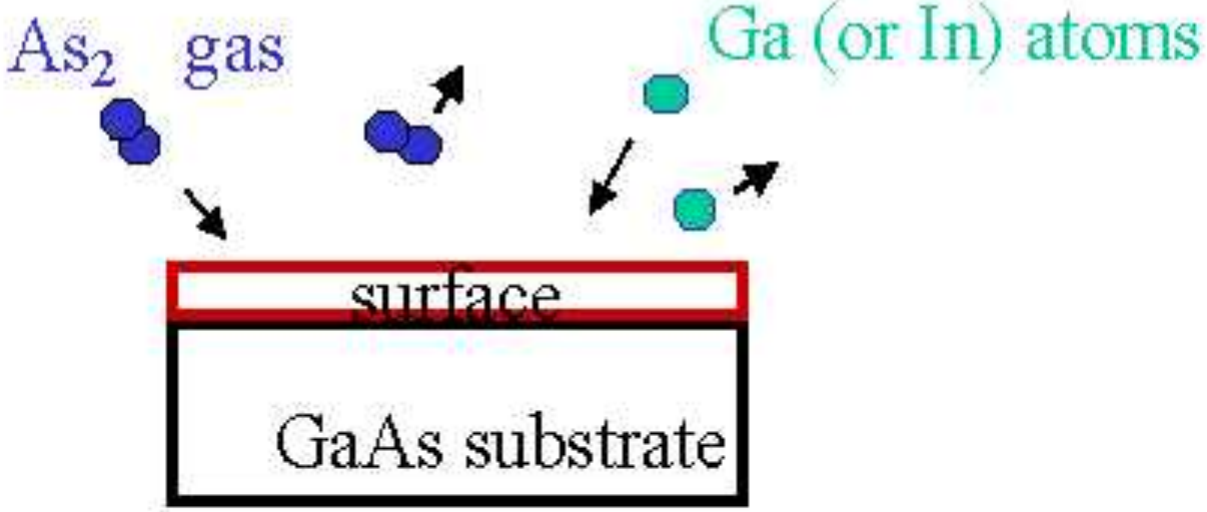
Surface diffusion, growth, and self-assembly of quantum dots at III-V semiconductor surfaces

Matthias Scheffler and Peter Kratzer
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin
http://www.fhi-berlin.mpg.de/th/th.html

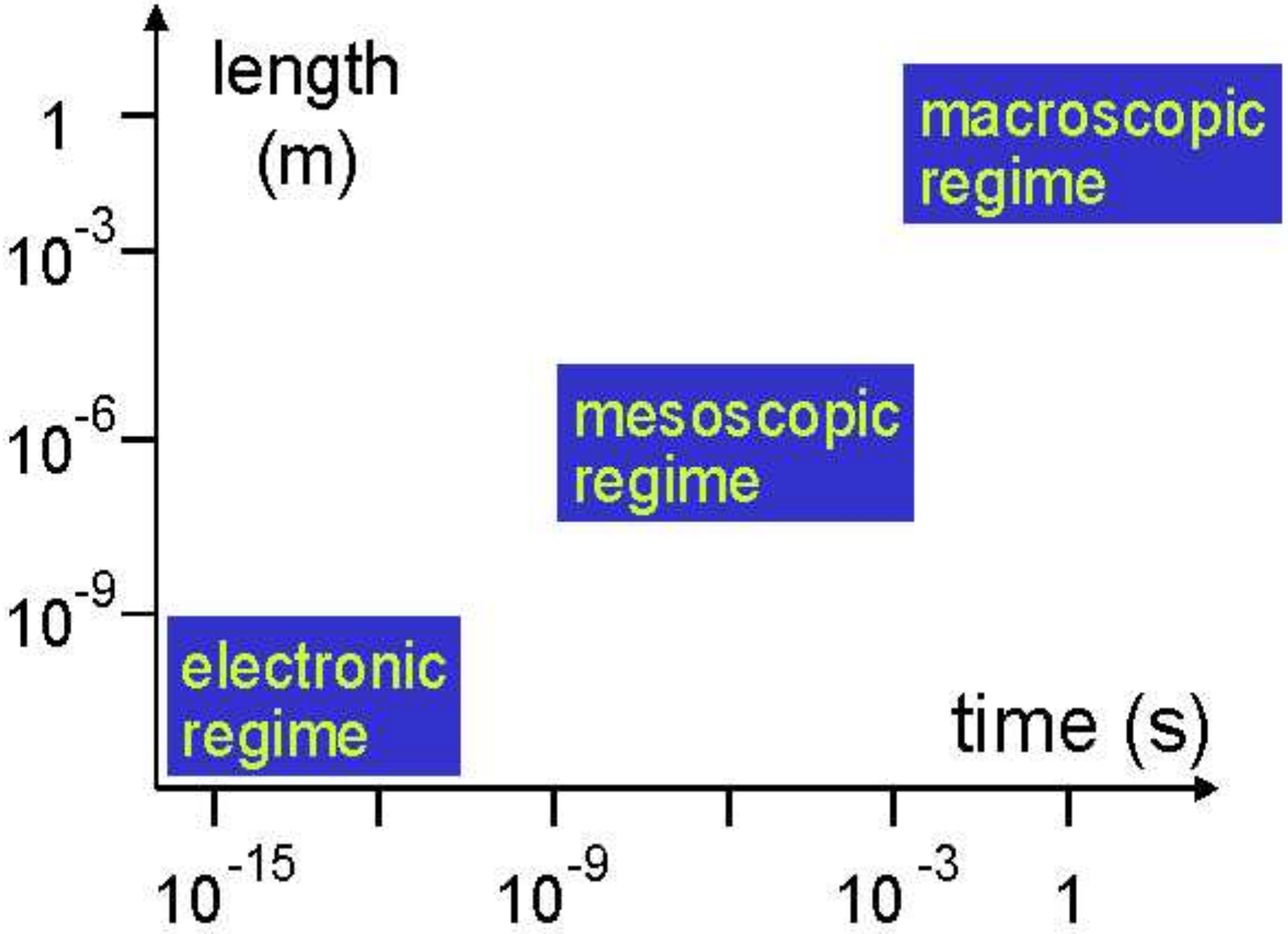
Microscopic processes controlling the growth of III-V semiconductors



1) deposition of Ga and As
2) adsorption of Ga
3) diffusion of Ga
4) desorption of Ga
5) adsorption of As_2 ?
6) dissociation of As_2 ?
7) diffusion of As
8) desorption of As
9) island nucleation
10) growth

key investigator: Peter Kratzer

- What are the microscopic processes to achieve stoichiometric growth?
- How do quantum dots form, and why do they assume a narrow size distribution (sometimes)


length
(m)
1
10-3
10-6
10-9
macroscopic
regime
mesoscopic
regime
electronic
regime
time (s)
10-15
10-9
10-3
1

Density Functional Theory

The energy of the ground state of a many-electron system : $E_0\,(\{\mathbf{R}_I\}) = \mathrm{Min}_{\Psi} \langle\Psi|H^e|\Psi\rangle$

Hohenberg and Kohn (1964): The functional

$$n(\mathbf{r}) \;=\; n[\Psi] \;=\; \langle\Psi| \sum_i \delta(\mathbf{r}-\mathbf{r}_i) \,|\Psi\rangle$$

can be inverted, *i.e.*,

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \Psi[n(\mathbf{r})] \quad .$$

This implies:

$$E_0\,(\{\mathbf{R}_I\}) = \mathrm{Min}_{n(\mathbf{r})}\, E_{\{\mathbf{R}\}}\,[n]$$

Kohn and Sham (1964):

$$E_{\{\mathbf{R}_I\}}[n] = T_s[n] + \int d^3r \; v^{\rm nuc}_{\{\mathbf{R}_I\}}(\mathbf{r}) n(\mathbf{r})$$

$$+ \frac{1}{2} \int\int d^3r d^3r' \; \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E^{\rm xc}[n]$$

with **local-density approximation**

or **generalized gradient approximation**

Accuracy of geometries is better than 0.1 Å. Accuracy of calculated energies (relative) is better than 0.2 eV [for special cases better than 0.01 eV].

