Ge/Si quantum dots and nanostructures

Nunzio Motta

INFM-Università di Roma TRE

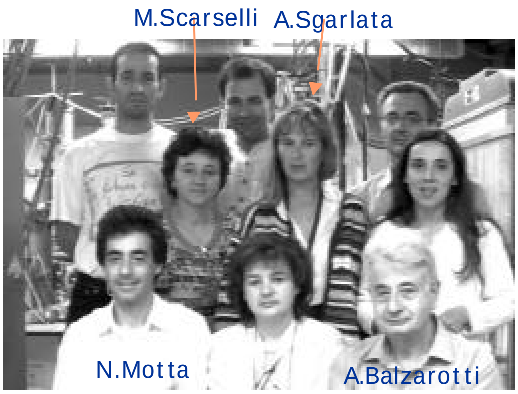
Coworkers

INFM-Dip. Fisica, Università di Roma Tor Vergata

Dr.Anna Sgarlata,

Dr. M.Scarselli

Prof. A.Balzarotti,



Dr. F.Rosei

CAMP, University of Århus, Denmark

Introduction

- **Semiconductor quantum dot:**
  - the ultimate quantum confined structure
- **Unique electronic properties:**
  - d - function like energy dependence of the density of states
  - quantum confinement of carriers in all 3 dimensions
- **Needs:**
  - lateral dimensions < l De Broglie (50 nm)
  - Uniformity in shape and dimensions
  - Reliable ordered distribution
  - direct synthesis of devices by epitaxial growth
- **Self assembled epitaxial growth:**
  - Damage-free structures
  - Coherent crystals
  - Good integration with microelectronic fabrication

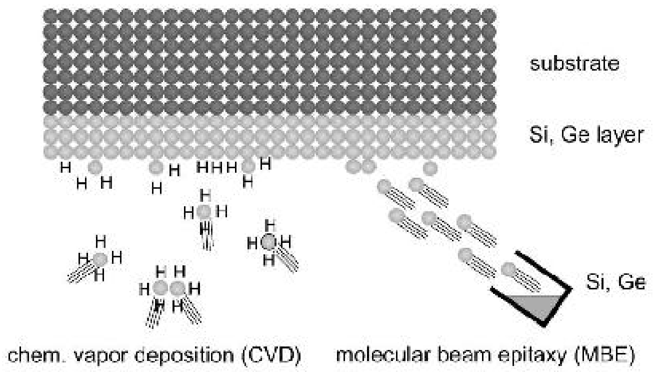
Outline

- **Growth techniques**
- **Heteroepitaxy**
- **Lattice strain and Stranski-Krastanov growth**
- **Coherent islands:**
  - Nucleation, growth, evolution
- **Stabilization of the island shape**
- **Growth on special substrates**
- **Conclusions**

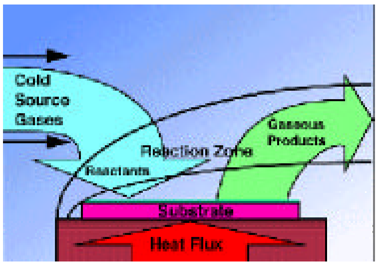
Growth techniques

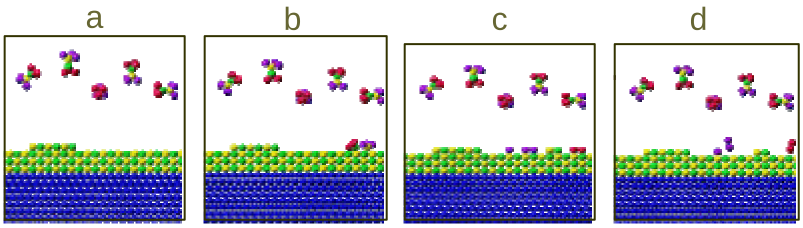
- **CVD:**
  - **Chemical Vapour Deposition (CVD)**
    - **0.1 - 100 nm/min**
- **MBE:**
  - **Molecular Beam Epitaxy**
    - **0.01 - 20 nm/min**
- **PVD:**
  - **Physical Vapour Deposition**
    - **0.001 – 0.5 nm/min**

