Semiconductor Quantum Nanostructures for Optoelectronic Applications
(PhD Oral Defense Examination)

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Presentation Overview

1. Thesis Introduction, Motivation and Objective
2. Optoelectronic Theory of Semiconductors
3. II-VI CdSe/CdS Nanoplatelets & Quantum Ring
   - Dimension Effect
   - Temperature Effect
   - Alloying Effect
   - Excitonic Absorption
   - Quantum Ring
4. Dilute-Nitride-Bismide III-V Quantum Dots & Wells
   - GaNBiAs/GaAs Quantum Dots
   - GaNBiAs/GaAs Quantum Wells
   - InNBiAs/InP Quantum Dots
   - InNBiSb/InSb Quantum Wells
5. Thesis Conclusion and Closing Remarks
Semiconductor Quantum Nanostructures for Optoelectronic Applications

Thesis Introduction, Motivation and Objective

History | Major Breakthroughs in Semiconductors

- Semiconductor amplifier (Shockley, 1945)
- Semiconductor transistor (Bell Labs, 1947)
- n-p-n junction transistor (Teal 1951)
- Transistorized computer (1953)
- Integrated circuit (Texas Instruments, 1958)
- LED (Texas Instruments, 1961)
- Laser diode (IBM, 1962)
- Quantum-well laser (1975)
- Quantum dot coined (1986)
- Quantum cascade laser (1994)
- Gallium-nitride blue laser (Nakamura, 1997)
- IL-VI Nanoplatelets (2009)

1 W. Shockley, J. Bardeen and W. Brattain were awarded the 1956 Nobel Prize for Physics for this work.
2 S. Nakamura was awarded the 2014 Nobel Prize for Physics for this work.
**Atoms, Discrete Energy States & Bands**

Fig. 1: Discrete energy states of an atom; and formation of energy bands.

Band Theory of Solids

- A solid is formed by bringing together isolated atoms.
- When atoms come together, electron wavefunctions overlap and energy levels shift, creating ‘bands.'
Categories of Solids | Semiconductors | Quantization

- 3 categories based on conductance:
  - Insulators, Semiconductors, Conductors.
- Electrical conductivity order: Insulators < Semiconductors < Conductors.

<table>
<thead>
<tr>
<th>Insulators</th>
<th>Semiconductors</th>
<th>Conductors</th>
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<tr>
<td>$10^{-18}$ Ω$^{-1}$m$^{-1}$</td>
<td>$10^{-8}$ Ω$^{-1}$m$^{-1}$</td>
<td>$10^{-3}$ Ω$^{-1}$m$^{-1}$</td>
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**Quantization effect:** When semiconductor crystal size is reduced to $\sim$ 10 nm, new material properties emerge.

**Fig. 2:** Semiconductors conductance range and properties.

**Fig. 3:** Band structure of insulators, semiconductors, conductors.

**Fig. 4:** Size range of quantum dot in comparison to macroscopic, waveguide & atom.
Semiconductors | Dimensionality and Density of States

**Fig. 5:** Density of states (DOS) vs. dimensionality of semiconductor nanostructures. Range: $\sim 1 - 10$ nm.

**Fig. 6:** Energy level splitting in QDs with size effect on the energy band. ([sigmaaldrich.com](http://sigmaaldrich.com))

- **DOS:** # of states available per energy interval at each energy level to be occupied by the charge carriers. DOS evolves with dimensionality. [see Fig. 5]³

³Fig. 5 is reprinted from “J. Kováčč, et al., Optoelectronics, 2009” with permission of Springer US.
Quantum Dots | Introduction

Quantum dots (QD) are nanoparticles in the $\sim 10$ nm size range, with unique electronic and optical properties.

**Applications:** LEDs, Optical Storage, Organic Dyes, Quantum Computing, Security, Solar Power, etc.

Fig. 7: Types and Size of Quantum Dots.
Nanoplatelets and Quantum Rings | Introduction

Fig. 8: Schematic and atom-by-atom view of NPL.

Fig. 9: Schematic and atom-by-atom view of QR.

- **Nanoplatelets (NPLs):** Atomically flat quasi-2D nanocrystals of wide bandgap II-VI semiconductors such as CdSe, CdS, etc.
- **Quantum rings (QRs):** Topologically inverted type-I core/crown NPL heterostructure. Example: CdS/CdSe QRs.
Quantum Confinement Effect on QDs, NPLs & QRs

QDs, NPLs & QRs are bandgap tunable by size to emit different colors wavelength.

We can engineer their optical and electrical properties.

Larger nanocrystals have a small bandgap, emitting at red end.

Smaller nanocrystals have a large bandgap, emitting at blue end.

**Fig. 10:** Quantum confinement effect on QDs, NPLs & QRs.
Motivation and Thesis Objective

Motivation

Among the wide range of semiconductor nanocrystals, two families have emerged as very promising for novel semiconductor applications:

1. NPLs and QRs of II-VI semiconductors/alloys.
2. QDs and QWs of dilute nitride/bismide III-V semiconductors.

Focus: To study and contribute in these research domains.

Thesis Objective

To characterize, simulate and study new optoelectronic properties of II-VI NPLs/QRs and dilute nitride/bismide III-V QDs/QWs for optoelectronic applications.
1 Thesis Introduction, Motivation and Objective

2 Optoelectronic Theory of Semiconductors

3 II-VI CdSe/CdS Nanoplatelets & Quantum Ring
   - Dimension Effect
   - Temperature Effect
   - Alloying Effect
   - Excitonic Absorption
   - Quantum Ring

4 Dilute-Nitride-Bismide III-V Quantum Dots & Wells
   - GaNBiAs/GaAs Quantum Dots
   - GaNBiAs/GaAs Quantum Wells
   - InNBiAs/InP Quantum Dots
   - InNBiSb/InSb Quantum Wells

5 Thesis Conclusion and Closing Remarks
The bandstructure of InAs.

Solution of energy-eigenvalue eq. of semiconductor gives bandstructure ($E-k$ diagram/dispersion curve).

Ex.: Fig. 11.  

- Highest point of VB: $\Gamma$-point.
- Lowest point of CB:
  - at $\Gamma$-point: direct bandgap.
  - not at $\Gamma$-point: indirect bandgap.

- Study near $\Gamma$-point reveals electronic, magnetic, optical properties.

**Framework:** $k\cdot p$ perturbation theory.
The Schrödinger equation for an electron wavefunction $\psi_{nk}$ in the $n^{th}$ band with a wavevector $k$ is

$$\hat{H}\psi_{nk}(r) = \left( \frac{p^2}{2m_0} + U(r) \right) \psi_{nk}(r) = E_n(k) \psi_{nk}(r)$$

Written in terms of the Bloch function $u_{nk}(r)$, it becomes

$$\hat{H}\psi_{nk}(r) = \left( \frac{p^2}{2m_0} + \frac{\hbar}{m_0} k \cdot p + U(r) \right) u_{nk}(r) = \left( E_n(k) - \frac{\hbar^2 k^2}{2m_0} \right) u_{nk}(r)$$

Expanding the above eq. at $k_0 = 0$ in the $k$-space, it holds for $E_n(0)$.

$$\hat{H}\psi_{nk}(r) = \left( H_0 + \frac{\hbar}{m_0} k \cdot p \right) u_{nk}(r) = \left( E_n(k) - \frac{\hbar^2 k^2}{2m_0} \right) u_{nk}(r)$$

where $H_0 = \frac{p^2}{2m_0} + U(r)$ is the Hamiltonian and $H_0$ $u_{nk}(r) = E_n(0)$ $u_{nk}(r)$.

