STM of nanostructures on semiconducting substrates

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Collaborations.

LEPES:

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- L. Juré, S. Pons (students).

Collaborations:

- UAM, Madrid: J.M. Gomez-Rodriguez.
- CSIC, Madrid: J.A. Martin-Gago.
- Univ. Roma II/III: N. Motta.

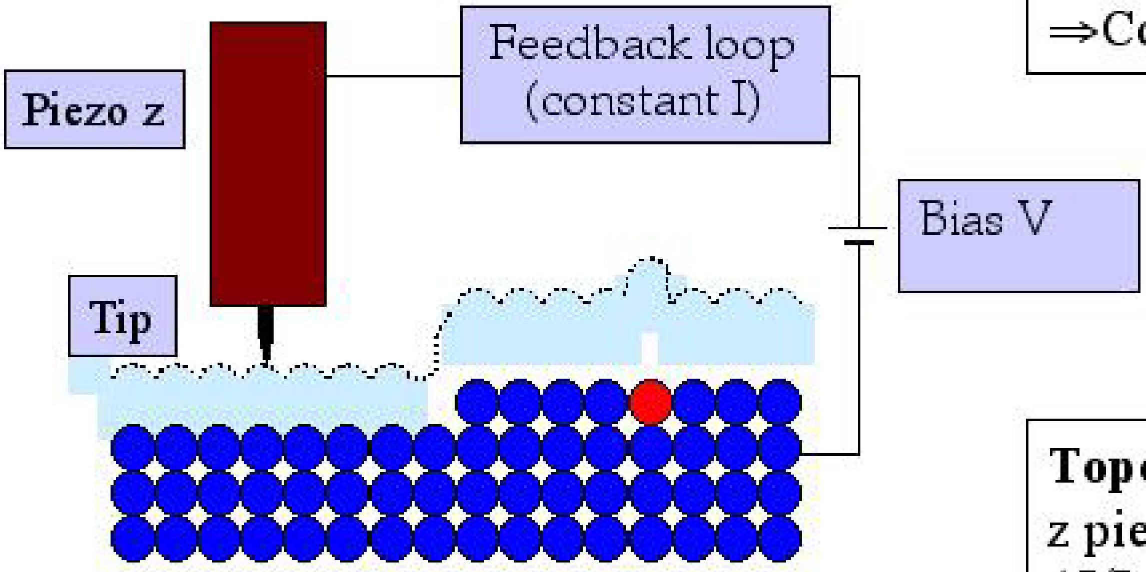
STM (introduction)

- **Principle of constant current imaging.**

In a simple 1D model (V<<Φ):

$$I \propto V \cdot \exp(-2\kappa d) \quad \kappa \approx 1\ \text{Å}^{-1}$$

Topographic image:
•Scanning the tip at constant V and constant I (feedback).
⇒Constant tip-sample distance



Topography: displacement of the z piezo to keep I constant.
$\Delta I/I = 10\% \Rightarrow \Delta d = 0.05$ Å

STM (introduction)

- **Role of the electronic structure.**

Tersoff-Hamann theory (PRL 50, 1988 (1983)).

Full 3D theory: spherical tip (radius R) .

At Low bias (V) and low temperature, the tunneling current is given by:

$$I = \frac{e^2 V}{\hbar} \beta \, e^{2kR} \rho_s(\vec{r}, E_f) \rho_t(E_f) \qquad \beta = \frac{2\pi^3 \hbar^4 R^2}{m^2}$$

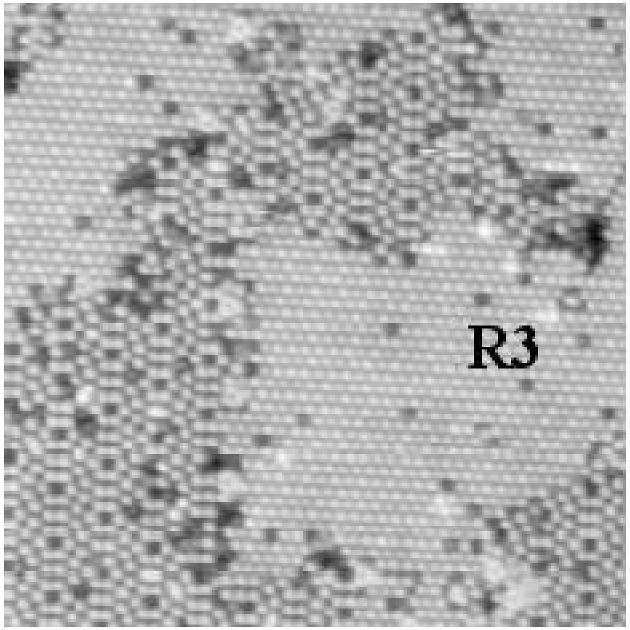
$\rho_s(\vec{r}, E_f)$:LDOS of the sample at E_f, evaluated at the **center** of the tip.

$\rho_t(E_f)$: DOS of the tip at E_f.

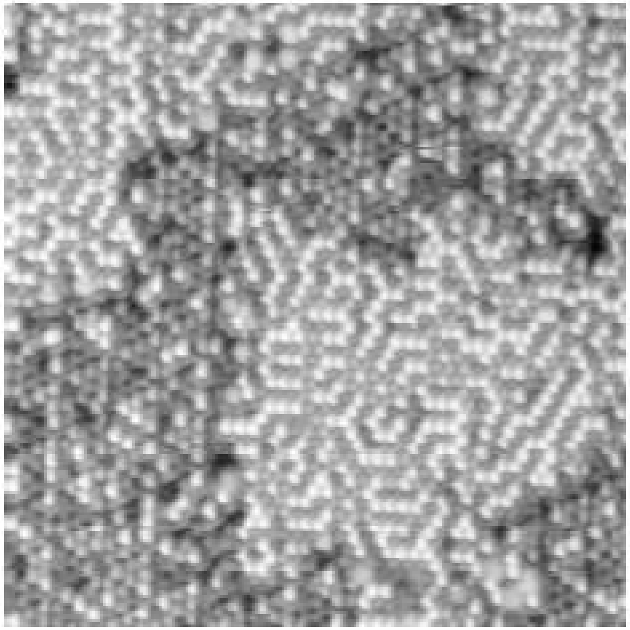
Both the topography and the spatial variations of the LDOS of the sample contribute to the current.

STM

- **Voltage dependent imaging: electronic effects.**



Empty states : V=1V



Occupied states : V=-1 V

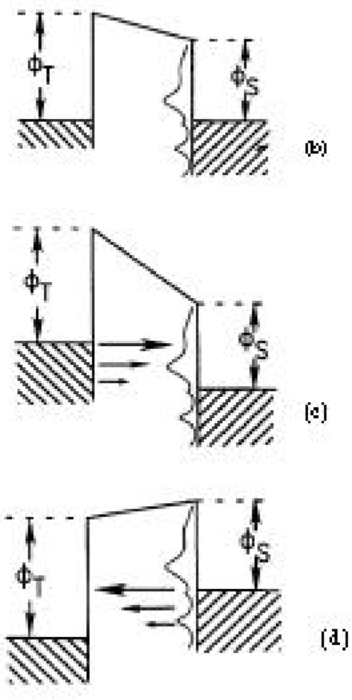
γ (mixed) phase of Pb/Si(111) (R3 type)

Same area. Size : 30x30 nm_

Gòmez-Rodrìguez et al, Surf. Sci. 377, 45 (1997)

Spectroscopy

- **Principle: I(V) curves at constant tip-sample separation (feedback off).**



V_s=0 V. I=0

V_s>0 V. e flow from tip to sample. Empty states.

V_s<0 V. e flow from sample to tip. Occupied states

Tip Sample

For a structureless tip DOS, at low bias and temperature:

$$\frac{dI}{dV} \propto \rho_s(\vec{r}, eV)$$

Spectroscopy ⇔ LDOS of the sample

N. D. Lang, PRB 34, 5947 (1986)

Asymmetry between occupied and empty states.

Other normalisation (high bias):

$$\rho_s(eV) \propto \frac{V}{I}\frac{dI}{dV}$$

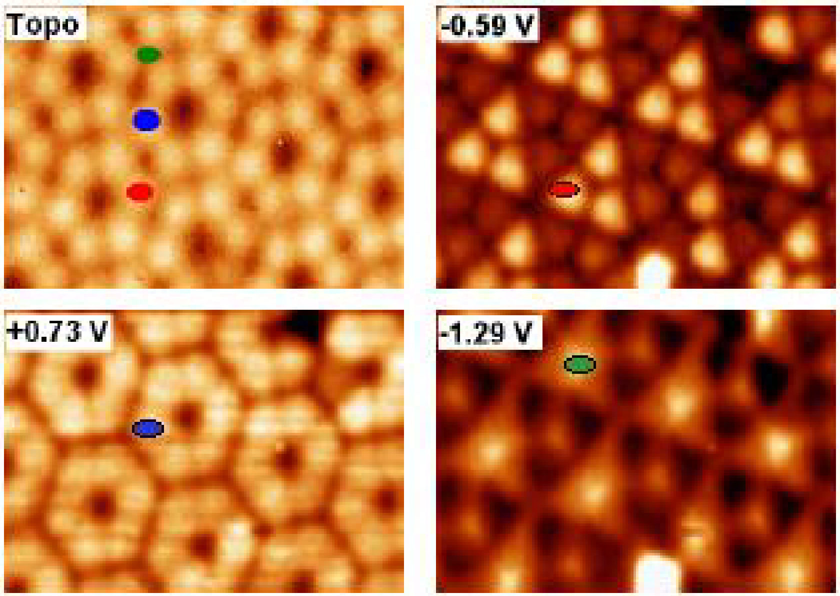
R. M. Feenstra et al. Surf. Sci. 181, 295 (87).