Growth techinques



Chemical Vapour Deposition

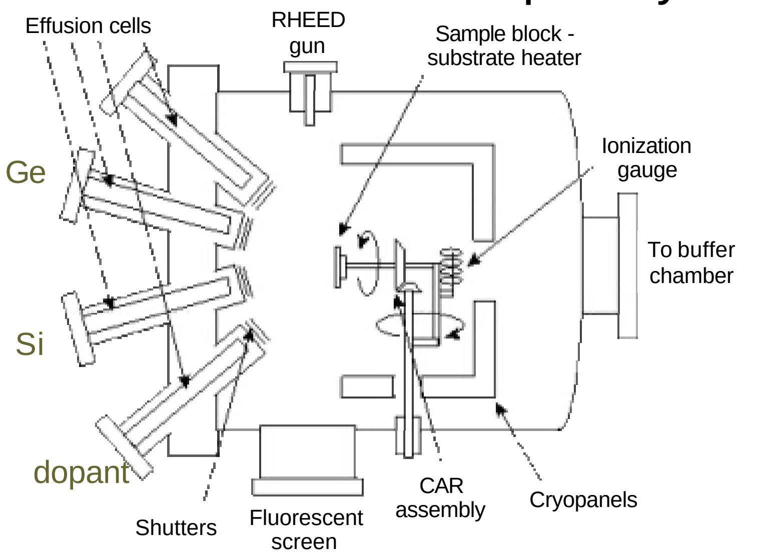




Base Pressure : 1 10^{-10} Torr

Growth Pressure: 10 -760 Torr

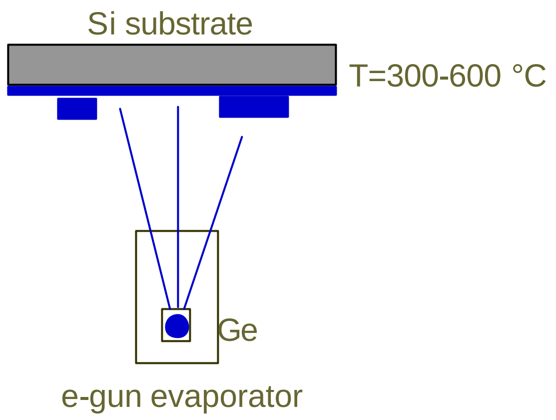
Molecular Beam Epitaxy



Base Pressure : 5 10^{-11} mbar

Growth Pressure: 10^{-8} -10^{-10} mbar

Physical Vapour Deposition



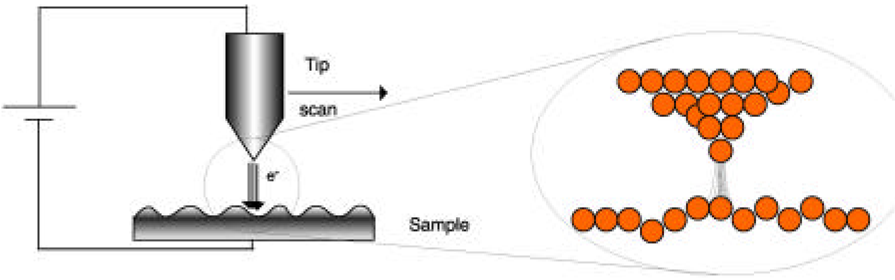
Base Pressure : 5 10^{-11}mbar

Growth Pressure: 10^{-9} -10^{-10}mbar

Characterization techniques

- **Scanning Probe Microscopies**
  - **QD size and distribution**
- **Electron microscopies (SEM-TEM)**
- **Electron diffraction (RHEED)**
  - **in situ check of the epitaxy**
- **X-Ray Absorption (XAFS)**
  - **QD composition**

Scanning Tunneling Microscopy



By putting a metallic tip very close to the surface of a solid, and applying a small bias voltage (0.02-2 V) the electrons can "tunnel" through the vacuum barrier.

This quantum mechanical effect can be exploited to visualize the atoms of a surface because of the exponential behavior of the tunneling current as a function of the tip-sample distance.

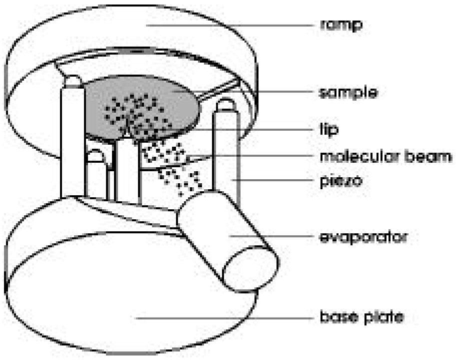
STM at work

SEM-movie during the STM measurement of a small Pb particle on Ru(001) (Voigtlaender - Juelich)

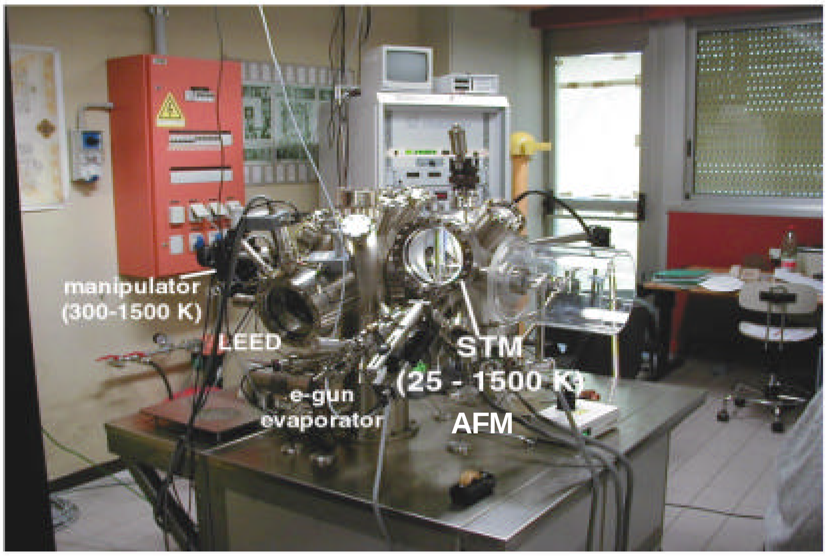
STM experimental set-up

for simultaneous MBE and STM imaging
(Voigtlaender - 1993)

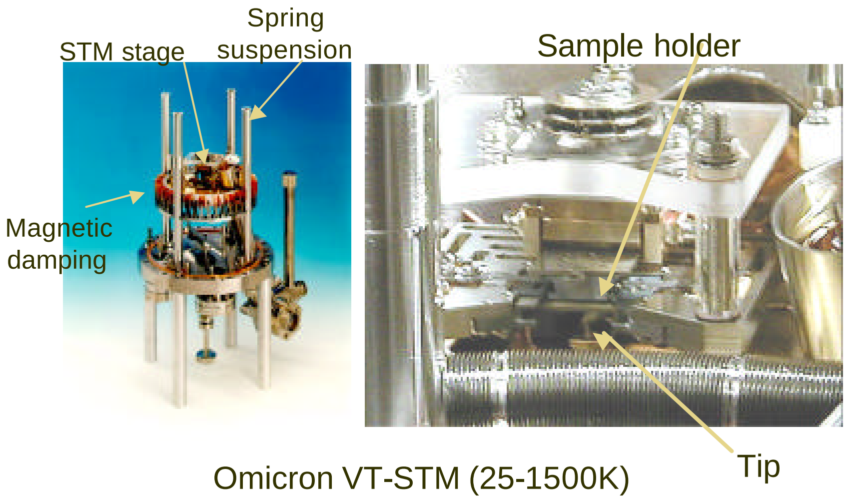
MBSTM: Simultaneous MBE and STM imaging at high temperature



