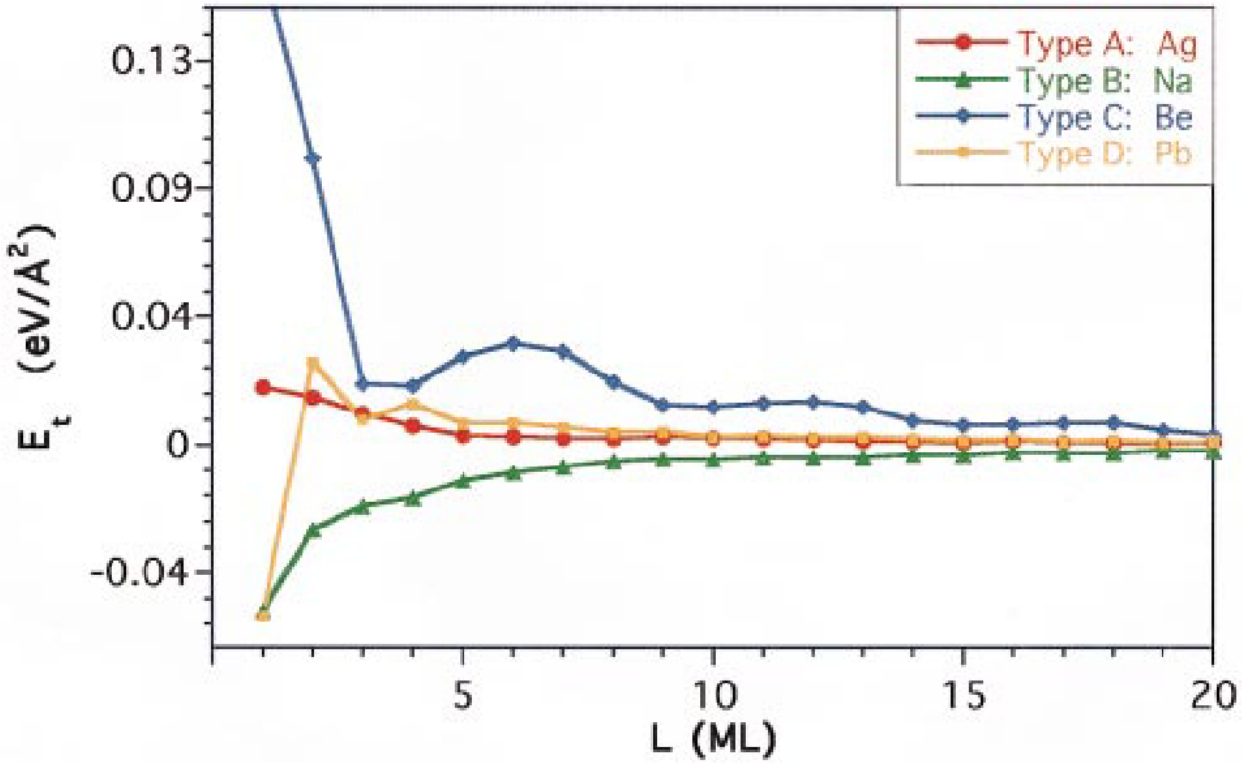


energy decrease
due to charge spill



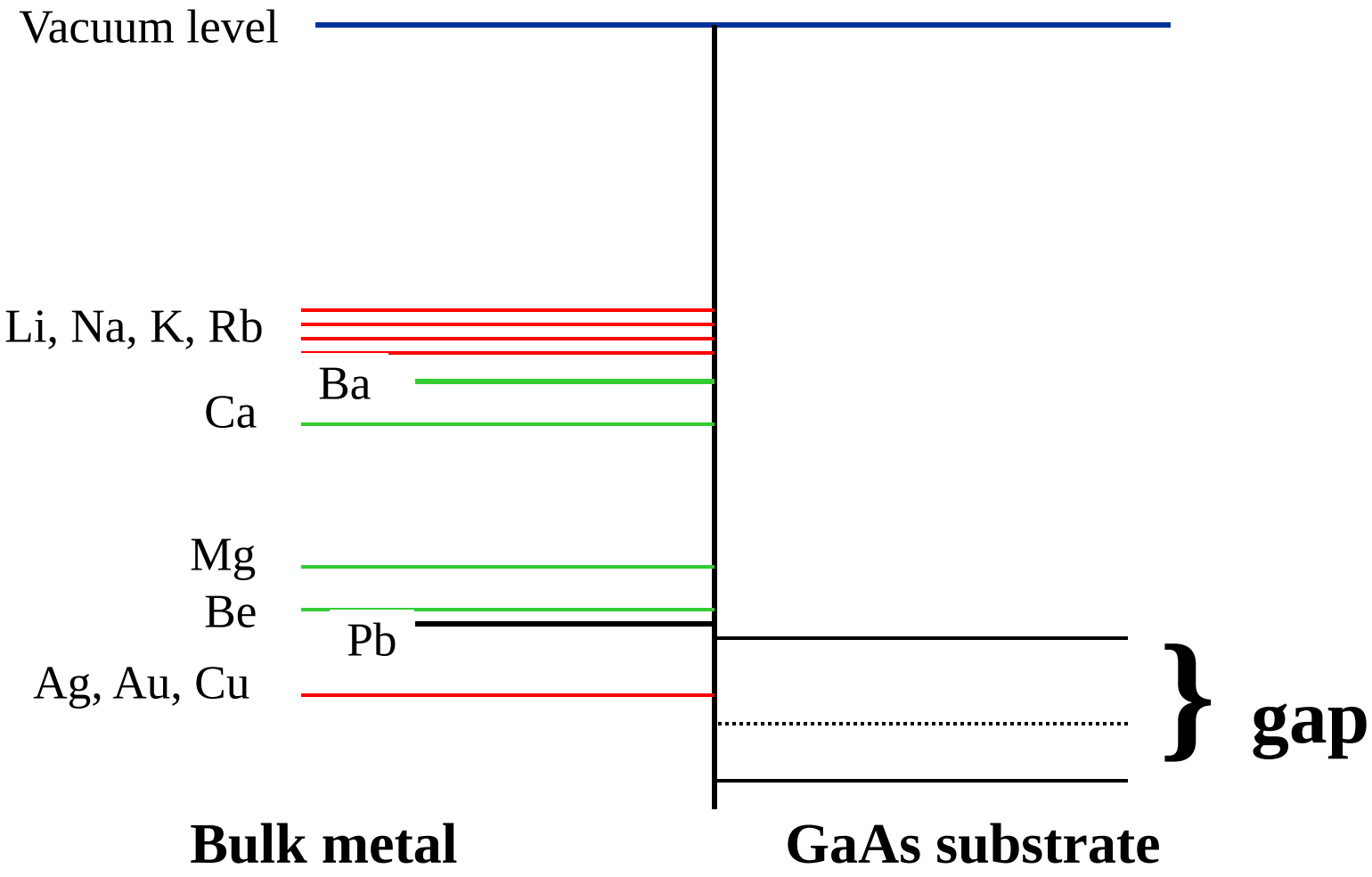
0th order model (electrons in a box)

Electronic Stability of Other Metals on GaAs(110)

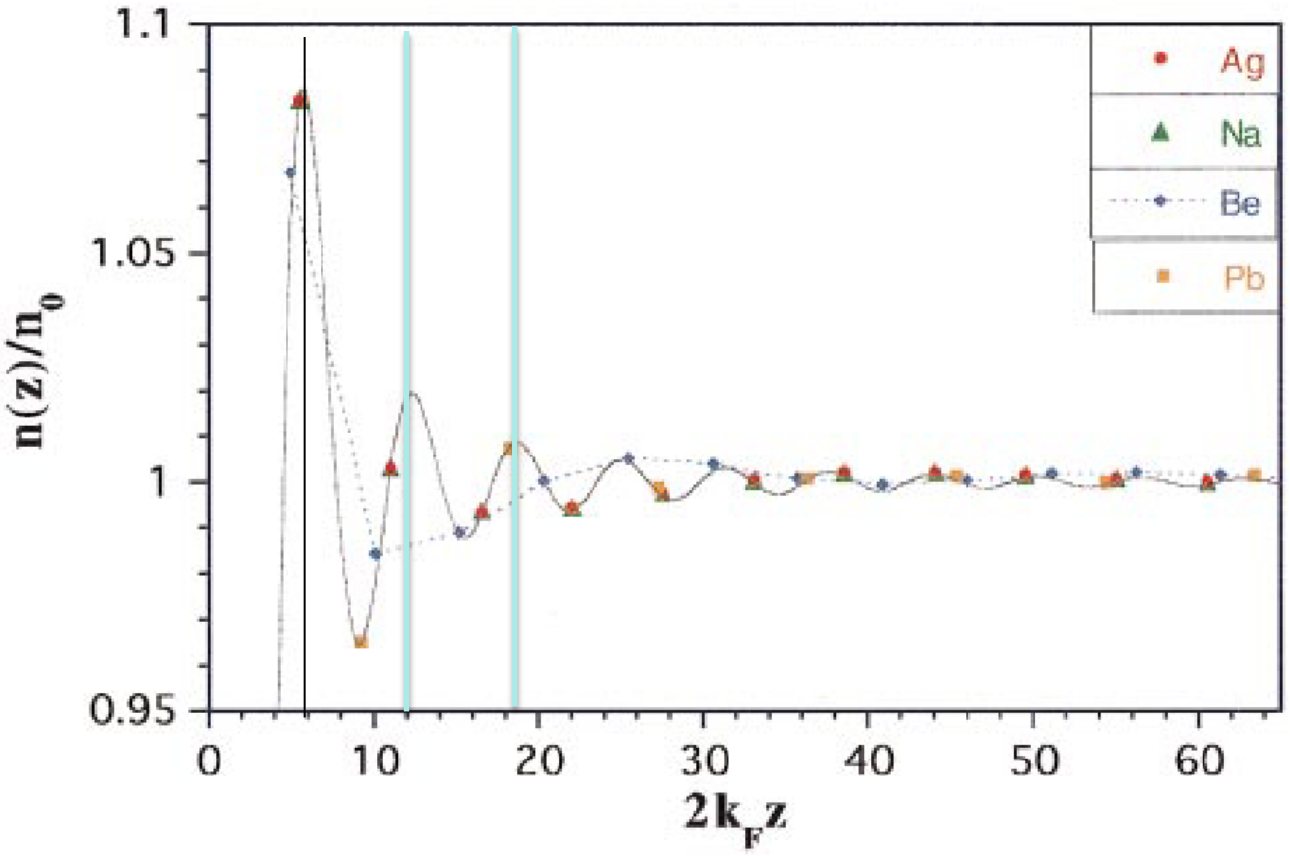


- Noble metals behave the same way if ignoring reactivity difference.
- Alkali metals behave qualitatively different.
- Multiple magic thicknesses for smooth growth of Pb & Be.

Why Noble Metals and Alkali Metals Behave So Differently?---Fermi Level Mismatch



Why Existing Magic Thickness?



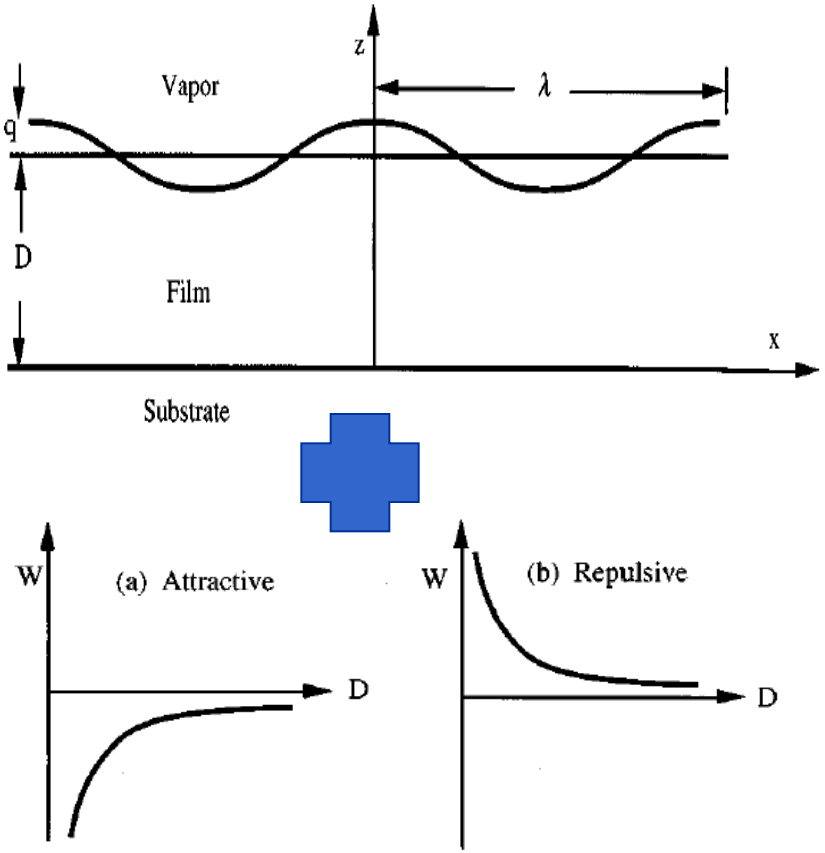
Magic thicknesses defined by commensurate length scales