CITS: Current Imaging Tunneling Spectroscopy

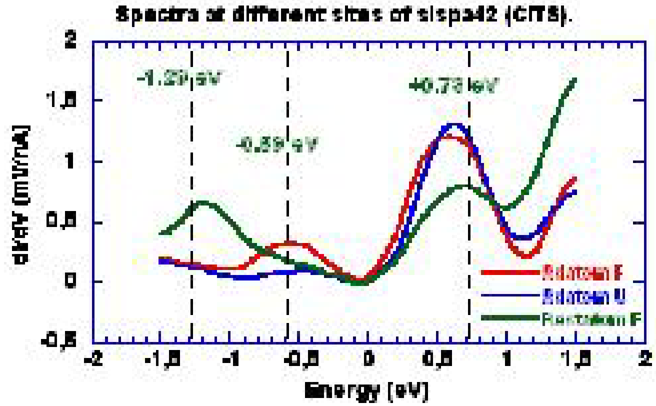
Spatial resolution of electronic structures (LDOS).

R. J. Hamers et al., PRL 56, 1972 (1986).

Si(111)5x5, 7nmx5nm, stabilization: +1.5V, 1.0 nA.



Topography and **current images** at selected voltages on the same area



Spectra on inequivalent sites

CITS: localization of the DOS features
⇒LDOS

Real time imaging by STM

- **Technique.**

  Scanning continuously the **same area** of the surface, event. during deposition and at high or low temperature.

  Observation of growth, decay, atom diffusion in « real time ».

  Main advantage:

  Direct observation of the mechanisms of formation of the deposit (nanostructures).

  Extraction of relevant parameters of growth (barriers, size dependent evolution).

  Problems:

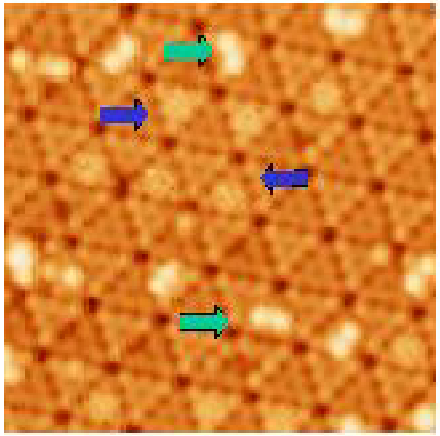
  Influence of the tip (expts at various biases…)

  Drift.

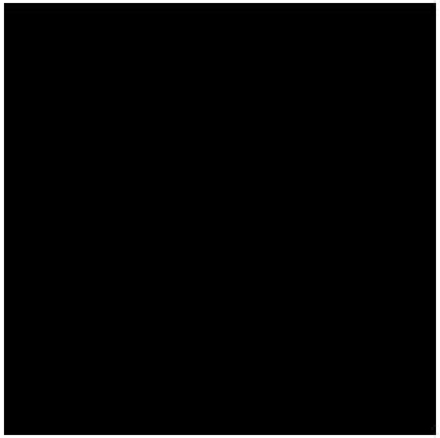
  Acquisition rate (STM is a low frequency technique).

Real time imaging by STM

- **Dynamics of single Pb atoms and pairs on the Si(111)7x7 surface .** (J.M. Gomez-Rodriguez et al., PRL 76, 799 (1996).



Initial frame.
Single atoms ( ) and pairs ( ).



Movie sipba23a.
58°C, -2.0 V, 0.2 nA, 16nmx16nm
156 frames for ~1h05', 25 s/frame.

Jumps of single atoms, formation of pairs, rotation of pairs…

Real time imaging by STM

- Detailed informations on the mechanisms of crystal growth.

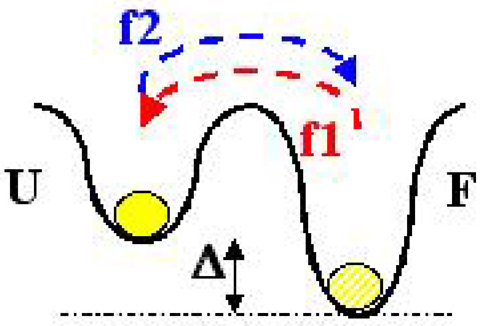
In the present case:

Activation energies, from Arrhenius plots (VT experiments).

- Ed=0.64±0.07 eV for the jumps of single atoms between adjacent (7x7) half-cells

Differences in binding energies from the asymetry of jump rates between U and F half-cells (factor 5).

- Pb atoms more « strongly bound » to the F than to the U half cells by ≈ 40 meV (for Si(111)7x7, same order of magnitude on 5x5).



$$f2/f1=\exp(\Delta/kT)$$

STM studies of nanostructures.

- **Imaging:**
  - -Shape, distribution and structure of the objects with high spatial resolution (atomic)
  - -Growth mechanism (real-time imaging)

•Spectroscopy:

-**Local** electronic structure (confined states).

•Creation of nanostructures.

-Patterning or direct writing.

•Benefit of STM: (sub)-nanometric resolution!

•Arbitrary selection of various exemples, for 0 D and 1 D systems.

Outline

- **0 dimensionnal objects:**

  -Growth of QD (Ge/Si): static and dynamics

  -Spectroscopy:

  Imaging the wave function

  Small metal clusters

- **1 dimensionnal objects:**

  -Lines of atoms on Si(100)2x1: Growth, stability and electronic structure.

  -Charge density wave in 1D atomic lines?

- **Fabrication by STM:**

  -Monohydride Si(100)2x1 surface.

  -Local CVD.

Growth of « Quantum dots ».

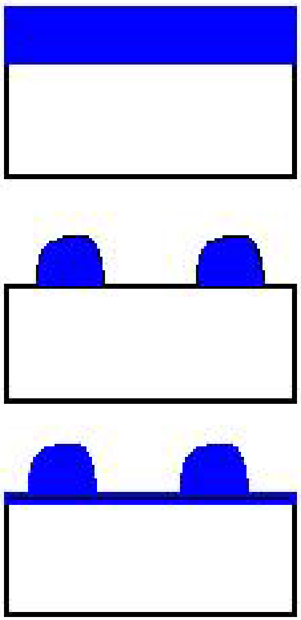
- **Ge/Si(100)2x1, InAs/GaAs(100).**

Famous exemples of « self-organized » growth.

Cf lecture by N. Motta..

Influence of misfit on crystal growth

Classical models, in terms of surface (γ_s, γ_d) and interface γ_i energies (without strain).



Franck van der Merwe (2D)

$\gamma_s > \gamma_d + \gamma_i$

Volmer Weber (3D)

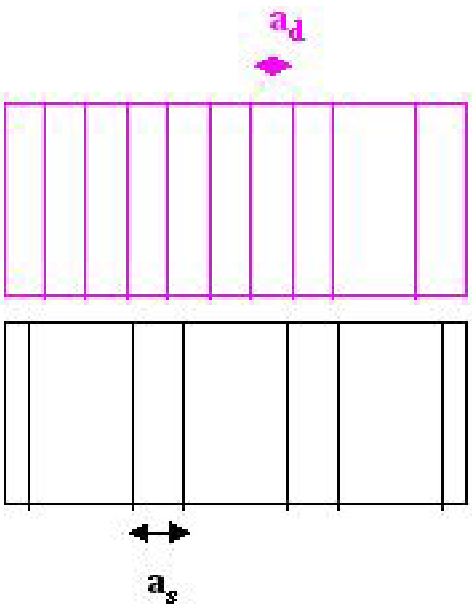
$\gamma_s < \gamma_d + \gamma_i$

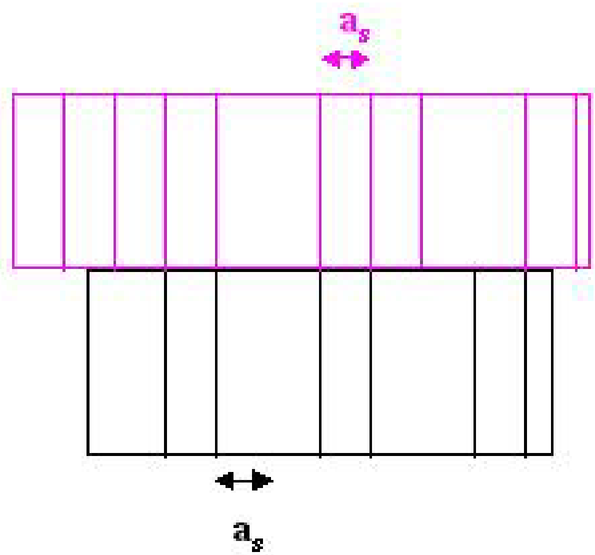
Stranski Krastanov (mixed)

Deposit **Substrate**

Influence of misfit on crystal growth

Deposit (Ge): lattice parameter a_d, Substrate (Si): lattice parameter a_s, Misfit: $f=(a_d-a_s)/a_s$



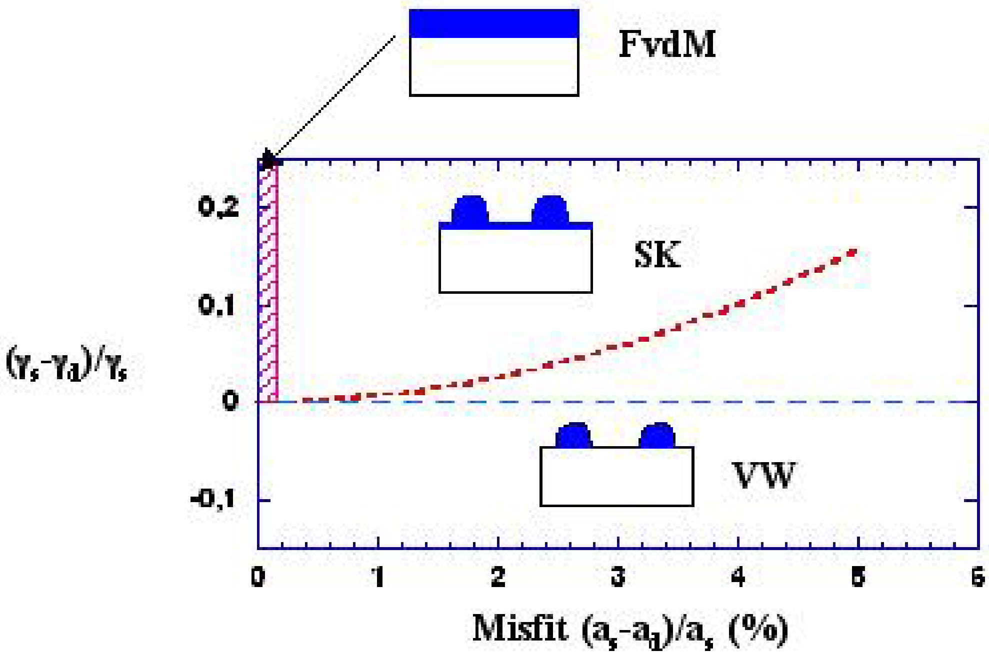


Elastic deformation
$a_d(//)$ increases
$a_d(\perp)$ decreases

- **How to satisfy the bonding across the interface?**

Elastic (coherent) deformation or misfit dislocations

Influence of misfit on crystal growth



Adapted from:
M. H. Grabow et al. , Surf. Sci. 194, p. 333 (1988)
K. N. Tu, IBM JRD 34, p.868 (1990).