VT-STM Lab
INFM-Roma Tor Vergata



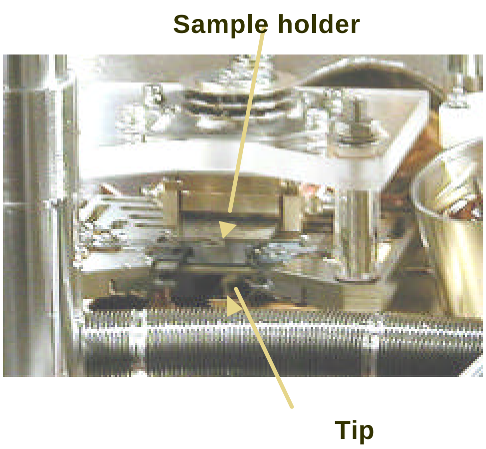
VT STM (Tor Vergata)

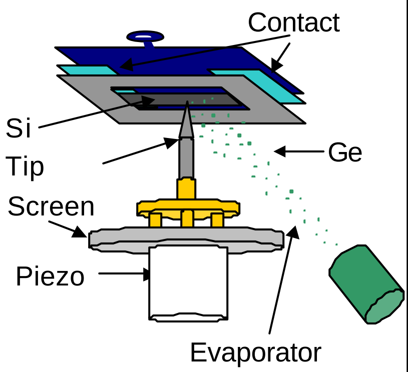


Omicron VT-STM (25-1500K)

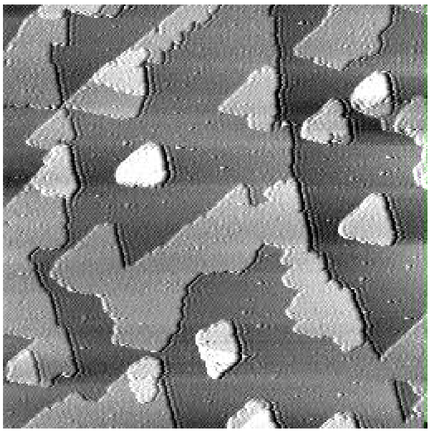
VT-STM Lab
INFM-Roma Tor Vergata

STM with direct current heating (300-1500 K)



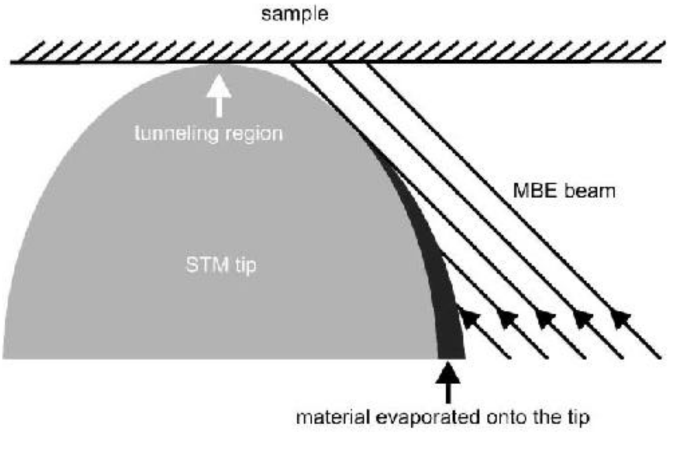


Growth of the wetting layer

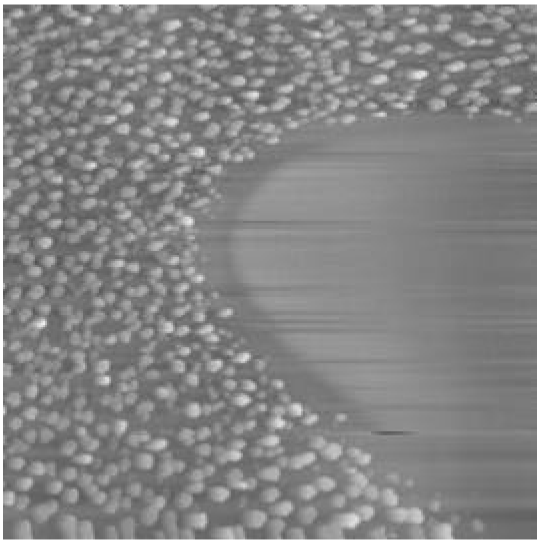


Video: Growth of Ge/Si(111) wetting layer
Voigtlaender, 1995

Tip shadow



Tip shadow (during the scan)



4 µm

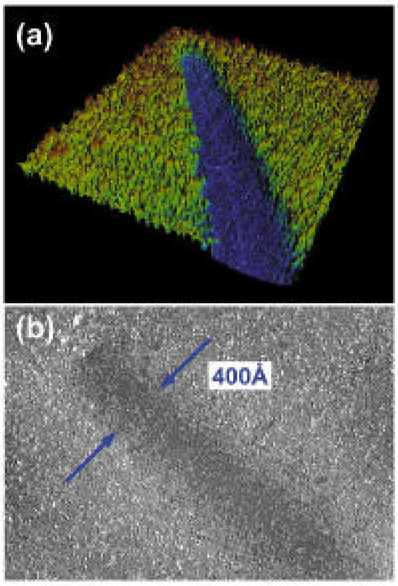
Ge/Si(111)

T=400°C
Ge flux = 0.15 ML/min
Final coverage: 20 ML

Total time: 1h 30min

A.Sgarlata et al: to be published

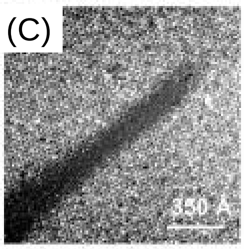
Tip shadow



Ge/Si
T=300K
Shadow images of STM tips

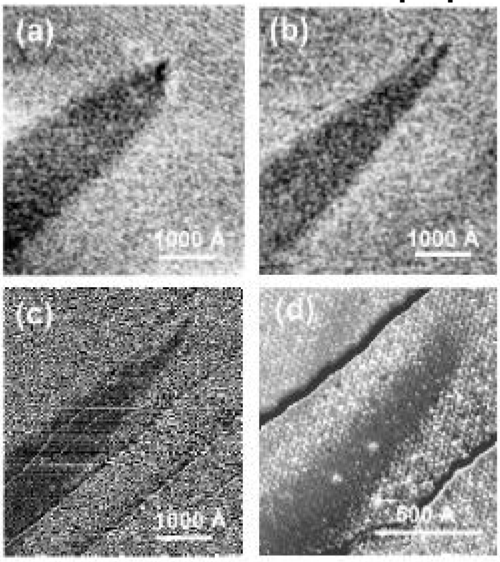
a) Tip diameter: 1000 Å
b) Tip diameter: 400 Å
c) Tip diameter: 100 Å