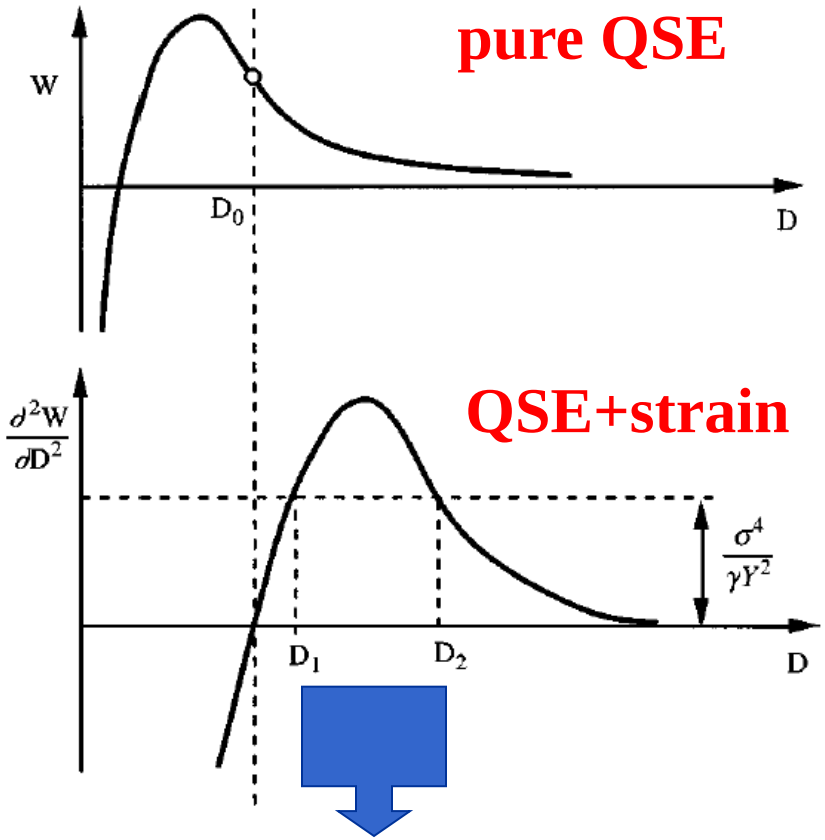
(wavelength for electron density oscillations

⟷ intrinsic interatomic layer spacing)

Quantum Size Effect (QSE) versus Strain

(Suo & Zhang, PRB 58, 5116 (1998))



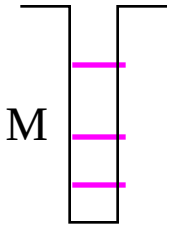


"Window of opportunity" for smooth growth

Electronic Growth: Conceptual Developments

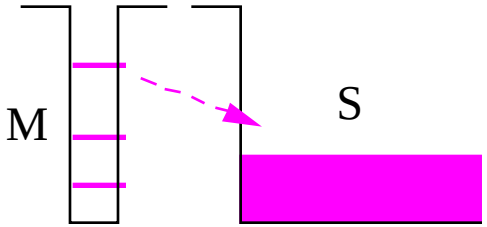
PRL 80, 1026 (’98); 80, 3582 (’98); 80, 5381 (‘98); PRB 58, 5116 (‘98)

Quantum-Size Effects



energy increase
due to confinement

Substrate Effects



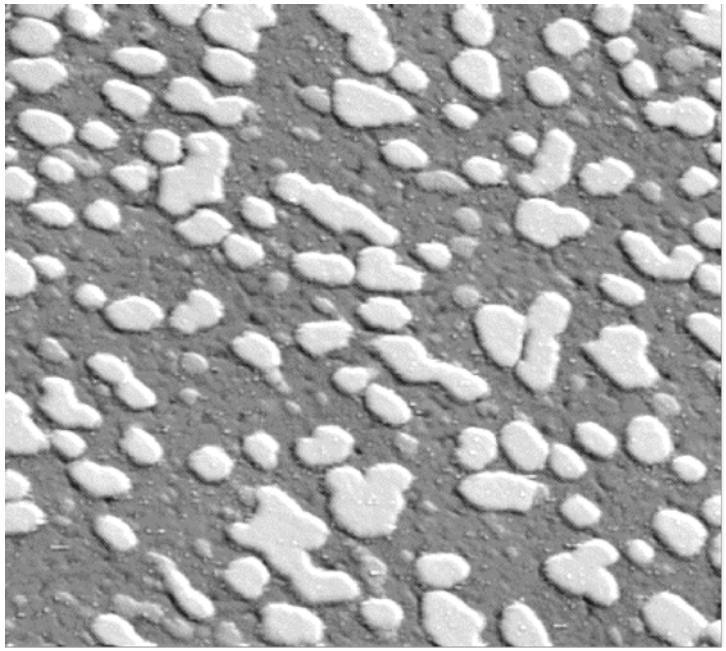
energy decrease
due to charge spill

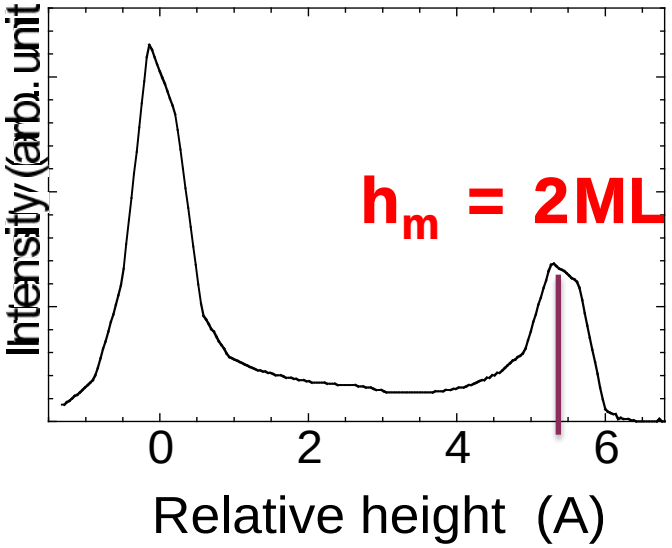
- Competition between quantum confinement and charge spilling leads to critical thickness for smooth growth.
- Commensuration between the standing wavelength and interlayer spacing determines the magic thickness (closed shells for 2D systems).
- In the ultrathin (quantum) regime, the electronic effects easily overwhelm the stress effects.
- 2D magic islands may be formed in the submonolayer regime.

Evidence for “Electronic Growth”

Formation of Quantum Platelets in Ag/Si(111)

Gavioli, Kimberlin, Tringides, Wendelken, Zhang, PRL (’99)





Low-T deposition, followed by annealing

Resistivity measurement: a bad metal out of a good conductor.

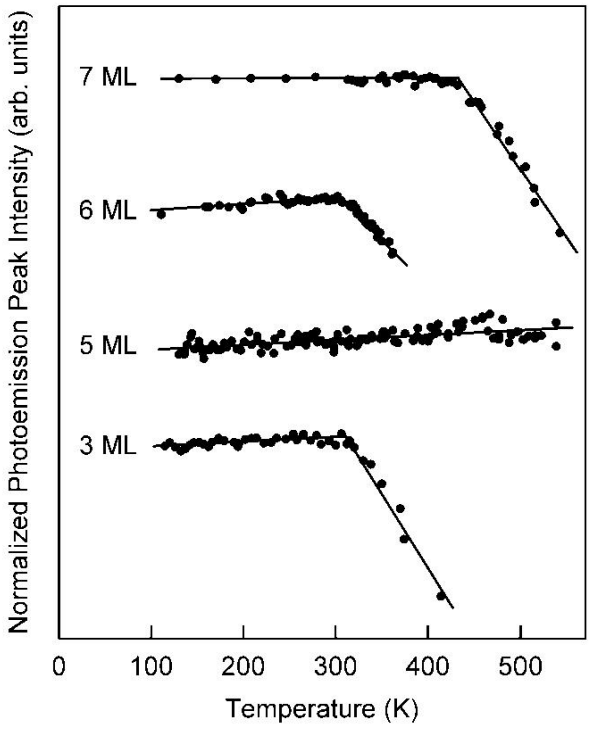
Evidence for “Electronic Growth”

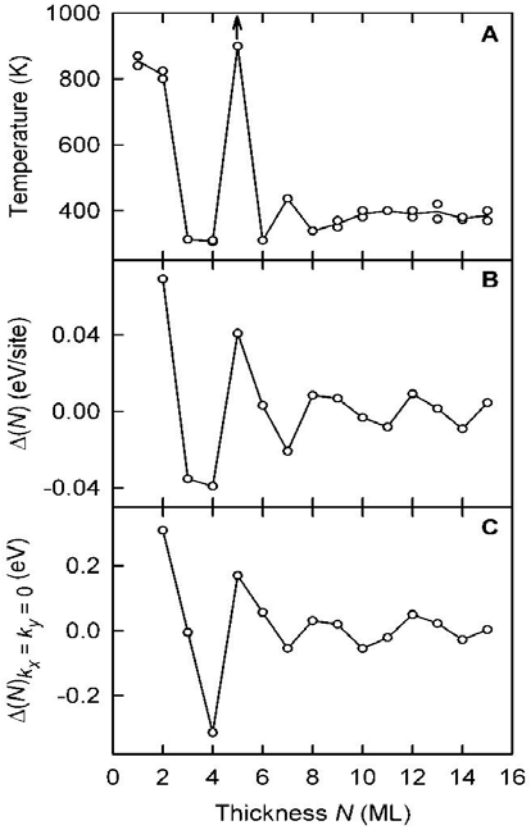
Quantum Electronic Stability of Atomically Uniform Films

Luh, Miller, Paggel, Chou, Chiang, Science (’01)

Ag-on-Fe(100):
A New Class of Systems

“Shell Structures”
Science (2001)



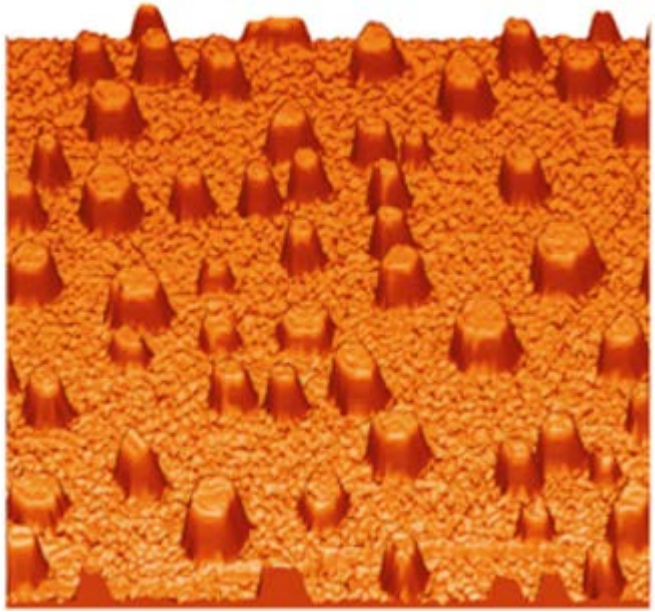


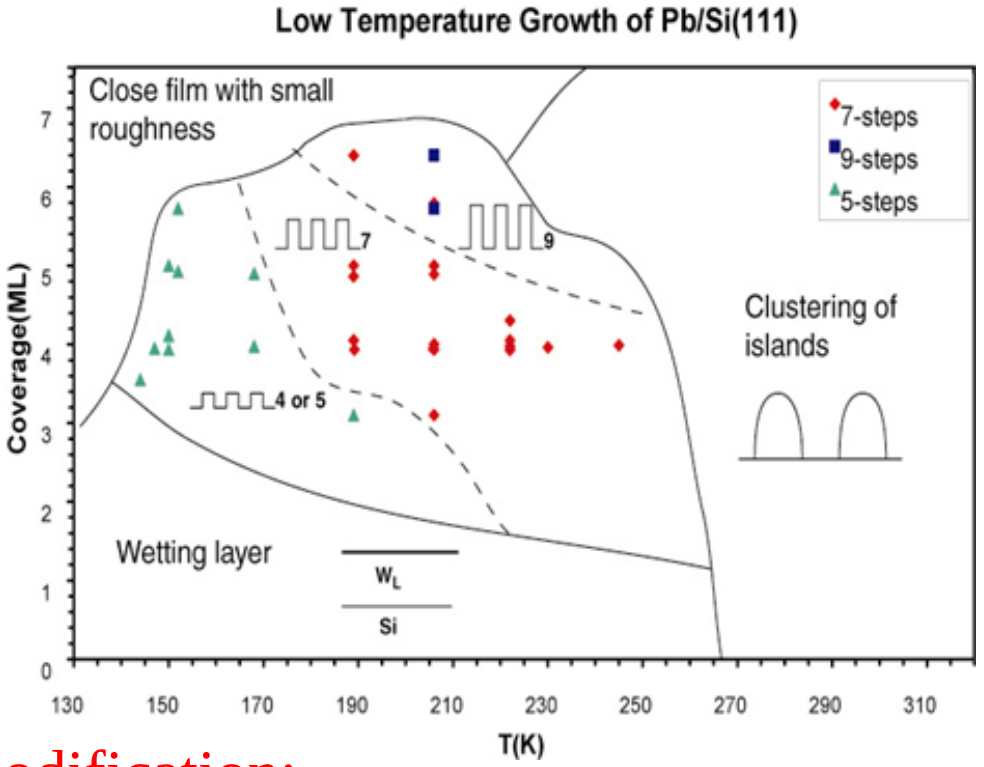
Film with h=5 ML too stable to be destroyed!

