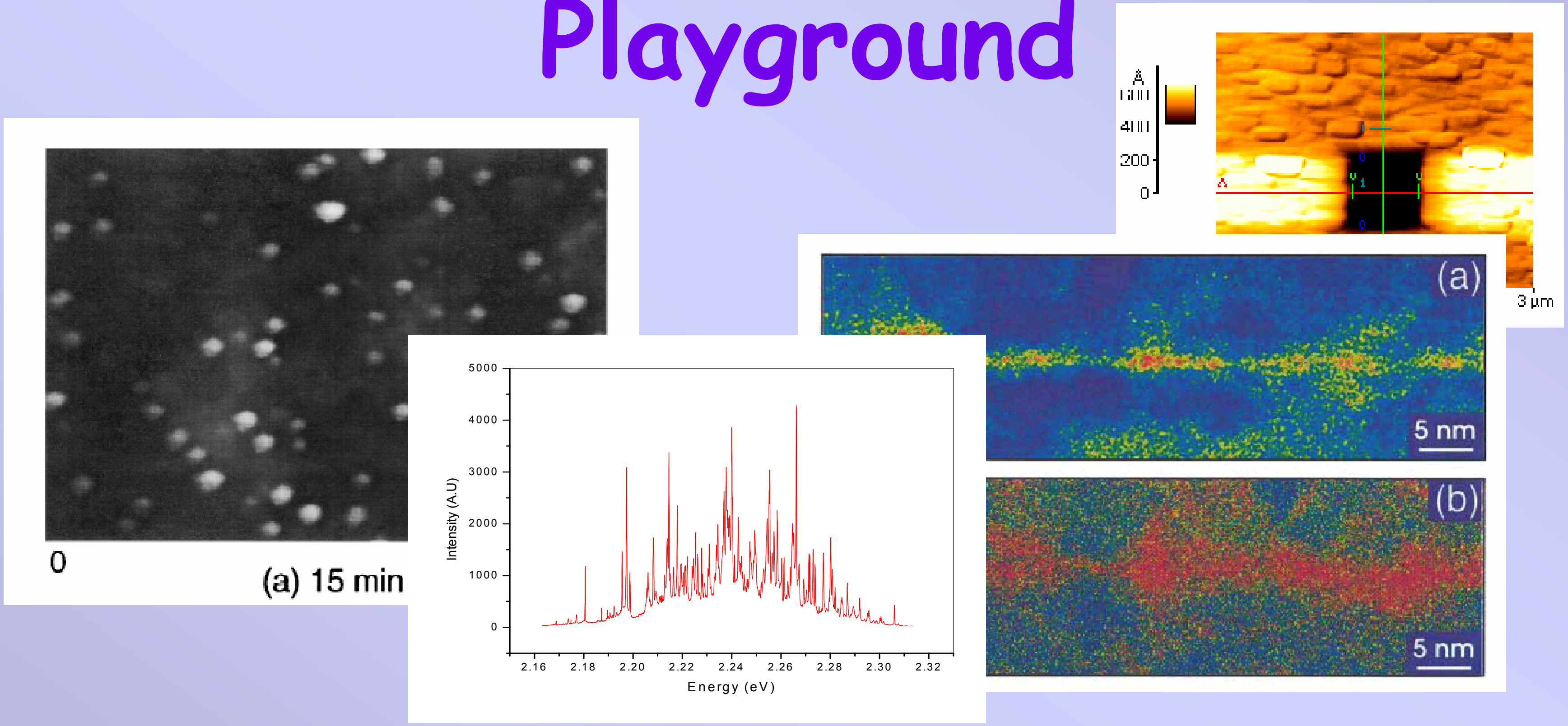
Quantum Dots: A Physicist's (& Chemist's) Playground



Jan Yarrison-Rice, Physics Dept.
Miami University

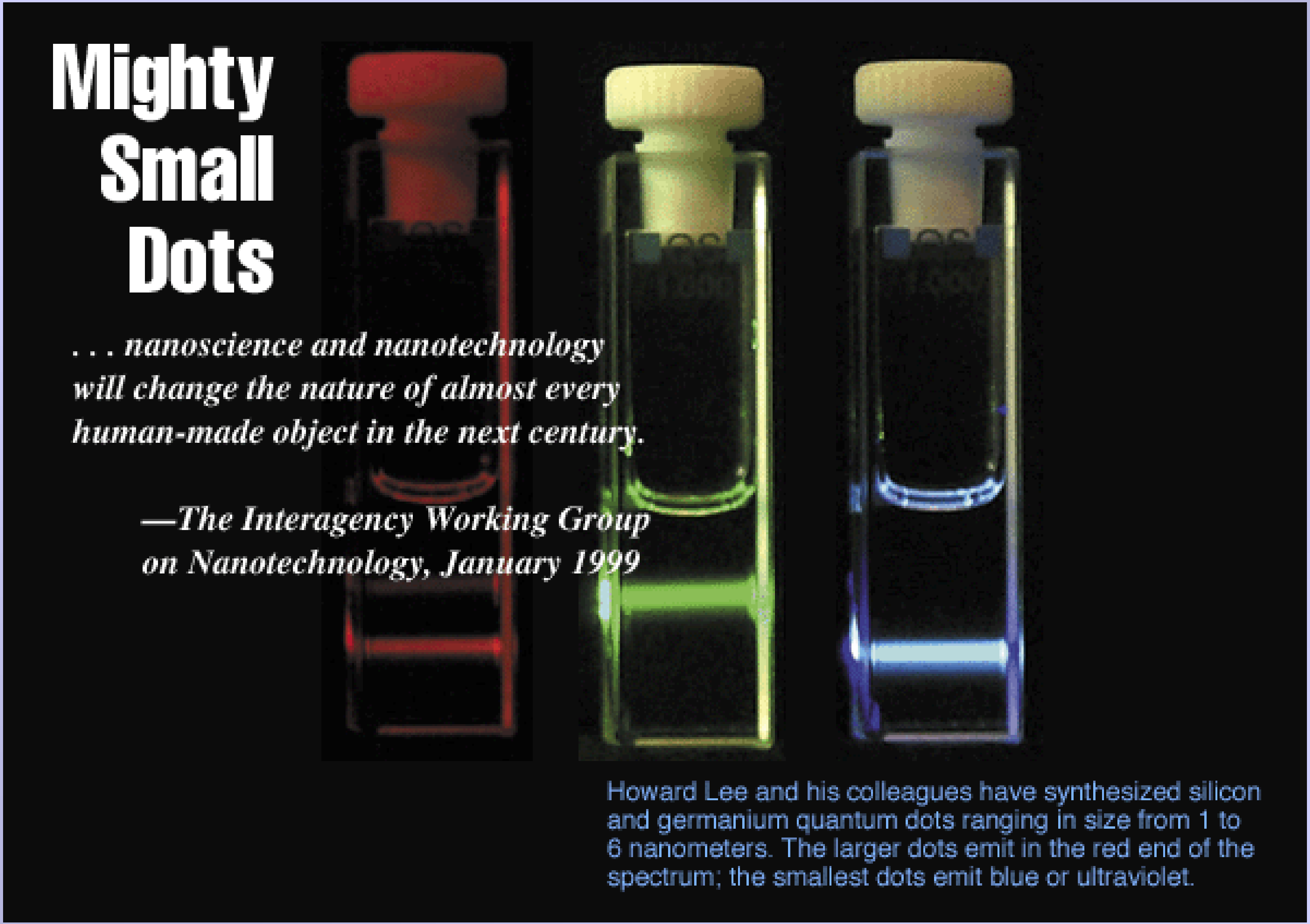
Thanks to Colleagues at University of Cincinnati:

Graduate Students	Faculty
Bob Jones	Leigh Smith
Aditi Sharma	Howard Jackson
Laurie Robinson	

Thanks to Colleagues at Notre Dame:

Jacek Furdyna
Margaret Dobrowalska

Thanks to NSF and DOE for their support



Mighty Small Dots

> *. . . nanoscience and nanotechnology will change the nature of almost every human-made object in the next century.*
>
> *—The Interagency Working Group on Nanotechnology, January 1999*

Howard Lee and his colleagues have synthesized silicon and germanium quantum dots ranging in size from 1 to 6 nanometers. The larger dots emit in the red end of the spectrum; the smallest dots emit blue or ultraviolet.

Lawrence Livermore Lab

Quantum Dots - A Playground?

- Fundamental Science on a Nanoscale
  - Self-assembled quantum dots (SAQDs)

  - Chemically prepared (Spherical QDs)

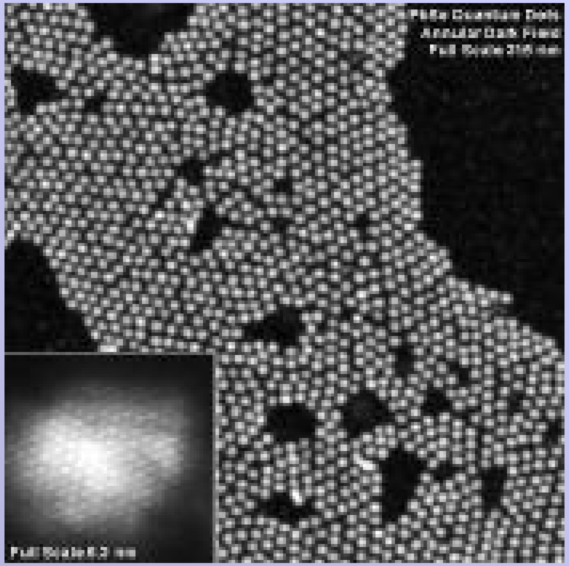
- Applied Science
  - QD LEDs and Lasers

  - QD sensors

"Nanotechnology has given us the tools...to play with the ultimate toy box of nature -- atoms and molecules. Everything is made from it...The possibilities to create new things appear limitless..."

Horst Stormer, Nobel Laureate
Columbia University
Lucent Technologies

QDs come in all shapes and sizes!



www.aep.cornell.edu/ gif/QdotsPbSe.jpg

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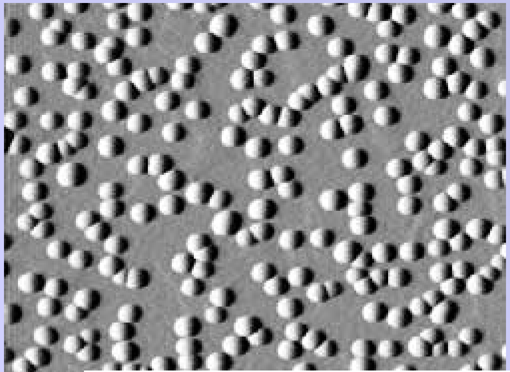
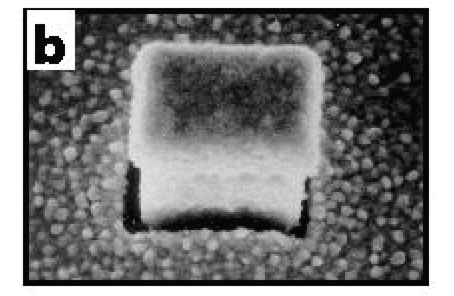
Top.quant.dot.htm





qt.tn.tudelft.nl/news/
NN6fig1b.gif

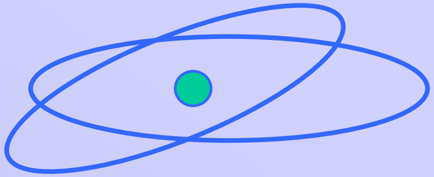
Why Study Semiconductor Quantum Dots?

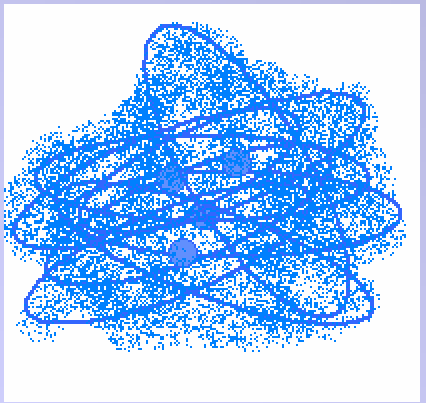
- To understand the physics of quantum confinement

- Is there anything *atomic* about “artificial atoms” in a solid?

- Potentials for technology applications

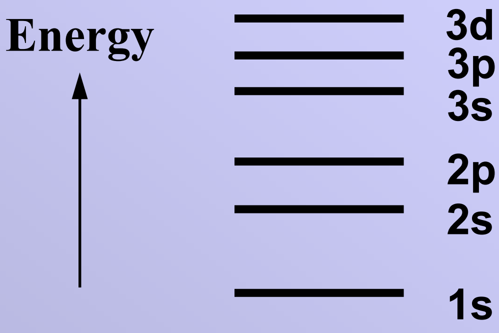
From atomic levels to bands…

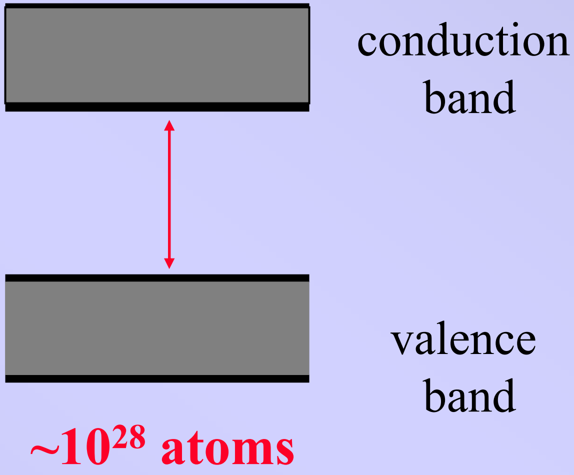




Discrete "atomic" Levels

Smeared energy bands





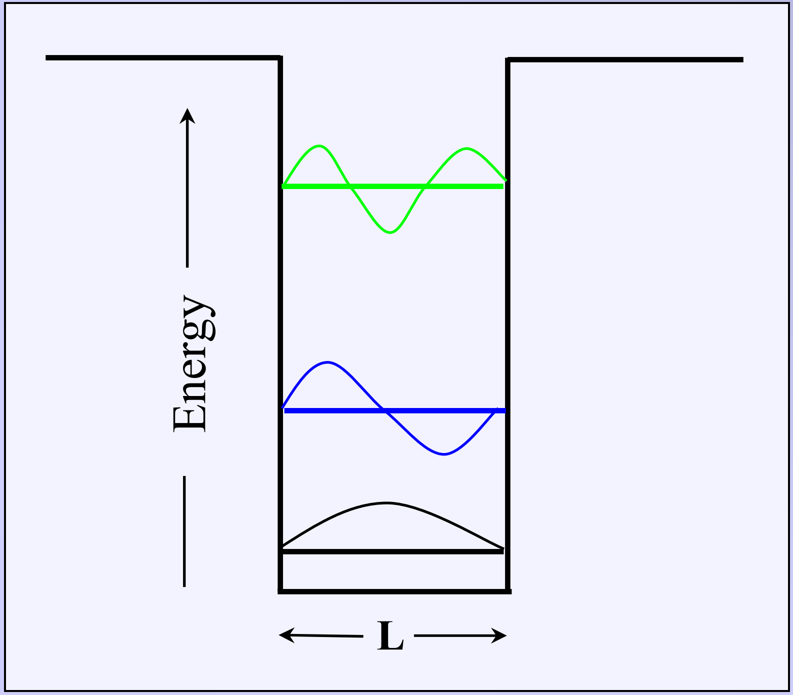
And back again…. .