---

### $k \cdot p$ Hamiltonian Models | Variants\(^6\)

#### 8-band $k \cdot p$ Kane’s Basis:

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#### 16-band $k \cdot p$ Kane’s Basis:

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#### Luttinger-Kohn’s Model

Expressions and interpretation of Hamiltonian terms can be referred to in Sec. 2.3 in the thesis.
8-band $k \cdot p$ Model: First Basis Type (Appendix)

Basis

$|S\rangle \uparrow, |1+1\rangle \uparrow, |1,0\rangle \uparrow, |1-1\rangle \uparrow$ and $|S\rangle \downarrow, |1+1\rangle \downarrow, |1,0\rangle \downarrow, |1-1\rangle \downarrow$

Hamiltonian\(^7\)

$$H_{8 \times 8} =$$

$$
\begin{pmatrix}
A & i\hbar \sqrt{E_p} (k'_x + i k'_y) / \sqrt{2m_0} & i\hbar \sqrt{E_p} (k'_x - i k'_y) / \sqrt{2m_0} & 0 & 0 & 0 & 0 \\

B & C & D & 0 & 0 & 0 & 0 \\

c.c. & c.c. & E & C & 0 & 0 & 0 \\

c.c. & c.c. & c.c. & B & 0 & 0 & 0 \\

c.c. & c.c. & c.c. & c.c. & A & i\hbar \sqrt{E_p} (k'_x + i k'_y) / \sqrt{2m_0} & i\hbar \sqrt{E_p} (k'_x - i k'_y) / \sqrt{2m_0} \\

c.c. & c.c. & c.c. & c.c. & c.c. & B & C \\

c.c. & c.c. & c.c. & c.c. & c.c. & E & C \\

c.c. & c.c. & c.c. & c.c. & c.c. & c.c. & B \\
\end{pmatrix} + H_{so} + V_{NPL}
$$

Transition Matrix Element (TME)\(^7\)

$$P_{cv, i} = \langle \Psi_{c,k} | \hat{e} \cdot \mathbf{p}_i | \Psi_{v,k} \rangle \ , \ i = x, y, z$$

\(^7\)Expressions and interpretation of Hamiltonian terms and TME can be referred to in Sec. 2.3.1 in the thesis.
8-band $k \cdot p$ Model: Second Basis Type (Appendix)

\[ H_{k} + H_{\varepsilon} = \begin{bmatrix} H_{cb} & c.c. & c.c. & c.c. & c.c. & c.c. & c.c. & c.c. \\ 0 & H_{cb} & c.c. & c.c. & c.c. & c.c. & c.c. & c.c. \\ \frac{1}{\sqrt{2}} P_{-} & 0 & H_{hh} & c.c. & c.c. & c.c. & c.c. & c.c. \\ -\sqrt{\frac{2}{3}} P_{z} & \frac{1}{\sqrt{6}} P_{-} & S^{*} & H_{lh} & c.c. & c.c. & c.c. & c.c. \\ -\frac{1}{\sqrt{6}} P_{+} & -\sqrt{\frac{2}{3}} P_{z} & -R^{*} & 0 & H_{lh} & c.c. & c.c. & c.c. \\ 0 & -\frac{1}{\sqrt{2}} P_{+} & 0 & -R^{*} & -S^{*} & H_{hh} & c.c. & c.c. \\ -\frac{1}{\sqrt{3}} P_{z} & -\frac{1}{\sqrt{3}} P_{-} & S^{*} & -D & -\sqrt{\frac{3}{2}} S & \sqrt{2} R & H_{so} & c.c. \\ -\frac{1}{\sqrt{3}} P_{+} & \frac{1}{\sqrt{3}} P_{z} & -\sqrt{2} R^{*} & -\sqrt{\frac{3}{2}} S^{*} & D & \frac{5}{\sqrt{2}} & 0 & H_{so} \end{bmatrix} \]

\[ P_{cv,i} = \langle \psi_{c,k} | \hat{e} \cdot \hat{p}_{i} | \psi_{v,k} \rangle \quad , \quad i = x, y, z \]

---

Expressions and interpretation of Hamiltonian terms and TME can be referred to in Sec. 2.3.2 in the thesis.
16-band $k \cdot p$ Model: First Basis Type (Appendix)

Basis

$|S\rangle \uparrow, |S\rangle \downarrow, |1 + 1\rangle \uparrow, |1, 0\rangle \uparrow, |1 - 1\rangle \uparrow, |1 - 1\rangle \downarrow, |1, 0\rangle \downarrow, |1 + 1\rangle \downarrow, |S_N\rangle \uparrow, |S_N\rangle \downarrow, |1 + 1_{Bi}\rangle \uparrow, |1, 0_{Bi}\rangle \uparrow, |1 - 1_{Bi}\rangle \uparrow, |1 - 1_{Bi}\rangle \downarrow, |1, 0_{Bi}\rangle \downarrow, |1 + 1_{Bi}\rangle \downarrow$. Here $|1, \pm 1\rangle \uparrow\downarrow = (|X\rangle \pm i|Y\rangle) / \sqrt{2} \uparrow\downarrow$, $|1, \pm 1\rangle \uparrow\downarrow = (|X_{Bi}\rangle \pm i|Y_{Bi}\rangle) / \sqrt{2} \uparrow\downarrow$ and $|1, 0_{Bi}\rangle \uparrow\downarrow = |Z_{Bi}\rangle \uparrow\downarrow$.

Hamiltonian$^9$

$$H_{16 \times 16} = \begin{pmatrix} H_{10 \times 10} & H_{10 \times 6} \\ H_{6 \times 10} & H_{6 \times 6} \end{pmatrix} + V_0. \text{ And } H_{10 \times 10} = \begin{pmatrix} E^C & i \sqrt{2} P^* & i P_z & i \sqrt{2} P^* & 0 & 0 & 0 & V_N & 0 \\ 0 & E^C & 0 & 0 & 0 & \sqrt{2} P^- & i P_z & i \sqrt{2} P^* & 0 & V_N \\ -i \sqrt{2} P^- & 0 & H H & S & R & 0 & 0 & 0 & 0 \\ -i P_z & 0 & S^* & Q - 2 \lambda & S & -\sqrt{2} \lambda & 0 & 0 & 0 & 0 \\ -i \sqrt{2} P^* & 0 & R^* & S^* & H H - \lambda & \sqrt{2} \lambda & 0 & 0 & 0 & 0 \\ 0 & -i \sqrt{2} P^- & 0 & -\sqrt{2} \lambda & 0 & H H - \lambda & S & R & 0 & 0 \\ 0 & -i P_z & 0 & 0 & \sqrt{2} \lambda & S^* & Q - 2 \lambda & S & 0 & 0 \\ 0 & -i \sqrt{2} P^* & 0 & 0 & 0 & R^* & S^* & H H & 0 & 0 \\ V_N & 0 & 0 & 0 & 0 & E^N & 0 \\ 0 & V_N & 0 & 0 & 0 & 0 & E^N & 0 & 0 \end{pmatrix}$$

Transition Matrix Element (TME)$^9$

$$P_{cv,i} = \langle \psi_{c,k} | \hat{e} \cdot \mathbf{p}_i | \psi_{v,k} \rangle, \quad i = x, y, z$$

$^9$Expressions and interpretation of Hamiltonian terms and TME can be referred to in Sec. 2.3.3 in the thesis.
16-band $k\cdot p$ Model: Second Basis Type (Appendix)

### Basis

$$
|S_N \uparrow\rangle, |S_N \downarrow\rangle, |S \uparrow\rangle, |S \downarrow\rangle, -\frac{i}{\sqrt{2}} |(X + iY) \uparrow\rangle, -\frac{i}{\sqrt{6}} |(X + iY) \downarrow -2Z \uparrow\rangle, \frac{i}{\sqrt{6}} |(X - iY) \uparrow +2Z \downarrow\rangle, \frac{i}{\sqrt{2}} |(X - iY) \downarrow\rangle \\
\frac{i}{\sqrt{3}} |(X + iY) \downarrow +Z \uparrow\rangle, \frac{i}{\sqrt{3}} |(X - iY) \uparrow -Z \downarrow\rangle, -\frac{i}{\sqrt{2}} |(X_{Bi} + iY_{Bi}) \uparrow\rangle, -\frac{i}{\sqrt{6}} |(X_{Bi} + iY_{Bi}) \downarrow -2Z_{Bi} \uparrow\rangle \\
\frac{i}{\sqrt{6}} |(X_{Bi} - iY_{Bi}) \uparrow +2Z_{Bi} \downarrow\rangle, \frac{i}{\sqrt{2}} |(X_{Bi} - iY_{Bi}) \downarrow\rangle, \frac{i}{\sqrt{3}} |(X_{Bi} + iY_{Bi}) \downarrow +Z_{Bi} \uparrow\rangle, \frac{i}{\sqrt{3}} |(X_{Bi} - iY_{Bi}) \uparrow -Z_{Bi} \downarrow\rangle
$$

