Semiconductor Quantum Dots

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Outline

- **Introduction**
- Fabrication – Experiments – Applications
  - Porous Silicon
  - II-VI Quantum Dots
  - III-V Quantum Dots
    - Cleaved Edge Overgrowth (CEO)
    - Self Assembling Quantum Dots
    - Electronic Structure

Introduction
Low Dimensional Systems

- Motion of electron in conduction band is described by the effective mass concept

$$E = \frac{p^2}{2m^*}$$

- Dispersion relation with $p = \hbar k$

$$\Rightarrow E(k) = \frac{\hbar^2 k^2}{2m^*}$$

- In low dimensional systems the carrier motion is quantized in one or more spatial directions

Inroduction
Density of States – 3D

- Wave function in 3D box of volume $\Omega = L_x L_y L_z$

$$\Phi_{lmn}(\mathbf{R}) = \frac{1}{\sqrt{\Omega}} \exp\left(i\mathbf{K}\bullet\mathbf{R}\right) \qquad \mathbf{K} = \left(\frac{2\pi l}{L_x}, \frac{2\pi m}{L_y}, \frac{2\pi n}{L_z}\right)$$

- Density of states / per unit volume

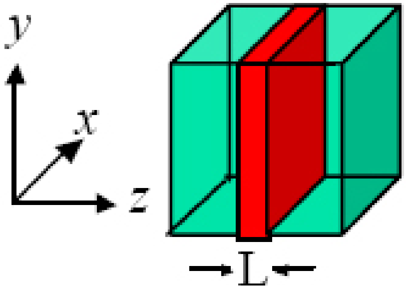
$$N_{3D}\left(\mathbf{K}\right) = \frac{2\Omega}{\left(2\pi\right)^3} \frac{4}{3} \mathbf{K}^3 \pi \qquad n_{3D}\left(\mathbf{K}\right) = \frac{1}{3\pi^2} \mathbf{K}^3$$

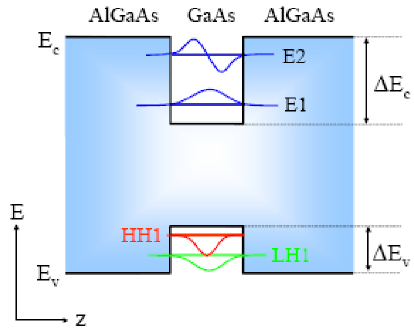
- Density of states in Energy

$$D_{3D}\left(E\right) = \frac{d}{dE} n_{3D}\left(\mathbf{K}\right) = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{\frac{3}{2}} \sqrt{E - E_g}$$

Introduction
Density of States – 2D

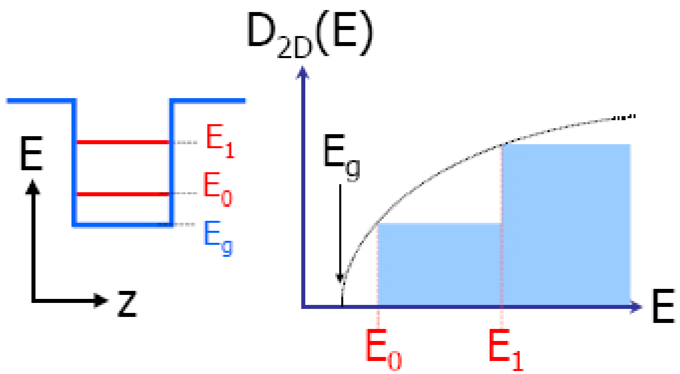
- For example $GaAs / Al_x Ga_{1-x} As \left(x < 0.4 \right)$ quantum well





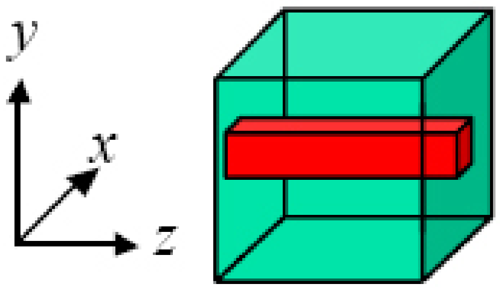
- Density of states

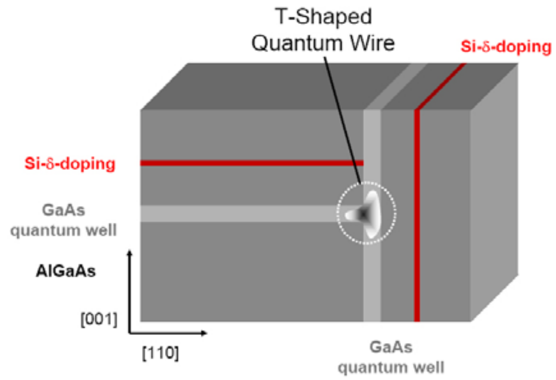
$$D_{2D}\left(E\right) = \frac{m^*}{\pi \hbar^2}$$



Introduction
Density of States – 1D

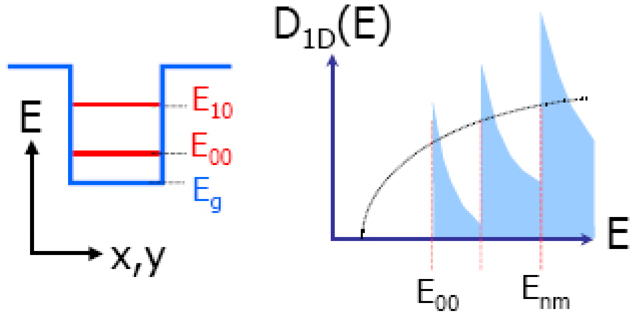
- Quantum wire through cleaved edge overgrowth





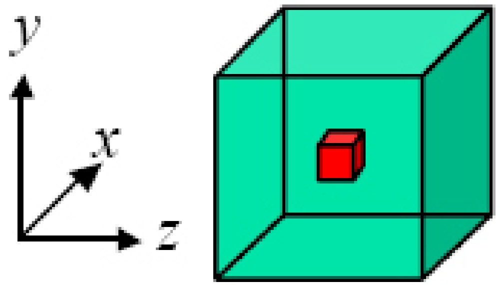
- Density of states

$$D_{1D}(E) = \frac{\sqrt{2m^*}}{2\pi\hbar} \frac{1}{\sqrt{E - E_{nm}}}$$



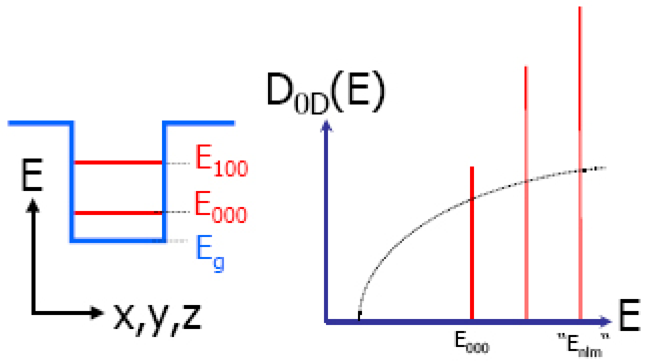
Introduction
Density of States – 0D

- Kinetic quantization along x, y and z-direction

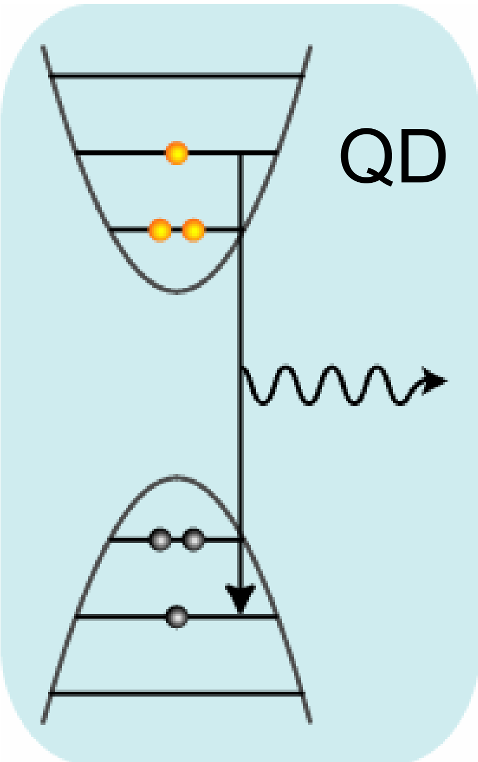


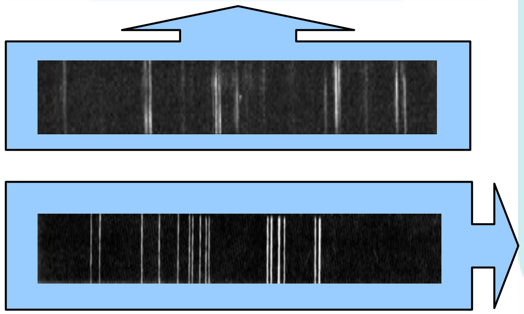
- Energy spectrum fully quantized
- Density of States

$$D_{0D}\left(E\right) = discrete$$

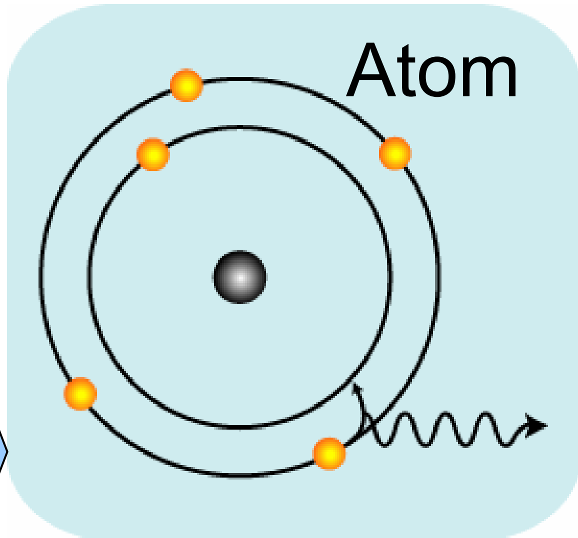


Introduction
Quantum Dots as Artificial Atoms





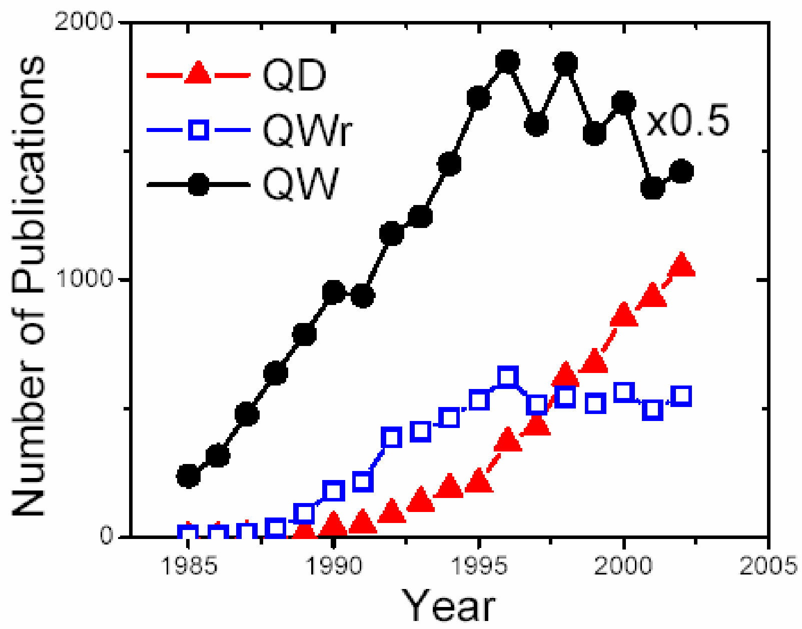
	Atom	QD
Particle:	Electron	Exciton
Energy scale:	13eV – 100keV	Typ. 1 eV
Length scale:	0.1 – 0.3 nm	Typ. 10 nm
Potential:	V(r) ~ 1/r	Tunable



Tunable properties in QDs

Introduction
Interest in Quantum Dots

- Applications
  - Lasers in visible and near infrared spectrum
  - Optical data storage
  - Optical detectors
  - Quantum information processing and cryptography
- Publications



Introduction
Requirements for Applications

- Size $\Delta E > 3k_B T \sim 75meV$
- Crystal quality
- Uniformity
- Density
- Growth compatibility
- Confinement for electrons and/or holes
- Electrically active matrix material

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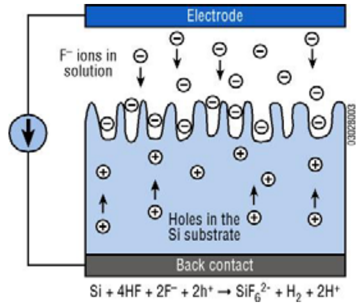
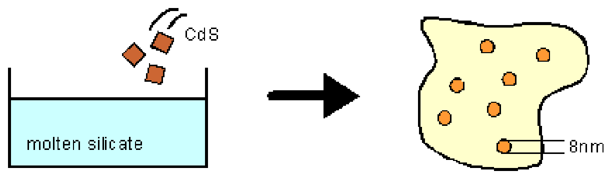
Fabrication – Experiments – Applications
Introduction

Several approaches:

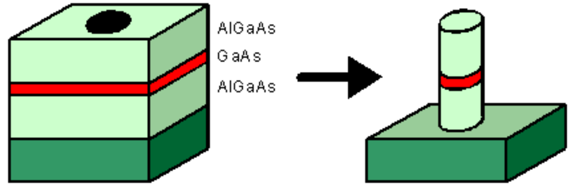
- Porous Silicon



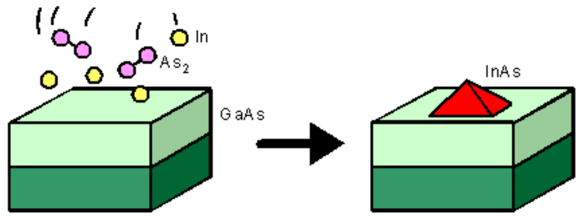
- Nanometer semiconductor inclusions in matrices



- Lithographic patterning of higher dimensional systems



- Strain driven self-assembly



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Porous Silicon
Introduction

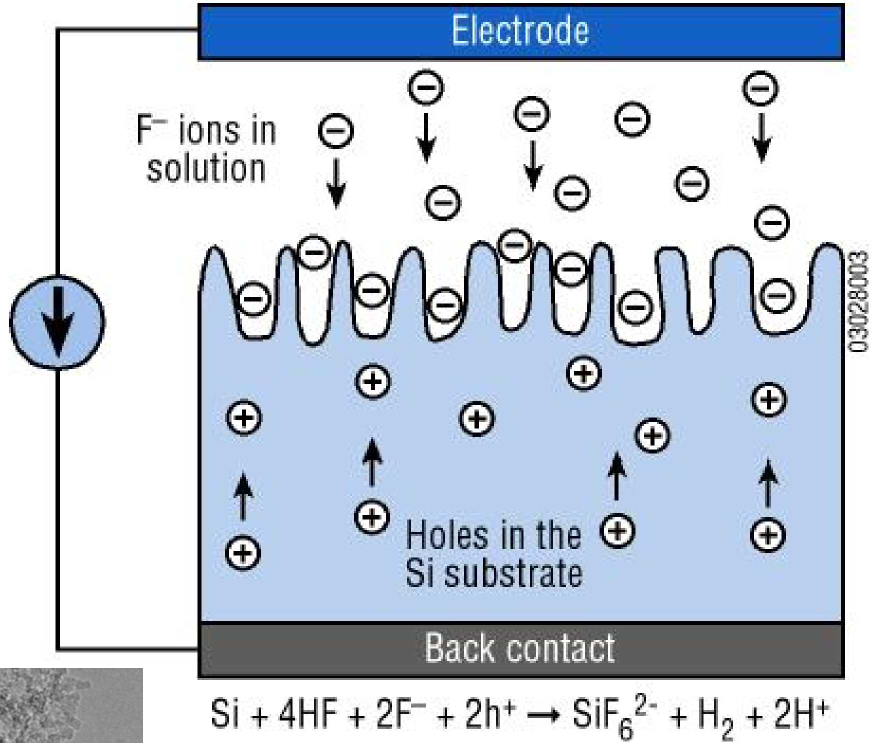
- C-Si: indirect bandgap → inefficient emitter even at 4K
- P-Si: emission efficiency up to 10% (optical excitation)
- Nanocrystals of different size and shape
- Structure of high complexity
- Confinement leads to bandgap widening and higher overlap of wavefunctions
- Light emission: surface ↔ core nanocrystal
- Easy fabrication of p-Si
- Pure Si optoelectronic devices possible

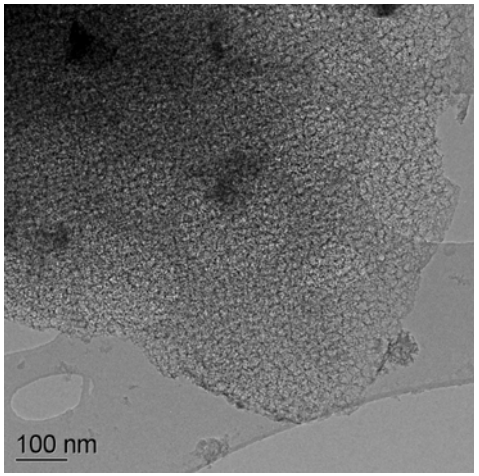
Porous Silicon Fabrication

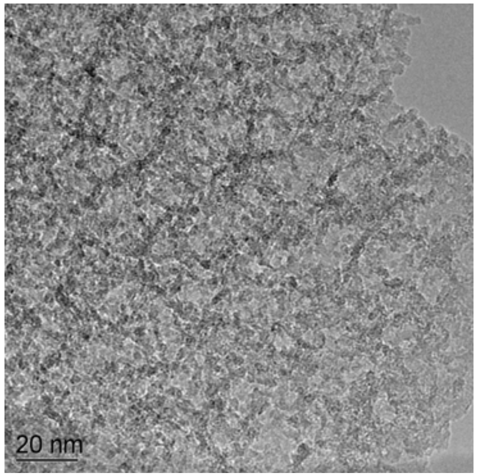
- Anodic biased c-Si in hydrofluoric acid (HF)

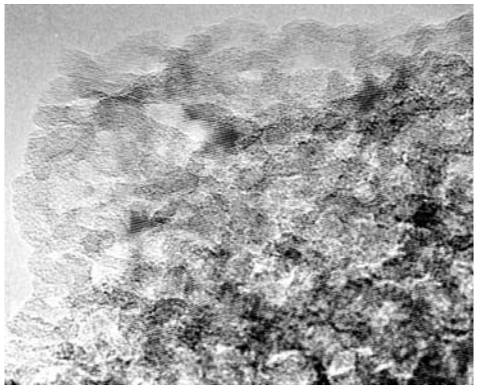
Structure depends on:

- Doping
- Etching conditions
- Illumination conditions

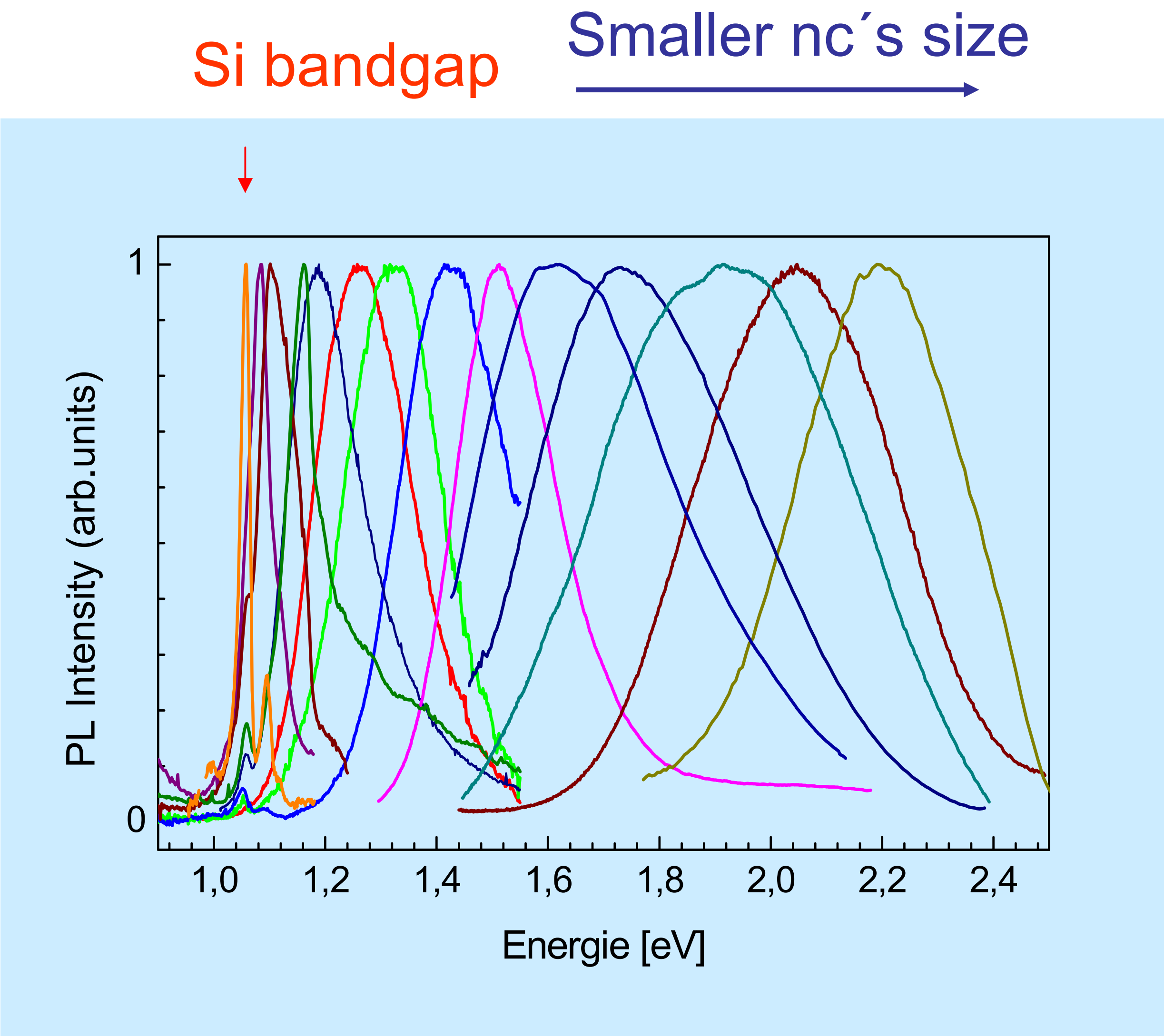








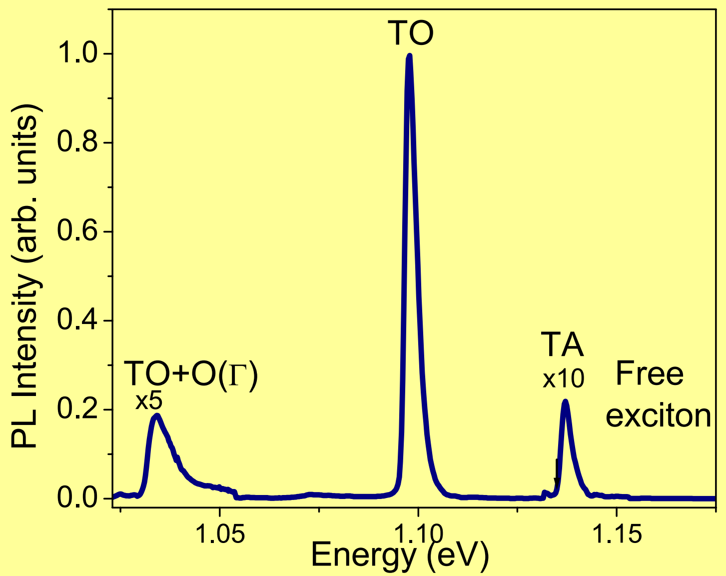
Porous Silicon
Optical Properties

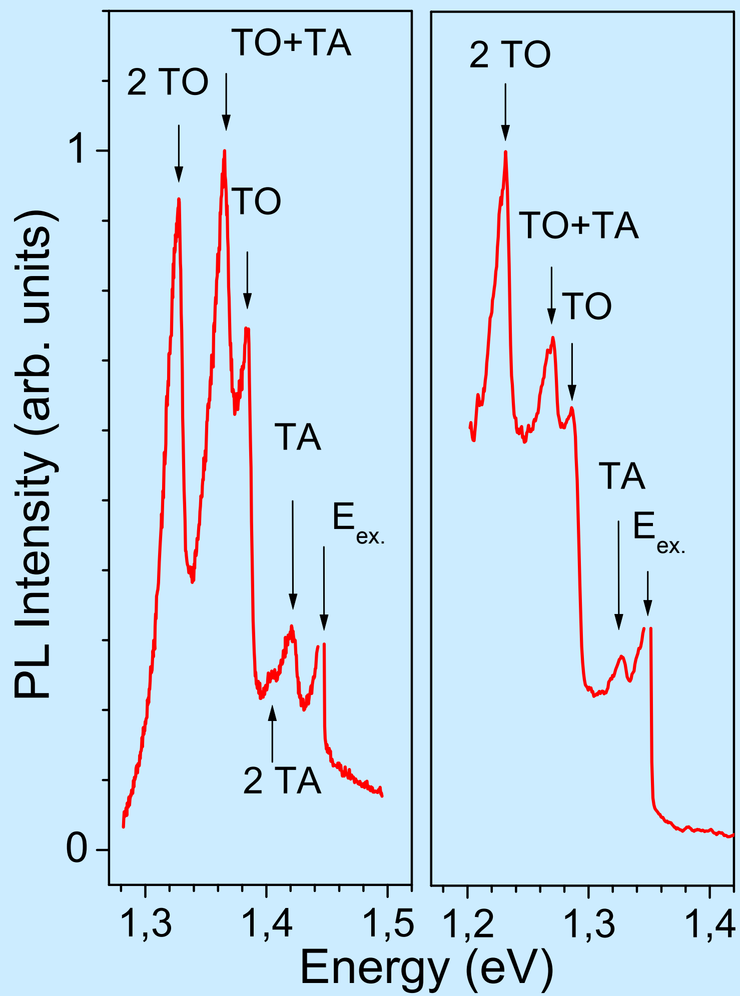


Widely tunable emission band due to quantum size effect: all emission energies are available

Broad spectrum → line narrowing

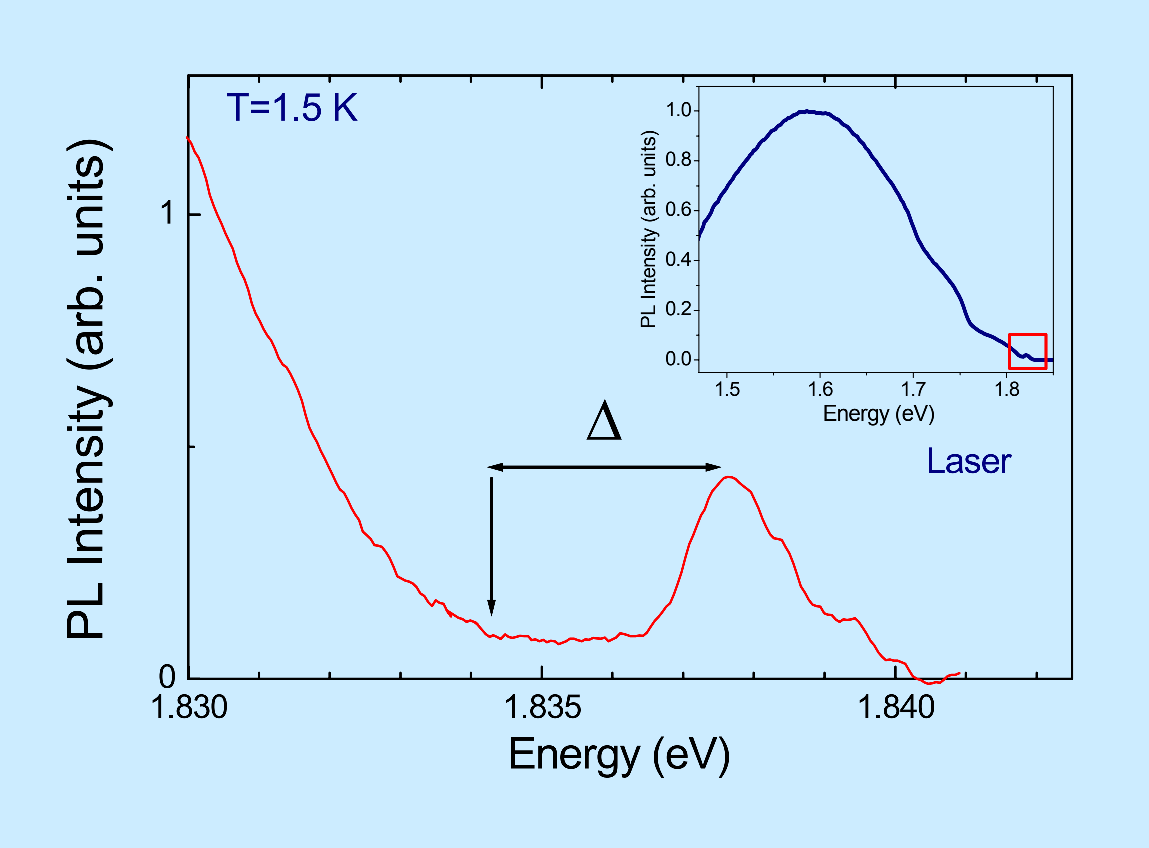
Porous Silicon
k-space

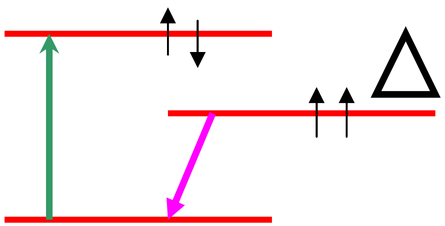




- P-Si has indirect nature
- ***k***-conservation rule breaks down due to confinement

Porous Silicon
Electron-Hole Exchange Interaction





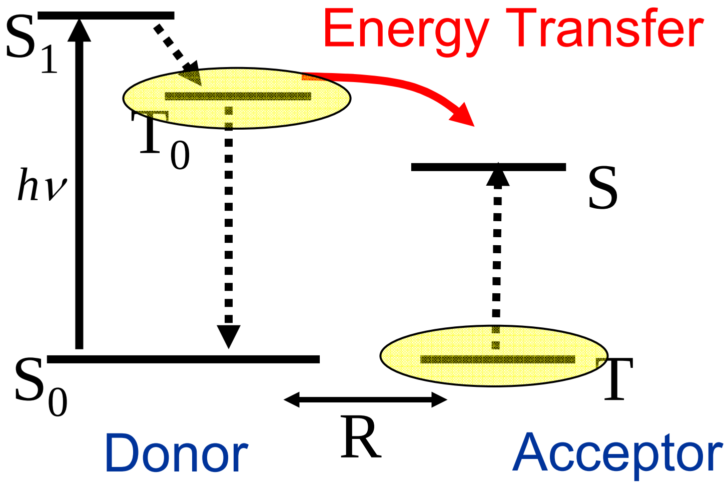
Absorption
in a singlet state

After spin flip
emission via
triplet state

Electronic structure of excitons is very similar to dye molecules

Porous Silicon
Indirect Excitation: Photosensitization

- Basic principle:



Energy transfer (dipole-dipole or direct electron exchange) is efficient if:

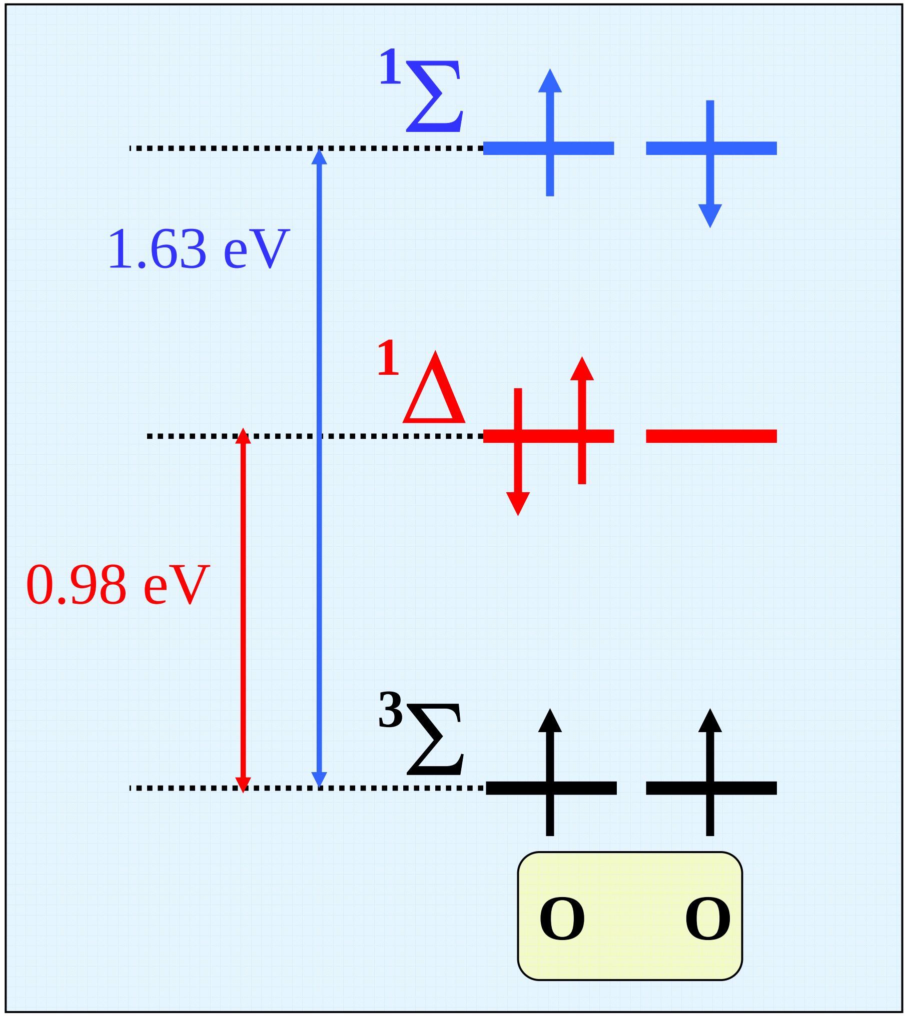
- photoexcited donor has long lifetime
- overlap of energy bands of D/A is good
- space separation of D/A is small

Silicon nanocrystals (almost ideal donor):

- ground state is triplet
- long exciton lifetime (10^{-5}-10^{-3} s)
- wide emission band
- huge internal surface area (10^3 m^2/cm^3)

Acceptor having triplet ground state?

Porous Silicon
Molecular Oxygen: Electronic Structure



ground gtate:

- spin triplet
- chemically inert

(reaction S+T → S is forbidden)

excited states:

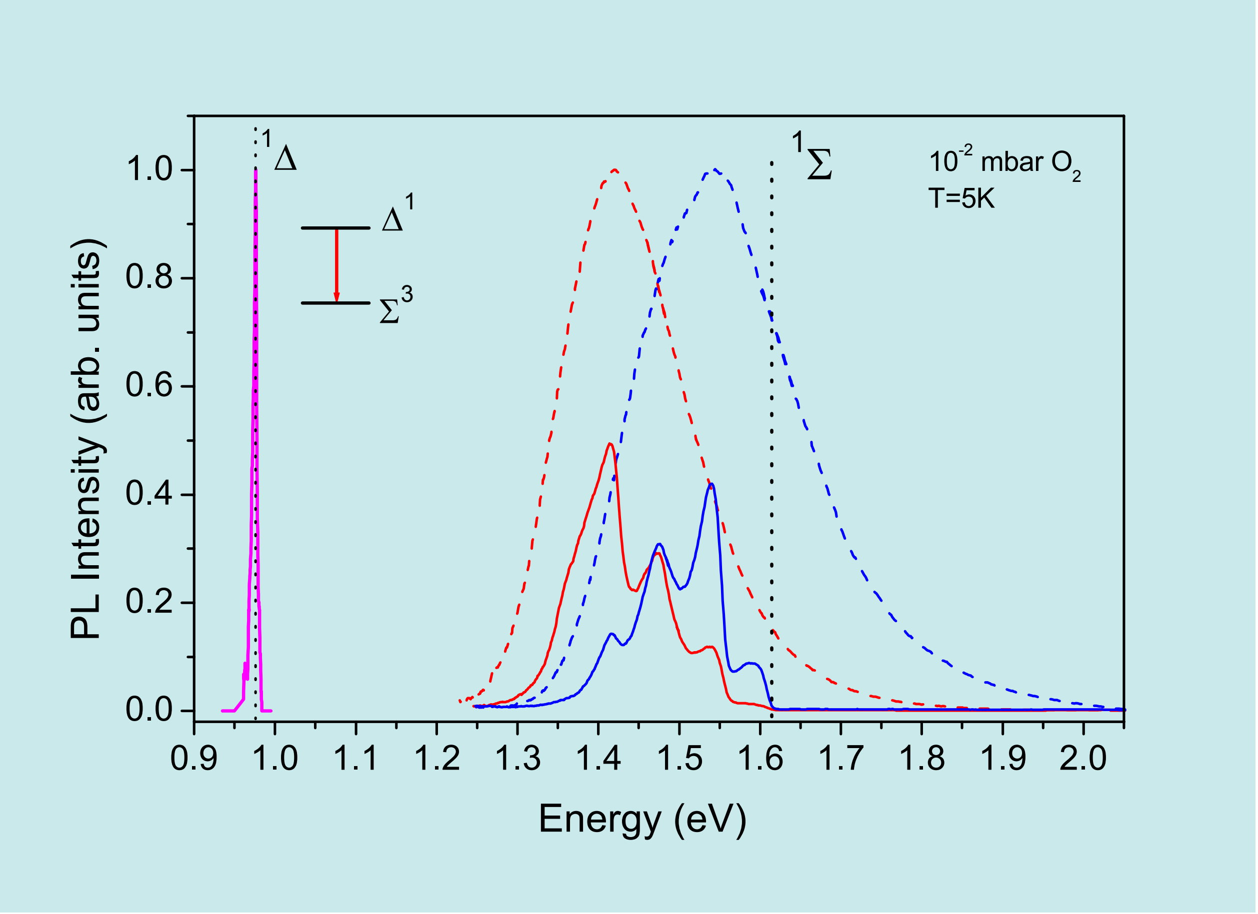
- spin singlet
- energy-rich
- high chemical reactivity

(reaction S+S → S is allowed

oxidation reactions in organic chemistry, biology, life science
photodynamic cancer therapy
oxygen-iodine laser

Optical excitation is impossible → Photosensitizer is required
→ Silicon nanocrystals

Porous Silicon
PL Quenching by Oxygen Molecules



→ Adsorption of O_2: PL Quenching

→ low temperature: • fine structure appears

• $^1D \rightarrow {}^3S$ emission line of O_2

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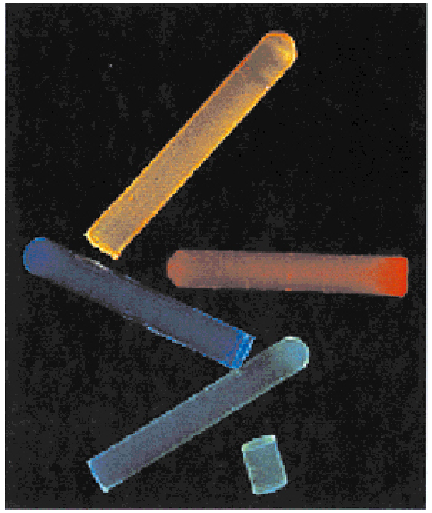
II-VI Quantum Dots
Introduction

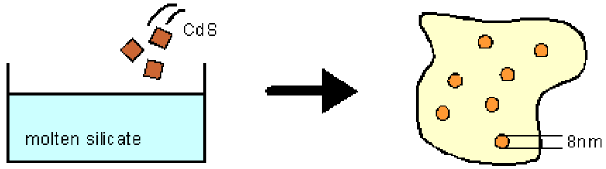
- First hints of quantum dots: CdSe and CdS in silicate glasses (X-ray 1932)
- Since 1960s semiconductor doped glasses used as sharp-cut color filter
- Quantum dots in glassy matrices
- Ideal model for the study of basic concepts of 3D confinement in semiconductors



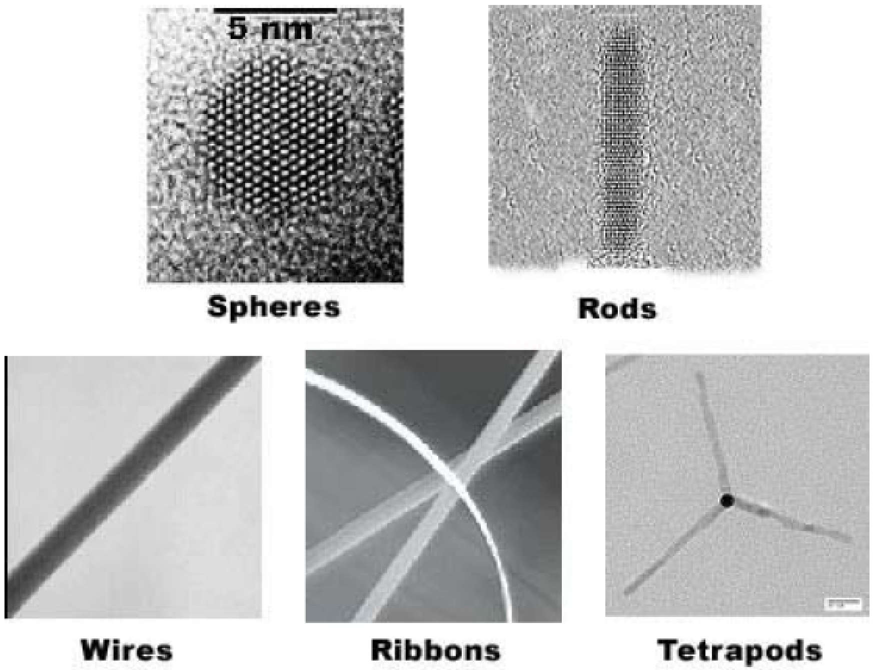
- Many different matrices: glasses, solutions, polymers, even cavities of zeoliths
- Many promising applications already on the way