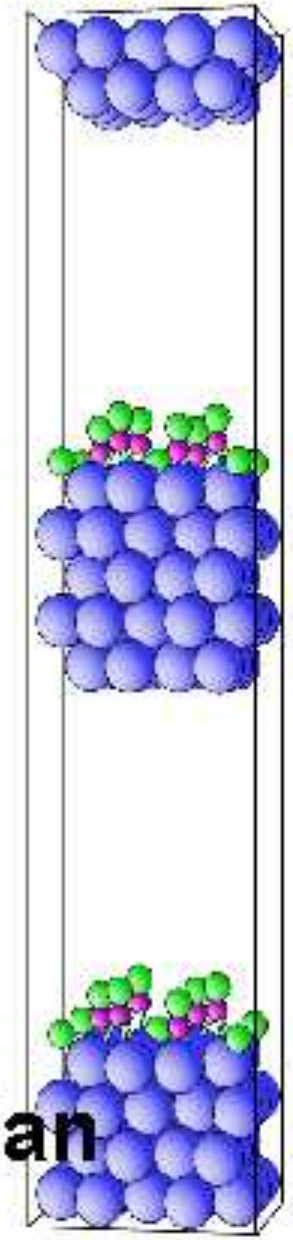
Methods

I

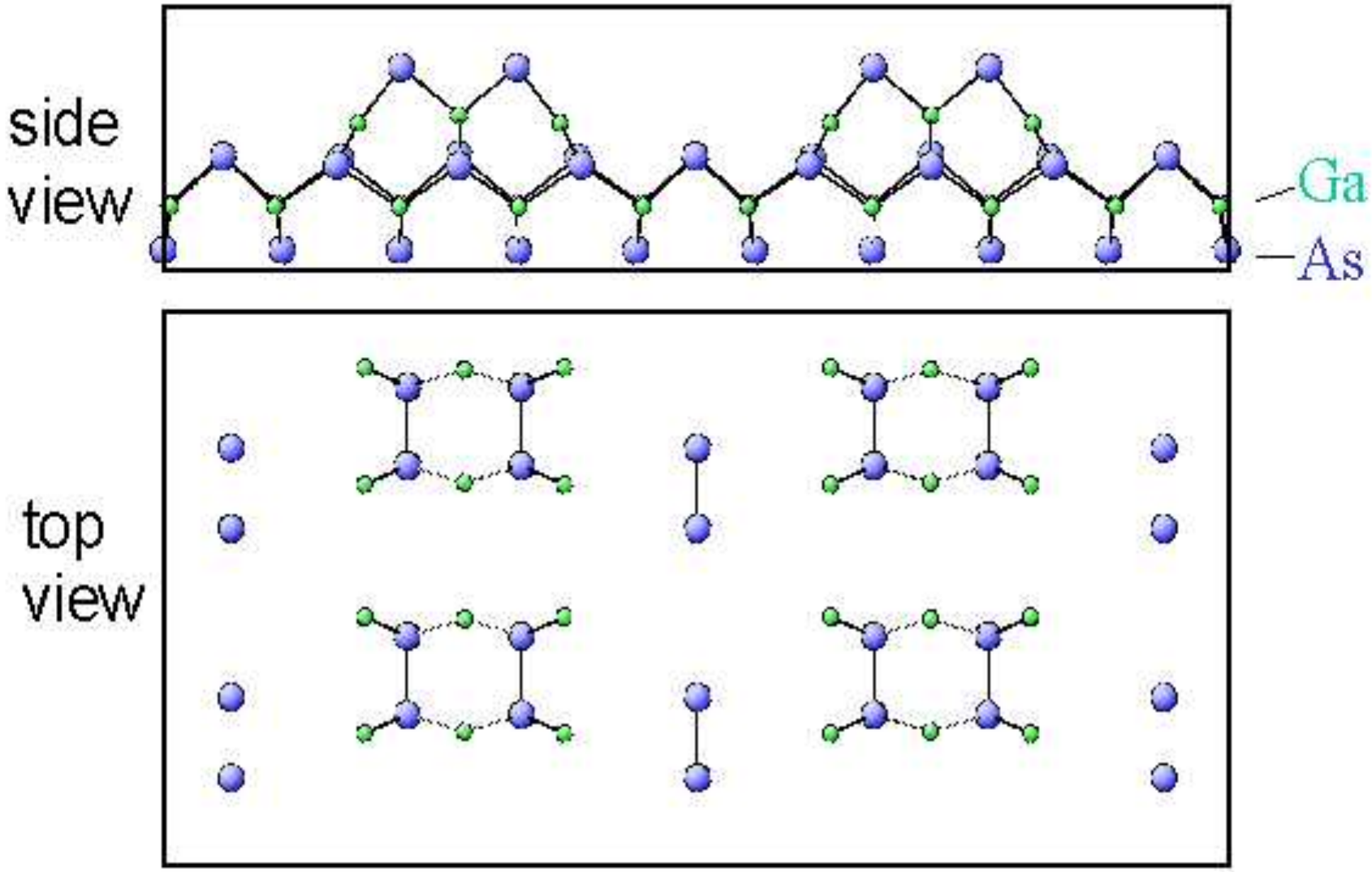
- **Density functional theory**
  - -- ***ab initio*** **pseudopotentials**
    (fhi96md --- *http://www.fhi-berlin.mpg.de/th/th.html*)
  - -- **FP-LAPW**
    (the WIEN - code by *P. Blaha, K. Schwarz, et al.; M. Petersen et al., CPC XX (2000)*)

II

- ***ab initio*** **Molecular Dynamics**
- ***ab initio*** **Quantum Dynamics**
- ***ab initio*** **Lattice Gas Hamiltonian**
- ***ab initio*** **kinetic Monte Carlo**



β2 reconstruction of GaAs (001)
(2x4) unit cell

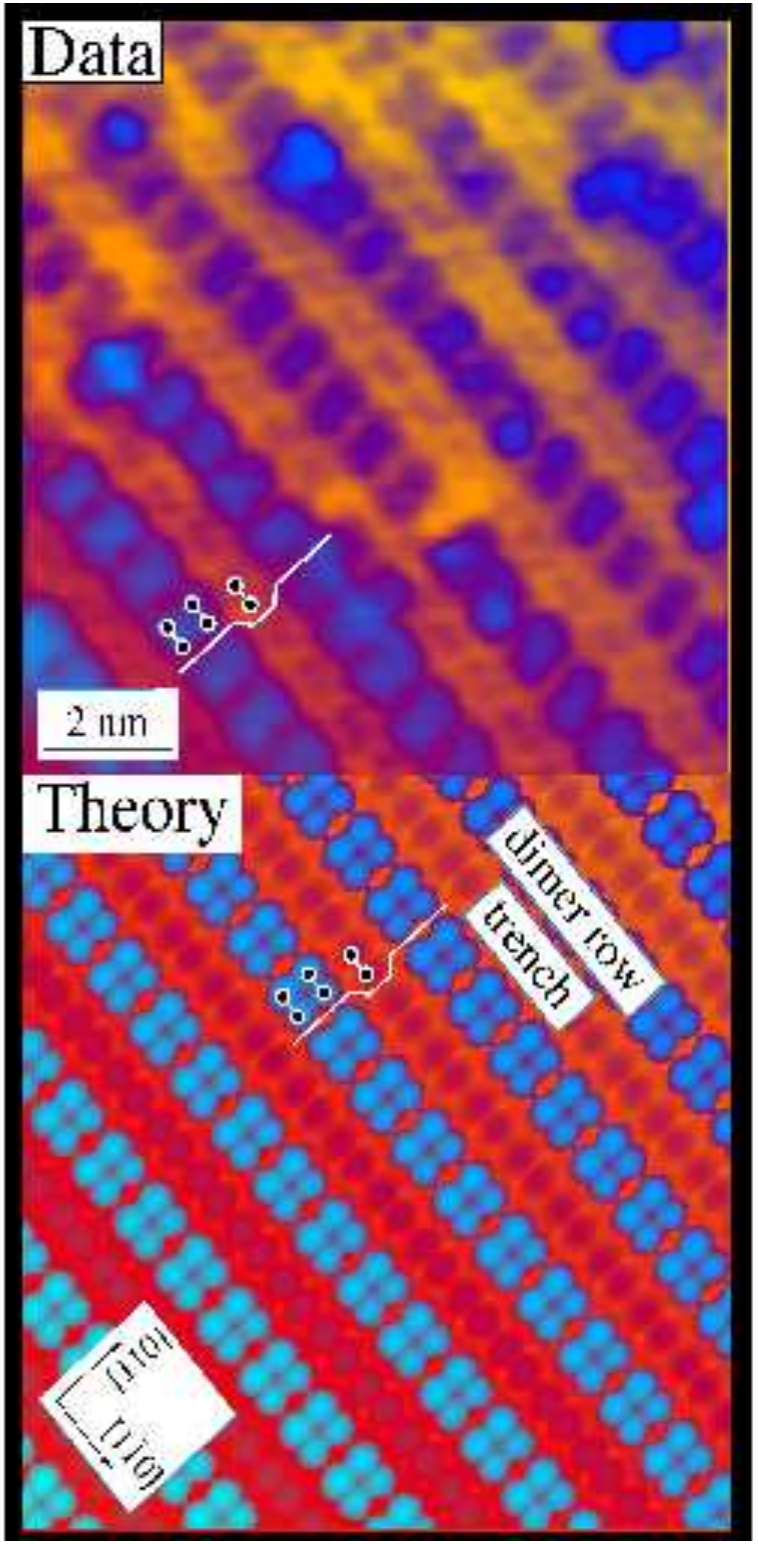


STM imaging of GaAs(001)

measured filled state image at V_{tip} = - 2.1eV

simulated image local density of states integrated to 0.3 eV below the valence band maximum

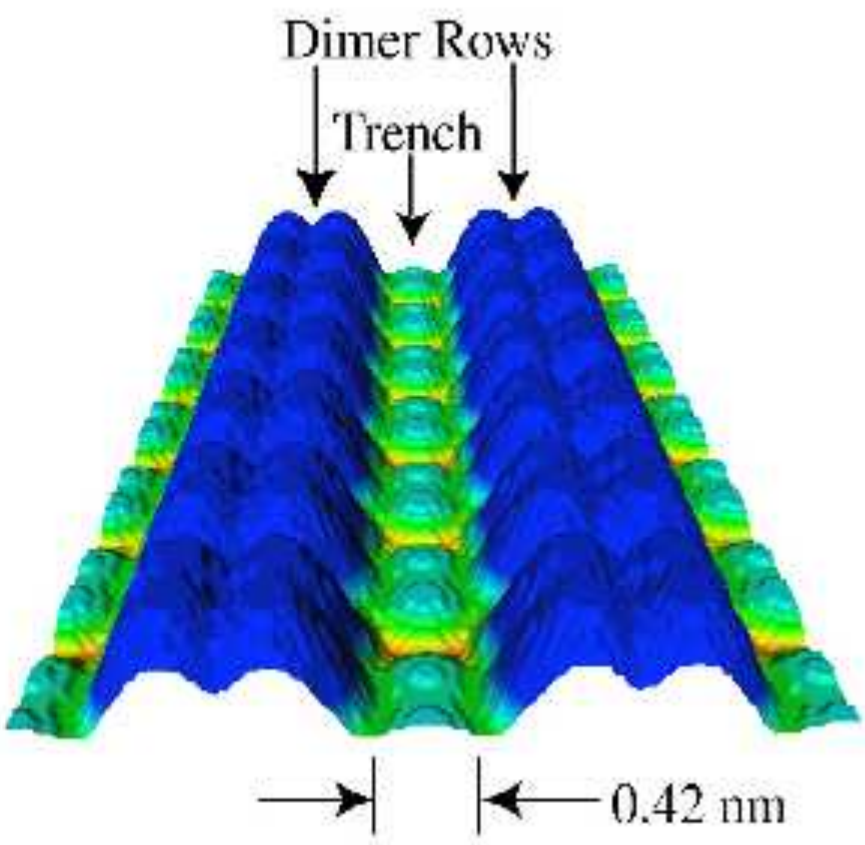
LaBella, Yang, Bullock, Thibado, Kratzer & Scheffler, PRL ***83****, 2989 (1999).*