Validation of "Electronic Growth":

Thickness Tuning of Quantum Platelets in Pb/Si(111)

(Yeh, Berbil-Bautista, Wang, Ho, Tringides, PRL (2000))



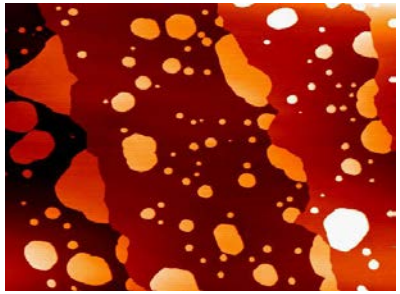


"7" ➡ "5" via interface modification:

Si(111)-(7x7) ➡ Si((111)-($\sqrt{3} \times \sqrt{3}$)Au.

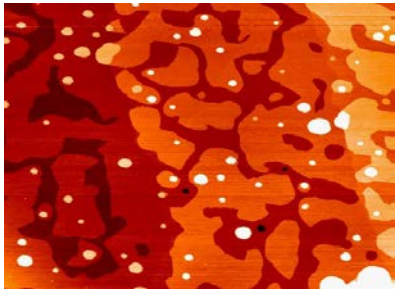
Bilayer-by-bilayer growth of Pb/Si(111)

5 & 7 ML



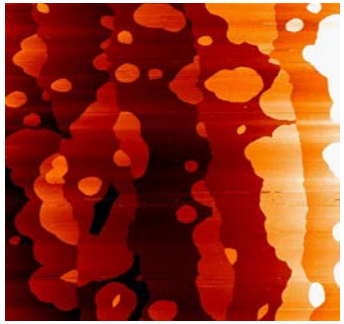
7 & 9 ML

9 & 11 ML

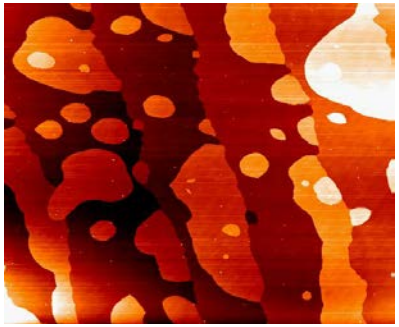


13 & 14 ML

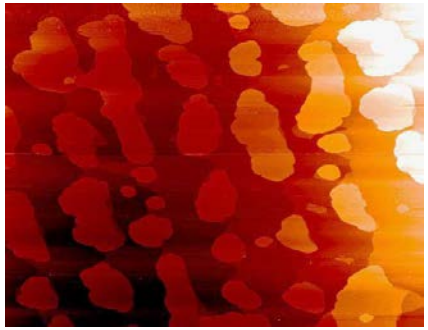
16 &18 ML



18 & 20 ML



20 & 22 ML



22 & 25 ML

(Ozer, Jia, Wu, Zhang, & Weitering, *PRB* 72, 113409,2005)

Stable layers: 4-5-7-9-11-13-14-16-18-20-22…25 ML

QSE: "Beating Effect"

$$E_s = A\frac{\cos[2k_f(N+\Delta N)t_0]}{(N+\Delta N)^{\alpha}} + B$$

$$E_{lattice} = A_0\cos(2k_{BZ}t_0 + \varphi)$$

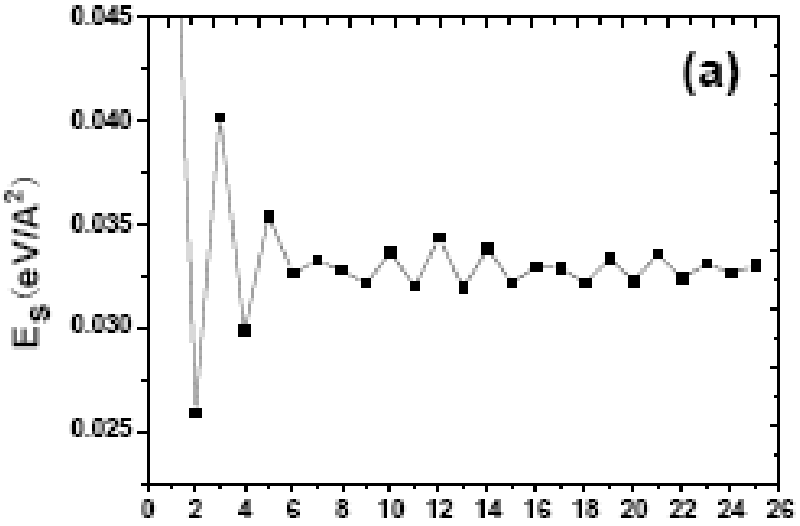


FIG. 5: (a) Surface energies of free standing Pb films.

$$k_f = 1.59A^{-1}; t_0 = 2.84A$$

$$k_{BZ} = \frac{\pi}{t_0}$$

$$2.07 \times t_0 = 3 \times \frac{\lambda_f}{2}$$

slight mismatch

$$\lambda_{beating} = \frac{\pi}{3k_{BZ} - 2k_f}$$

$$\lambda_{beating} = 9.6ML$$

$$with \quad k_f \uparrow, \quad \lambda_{beating} \uparrow$$

Quantum Tuning of Functional Properties

- **Philosophy:**

  Film thickness L => density of states $\rho(E_F)$
  => many properties

- **Examples of properties:**

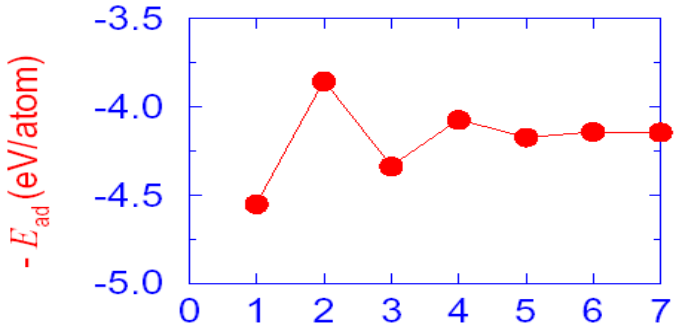
  - lattice relaxation
  - work function
  - ***electrical conductivity***
  - superconductivity
  - adatom diffusivity
  - chemical reaction rates
  - electronic friction/quantum tribology
  - ...

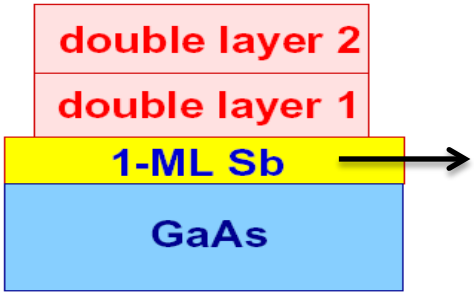
Sb/GaAs(110): From Structures to Transport

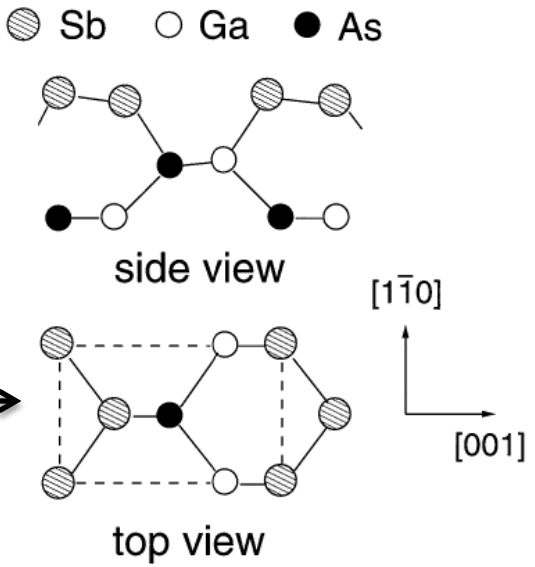
(Cho, Niu, Zhang, PRL 80, 3582 (1998); & Physical Review Focus)

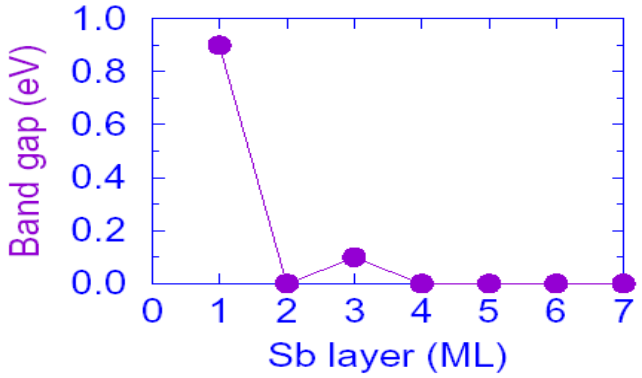
Signature for quantum-size growth

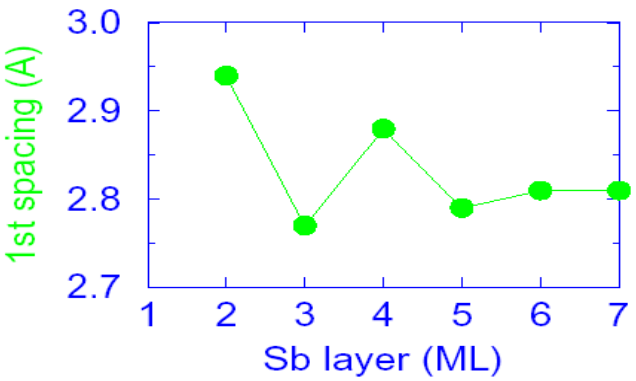
$$E_{ad} = [E(\theta_{Sb} = n - 1\ ML) - E(\theta_{Sb} = n\ ML) + 4E_{a,Sb}]/4$$







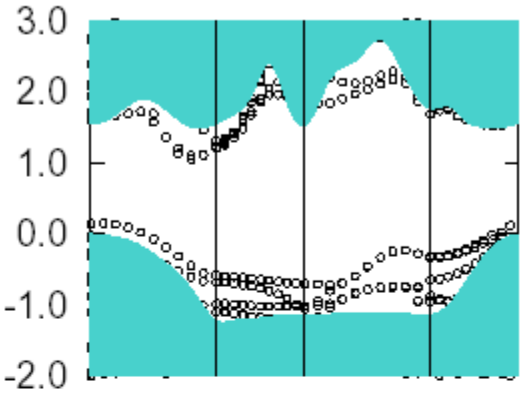




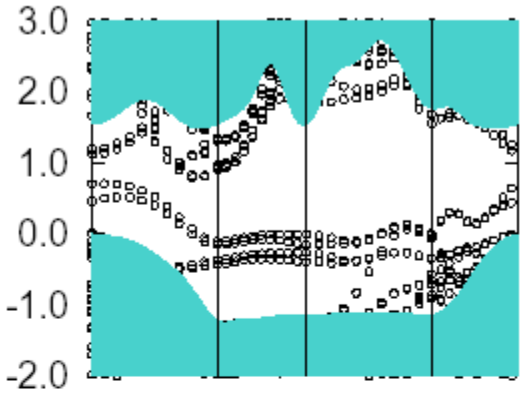
	d_{01}
1 ML	2.39
2 ML	2.54
3 ML	2.41
4 ML	2.44
5 ML	2.43
6 ML	2.44
7 ML	2.43