(C)



B.Voigtlaender, Surf.Sci. Rep. 43 (2001) 127

In situ tip preparation

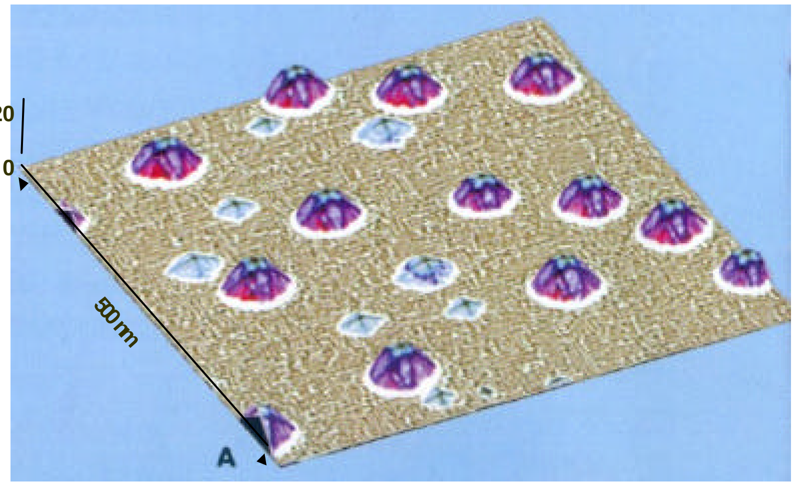


Shadow images of STM tips

a) As etched
b) After 10 min self sputt. + anneal. at 925 K
c) After heating at 1175 K
d) Close up of c).

B.Voigtlaender, Surf.Sci. Rep. 43 (2001) 127

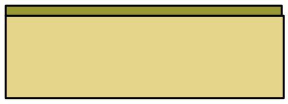
Heteroepitaxy



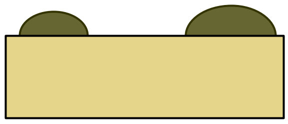
AFM image of self assembled Ge islands on Si(100)
G.Medeiros-Ribeiro et al. Science 279, 353 (1998)

Epitaxial growth modes

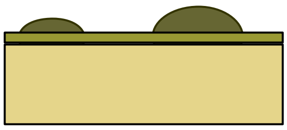
- Frank-Van der Merwe



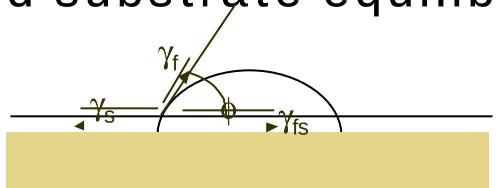
- Volmer-Weber



- Stranski-Krastanow



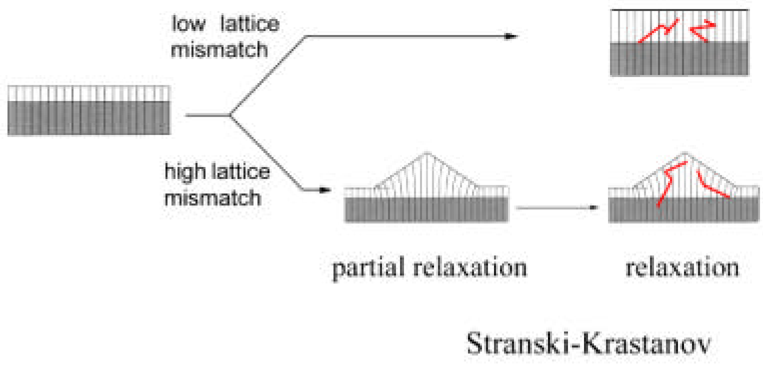
Island-substrate equilibrium



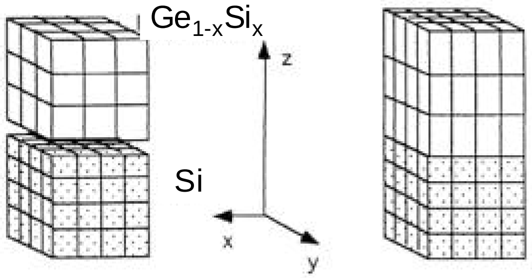
$\gamma_s = \gamma_f \cos\phi + \gamma_{fs}$ (Young-Duprè)

- **Layer by layer:** $\gamma_s \geq \gamma_f + \gamma_{fs} \Rightarrow \phi = 0$
- **Volmer-Weber:** $\gamma_s < \gamma_f + \gamma_{fs} \Rightarrow \phi > 0$
- **Stranski-Krastanow: mix of the two:**
  - before the critical thickness: $\gamma_s \geq \gamma_f + \gamma_{fs}$
  - after the critical thickness: $\gamma_s < \gamma_f + \gamma_{fs}$

Evolution of a strained heterostructure



Pseudomorphic growth



Lattice parameter { Ge = 5.65 Å, Si = 5.43 Å }

Lattice Mismatch $e = \frac{d_{Ge} - d_{Si}}{d_{Ge}} = 4.2\%$

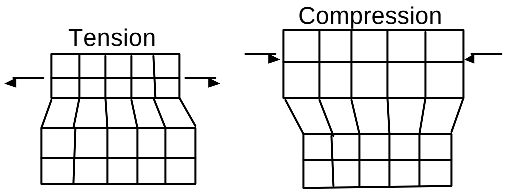
Lattice mismatch and deformation

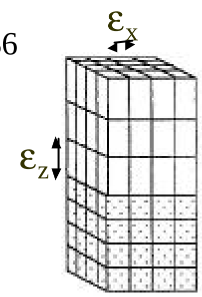
- The lattice mismatch is the cause of the deformation
- The energy accumulated in the deformation is: $E \sim k\varepsilon^2$ and it is proportional to the number of layers
- When no dislocations appear we have a “coherent strain”.