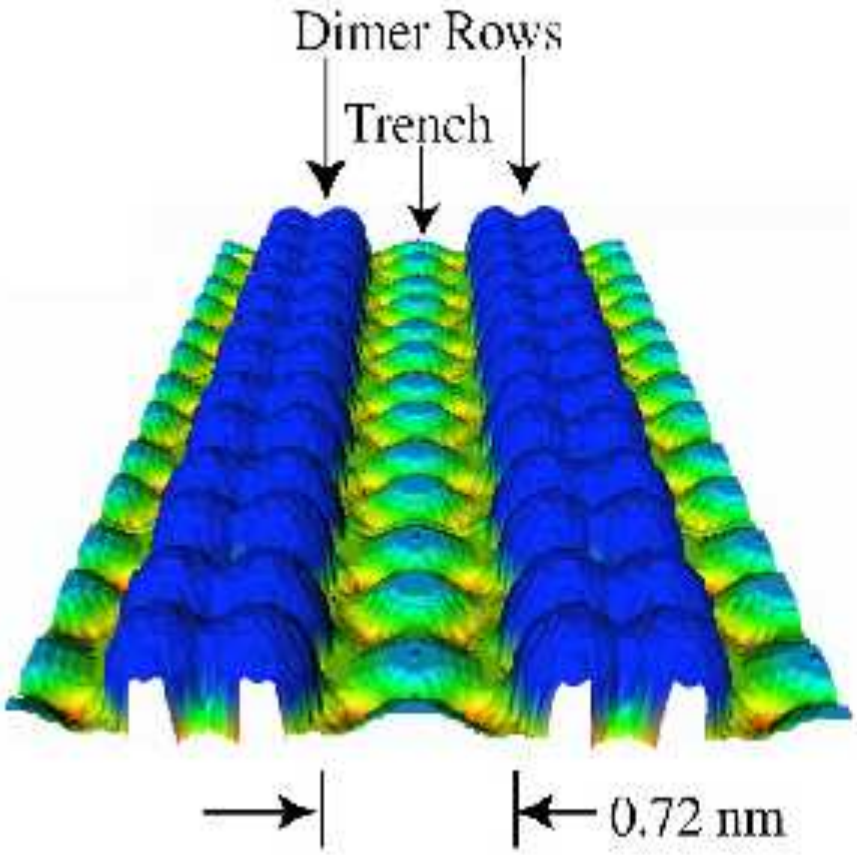
Voltage dependence of the STM current

STM simulation

-3.0 eV (high)



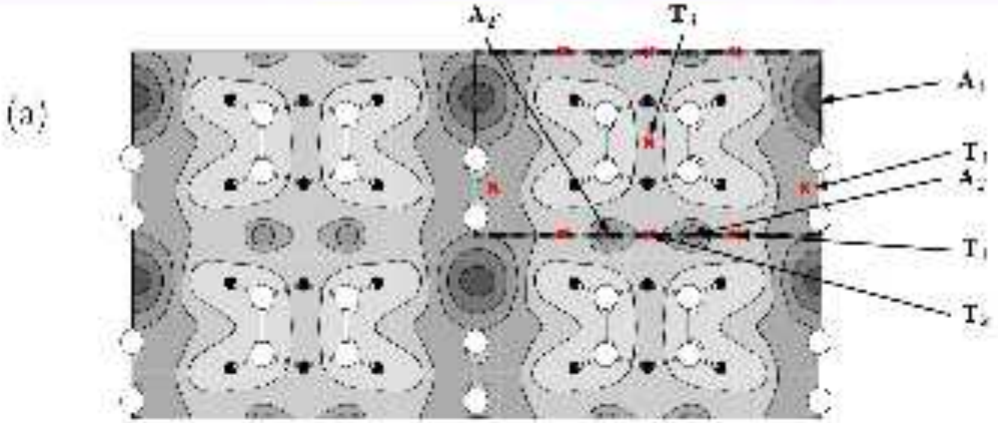
-2.1 eV (low)



LaBella, Yang, Bullock, Thibado, Kratzer & Scheffler, PRL **83**, *2989 (1999).*

Total energy of a diffusing Ga atom at GaAs (001)

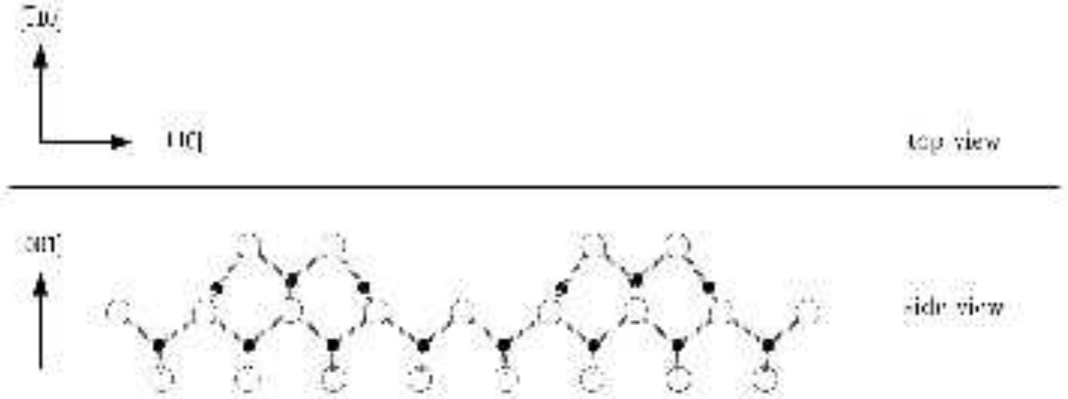
top view



E_{A1} = -2.5 eV
E^{TS} = -2.0 eV

E_{A2} = -2.2 eV
E^{TS} = -1.8 eV

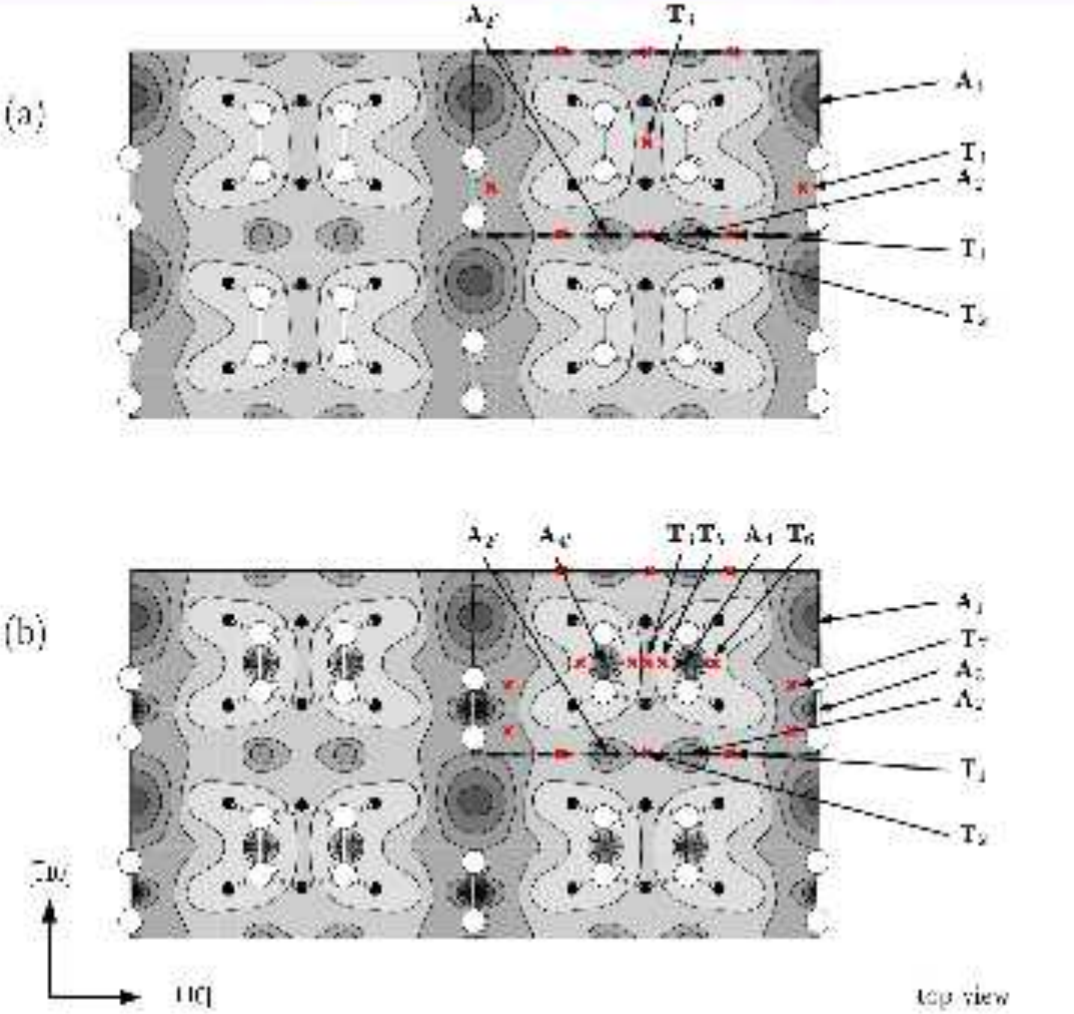
side view



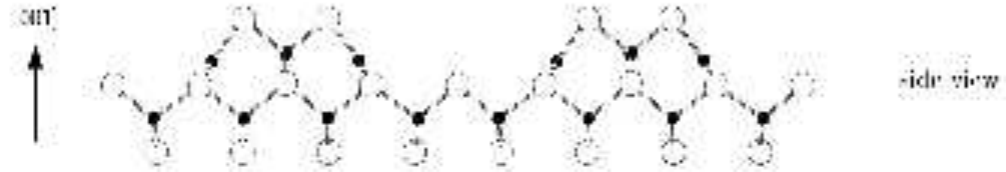
A. Kley, P. Ruggerone, and M.S., PRL **79** (1997)