Sb/GaAs(110): Gap Evolution

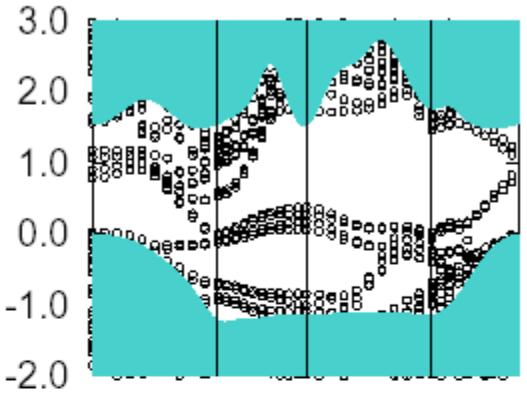
1 ML



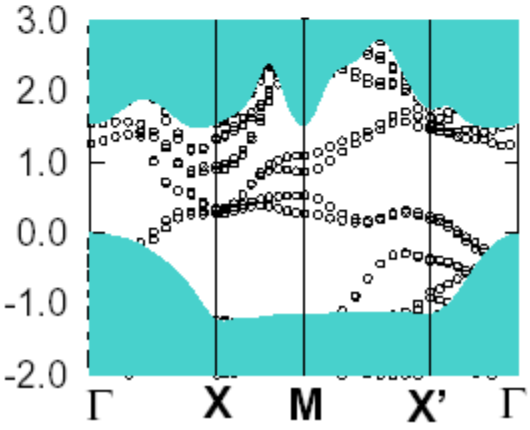
3 ML



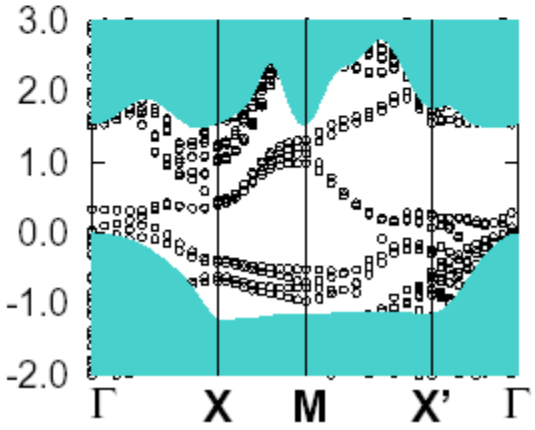
5 ML

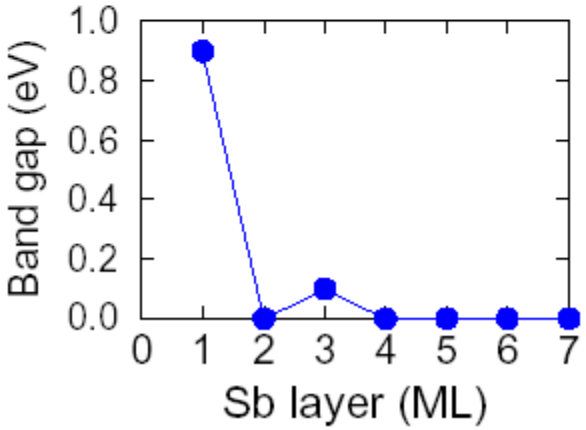


2 ML



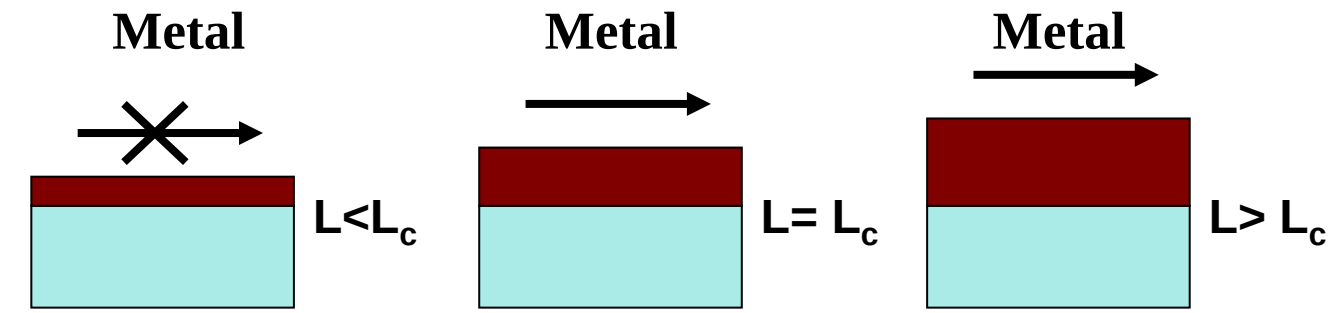
4 ML



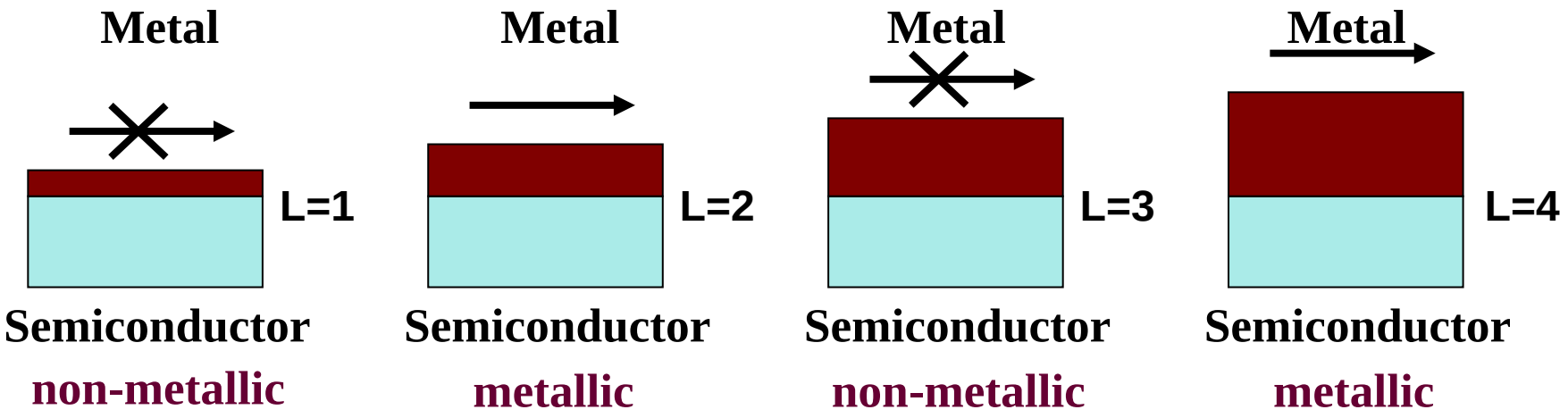


Oscillatory Nonmetal-Metal Transitions

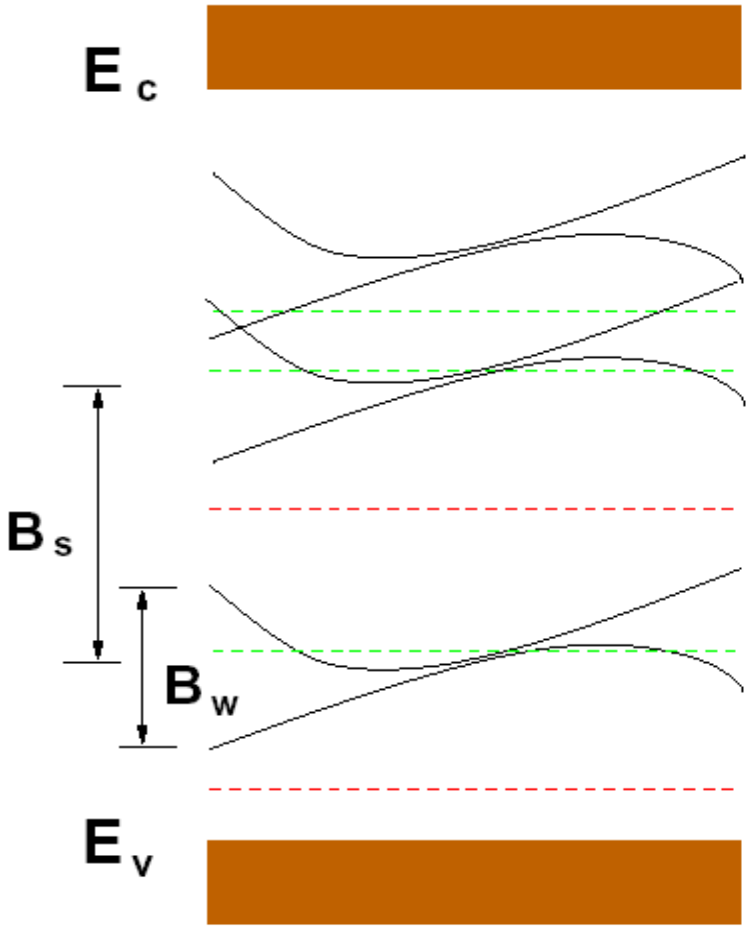
Traditional Belief:



New Finding:



Schematic diagram of oscillatory NM-M transitions



Above L_c = 5 ML
band gap disappearance
($B_w > B_s$)

5 ML (N = 8) : metallic
4 ML (N = 6) : metallic
3 ML (N = 4) : nonmetallic
2 ML (N = 2) : metallic
1 ML (N = 0) : nonmetallic

- The adsorption energy per layer oscillates with the overlayer thickness, making stable flat films at 1, 3, and 5 ML coverages.
- For films at different thicknesses, there exist strong oscillations in the topmost interlayer spacings.
- There are oscillatory nonmetal-metal transitions as the film thickness increases.

Quantum Tuning of Functional Properties

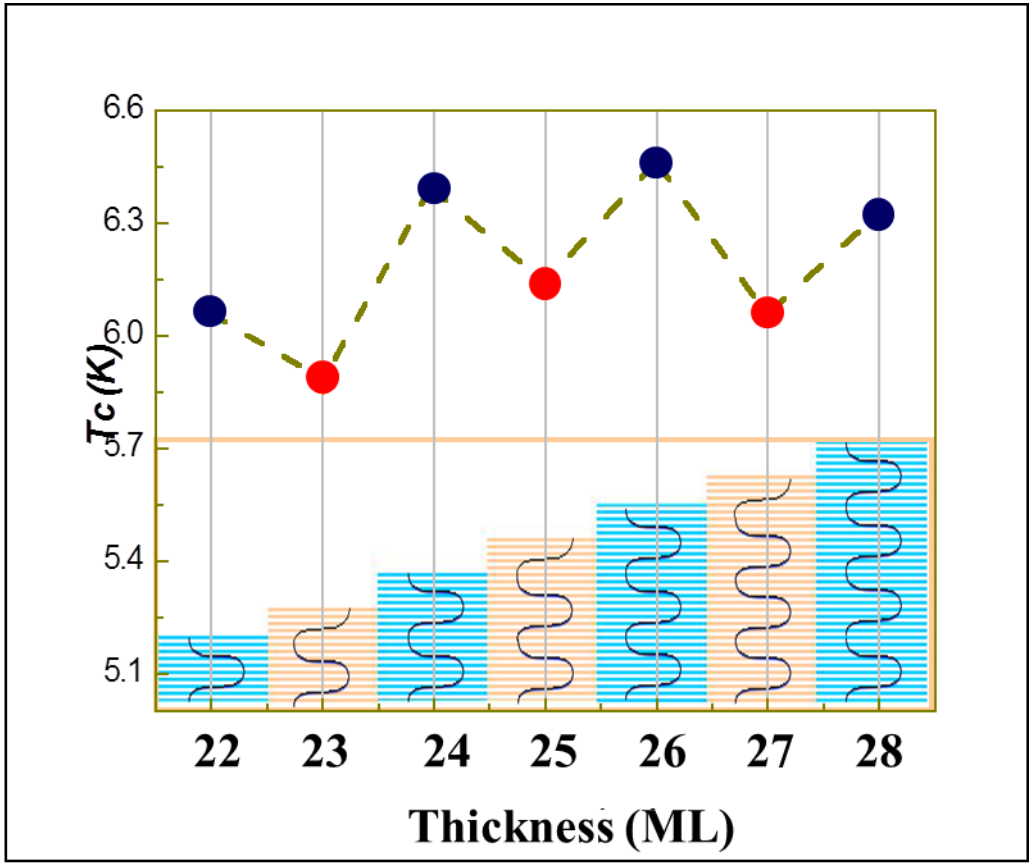
- **Philosophy:**

  Film thickness L => density of states $\rho(E_F)$
  => many properties

- **Examples of properties:**

  - lattice relaxation
  - work function
  - electrical conductivity
  - ***superconductivity***
  - adatom diffusivity
  - chemical reaction rates
  - electronic friction/quantum tribology
  - ...