### Hamiltonian

$$
H_{16 \times 16} = \begin{bmatrix}
H_{2 \times 2} & H_{2 \times 8} & 0 \\
H_{8 \times 2} & H_{8 \times 8} & H_{6 \times 6} \\
0 & H_{8 \times 8} & H_{6 \times 6}
\end{bmatrix}
$$

And $H_{8 \times 8} =$

$$
\begin{bmatrix}
E^c & c.c. & c.c. & c.c. & c.c. & c.c. & c.c. & c.c. \\
0 & E^c & c.c. & c.c. & c.c. & c.c. & c.c. & c.c. \\
\frac{1}{\sqrt{2}}P_- & 0 & P + Q & c.c. & c.c. & c.c. & c.c. & c.c. \\
-\sqrt{\frac{2}{3}}P_z & \frac{1}{\sqrt{6}}P_- & S^* & P - Q & c.c. & c.c. & c.c. & c.c. \\
-\frac{1}{\sqrt{6}}P_+ & -\sqrt{\frac{2}{3}}P_z & -R^* & 0 & P - Q & c.c. & c.c. & c.c. \\
0 & -\frac{1}{\sqrt{2}}P_+ & 0 & -R^* & -S^* & P + Q & c.c. & c.c. \\
-\frac{1}{\sqrt{3}}P_z & \frac{1}{\sqrt{3}}P_- & \frac{S^*}{\sqrt{3}} & -\sqrt{2}Q & -\sqrt{\frac{2}{3}}S & \sqrt{2}R & P - \Delta & c.c. \\
-\frac{1}{\sqrt{3}}P_+ & \frac{1}{\sqrt{3}}P_z & -\sqrt{2}R^* & -\sqrt{\frac{3}{2}}S^* & \sqrt{2}Q & \frac{S}{\sqrt{2}} & 0 & P - \Delta
\end{bmatrix}
$$

### Transition Matrix Element (TME)

$$
P_{cv,i} = \langle \Psi_v, k | \hat{\mathbf{e}} \cdot \mathbf{p}_i | \Psi_v, k \rangle \quad , \quad i = x, y, z
$$

---

10 Expressions and interpretation of Hamiltonian terms and TME can be referred to in Sec. 2.3.4 in the thesis.
Strain Effects on Bandstructure (1/2) | Impact

- Strain changes the energy bandstructure profile.

**Fig. 12:** $HH$ and $LH$ degeneracy fails to exist during strain. In compressive strain $E_{HH} > E_{LH}$, and in tensile strain $E_{HH} < E_{LH}$. But $|\delta E_{LH}| > |\delta E_{HH}|$ always holds.

**Fig. 13:** (a) Bandstructure of bulk Ge, (b) Bandstructure of tensile strained Ge, (c) Bandstructure of tensile strained $n^+$ Ge with n-type doping to fill $e^-$ in L valley.

- Bulk Ge has 136 meV difference between direct & indirect bandgap.  

11 Image Courtesy: Fig. 13 is from J. Liu, et al., Thin Solid Films, 520, 8, 3354 (2012)
Strain Effects on Bandstructure (2/2) | Calculations

For a quantum well growing along the $z$ direction, the strain components are

$$\epsilon_{xx} = \epsilon_{yy} = \frac{a_{subs} - a_{well}}{a_{well}}$$

where $a_{subs}$ and $a_{well}$ are the lattice constants of the substrate and the well materials respectively.

However, for non-uniform strain (such as in QDs), to calculate the strain we use Valence Force Field (VFF) model based on atomistic elasticity.\(^{12}\)

$$E_{strain} = \sum_{i(j)} \varepsilon_{2B}(r_i - r_j) + \sum_{i(j,k)} \varepsilon_{3B}(\hat{\theta}_{ijk})$$

$$E_{strain} = \frac{1}{2} \sum_{i(j)} \frac{3\alpha_{i-j}}{8d_{0,i-j}^2} \left( |r_i - r_j|^2 - d_{0,i-j}^2 \right)^2$$

$$+ \sum_{i(j,k)} \frac{3\beta_{j-i-k}}{8d_{0,i-j}d_{0,i-k}} \left( |r_i - r_j||r_i - r_k| - \cos \hat{\theta}_{ijk} \cdot d_{0,i-j} d_{0,i-k} \right)^2$$

where $i$, $j$ and $k$ index the atom indices; $d_{0,i-j}$ is the ideal bond length between atom $i$ & atom $j$. The force on atom $i$ is given by $F_i = -\nabla_i (E_{strain})$ and each atom vibrates and moves along the force direction, until net-force = 0.

Fermi level and Fermi function

- ‘Fermi level’ is the term used to describe the top of the collection of electron energy levels at absolute zero temperature.
- The Fermi function \( f = 1/[1 + e^{(E-E_f)/k_B T}] \) gives the probability that a given available electron energy state will be occupied at a given temperature.

Quasi-Fermi energy distribution

\[
f_c = \frac{1}{1 + e^{(E-E_{f_c})/k_B T}} \\
f_v = \frac{1}{1 + e^{(E-E_{f_v})/k_B T}}
\]

- \( f_c \) and \( f_v \) are the probability of electron occupation in the CB \& VB respectively.
- \( E_{f_c} \) and \( E_{f_v} \) are the quasi-Fermi energy level for CB \& VB. \( \Delta F = E_{f_c} - E_{f_v} \).
- Optical gain \( \propto \text{Fermi factor}^{13} \)
  \( = (f_c - f_v) = f_c(1 - f_v) - f_v(1 - f_c) \).

13 Gain Fermi factor = \( f_c - f_v \) and Spontaneous Radiative Fermi factor = \( f_c(1 - f_v) \). [Sec. 2.5.2 in thesis].

Optical Processes in Semiconductors
Optical Absorption, Emission and Gain

Optical gain = growth ratio of light intensity (photon density) per unit length of light propagation. Unit: (1/cm).

When a photon is incident of an semiconductor media, it could either
(1) get absorbed or (2) generate gain.

1. Absorption of photon: Transition of an e− from a lower to a higher energy band creates an e−/h+ pair.
2. Stimulated recombination of an existing e−/h+ pair: Generates a second photon ⇒ Gain.

The generated photon has the same phase/wavelength as the incident photon ⇒ doubling the monochromatic wave amplitude ⇒ Amplification/Gain.
Non-Excitonic Optical Gain (Appendix)

For 0D QDs (based on the density-matrix theory eqn.)

\[
\mathcal{G}(\hbar \omega) = \frac{2\pi e^2}{cn_r \varepsilon_0 m_e^2 \Omega} \sum_{c,v} \frac{|P_{cv}|^2 (f_c - f_v)}{\omega_{cv}} \times L_{cv}(\hbar \omega - \hbar \omega_{cv})
\]

\[
L_{cv}(\hbar \omega - \lambda) = \frac{1}{\pi} \frac{\hbar/\tau_{in}}{(\hbar \omega - \lambda)^2 + (\hbar/\tau_{in})^2}
\]

For 2D NPLs & QWs (based on the density-matrix theory eqn.)

\[
\mathcal{G}(\hbar \omega) = \left[ 1 - \exp \left( \frac{\hbar \omega - \Delta F}{k_B T} \right) \right] \frac{\pi^2 c^2 \hbar}{n^2 \omega^2} \mathcal{R}_{sp}(\hbar \omega)
\]

\[
\mathcal{R}_{sp}(\hbar \omega) = \frac{ne^2 \omega}{\pi m_e^2 \varepsilon_0 \hbar c^3} \sum_c \sum_v \int \int \frac{|P_{cv}|^2}{4\pi^2 d} f_c f_v \times L_{cv}(\hbar \omega_{cv} - \hbar \omega) dk_x dk_y
\]

\[
\mathcal{R}_{st}(\hbar \omega) = \left[ 1 - \exp \left( \frac{\hbar \omega - \Delta F}{k_B T} \right) \right] \cdot \mathcal{R}_{sp}(\hbar \omega)
\]
Excitonic Optical Gain for 0D QDs\textsuperscript{14} (Appendix)

Excitonic bound state contributions

$$G^{\text{ex}, b} (\hbar \omega) = \frac{\pi e^2}{n_r c \varepsilon_0 m_0^2 \omega d} \sum_{c, v} |\psi_1^{cv} (0)|^2 |P_{cv}|^2 |I_{cv}|^2 \times (f_c - f_v) \mathcal{L} (\hbar \omega - \hbar \omega_{cv} - \hbar \omega_b)$$

$$\psi_{1s} (x) = \frac{4 \beta}{a_B \sqrt{2 \pi}} e^{-2x \beta / a_B} \text{ and } \hbar \omega_b = -4\beta^2 R_y$$