Total energy of a diffusing Ga atom at GaAs (001)

top view



side view



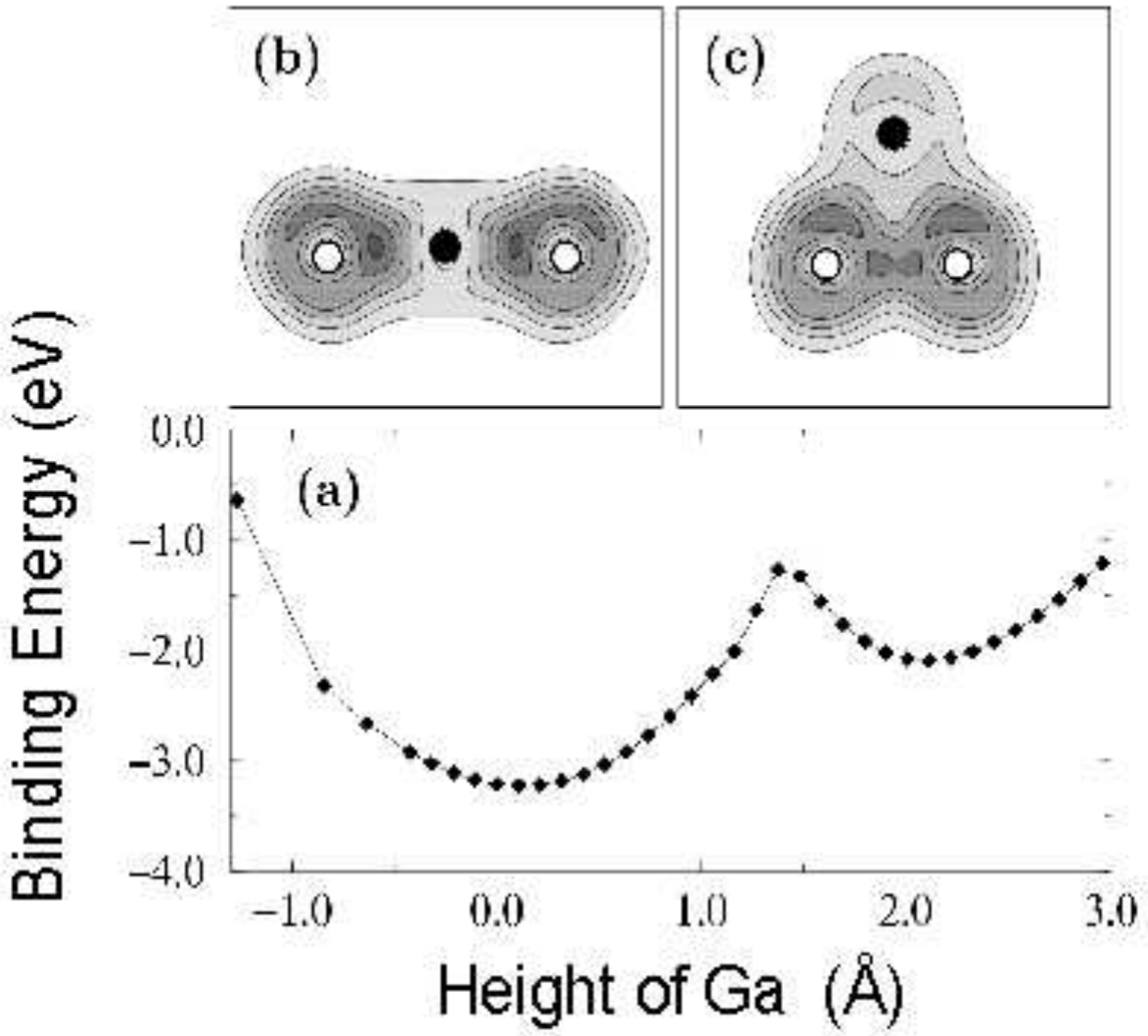
E_{A1} = -2.5 eV
E^{TS} = -2.0 eV

E_{A2} = -2.2 eV
E^{TS} = -1.8 eV

E_{A3} = -3.2 eV

A. Kley, P. Ruggerone, and M.S., PRL **79** (1997)

Unusally stable site for Ga adatom inside the trench-site As-dimer

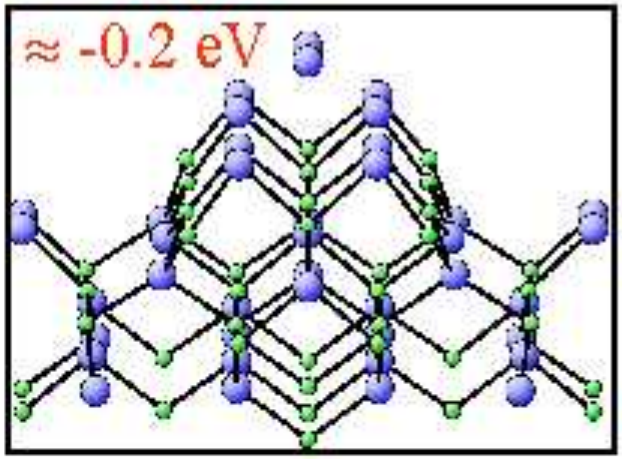


A. Kley, P. Ruggerone, M.S., PRL 79 (1997)

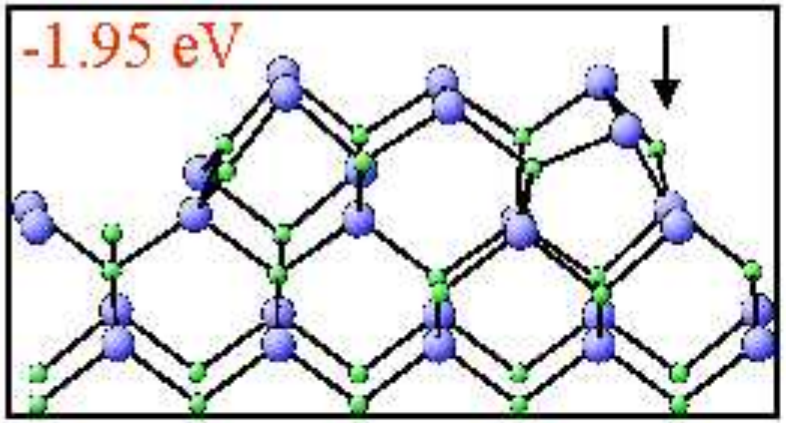
As_2 Adsorption

C. Morgan, P. Kratzer, M.S., PRL **82** (1999)

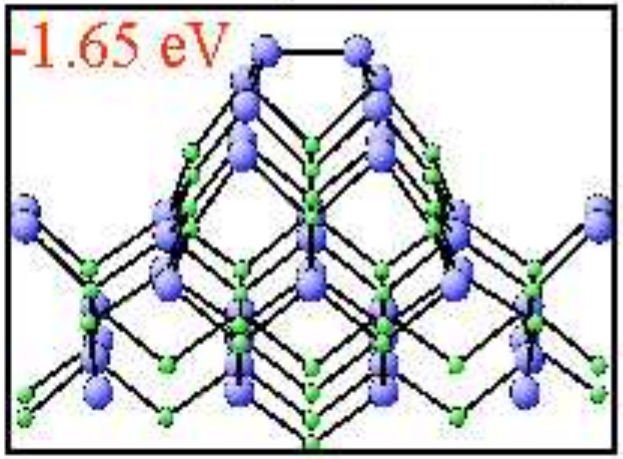
molecular As_2 adsorption



As_2 chemisorption at Ga adatom



As_2 chemisorption in top layer



As_2 does not need to break up to become incorporated. As_2 is readily available everywhere on the surface

Theory of the kinetics of growth

1) Analysis of all possibly relevant processes
2) Calculate the rates of all important processes

$$\Gamma^{(i)} = \Gamma_0^{(i)} \exp\left(\Delta E^{(i)} / kT \right)$$

3) Statistical approach to describe
   - deposition
   - diffusion
   - nucleation
   - growth

➡ **kinetic Monte Carlo method**

movie

Adsorption, diffusion, island nucleation,
and growth of GaAs

DFT-GGA calculations

goto
http://www.fhi-berlin.mpg.de/th/Highlights
to see the movie

we display:

1/60 of the full simulation cell
total time = 1 sec
As_2 pressure = 1.33×10^{-3} Pa = 1.33×10^{-8} bar
Ga deposition rate = 0.1 ML/s
T=700 K (somewhat low; exp. uses about 850 K)

Summary

What makes GaAs(001) the preferred substrate?

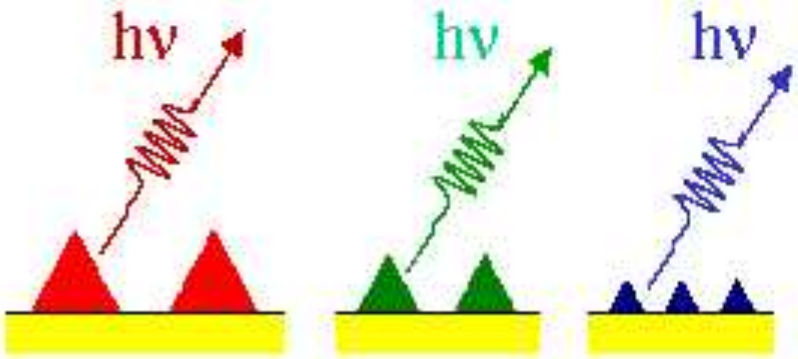
- principal structural element: As dimers
  - As_2 molecules are incorporated undissociatedly and without an activation barrier
  - several intermediate binding sites enhance the As_2 surface lifetime
- unusually stable two-fold coordinated cation adsorption state
  - cation evaporation is negligible even at high growth temperatures

Self-Assembly of Nano-Scale Structures at Semiconductor Surfaces

Motivation:

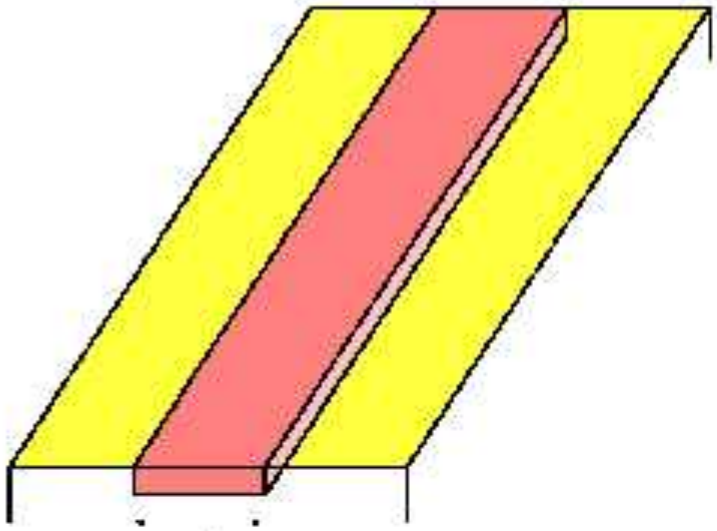
Single-electron transistor

LEDs and
laser diodes

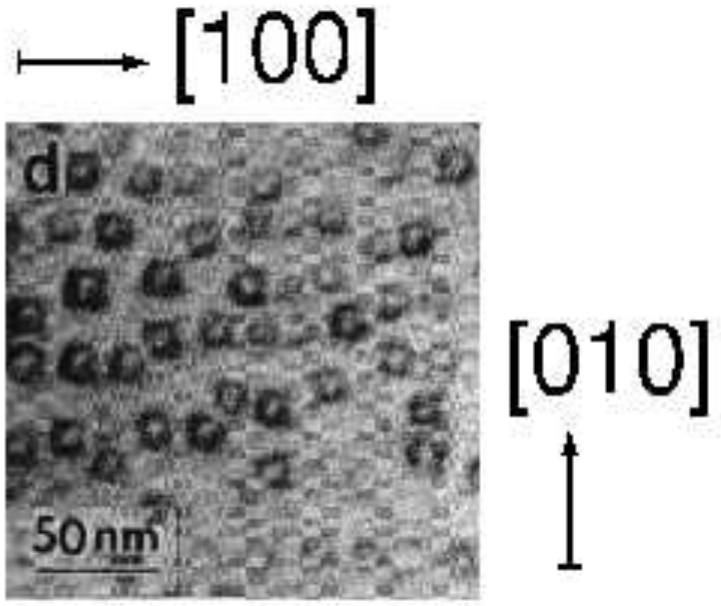


required dimensions: 50 - 200 Å

lithography ends at d > 300 Å, and has rough edges



self-assembly of InAs quantum-dots on GaAs (100)