II-VI Quantum Dots
Growth of Nanocrystals

- Colloidal QDs can be further processed and incorporated in a variety of media

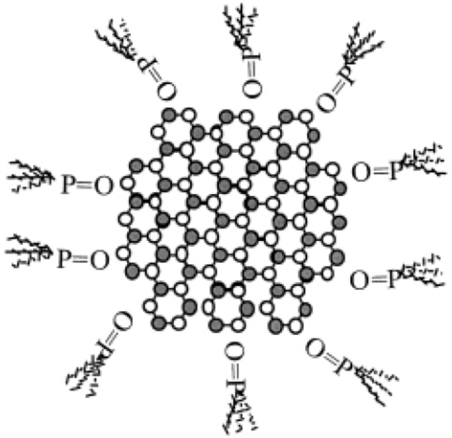


- CdSe can be prepared in a wide range of shapes

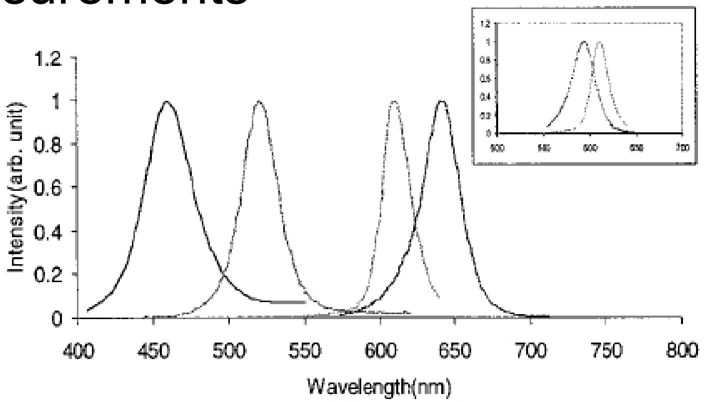


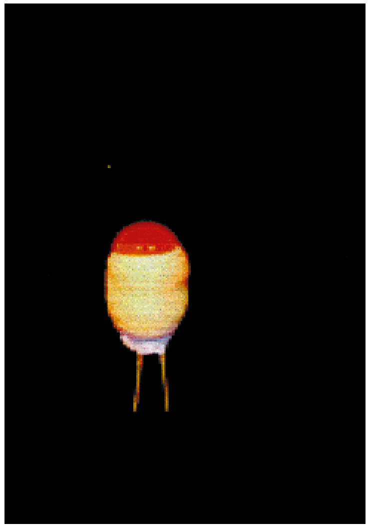
II-VI Quantum Dots
Growth of Nanocrystals

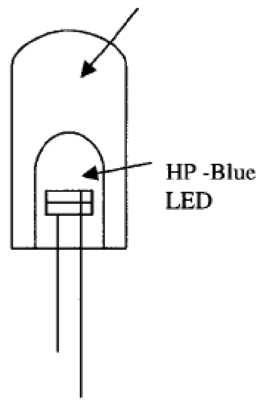
- In polymer composites
  - Nearly full color emitting LEDs
  - (CdSe)ZnS in PLMA (green – red)
  - (CdS)ZnS in PLMA (violet – blue)
  - (CdS)ZnS in PLMA for temperature measurements



CdSe in TOPO

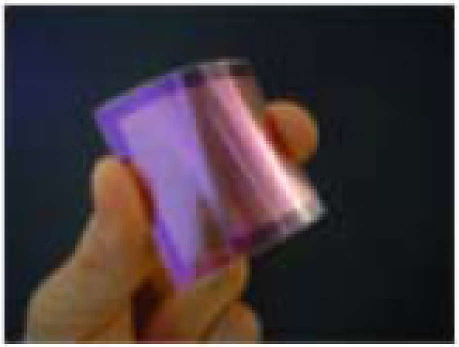




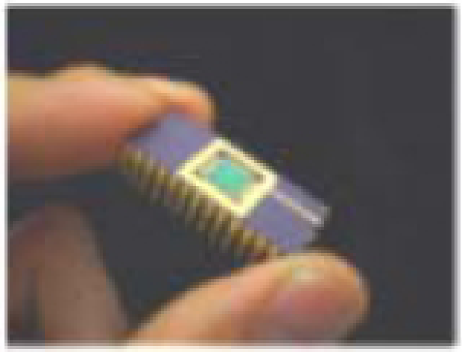


II-VI Quantum Dots
Applications

- Coupled to bio-molecules → biological sensors

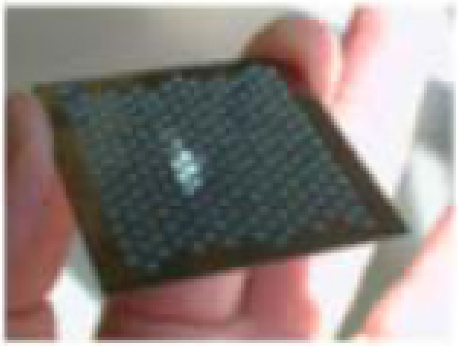


Conformal Solar Cells



Memory

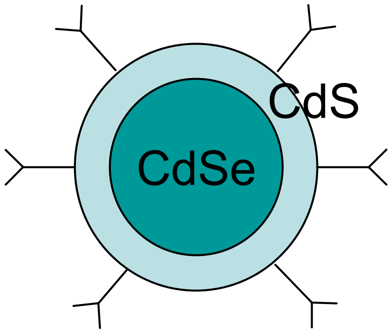
Flexible Electronics

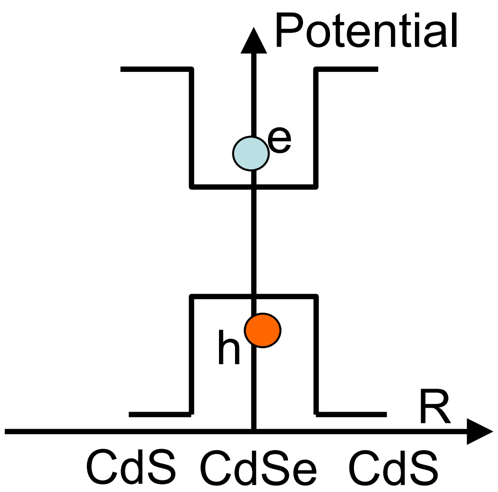


Drug Discovery Substrates

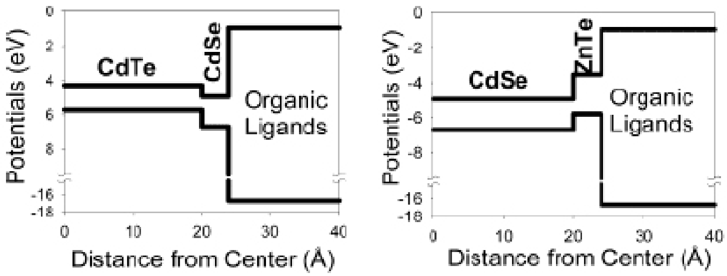
II-VI Quantum Dots Bandstructure

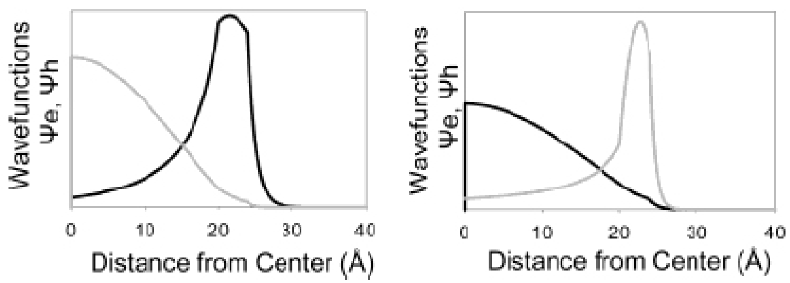
- Type-I core-shell structure (CdSe)CdS
  - Display devices and lasers





- Type-II (CdTe)CdSe and (CdSe)ZnTe
  - Esp. photovoltaic photoconducting devices
  - Energies smaller than bandgap of each material possible
  - Tunable bandgap – low yield (<5%)





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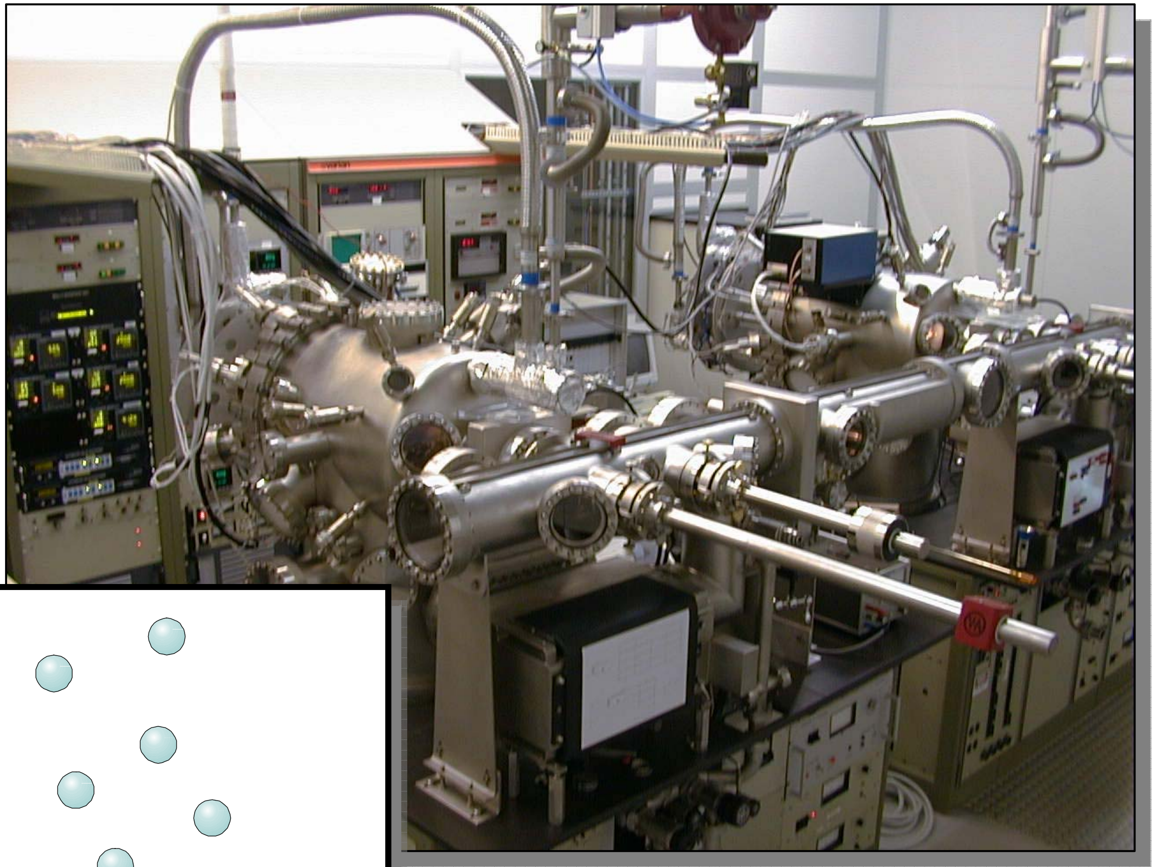
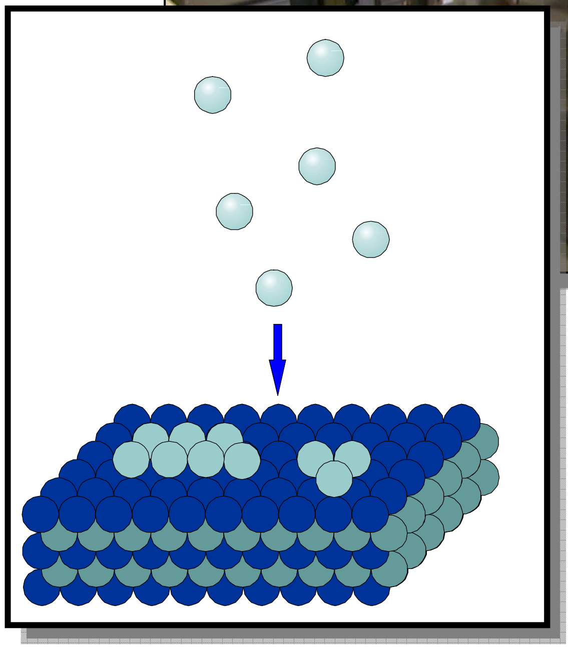
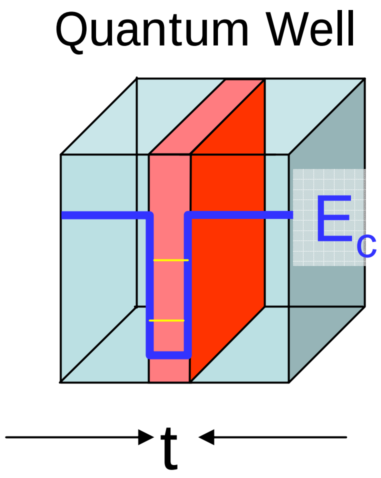
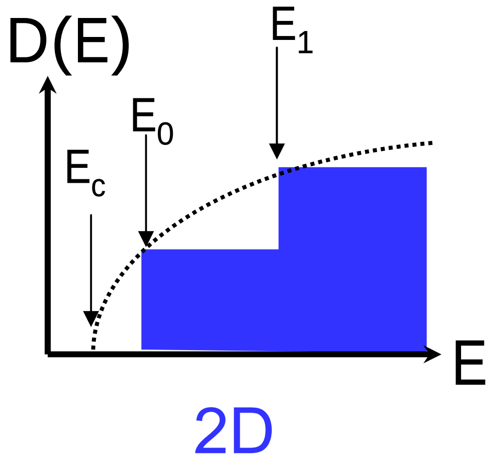
CEO
Molecular-Beam-Epitaxy (MBE)



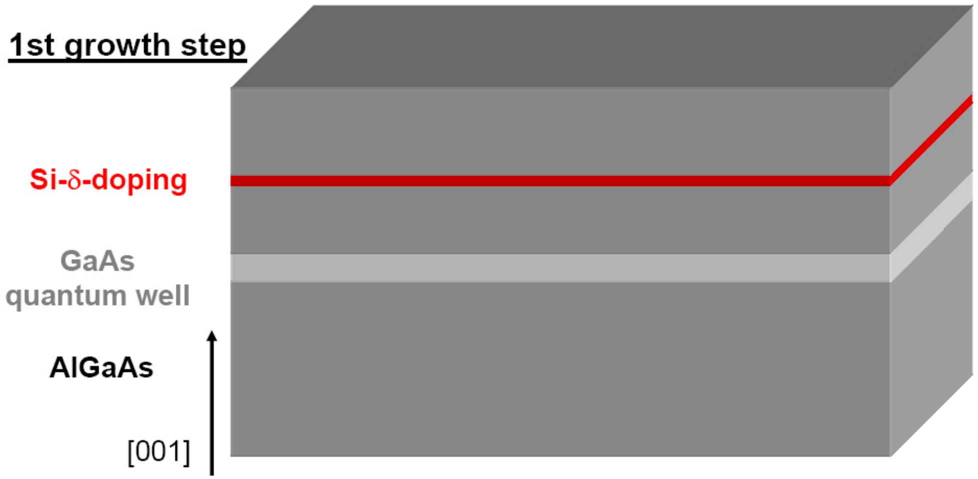


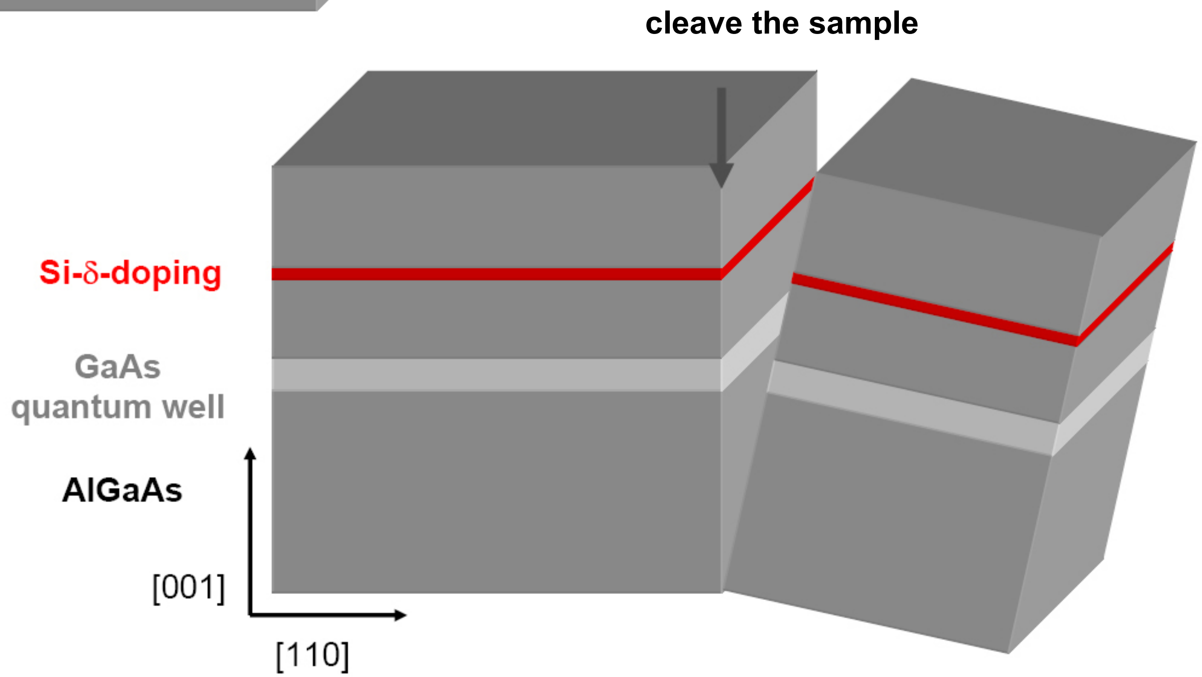




MBE→ Atomically precise deposition of layers with different composition and/or doping

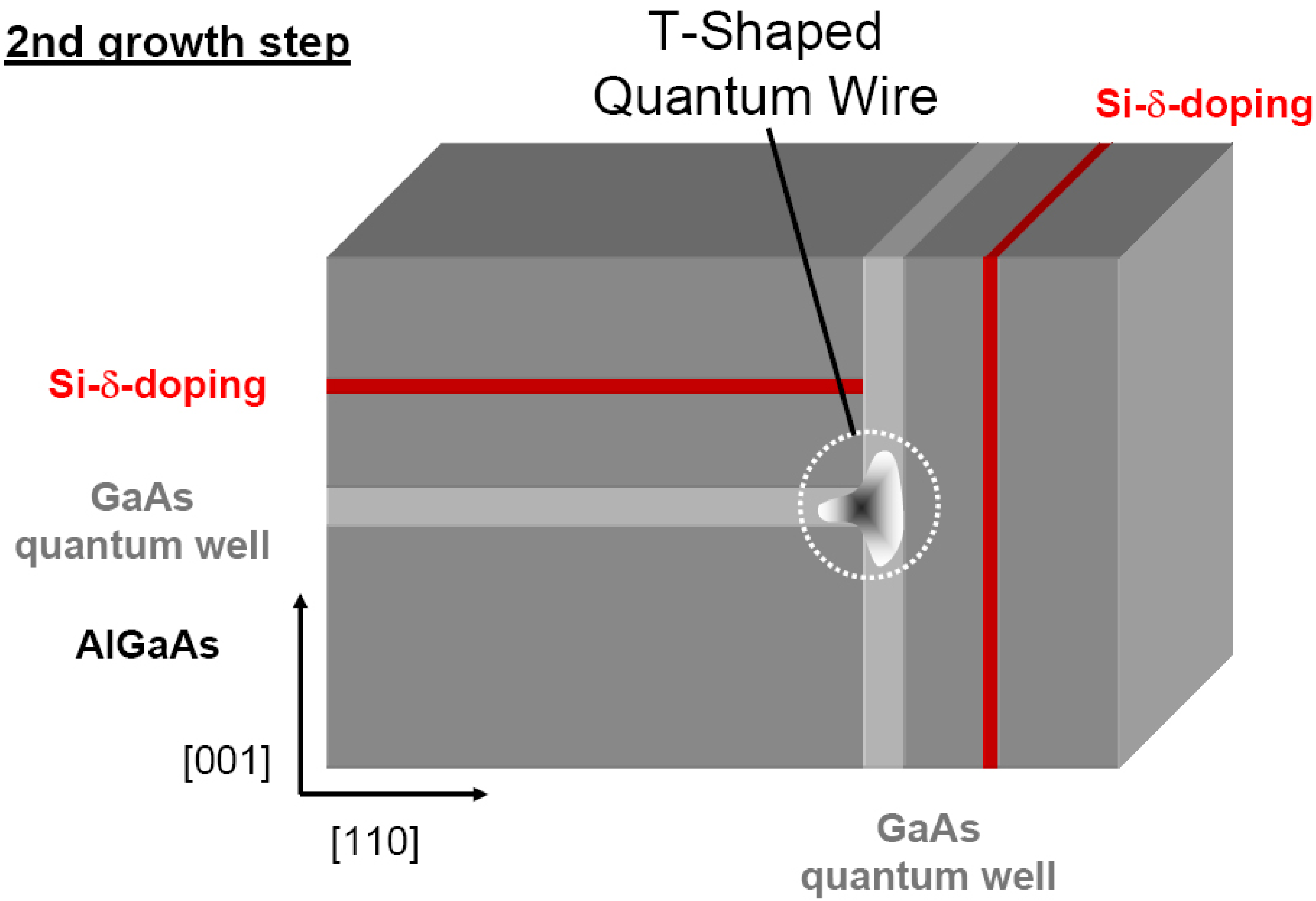
CEO Process


1st growth step
Si-δ-doping
GaAs
quantum well
AlGaAs
[001]