At equilibrium, SK may be favored even in « wetting conditions » for non zero misfit.

Ge/Si(100) 2x1: SK growth mode.

Ge « wets » Si, but misfit ~4% ⇒SK growth mode.

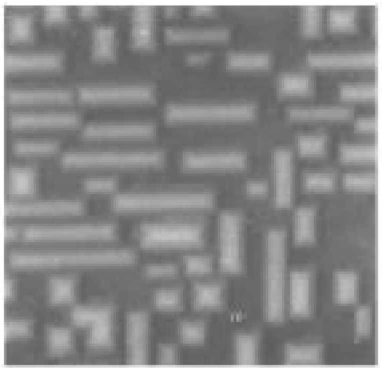
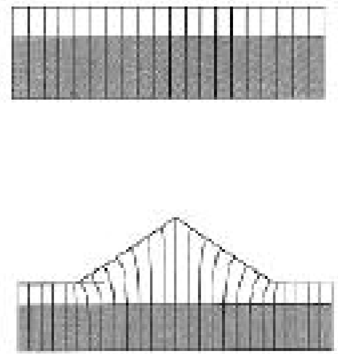


FIG. 1. STM and SEM images of two types of Ge clusters on Si(001). (a) STM image, 2500×2500 Å. "Hut" clusters have rectangular or square bases, in two orthogonal orientations, corresponding to ⟨100⟩ directions in the substrate. Clusters are ≲1000 Å long and 20–40 Å high. (b) STM image



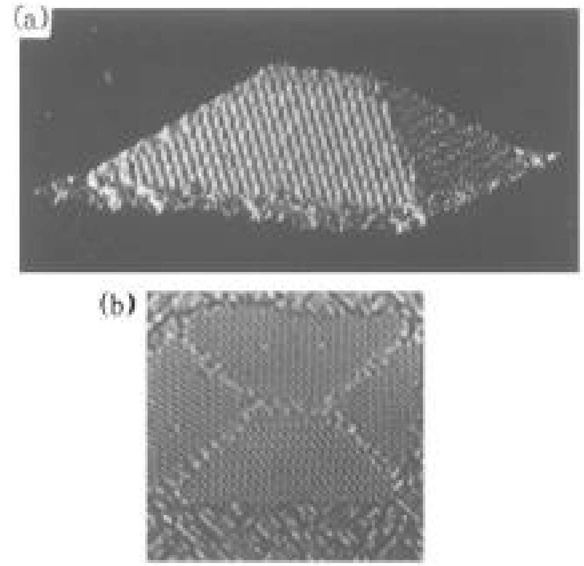


FIG. 2. STM images of single "hut" cluster. (a) Perspective plot. Scan area is 400 Å×400 Å. The height of the hut is 28 Å. (b) Curvature-mode grey-scale plot. The crystal structure on all four facets as well as the dimer rows in the 2D Ge layer around the cluster are visible. The 2D layer dimer rows are 45° to the axis of the cluster.

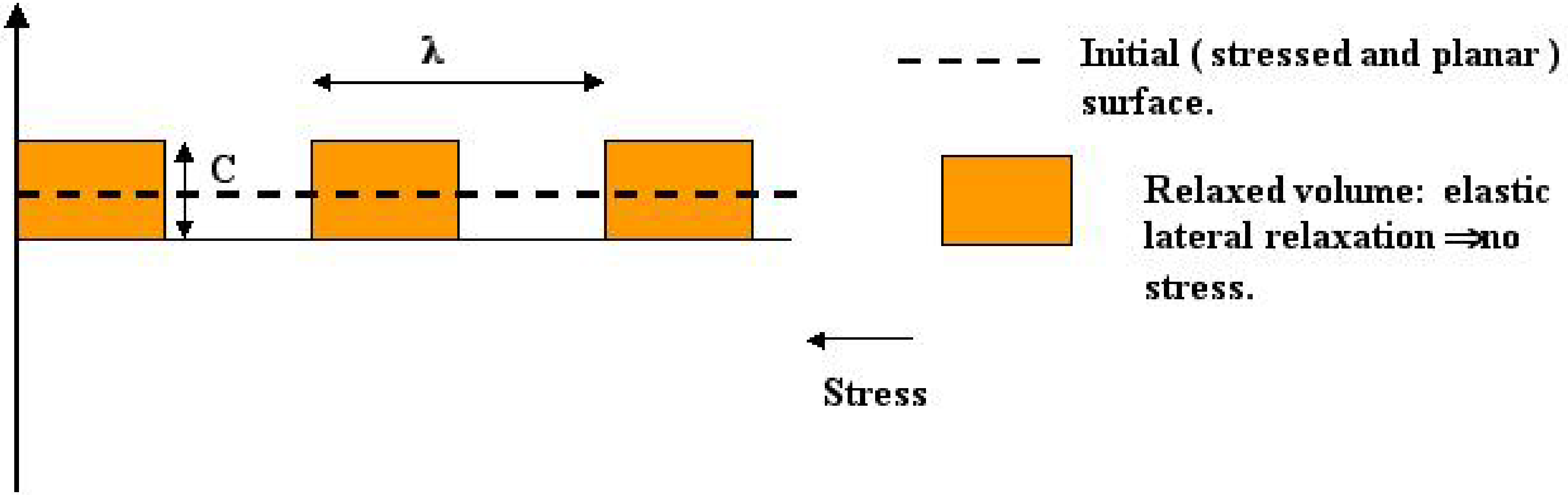
Sides: perfect {105} facets, tilted by 11.5° relative to the (100) surface plane.

From Mo et al., PRL 65, p 1020 (90).

Coherent Ge « hut » clusters above a 3 ML thick stained 2D layer.

SK growth due to lateral relaxation of the strain in the islands.

Influence of strain on crystal growth



Energy gain for a rough surface: $$\Delta\varepsilon = \frac{-\sigma^2}{2E}\frac{c\lambda}{2} + 2\gamma c$$

σ: stress, γ: surface energy, E: Young modulus, (σ~E*f, f: misfit).

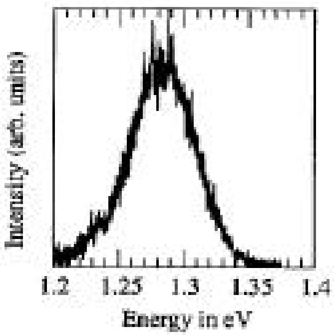
- **The flat surface is unstable for large values of λ**

From D. J. Srolovitz, Acta Metall. 37, p 621 (1989)

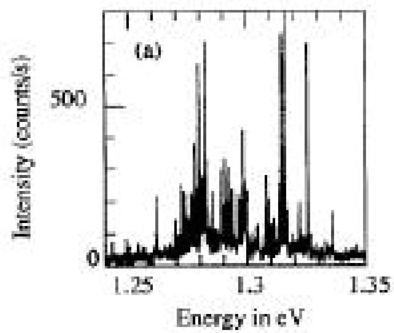
Ge/Si(100): growth of nanostructures with similar sizesans shapes: « self-organized » quantum dots. Also found for InAs/GaAs(001)

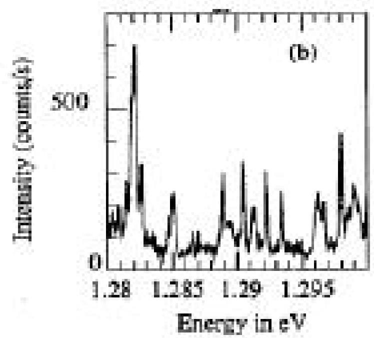
Interest of STM (and other near-field techniques) in this context:

- Investigation ofthe growth mechanism, thermal stability and ordering mechanism of the islands ⇒ distribution of clusters ashomogeneous as possible (applications).
- Influence of the distribution of sizes on the electronic properties InAs/GaAs: PL spectra of QD (J-Y Marzin et al., PRL 73, p. 716 (1994)).

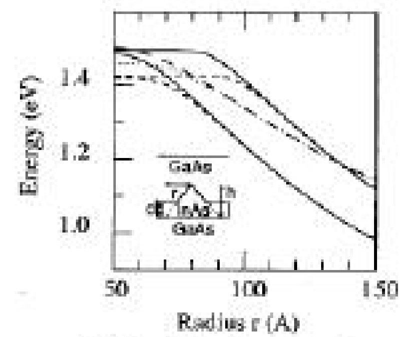


Size: 5000 nm, 10 K





↑ Size: 500 nm, 10 K ↑



Calculated energies of optical transitions

Very narrow lines are resolved when the number of dots decreases: Broadening due to an inhomogeneous distribution of clustersizes Δr≈±0.5 nm.

