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
• 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 \( \Omega = L_x L_y L_z \)

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

• Density of states / per unit volume

\[
N_{3D}(\mathbf{K}) = \frac{2\Omega}{(2\pi)^3} \frac{4}{3} K^3 \pi \quad n_{3D}(\mathbf{K}) = \frac{1}{3\pi^2} K^3
\]

• Density of states in Energy

\[
D_{3D}(E) = \frac{d}{dE} n_{3D}(\mathbf{K}) = \frac{1}{2\pi^2} \left( \frac{2m^*}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{E - E_g}
\]
• For example \( \text{GaAs/Al}_{x}\text{Ga}_{1-x}\text{As} (x < 0.4) \) quantum well

\[
D_{2D}(E) = \frac{m^*}{\pi \hbar^2}
\]
Introduction
Density of States – 1D

- Quantum wire through cleaved edge overgrowth

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

- Density of states
Introduction
Density of States – 0D

- Kinetic quantization along x, y and z-direction
- Energy spectrum fully quantized
- Density of States

\[ D_{0D}(E) = \text{discrete} \]
**Introduction**

**Quantum Dots as Artificial Atoms**

<table>
<thead>
<tr>
<th>Particle</th>
<th>Atom</th>
<th>QD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy scale</td>
<td>13eV – 100keV</td>
<td>Typ. 1 eV</td>
</tr>
<tr>
<td>Length scale</td>
<td>0.1 – 0.3 nm</td>
<td>Typ. 10 nm</td>
</tr>
<tr>
<td>Potential</td>
<td>V(r) ~ 1/r</td>
<td>Tunable</td>
</tr>
</tbody>
</table>

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
• Introduction

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

Si + 4HF + 2F⁻ + 2h⁺ → SiF₆²⁻ + H₂ + 2H⁺
Porous Silicon
Optical Properties

Si bandgap → Smaller nc´s size

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

Broad spectrum → line narrowing
- P-Si has indirect nature
- $k$-conservation rule breaks down due to confinement
Porous Silicon
Electron-Hole Exchange Interaction

Electronic structure of excitons is very similar to dye molecules

Absorption in a singlet state
After spin flip emission via triplet state

T=1.5 K

Laser

Energy (eV)

PL Intensity (arb. units)

Absorption in a singlet state
After spin flip emission via triplet state
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

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

Silicon nanocrystals (almost ideal donor):
- ground state is triplet
- long exciton lifetime \((10^{-5}-10^{-3} \text{ s})\)
- wide emission band
- huge internal surface area \((10^3 \text{ m}^2/\text{cm}^3)\)

Acceptor having triplet ground state?
Optical excitation is impossible $\rightarrow$ Photosensitizer is required $\rightarrow$ Silicon nanocrystals

**Porous Silicon**

**Molecular Oxygen: Electronic Structure**

- **Ground state:**
  - spin triplet
  - chemically inert
  (reaction $S + T \rightarrow S$ is forbidden)

- **Excited states:**
  - spin singlet
  - energy-rich
  - high chemical reactivity
  (reaction $S + S \rightarrow S$ is allowed)

oxidation reactions in organic chemistry, biology, life science, photodynamic cancer therapy, oxygen-iodine laser
→ Adsorption of O₂: PL Quenching
→ low temperature: • fine structure appears
    • \(^1\text{D} \rightarrow \text{^3S}\) emission line of O₂
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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
• 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
II-VI Quantum Dots Applications

- Coupled to bio-molecules → biological sensors
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%)

![Potential Diagram](image)
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MBE $\rightarrow$ Atomically precise deposition of layers with different composition and/or doping.
Cleave the sample
2nd growth step

T-Shaped Quantum Wire

Si-δ-doping

GaAs quantum well

AlGaAs

[001]

[110]

GaAs quantum well
Two cleaving steps enable fabrication of QDs and artificial molecules

- 1st growth on (001) GaAs
- 2nd growth on (011)
- 3rd growth on (011)

At intersection between three quantum wells
- Weaker localisation
- Lower energy state

▶ QUANTUM DOT
1st: grow AlAs layers in GaAs matrix
2nd: cleave in MBE machine
3rd: grow InAs Dots on MBE patterned (110) surface
### Quantum Dot Size Correlated with AlAs-Width

- **AlAs-width [nm]**
  - SL1: 32
  - SL2: 20
  - SL3: 11
  - SL4: 20

- **Dot Width [nm]**
  - SL1: 35
  - SL2: 22
  - SL3: 12
  - SL4: 22

- **Dot Height [nm]**
  - SL1: 13 ±4
  - SL2: 7 ±1
  - SL3: 3
  - SL4: 7 ±1

- **Density [dots/µm]**
  - SL1: 17
  - SL2: 14
  - SL3: ----- 
  - SL4: ----- 

- Create chessboard-structure?
Advantages

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

Disadvantages

• Relatively low confinement energies ($\Delta \sim 10\text{meV}$)
• Complex crystal growth and fabrication
• (011) surface not purely As or Ga terminated like (100)
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Self Assembling QDs
Epitaxial Growth Modes

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

\[ \alpha_2 + \beta_{12} < \alpha_1 \]

Deposited Material Wet Substrate

\[ \alpha_2 + \beta_{12} > \alpha_1 \]