Pb/Si(111): T_c Oscillation vs film thickness

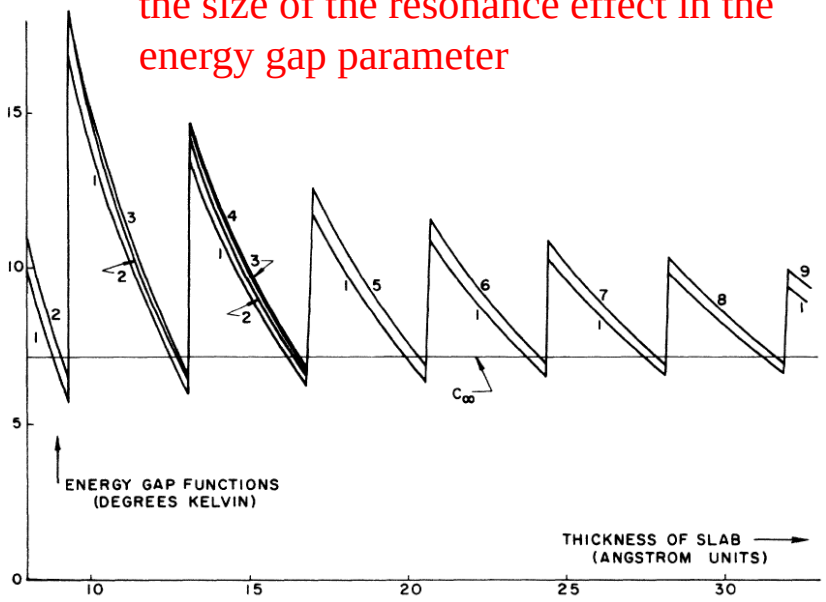


This oscillating behavior originates from the Fabry-Perot interference modes of electron de Broglie waves in the films, which modulate the electron density of states near the Fermi level and the electron-phonon coupling. Q. K. Xue, *et al.* Science 12/10/2004.
M. Ozer, Y. Jia, B. Wu, ZZ, HH Weitering, PRB 72, 113409 (2005).

Blatt and Thompson, Phys. Rev. Lett. 10, 332 (1963)

Superconductor equation is solved for a slab with thickness ***a***. Resonance effects are expected whenever an energy level (for motion perpendicular to the slab faces) passes through the Fermi surface as the thickness ***a*** is varied.

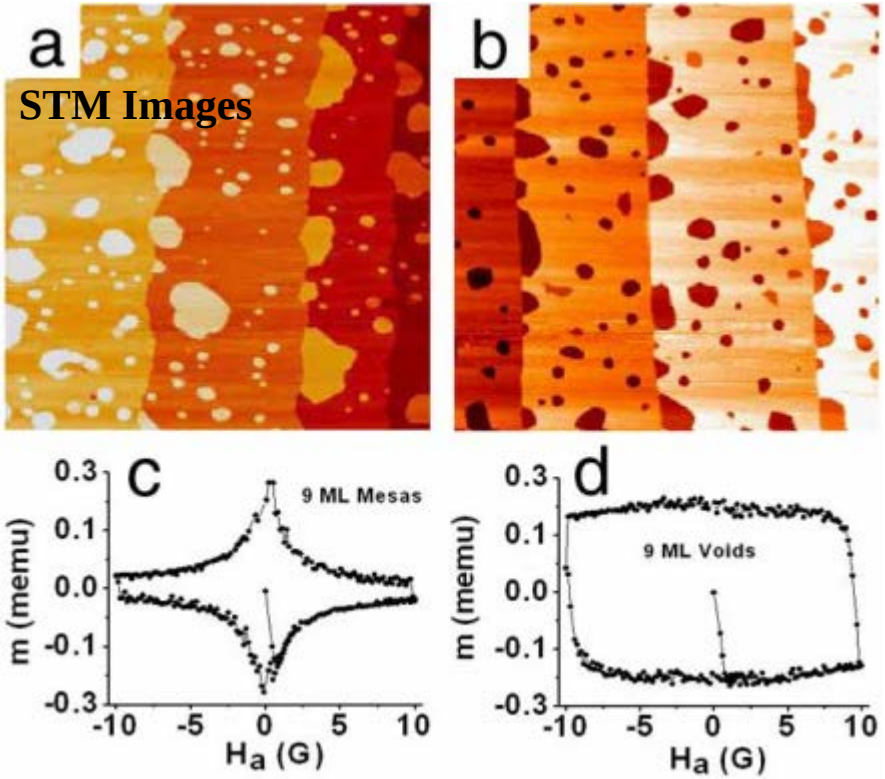
the size of the resonance effect in the energy gap parameter

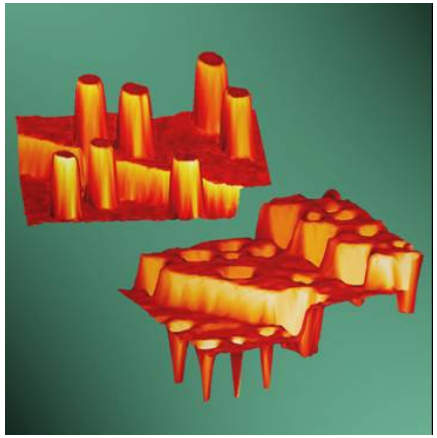


Hard Superconductivity in a Soft Metal Film with Quantum Defects

Nature Physics (2006)

MUSTAFA M. ÖZER[1], JAMES R. THOMPSON[1,2] AND HANNO H. WEITERING[1]

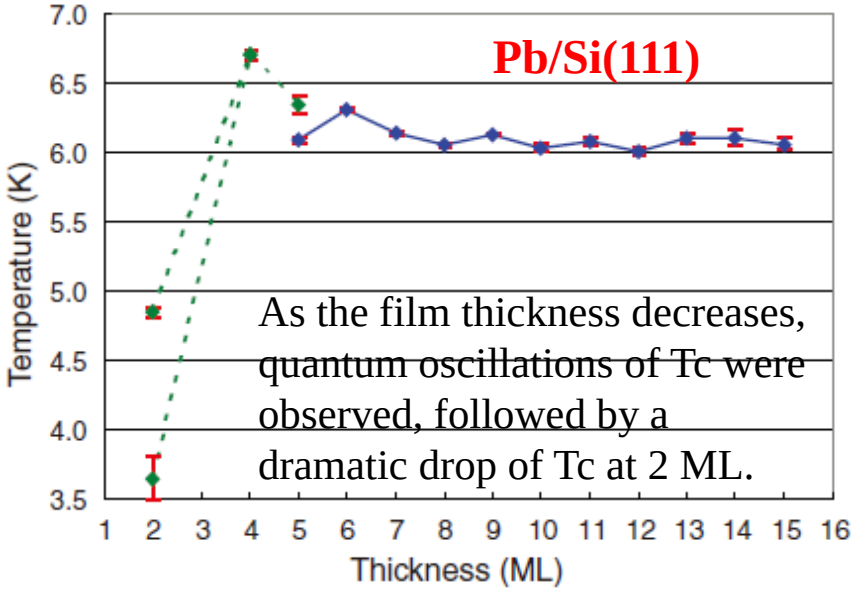


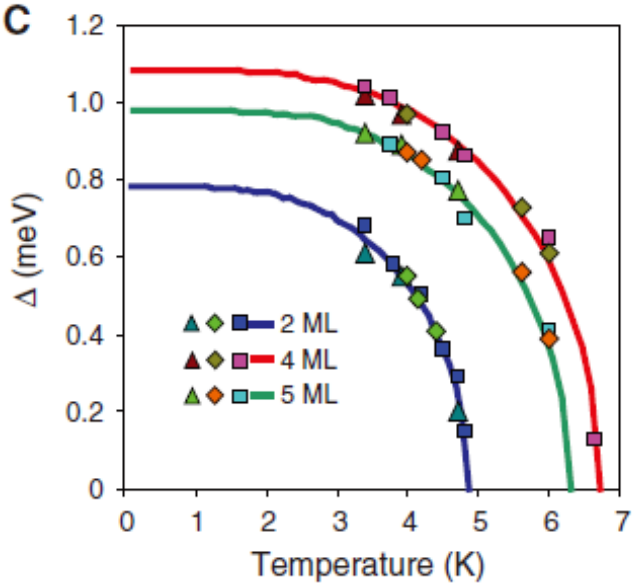


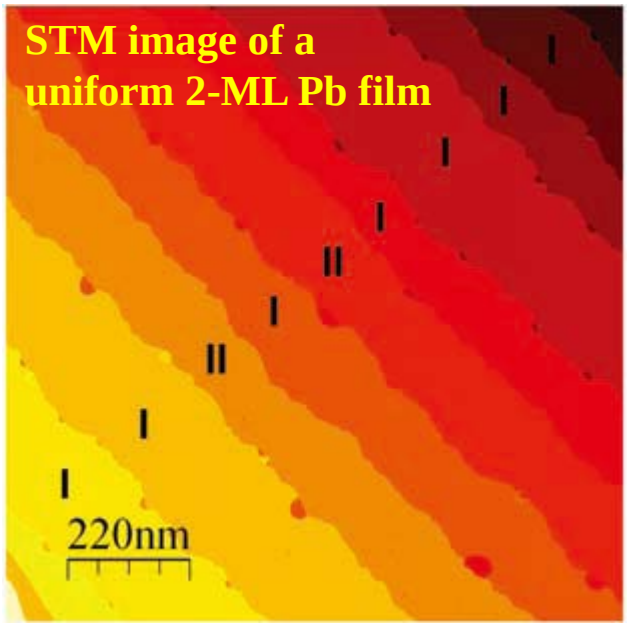
DC magnetic response of these films: Quantum voids produce “hard” hysteresis loops (d), while quantum mesas produce “soft” hysteresis loops (c).

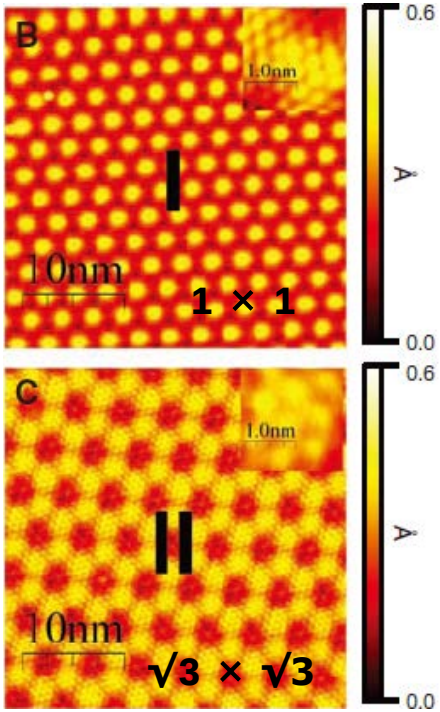
Superconducting state in quantum-confined geometries: Quantum confinement of itinerant electrons in a soft metal stabilizes superconductors with vertical dimensions of only a few atomic layers. The extreme hardness of the critical state is attributed to quantum trapping of vortices.

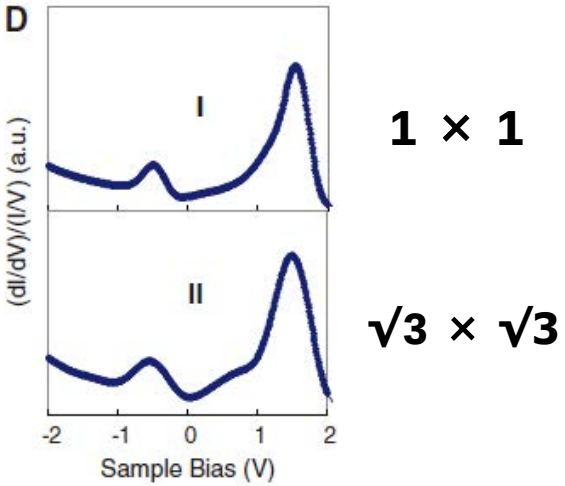
Superconductivity at the Two-Dimensional Limit





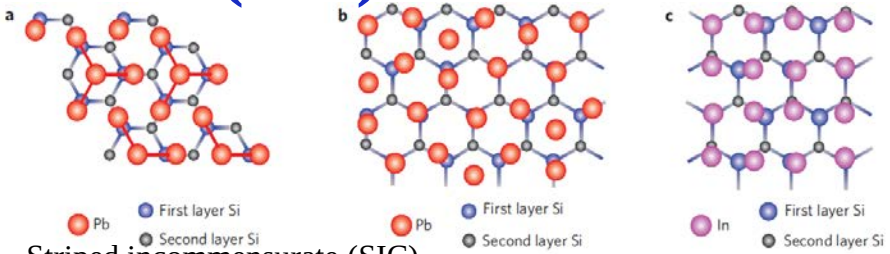




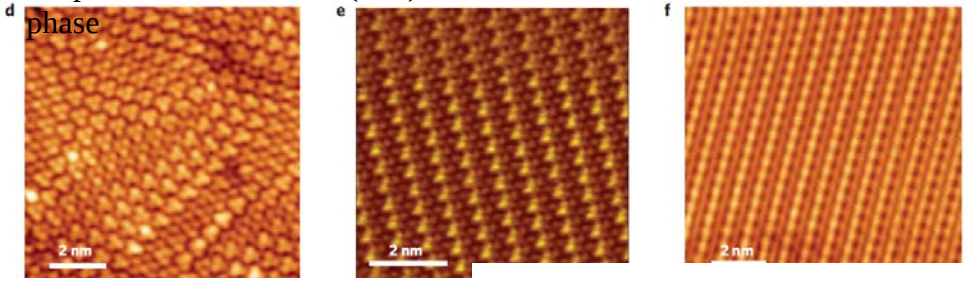


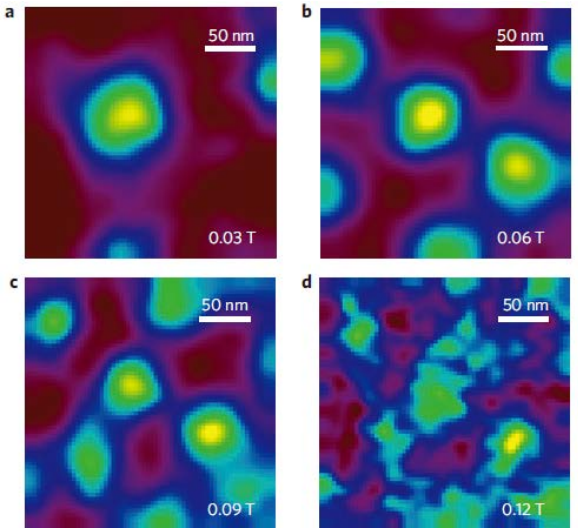
Shih et al, SCIENCE, 324 , 1314（2009）
Hanno H. Weitering, Chem. Phys. Chem. 2009, 10, 3183