(NB: 1 peak ≡ 1 cluster). Encapsulated dots.

STM for crystal growth: kinetically self-limiting growth of Ge islands on Si(100).

M. Kästner et al., PRL 82, p. 2745 (1999),
B. Voigtländer, SSR 43 p.127 (2001).

« Real time » evolution of « hut » clusters during growth at 575 K.

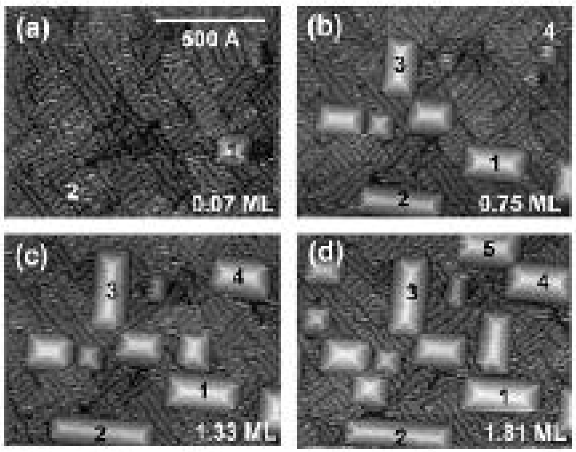


FIG. 1. STM sample images of the hut cluster growth as a function of coverage (beyond the wetting layer). The hut clusters are imaged as rectangular bright areas (image area: 1300 × 1000 Å^2, $T = 575$ K). Identical islands are numbered in (a)–(d). The complete growth sequence is available as a movie [17].

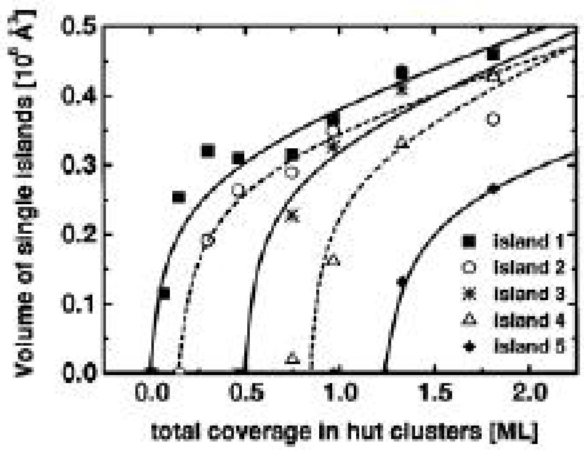
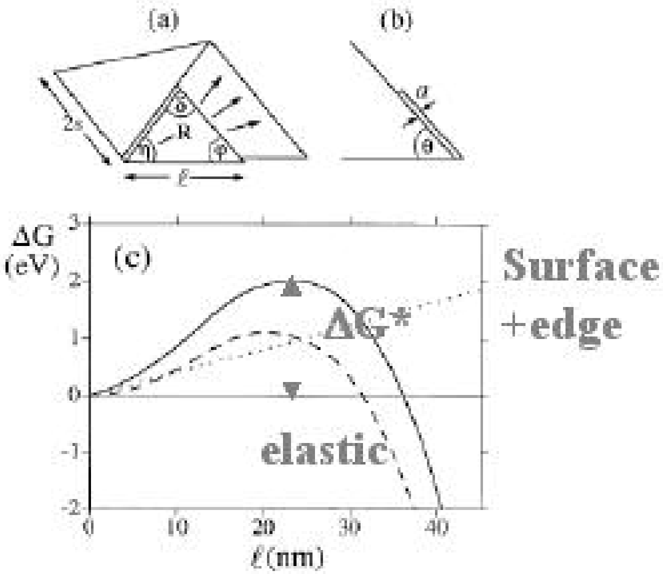


FIG. 2. Evolution of the volume of individual hut clusters. The different symbols correspond to different individual islands as numbered in Fig. 1. The size evolution shows self-limiting behavior. The initially larger growth rate (large slope) just after the nucleation decreases when the islands grow larger. Results of a model calculation of kinetically self-limiting growth including an energy barrier for the nucleation of new material on the facets are shown as solid and dashed lines.

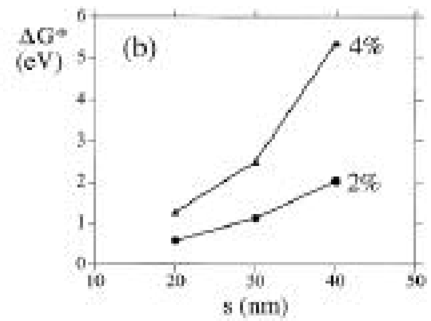
Small islands grow faster than large ones⇒self limited growth, that should favor a narrow size distribution of the islands.

Self limited growth: interpreted in terms of nucleation energy.

- **Increase of the cluster size ⇔ growth of a new {105} facet.**
- **There is a size dependent nucleation barrier to form a new facet**
- D. E. Jesson et al. PRL 80, p. 5156 (1998),



Energy to form a portion of facet of size l from the WL. ΔG decreases at large l as the added material reaches the « relaxed » area close to the apex of the pyramid .



Evolution of the Nucléation energy With size and misfit .

The nucleation rate of a new facet decreases with increasing islandsize:
⇒small islands grow faster thanlarge ones.
⇒Self-limited growth

Spectroscopy of 0D nanostructures.

Confinement effects.

Introduction

Pb/Si(111): confinement ⊥ surface (2D like)

InAs/GaAs(100): imaging the wavefunction in QD

Fe/GaAs(110): size effects and deposit/substrate interaction.

Coulomb blockade.

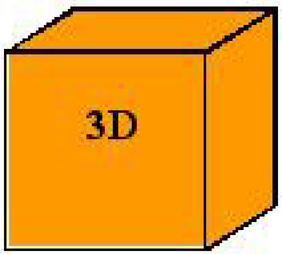
Basic features

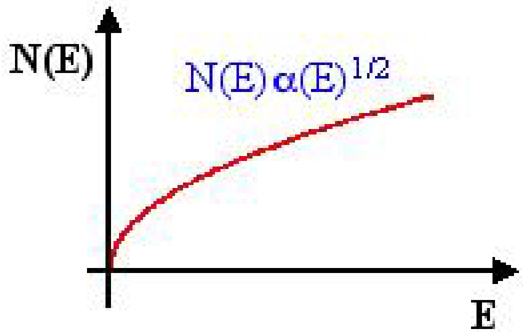
Metal grains on SC surfaces.

Confinement effects.

- **Introduction.**

Free electrons model.



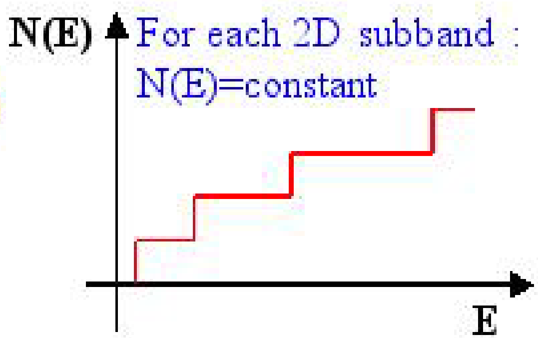


bulk crystal

$$E=\frac{\hbar^2}{2m}\left(k_x^2+k_y^2+k_z^2\right)$$

2D. Film thickness: L

$k_\perp(n)=n\pi/L$

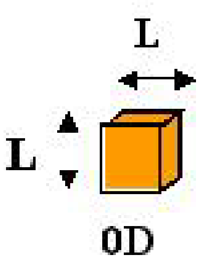


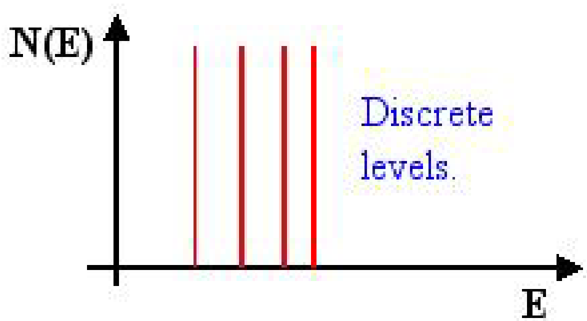
+ ideal 2D confinement

$$E=E_n+\frac{\hbar^2}{2m}\left(k_x^2+k_y^2\right)$$

2D subbands with onset energy:

$$E_n=\frac{\hbar^2}{2m}\left(\frac{n\pi}{L}\right)^2$$





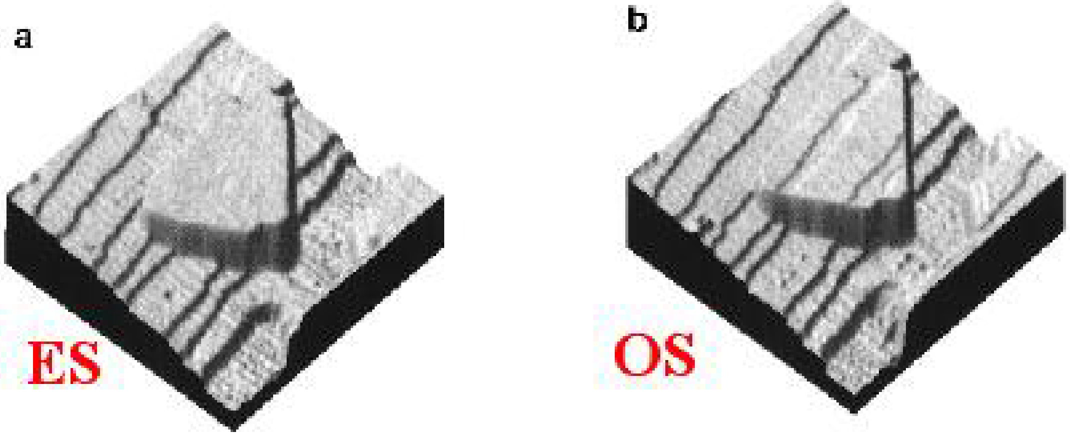
+ideal 0D confinement

$$E=\frac{\hbar^2}{2m}\left[\left(\frac{l\pi}{L}\right)^2+\left(\frac{m\pi}{L}\right)^2+\left(\frac{n\pi}{L}\right)^2\right]$$

Quantized states in Pb islands on Si(111).