Artificial atoms (a.k.a. quantum dots!)
the "particle in a box"

- Quantum Mechanics requires that particles have wave properties

- An electron confined to a box has allowed frequencies

- We can solve a wave equation, called the Schrodinger equation, for particle-waves

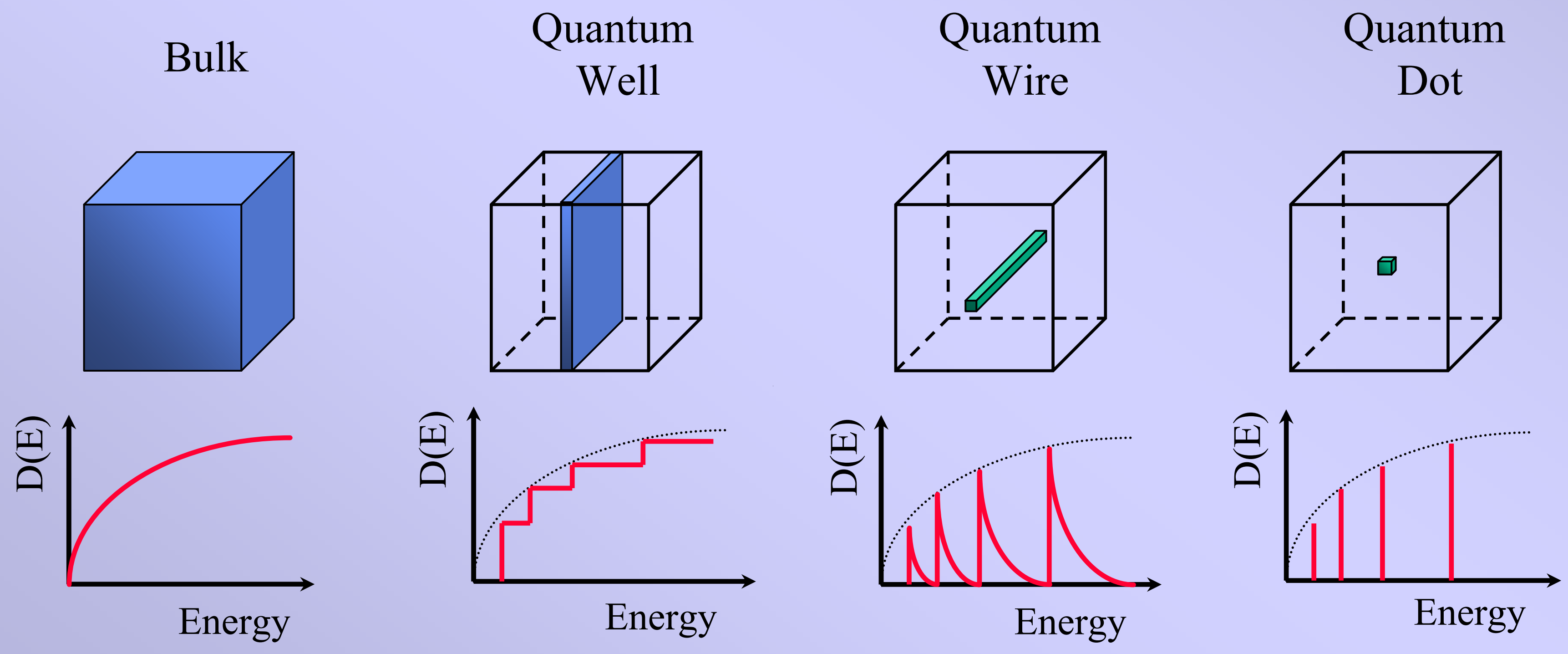


$$\frac{d^2\Psi}{dx^2}+\left(\frac{2mE}{\hbar^2}-V\right)\Psi=0$$

$$E_n=\frac{\hbar^2(\pi n)^2}{2mL^2}$$

Reduced Dimensionality

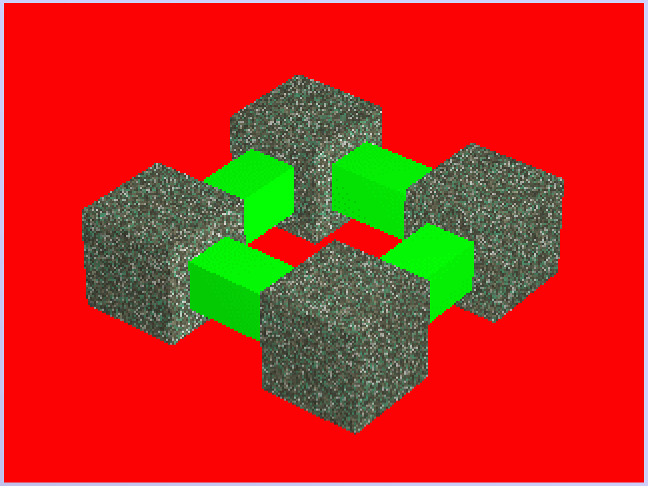
- Confining a carrier in at least one spatial dimension at scale of the order of de Broglie wavelength leads to quantum size effects

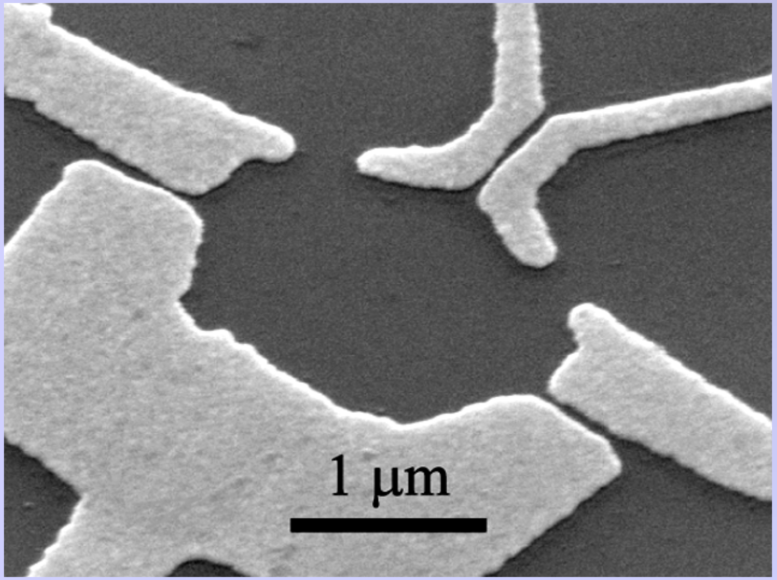


Electronic density of states in different structures

QD Fabrication Techniques

- Photolithographic Fabrication of QDs


McMaster University



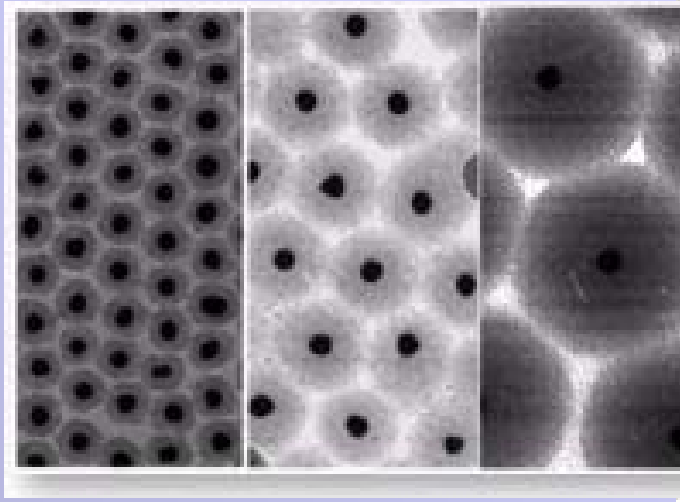
University of Stuttgart

- Chemical Synthesis of QDs
- Molecular Beam Epitaxial Growth of QDs

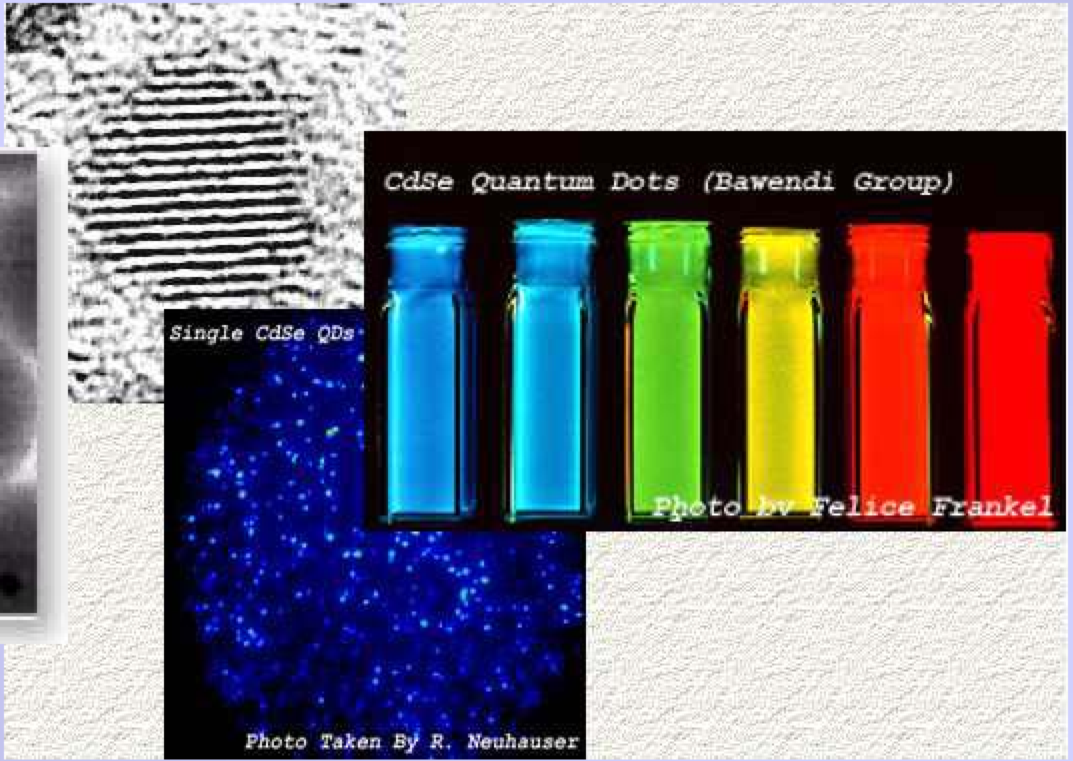
Chemical Synthesis of QDs

- Pyrolysis of organometallic precursors in a coordinating solvent
- Size-selected by precipitation
- Result in 5% monodispersed spherical 23-100 Å QDs

(oblateness 1.1-1.3)