- The deformation is partially compensated by a tetragonal distortion

$$e_z = \frac{a_z - a_{Ge}}{a_{Ge}} = 0.15$$

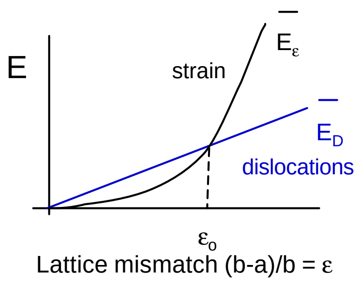
$$a_z = a_{GeSi}^{def} = 5.86$$

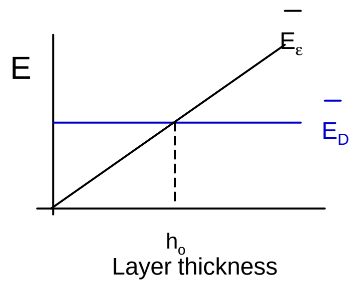




Lattice mismatch and dislocations

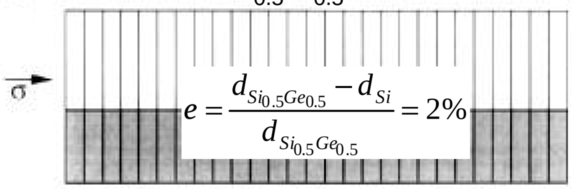
- It is interesting to compare the energy density accumulated in the wetting layer
  - in the lattice distorsion
  - in the dislocations
- as a function of the deposited thickness





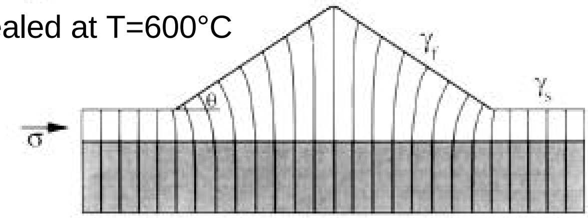
Accommodation of the strain

2 nm $Ge_{0.5}Si_{0.5}$ at T=400°C



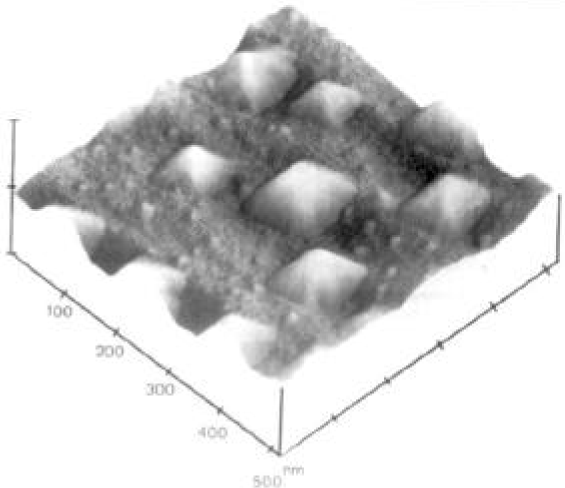
$$e = \frac{d_{Si_{0.5}Ge_{0.5}} - d_{Si}}{d_{Si_{0.5}Ge_{0.5}}} = 2\%$$

Annealed at T=600°C



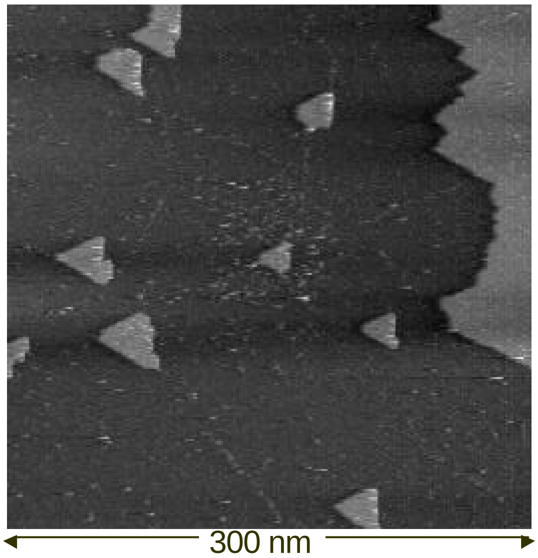
From Jesson, Chen and Pennicook, MRS bull 4/96

Accommodation of the strain



AFM image of an initially planar 2-nm-thick $Si_{0.5}Ge_{0.5}$ alloy layer on Si(100) annealed for 5 min at T=600°C

Growth of the wetting layer



Ge/Si(111)

Flat substrate

T=400°C

Ge flux = 0.02 ML/min
Final coverage: 2 ML

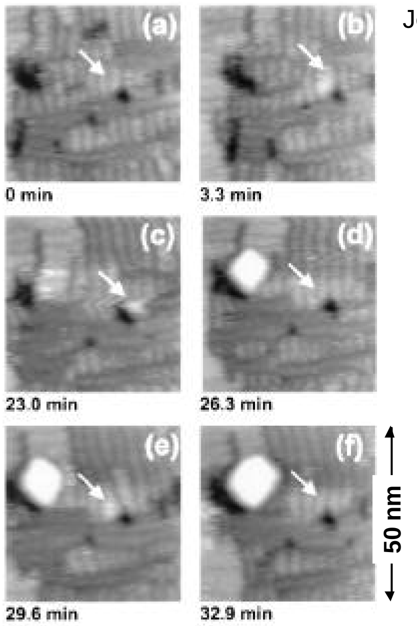
Total time: 2h
~1 image/min

A.Sgarlata et al: to be published

Nucleation of coherent islands

- **Coherent and strained layer by layer growth is favoured:**
  - **for** $e < e_o$
  - **for** $h < h_o$
- **for** $h > h_o$ **coherent islands can nucleate**
- **Chen and Washburn (PRL 77, 4046 (1996)**
  - **2D platelets grown over the critical size** N_c **become unstable**
  - **the adatoms deposited on the wetting layer tend to diffuse and hop to the top of the platelet**
  - **3D islands are formed abruptly**

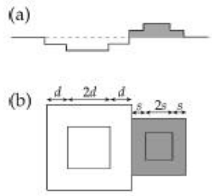
Nucleation of the islands



Jesson, Kastner, Voigtlaender, PRL 84, 330 (2000)

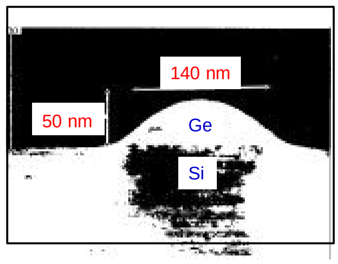
2D-3D transition
Ge deposition on Si(001)
T=300 °C.