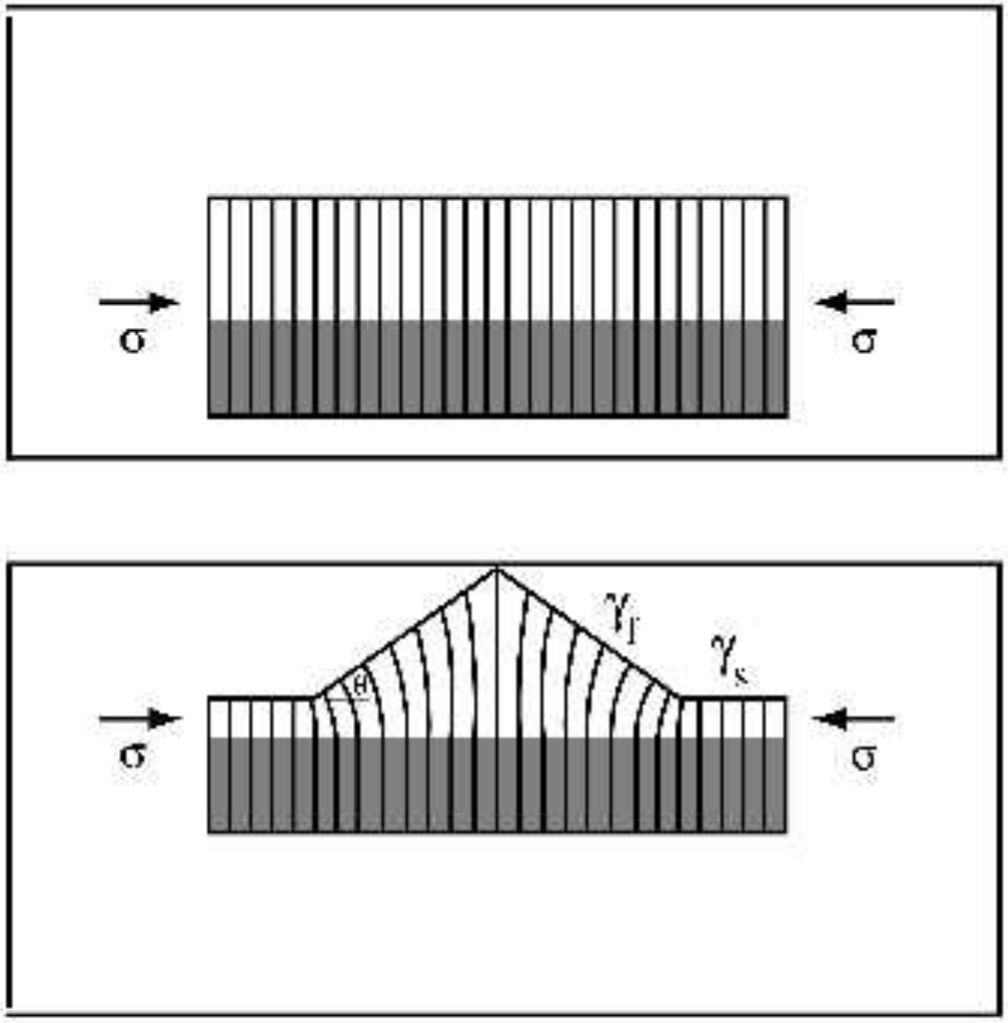
Ruvimov et al., PRB 1995

Thermal Equilibrium Shapes of InAs Quantum Dots on GaAs(100)

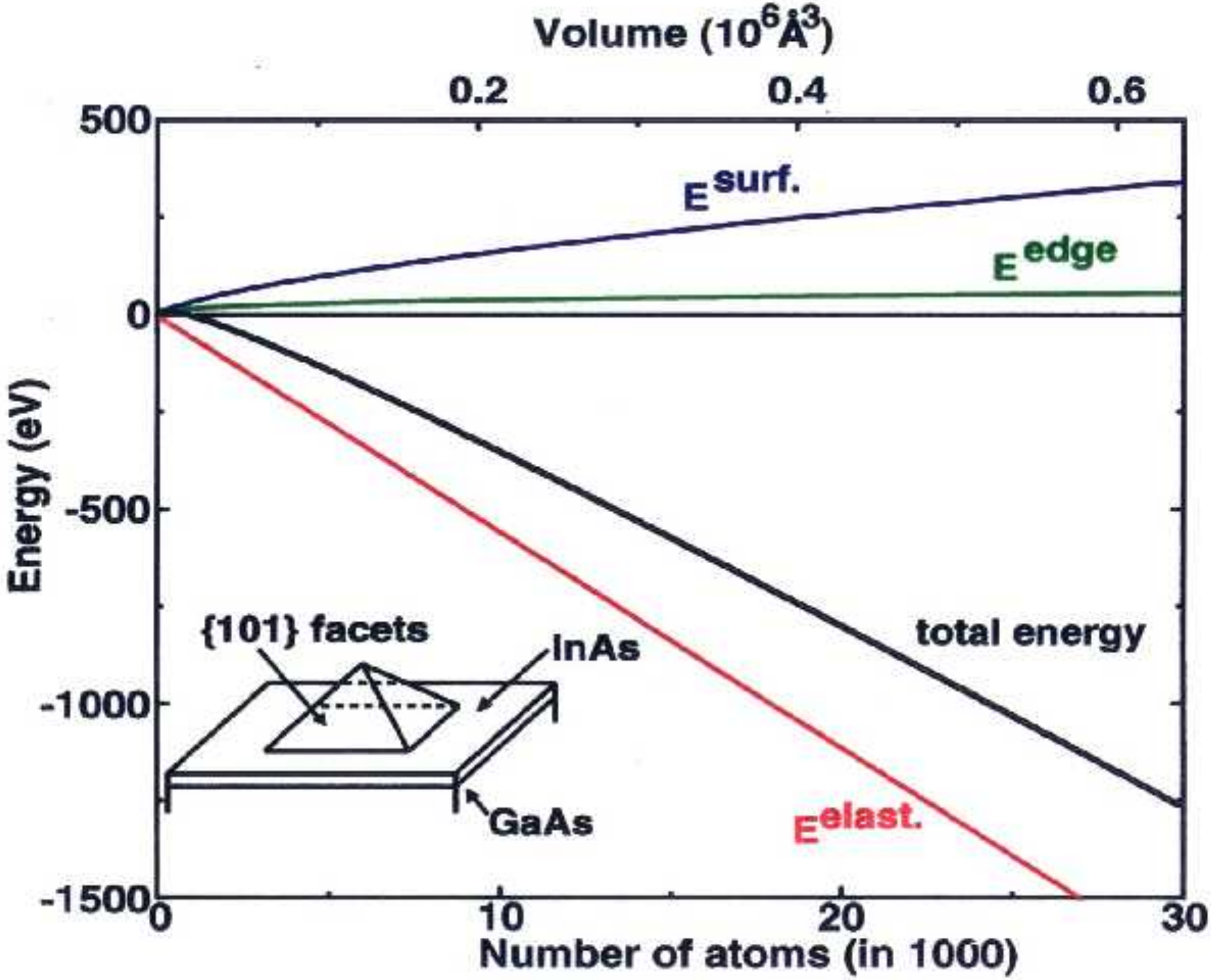
Stranski-Krastanov Growth Mode

If the experimental quantum dot shape deviates from the equilibrium shape, equilibrium thermodynamics is not adequate to describe the island formation and size distribution

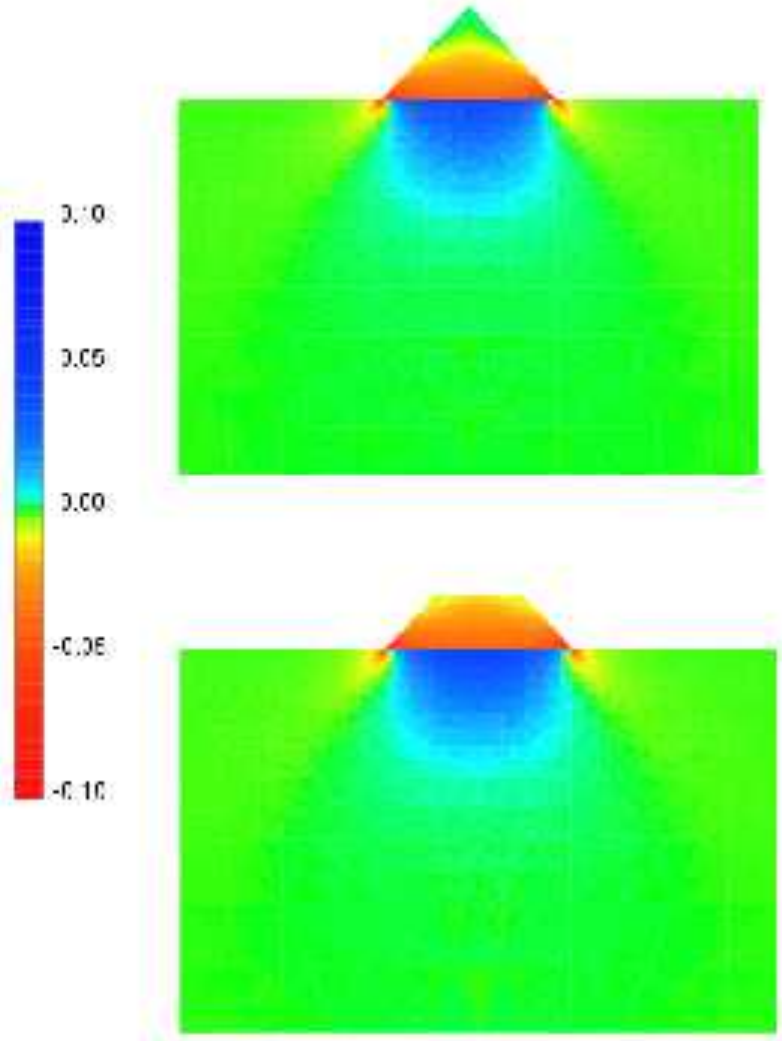
Stranski-Krastanov morphology
as one way to reduce misfit strain energy