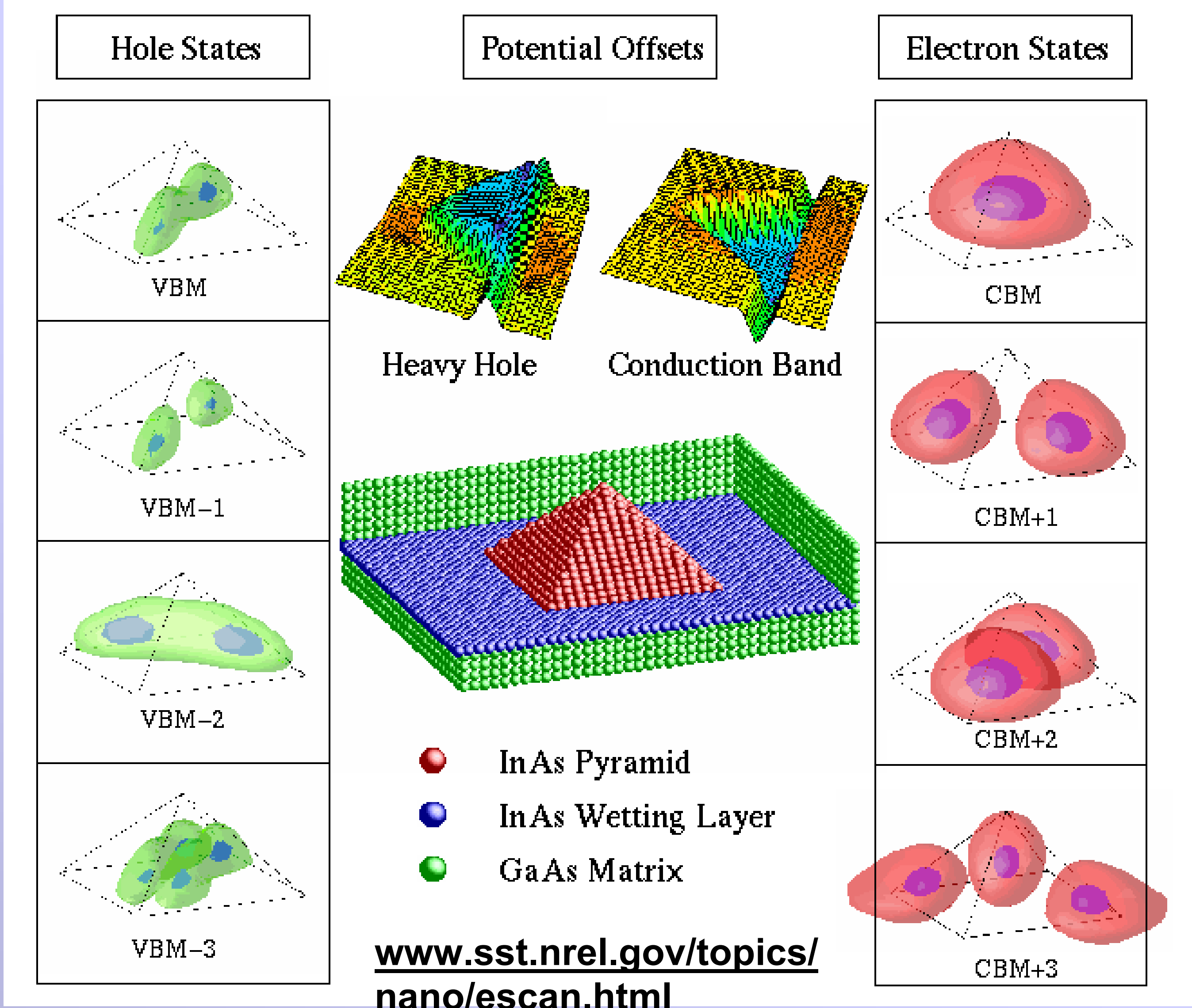


The University of Melbourne



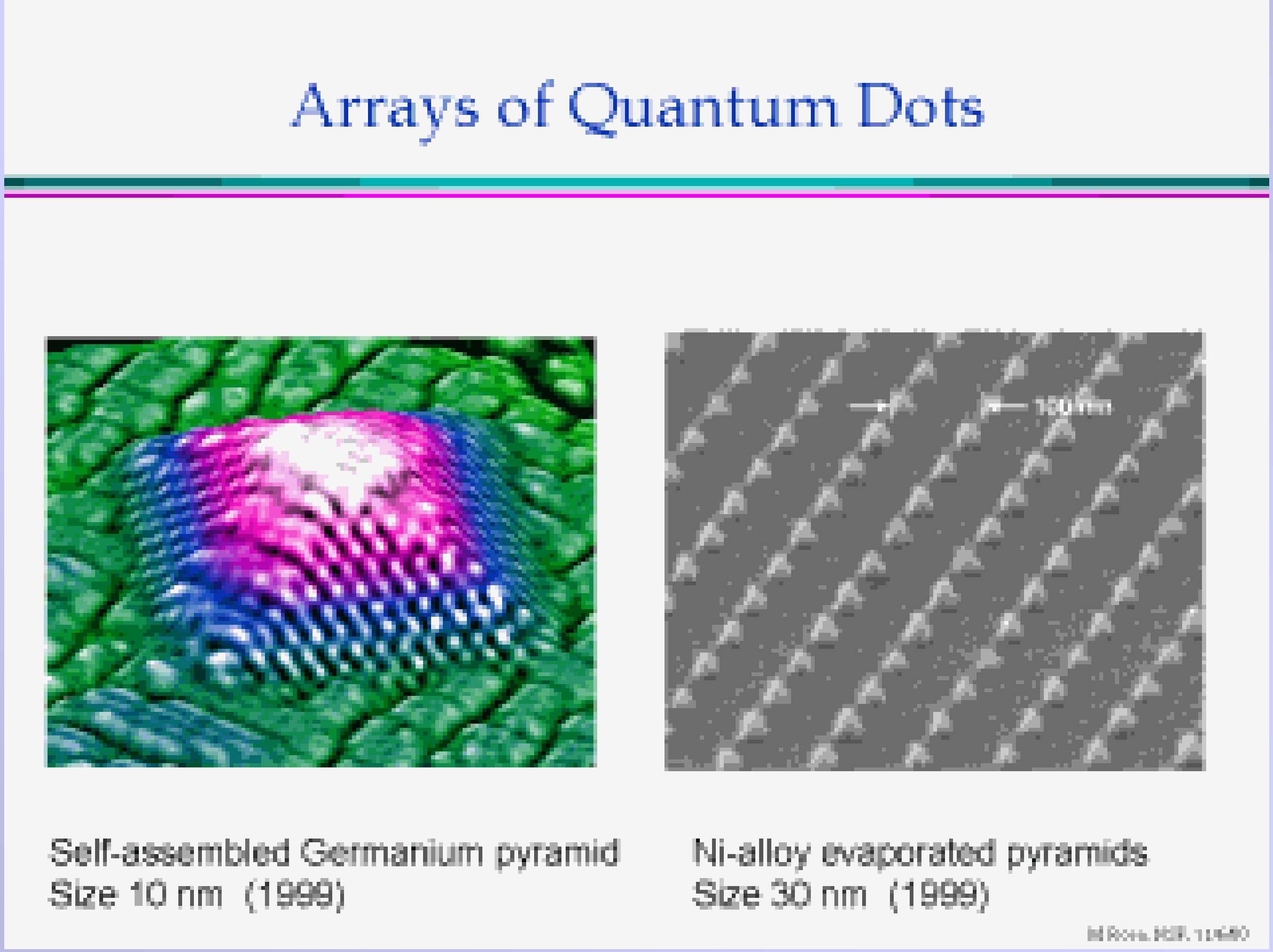
Bawendi, MIT

Growth of III-V QDs



www.sst.nrel.gov/topics/nano/escan.html

Some QD Pyramids

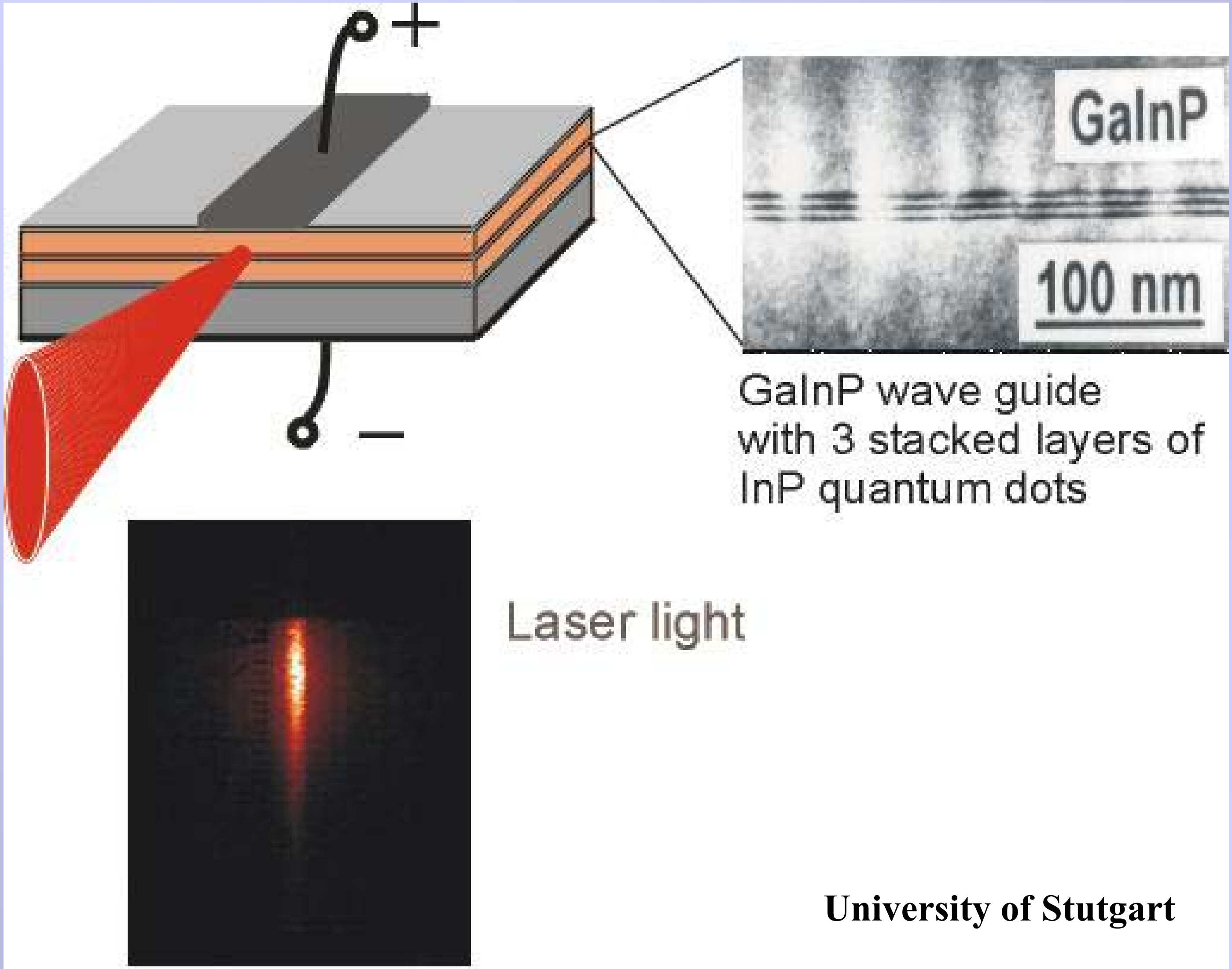


Arrays of Quantum Dots

Self-assembled Germanium pyramid
Size 10 nm (1999)

Ni-alloy evaporated pyramids
Size 30 nm (1999)

InP QD Laser

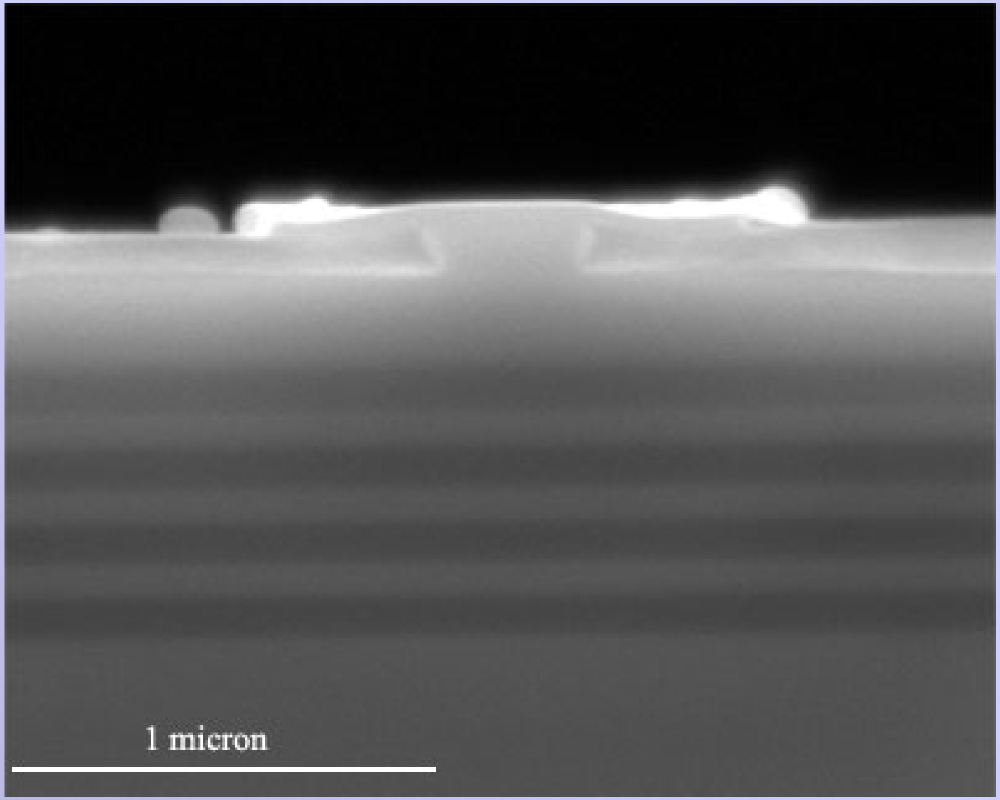


GaInP wave guide with 3 stacked layers of InP quantum dots

Laser light

University of Stutgart

InAs QD LEDs

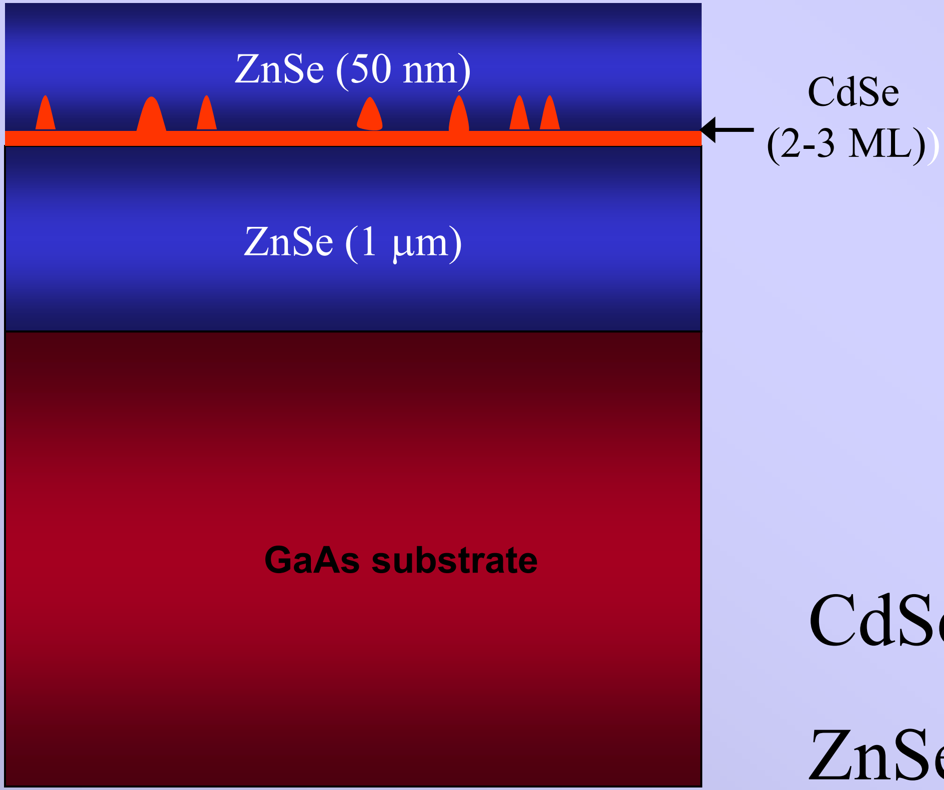


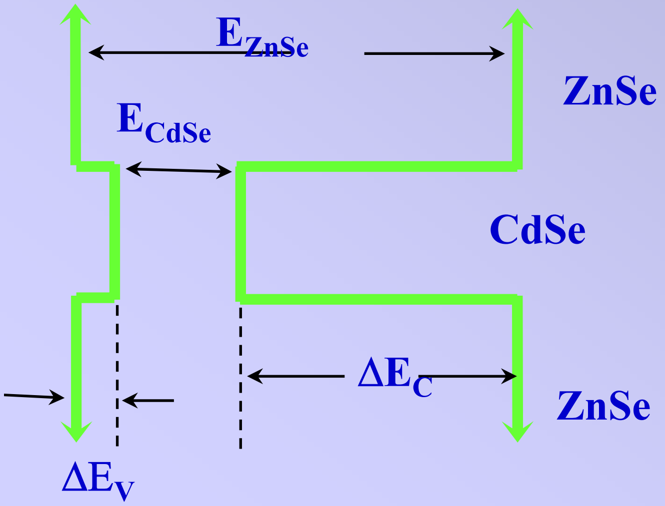
Source: Swiss Federal Institute of Technology at Lausanne

Description: This electron microscope image shows a side view of a light-emitting diode that is just one tenth the size of a red blood cell

25 nm x 7 nm QDs

Molecular Beam Epitaxy Growth of CdSe on ZnSe (SAQDs)