I. B. Altfeder et al. PRL 78, p 2815 (1997), W. B. Su et al. PRL 86, p. 5116 (2001). D. M. Chen, J. Elec. Spec. And Re. Phenomena 109, p 85 (2000).

- **Pb/Si(111) 7x7: SK Growth mode with a 2 ML thick wetting layer. Pb(111) crystallites.**
- **High bias imaging (± 5V!) of the same island.**

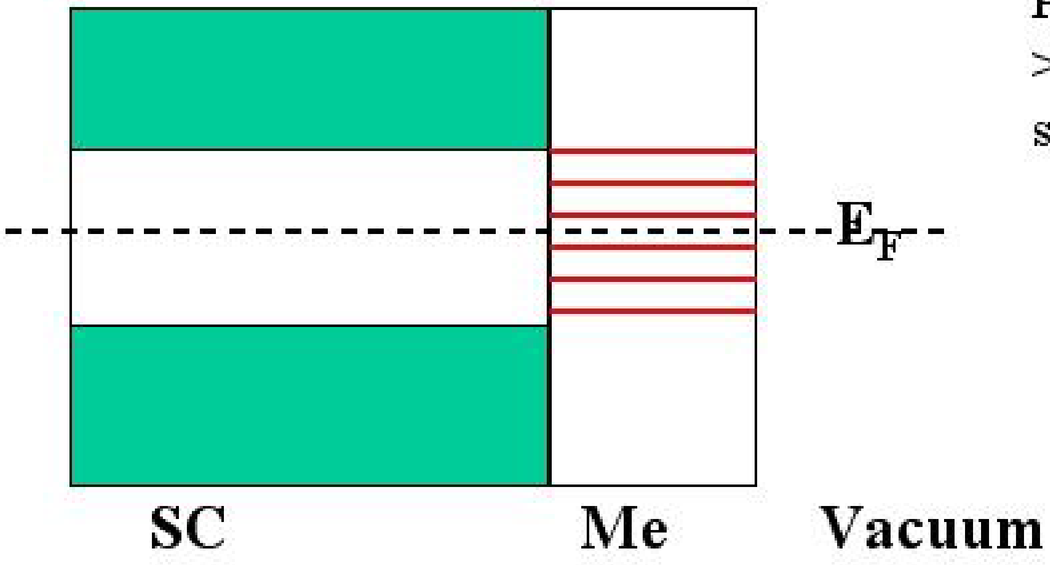


Size of the image: 500x500 nm^2.
Height of the island: 8 to 12 ML above WL.

Fringes in OS images, precisely aligned with substrate steps
⇔ **Quantized states** in the Pb layer due to **confinement** ⊥ **surface**.

Confinement ⊥ surface.

- ⊥ to the surface, the electrons are confined on one side by the vacuum barrier and on the other by the interface (gap of the SC wthin 1 eV from the Fermi level).
- This will lead to a quantization of the wave vector ⊥ surface:
  $k_{\perp}=n\pi/H$, n integer ≥1 and H: thickness of the layer. (assuming perfect confinement: hard wall model).



Provided the width of the layer is >> H: 2D subbands, delocalized // surface (it is the case here).

Confinement ⊥ surface.

- **In an hard wall model, close to E_F:**

  $k_\perp = n\pi/H \approx 2\pi/\lambda_F \Rightarrow n_{occ} \approx 2H/\lambda_F$ **(number of occupied levels).**

  Separation between levels: $\Delta = \frac{fE}{fk}(E_F) \times \Delta k_\perp = \frac{\hbar \times v_F \times \pi}{H}$

  Significant effect when H ≈a few λ_F and v_F is large.

For a simplemetal (1 half filled band), with interplane spacing d_0. $\lambda_F = 4 \times d_0$, $H = N \times d_0$ and $k_\perp = 2 \times n \times k_F/N$ ($n_{occ} = N/2$).
2D subbands appear right at the Fermi level for each additionnal bilayer

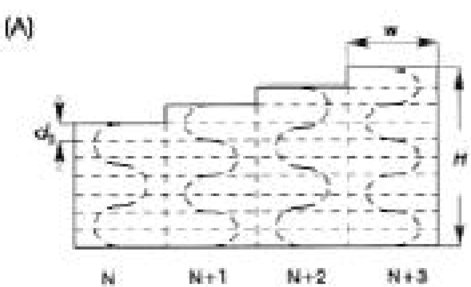
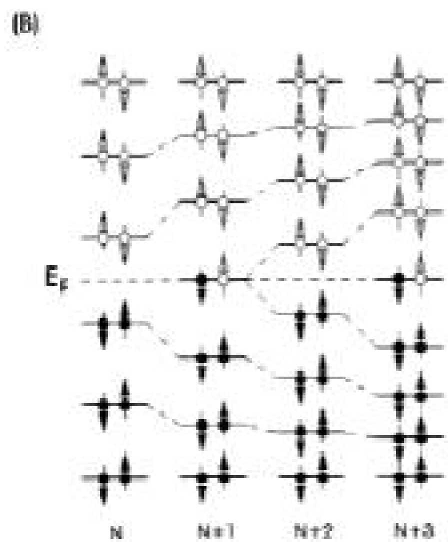
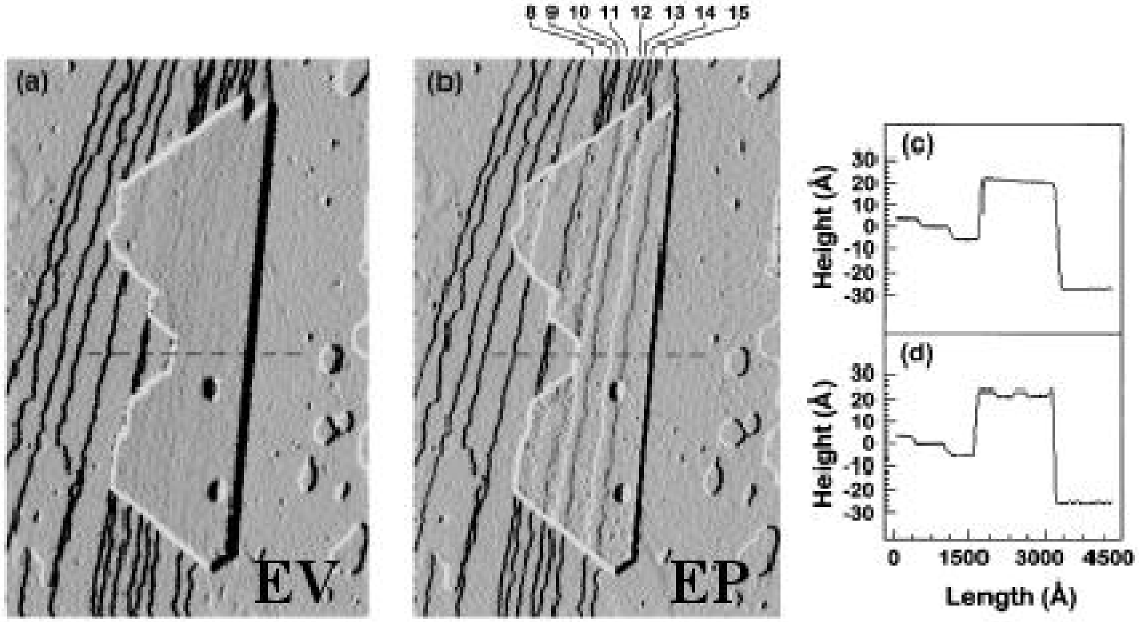


Fig. 1. (a) A quantum wedge consisting of four quantum wells with incremental atomic layers (the width is compressed disproportionally). The standing wave of the highest occupied quantum state for each element is illustrated. (b) One dimensional energy spectra for electrons in each of the four quantum wells. The metal has an ideal half-filled band and the Fermi wavelength is four times the lattice spacing.



Confinement ⊥ surface.

- Spectroscopy on a « wedge ».



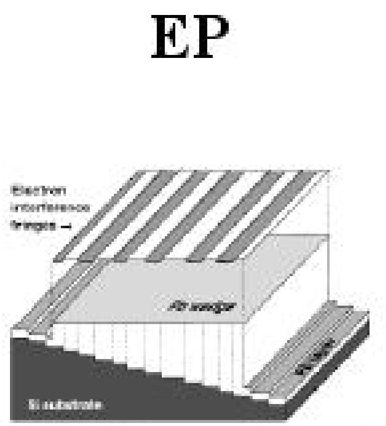


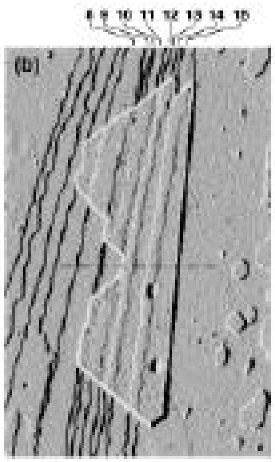
FIG. 2. Schematic of a quantum wedge on a stepped substrate. Electron interference fringes are shown above the wedge. Vertical scale is enlarged by a factor of 100.

FIG. 1. (a) 7300 × 11 000 Å STM image taken with a tip bias of −5 V, showing a topography of the Pb wedge grown on a stepped Si(111) substrate. (b) STM image of the same wedge obtained with +5 V tip bias, showing the electron fringes on the surface of the wedge. Both images are differentiated with respect to the horizontal axis to enhance the step edges. (c),(d) Cross sections taken, respectively, from the originals of (a) and (b) as marked by the dashed lines.