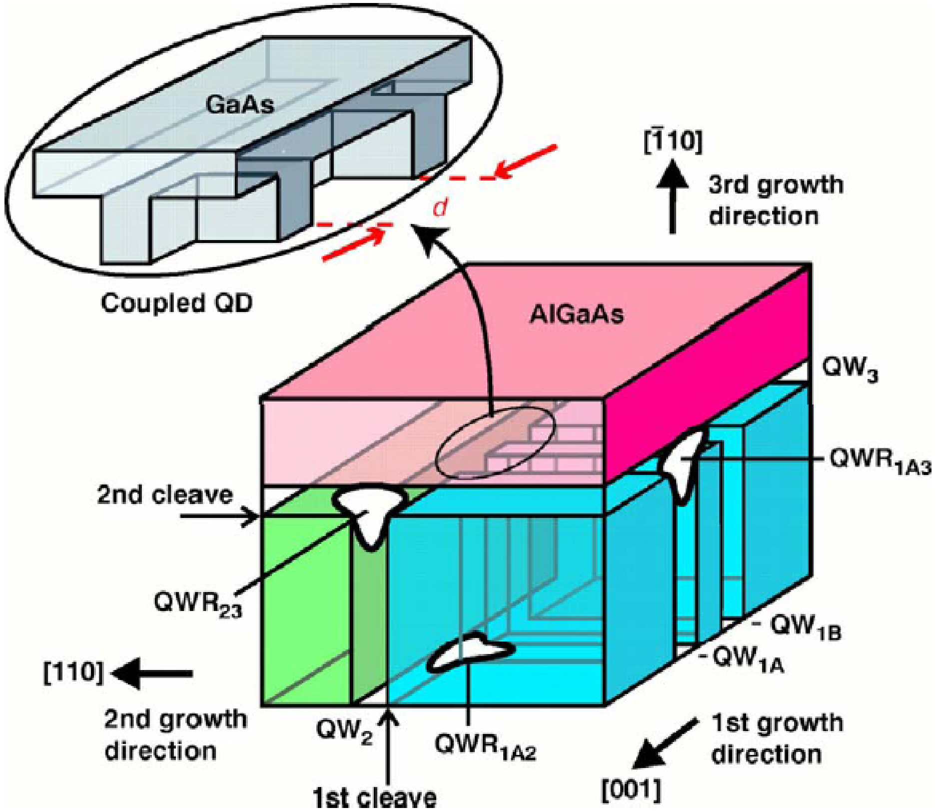

cleave the sample
Si-δ-doping
GaAs
quantum well
AlGaAs
[001]
[110]

CEO Process

2nd growth step



CEO
QDs via 2x CEO



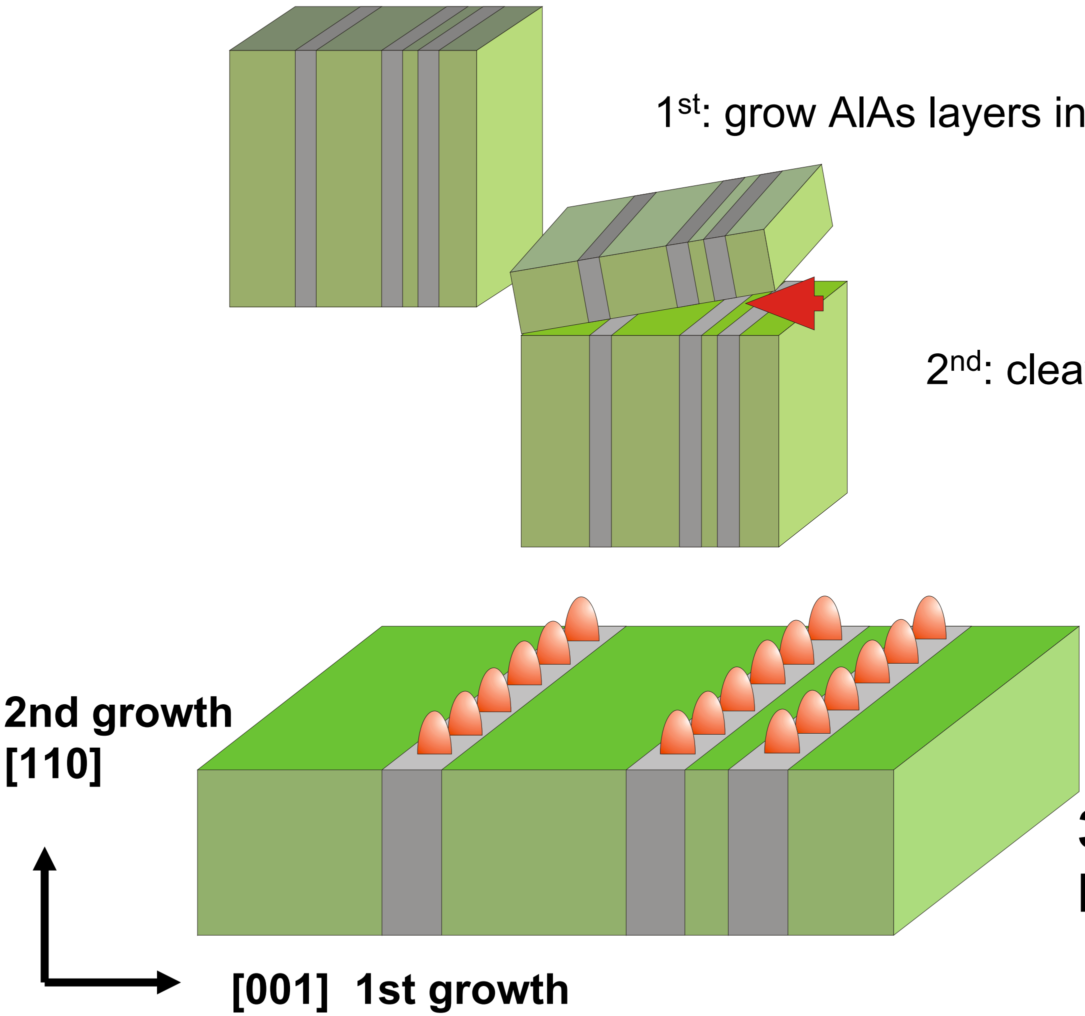
- Two cleaving steps enable fabrication of QDs and artificial molecules
  - 1st growth on (001) GaAs
  - 2nd growth on (011)
  - 3rd growth on (0$\bar{1}$1)
- At intersection between three quantum wells
  - Weaker localisation
  - Lower energy state

→QUANTUM DOT

CEO
Lateral Aligned Quantum Dots

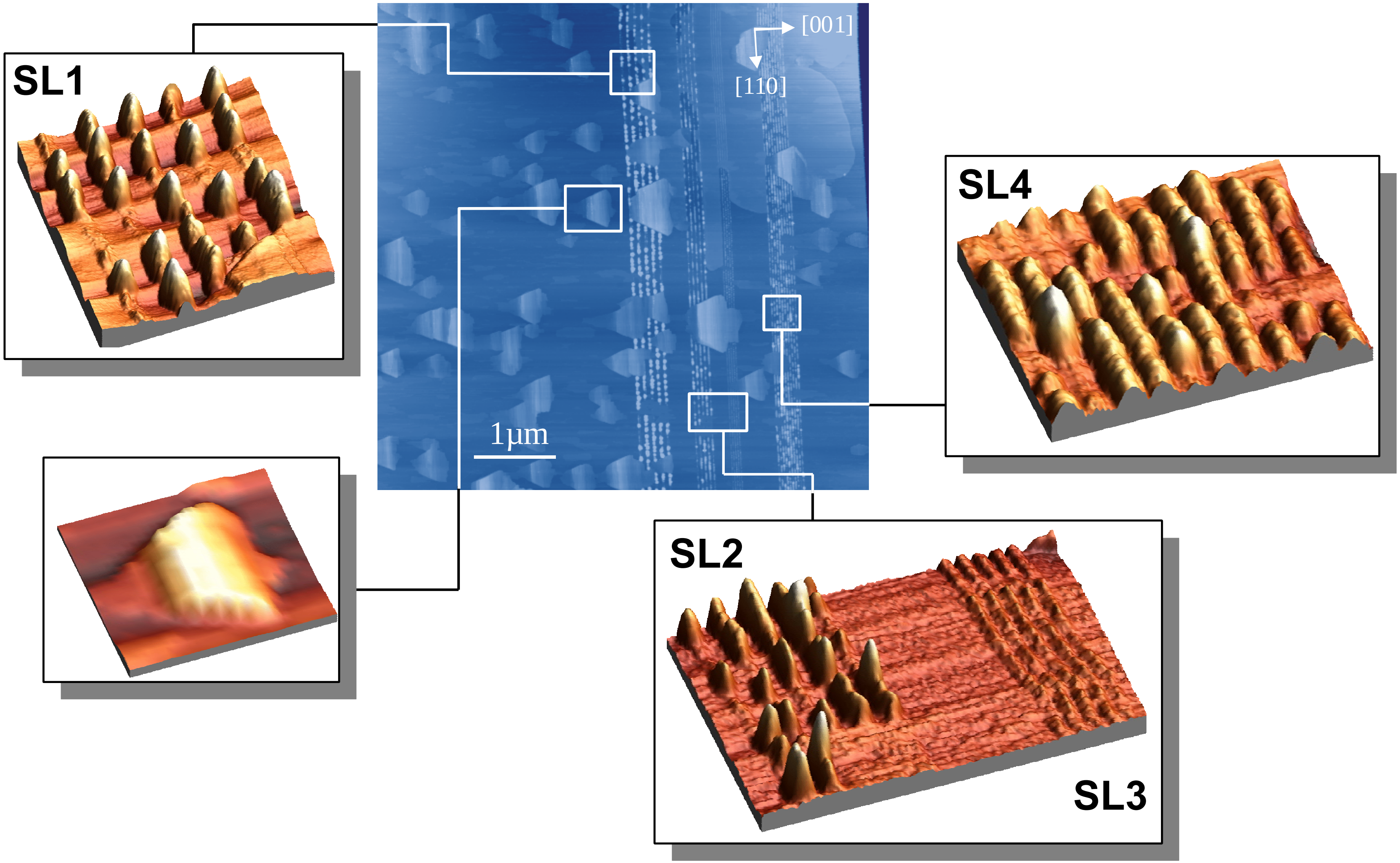
1st: grow AlAs layers in GaAs matrix

2nd: cleave in MBE machine

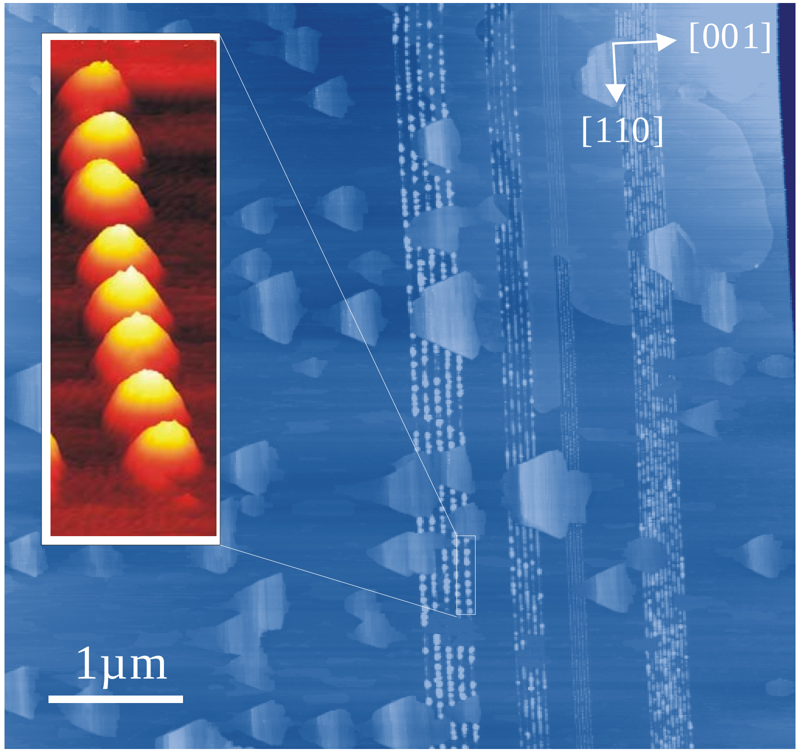


3rd: grow InAs Dots on MBE patterned (110) surface

CEO
Atomic Force Microscopy I



CEO
Atomic Force Microscopy II



SL 1 2 3 4

	SL1	SL 2	SL3	SL4
AlAs-width [nm]	32	20	11	20
dot width [nm]	35	22	12	22
dot height [nm]	13 ±4	7 ±1	3	7 ±1
density [dots/µm]	17	14	-----	-----

- **quantum dot size correlated with AlAs-width**
- **create chessboard-structure?**

Fabrication Methods – CEO Conclusions

Advantages

- Very high crystal quality
- Confinement for both electrons and holes
- Flexibility

Disadvantages

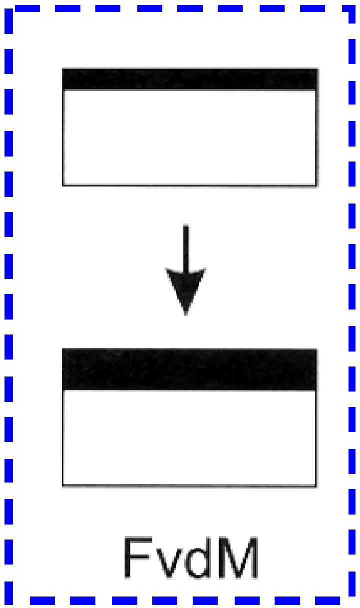
- Relatively low confinement energies (Δ~10meV)
- Complex crystal growth and fabrication
- (011) surface not purely As or Ga terminated like (100)

Outline

- Introduction
- **Fabrication – Experiments – Applications**
  - Porous Silicon
  - II-VI Quantum Dots
  - **III-V Quantum Dots**
    - Cleaved Edge Overgrowth (CEO)
    - **Self Assembling Quantum Dots**
    - Electronic Structure

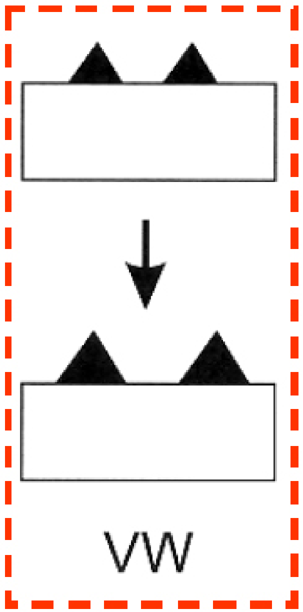
Self Assembling QDs
Epitaxial Growth Modes

- Equilibrium crystal growth driven by thermodynamic forces
  - Surface (α) and interface (β) energies
  - Two growth modes = Frank-van der Merwe (FvdM), Volmer-Weber (VW)