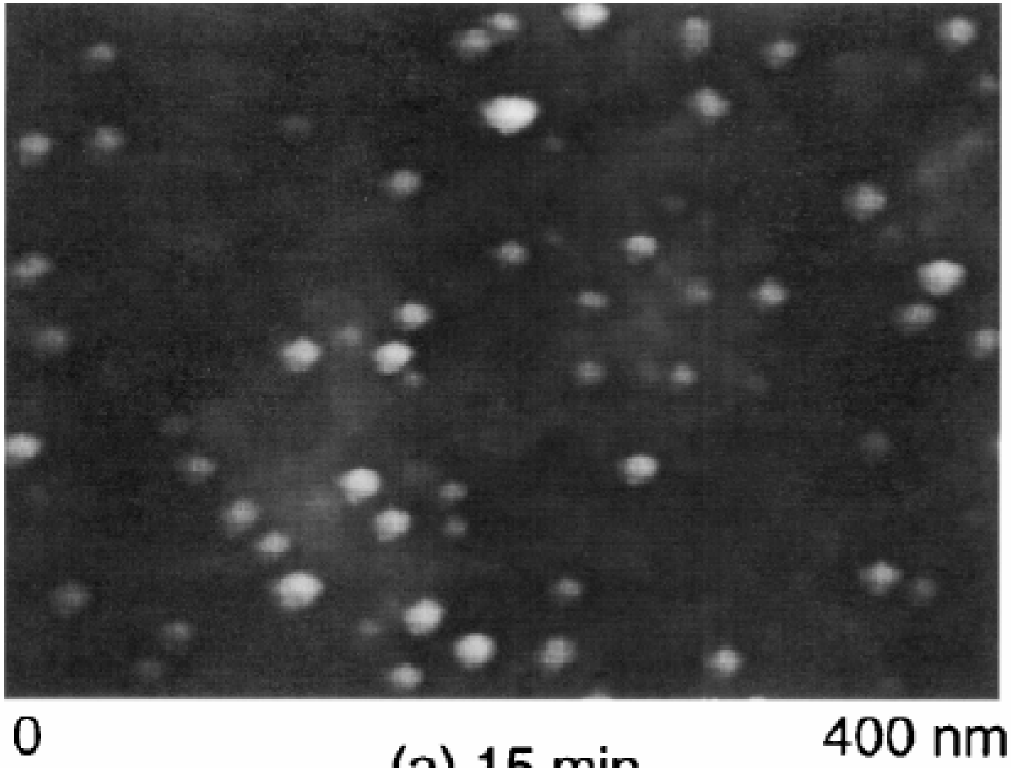
CdSe E_{Gap} = 1.84 eV (2 K)

ZnSe E_{Gap} = 2.82 eV (2 K)

7% lattice mismatch between CdSe & ZnSe

AFM Image of QDs before Cap

- 10-30 nm diameter
- 2-4 nm high
- 700 QDs μm^{-2}

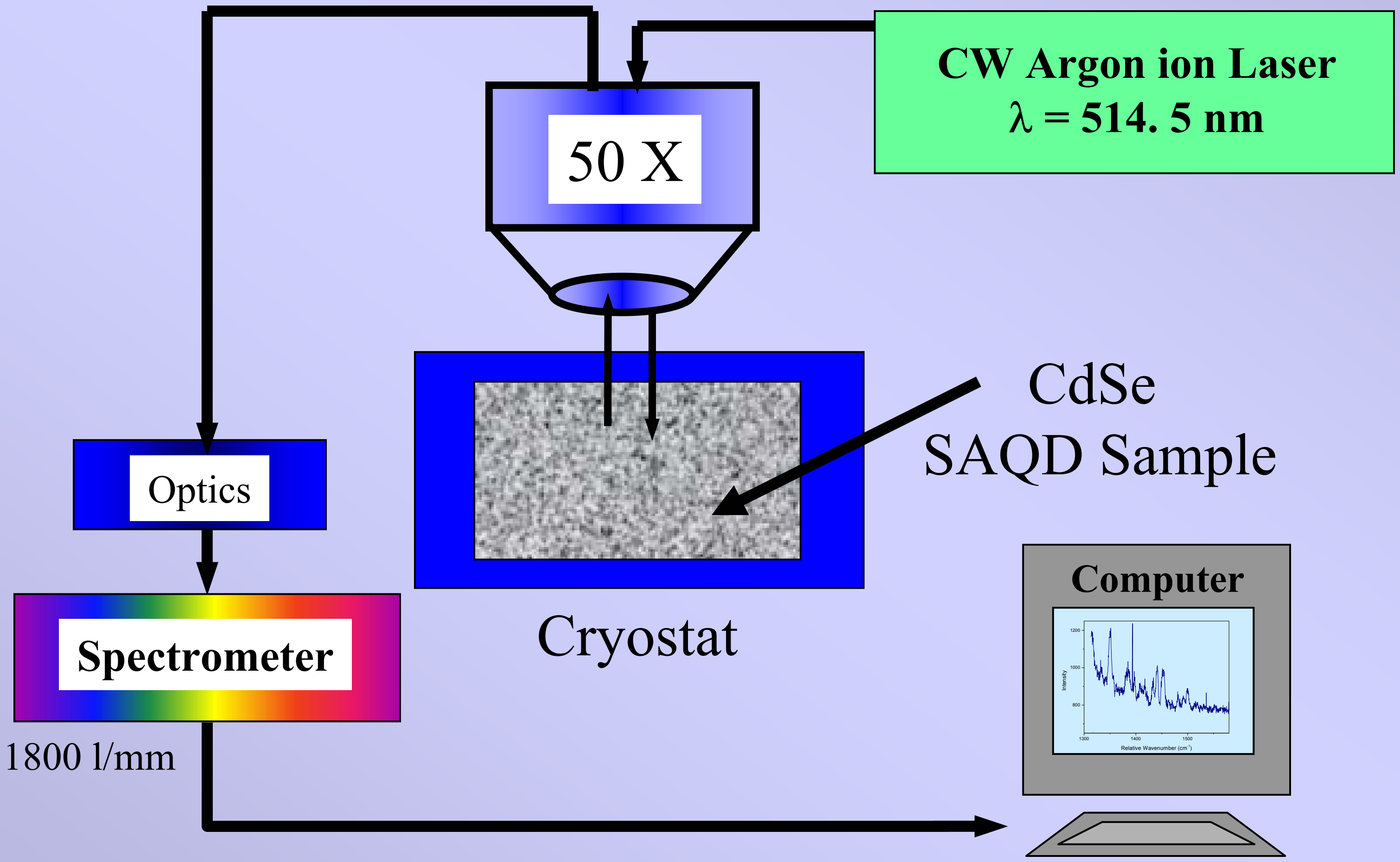


(a) 15 min

Now that we have made QDs, How do we probe these structures?

- Optically via Photoluminescence
  - Non-destructive

Photoluminescence Set-Up



CW Argon ion Laser
λ = 514. 5 nm

50 X

CdSe
SAQD Sample

Optics

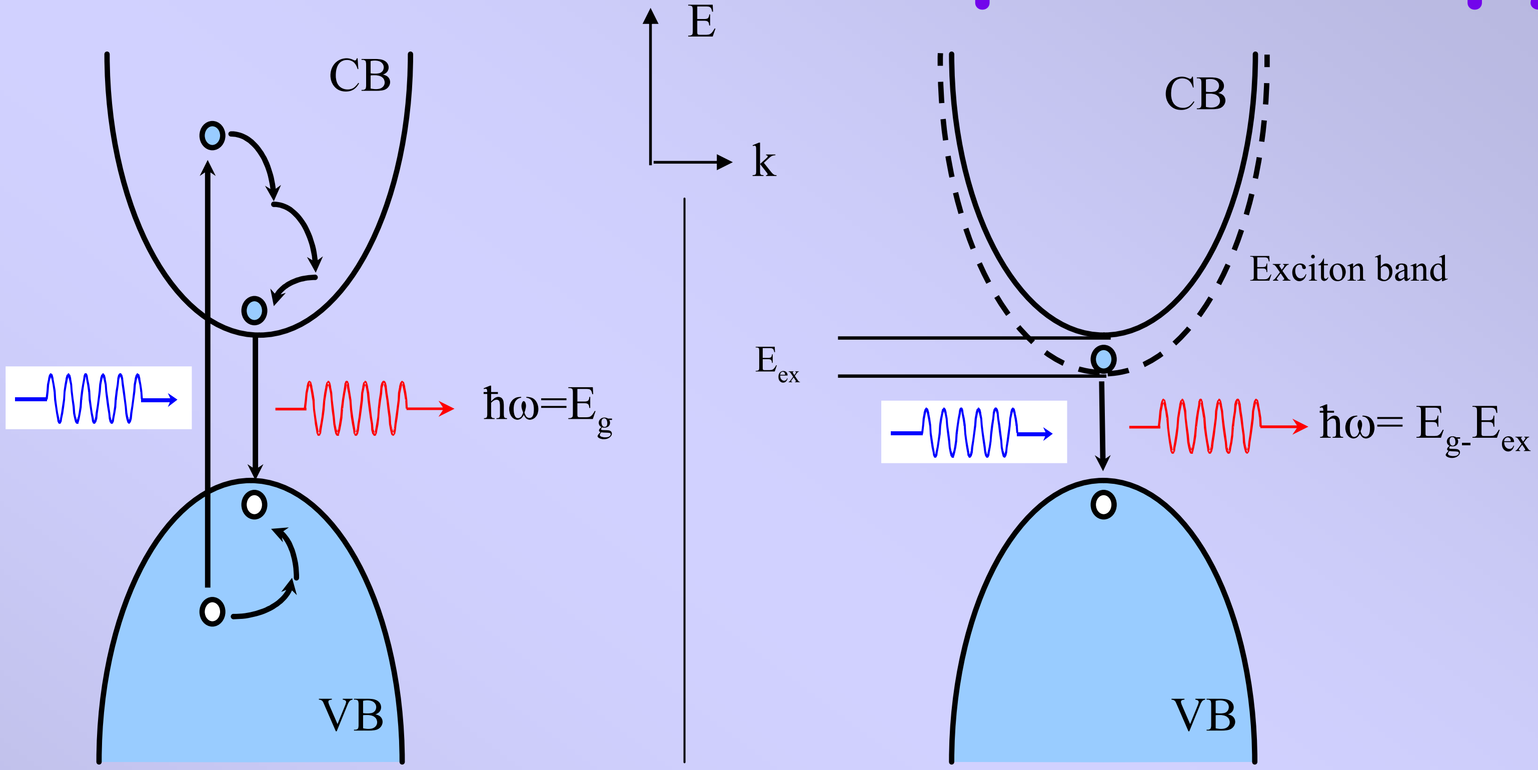
Cryostat

Spectrometer

1800 l/mm

Computer

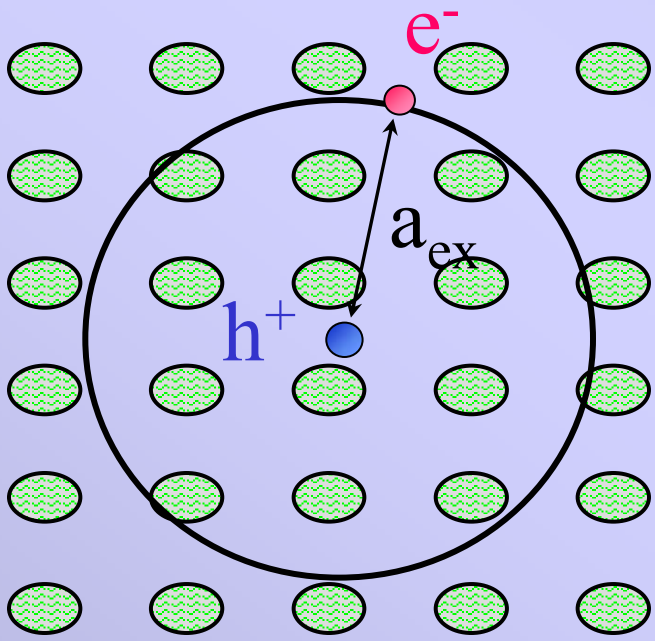
Photoluminescence Spectroscopy



- A laser excites electrons from the valence band into the conduction band, creating *electron-hole pairs.*
- These electrons and holes recombine and emit a photon.
- We measure the number of emitted photons (intensity) as a function of energy.

Excitons:

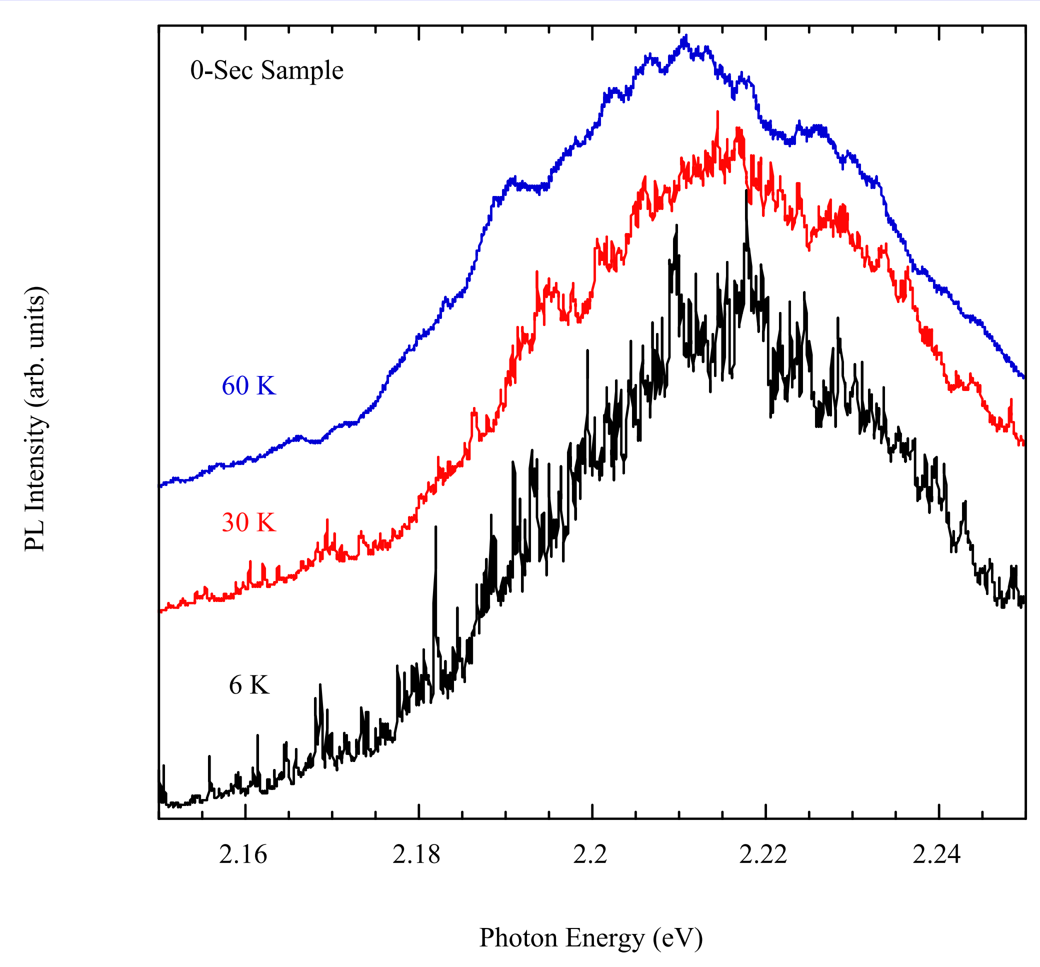
Hydrogen-like bound state of an electron and hole.



