Ge/Si quantum dots and nanostructures

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Introduction

- Semiconductor quantum dot: the ultimate quantum confined structure
- Unique electronic properties:
  - δ-function like energy dependence of the density of states
  - quantum confinement of carriers in all 3 dimensions
- Needs:
  - lateral dimensions < λ 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
Chemical Vapour Deposition

Base Pressure: $1 \times 10^{-10}$ Torr

Growth Pressure: 10^-760 Torr

Molecular Beam Epitaxy

Base Pressure: $5 \times 10^{-11}$ mbar

Growth Pressure: $10^{-8} - 10^{-10}$ mbar
Physical Vapour Deposition

Si substrate \[ T = 300-600 \, ^\circ \text{C} \]

Ge

e-gun evaporator

Base Pressure: \( 5 \times 10^{-11} \text{mbar} \)  
Growth Pressure: \( 10^{-9} - 10^{-10} \text{mbar} \)

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) (Voigtländer - 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
Voigtländer, 1995

Tip shadow

Sample

Tunnelling region

STM tip

MBE beam

Material evaporated onto the tip
Tip shadow (during the scan)

Ge/Si(111)

T = 400°C
Ge flux = 0.15 ML/min
Final coverage: 20 ML
Total time: 1 h 30 min

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

**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).


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**Heteroepitaxy**

AFM image of self assembled Ge islands on Si(100)

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
\[
\left\{
\begin{array}{l}
\text{Ge} = 5.65 \, \text{Å} \\
\text{Si} = 5.43 \, \text{Å}
\end{array}
\right.
\]

Lattice Mismatch
\[
\varepsilon = \frac{d_{\text{Ge}} - d_{\text{Si}}}{d_{\text{Ge}}} = 4.2\%
\]
Lattice mismatch and deformation

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

\[
\varepsilon_z = \frac{a_z - a_Ge}{a_Ge} = 0.15
\]
\[
a_z = a_{Ge}^{def} = 5.86
\]

Lattice mismatch and dislocations

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

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 $\varepsilon < \varepsilon_o$
  – 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 °C
  – 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


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 nm²
(Kastner, Voigtlaender, PRL 82 (1999))
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)

High repulsion

Low repulsion

{501} facet
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 $T=600 \, ^\circ$C
Gradient mode image: the colours represent the local surface curvature
Island shapes
10 ML Ge/Si(001) T= 600 °C

- 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

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

Pyramid
Dome

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.

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

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

- \(\Delta E\) = 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)
- \(a_n\) = elastic cutoff parameter
- Energy of an ensemble of nanocrystals [(N/n) = area density]:

\[
(N/n)\Delta E[n] = N \left( C + Bn^{-1/3} + An^{-2/3} \ln \left( \frac{a_n}{n^{1/3}} \right) \right)
\]
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 grow up to their max size
  - Diffusion of Ge atoms from the extra 2D layer to the island
  - Abrupt transition: pyramid -> dome