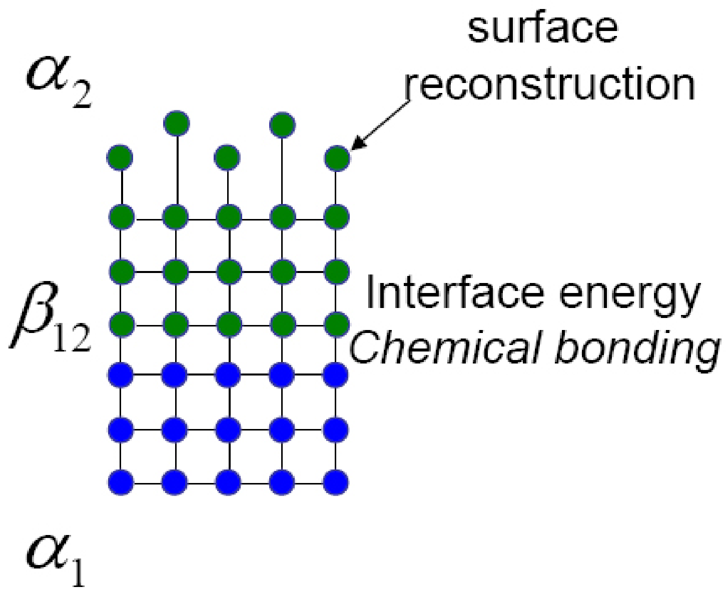
$$\alpha_2 + \beta_{12} < \alpha_1$$

Deposited Material Wets Substrate

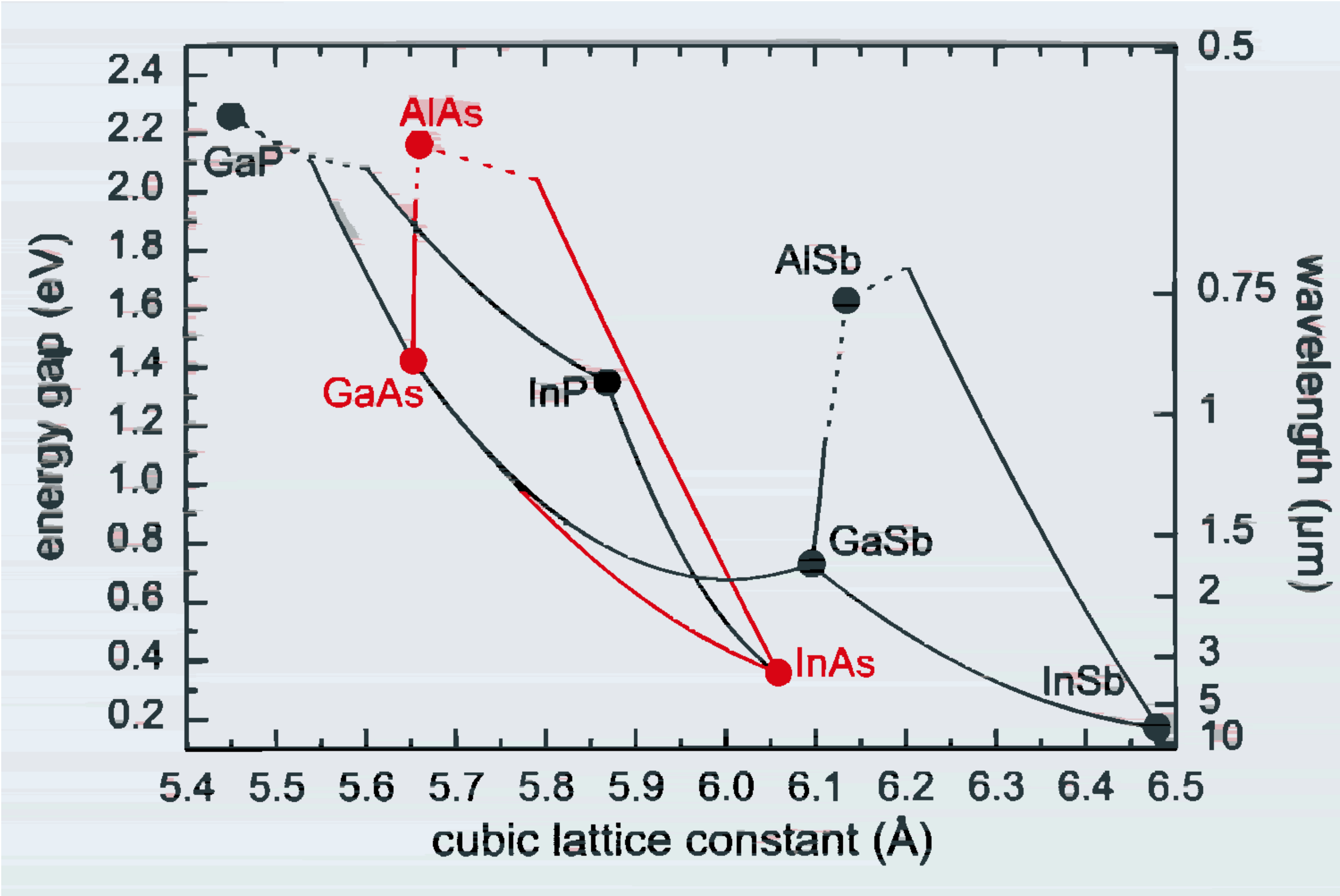


$$\alpha_2 + \beta_{12} > \alpha_1$$

Clustering reduces free energy

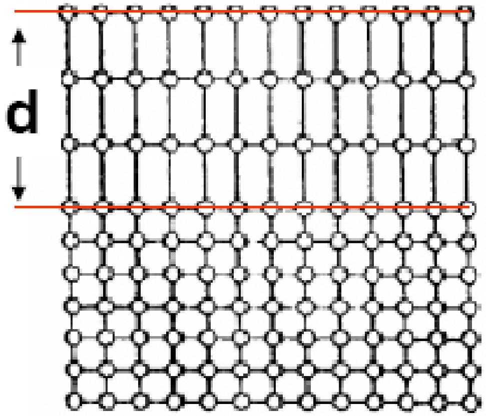


Self Assembling QDs
Energy Gap vs. Lattice Constant

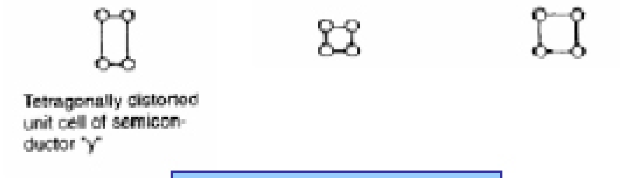


Self Assembling QDs
Strained Layer Epitaxy

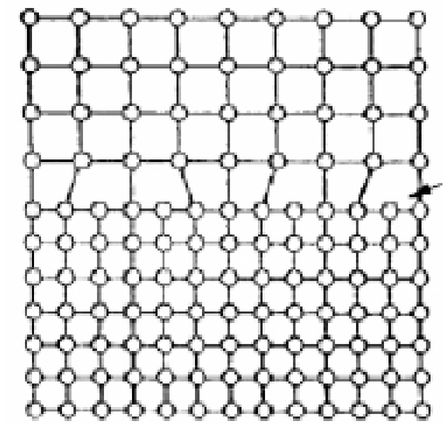
Pseudomorphic



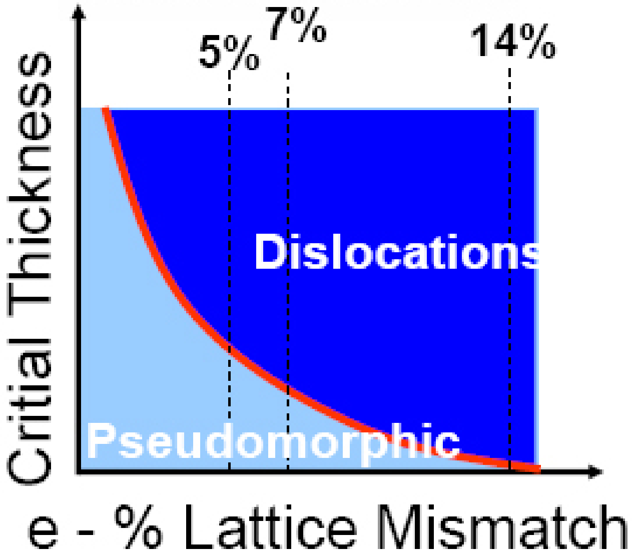
a_1 a_2



Dislocated



$$\varepsilon = \frac{a_1 - a_2}{a_1}$$



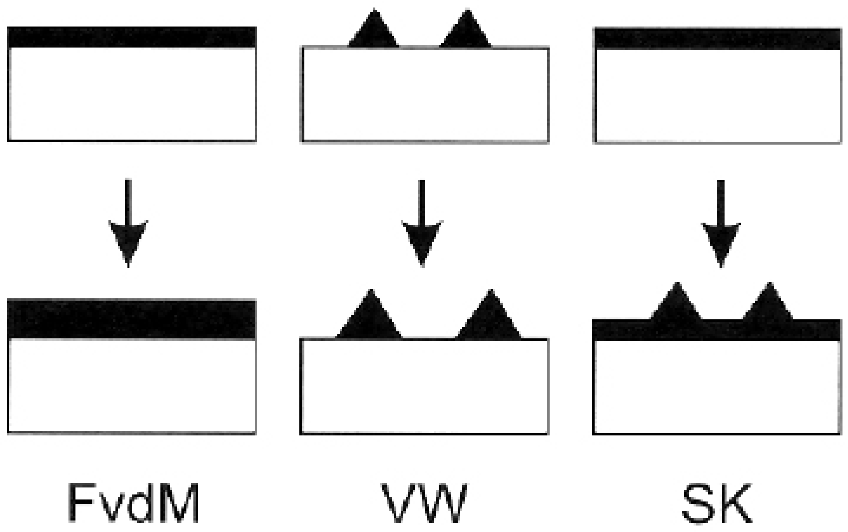
For (001) growth
Strain Energy

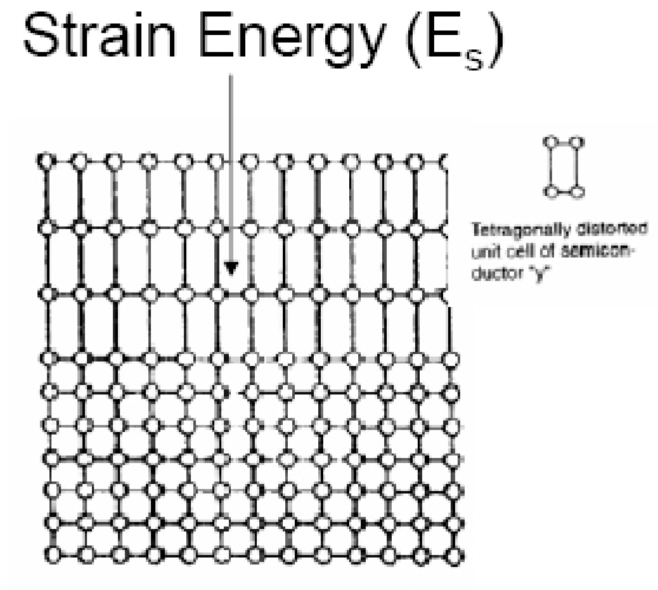
$$E_s \propto \varepsilon^2 d$$

- Pseudomorphic growth
  - Strain energy increases ~ linearly with d

Self Assembling QDs
Growth Modes in Strained Systems

- Switching between FvdM and VW growth possible due to increase of strain energy during heteroepitaxy…

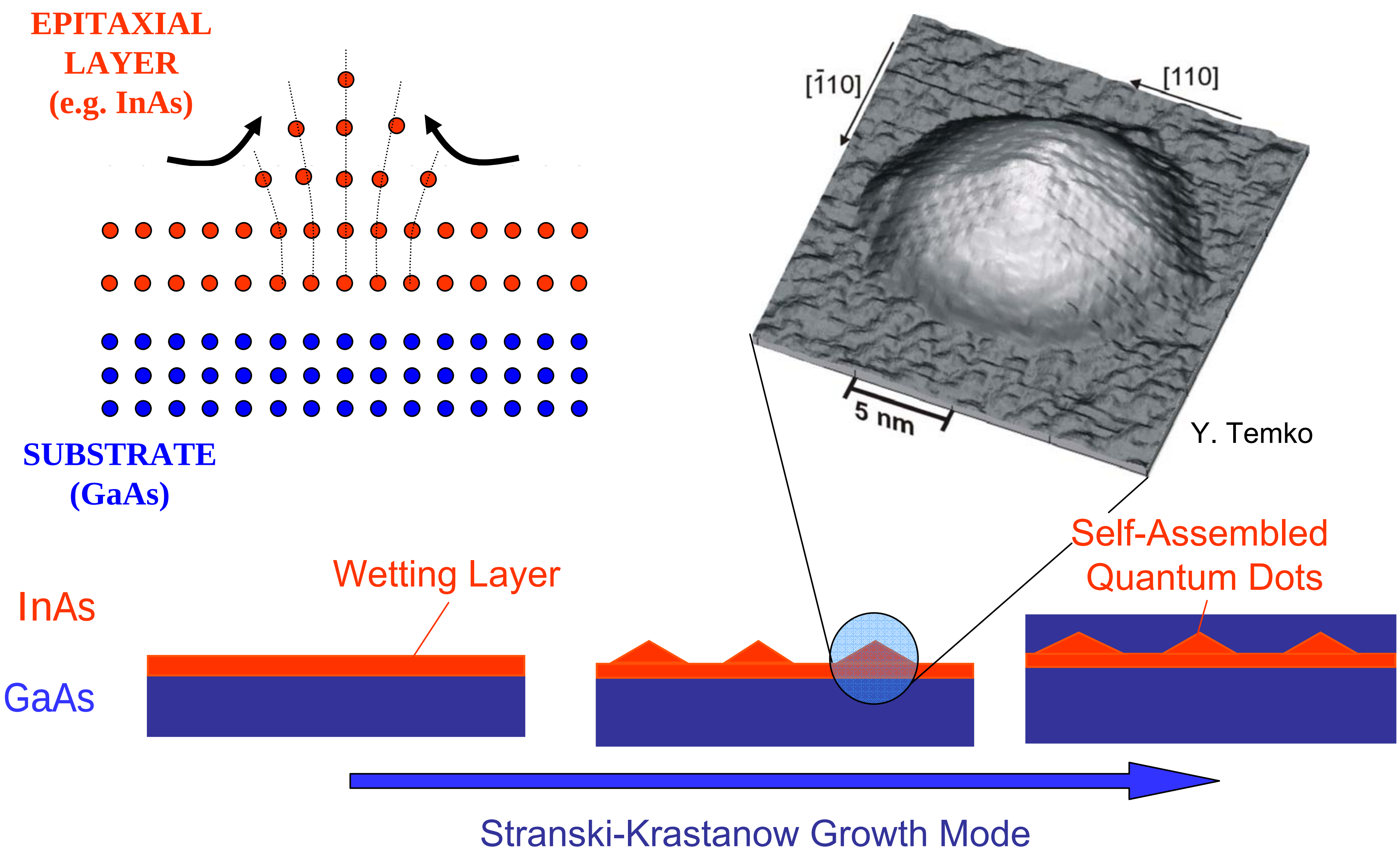




Planar FvdM growth at start ($\alpha_2 + \beta_{12} < \alpha_1$) but growing strain energy (E_S) drives a change from FvdM to VW like growth → Stranski-Krastanow Mechanism

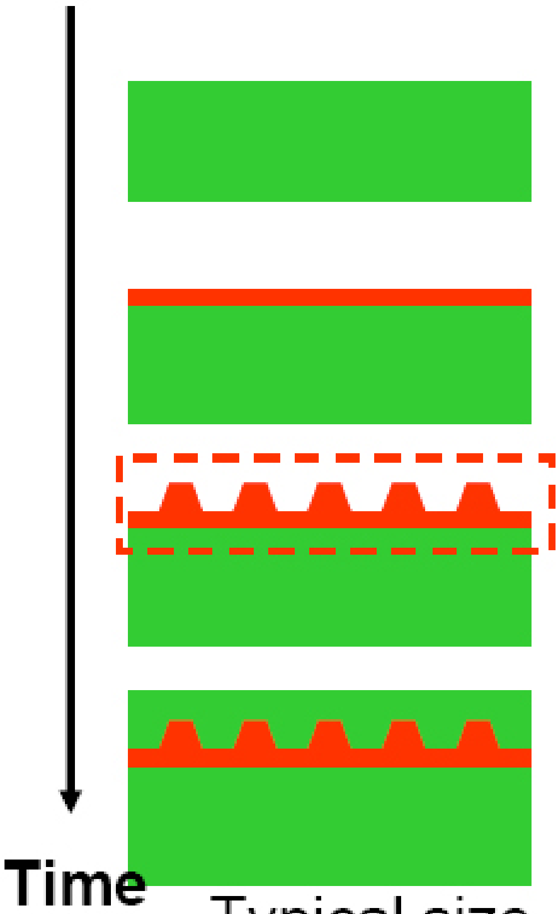
Self Assembling QDs
Stranski-Krastanov Growth

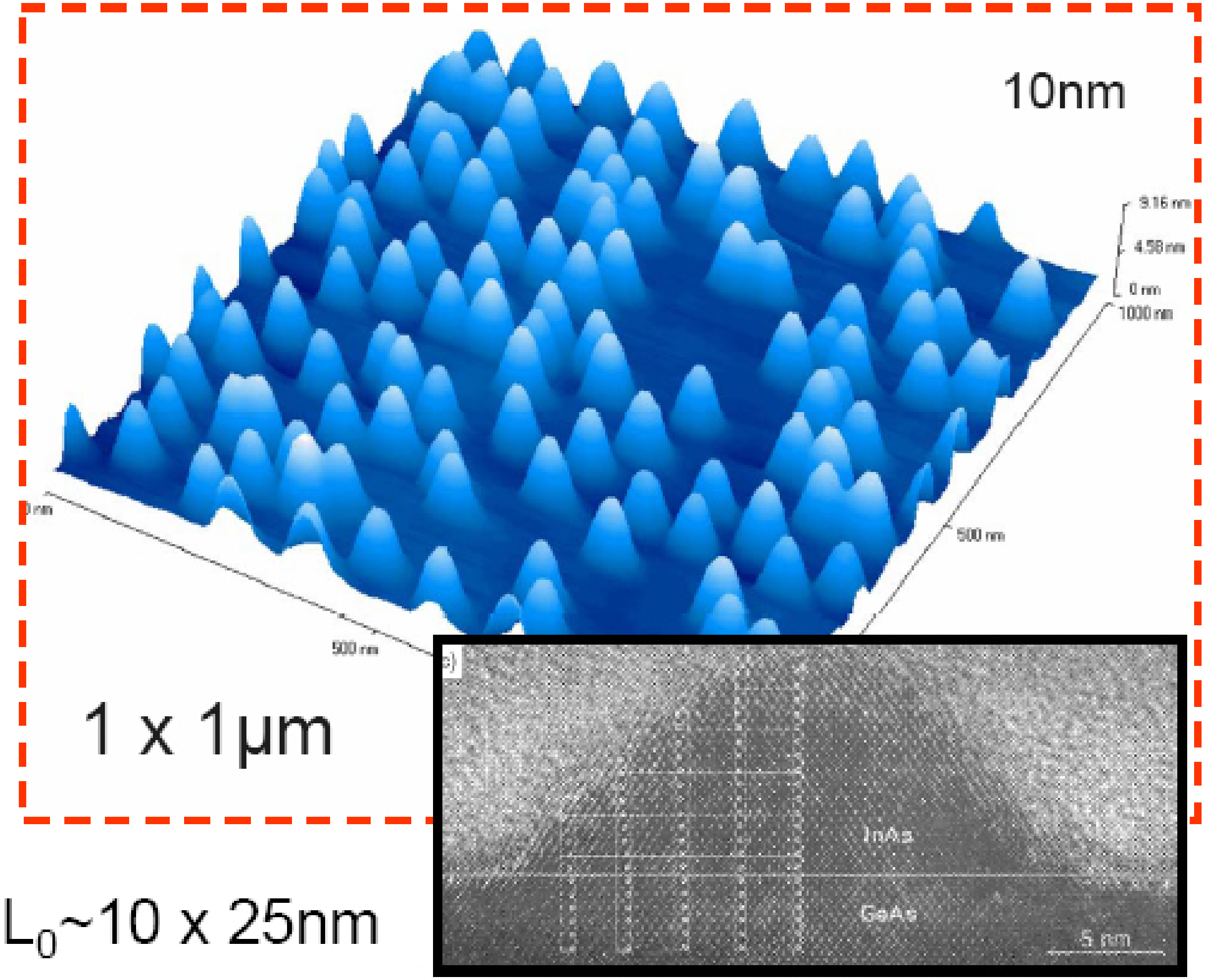
- Nanostructures formed during lattice mismatched epitaxy (e.g. InAs on GaAs)



Self Assembling QDs
Islands → Quantum Dots

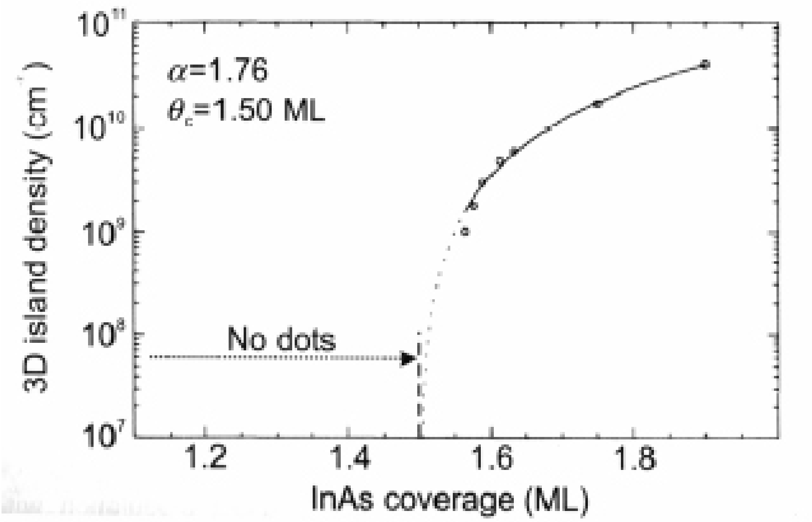
- Formed during Stranski-Krastanow growth of lattice mismatched materials
    - e.g. GaAs substrate + InAs islands + GaAs cap