- Screened Coulomb attraction
- Small Binding energy
- Large Bohr radius

Material	m_e^*	m_h^*	m_{ex}^*	ε	a_{ex}	E_{ex}
ZnSe	$0.16\ m_0$	$0.78\ m_0$	$0.13\ m_0$	9	37 Å	15 meV
CdSe	$0.13\ m_0$	$0.9\ m_0$	$0.11\ m_0$	10	**48 Å**	**22 meV**

Temperature Dependent Micro-Photoluminescence

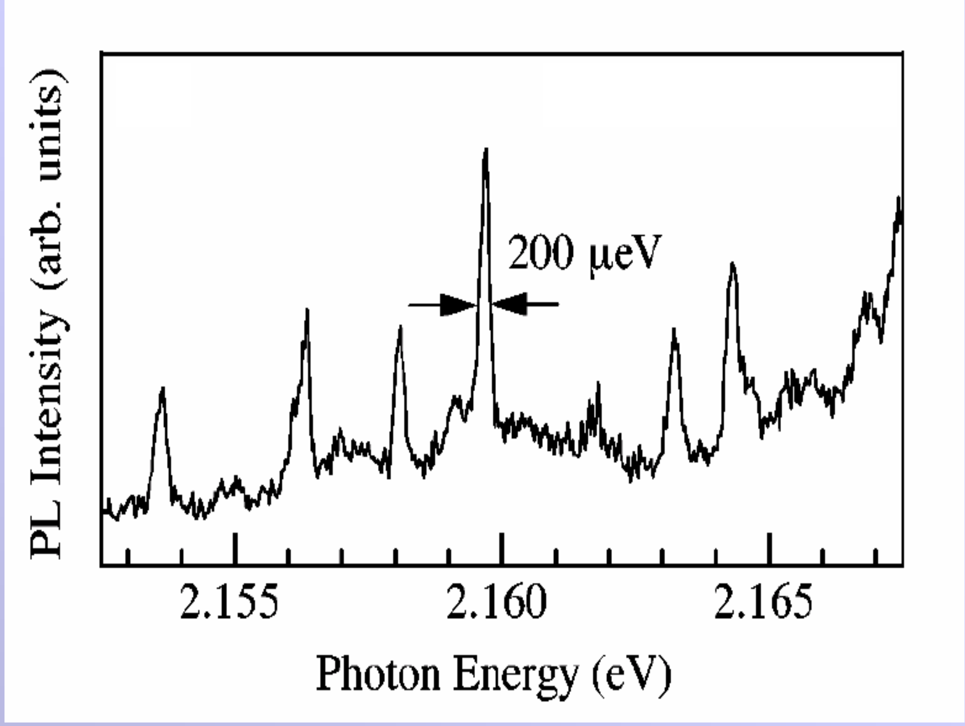


Broad peak remains strong at 60 K

Sharp peaks disappear at once

i.e. an ensemble behavior is observed over ~ 70 meV

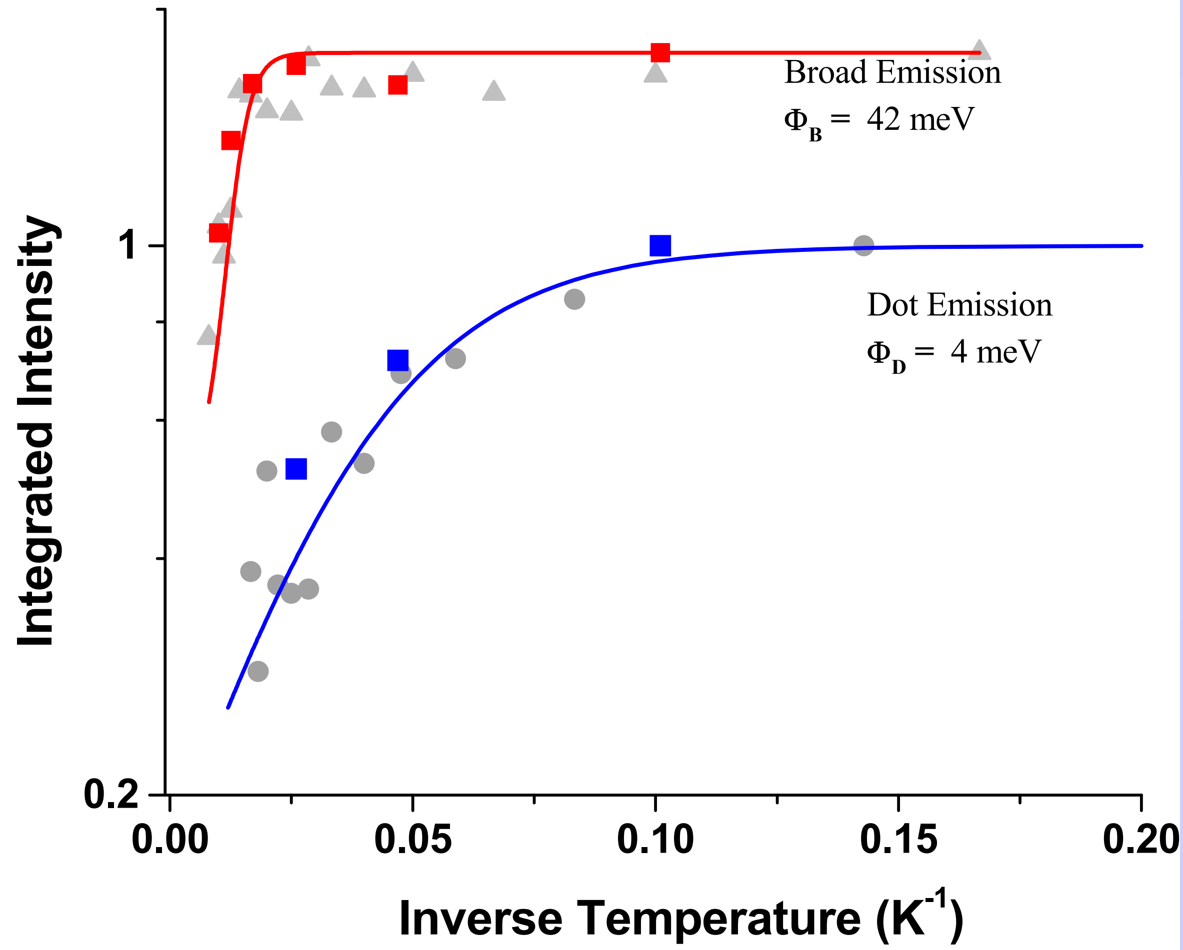
Expanded PL Spectra



- Individual delta-like peaks corresponding to single QD emission
- Recall “particle in a box”

Sharp vs. Broad Features

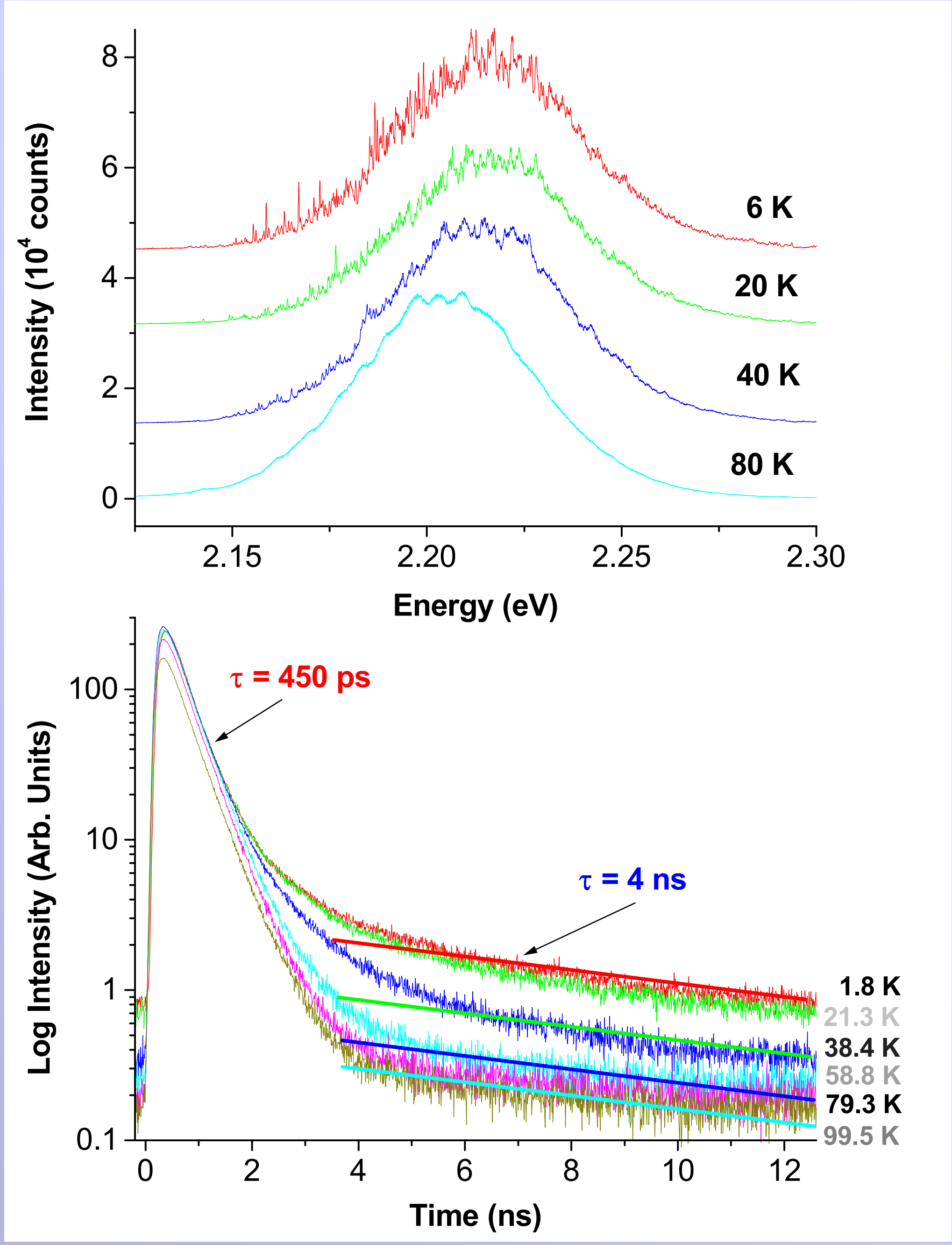
$$I(T) = I_o[1 + C \exp\{-\phi/kT\}]^{-1}$$



- Temperature dependence of two components is the same under both cw and pulsed excitation.

- What are the lifetime associated with these two different activation energies?

Exciton Decays vs Temperature



- Evidence for two states is also seen in the PL decay-times

- Broad PL → short lifetime

- Narrow PL → long lifetime

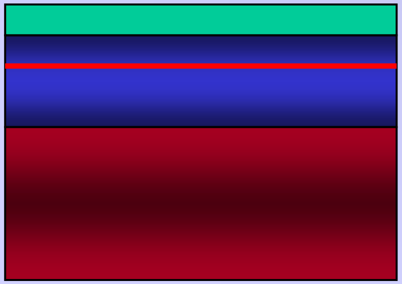
Can we isolate the QDs & then do PL?

- **Micro-PL** – already accomplished with microscope objective - 0.7 micron spotsize

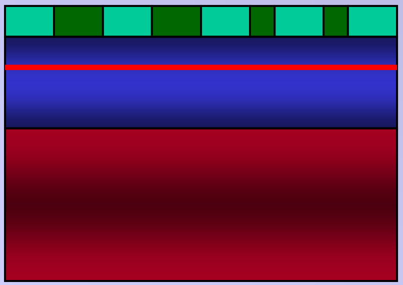
- **Nano-PL** – accomplished with apertures etched into an overlayer – 5 micron per side to 0.07 micron per side