Islands appear essentiallyflat in ES images, except for the mismatch between $a_\perp$ for Pb(111) and the Si steps (slope). Up and down bands ($\Delta z \approx 0.5$-1Å) in OS images.

Confinement ⊥ surface.

- **Spectroscopy on a « wedge ».**



Spectra on different bands The number of Pb layers **above** the WL is indicated

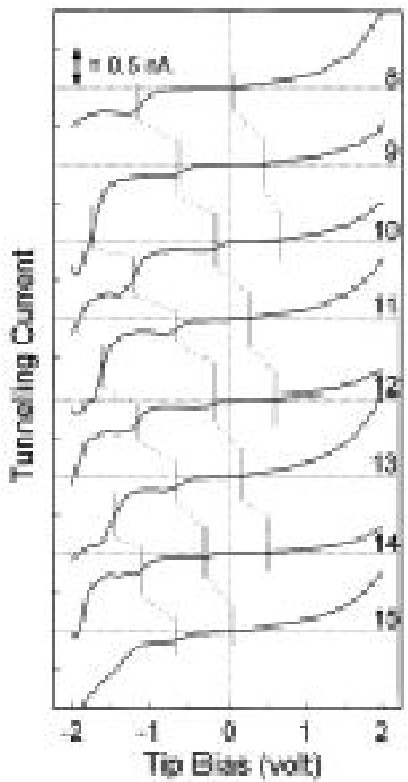
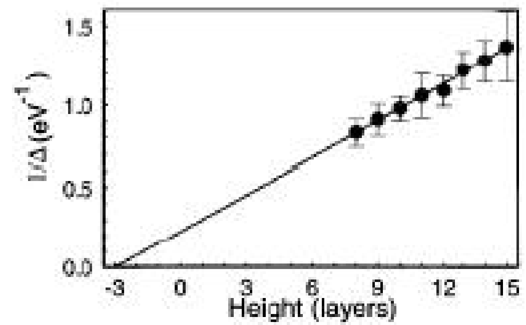


FIG. 3. A series of I-V spectra measured at 4.8 K over different numbered bands on the surface of the Pb-wedge shown in Fig. 1(b). Progression of the quantized steps is marked.

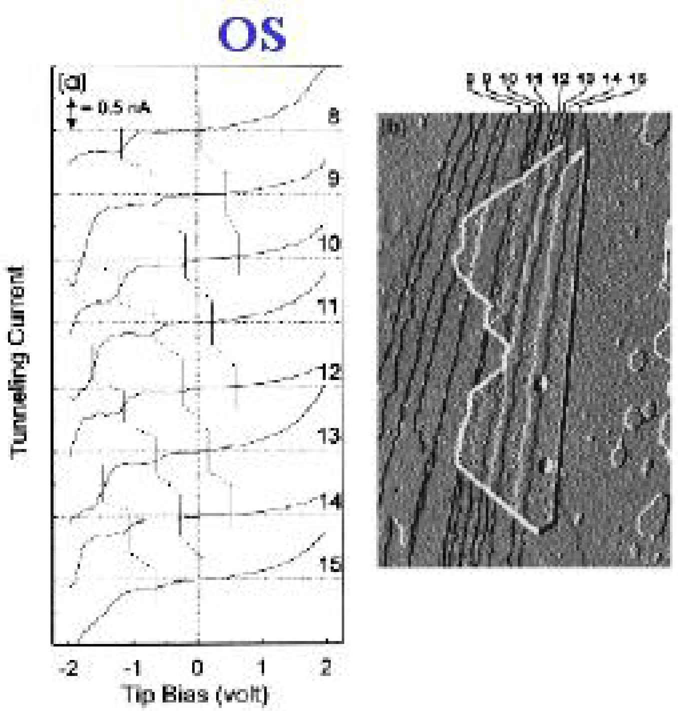
Sharp steps corresponding to different n levels (2D subbands). Δ (separation at E_F) ↘ with N.



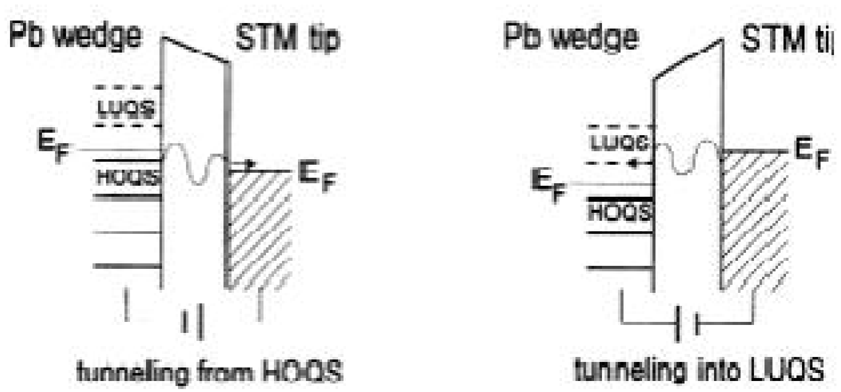
$1/\Delta$ vs N$\Rightarrow v_F=1.9\ 10^8$ cm/s along (111), in agreement with previous data (photoemission). **Confirms QWS.**

Confinement ⊥ surface.

- Contrast (fringes) in OS images at high bias.



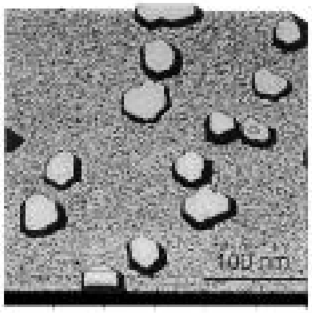
Correlation between the current at high bias (OS) and the position of the first occupied state
⇒Contrast in OS images (thickness)
⇒Characterization of a buried interface.
The highest occupied state gives the main contribution to the current (OS) since it has the lowest barrier.



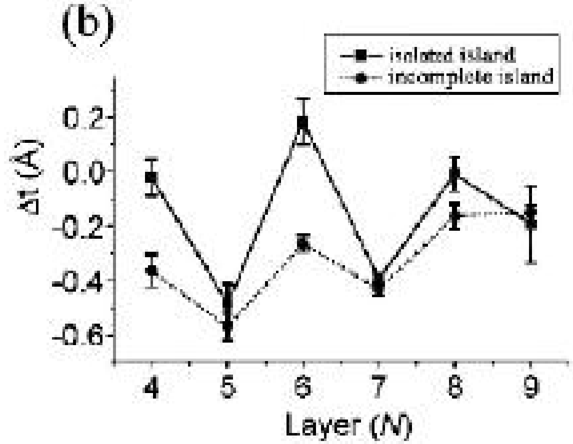
OS images high bias (5 V)
Spectra at constant separation.

Confinement ⊥ surface.

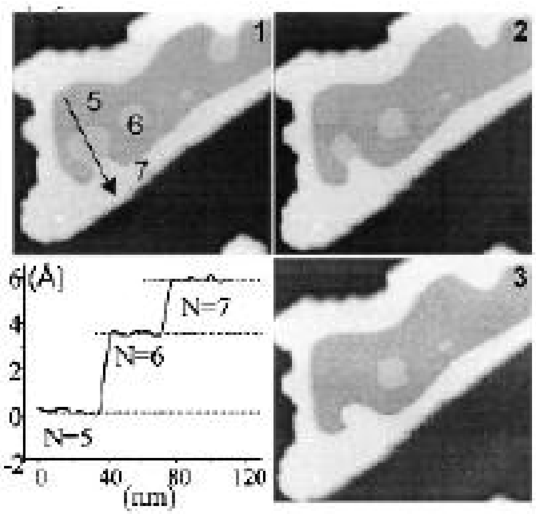
- **Influence of quantized states on the structure of Pb islands.** (W. B. Su et al, PRL 86, p 5116 (2001))



300nmx300nm
Island heights :
4-9 AL above a
2ML WL.
Pb(111) surface



Δt=measured thickness $-N*d_0$



300nmx300nm, +2.0V
5 to 7 AL above WL.

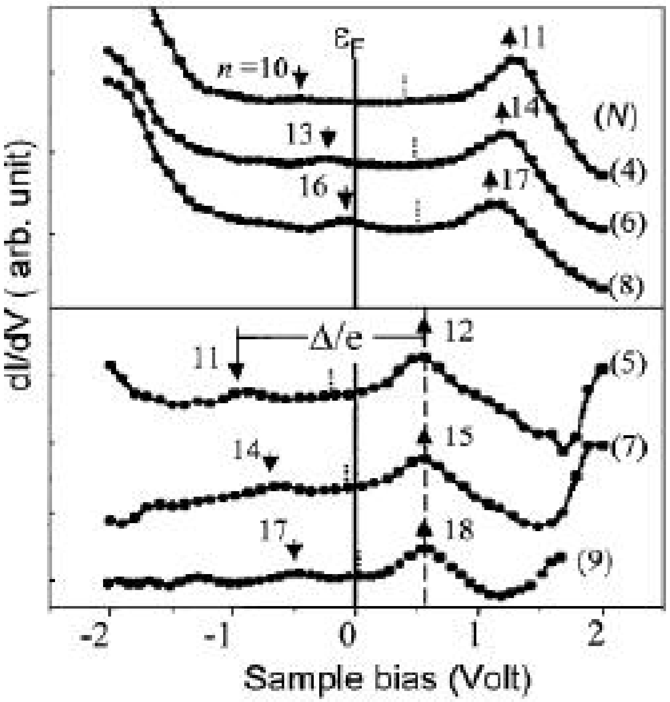
Variation of the apparent height of the islands, with a period of 2 AL. These changes are not due to electronic effects only (observed at ≠ biases)

⇒ **structural oscillations.**

Oscillations of monoatomic steps also observed for Pb/Ge(001) by He scattering. A. Crottini et al., PRL 79 1527 (1997)

Confinement ⊥ surface.

- **Influence of quantized states on the structure of Pb islands.** (W. B. Su et al, PRL 86, p 5116 (2001))



N: number of AL in the island (above WL)

n: index of the QW state (assigned here).