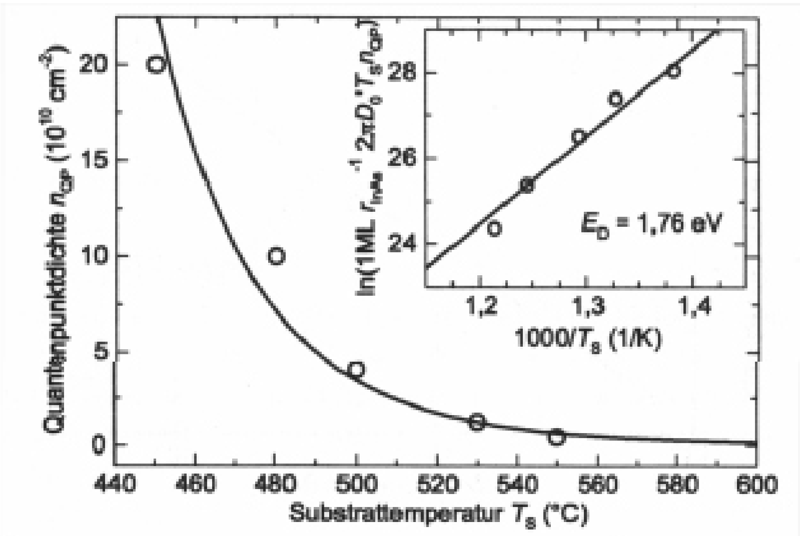


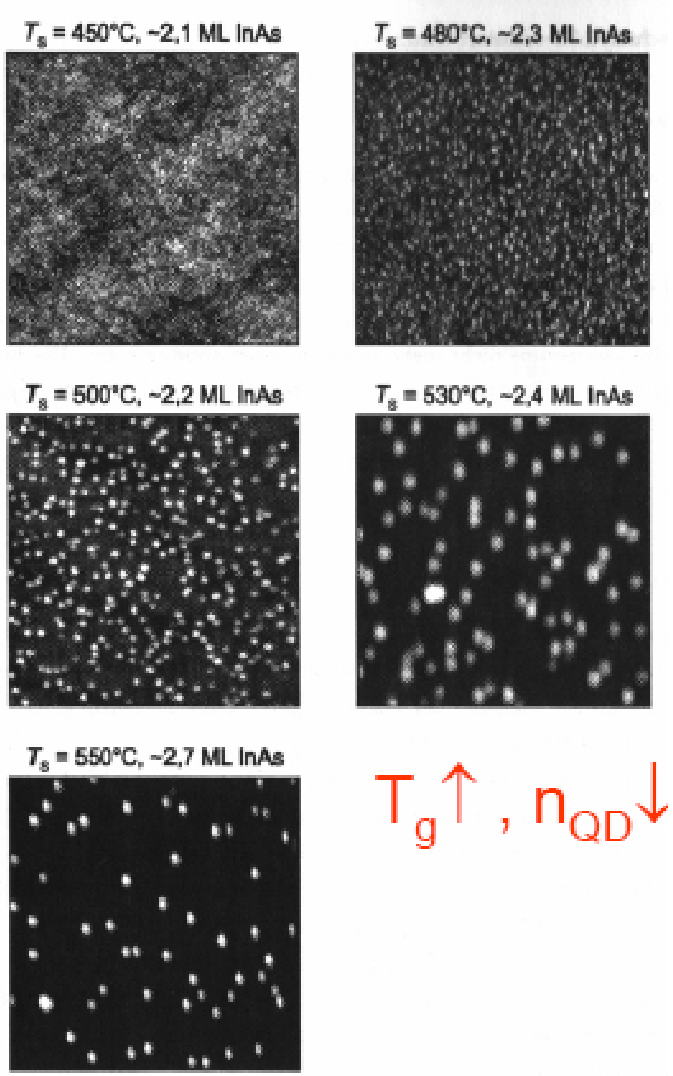


Typical size – L_0~10 x 25nm

Self Assembling QDs
Influence of Growth Parameters







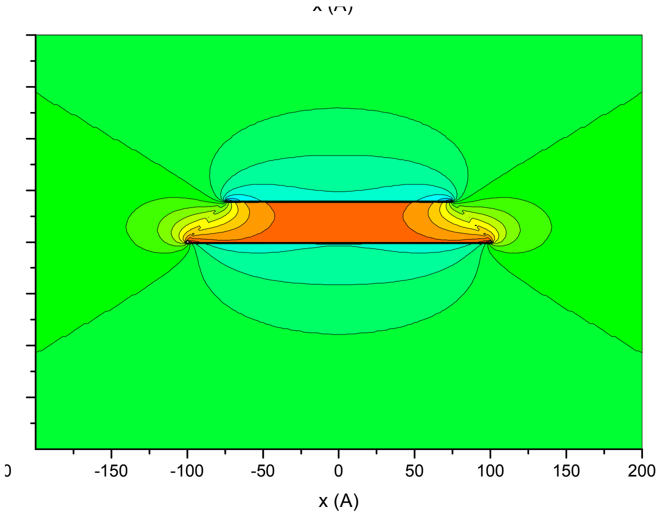
$T_g\uparrow$, $n_{QD}\downarrow$

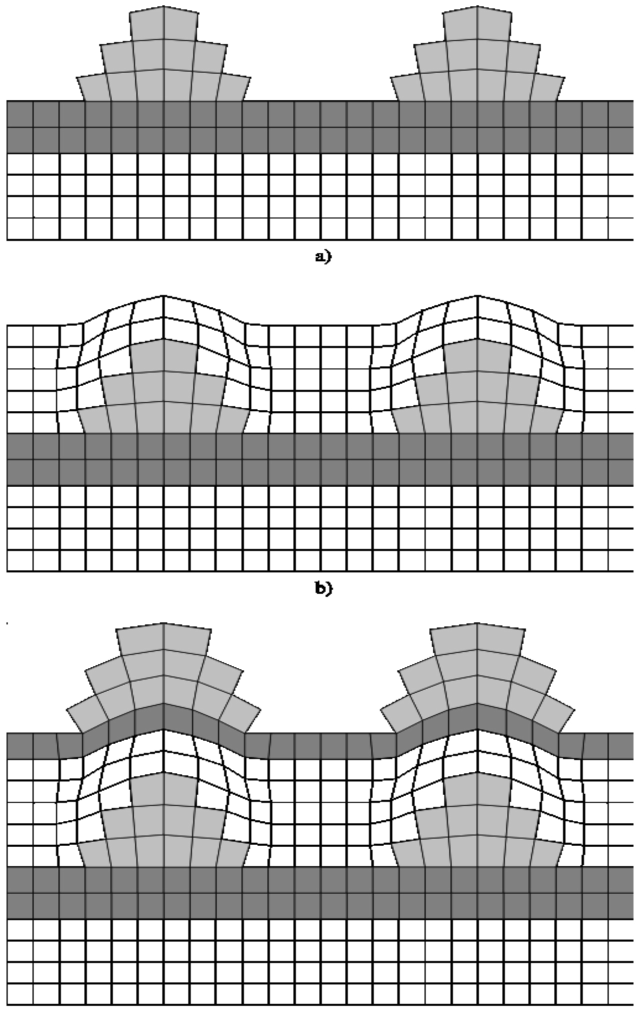
- Growth conditions control QD size, density and composition

Self Assembling QDs
Strain

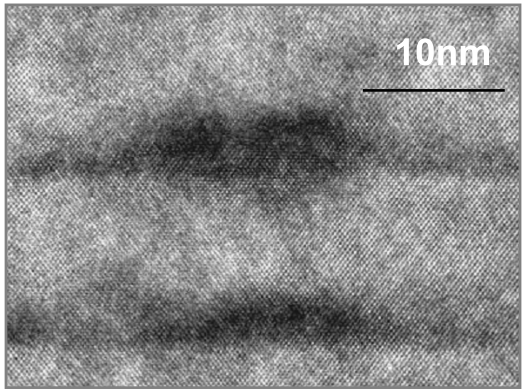
Upper layers of dots tend to nucleate in strain field generated by lower layers

Strain field extends outside buried QD



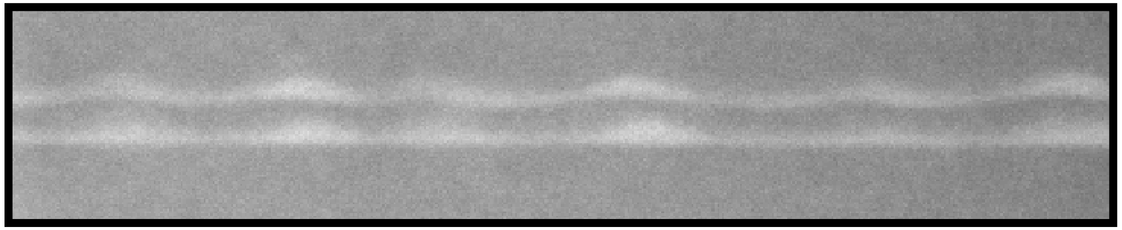


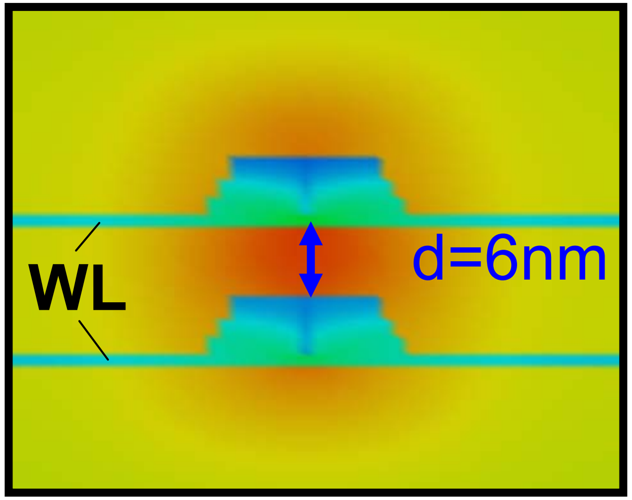
Transmission Electron Micrograph of single coupled QD molecule

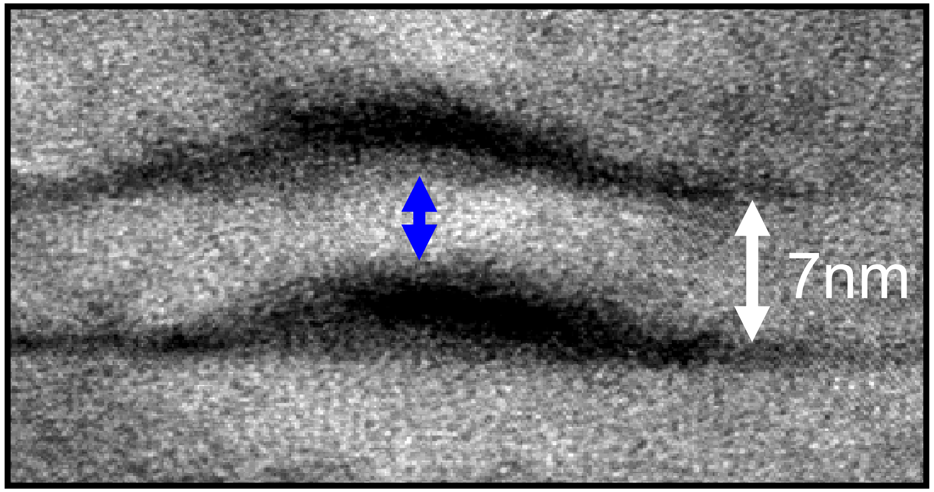


Self Assembling QDs
Strain

- InGaAs-GaAs self assembled QD-molecules
- Self alignment via strain field



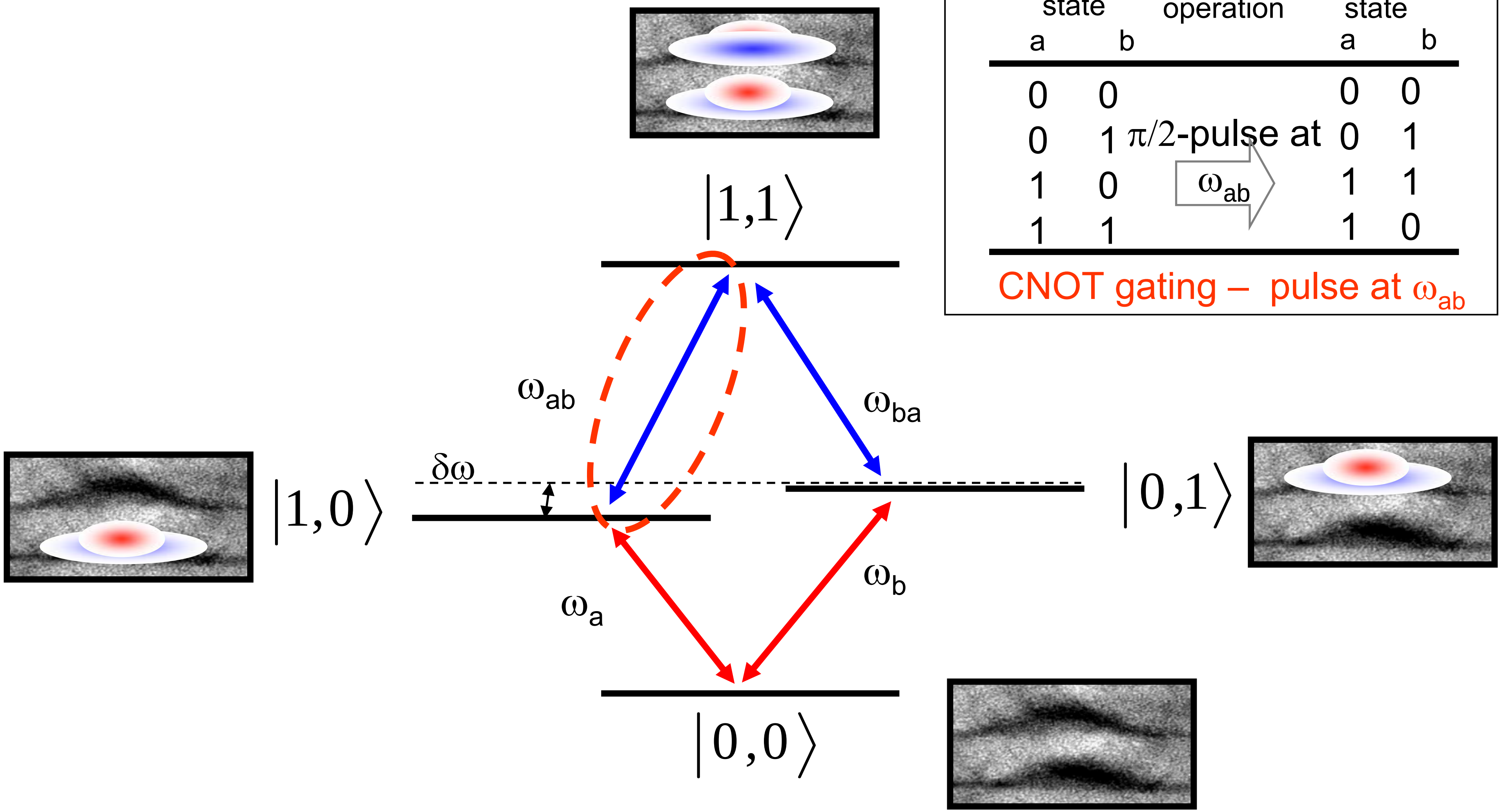




Self Assembling QDs
Quantum Logic

Initial state a	Initial state b	CNOT operation	Final state a	Final state b
0	0	$\pi/2$-pulse at ω_{ab}	0	0
0	1		0	1
1	0		1	1
1	1		1	0

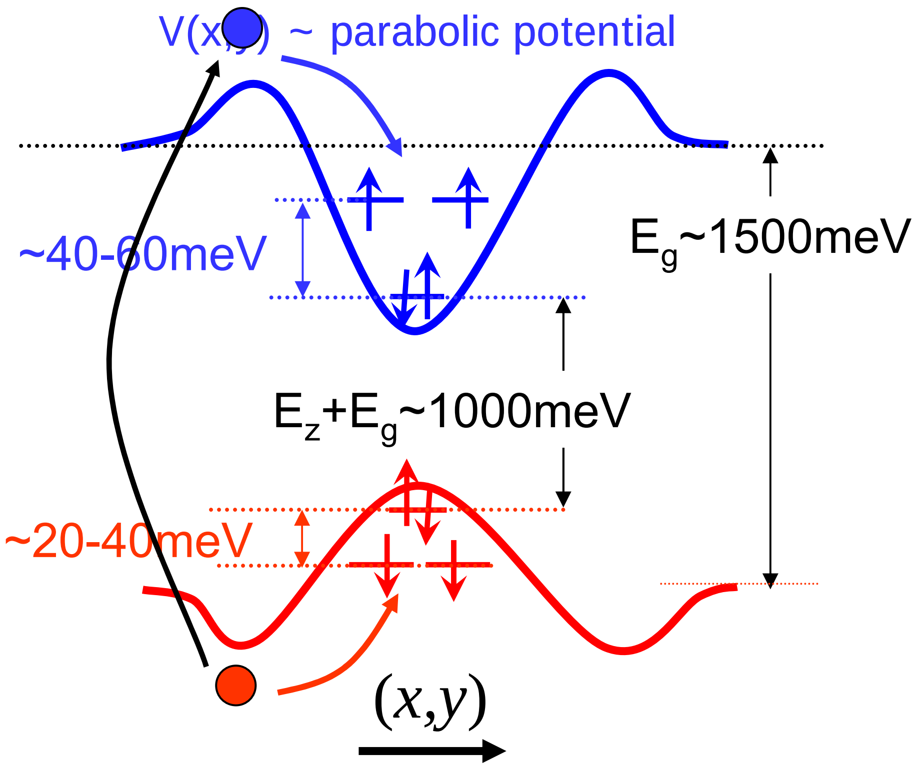
CNOT gating – pulse at ω_{ab}

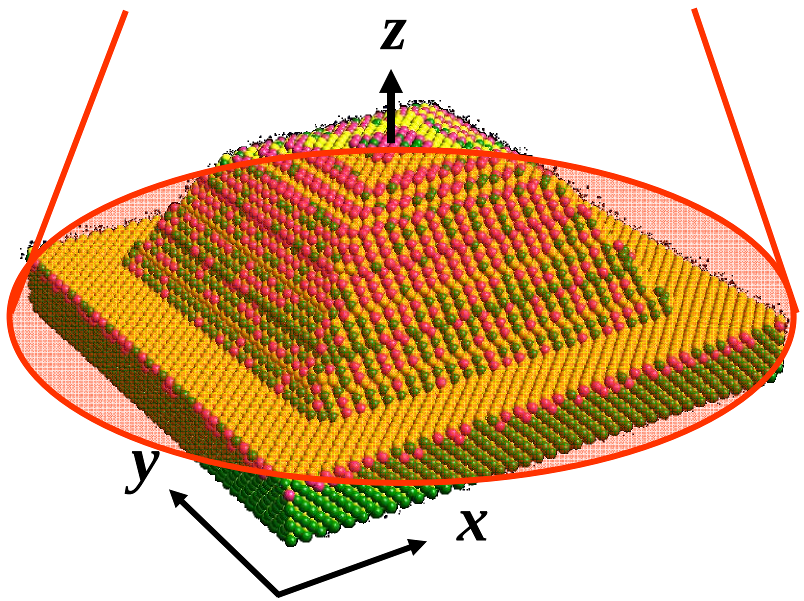


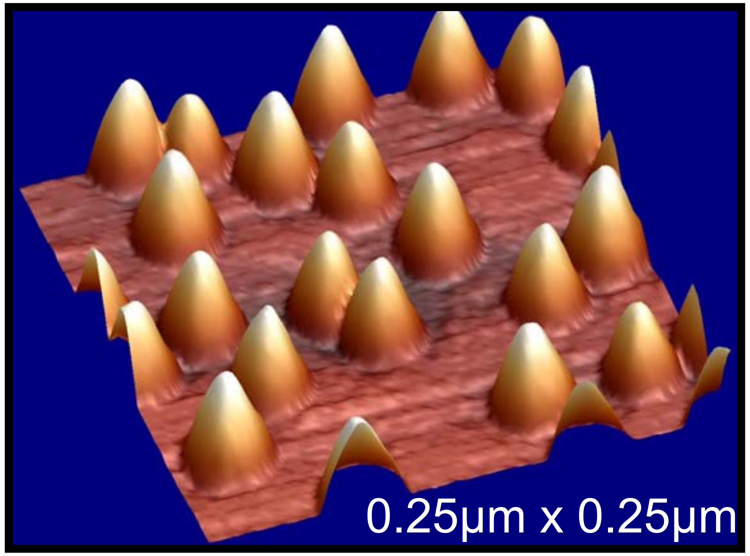
Outline

- Introduction
- **Fabrication – Experiments – Applications**
  - Porous Silicon
  - II-VI Quantum Dots
  - **III-V Quantum Dots**
    - Cleaved Edge Overgrowth (CEO)
    - Self Assembling Quantum Dots
    - **Electronic Structure**