Superconductivity in one-atomic-layer metal films grown on Si(111)

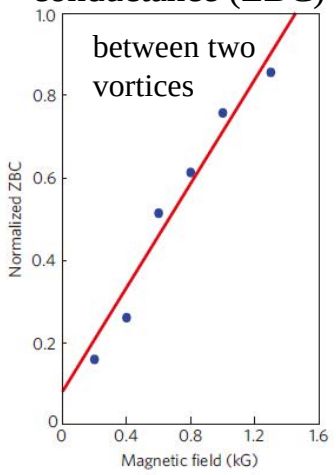


Striped incommensurate (SIC) phase

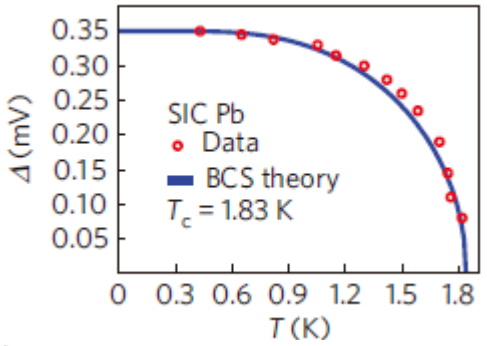


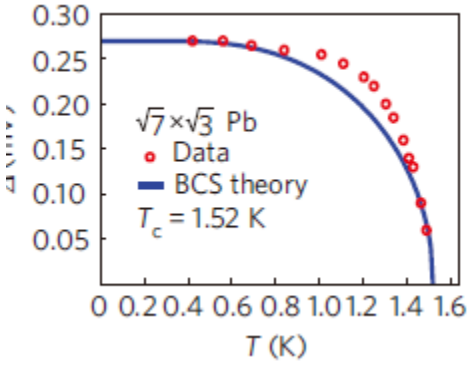


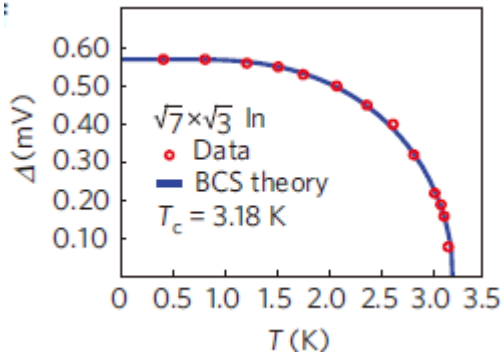
the zero bias conductance (ZBC)

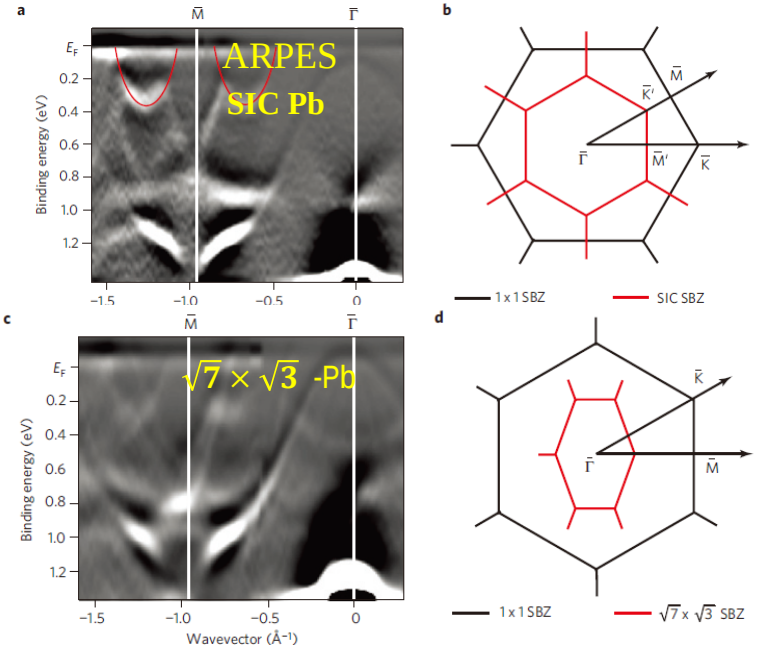


Superconducting vortices in the SIC-Pb phase









Xue et al, Nature Physics, 6, 104 (2010)

Quantum Alloying

Doping Bi, Ga and Hg in Pb: Pb-based alloy films

?

Change k_f → **$\lambda_{beating}$ Change**

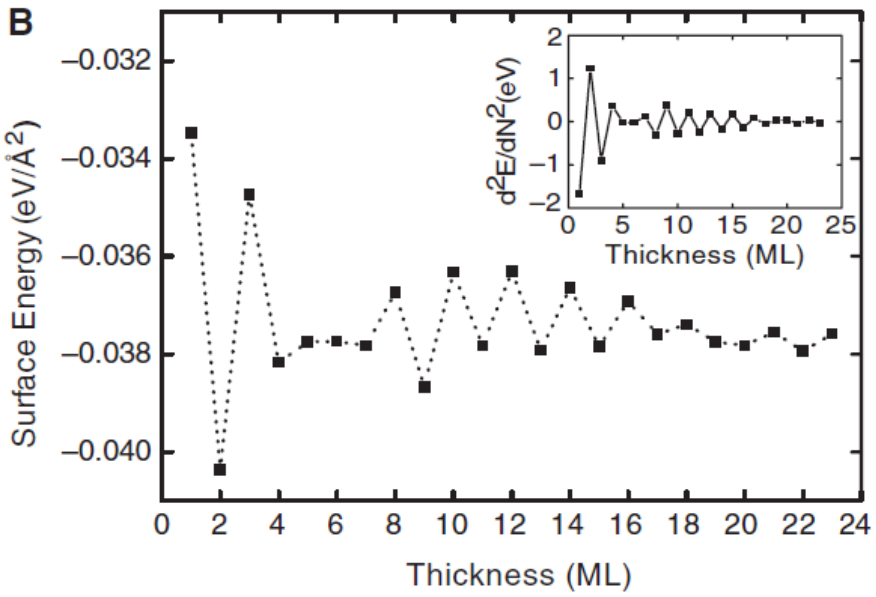
Altering Growth Mode

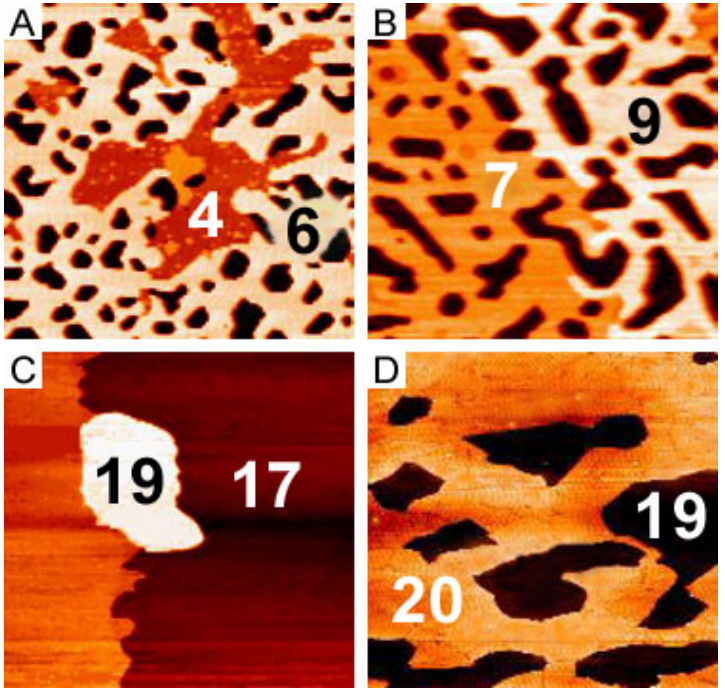
Quantum Alloy of $Pb_{0.89}Bi_{0.11}$ on Si(111)

Ozer, Jia, Zhang, Thompson, & Weitering, Science (06/15/07)

It has been shown that quantum confinement of itinerant electrons in atomically smooth ultrathin Pb films produces oscillations in the thickness-dependent film energy.

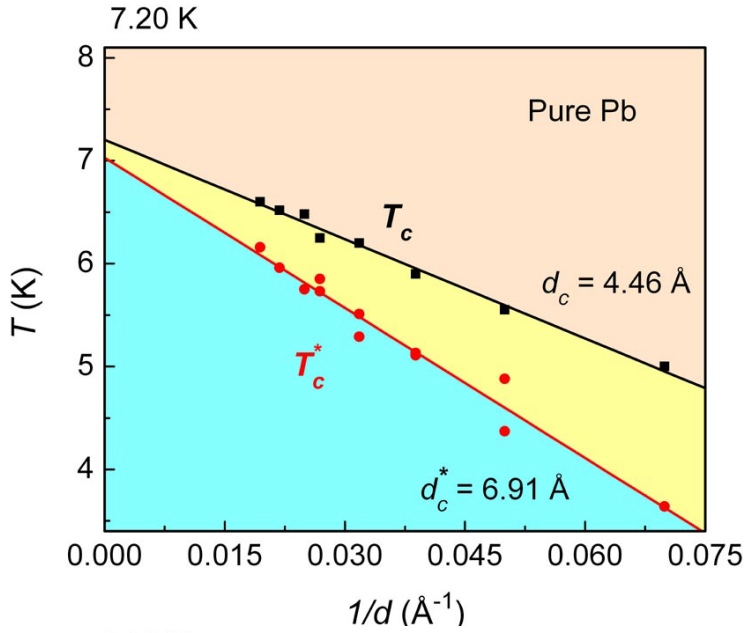
What might be changed by adding extra electrons via bismuth alloying?