Fabrication of Nano-Apertures

(1) CdSe/ZnSe sample

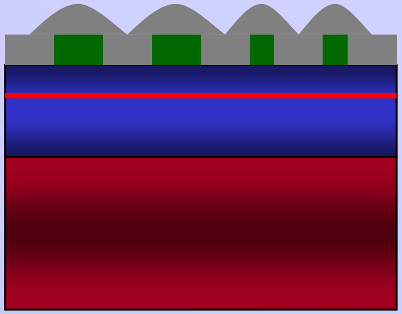


(2) Resist

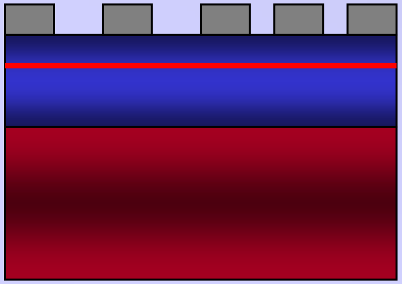


(3) E-beam writing

(4) Development of exposed resist

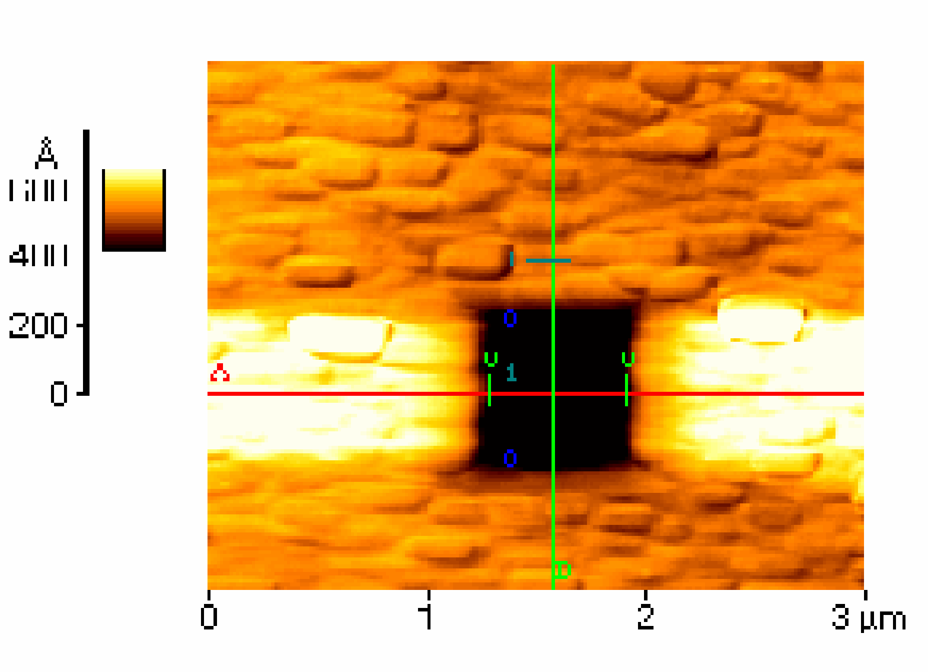


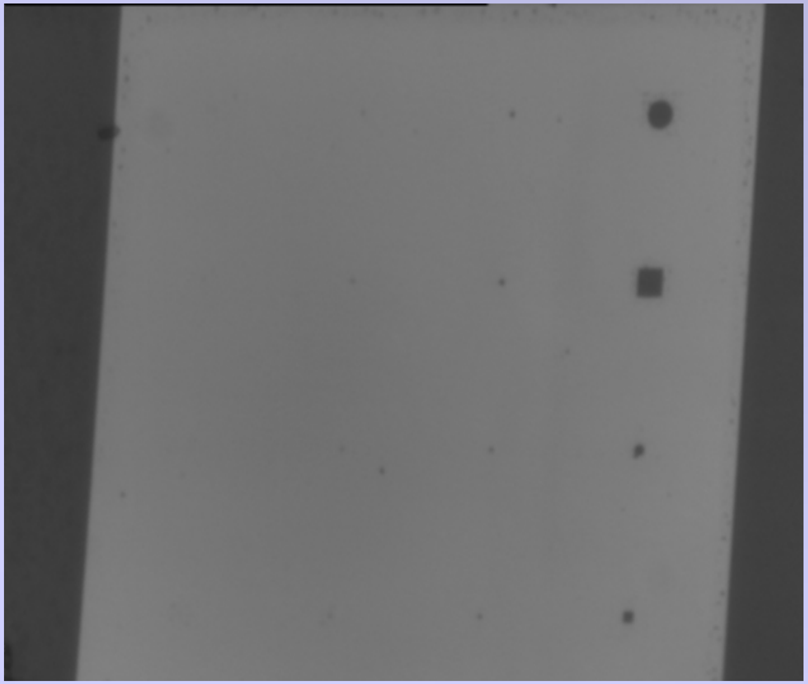
(5) Electron beam evaporation deposition



(6) Lift off

Nano-Aperture Profile



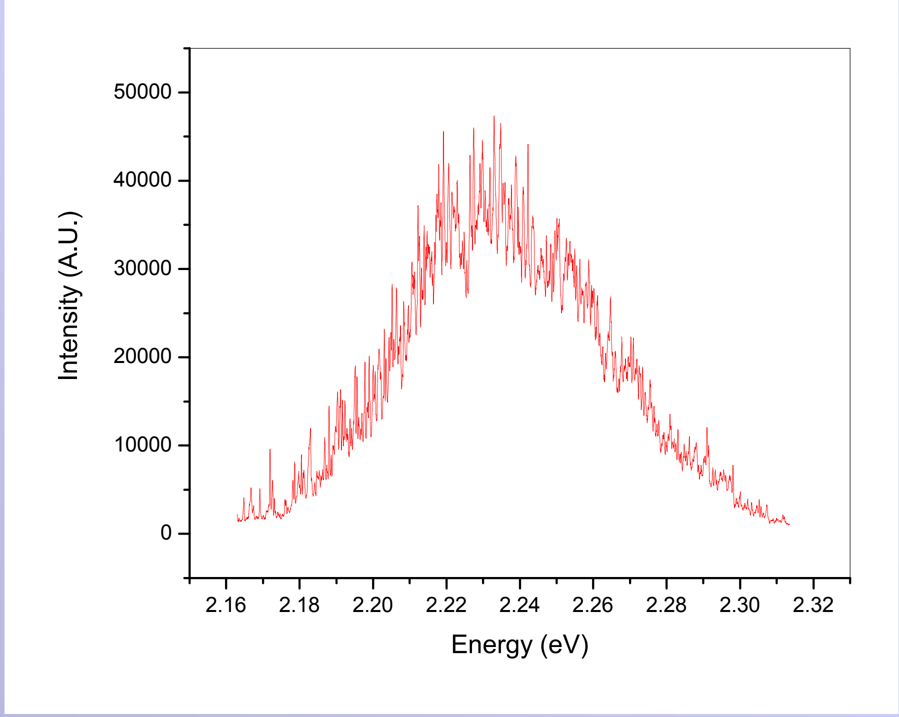


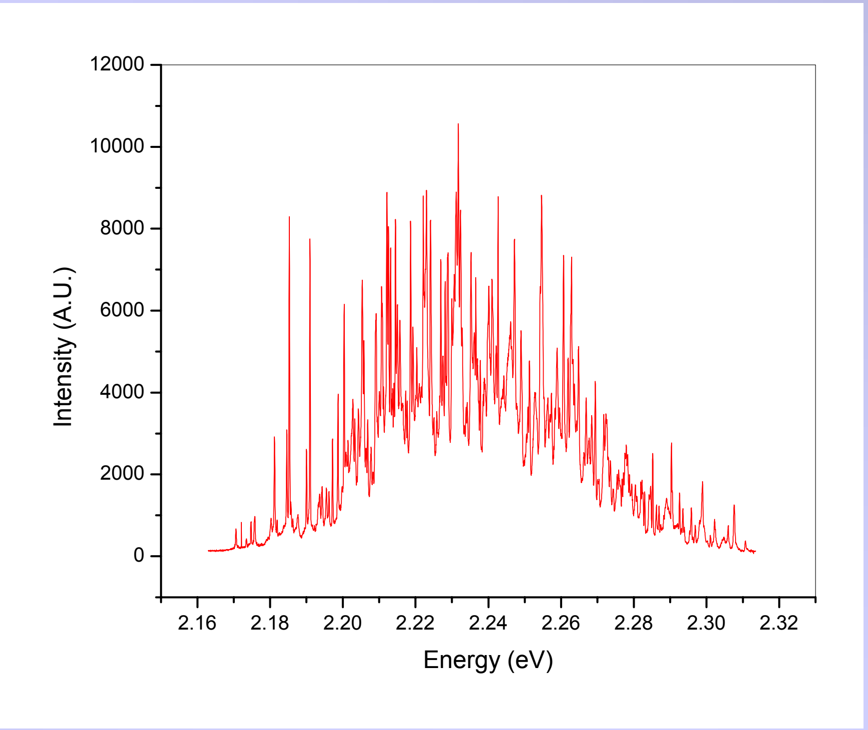
- Atomic Force Microscope image of a 0.51 µm^2 aperture

- Optical image an aluminum pad ~ 40 nm thick fabricated on top of the the CdSe

Apertures made by K. Leosson, COM/DTU Lyngby, DK

Experimental Nano-PL Spectra

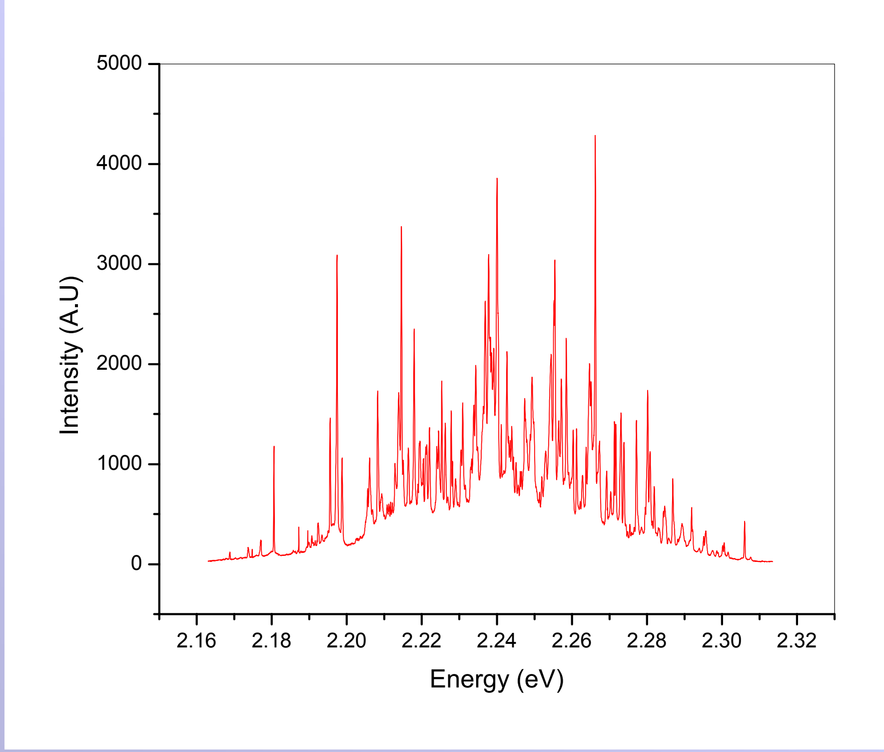


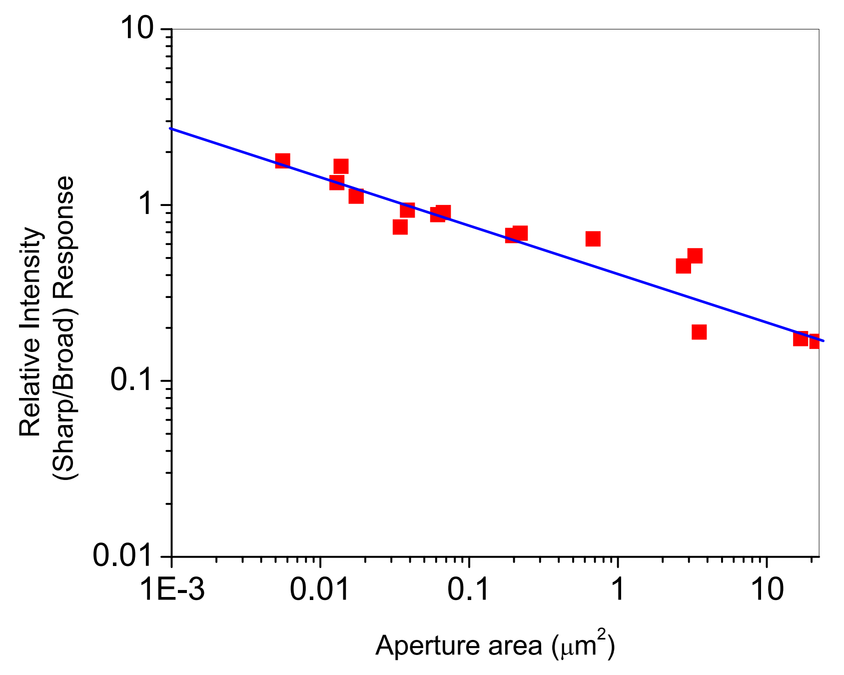


3.53 μm^2 (2500 QDs)

0.062 μm^2 (45 QDs)

Experimental Nano-PL Spectra & Analysis





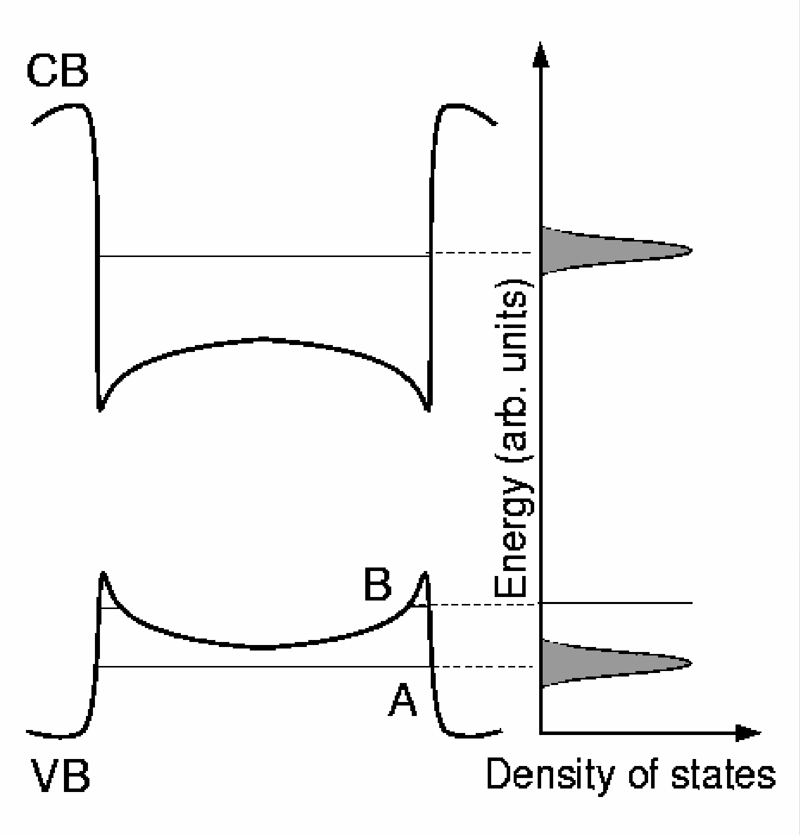
0.013 μm^2 (10 QDs)

Fractional Integrated Intensity

(Narrow Peak to Broad Feature)

One *Possible* Explanation:

Strain-induced local potential minima results in *two distinct VB states*



- Highly localized "0-D" ground state (B)
- Inhomogeneously broad excited state (A)

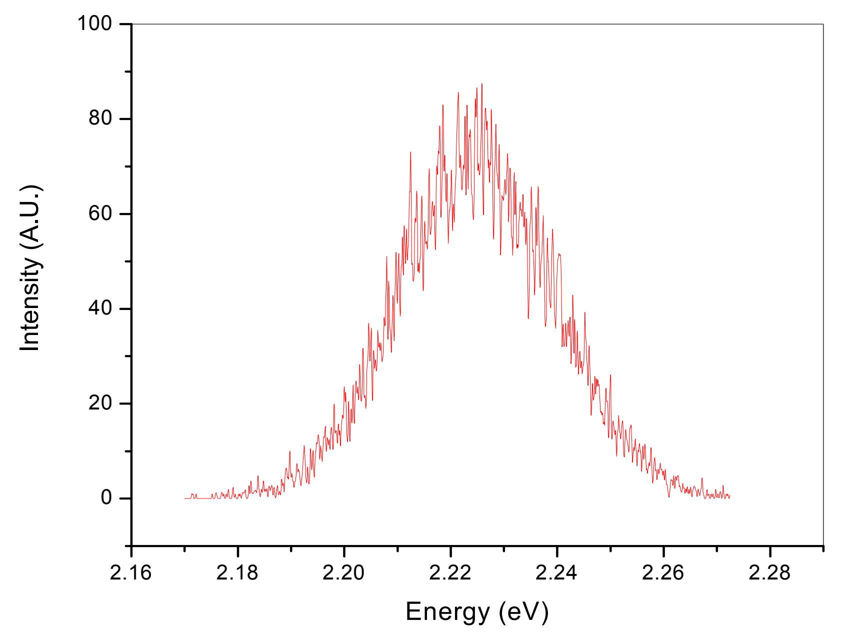
Two Distinct States mean :