Clustering reduces free energy
Self Assembling QDs
Energy Gap vs. Lattice Constant

![Graph showing the relationship between energy gap and lattice constant for various materials.](image-url)
Self Assembling QDs
Strained Layer Epitaxy

Pseudomorphic

\[ \varepsilon = \frac{a_1 - a_2}{a_1} \]

Dislocated

For (001) growth
Strain Energy

\[ E_s \propto \varepsilon^2 d \]

- Pseudomorphic growth
- Strain energy increases \( \sim \) linearly with \( d \)

\( d \) - Critical Thickness

e - % Lattice Mismatch

- 5%
- 7%
- 14%

Dislocations
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)

EPITAXIAL LAYER (e.g. InAs)

SUBSTRATE (GaAs)

InAs

GaAs

Wetting Layer

Self-Assembled Quantum Dots

Stranski-Krastanow Growth Mode
Self Assembling QDs
Islands $\rightarrow$ Quantum Dots

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

Time

Typical size $- L_0 \sim 10 \times 25$ nm
Self Assembling QDs
Influence of Growth Parameters

- Growth conditions control QD size, density and composition
Upper layers of dots tend to nucleate in strain field generated by lower layers.
Self Assembling QDs
Strain

- InGaAs-GaAs self assembled QD-molecules
- Self alignment via strain field
Self Assembling QDs
Quantum Logic

<table>
<thead>
<tr>
<th>Initial state</th>
<th>CNOT operation</th>
<th>Final state</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>b</td>
<td>a</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>1/2-pulse at $\omega_{ab}$</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>$\omega_{ab}$</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
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CNOT gating – pulse at $\omega_{ab}$
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Electronic Structure
Single Dot Spectroscopy

\[ V(x, y) \sim \text{parabolic potential} \]

\[ E_{z} + E_{g} \sim 1000 \text{meV} \]

\[ E_{g} \sim 1500 \text{meV} \]

\[ \sim 20-40 \text{meV} \]

\[ \sim 40-60 \text{meV} \]

Inhomogeneous broadening

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

0.25µm x 0.25µm
Electronic Structure
Photoluminescence of QD Ensemble

T=4.2 K
- 100 mW
- 40 mW
- 10 mW
- 1 mW

Energy (eV)

PL-Intensity (a. u.)

GaAs

WL

s-s

p-p

WL

WL
Electronic Structure
Ensemble $\rightarrow$ Single Quantum Dot

$T = 10 \, \text{K}$

Ensemble PL
$\sim 10^7$ QDs

- S-S
- P-P
- $<10 \mu\text{eV}$
- 70 meV

PL Intensity (arb. units)

Energy (meV)

Typical areal QD density 10-100$\mu\text{m}^2$

$\rightarrow$ Require low density QD material and spatially resolved spectroscopic techniques
Electronic Structure
Low Quantum Dot Density

PL "Wafer Mapping" (T=300 K)

- 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

\[ h \omega \]

\[ < \lambda \]

500nm

Electrical contacts

Objective

Sample

Scanner

x-y positioning

Shadowmask Apertures + Cryogenic Microscope

Cryogenic Microscope

He3 Sorb-Pump

He4 1K-Stage

15T Magnet and Cryo-Microscope
Each occupancy state \((1e + 1h, 2e + 2h\ldots)\) 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 \(\rightarrow\) Single emission line
  - High \(\rightarrow\) Two groups of lines

- Two “energy scales”
  - Quantisation energy \(\sim 40\text{meV}\)
  - Few particle interactions \(\sim\text{meV}\)
**Electronic Structure**

**Identification of Occupancy States**

- QD occupancy states (X, 2X, 3X…)
- Identified from power characteristics

QD occupancy states (X, 2X, 3X…)

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

- Prob. dot occupied with “q” e-h pairs
- \( N = \) exciton generation rate

\[ I(X) \propto P_{ex}^{0.5} \]

\[ I(X^*) \propto P_{ex}^{0.25} \]

\[ I(2X) \propto P_{ex}^{2} \]

\[ I(mX_{s1}) \propto P_{ex}^{2.5} \]

\[ E_{ex} = 1524 \text{meV} \]

\[ P_{ex} \text{ (W cm}^{-2}\text{)} \]

\[ \text{PL Intensity (1000 counts s}^{-1}\text{)} \]
Electronic Structure
Single Photon Generation

- Pulsed optical excitation of a single dot

- Each external laser pulse produces single photon at X0 energy
Electronic Structure
Calculate Strain

Minimization of elastic energy in continuum model.

\[ E_{el} = \frac{1}{2} \int \nabla \varepsilon \cdot \varepsilon \, dV \]

**Enhanced lateral confinement**

-2 -1 0 1 [%]
-2 -1 1 2

GaAs
InGaAs
tensile
compressive

Lead to Piezo electric polarization
Electronic Structure
Calculate the Quantum States

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

\[ \nabla \frac{1}{m^*(r)} \nabla \Psi(r) + E_c(r) - e\Phi(r) = E\Psi(r) \]

**Electron** wavefunctions

s  \hspace{1cm} p  \hspace{1cm} p  \hspace{1cm} d  \hspace{1cm} d

**Hole** wavefunctions
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
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

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• References: Please ask for special topics.