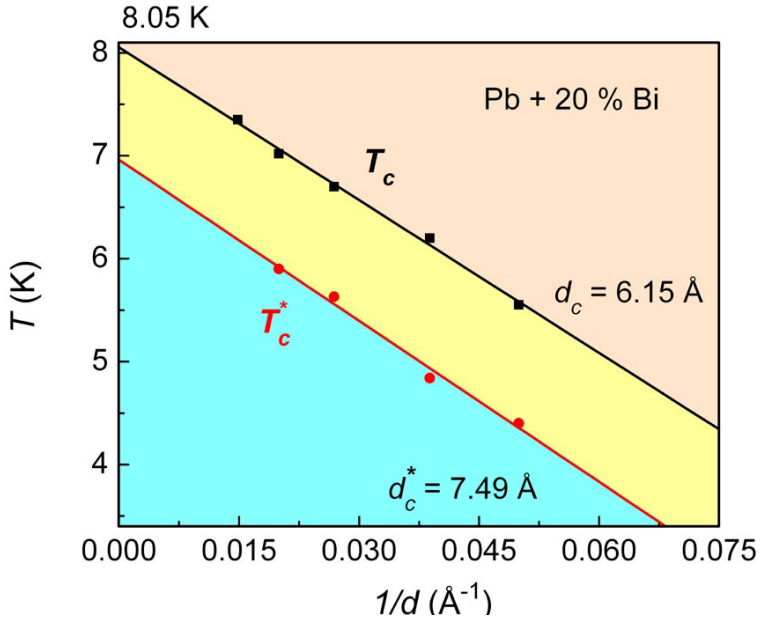


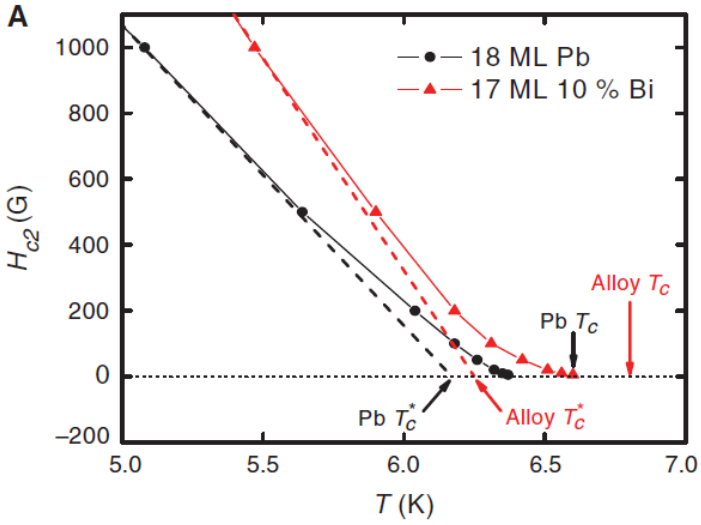


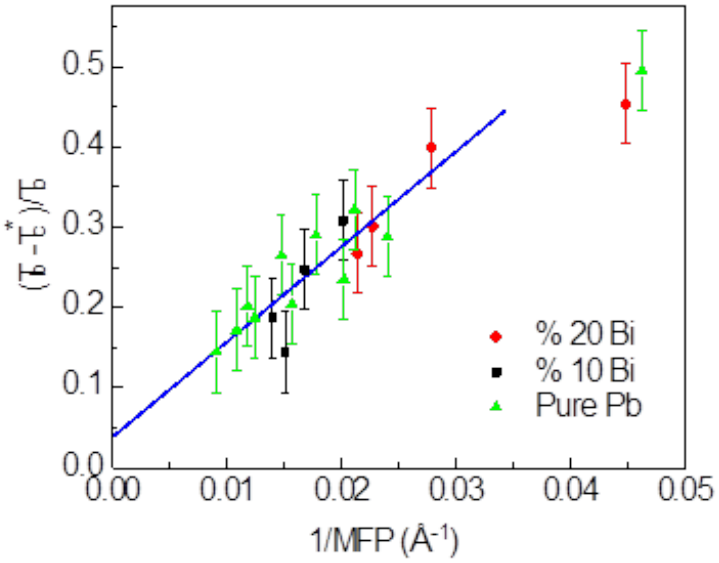
- **Stable layer: 2-4-6-7-9-11-13-15-17-19-20-22-24-26…ML**
- **in precise agreement with experimental results.**

Quantum Alloying









The isotropic nature of the superconductive pairing in bulk lead-bismuth alloys is altered in the quantum regime.

Quantum Tuning of Functional Properties

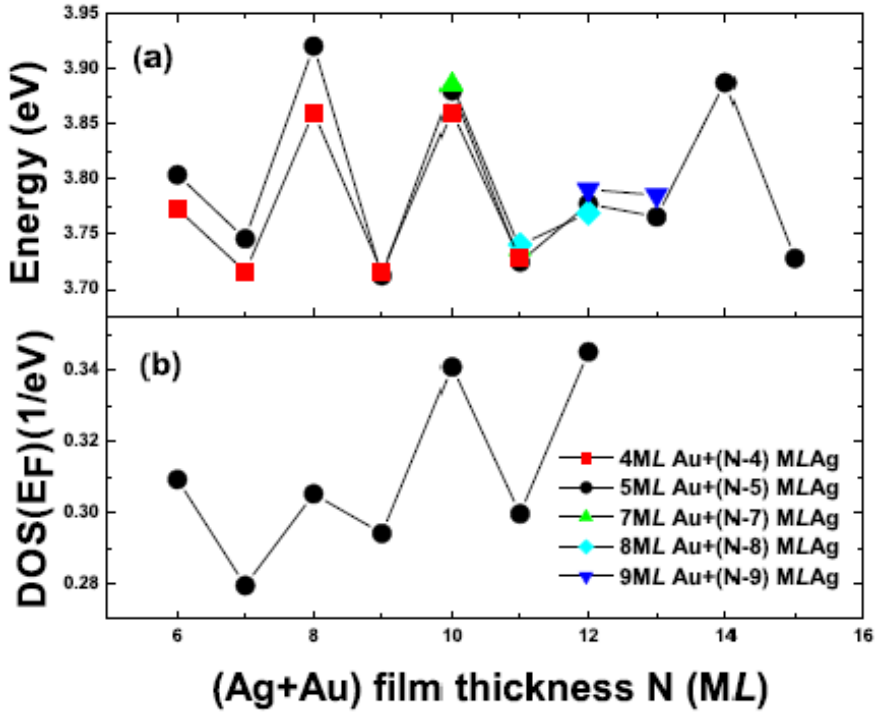
- **Philosophy:**

  Film thickness L => density of states $\rho(E_F)$
  => many properties

- **Examples of properties:**

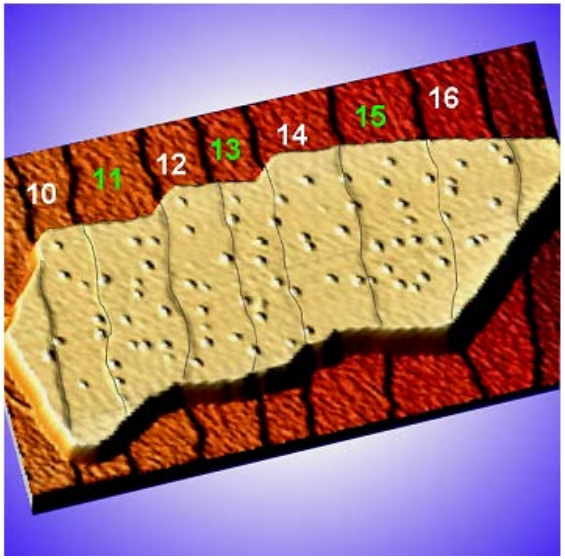
  - lattice relaxation
  - work function
  - electrical conductivity
  - superconductivity
  - adatom diffusivity
  - ***chemical reaction rates***
  - electronic friction/quantum tribology
  - ...

Quantum Oscillations of Chemical Adsorption of O and CO on Synergetic (Au+Ag)(111) Films

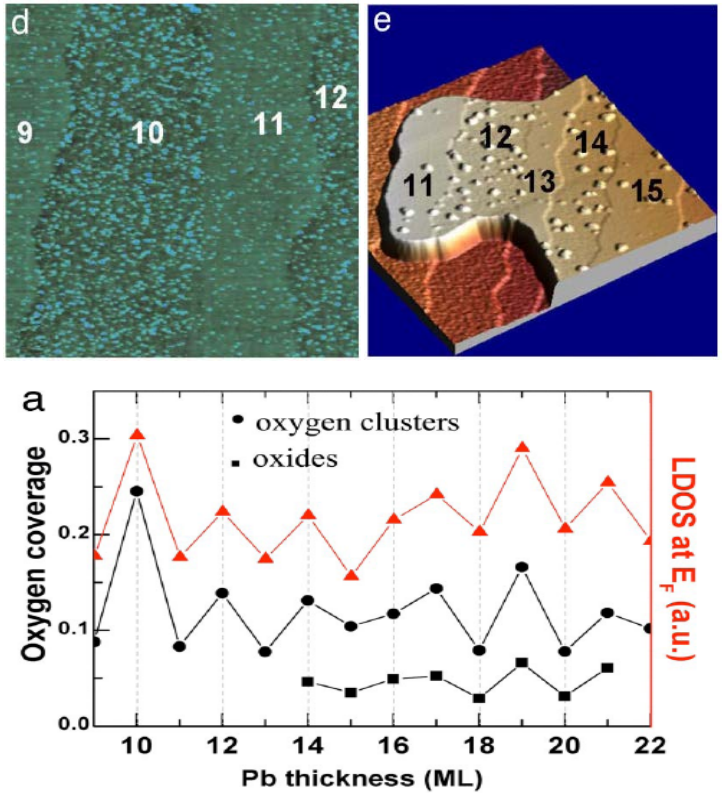


- Enhanced O or CO (~0.2 eV) binding on Au or Ag side
- Binding energy oscillates with the TOTAL film thickness
- Correlated oscillations in binding energy and $\rho(E_F)$
- DOE H initiative based on quantum metal alloys

Quantum Oscillations of Chemical Adsorption

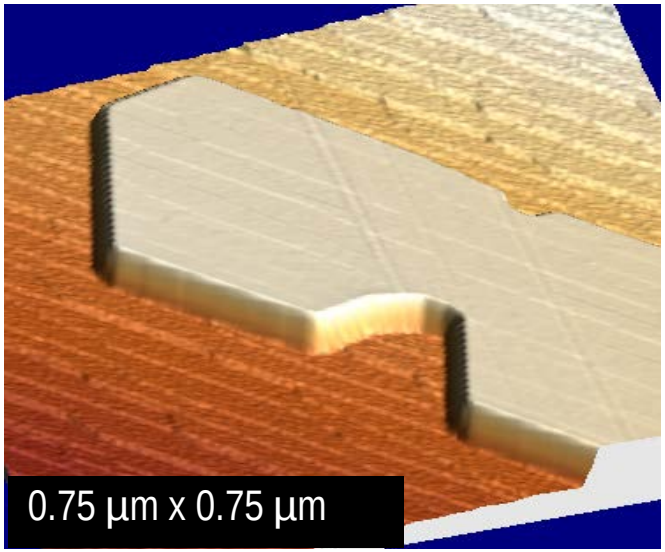


Fe on Pb/Si(111)
Ma et al., PRL 97, 266102 (2006)

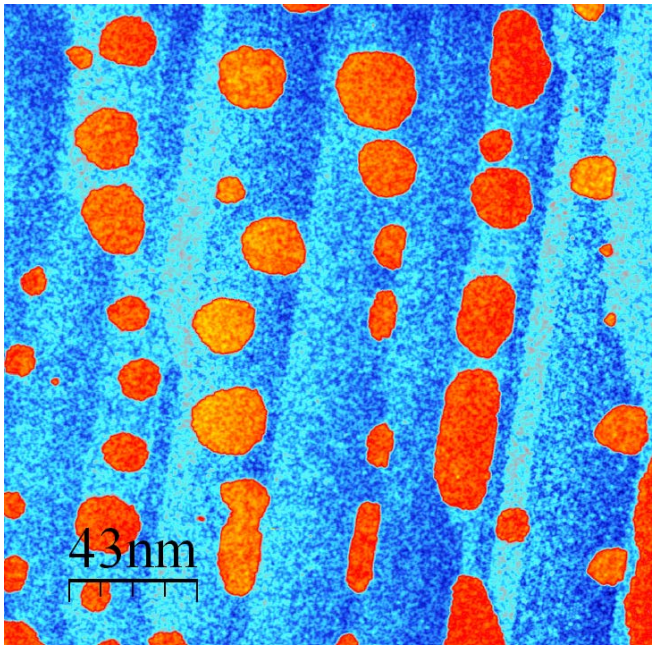


O on Pb/Si(111)
Ma et al., PNAS 104, 920 (2007)

Adsorbate-Induced Restructuring of Pb Nanomesa in the Quantum Regime

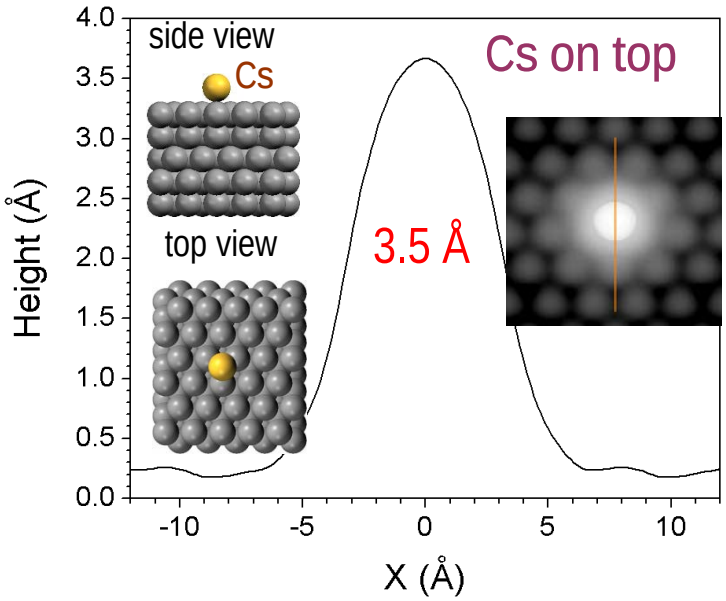


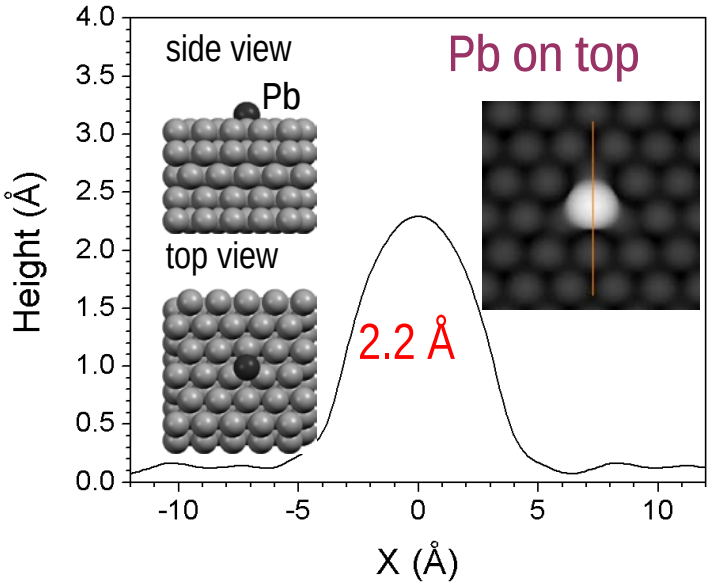
Bare Pb nanomesa on vicinal Si(111)