Same Fermi velocity as in prev. work

The oscillating relaxation is correlated to changes in the electronic structure (position of the subbands relative to E_F).

The appearance of a new QW state below E_F when N increases will change the electron distribution in the film and will affect the electronic (WF, resistivity) and the structural properties*.

Origin of the bilayer oscillation:

For Pb(111): $2d_0 \approx 3\ (\lambda_F/2)$

1 new state at E_F for $\Delta H = \lambda_F/2 = 2d_0/3$, or:

$\Delta H = 2d_0 = 3 \times \lambda_F/2$, ($\Delta H = d_0 = 3 \times \lambda_F/4$)

⇒+3 states for +2 AL: bilayer periodicity

⇒1 or 2 new states below E_F for +1 AL, sequentially

* Jalochowski et al., PRB 38 (1988), Yeh et al., PRL 85 (2000)

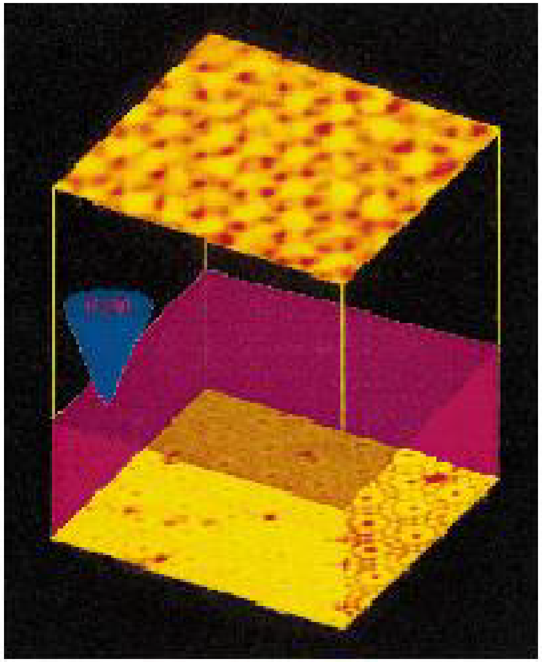
Confinement ⊥ surface.

Summary.

Observation and analysis of confined (QW) states

Characterization of the buried Interface (monoatomic steps).

Influence of the confinement on the Structural parameters.

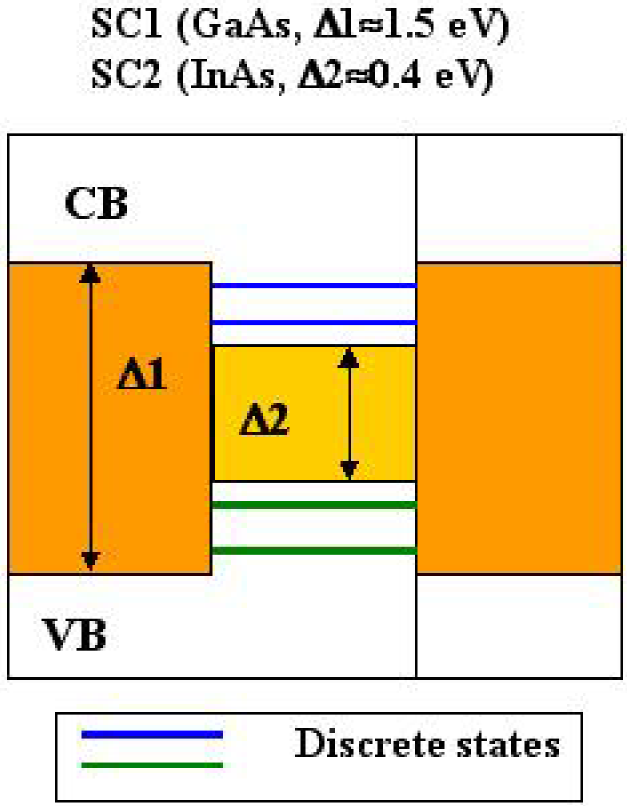


The interfacial Si(111)7x7 lattice buried under 100 Å of Pb (purple block imaged with STM on top of bhe Pb at 77 K.
D. Chen, JESRP 2000.

Imaging of the wave function.

Wave functions in QD of InAs/GaAs (100)

B. Grandidier et al., PRL 85, 1068 (00), see also: Oded Millo, PRL 86, 5751 (01)



Electrons at the top of the VB and at the bottom of the CB in the small gap SC can not propagate in the large gap SC.

⇒ Confinement of the electrons and holes by the band offest

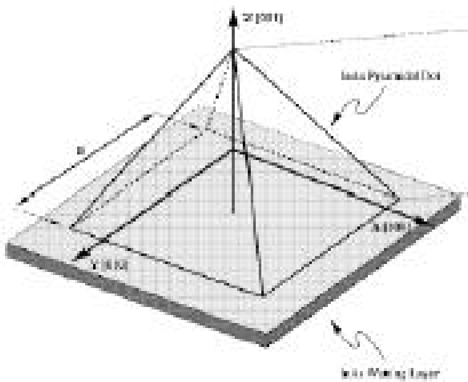
⇒ **discrete states in a 0D object.**

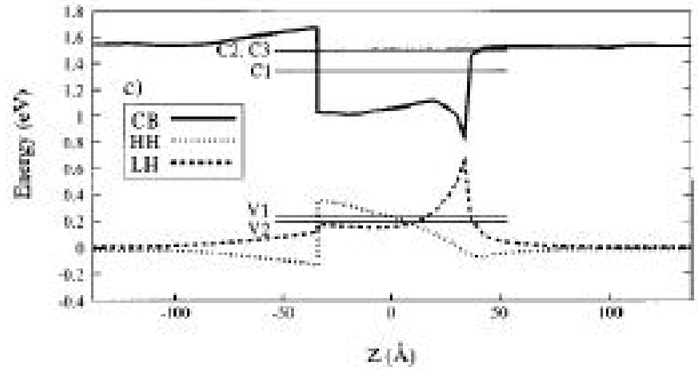
0D objects: InAs islands in GaAs (« self organized » SK growth mode).

Imaging of the wave function.

Confined states: more realistic calculations.

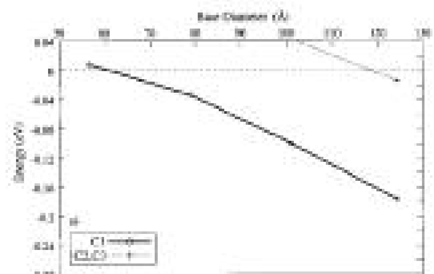
Calculations by M. A. Cusak et al., PRB 54, R2300 (1996). Includes strain,…





Confining potential
For electrons and holes.
Ground and first excited e (C1, C2, C3) and h energy levels

System : pyramid of base 12.4 nm, of height 6.2 nm above a 1.5 ML thick WL. Elastic relaxation of atomic positions



Electron energy levels relative to the GaAs VB (----) for different sizes of the base.

Electrons are confined in InAs QD

Imaging of the wave function.

« Topography » of the QD.

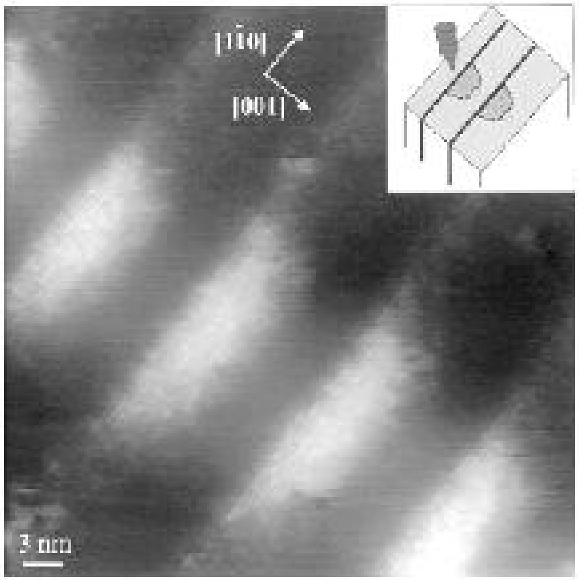


FIG. 1. STM image of the (110) face of an InAs box-stack layer in GaAs. The image was acquired at a sample bias of 1.86 V. Inset: Schematic diagram of the cleave.

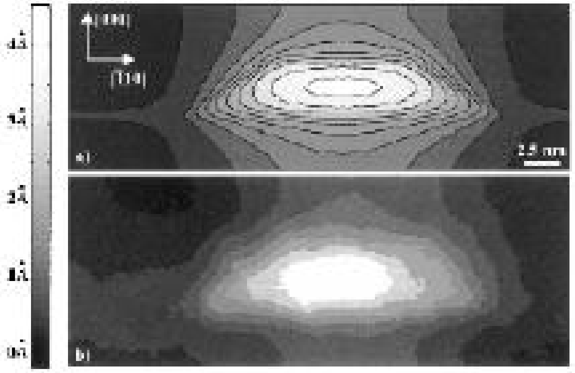


FIG. 2. Comparison of the height variation between (a) a simulated topographical image and (b) a STM image of the cleaved InAs box located in the center of Fig. 1. A low pass filter was used to remove the atomic corrugation from (b). For clarity, a contour line plot is displayed.

Arrays of InAs QD separated by GaAs
MBE Growth
Cleaved « in-situ » ⊥ surface
InAs boxes appear bright (GaAs: dark)
InAs QD: length ≈20 nm, height ≈4-6 nm.

Contrast of the InAs boxes: Structural height variation due to strain relaxation. (No electronic Effect at biases ~ +2.0 V

Δh≈4 Å for experiment and computation (elasticity theory).

Imaging of the wave function.

Technique: Current imaging tunneling spectroscopy (CITS)

For each point of a **topographic image** (I and V constant), a full I(V) spectrum is recorded **at constant tip sample separation d** (d is often given by the topographic image) after turning the **feedback loop off**.