Band-to-band continuum state contributions

$$G^c (\hbar \omega) = \frac{\pi e^2}{n_r c \varepsilon_0 m_0^2 \omega V} \sum_{c, v} |P_{cv}|^2 (f_c - f_v) \times S_{2D} (\hbar \omega - \hbar \omega_{cv}) \mathcal{L} (\hbar \omega - \hbar \omega_{cv})$$

$$S_{2D} (\hbar \omega - \hbar \omega_{cv}) = \frac{2}{1 + \exp \left( -2\pi \sqrt{R_y} / (\hbar \omega - \hbar \omega_{cv}) \right)} \quad (2D \text{ Sommerfeld enhancement})$$

\textsuperscript{14}Exciton binding energy of CdSe = 15 meV, CdS = 26 meV [J. Voigt, et al., Physica Status Solidi (B), 91, 1, 189 (1979)]
Excitonic Optical Gain for 2D NPL & QWs\textsuperscript{15} (Appendix)

**Excitonic bound state contributions**

\[
\alpha^{\text{ex}, b} (\hbar \omega) = \frac{\pi e^2}{2 \omega n_r m_0 \varepsilon_0 c} \sum_{n_c, n_v} \frac{|P_{cv}|^2}{d} \left| l_{cv} \right|^2 \left| \varphi_{ns} (0) \right|^2 \frac{\tau_{\text{ex}}}{n_c n_v \hbar} \text{sech} \left[ \frac{\hbar \omega_{cv} - \hbar \omega_b - \hbar \omega}{n_c n_v \hbar / \tau_{\text{ex}}} \right]
\]

\[
\hbar \omega_b = \frac{\hbar \omega_{3D}^B}{[n - (1/2)]^2} \quad \text{and} \quad \left| \varphi_{ns} (0) \right|^2 = \frac{1}{\pi a_B [n - (1/2)]^2}
\]

**Band-to-band continuum state contributions**

\[
\alpha^c (\hbar \omega) = \frac{\pi e^2 n_r^{-1}}{2 \omega m_0 \varepsilon_0 c} \sum_{n_c, n_v} \int \int \frac{|P_{cv}|^2}{4 \pi^2 d} S_{2D} (\hbar \omega - \hbar \omega_{cv}) \times \frac{\tau}{n_c n_v \hbar} \text{sech} \left[ \frac{\hbar \omega_{cv} - \hbar \omega}{n_c n_v \hbar / \tau} \right] dk_x dk_y
\]

\textsuperscript{15} Exciton binding energy of CdSe = 15 meV, CdS = 26 meV [J. Voigt, et al., \textit{Physica Status Solidi (B)}, 91, 1, 189 (1979)]
Temperature Effect on Bandgap

- Semiconductor band gap, $E_g$ varies $\sim 10^2$ meV from 10 K to RT.
- $dE_g/dT < 0$ due to (i) the thermal dilatation of the lattice $\propto T$ at high temp, and (ii) electron-phonon interaction $\propto T^2$ at low temp and $\propto T$ at high temp.

Relation between band gap and temperature

Varshni reln.: $E_g(T) = E_g(0) - \frac{\alpha T^2}{\beta + T}$

O’Donnell reln.: $E_g = E_g(0) - \frac{2S\langle\hbar\omega\rangle}{e^{\langle\hbar\omega\rangle/k_BT} - 1}$

Cardona reln.: $E_g = E_g(0) - \frac{2a_{ep}}{e^\Theta/T - 1}$

- $\alpha$ and $\beta$ are material constants.
- O’Donnell and Cardona consider the Bose-Einstein statistical factors for phonon emission and absorption.
- $S$ is a dimensionless electron-phonon coupling constant (vibronic model of Huang and Rhys). $\langle\hbar\omega\rangle$ is the average phonon energy.
- $a_{ep}$ is the exciton-phonon coupling constant and $\Theta$ is the average phonon temperature, the average phonon energy being $k_B\Theta$.

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# II-VI CdSe/CdS Nanoplatelets & Quantum Ring

## Literature Review

**NPLs:** Atomically flat quasi-2D quantum confined nanocrystals, synthesized using wide bandgap II-VI semiconductors such as CdSe, CdS, etc.\(^{17}\)

- Colloidal synthesis: High quantum efficiency and cost-effective.

**Properties:**
- Wide bandgap tunability
- Fast fluorescence lifetime
- Narrow emission spectra (FWHM)
- Range: near IR to visible
- Thickness ~ Bohr radius
- High quantum yield: > 80%
- Low auger recombination
- Low inhomogeneous broadening
- Low coulomb blockade
- Efficient carrier injection
- Femtosecond cooling dynamics
- Giant oscillator strength transition (GOST)
- Low threshold emission

**Recent report:** Emission threshold 41µJ/cm\(^2\) & PL FWHM 2 nm.\(^{18}\); CW laser.\(^{19}\)

**NPLs vs. QWs:** NPLS have enhanced splitting between bright and dark excitons due to dielectric confinement & giant GOST.\(^{20}\)

**NPLs vs. QDs:** NPLs have smaller (~ 2 orders of magnitude) fluorescent lifetimes than QDs due to fast band-edge exciton recombination.

**NPL applications:** photovoltaics, photodetectors, laser, solar cells, etc.

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II-VI Quantum Rings (QRs) | Literature Review

QRs: Topologically inverted type-I core/crown NPL heterostructure. Active material of lower $E_g$ laterally grown around barrier of higher $E_g$ (Ex: CdS/CdSe).

QRs vs. NPLs: Emission window of QRs are extended over NPLs due to excitonic recombinations in QR crown (band alignment).

Properties:
- Non-trivial topology
- High optical tunability
- High charge injection efficiency
- Enhanced absorption range

Recent report: Type-I CdS/CdSe QRs have an emission range spanning from that of core CdS NPLs to that of core CdSe NPLs.

QR applications:
- Phosphors for color conversion in white light LEDs.
- Magneto-optical device applications (Aharonov-Bohm effect.)
- Charge separator for solar cells and LEDs.

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21 S. Lamarre, et al., arXiv:1509.07793v2
Thesis Introduction, Motivation and Objective

Optoelectronic Theory of Semiconductors

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- GaNBiAs/GaAs Quantum Dots
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Thesis Conclusion and Closing Remarks
Research Problem and Objective

- Optoelectronic properties of II-VI NPLs are strongly geometry dependent.
- But most studies on CdSe and CdS NPLs are characterized only by thickness. Emission wavelength is claimed to be only dependent on atomic-layer thickness.\(^{24}\)
- Lateral sizes often vary in these observations but are commonly neglected.
- Chapter objective: To study of the effect of vertical thickness and lateral size for CdSe and CdS NPLs.

We have studied CdSe and CdS NPLs in the ZB phase, assuming they are colloidally synthesized.

The thickness and lateral sizes are varied to study the electronic bandstructure and optical properties.

Variation in size: 7, 11, 15, 20 nm; and thicknesses: 5 to 8 ML.
**Fig. 15:** For CdSe and CdS NPLs: E1–H1 transition energy/wavelength and TME: (a) and (b) vs. lateral size; and (c) and (d) vs. thickness.

- CdSe has lower emission energy due to smaller $E_g$. It is also marginally more sensitive to size effect.
- CdSe has a higher TME as its CB $e^-$ strongly couple with VB $h^+$.
- For CdSe ($m_e^* = 0.13$) < For CdS ($m_e^* = 0.25$) $\Rightarrow$ more concave dispersion curve relating from $m^* = \hbar^2 \left( \frac{\partial^2 E}{\partial k^2} \right)^{-1}$. 
Fig. 16: Electronic bandstructure and band mixing probability for CdSe NPLs of (a) 15 nm × 15 nm × 5 ML, (b) 20 nm × 20 nm × 5 ML, (c) 15 nm × 15 nm × 6 ML, (d) 20 nm × 20 nm × 6 ML.