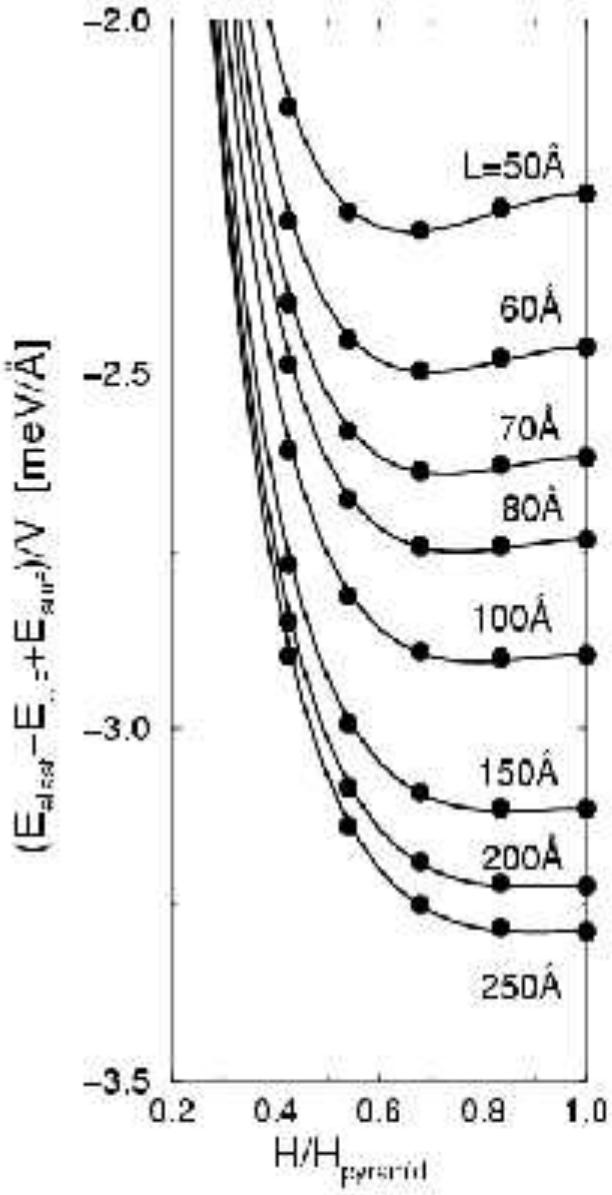


e.g.
InAs on
GaAs


Volume (10^6Å^3)
0.2
0.4
0.6
500
0
-500
-1000
-1500
Energy (eV)
$E^{surf.}$
E^{edge}
total energy
$E^{elast.}$
{101} facets
InAs
GaAs
0
10
20
30
Number of atoms (in 1000)

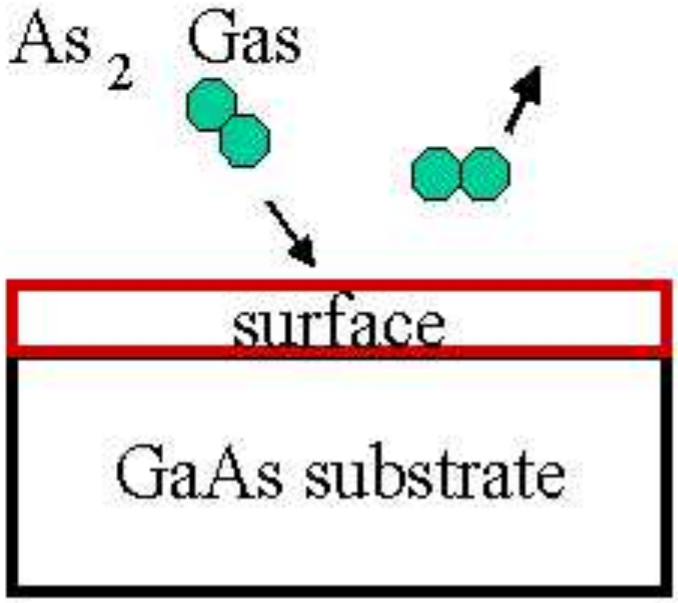
Stress tensor at strained InAs on GaAs





Stoichiometry and structure of the surface depend on the environment

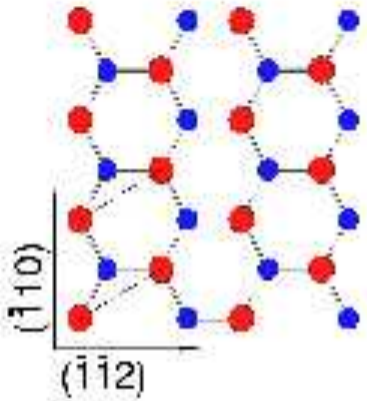
(atomic chemical potentials)

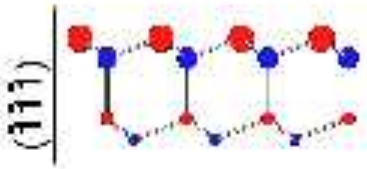


$$\mu_{\mathrm{As}} \leq E^{\mathrm{bulk}}(\mathrm{As})$$
$$\mu_{\mathrm{Ga}} \leq E^{\mathrm{bulk}}(\mathrm{Ga})$$

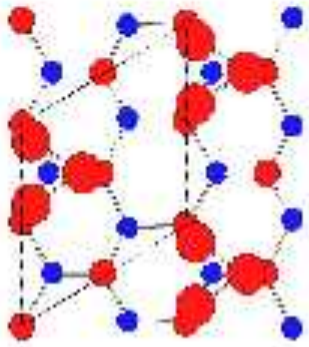
$$\mu_{\mathrm{Ga}} + \mu_{\mathrm{As}} = E^{\mathrm{bulk}}(\mathrm{GaAs})$$

DFT Calculations of Surface Energies Example: InAs (-1-1-1)

