Aim of lecture

- Short review of physics of quantum dots
- What can be learnt from single quantum dot spectroscopy?
- Our own work on silicon QDs – compared to direct bandgap QD’s

Acknowledgements:

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Outline

Introduction
Quantum dot – “artificial atom”
The zoo of quantum dots: III-V/ II-VI / Si

Theory
Quantum confinement - Schrödinger equation
Recombination, surface passivation

Single-dot spectroscopy
Techniques to probe single dots
The unexpected: Spectral diffusion, blinking
High excitations
STM of single quantum dots

Spectroscopy of single silicon quantum dots (our work)
QDs from lithography
Linewidth, blinking
Time resolved and high excitations measurements

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Quantum dot – ‘artificial atom’

Atom

Quantum dot

Bulk semiconductor

Energy

\[ \lambda \]

\[ kT \]

\[ e^- h^+ \]
When size is reduced quantized states begin to form at band edges. This means that a semiconductor nanocrystal forms discrete states while a metal particle still has a very high density of states near Fermi level. Thus, metals turn to quantum dots only at very small sizes (< 1 nm).
Quantum confinement

Effective bandgap

Quantum dot

Size - d [nm]

Band gap [eV]
Photon emission/absorption – quantum size effect

Emission

Absorption

Murray, Norris, Bawendi, MIT
'zoo' of nanocrystals/QDs
Fig. 33. Semiconductor nanocrystals in various environments. (a) CdS crystallites in polyvinylpyrrolidone (Gaponenko, Germanenko et al. 1996); (b) InP islands on a GaInP surface (Carlsson et al. 1995); (c) Ge single nanocrystals in a composite semiconductor-glass film (Kanemitsu et al. 1992); (d) GaAs single nanocrystals in a polymer matrix (Mioč and Nozik 1996). Note pronounced crystallographic planes in (c) and (d).
**Stranski-Krastanov growth: In(Ga)As QDs**

- In(Ga)As – grown on GaAs
- Lattice mismatch ~7.2 %
- Compressive strained layers
  - up to a few monolayers
- Relaxation => island growth
- Size: lateral: 10 – 20 nm; height: 5 – 8 nm

![Diagram of InAs growth on GaAs](image)

**Fig. 1**  
a) AFM image of a sparse array of In(Ga)As S–K QDs deposited on GaAs. b) High resolution TEM cross-section of vertically correlated InAs–GaAs QDs via multilayer Stranski–Krastanov growth.
Gates 1, 2, 3, 4 are reverse-biased. This forms restrictions in an underlying 2-dimensional electron gas (GaAs layer embedded in AlGaAs). Thus, a quantum dot is formed below electrodes!
Porous silicon

Leigh Canham 1990, APL

Porous Si structure
TEM, from Cullis et al.
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12.5.1 Quantum dot with spherically symmetric potential

A quasi-zero-dimensional quantum dot with radius $R$, exhibiting the quantum-confinement effect in all directions, can be most easily described using a spherically symmetric potential well, defined by

$$
V(r) = \begin{cases} 
0 & \text{for } r \leq R, \\
V_0 & \text{for } r > R,
\end{cases}
$$

(12.25)

where $r^2 = x^2 + y^2 + z^2$. The treatment of such a spherically symmetric well with finite depth can be carried out using separation of variables and finding an analytical solution; more details can be found, e.g., in [17].

In view of the symmetry of the problem, it is useful to employ the transformation of the Cartesian coordinate system into spherical coordinates (see Fig. 12.21):

$$
x = r \sin \vartheta \cos \varphi, \quad y = r \sin \vartheta \sin \varphi, \quad z = r \cos \vartheta.
$$

The transformation changes the relevant Hamiltonian into

$$
H = -\frac{\hbar^2}{2m} \nabla^2 + V(r) \quad \Rightarrow \quad -\frac{\hbar^2}{2mr^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) - \frac{\hbar^2 \Lambda}{2mr^2} + V(r),
$$

where the operator $\Lambda$ stands for

$$
\Lambda = \frac{1}{\sin \vartheta} \left[ \frac{\partial}{\partial \vartheta} \left( \sin \vartheta \frac{\partial}{\partial \vartheta} \right) + \frac{1}{\sin \vartheta} \frac{\partial^2}{\partial \varphi^2} \right].
$$
Schrödinger eq. for quantum dot