- For CdSe NPLs, increasing thickness from 5 to 6 ML red shifts the emission energy by 900 meV, while increasing size from 15 to 20 nm shifts by 100 meV.
- The effective heavy hole mass is much more than the effective electron mass.
- First 10 h+ spans ~10–12 meV, while first 10 e− spans ~400–500 meV.
**Fig. 17:** Spatial charge density of first 10 CB $e^-$ and VB $h^+$ for CdSe NPLs of $15 \text{ nm} \times 15 \text{ nm} \times 5 \text{ ML}$ at 300 K ($x$-$y$ plane at $z = 0$). $hh = $ heavy hole, $lh = $ light hole.

- E4 & H4: $d_{xy}$-like. E5 & H6: $d_{x^2-y^2}$-like. E6 & H5: $d_{z^2}$-like.
- H1 to H8: $hh$ dominated. H9 and H10: $lh$ dominated [see Fig. 16 (a)].
- In TE mode, E1–H1 ($hh$) transition is strongest ($\text{TME} = 0.45$), followed by the TM mode E1–H9 ($lh$) transition ($\text{TME} = 0.44$).
- Both H1 & H9 are $s$-like having favorable spatial wavefunction overlap with E1.
For CdS NPLs, increasing thickness from 5 to 6 ML red shifts the emission energy by 600 meV, while increasing size from 15 to 20 nm shifts by 100 meV.

First 10 \( h^+ \) spans \( \sim 6-8 \) meV, while first 10 \( e^- \) spans \( \sim 300-400 \) meV.

Spin-orbit splitting energy of CdS is over six times smaller than that of CdSe \( \Rightarrow \) it has a much higher contribution from split-off \( h^+ \).
**Dimension Effect** | **Spatial Charge Density (CdS)**

**Fig. 19:** Spatial charge density distributions of the first 10 CB e$^{-}$ and VB h$^{+}$ for CdS NPLs of 15 nm $\times$ 15 nm $\times$ 5 ML at 300 K (x-y plane at $z=0$). $hh =$ heavy hole, $lh =$ light hole, $so =$ split off hole.

- E4 & H4: $d_{xy}$-like. E5 & H8: $d_{x^2-y^2}$-like.
- H5, H9 and H10: varying ratios of $hh$, $lh$ and so holes.
- Dominant contributors: 44% so (H5), 43 % $hh$ (H9) and 34 % so (H10).
- In TE mode, E1–H1 ($hh$) transition is strongest (TME = 0.43), followed by the TM mode E1–H5 ($lh$/so) transition.
### Dimension Effect | Optical Gain Spectra (CdSe)

**Fig. 20:** Optical gain (cm\(^{-1}\)) of CdSe NPLs of lateral sizes (7, 11, 15, 20 nm) and thickness (5, 6, 7, 8 ML) for injection carrier density (1.0, 1.5, 2.0, 2.5 \(\times\) 10\(^{19}\) cm\(^{-3}\)) at 300 K. Across: ↑ thickness; Down: ↑ size.

- **Optical gain factors:**
  - TME, carrier density, Fermi factor, NPL dimensions, material, dephasing/scattering rate.
  - Increase in size and thickness ⇒ red shift in emission \(\lambda\).
  - **Dimension gradient of red shift:** \(< 0\).
  - \(\Delta \lambda \text{11nm–7nm} \approx 15 – 20\) nm,
  - \(\Delta \lambda \text{15nm–11nm} \approx 5 – 6\) nm,
  - \(\Delta \lambda \text{20nm–15nm} \approx 4 – 5\) nm.
  - \(\Delta \lambda \text{6ML–5ML} \approx 19 – 23\) nm,
  - \(\Delta \lambda \text{7ML–6ML} \approx 13 – 15\) nm,
  - \(\Delta \lambda \text{8ML–7ML} \approx 8 – 9\) nm.
  - **Injection carrier density \(\nabla\) of gain > 0 and \(\nabla^2 < 0\) (Band filling effect).
Fig. 21: For CdSe NPLs: Maximum gain at 300 K for carrier density (a) 2 and (b) $2.5 \times 10^{19}$ cm$^{-3}$; and Differential gain at 300 K for carrier density (c) 2 and (d) $2.5 \times 10^{19}$ cm$^{-3}$.

- Maximum peak gain depends on the TME, Fermi factor and volume of the NPL.
- It is higher for larger and thicker NPLs due to higher E and H wavefn. overlap.
- Differential gain: measure of the effectiveness of transforming injected carriers to photon emission. It’s smaller for higher density as we approach saturation.
**Fig. 22:** For CdSe NPLs: Fermi factor at 300 K with carrier density (a) 2 and (b) $2.5 \times 10^{19}$ cm$^{-3}$; and (c:) Transparency carrier density ($\times 10^{19}$ cm$^{-3}$) at 300 K.

- **Fermi factor:** Positive co-relation with size and thickness & carrier density.
- $(\Delta F - E_{\text{eff}}^g) \propto$ carrier density and size/thickness.
- **Note:** Gain spectrum is limited to $E_g < \hbar \omega < \Delta F$, which increases with density and size/thickness.
For geometrically identical NPLs with the same carrier density, CdS NPLs have a lower gain spectrum, maximum gain and a lower Fermi factor.

CdS needs higher carrier density than CdSe to obtain a near identical gain.

The peak positions of the CdS NPLs are less affected by dimension change.

**Fig. 23:** Optical Gain (cm$^{-1}$) of CdS NPLs of lateral sizes (11, 15 nm) and thickness (5, 6, 7, 8 ML) for injection carrier density ($1.0, 2.5, 4.0, 5.5 \times 10^{19}$ cm$^{-3}$) at 300 K. Across: ↑ thickness; Down: ↑ size.
Both thickness and lateral size significantly impact emission energy and TME, but differential change for thickness is larger.

\[ \Delta \text{Thickness} \geq \Delta \text{Size} \geq 0 \Rightarrow \text{red shift. Similar } \% \text{ variations } \Rightarrow \text{comparable red shift } \Rightarrow \text{lateral size is important parameter NPLs’ optical properties.} \]

\[ m_{hh}^* > m_e^* \Rightarrow hh \text{ dispersion curve is flatter than } e \text{ dispersion curve.} \]

For spatial charge density, material properties determines \( hh, lh \) and so-hole \( \% \) and \( s-p-d \) mixing.

Optical gain depends on TME, carrier density, Fermi factor, NPL dimensions, material, dephasing/scattering rate, etc.

Transparency carrier density decreases with increasing thickness and size.

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Temperature Effect | Chapter Objective

Research Problem and Objective

- In last 3–4 years, NPLs have been used in optoelectronic devices.\(^\text{25}\)
  Operating temperature affects the bandstructure and luminescence.

- Achtstein \textit{et al.} studied NPLs at the cryogenic range.\(^\text{26}\) Others have studied QDs, etc in varying temperature ranges.\(^\text{27}\)

- At elevated operating temperature (> RT), both reversible and irreversible luminescence quenching processes exist.\(^\text{28}\)

- \textbf{Chapter Objective}: To study NPL’s optoelectronic properties at elevated temperatures > RT (not reported yet).

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Temperature Effect | Band Energy/Mixing Probability

- We have studied quasi-2D CdSe NPLs of 22 nm x 8 nm x 4 ML, in temperature range 25°C to 90°C.

![Graph showing theoretical E1–H1 transition energy/wavelength vs. temperature.](image)

**Fig. 24:** Theoretical E1–H1 transition energy/wavelength vs. temperature.

- First 10 h⁺ spans ~140 meV, and first 10 e⁻ spans ~425 meV.

- In VB, first few levels are hh dominated followed by increased lh and so influence.

- Increase in temperature:
  - induces a faster reduction in the intra-CB state gaps compared to the intra-VB state gaps.
  - promotes e⁻ – h⁺ quantum state coupling

![Graph showing electronic bandstructure and band mixing probability for 4 ML CdSe NPLs.](image)

**Fig. 25:** Electronic bandstructure and band mixing probability for 4 ML CdSe NPLs at (b) 30 (c) 50 (d) 70°C.
**Fig. 26:** (a) Fermi factor for E1–H1 transition, and (b) $\Delta F$ compared with the E1–H1 transition energy in 4 ML CdSe NPLs vs. temperature for varying carrier densities.