Electronic Structure
Single Dot Spectroscopy



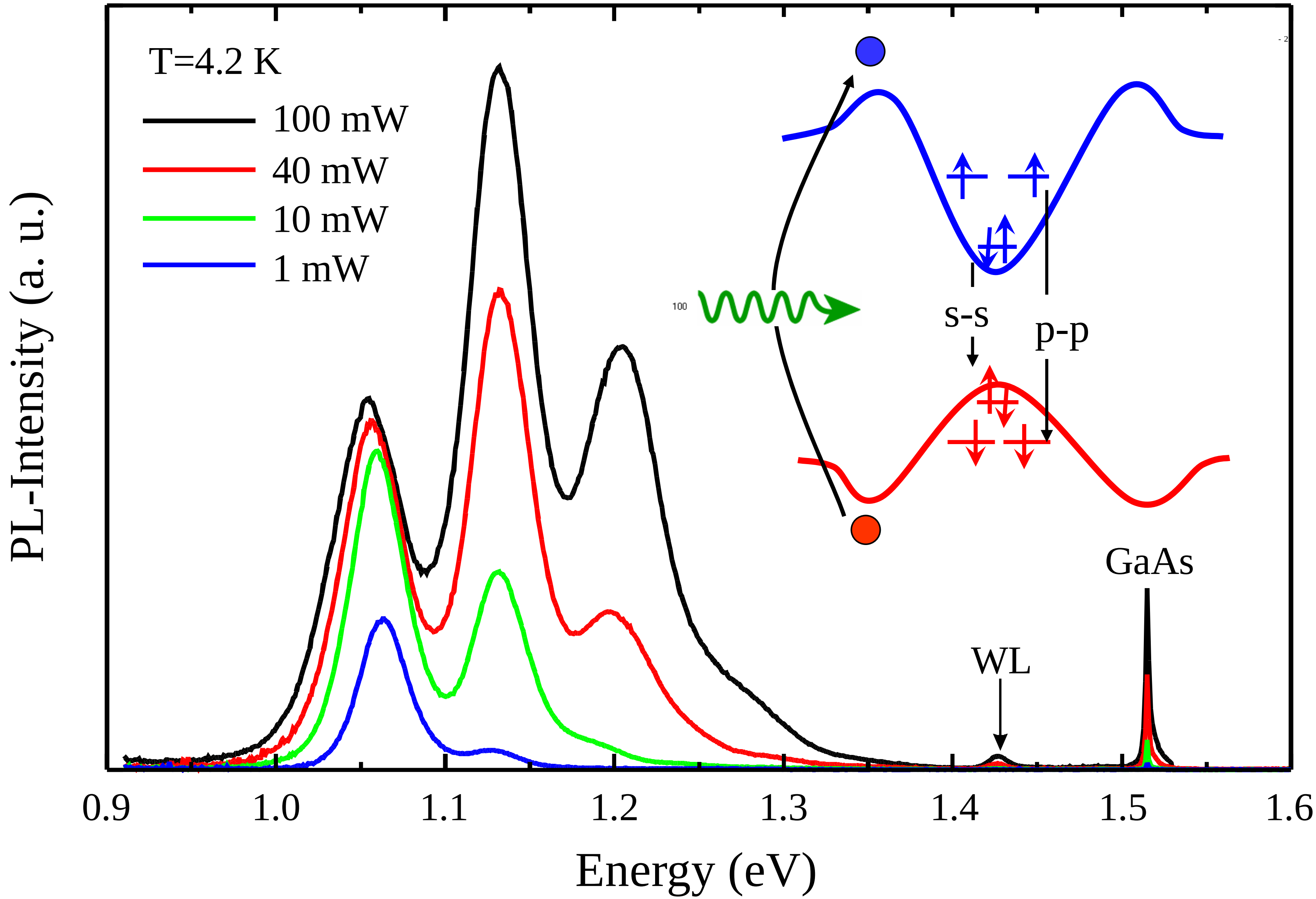




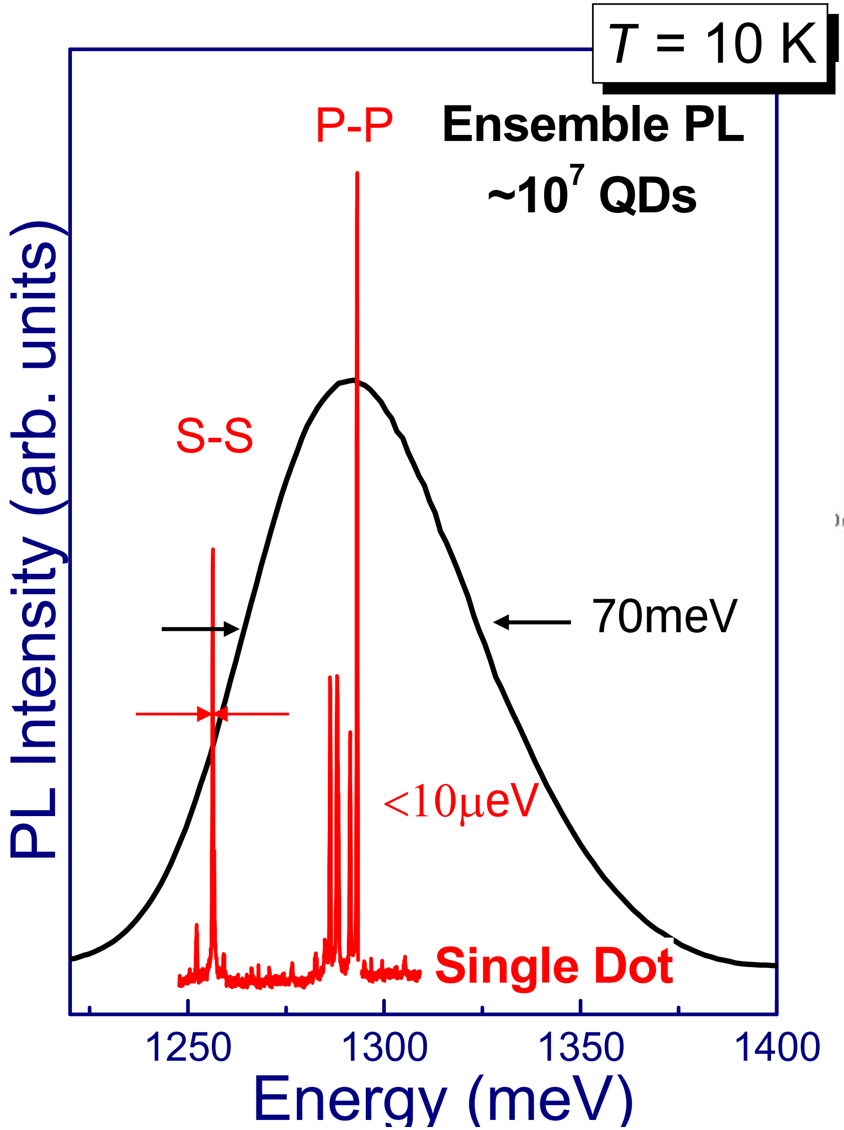
Inhomogeneous broadening

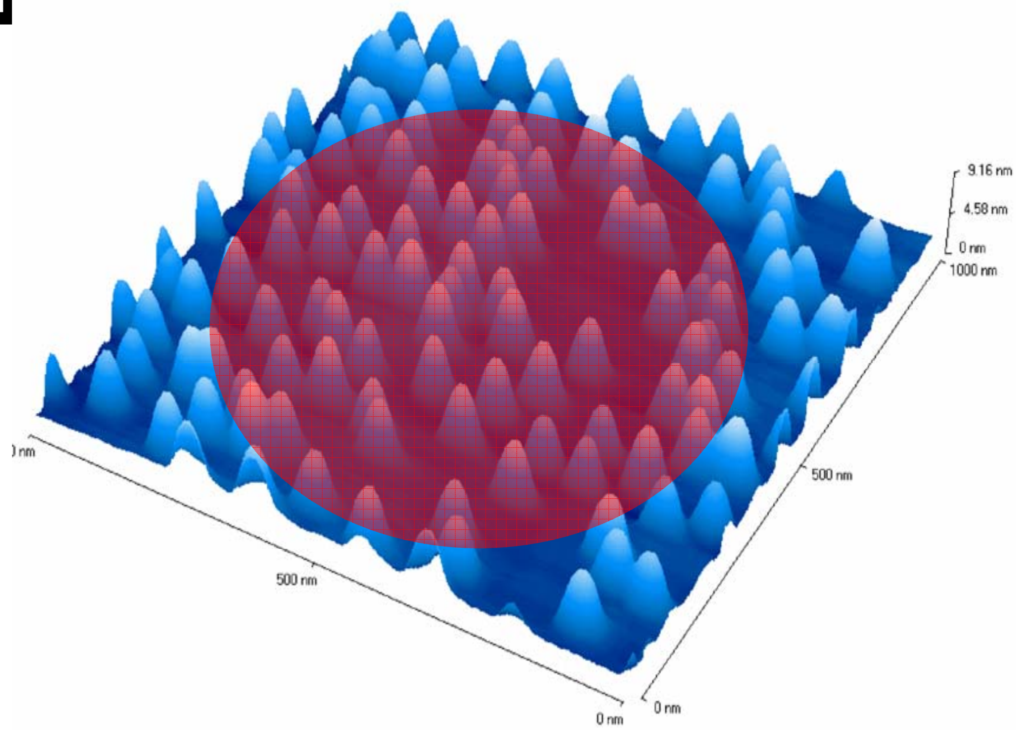
→Size, shape and composition fluctuations
→Limits range of physical phenomena investigable

Electronic Structure
Photoluminescence of QD Ensemble



Electronic Structure
Ensemble → Single Quantum Dot

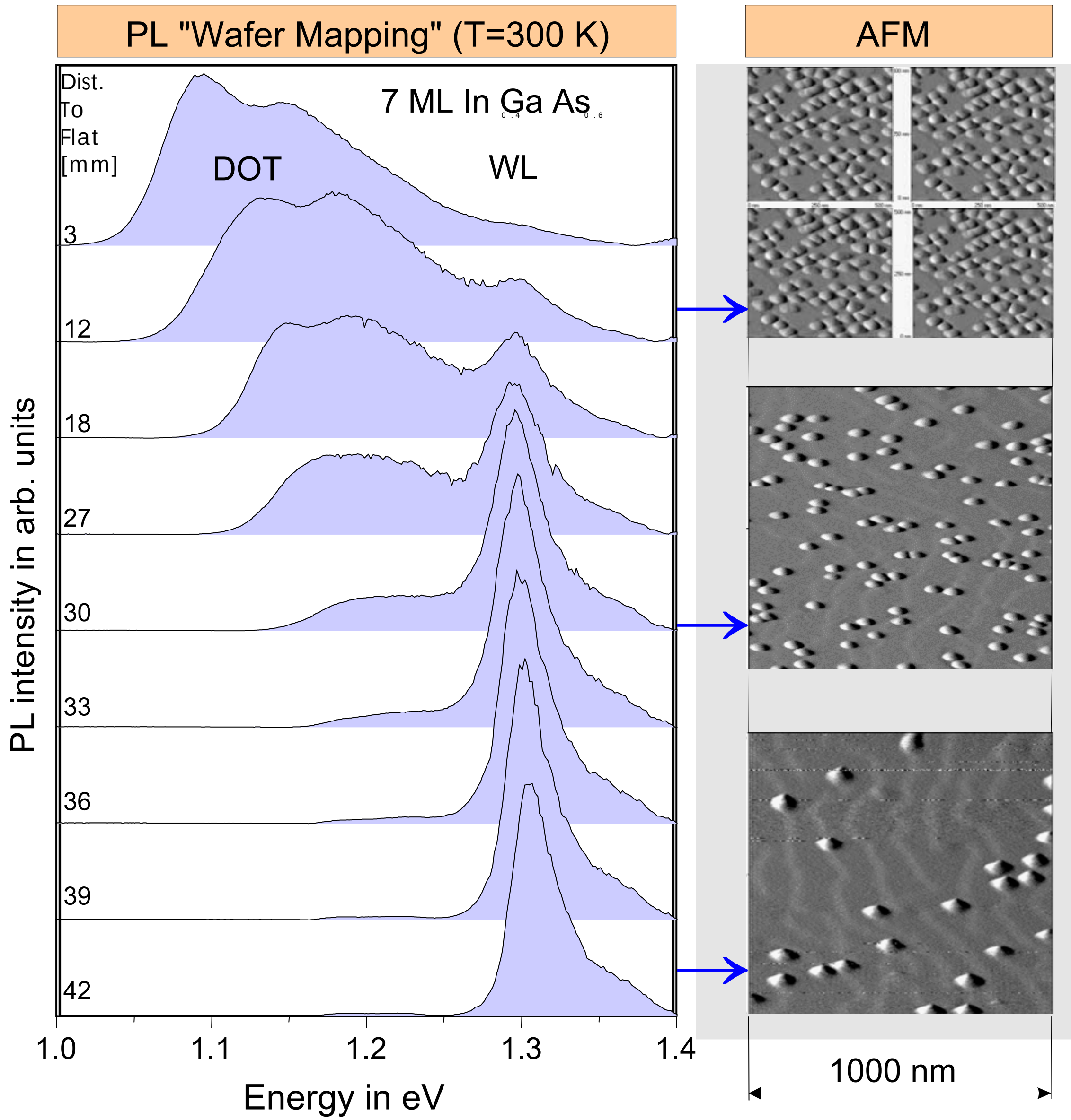


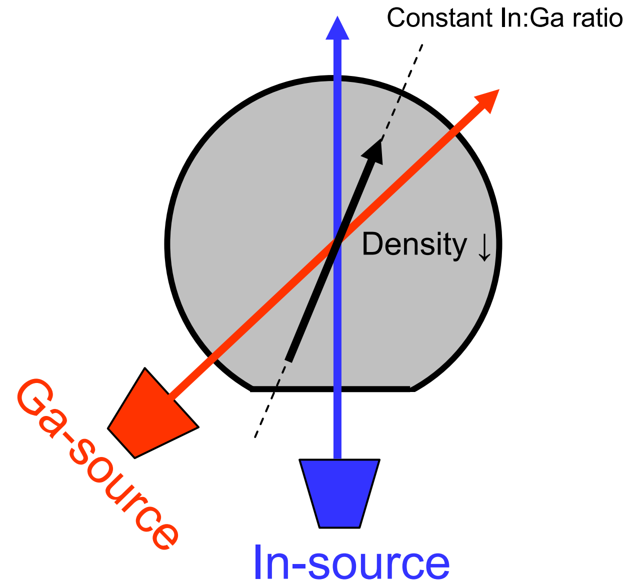


Typical areal QD density 10-100µm^{-2}

→Require low density QD material **and** spatially resovled spectroscopic techniques

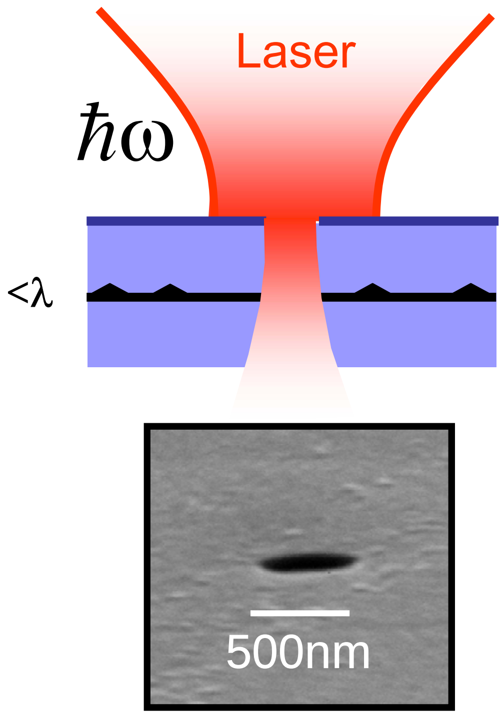
Electronic Structure
Low Quantum Dot Density





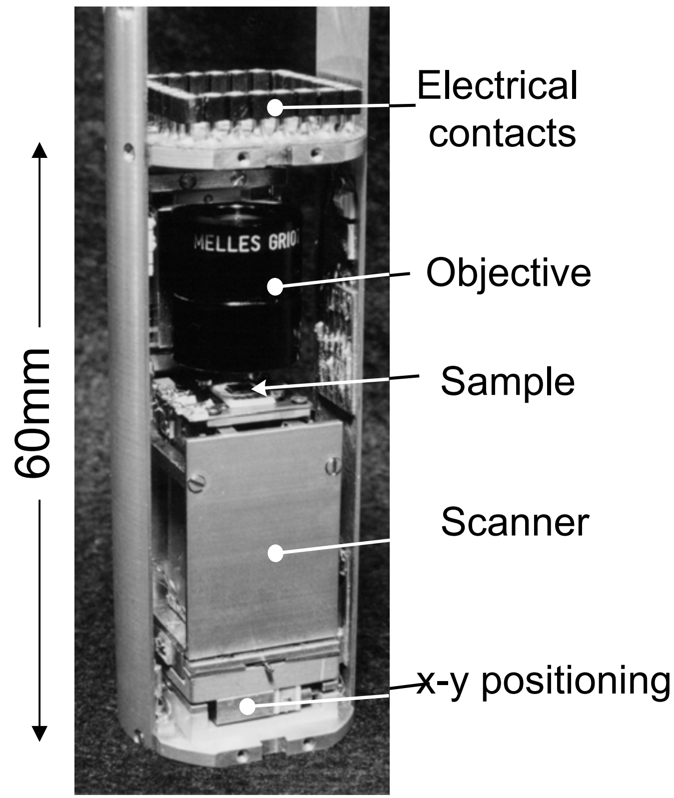
- Growth without substrate rotation
  - Control of In-gradient and In:Ga Ratio
- QD density - 300-10μm^{-2}
- Characterization using PL and AFM

Electronic Structure
Spatially Resolved Spectroscopy

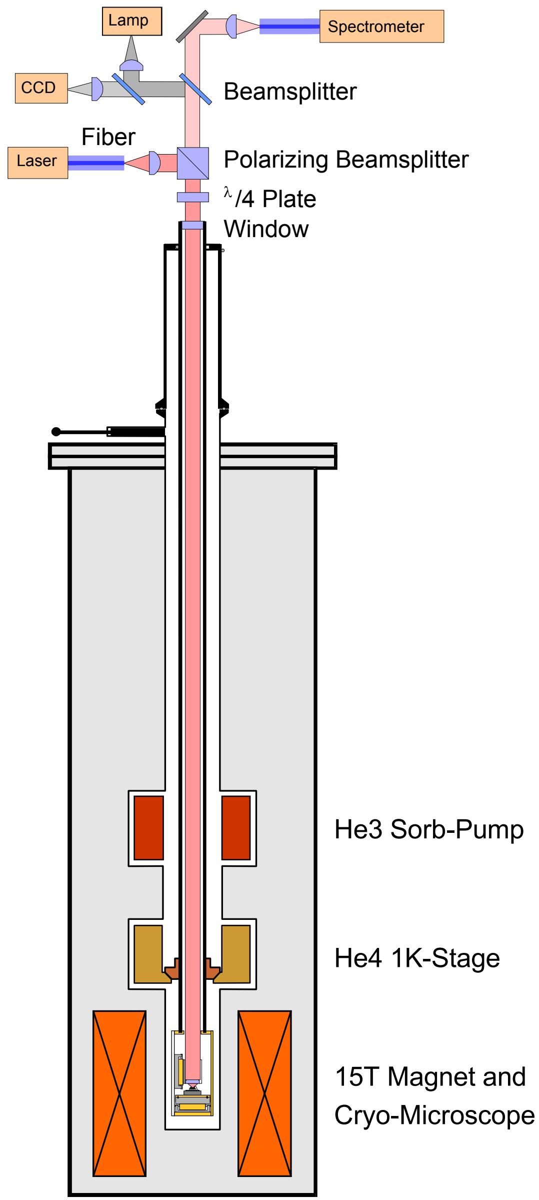


Shadowmask Apertures

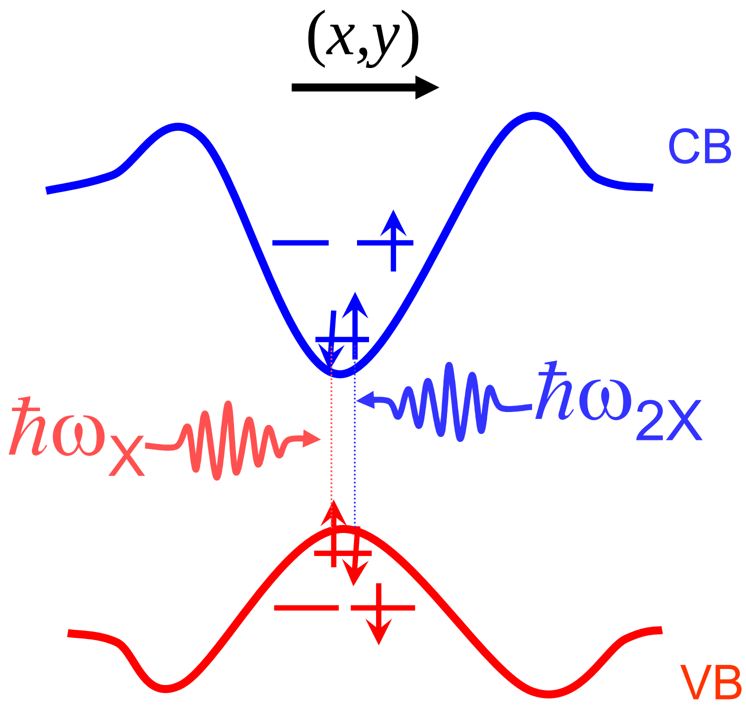
+

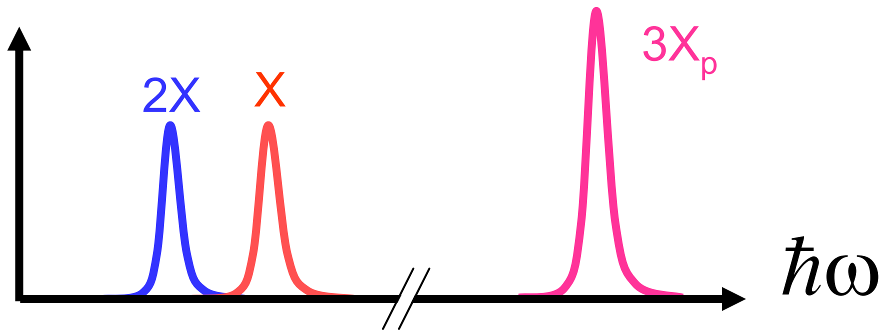


Cryogenic Microscope



Electronic Structure
Optical Nonlinearities





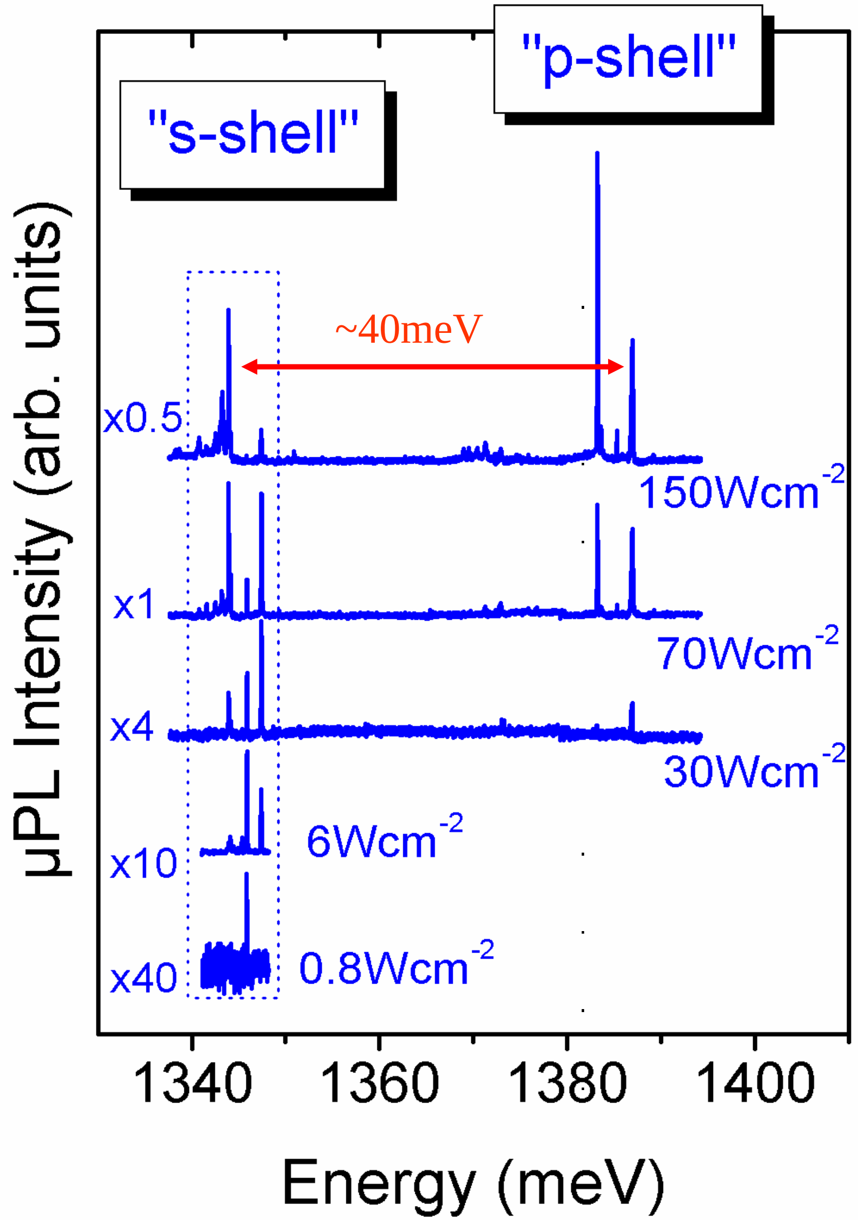
Each occupancy state (1e + 1h, 2e + 2h…) has distinct transition frequency

Application of single dots for quantum information science ?