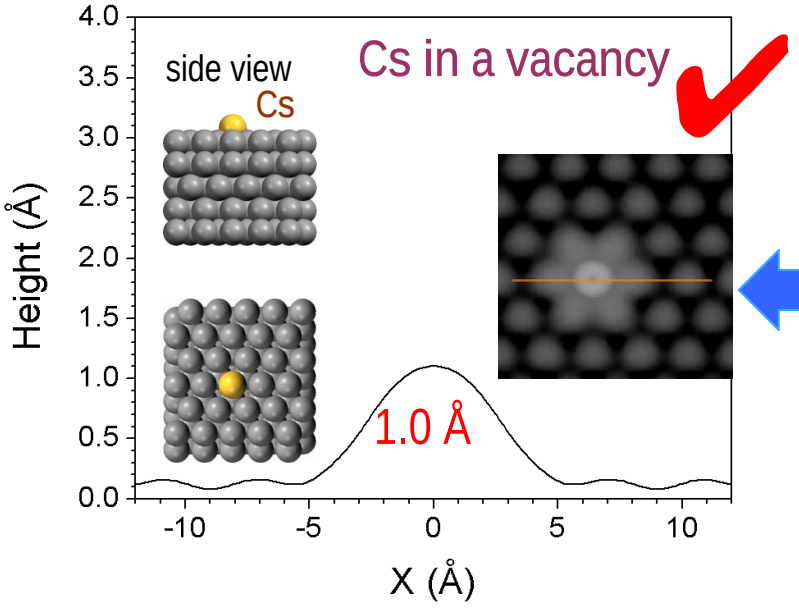


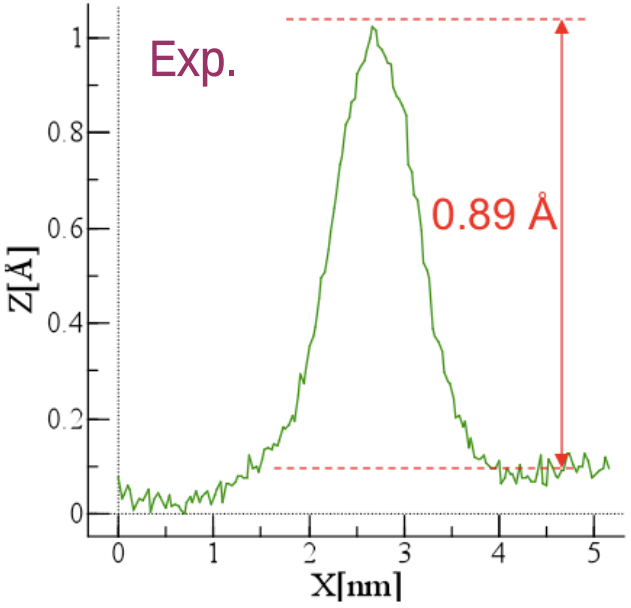
0.057 ML Cs adsorbed

Identity of the Adatoms

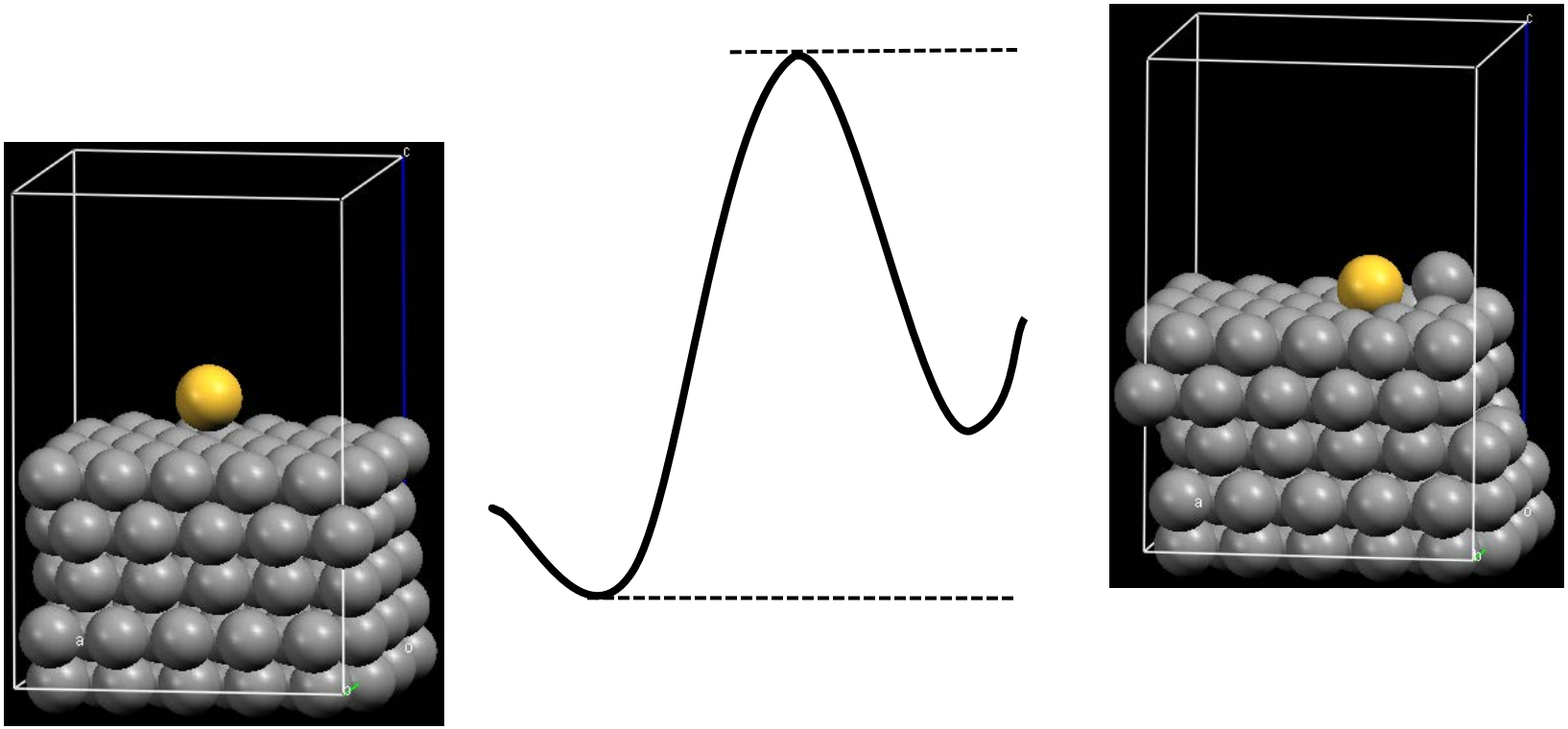






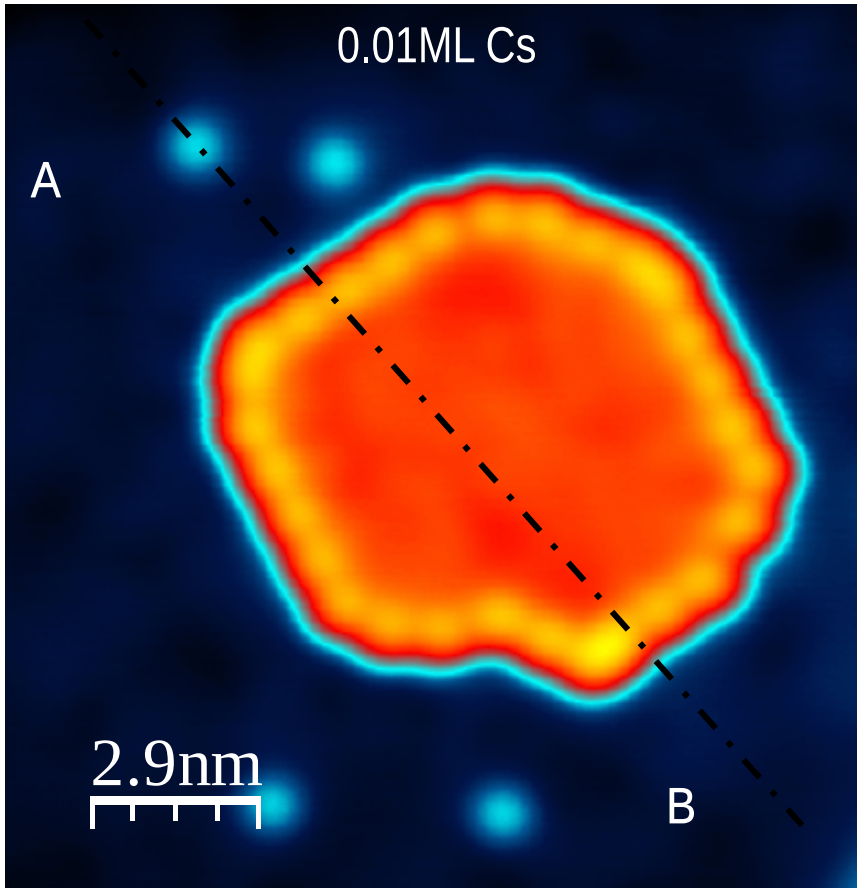


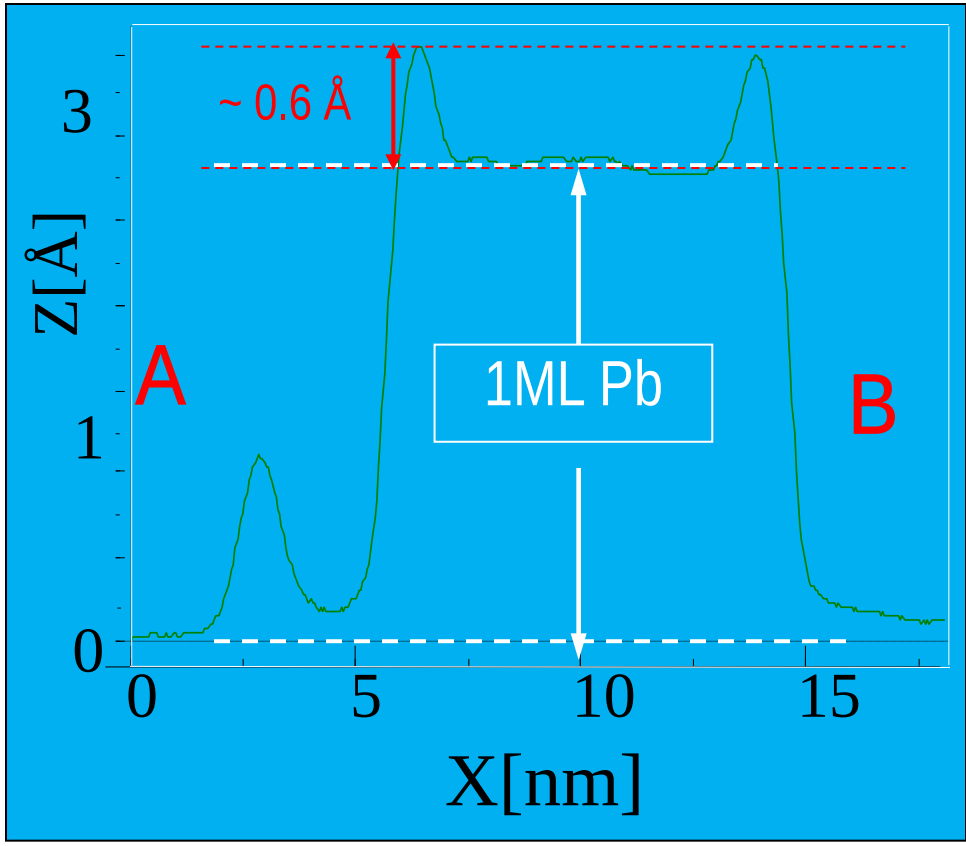
Fast Enough Kinetics for Surface Alloying



Activation barrier for position exchange: 0.8 eV.

Elemental Identity of the Emerging Islands





Pb islands with Cs decorated around the steps

Formation Mechanism of the Emergent Islands

- Cs atoms deposited on the surface of flat-top Pb mesas squeeze out Pb atoms from the top layer (surface alloying), and the expelled Pb atoms nucleate to form the islands (confirmed by counting).
- Due to the relatively lower surface formation energy, the islands prefer to form on the quantum mechanically unstable layers.
- Cs step decoration further reduces the energy cost on the step formation energy of the islands.