- Both, Fermi factor $f_c(1 - f_v)$ and $\Delta F$ have a negative temperature gradient.
- $\Delta F > E1$–H1 ⇒ Bernard-Duraffourg inversion condition (population inversion) necessary for lasing.\(^{29}\)


**Fig. 27:** Quasi Fermi energy levels of the CB ($E_{fc}$) and VB ($E_{fv}$) in 4 ML CdSe NPLs vs. temperature under varying carrier densities.

- With increasing temperature, $E_{fc}$ and $E_{fv}$ approach each other and Fermi energy separation $\Delta F = E_{fc} - E_{fv}$ falls.
- Also fermions ($e^-/h^+$) get thermally excited.∴ probability of occupying higher CB and VB energy states is increased ⇒ $f_c$ falls & $f_v$ rises ⇒ Fermi factor falls.
**Temperature Effect | Fermi factor/energy & TME**

**Fig. 28:** (a) Fermi factor $f_c(1 - f_v)$ for E1–H1 transition, and (b) Fermi energy separation $\Delta F = E_{fc} - E_{fv}$ (eV) vs. temperature and carrier concentration in 4 ML CdSe NPLs.

- Fermi factor and $\Delta F$ increases with:
  - increasing carrier density.
  - decreasing temp.

- At higher temp., $f_c$ falls & $f_v$ rises $\Rightarrow$ Fermi factor falls.

- And thermally excited fermions occupy higher energy states $\Rightarrow$ E1–H1 TME falls.

- **TME**~ oscillator strength $f_{cv} \propto \mu_{cv}^2$.
  - $\mu_{cv} =$ transition dipole moment $= e\hbar P_{cv} / im_0 E_{cv}$.
  - $|c\rangle$ to $|v\rangle$ transition strength decreases with a rise in temp.

**Fig. 29:** TE mode TME for the E1–H1 transitions vs. temperature in 4 ML CdSe NPL.
**Temperature Effect | $\Delta E_n - H_m$, Fermi factor & TME**

**Fig. 30:** For 4 ML CdSe NPLs at 30°C: (a) $\Delta E_n - H_m$ – $min$ (2.42 eV) at $\Delta E1 – H1$, (b) Fermi factor for carrier density $3 \times 10^{19}$ cm$^{-3}$ – $max$ = 0.768 at $E1 – H1$, (c) TE mode TME – strongest (0.455) at $E1 – H1$, and (d) TM mode TME – strongest (0.358) at $E1 – H9$.

- $min(\Delta E_n – H_m) = 2.42$ eV at $\Delta E1 – H1$.
- $min(\text{Fermi factor}) = 0.768$ at $E1 – H1$.
- Transitions with Fermi factor $> 0$ contribute to the radiative recombination.
- TE mode TME – strongest (0.455) at $E1 – H1$ [heavy hole].
- TM mode TME – strongest (0.358) at $E1 – H9$. [light hole].
Temperature Effect | Spatial charge density

Fig. 31: Spatial charge density of first 10 e\(^-\) & h\(^+\) of 4 ML CdSe NPLs at 30\(^\circ\)C in the x-y plane (z = 0).

- Spatial charge density: square of e\(^-\) & h\(^+\) wavefunction |\(\psi^2\)|.
- Warmer (reddish) \(\Rightarrow\) higher & Cooler (bluish) \(\Rightarrow\) lower occupation probability.
- Rectangular boundary: our studied NPL (22 nm \(\times\) 8 nm)
- Temperature has inconsequential variation on spatial charge density. Major factors: piezoelectric strain and external electric fields.
Two NPL orientations in TEM: face view (flat) and edge view (stacked).

PL excitation wavelength = 350 nm. PL peak = 512 nm.\(^{30}\)

1\(^{st}\) absorption = 509 nm \([hh]\) (Stokes = 3 nm), 2\(^{nd}\) absorption = 480 nm \([lh]\).

TRPL: \(I(t) = a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2}\). PL decay lifetimes: \(\tau_1 = 0.34\) ns (radiative) & \(\tau_2 = 2.27\) ns (non-radiative) with 30% and 70% contribution.

Average lifetime = \(\tau_{avg} = (a_1 \tau_1^2 + a_2 \tau_2^2) / (a_1 \tau_1 + a_2 \tau_2) = 2.15\) ns.\(^{31}\)

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\(^{30}\) PL peak at 512 nm matches with E1–H1 energy prediction of 2.42 eV by our model.

\(^{31}\) Consistent with previous \(\tau_{avg}\) of CdSe NPLs at RT by M. D. Tessier, \textit{et al.}, \textit{Nano Lett.}, 13, 7, 3321 (2013).
Fig. 34: PL spectra of 4 ML CdSe NPLs while (a) ascending, and (b) descending temperature, respectively.

- **Measurements:** NPLs in thin-film form using a laser excitation wavelength of 355 nm at 0.5 mW power.
- **For every 10°C rise in temperature:**
  - Emission wavelength red-shifts by $\sim 2$ nm
  - PL intensity falls as the sample quality degrades
  - Spectrum broadens due to intraband scattering effect.
- **Upon decreasing the temperature to RT,** peak position and linewidth retrace substantially, but not the intensity.
Fig. 35: While ascending (black □) and descending (red ×) temp.: (a) PL emission energy/wavelength compared with E1–H1 values; (b) PL linewidth and intraband relaxation time $\tau_{in}$; (c) PL intensity compared with theoretical relative PL intensity; and (d) Arrhenius plot for PL integrated intensity. Symbols: blue + for theoretical data; green · · · dotted lines for fitted plots with the ascending temp. data.

- For a particular temp., emission energy & linewidth are almost identical in both.
- While cooling back to RT, intensity increases, but recovery is < 14%.
Temperature Effect | Emission energy, PL width & intensity

**Excitonic emission energy**

\[ E_{\text{exc}}(T) = E_{\text{exc}}(0) - 2a_{ep}/(e^{\Theta/T} - 1) \]

Upon fitting: \( E_{\text{exc}}(0) = 2.727 \text{ eV}, a_{ep} = 18.2 \pm 2.8 \text{ meV} \) and \( \Theta = 36 \pm 0.4 \text{ K} \).

Increased confinement (vs. QD) \( \Rightarrow \) ↑ \( E_{\text{exc}}(0) \), ↓ \( a_{ep} \) and ↓ \( \Theta \).

**PL linewidth**

\[ \Gamma(T) = \Gamma_0 + \gamma_{AC} T + \Gamma_{LO}/[e^{(\hbar\omega_{LO}/k_B T)} - 1] \]

Used \( \Gamma_0 \) (inhomogeneous broadening) = 32.5 meV and \( \hbar\omega_{LO} \) (exciton-longitudinal optical) = 25 meV.\(^{32}\) Upon fitting: \( \Gamma_{LO} = 236.3 \pm 11.8 \text{ meV} \) and \( \gamma_{AC} \) (exciton-acoustical) = 0.38 ± 0.03 meV [negligible \( \sim 0 \)]. \( \Gamma_{LO} >> \gamma_{AC} \).

**PL integrated intensity**

\[ I(T) = I(0)/[1 + C \cdot e^{-E_a/k_B T}] \]

Upon fitting, \( E_a = 494 \pm 6 \text{ meV} \). Irreversible losses (ligand loss/oxidative degradation) at high temp. \( \Rightarrow \) Nonretraceability in intensity. Reversible losses (dynamic/static quenching) \( \Rightarrow \) minimal retraceability.

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Temperature Effect | Experiment & Theory Comparison

Fig. 36: Comparison of normalized experimental (solid black) vs. theoretical (dotted blue) PL spectra of 4 ML CdSe NPLs at 30, 50 and 70°C.

- **PL peak position**: Theoretically calculated the temp. dependent E1–H1. Matched excellently with the experimental PL peak.
- **PL linewidth**: Used experimental linewidth to extract intraband relaxation time ($\tau_{in} = 2\hbar/$FWHM). Used to calculate spontaneous radiative rate from excitonic bound states and continuum-states.
- **PL intensity**: Theoretically calculated relative PL intensity, which exponentially falls with temp., as verified experimentally.
Temperature Effect | Low Temperature Comparison

**Fig. 37:** Comparison/extension of low $T$ PL emission energy by Achtstein et al.$^{33}$ ($L$) with our high $T$ E1–H1 transition energy ($R$).