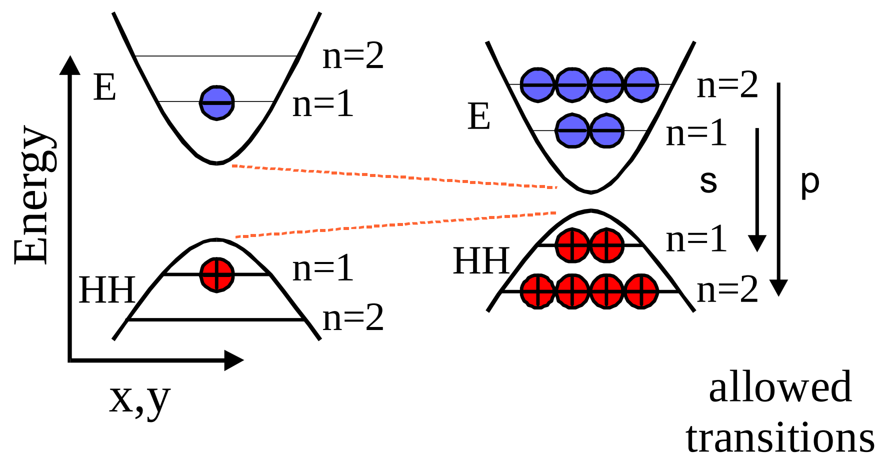
Charge and spin qubits…

Deterministic single photon sources…

Electronic Structure
Single QD Photoluminescence

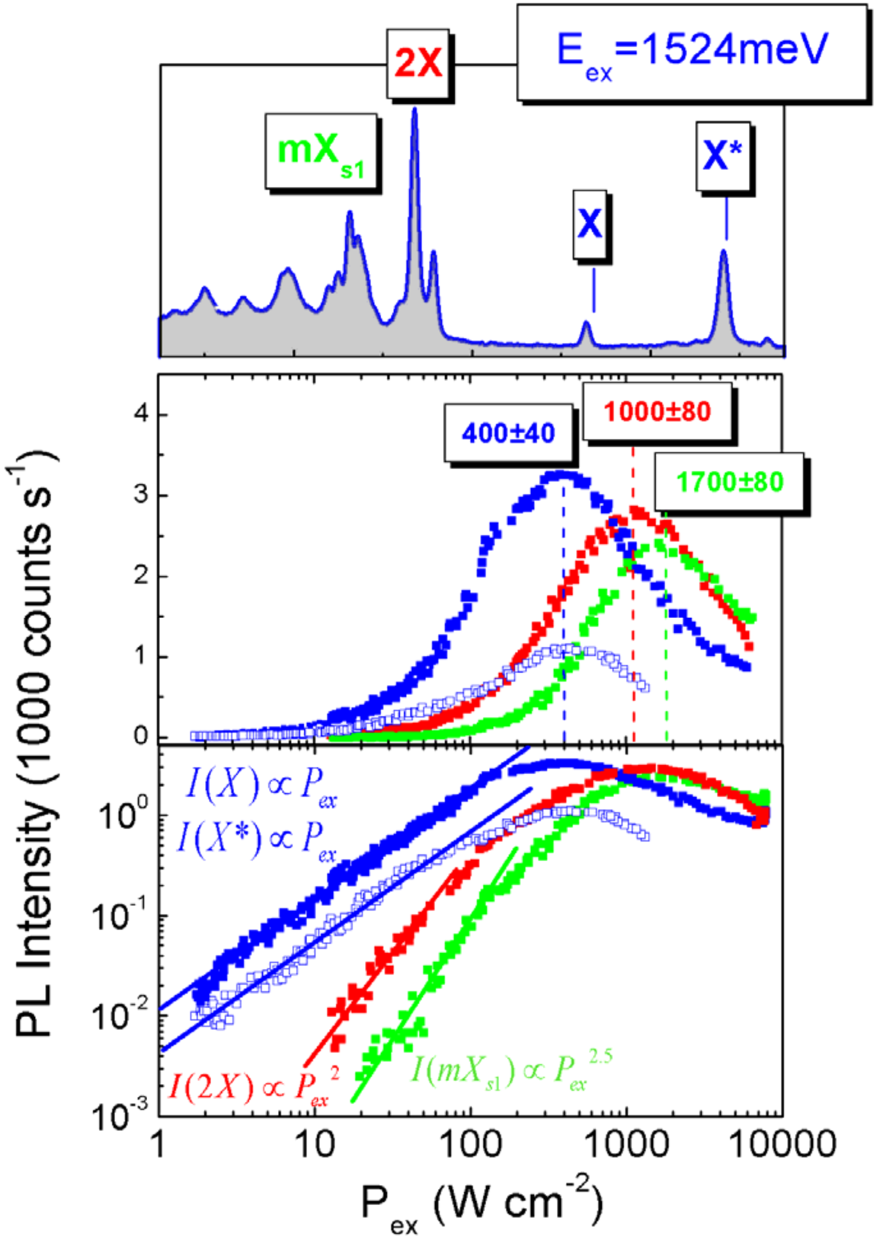


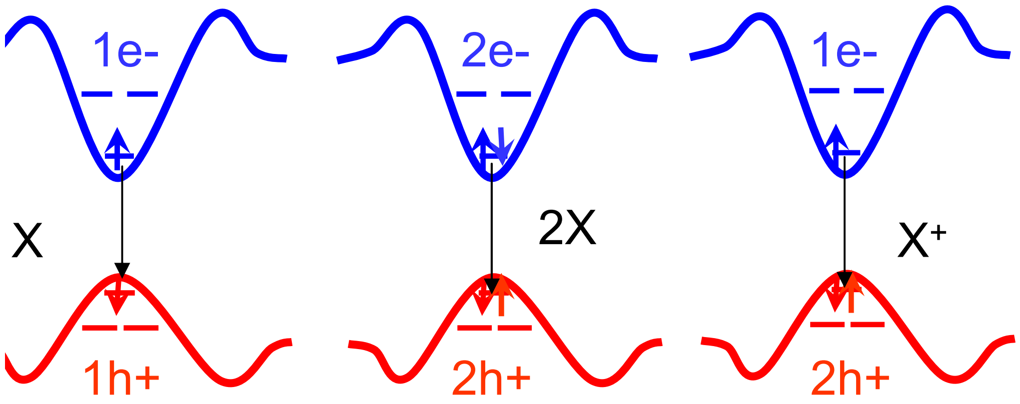
- Power controls occupancy
  - Low → Single emission line
  - High → Two groups of lines



- Two "energy scales"
  - Quantisation energy ~40meV
  - <u>Few particle interactions</u> ~meV

Electronic Structure
Identification of Occupancy States





QD occupancy states (X, 2X, 3X…)

→Identified from power characteristics

$$P(q) = \frac{N^{q} \exp(-N)}{q!}$$

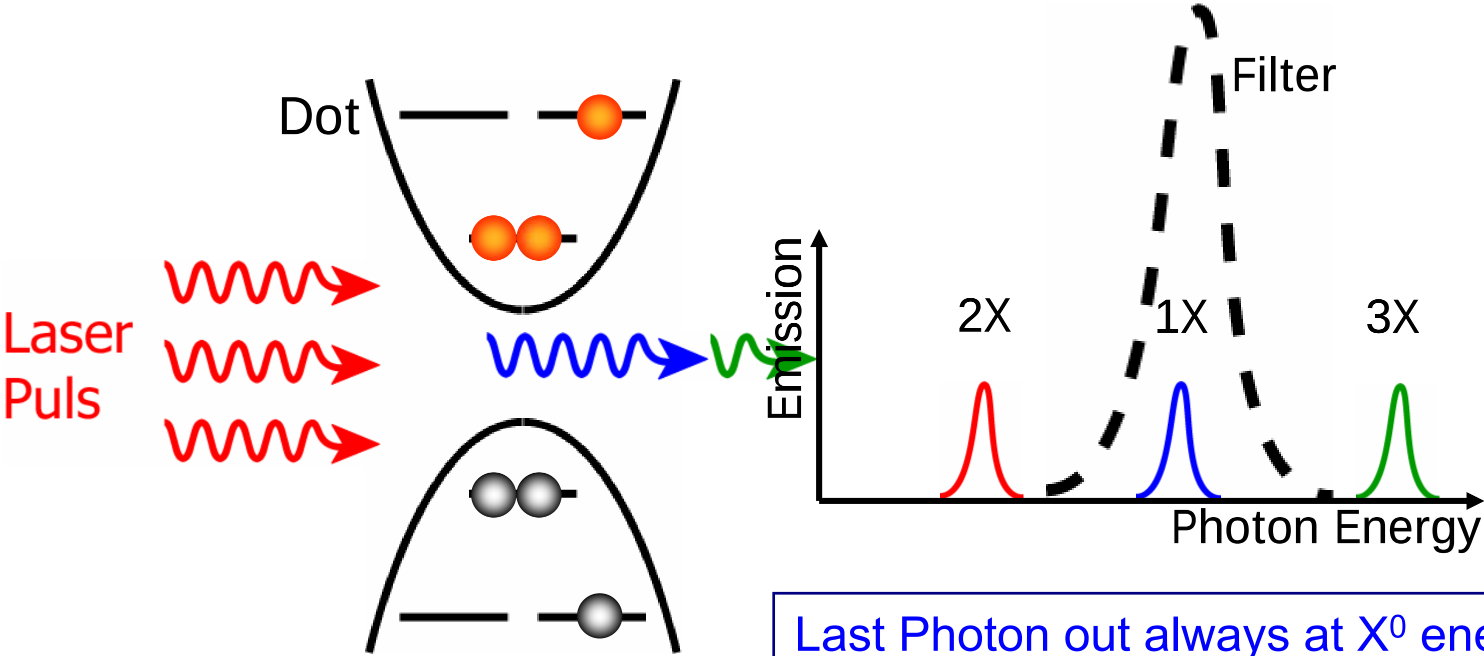
Prob. dot occupied with "q" e-h pairs

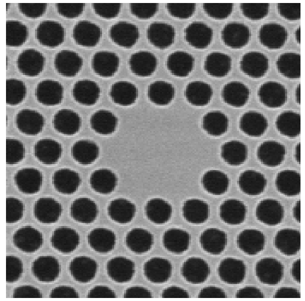
N=exciton generation rate

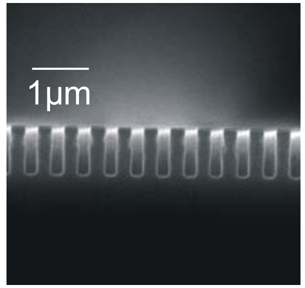
→Two "single exciton" lines (X and X*)

Electronic Structure
Single Photon Generation

- Pulsed optical excitation of a single dot







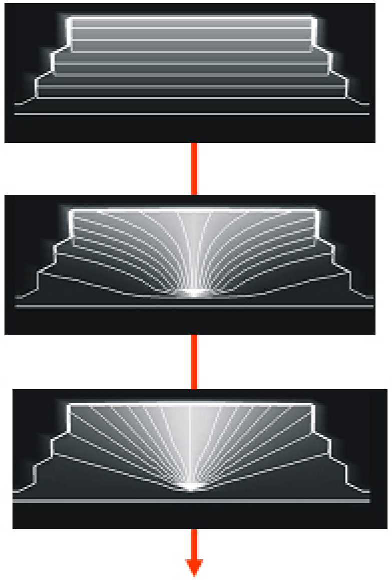
Last Photon out always at X^0 energy

- Each external laser pulse produces single photon at X0 energy

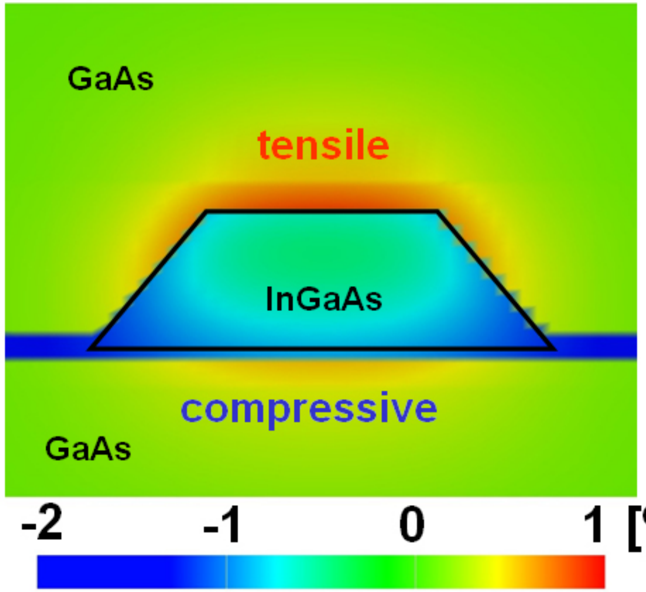
Electronic Structure
Calculate Strain

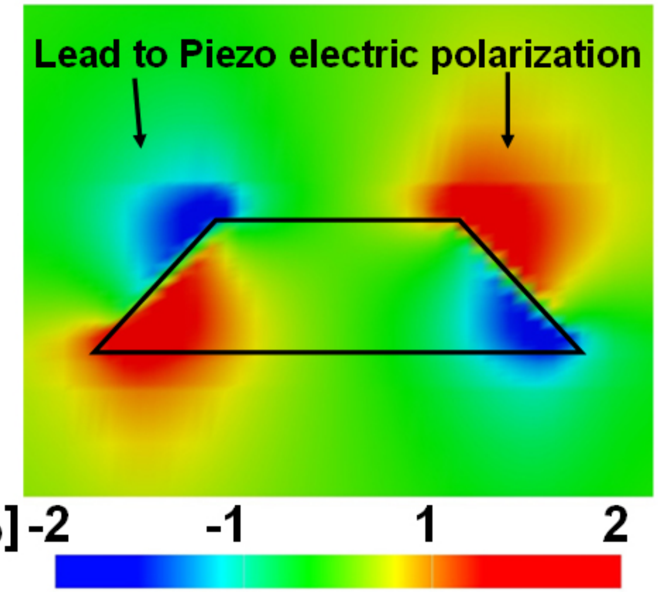
Minimization of elastic energy in continuum model.

$$E_{EL} = \frac{1}{2}\int_V C_{ijkl}\,\varepsilon_{ij}(\mathbf{r})\varepsilon_{kl}(\mathbf{r})\,dV$$



Enhanced lateral confinement



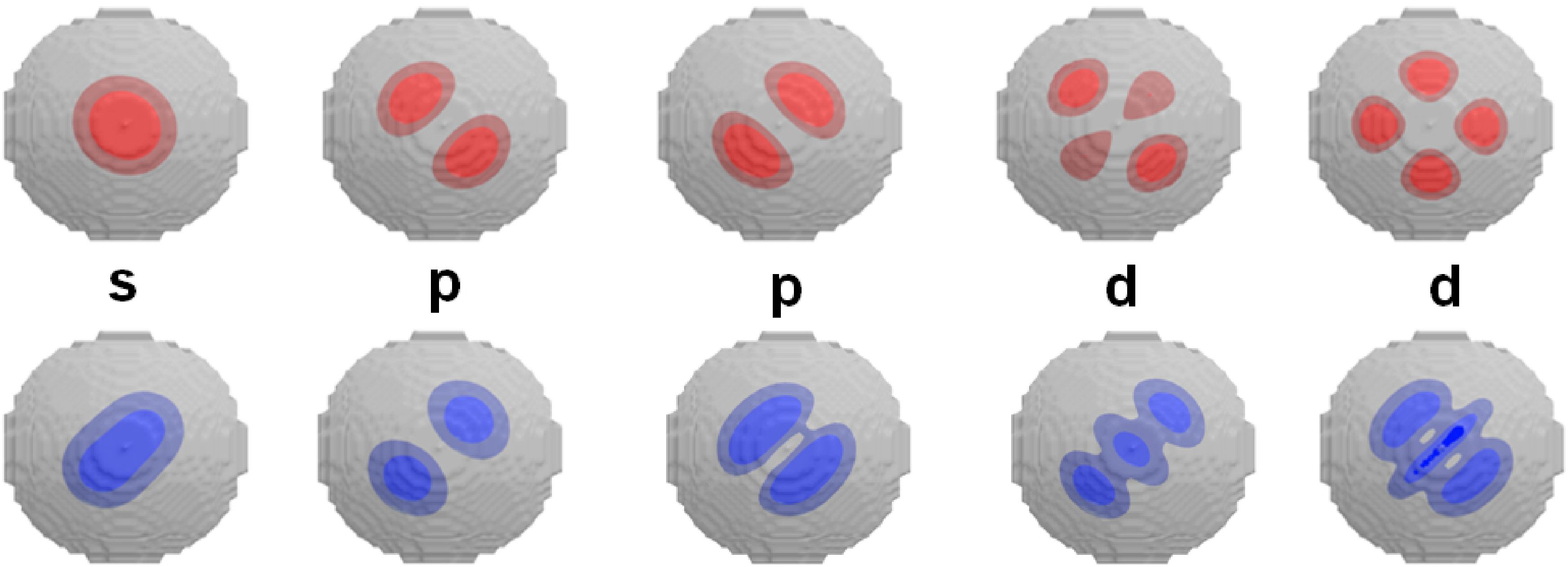


Electronic Structure
Calculate the Quantum States

Solve single- or multi-band (**k.p**) Schrödinger equation

$$\nabla \frac{1}{m_c^{*}(\mathbf{r})}\nabla\Psi(\mathbf{r}) + E_c(\mathbf{r}) - e\Phi(\mathbf{r}) = E\Psi(\mathbf{r})$$

Electron wavefunctions



Hole wavefunctions

Self Assembling QDs Conclusions

Nanoscale islands form during strain driven self-assembly

- Formation is driven by thermodynamic forces
- Size of islands is self-limiting – 10-100nm range
- Realised in many materials systems
  - (e.g. InAs on (Al)GaAs, Ge on Si, InAs on InP…)
- Already incorporated into many optoelectronic devices
  - Lasers, LEDs, Detectors, Non-Classical Light emitters, Hardware for quantum computation

Self Assembling QDs
Conclusions

Advantages

- Large confinement energies (>60meV)
- High crystal (optical) quality
- High areal density (10^{10}-10^{11}cm^{-2})
- Weak coupling to their environment
- Multiple layers of dots can be readily fabricated

Disadvantages

- Homogeneity - size, shape and morphology fluctuations

Acknowledgement

- Jon Finley
- Dimitri Kovalev
- Martin Stutzmann
- Andreas Kress, Felix Hofbauer, Michael Kaniber
- WSI (E24)

- References: Please ask for special topics.