- Different Spectral Widths
- Different Exciton Lifetimes
- Different Temperature Dependence (activation energies)

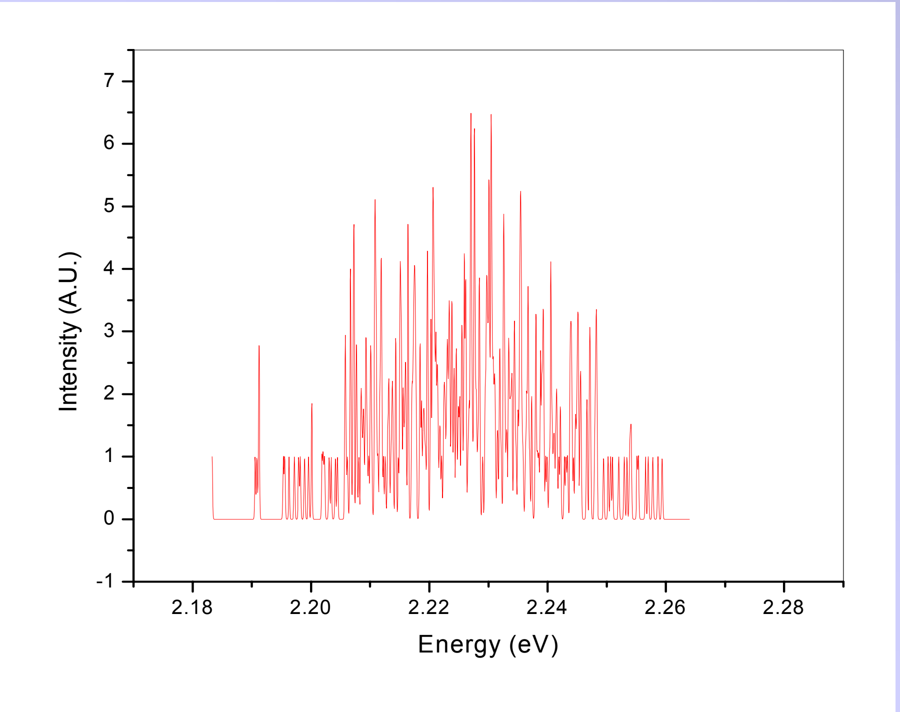
While this is consistent with experimentally observed behavior, is it theoretically consistent?

Single State Model Simulated Spectra

Multiple individual peaks with 250 μeV linewidths

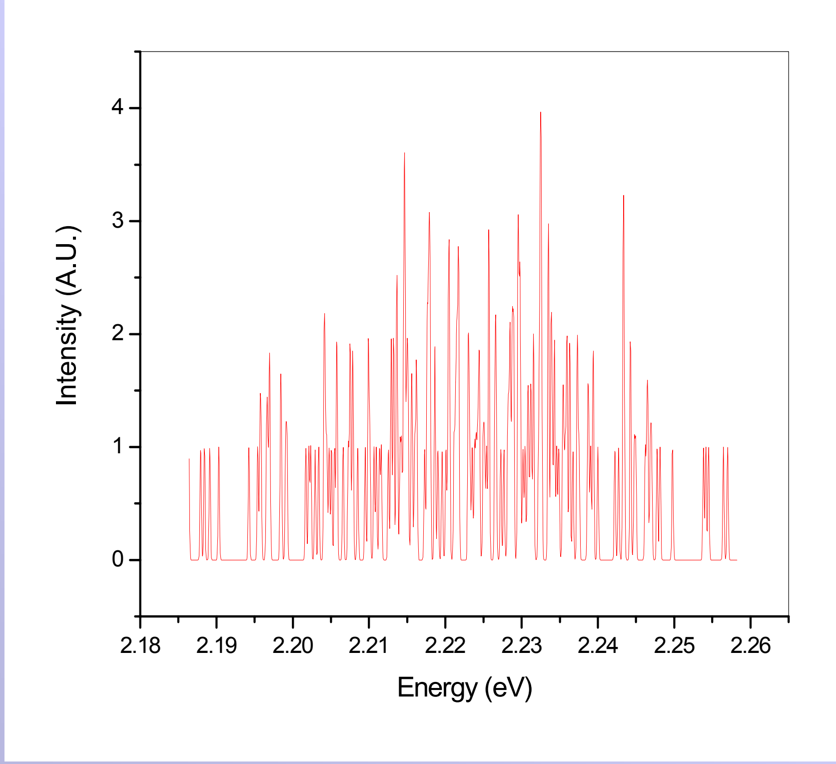


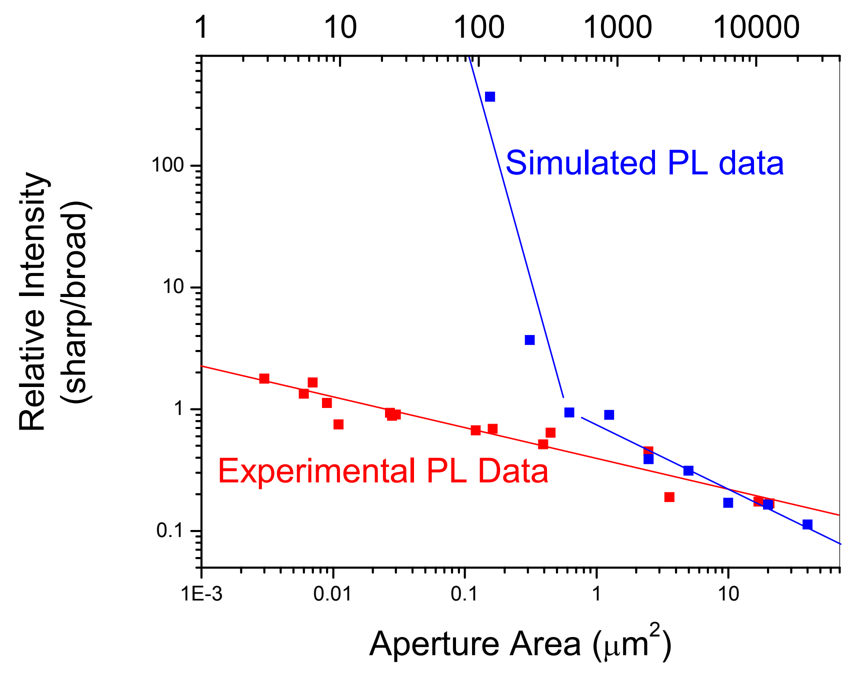
12,500 Single Peaks (2100 QDs)



400 Single Peaks (50 QDs)

Single State Model Simulated Spectra & Analysis





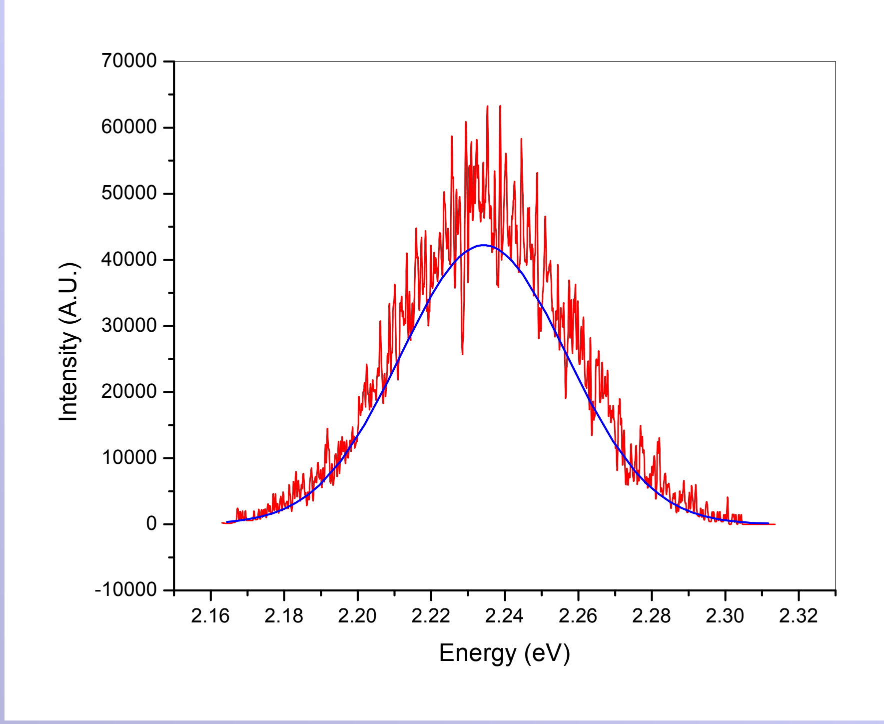
200 Single Peaks (30 QDs)

Fractional Integrated Intensity

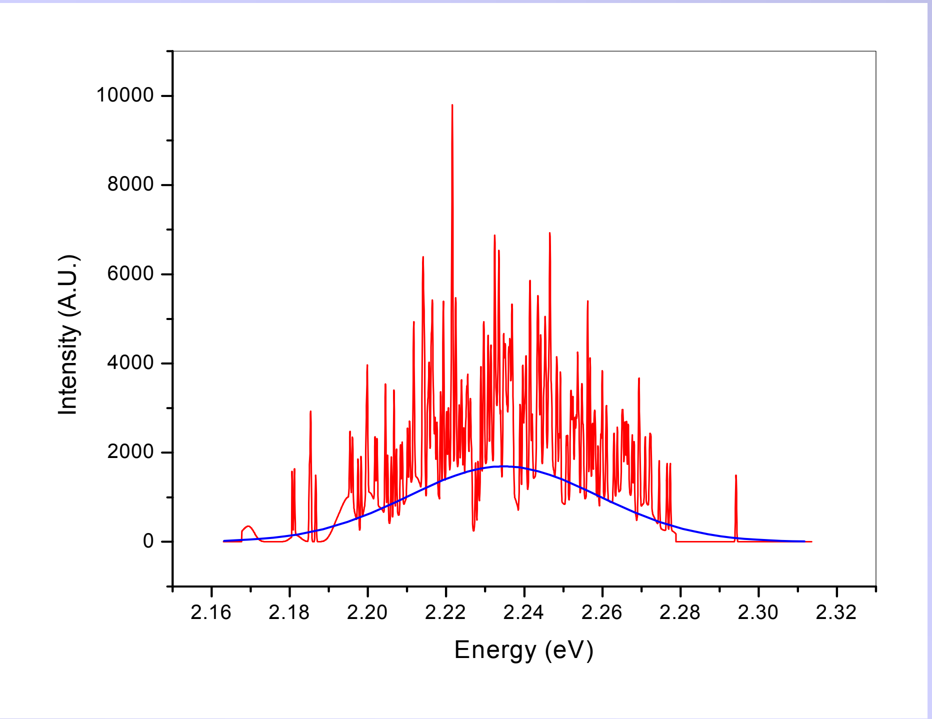
(Narrow Peak to Broad Feature)

Two State Model Simulated Spectra

Multiple pairs of peaks with 300 μeV & 3000 μeV linewidths

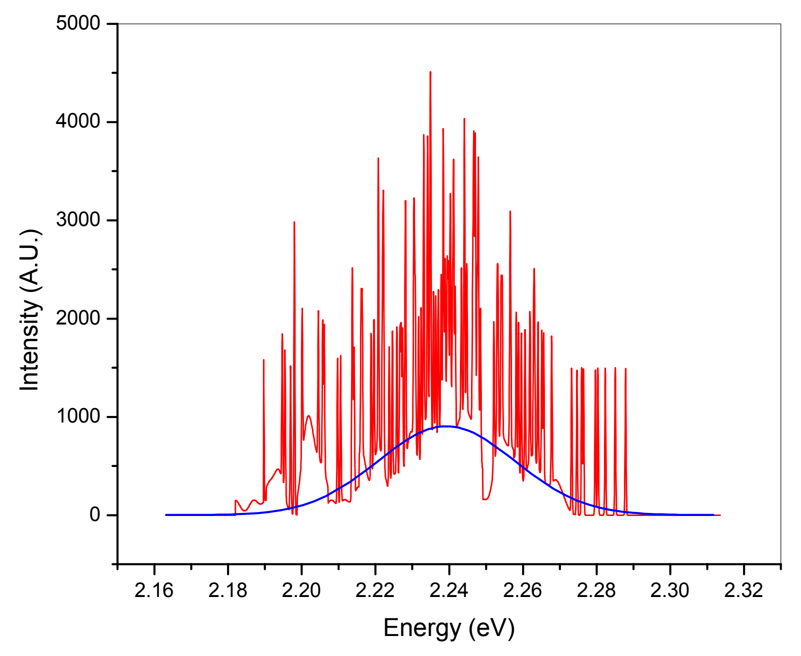


3000 Peak Pairs (500 QDs)

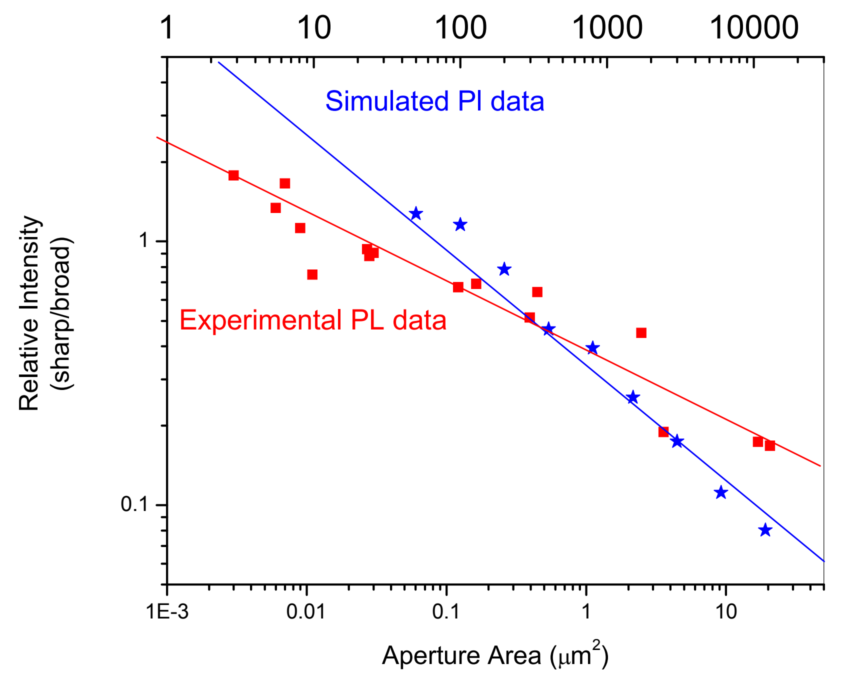


200 Peak Pairs (50 QDs)

Two State Model Simulated Spectra & Analysis



100 Peak Pairs (15 QDs)



Fractional Integrated Intensity

(Narrow Peak to Broad Feature)

What have we learned about QD systems?