- **Fig. 37:** PL emission at $512\pm3$ nm ($\sim 2.42$ nm) is from 4 ML NPLs. Comparison shows continuity in the PL emission energy.$^{33}$

- **Fig. 38:** Smooth continuity in the emission peak positions and linewidths.$^{34}$

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$^{33}$ Fig. 37: reprinted (adapted) w. permission fr. Achtstein, et al., *Nano Lett.*, 12, 6, 3151 (2012) © ACS.

$^{34}$ Fig. 38: reprinted (adapted) w. permission fr. Erdem, et al., *J. Phys. Chem. Lett.*, 7, 3, 548 (2016) © ACS.
Implications of rise in NPL operation temperature:

- Reduction in effective band-edge transition energy.
- Fall in optical TME strength.
- Reduction in intraband state gaps, faster in CB compared to VB.
- Promotion of interband $e-h$ coupling.
- Modification in $hh$-$lh$-$so$ band mixing probabilities.
- Reduction in Fermi factor.
- Reduction in quasi Fermi separation.
- Invariance in the charge density.
- Redshift in peak photon emission energy in PL spectra.
- Widening of PL spectral linewidth owing to intraband scattering.
- Exponential fall in PL intensity.
- Reversible and irreversible losses in PL traceability.

Chapter Publication

Research Problem and Objective

- Optoelectronic properties of II-VI NPLs are strongly dependent on type of semiconductor material.
- Traditionally, NPL thickness determined emission wavelength.
- But most studies on CdSe and CdS NPLs are characterized only by thickness. Emission wavelength is claimed to be only dependent on atomic-layer thickness.\(^{35}\)
- But, this can be bypassed by alloying NPL composition for continuous emission tunability.\(^{36}\)

- **Chapter objective**: To study of the effect of alloying CdS\(_x\)Se\(_{1-x}\) NPLs in contrasting sizes, thicknesses and temperature.


Alloying Effect | Energy & TME vs. alloy composition

- We have studied CdS$_x$Se$_{1-x}$ NPLs of varying the alloy composition, varying $x$ from 0 to 1, in steps of 0.2.
- NPLs: (i) 12 nm $\times$ 12 nm $\times$ 5 ML/300K, (ii) 15 nm $\times$ 15 nm $\times$ 5 ML/300K, (iii) 15 nm $\times$ 15 nm $\times$ 5 ML/350K and (iv) 15 nm $\times$ 15 nm $\times$ 6 ML/300K.

![Graphs showing transition energy and TME vs. Se fraction](image)

**Fig. 39:** For CdS$_x$Se$_{1-x}$ NPLs: (a) E1–H1 transition energy with bowing parameter = 0.28 eV, and (b) TE mode TME of E1-H1 vs. Se fraction (1 $-$ x).

- E1–H1 of CdS $>$ CdSe. E1–H1 concavity due to optical bowing coefficient.
- E1–H1 decreases with Se fraction (1 $-$ x), and increasing NPL volume.
- TME increases with Se fraction (1 $-$ x), and increasing NPL volume.

---

Alloying Effect | Band Energy/Mixing Probability

- $m_{h,\text{CdS}}(0.98) > m_{h,\text{CdSe}}(0.62) \Rightarrow$ flatter dispersion curve in CdS $\Rightarrow$ first 10 $h^+$ range $\sim 105 \text{ meV}$ in CdS & $\sim 120 \text{ meV}$ in CdSe.
- $m_{e,\text{CdS}}(0.25) > m_{e,\text{CdSe}}(0.12) \Rightarrow$ flatter dispersion curve in CdS $\Rightarrow$ first 9 $e^-$ range $\sim 125 \text{ meV}$ in CdS & $\sim 216 \text{ meV}$ in CdSe.
- $m^* = \hbar^2 \left( \frac{\partial^2 E}{\partial k^2} \right)^{-1}$
- $\therefore m_{h}^* > m_{e}^*$ for both, H states are closely packed than E states.
- $\therefore \Delta_{so,\text{CdS}} > 6 \times \Delta_{so,\text{CdSe}}$, band-mixing probabilities in CdS has higher contribution from so holes than in CdSe.

Fig. 40: Bandstructure and band-mixing probability for 5 ML (a) CdS and (b) CdSe NPLs of size 12 nm at 300 K.

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Alloying Effect | Spatial charge density

Fig. 41: Spatial charge density of first 10 CB $e^-$ and VB $h^+$ of 5 ML (a) CdS and (b) CdSe NPLs of size 12 nm at 300 K ($x$-$y$ plane at $z = 0$). $hh$ = heavy hole, $lh$ = light hole, $so$ = split-off hole.

- In CdS: H1 to H3 & H9: $hh$ dominated. Others: H4 (38% $hh$), H5 (47% $hh$), H6 (41% $so$), H7 (46% $hh$), H8 (36% $so$), H10 (49% $hh$).
- In CdSe: H1 to H7 & H9: $hh$ dominated. Others: H8 (88% $lh$), H10 (49% $lh$).
Alloying Effect | $\Delta E_n - H_m$, Fermi factor & TME

Fig. 42: For 5 ML CdS NPLs of size 12 nm (a) $\Delta E_n - H_m = \min (2.82 \text{ eV})$ at $\Delta E_1 - H_1$, (b) Fermi factor for carrier density $2.5 \times 10^{19} \text{ cm}^{-3} - \max = 0.38$ at $E_1 - H_1$, (c) TE mode TME – strongest (0.427) at $E_1 - H_1$ [heavy hole], and (d) TM mode TME – strongest (0.02) at $E_1 - H_8$ [mix].
**Alloying Effect**

\[ \Delta E_{n-H_m}, \text{Fermi factor & TME} \]

- **min(\(\Delta E_{n-H_m}\)) = 2.29 eV at \(\Delta E_{1-H1}\).**
- **min(Fermi factor) = 0.69 at \(E_{1-H1}\).**
- Transitions with Fermi factor > 0 contribute to the radiative recombination.
- TE mode TME – strongest (0.447) at \(E_{1-H1}\) [heavy hole].
- TM mode TME – strongest (0.429) at \(E_{1-H8}\) [light hole].

**Fig. 43:** For 5 ML CdSe NPLs of size 12 nm (a) \(\Delta E_{n-H_m} - \text{min}\) (2.29 eV) at \(\Delta E_{1-H1}\), (b) Fermi factor for carrier density \(2.5 \times 10^{19} \text{ cm}^{-3}\) – max = 0.69 at \(E_{1-H1}\), (c) TE mode TME – strongest (0.447) at \(E_{1-H1}\), and (d) TM mode TME – strongest (0.429) at \(E_{1-H8}\).

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**II-VI CdSe/CdS Nanoplatelets & Quantum Ring**

**Semiconductor Quantum Nanostructures for Optoelectronic Applications** | Sumanta Bose | sumanta001@e.ntu.edu.sg
Alloying Effect | Optical Gain Spectra

**Fig. 44:** Optical gain (cm$^{-1}$) of (a) CdS (b) CdS$_{0.8}$Se$_{0.2}$ (c) CdS$_{0.6}$Se$_{0.4}$ (d) CdS$_{0.4}$Se$_{0.6}$ (e) CdS$_{0.2}$Se$_{0.8}$ and (f) CdSe NPLs of size 15 nm & thickness 5 ML at 300 K, for carrier densities (1 to 3 $\times$ 10$^{19}$ cm$^{-3}$).

- From CdS to CdSe, peak position redshifts.
- From CdS to CdSe, gain increases $\because$ CdSe NPLs have higher Fermi factor compared to CdS NPLs.
- With increase in the carrier density, the peak position slightly blueshifts.
- Injection carrier density $\nabla$ of gain $> 0$ and $\nabla^2 < 0$ (Band filling effect).
Alloying Effect | Fermi factor, Max. & Diff. Gain

- $m_{h,CdS}^{*}(0.98) > m_{h,CdSe}^{*}(0.62)$ & $m_{e,CdS}^{*}(0.25) > m_{h,CdSe}^{*}(0.12)$.
- CdSe has higher concavity of the dispersion curves → larger quasi Fermi level separation → higher Fermi factor.
- From CdS to CdSe transparency carrier density decreases.
- Max. gain increases, while diff. gain decreases (saturates) with carrier density.