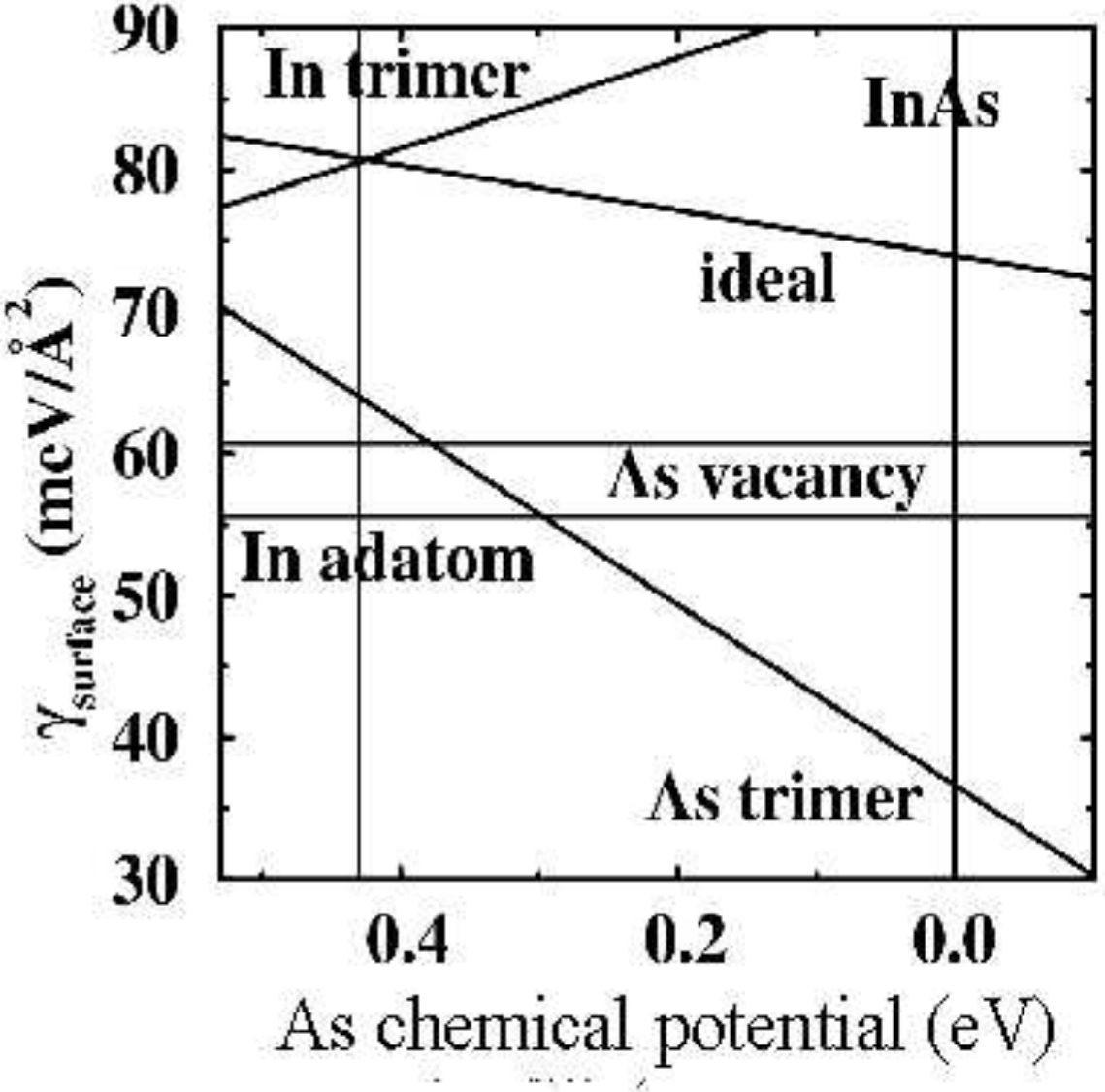




ideal

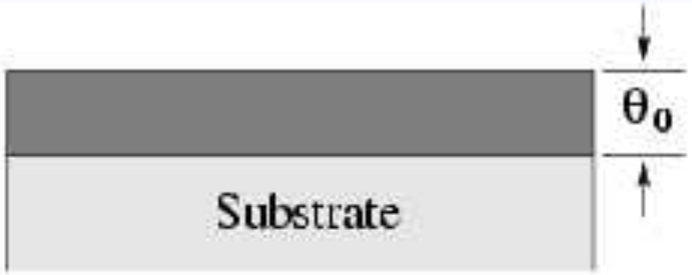


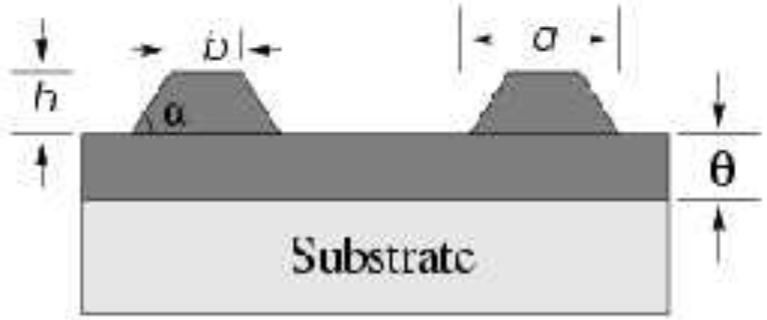
As trimer



What determines the volume and shape of quantum dots? (how q-dots eat from the wetting layer)

e.g. InAs on GaAs





L. Wang, P. Kratzer, and M.S., PRL **82** *(1999)*

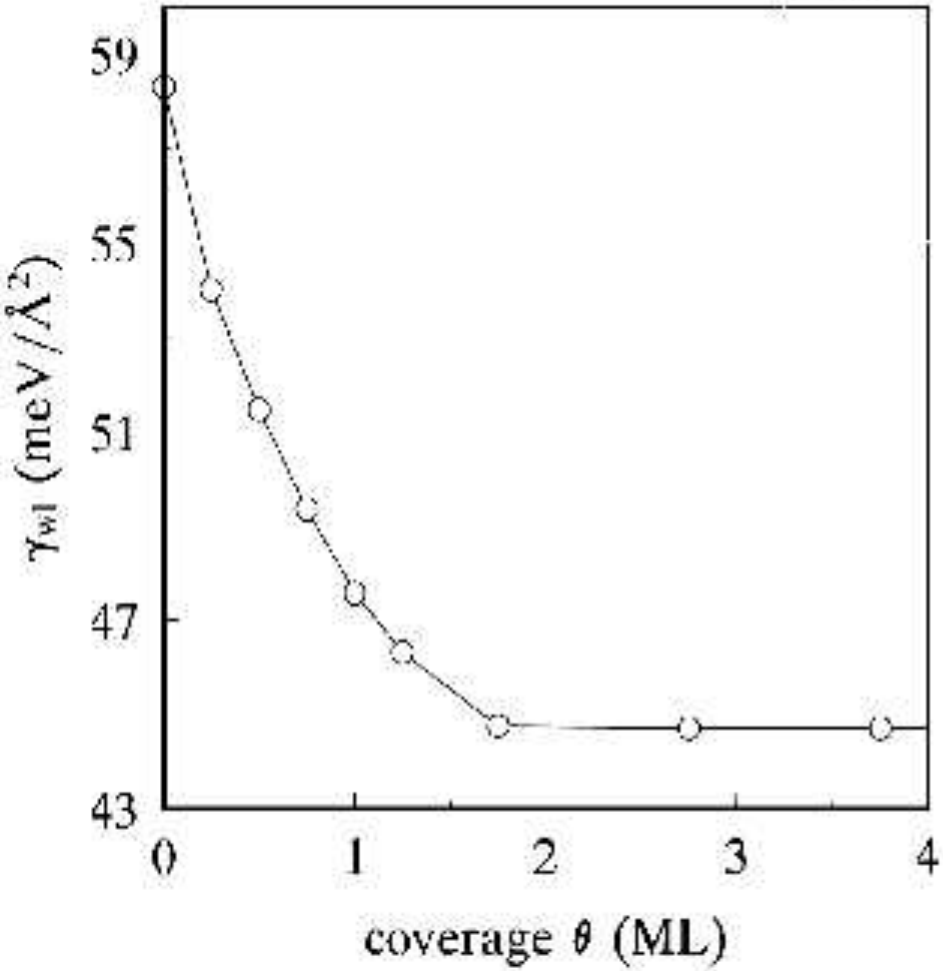
$$
\begin{aligned}
E/V &= E^{\mathrm{el}}_{\mathrm{is}}/V - \epsilon^{\mathrm{el}}_{\mathrm{film}} \\
&+ [S\gamma_{\mathrm{f}} + b^2\gamma_{\mathrm{top}} - a^2\gamma_{\mathrm{wl}}(\theta_0)]/V \\
&+ (1/n - a^2) \times [\gamma_{\mathrm{wl}}(\theta) - \gamma_{\mathrm{wl}}(\theta_0)]/V
\end{aligned}
$$

InAs on GaAs (100)

surface plus interface energies

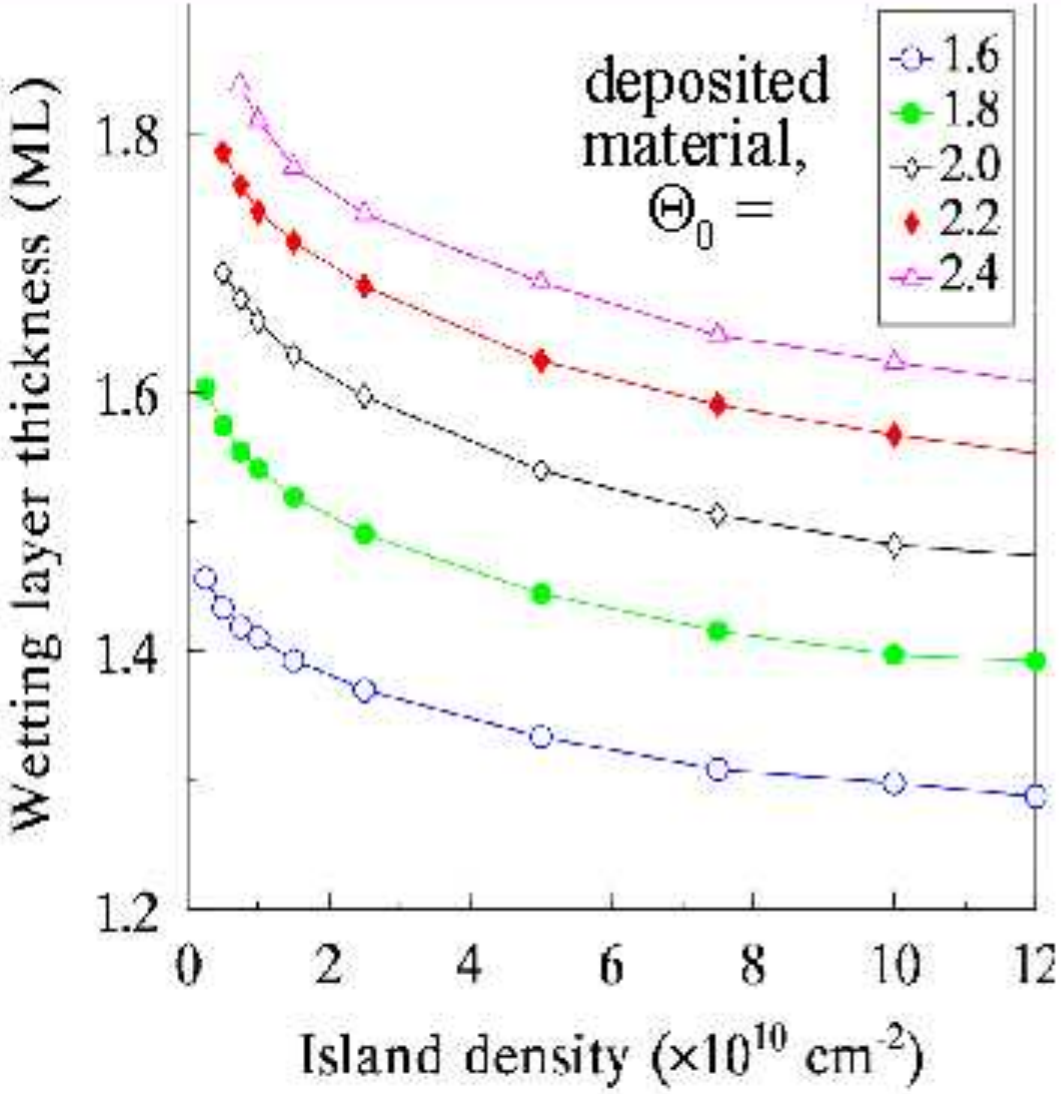
$$\gamma_{wl} A = E^{tot} - E^{bulk}(GaAs)\, N_{Ga} - E^{strained\text{-}bulk}(InAs)\, N_{In} - \mu_{As}\, \Delta N_{As}$$