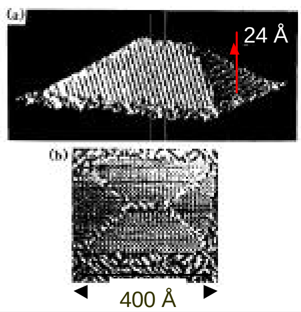
Two monolayer high fluctuations containing 270, 120, and 140 atoms occur at the arrowed pit after 3.3 min



Coherent islands of Ge/Si(001)

- **First discoveries**
  - **Eaglesham and Cerullo PRL 64,1943 (1990)**
    - **Dislocation-free islands imaged by TEM**
    - **~100 Å Ge deposited on Si(001) by MBE at 500 ºC**
  - **Mo, Savage, Swartzentruber, Lagally PRL 65, 1020 (1990)**
    - **PVD Ge on Si(001) at 500 °C**
    - **Atomic resolution STM**
    - **island shapes: hut clusters**





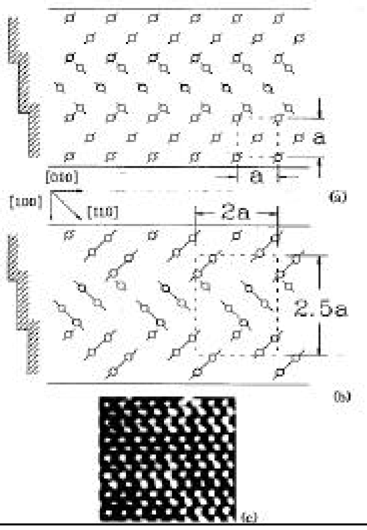
Coherent islands of Ge/Si(001)

- Mo, Savage, Swartzentruber, Lagally PRL 65, 1020 (1990)
  - Reconstruction of [501] facet

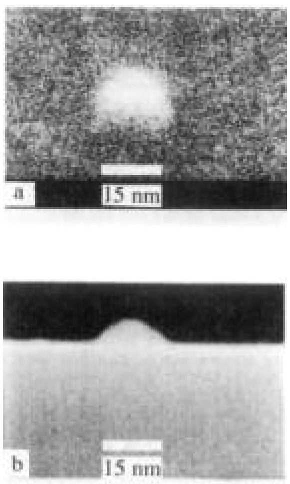
Unreconstructed [501] plane projected on [001] plane.

Reconstructed [501] plane projected on [001] plane.

STM scan on one of the [501] facets, 100x100 Å



Size vs strain

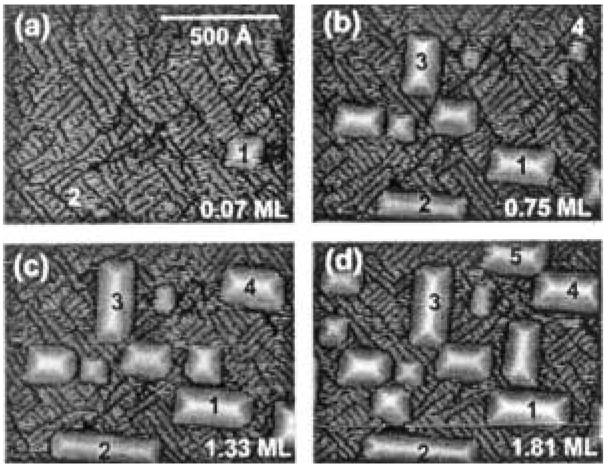


- **Island size**
  - **function of the strain**
- **Strain control**
  - **lattice mismatch**
  - **intermixing**
  - **growth temperature**
  - **growth speed**
  - **atom mobility**

A very small InGaAs /GaAs island grown by MBE
SEM images: Oshinowo et al. APL 65, 1422 (1994)

Ge/Si(100): 3D islands growth

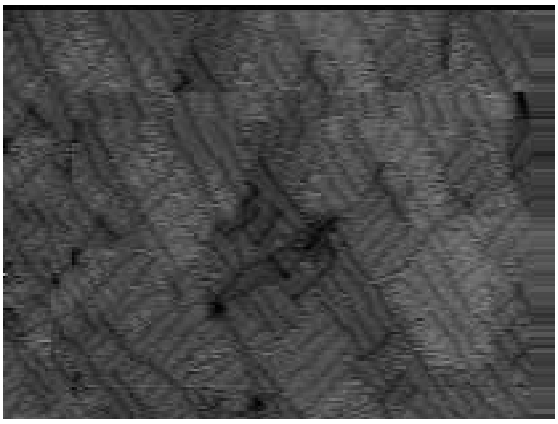
PVD (0.06ML/min) at T=300°C



STM Image: 130x100 nm^2

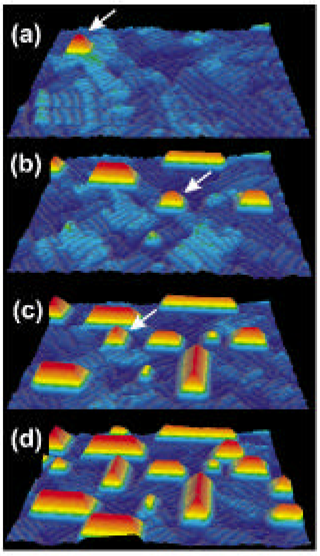
(Kastner, Voigtlaender, PRL 82 (1999))