⇒ **Spatially resolved tunneling spectroscopy**

⇒ **Maps of the LDOS at sub nm resolution.**

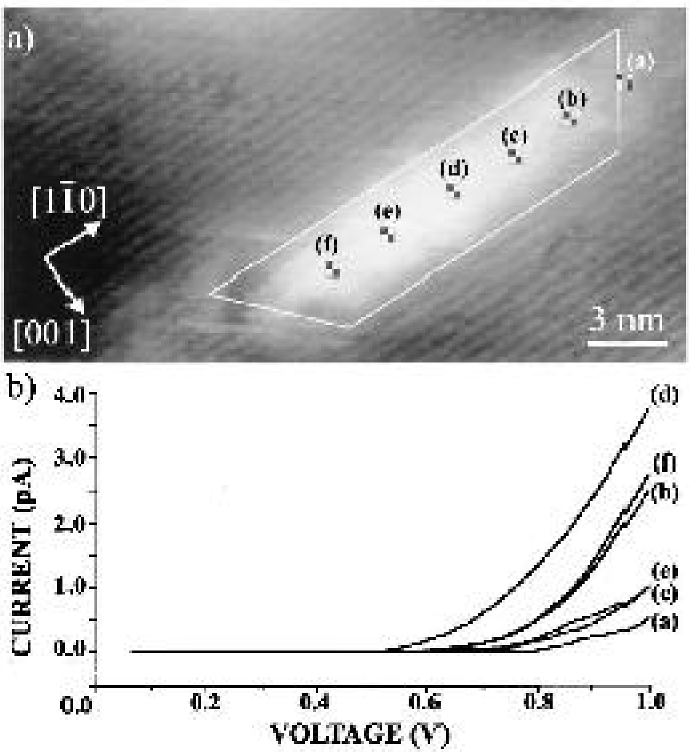
In the present case: Current images at different biases.

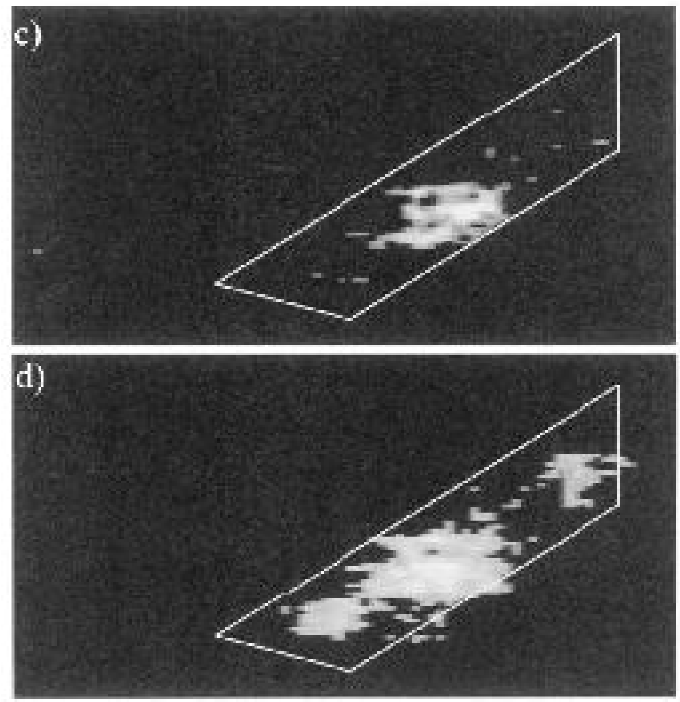
Stab. voltage: +2.15 V

Island: 20 nm (base) and 4 nm (height).

Imaging of the wave function.

Results, experiments at RT (300 K):





V range:

+0.63 to +0.74 V

V range:

+0.74 to +0.90 V

Topography and selected spectra :

-Onset voltage depends on the area.

-Mirror symetry

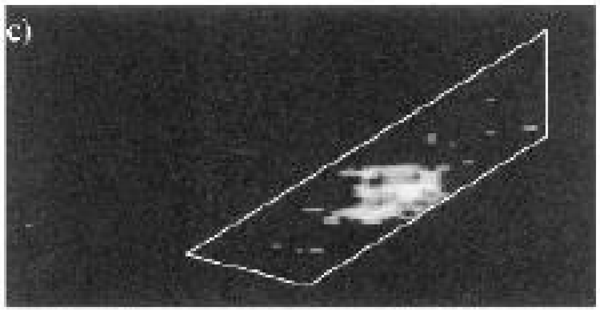
Current images at +0.69 V (c) and +0.82 V (d).

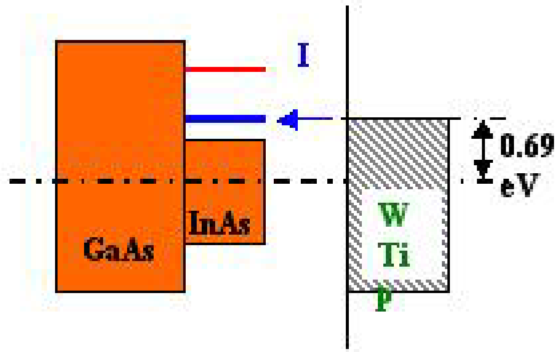
-Grey scale: 0.01-0.8 pA (c) and 0.01 to 1.5 pA (d)!!

⇒SW pattern in the box.

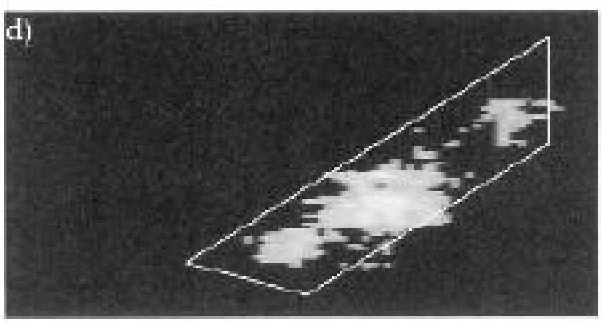
Imaging of the wave function.

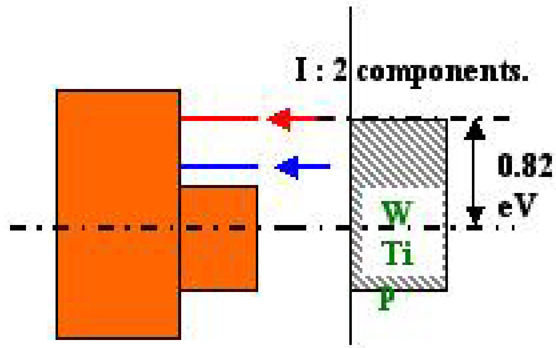
Interpretation of current images in terms of electron states.





Ground state for electrons in the box



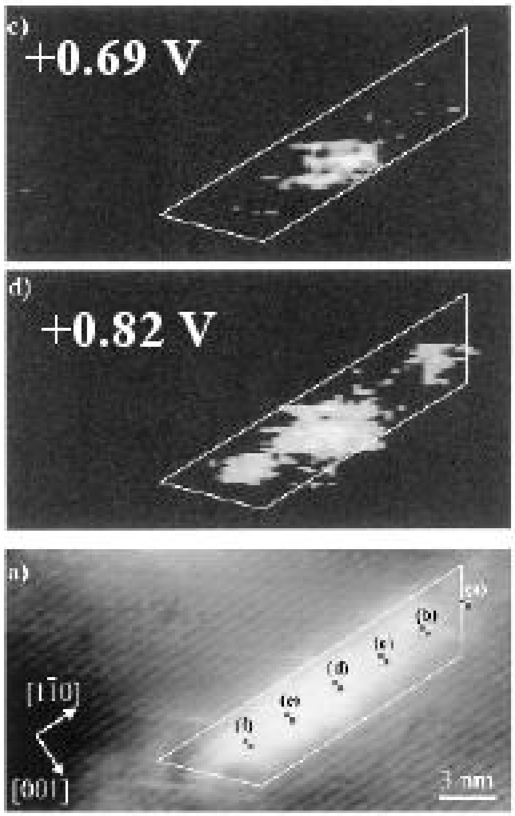


Ground state and first excited statefor electrons in the box

<u>Higher biases</u>: no other features in the box. Tunneling into the WL and the GaAS CB.
<u>No charging effects</u> in the box (small I, fast radiative recombination: 1.3 ns)

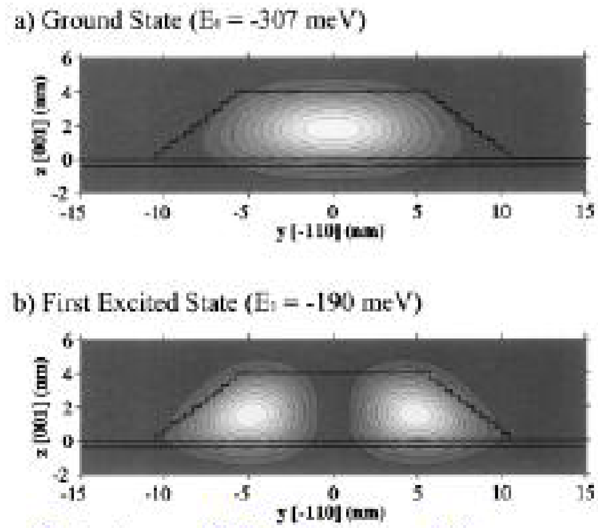
Imaging of the wave function.

Comparison with theory (with the same geometry):



Experiment

Computation of $|\Psi(R)|^2$ for the 2 lowest levels in the box: (|000> and |010>, with y// [1$\bar{1}$0])



Energy measured with to CB minimum of GaAs

Ground state: s-like (no node)

First excited state: p_y-like (nodal plane ⊥[1$\bar{1}$0])

ΔE≈110 meV, similar to expt. (130 meV), for ≠ geometries.

Good agreement, QS resolved at RT.

Wave function imaging ⇒ Understanding of electronic (optical) properties of nanoobjects.