$$\mu_{As} = E^{bulk}(As) - 0.2\ eV$$



L. Wang, P. Kratzer, and M.S., PRL **82** *(1999)*

Thickness of the wetting layer depends on the island density

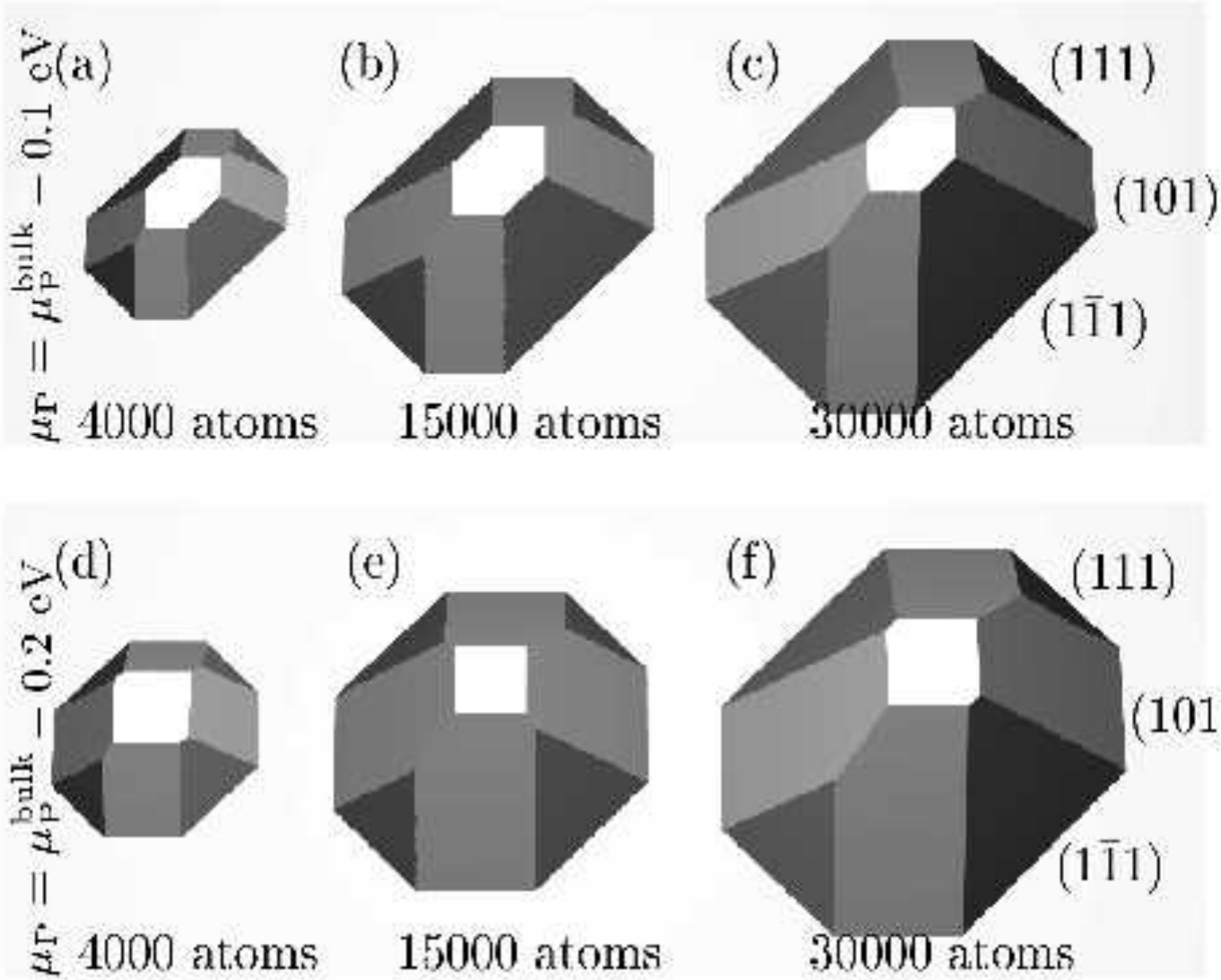


InAs on GaAs

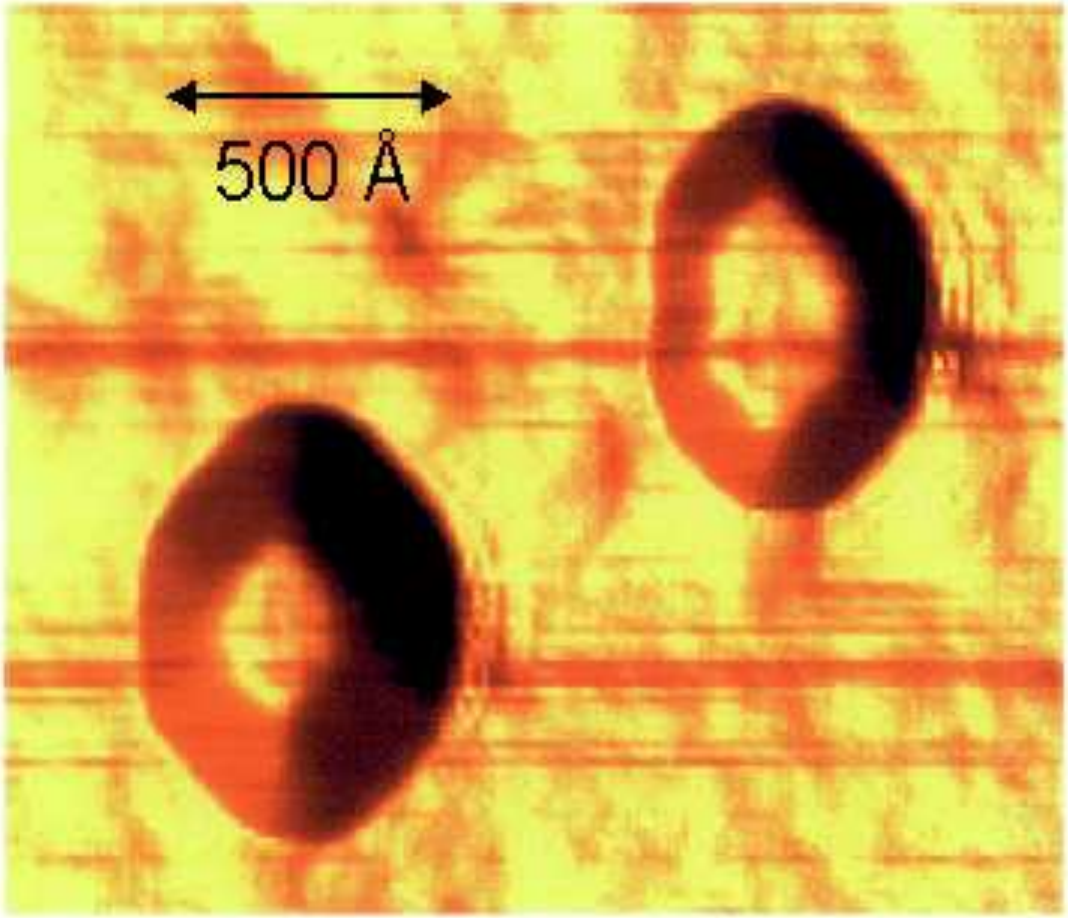
$$\mu_{As} = E^{bulk}(As) - 0.2\,eV$$

L. Wang, P. Kratzer, and M.S., PRL 82 (1999)

InP quantum dots on GaP(001)

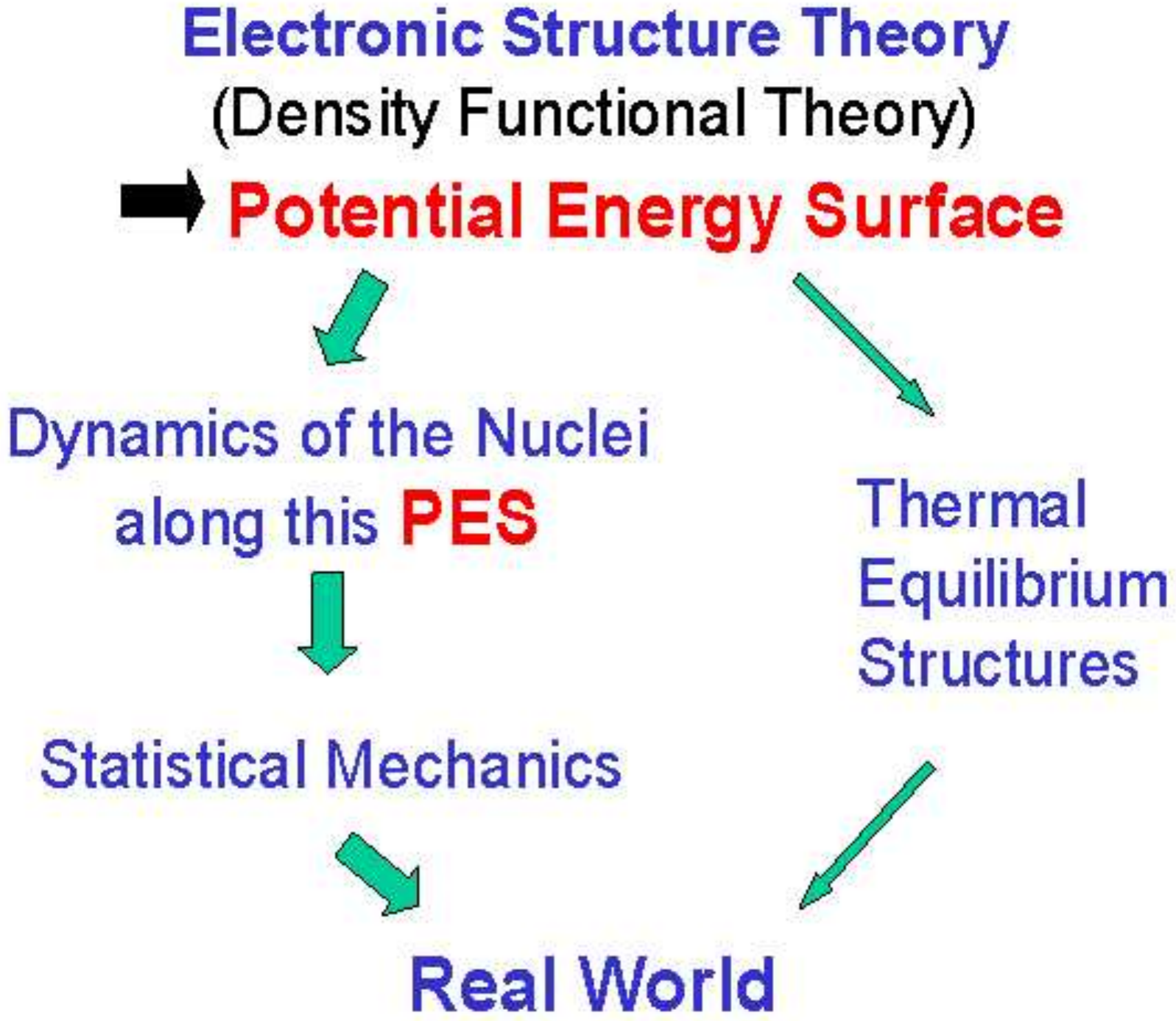


Q. Liu, E. Pehlke, N. Moll, M.S., PRB ***60****, (1999)*



Samuelson *et al.* (1996)

MOVPE grown InP islands on GaInP


Electronic Structure Theory
(Density Functional Theory)
Potential Energy Surface
Dynamics of the Nuclei
along this PES
Thermal
Equilibrium
Structures
Statistical Mechanics
Real World