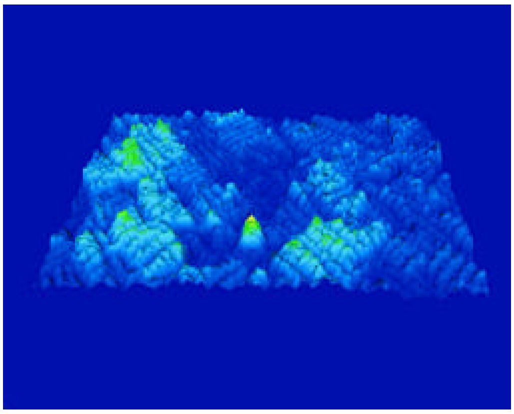
Ge/Si(100): 3D islands growth



3D islands growth by PVD of Ge/Si(100) at T=300 C
STM movie from: Kastner, Voigtlaender, PRL 82 (1999)
Ge flux: 0.06ML/min

Ge/Si(100): 3D islands growth

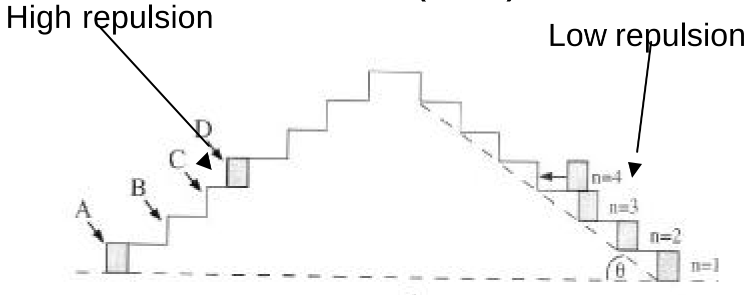


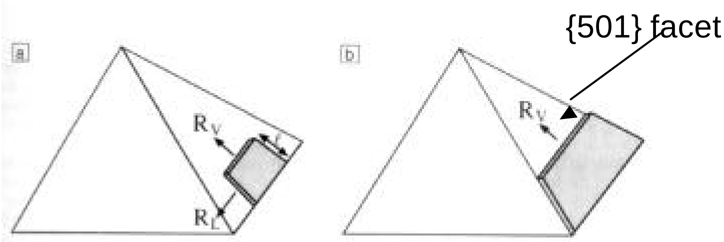


3D islands growth of Ge/Si(100) at T=300 C
STM movie from: Kastner, Voigtlaender, PRL 82 (1999)

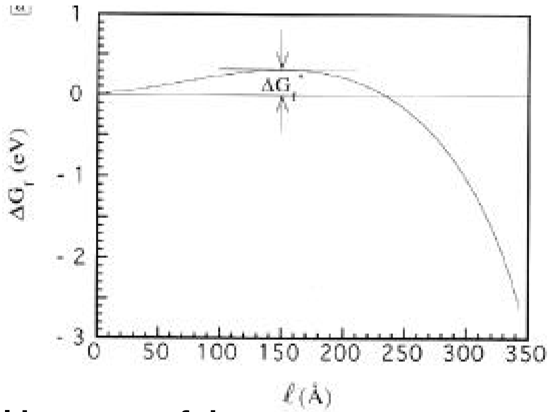
Island growth scheme

Ge/Si(001)





Energy change for a square nucleus of side *ℓ* on **{501} facet**



Initial increase of the energy

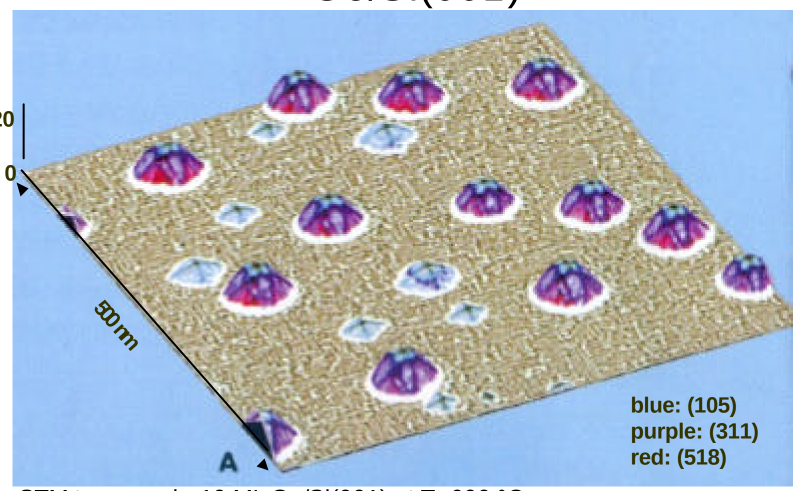
(concentration of stress at the base of the island)

At large coverage

the elastic energy released dominates

Distribution of island shapes

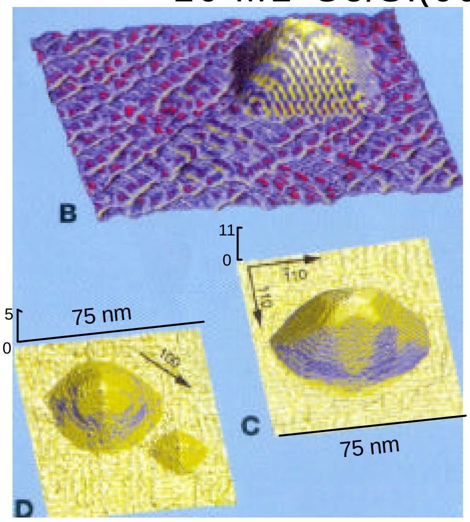
Ge/Si(001)



STM topograph: 10 ML Ge/Si(001) at T=600 °C
Gradient mode image: the colours represent the local surface curvature
Medeiros-Ribeiro et al. Science 279, 353 (1998)