The wavefunction can be separated into the functions of the individual variables $\psi = R(r) \Theta(\theta) \Phi(\varphi)$. It is often written down as

$$\psi_{n,l,m}(r, \theta, \varphi) = \frac{u_{nl}(r)}{r} Y_{lm}(\theta, \varphi),$$  \hspace{1cm} (12.26)

where $Y_{lm}$ denote the Laplace spherical harmonics and the radial part $u(r)$ is the solution of

$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[ V(r) + \frac{\hbar^2}{2mr^2} l(l+1) \right] u(r) = Eu(r), \hspace{1cm} l = 0, 1, 2, \ldots$$ \hspace{1cm} (12.27)

As long as the well is infinitely deep ($V_0 \to \infty$), the radial part of the wave function $u(r)$ will equal zero for $r = R$ and the energy levels corresponding to the localized states will be described by the simple equation [7, 9]

$$E_{nl} = \frac{\hbar^2}{2m} \left( \frac{\chi_{nl}}{R} \right)^2,$$ \hspace{1cm} (12.28)

where $\chi_{nl}$ stands for the $n$th root of the $l$th-order spherical Bessel function.
Energy states in a spherical well

Fig. 1.3. Energy levels of a particle in a spherical well with infinite barrier. Energy is scaled in the dimensionless units of $\hbar^2/(2ma^2)$, where $\chi_n$ values are the roots of the Bessel functions listed in the Table 1.1. The states are classified by the principal quantum number, $n$, and by the orbital quantum number, $l$. Every state is $(2l + 1)$ degenerate. For $l = 0$ (so-called s-states) $\chi_n = \pi n$ holds, and corresponding energies obey a series derived for a particle in a rectangular well [see Fig. 1.1(a)].

Fig. 2.1. A sketch of optical properties of an ideal spherical quantum dot with isotropic scalar effective masses of noninteracting electron and hole. Electron and hole energy levels (a) obey a series of states inherent for a particle in a spherical box with an infinite barrier. Selection rules allow optical transitions coupling the hole and the electron states with the same quantum numbers. Therefore, the optical absorption spectrum of the parent bulk crystal reduces to a number of discrete bands (b).
Excitation of electron-hole pair: Exciton

- **Exciton**
- **Excitation**

**Luminescence**

Exciton: +

Coulomb attraction =>

Binding energy!
Exciton – weak/strong confinement

Weak confinement: $a > a_B$

Strong confinement: $a < a_B$

with exciton Bohr radius: $a_B \sim \frac{\epsilon \hbar^2}{\mu e^2}$

where $\mu$ is the electron-hole reduced mass:

$\mu^{-1} = m_e^{-1} + m_h^{-1}$
**Exciton energy**

**Weak confinement: \( R > a_B \)**

The energy of an exciton in the weak confinement regime is:

\[
E_{\text{nnl}} = E_g - \frac{\text{Ry}^*}{n^2} + \frac{\hbar^2 \chi_{nl}^2}{2MR^2},
\]

where \( \chi_{nl} \) are roots of the spherical Bessel functions (\( n \) – number of the root, \( l \) – order of the function)

\( \text{Ry}^* \) is the exciton Rydberg energy given by:

\[
\text{Ry}^* = \frac{e^2}{2ea_B}, \quad \text{and} \quad M = m_e^* + m_h^*.
\]

Thus, the exciton levels in the quantum dot are characterized by the quantum numbers \( n, m \) and \( l \).

**Strong confinement: \( R < a_B \)**

The confined electron and hole in such a case have no bound states corresponding to the hydrogen-like exciton. Then, position of energy levels become:

\[
E_{nl} = E_g + \frac{\hbar^2}{2\mu R^2} \chi_{nl}^2.
\]

where \( \mu^{-1} = m_e^{*-1} + m_h^{*-1} \) is the electron-hole reduced mass.
Quantum confinement

Exciton Bohr radius: red arrows

$\text{r} = 0.7 \text{ nm}$
Surface states - passivation

Quantum dot surface

"dangling bonds"

"core shell quantum dot"
Recombination mechanisms

In a perfect nanocrystal at low excitation:

- **Radiative**
- **SRH**: Defect/impurity
- **Auger eeh** (hhe)