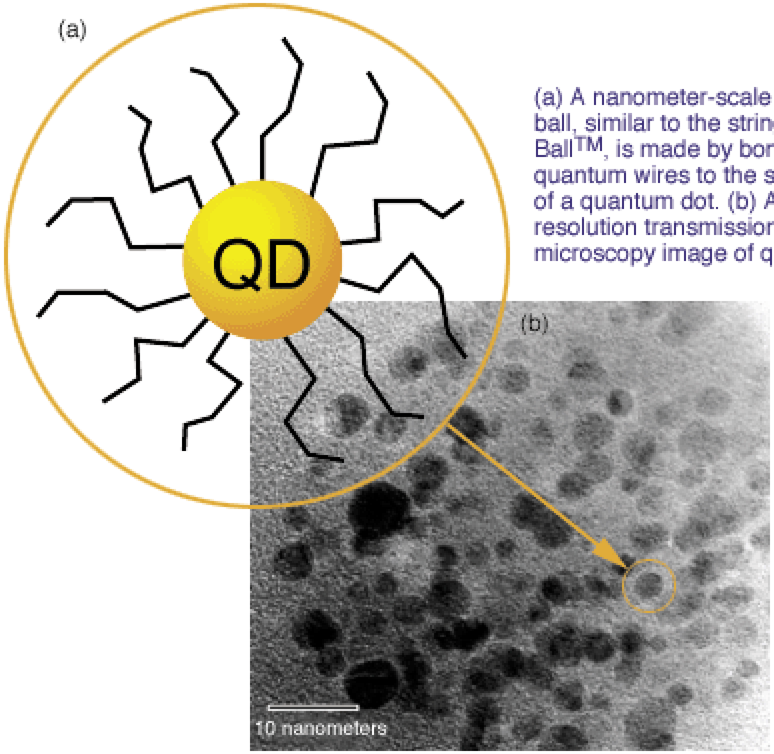
- Self-assembled quantum dots are nanometer structures which exhibit quantum effects
- Photo-luminescence emission is comprised of narrow peaks & broad features relating to two electronic states
- PLE demonstrates that excitons have different local energy landscapes within the quantum dots
- SAQDs show great promise both for studying fundamental science of quantum confined systems and for use as light sources in various applications.

Where do we go from here?

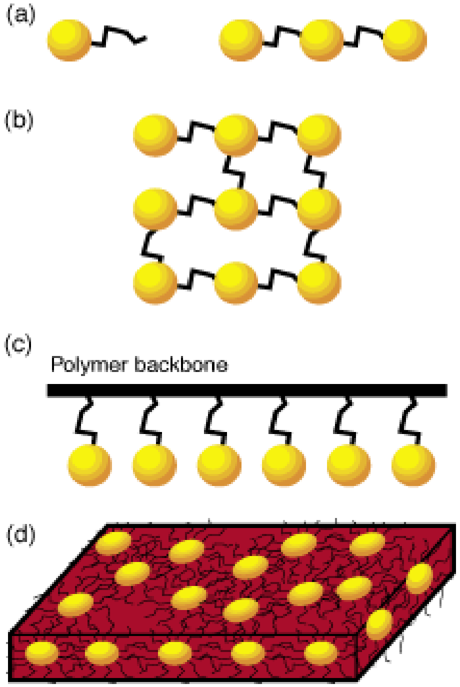
- **Photonic Structures**
  - Add chemically prepared QD spheres to self-assembled bi-block polymers
  - Incorporate SAQDs as an active medium in photonic band gap structures

- **Computing Structures**
  - Add magnetic material (eg. Mg) to SAQDs Magnetic spin control implies quantum computing applications
  - QDs can be used for making ultra-fast, all optical switches and logic gates

Spherical QDs with Quantum Wire Tethers form Building Blocks



(a) A nanometer-scale quantum ball, similar to the stringy Koosh Ball^{TM}, is made by bonding quantum wires to the surface of a quantum dot. (b) A high-resolution transmission electron microscopy image of quantum dots.



With molecular tethers to link them together, quantum dots become the building blocks of nanostructures. They can be linked together as (a) molecules, (b) lattices, (c) attached to a polymer backbone, or (d) incorporated into a polymer thin film.

Quantum Computing

Tokyo, July 29, 2002 - **Fujitsu Laboratories Ltd. announced today that it has succeeded in developing breakthrough technologies for fabricating quantum dot arrays as a basic element of quantum computers**

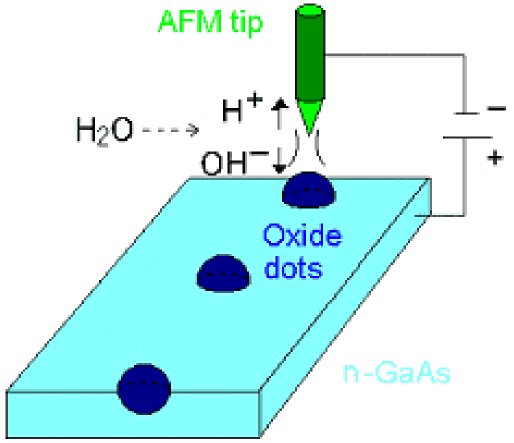
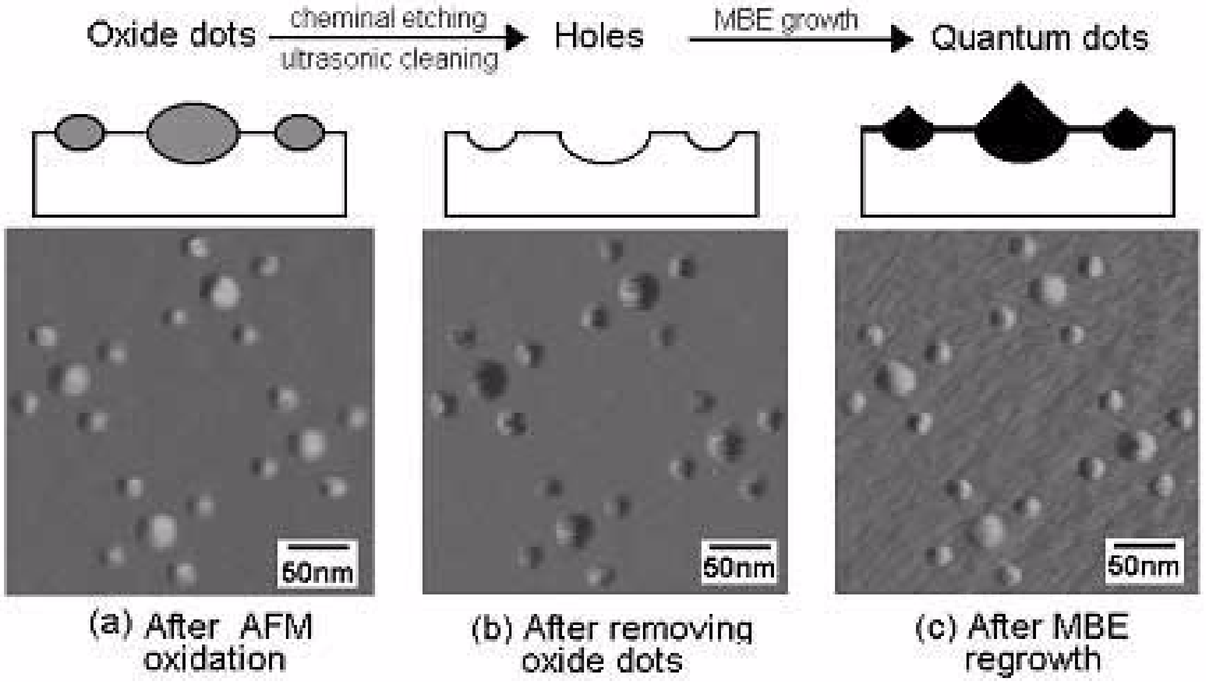


FIG. 2 Fabrication of oxide dots



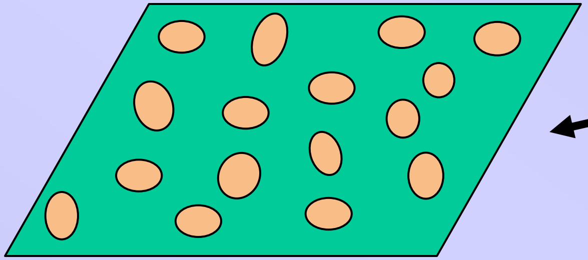
(a) After AFM oxidation

(b) After removing oxide dots

(c) After MBE regrowth

FIG. 1 Quantum dot fabrication processes and array of fabricated quantum dots

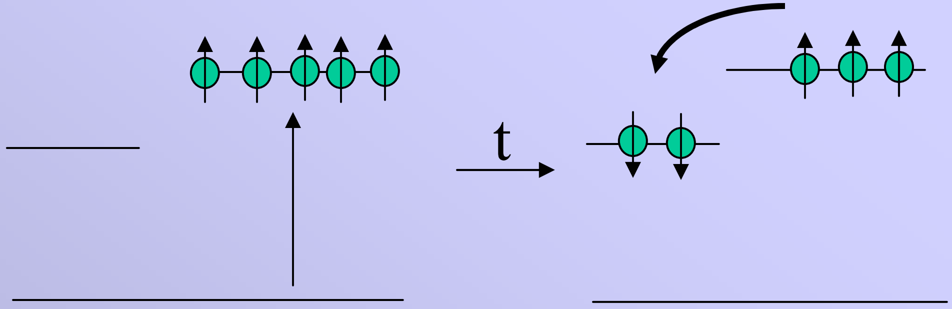
More Quantum Computing: Add Mg to CdSe & CdTe SAQDs



Quantum dots

Quantum Computer.

Single electron transistor



By analyzing Magneto-PL

Spin Relaxation Time

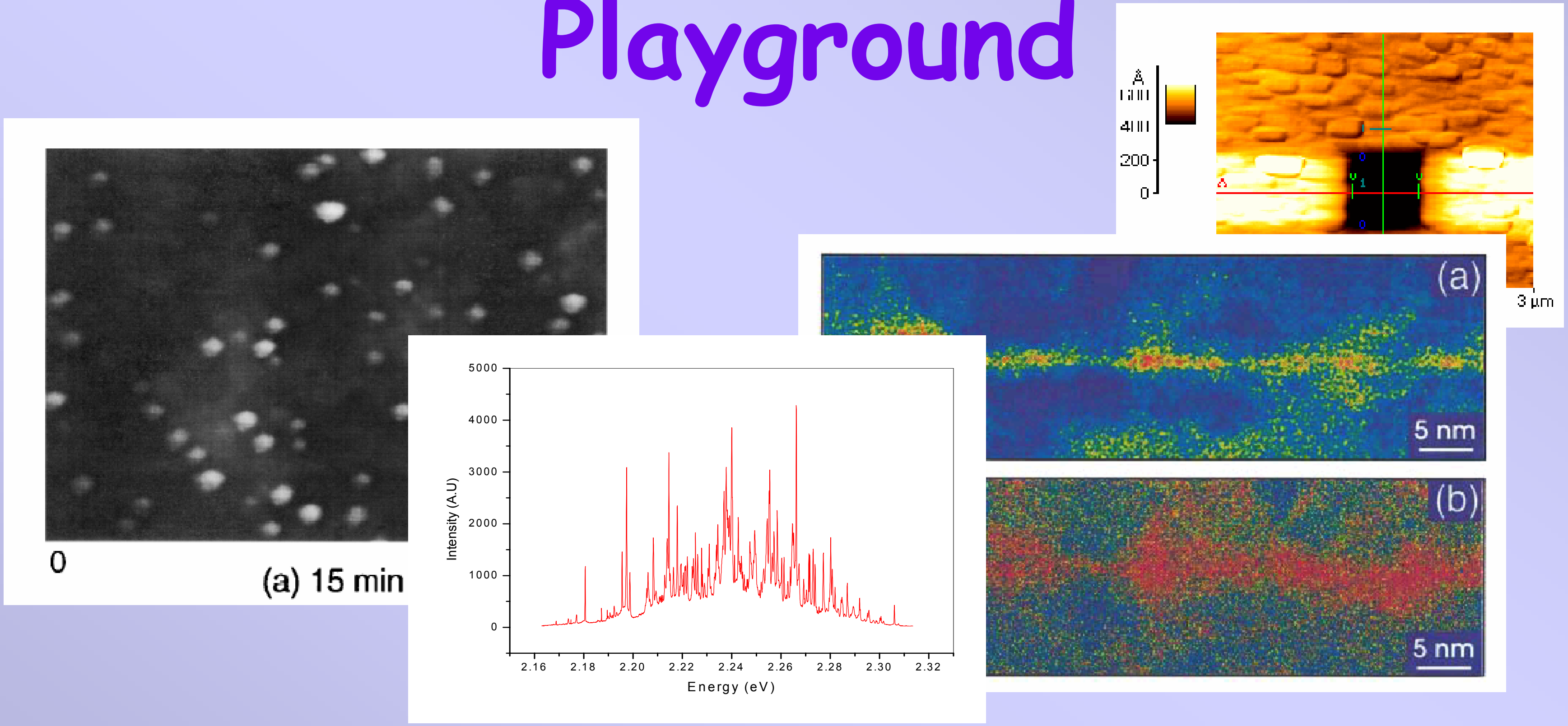
(Gyration Constant , diamagnetic shift)

Conclusion

"The National Nanotechnology Initiative is a big step in a vitally important direction. It will send a clear signal to the youth of this country that the hard core of physical science (particularly physics and chemistry) and the nanofrontiers of engineering have a rich, rewarding future of great social relevance. The coming high tech of building practical things at the ultimate level of finesse, precise right down to the last atom, has the potential to transform our lives. Physics and chemistry are the principal disciplines that will make this all happen. But they are hard disciplines to master, and far too few have perceived the rewards at the end of the road sufficient to justify the effort. The proposed NNI will help immensely to inspire our youth.“

Richard E. Smalley
Gene and Norman Hackerman Professor of Chemistry and Professor of Physics
Rice University Center for Nanoscale Science and Technology

Quantum Dots:
A Physicist's (& Chemist's) Playground



Jan Yarrison-Rice, Physics Dept.
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