Island shapes

10 ML Ge/Si(001) T= 600 ºC



- Physical Vapour deposition
  - 2-5 ML/min
- Ge/Si(001) nanocrystals
  - two different equilibrium shapes:
    - Pyramid (square based)
    - Dome

B. small pyramid (high resolution image)

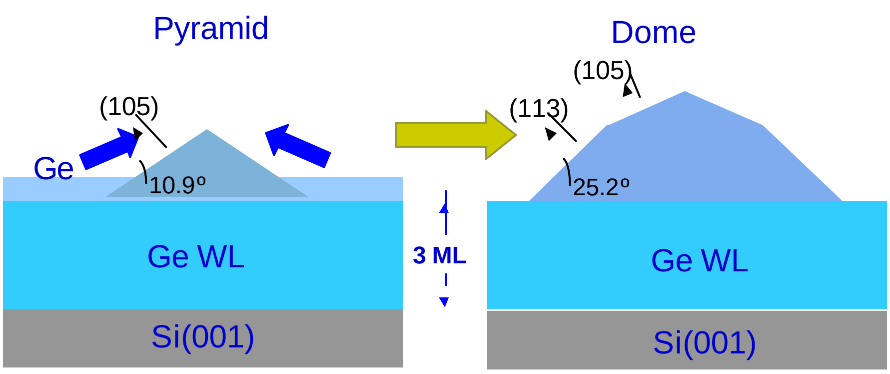
C. Mature dome

D. nanocrystal entering in the transition stage. Small pyramid

Medeiros Ribeiro et al. Science 279, 353 (1998)

From pyramids to domes

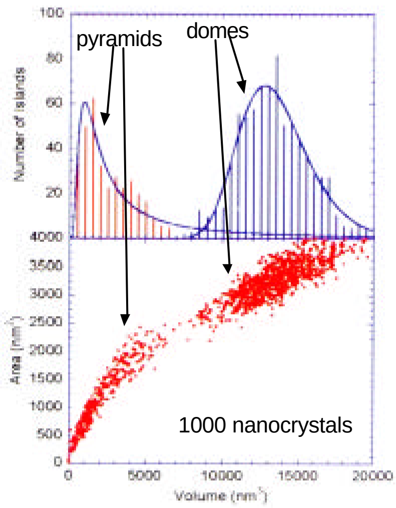
- Transition from the pyramid to dome shape
  - Pyramids nucleate and growth up to their max size
  - Diffusion of Ge atoms from the extra 2D layer to the island
  - Abrupt transition: pyramid -> dome



Medeiros Ribeiro et al. Science 279, 353 (1998)

Distribution of island shapes

Ge/Si(100)



- **At T<600°C**
  - **Hut clusters**
  - **Pyramids**
  - **Domes**
- **At T=600°C only:**
  - **Pyramids**
  - **Domes**
- **Max size and distribution widths independent by the amount of deposited Ge**
- **The distribution of the two shapes can be calculated from the energy of a strained nanocrystal containing n atoms and assuming a Boltzmann form**

Medeiros Ribeiro et al. Science 279, 353 (1998)

Distribution of island shapes

Ge/Si(100)

- **Energy of a strained nanocrystal - from Sckhukin (PRL 95):**

$$\Delta E[n] = Cn + Bn^{2/3} + An^{1/3}\ln\left[\frac{a_c}{n^{1/3}}\right]$$

- **DE = E(n atoms in a nanocrystal) - E(n atoms in a 2D island)**
- **C = negative coefficient: bulk energy**
- **B = coefficient from the facet energy difference :**
  - **atomic bonds on nanocrystal surface - atomic bonds on 2D layer**
    - **(positive)**
  - **relaxation of the surface bonds on nanocrystal with respect to 2D layer**
    - **(negative)**
- **A = positive coefficient (magnitude of the edge energy)**
- **a_c = elastic cutoff parameter**
- **Energy of an ensemble of nanocrystals [(N/n) = area density]:**

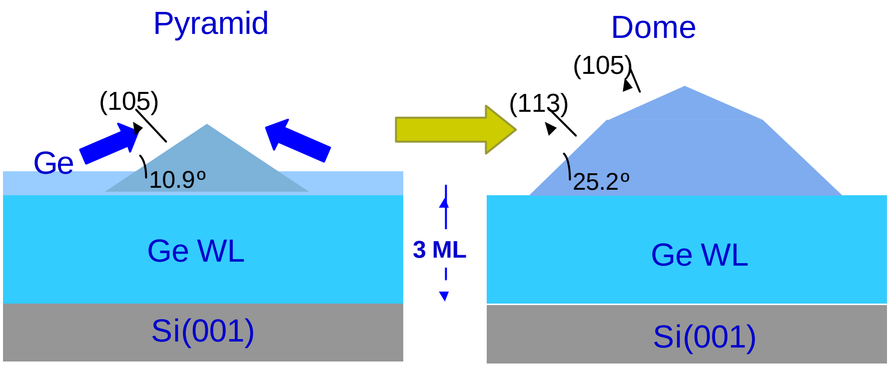
$$(N/n)\Delta E[n] = N\left(C + Bn^{-1/3} + An^{-2/3}\ln\left[\frac{a_c}{n^{1/3}}\right]\right)$$

Understanding the shape transition for Ge/Si(100)
(Medeiros et al.)

- **2D Ge islands on top of the wetting layer: reservoir**
- **Nanocrystal ensemble**
  - **open system**
  - **exchange energy and atoms with 2D islands**
  - **Distribution of 3d islands at equilibrium: Boltzmann form**
- **Pyramids nucleate and grow up to a max volume**
- **Max volume pyramids + atoms in the 2D islands:**
  - **Dome formation**
  - **Abrupt transition**
- **The island nucleation and evolution is independent from the growth method**
  - **but not on the growth parameters! (substrate T and deposition rates).**

From pyramids to domes

- **Transition from the pyramid to dome shape**
  - **Pyramids nucleate and growth up to their max size**
  - **Diffusion of Ge atoms from the extra 2D layer to the island**
  - **Abrupt transition: pyramid -> dome**



Medeiros Ribeiro et al. Science 279, 353 (1998)