**Common in**
- Direct-bandgap semiconductors => LEDs, lasers

**Shockley-Read-Hall**
- Recombination dominating in Si, Ge etc ($E_T$ = trap state energy)

**dominates at high carrier densities**
- (e.g. in lasers)
"Phonon bottleneck" ???

Bulk – conduction band

Quantum dot – discrete states
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  Techniques to probe single dots
  The unexpected: Spectral diffusion, blinking
  High excitations
  STM of single quantum dots

Spectroscopy of single silicon quantum dots (our work)
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Epilogue
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Need for single quantum dot studies

Inhomogenous broadening!  
Sharp linewidth
Techniques to probe single QD

- microscope
- SNOM
- metal mask
- mesa etching
- tip-enhanced

(dot spacing > λ)

Adapted after M. Sugisaki in 'Semiconductor quantum dots', Springer 2002
Spectroscopy of single CdSe nanocrystals

Empedocles, Norris, Bawendi
MIT, PRL 77, 3873, -96
To see individual quantum dots:

You need to:

- disperse QDs > ~1 um
- use high numerical aperture microscope lens
- in cryostat – window corrected lens
- filter out excitation light and background fluorescence
- cooled CCD camera (< -90 C)
- mechanically stable system
The unexpected.....

On/Off blinking
Blinking

Single CdSe nanocrystals

On/Off blinking observed in:
- II-VI nanocrystals
- single molecules
- in III-V Q-dots - rarely

Shimizu et al.
MIT, PRB 2001
The unexpected....

spectral diffusion
CdSe nanocrystals: Spectral diffusion

Conclusions:

• Randomly oriented local fields changing over time
• Increasing by high excitation
• Charges at the dot surface?

Empedocles, Norris, Bawendi
MIT, PRL 77, 3873, -96
high excitations
Multi-excitonic emission

In_{0.6}Ga_{0.4}As self-assembled dots on GaAs

Bayer et al.
Nature -00
Multi-excitonic emission

$\text{In}_{0.6}\text{Ga}_{0.4}\text{As}$ self-assembled dots on GaAs
STM of single quantum dots
Wave-Function Mapping of Strain-Induced InAs QDs

STS imaging - $|\psi|^2(x, y, V)$

- **0.89 V (000)**
- **1.14 V (100)**

Martin Janson, NANOSPECTRA2004
Wave-Function Mapping of Strain-Induced InAs QDs
STS imaging - \(|\psi|^2(x, y, V)\)

STM

$H=9.4\ \text{nm}$

$14\ \text{nm}$

$14\ \text{nm}$

$V_{\text{stab}}=2.4\ \text{V}$

$I_{\text{stab}}=70\ \text{pA}$

Martin Janson, NANOSPECTRA2004
InAs QD: atomic-like electronic states

STM I-V curve

Size evolution

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fabrication – our approach to see individual Si QD’s
Single Si quantum dots by lithography

Fabrication
1. e-beam lithography
2. plasma etching
3. oxidation (self limiting)
4. PL?
5. repeat 3 & 4.....

pillars 0D dots?

walls - 1D lines?

planes - 2D quantum wells?

SOI wafer
Pillar array – PL image

Each single light source can be traced down to a certain pillar

White light reflection image
(arrays of 30x30 pillars)

PL image
Pumping: 325 nm cw (HeCd)
Some structures after oxidation
100 nm
Make one or two dots?

Schematic of a wall with varying thickness (repeated continuously along line):

Bruhn et al, PSS (2010)
New setup for combined AFM/PL
Single-dot spectra – room temperature

- FWHM: 122 meV for A
- FWHM: 120 meV for B
- FWHM: 152 meV for C

Photon Energy [eV]
Low temperature spectra

35 K => 3 meV

Width less than $kT$!

Discrete lines!
– Quantum dot!

Sychugov et al. PRL (2005)
Narrow spectra - phonons

PL intensity [a.u.]

PL energy [eV]

FWHM 0.78 meV
E(13K) = 1.12 meV

pre1: 16.3 meV
pre2: 3.7 meV

60 meV

5.3 meV spacing
k-conservation relaxed

Silicon nanocrystals
– still indirect bandgap

Zero phonon line (ZPL)

$\Delta x \cdot \Delta p \geq \hbar$

Phonon line (TOL)

$c)$

Si nanocrystals

Sychugov
PRL 2005

CdSe nanocrystals

Empedocles
PRL 1996
Time resolved imaging

- Laser modulation
  - Delay: 0 µs, 5 µs, 10 µs, 15 µs

- Image intensifier
  - on, off
  - open, shut

- Delay: 20 µs

- Images at different delays:
  - 0 µs
  - 5 µs
  - 10 µs
  - 15 µs
Lifetimes

\[ \tau \sim 30 \, \mu s \]
Summary – single dot studies on Si

100 excitons/nanocrystal

1 exciton/nanocrystal
On/Off blinking
Blinking
Blinking - stability

Data for one Si nanocrystal

(a) Dot 80

(b) Average on-time vs. time
- 015mW
- 020mW
- 040mW
- 060mW
- 080mW

Time spent in on-state vs. time [slides]
Model for blinking

Light state

QD trap states
Model for blinking

Dark state

QD          trap
states
Model for blinking

Light state

For Gaussian trap distribution:

\[ P(t) = A \cdot t^{-\alpha} \]

with \( \alpha = 1.5 \)
Blinking at high excitation

(a) Intensity vs. excitation power density.
(b) Distribution of power law exponents.
Suppression of blinking using graded shell

Wang et al.
Nature 2009
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## Comparison - quantum dots

<table>
<thead>
<tr>
<th></th>
<th>ZnSe nanocrystals</th>
<th>InAs quantum dots</th>
<th>Si quantum dots</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>type of bandgap</strong></td>
<td>direct</td>
<td>direct</td>
<td>indirect</td>
</tr>
<tr>
<td><strong>lifetime</strong></td>
<td>ns - range</td>
<td>ns - range</td>
<td>10 µs - range</td>
</tr>
<tr>
<td><strong>on/off blinking</strong></td>
<td>YES</td>
<td>NO (rarely)</td>
<td>YES</td>
</tr>
<tr>
<td><strong>quantum efficiency</strong></td>
<td>10 – 60 %</td>
<td>?</td>
<td>10 – 80 % ?</td>
</tr>
<tr>
<td><strong>tuning</strong></td>
<td>visible</td>
<td>IR</td>
<td>visible - IR</td>
</tr>
</tbody>
</table>
Summary – single dot spectroscopy

- excellent for studying the physics of quantum dots
- has revealed new phenomena
- individual variation

But…..

- rich scenario of individual properties may exist:
  - size, shape, stress, passivation, local environment

=> large number of dots must be analyzed for proper conclusions

Silicon quantum dots:

- Similar physics as direct bandgap QD – less intense
- High quantum efficiencies?
- Nontoxic
Applications of quantum dots

- Labelling of (bio-) molecules (fluorescence tagging)
- Single-photon source: Quantum cryptography
- Luminescent devices: LED, laser
- "Dots in well" infrared detectors
- Phosphor for new lighting
Bleaching – QD’s vs dyes

Rhodamine Green Dextran

CdSe quantum dot

Dubertret et al.
Nature -02
nanosilicon group

seniors
- Jan Linnros (prof)
- Ilya Sychugov (ass prof)
- Torsten Schmidt (postdoc)

PhD students
- Benjamin Bruhn
- 'Mahtab' Sangghaleh
- Roodabeh Afrasiabi
- Yashar Hormozan
- Karolis Gulbinas
- Miao Zhang (starting March)

M.Sc. students
- Viktor Tullgren
- Fatjon Qejvanaj
Thank you for your attention!
Bibliography

**Books:**

- 'Optical properties of semiconductor nanocrystals'
  S.V. Gaponenko (Cambridge Univ. Press 1998)
- 'Semiconductor quantum dots: Physics, spectroscopy and applications'
  Y.Masumoto, T. Takagahara (Eds) (Springer 2002)
- 'Quantum dots' L.Jacak, P. Hawrylak, A. Wojs (Springer 1998)
- 'The physics of low-dimensional semiconductors'
  John Davies (Cambridge 1998)

**Articles:**

- 'The structural and luminescence properties of porous silicon'
  Cullis, Canham, Calcott, J. Appl. Phys. 82, 909 (1997)
- 'Overview of fundamentals and appl. of electrons, excitons and photons in confined structures’

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