**Fig. 45:** Fermi factor vs. carrier density for 15nm–5ML Cd$_x$Se$_{1-x}$ NPLs at 300 K.

**Fig. 46:** (a) Maximum gain (cm$^{-1}$) and (b) Differential gain (cm$^2$) vs. carrier density (cm$^{-3}$) for 15nm–5ML Cd$_x$Se$_{1-x}$ NPLs at 300 K.
Alloying Effect

**Fig. 47:** (a) Fermi factor vs. Se fraction \((1-x)\) in \(\text{CdS}_x\text{Se}_{1-x}\) NPLs with an injection carrier density of \(2.5 \times 10^{19} \text{ cm}^{-3}\) at 300 K; and (b) Transparency carrier density \((\text{cm}^{-3})\) vs. Se fraction \((1-x)\) in \(\text{CdS}_x\text{Se}_{1-x}\) NPLs.

- \(m^*_h,\text{CdS}(0.98) > m^*_h,\text{CdSe}(0.62)\) & \(m^*_e,\text{CdS}(0.25) > m^*_h,\text{CdSe}(0.12)\).
- CdSe has higher concavity of the dispersion curves \(\Rightarrow\) larger quasi Fermi level separation \(\Rightarrow\) higher Fermi factor.
- From CdS to CdSe transparency carrier density decreases.
Chapter Highlights

- Emission wavelength of CdS$_x$Se$_{1-x}$ NPLs can be continuously tuned by changing material composition.

- Variations in composition affects energy levels, band-mixing probabilities and optical gain.

- NPLs with higher Se fraction, have a larger TME due to a lower effective $e^-$ & $h^+$ masses; and produce larger gain due to their higher Fermi factors; and exhibit transparency at lower densities.

- For NPLs of the same composition, larger NPLs have lower E1–H1; and have a slight blueshift (and rise in intensity) with increasing carrier density due to band-filling effect.

Chapter Publication

Semiconductor Quantum Nanostructures for Optoelectronic Applications

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II-VI CdSe/CdS Nanoplatelets & Quantum Ring

Excitonic Absorption

Presentation Navigator

1. Thesis Introduction, Motivation and Objective
2. Optoelectronic Theory of Semiconductors
3. II-VI CdSe/CdS Nanoplatelets & Quantum Ring
   - Dimension Effect
   - Temperature Effect
   - Alloying Effect
   - Excitonic Absorption
   - Quantum Ring
4. Dilute-Nitride-Bismide III-V Quantum Dots & Wells
   - GaNBiAs/GaAs Quantum Dots
   - GaNBiAs/GaAs Quantum Wells
   - InNBiAs/InP Quantum Dots
   - InNBiSb/InSb Quantum Wells
5. Thesis Conclusion and Closing Remarks
Research Problem and Objective

- Quasi-2D NPLs experience strong 1D confinement $\Rightarrow$ Large $E_b^{ex}$ and increased exciton center-of-mass extension $\Rightarrow$ GOST.\(^{39}\)
- This significantly enhances the NPL’s absorption cross-section,\(^{39}\) affecting photon absorption and quantum yield.
- Absorption spectra of NPLs have a well recognized signature:\(^{40}\) higher intensity $HH$ peak, and blue-shifted lower intensity $LH$ peak.
- Ultrathin sub-nm (2 ML) NPLs: Anomalous properties – increased intrinsic absorption & inverted $HH/LH$ relative peak intensities.\(^{41}\)
- **Chapter Objective:** To study bandstructure and polarization dependent excitonic absorption of CdSe NPLs, with focus on 2 ML.

---


We study excitonic absorption CdSe NPLs of thicknesses: 2, 4, 6 and 8 ML.

**Fig. 48:** E1, H1 and E1–H1 energy for 2, 4, 6 and 8 ML CdSe NPLs. H1 is HH in all four cases.

- Vertical confinement reduces with increase in NPL thickness ⇒ E1–H1 falls.
- Intraband state-gaps in CB & VB falls.
- Rate of intraband state-gaps reduction: VB > CB, ∴ \( m_e^* = 0.12 \) < \( m_h^* = 0.62 \) from \( m^* = \hbar^2 \left( \frac{\partial^2 E}{\partial k^2} \right)^{-1} \)

**Fig. 49:** Energy dispersion of first 3 e\(^-\) & first 5 h\(^+\) in CdSe NPLs of (a) 2 ML; (b) 4 ML; (c) 6 ML; (d) 8 ML. E = e\(^-\), HH = heavy h\(^+\), LH = light h\(^+\), SO = split-off h\(^+\).

- E and H subbands are isotropic due to the isotropy \( m_e^* \) & \( m_h^* \).
- H1: HH dominated; H2: LH dominated.
CB states: primarily E, mild infusion of LH and SO.

H1: HH dominated. H2: LH dominated, more with thickness.

Higher VB states: SO contribution.

Lower the $\Delta_{so}$, higher the extent of SO contributions in VB states.

**Table 1:** Predominant hole-type for the first 5 VB levels for 2, 4, 6 and 8 ML CdSe NPLs.

<table>
<thead>
<tr>
<th>VB level</th>
<th>2 ML</th>
<th>4 ML</th>
<th>6 ML</th>
<th>8 ML</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1</td>
<td>Heavy</td>
<td>Heavy</td>
<td>Heavy</td>
<td>Heavy</td>
</tr>
<tr>
<td>H2</td>
<td>Light</td>
<td>Light</td>
<td>Light</td>
<td>Light</td>
</tr>
<tr>
<td>H3</td>
<td>Split-off</td>
<td>Split-off</td>
<td>Heavy</td>
<td>Heavy</td>
</tr>
<tr>
<td>H4</td>
<td>Heavy</td>
<td>Heavy</td>
<td>Light</td>
<td>Light</td>
</tr>
<tr>
<td>H5</td>
<td>Heavy</td>
<td>Light</td>
<td>Split-off</td>
<td>Heavy</td>
</tr>
</tbody>
</table>

**Fig. 50:** Band-mixing probability in CdSe NPLs of (a) 2 ML (b) 4 ML (c) 6 ML (d) 8 ML.
Fig. 51: Squared wavefunctions for first 3 e− & first 5 h+ in CdSe NPLs of (a) 2 ML (b) 4 ML (c) 6 ML (d) 8 ML vs. distance from the center along [001].

- As NPL thickness increases, E & H wavefunctions spreads out.
- E1 has a reasonable overlap with that of H1 (HH1).
- For other E-H transitions, optical selection rule is followed.42
- Used CB and VB offset, Φ(z) = 2 eV.43
- Peak: anti-node; Trough: node.
- Wavefunction Ψ_{nc} or Ψ_{nv}, corresponds to an energy level E_{nc} and E_{nv} at k = 0.

---

As the NPL thickness decreases, the extent of confinement increases and quantized energy levels, $E_{n_c}$ and $E_{n_v}$ get more spaced out in the energy spectrum.

Higher CB & VB states may have energy almost approaching the band offsets $\therefore$ are not quantum confined any longer.

**Fig. 52:** Band-lineup and squared wavefunctions for first 3 $e^-$ & first 5 $h^+$ in CdSe NPLs of (a) 2 ML (b) 4 ML (c) 6 ML (d) 8 ML vs. distance from the center along [001].
Excitonic Absorption | Band-lineup

Fig. 53: TME in CdSe NPLs of (a) 2 ML (b) 4 ML (c) 6 ML (d) 8 ML. Sub-frames in each frame show TE and TM TMEs from E1 and E2 to first 5 h⁺: (i) TE TME from E1; (ii) TM TME from E1; (iii) TE TME from E2; and (iv) TM TME from E2.

- Dominant hole-type are indicated.
- TE TME from E1: HH1 strongest.
- TM TME from E1: LH1 strongest.
- TE TME from E2: HH2 strongest.
- TM TME from E2: LH2 strongest.
- Optical selection rule ($\Delta n = 0$)
Excitonic Absorption

- Optical transitions must conserve momentum. Optical absorption must follow DOS.
- For band-edge absorption $HH \& LH$ results in two of $h^+$ subbands, with varying energy spacings.
- Energy spacing: $HH > LH$.
- $HH$ to $E$ starts at lower energy than $LH$ to $E$.
- 3 peaks: $HH1–E1$, $LH1–E1$, $SO1–E1$.
- Spectral anomaly: Avg. LH peak > HH peak for 2 ML.

![Optical Absorption Spectra](image)

**Fig. 54:** Excitonic TE mode (red), TM mode (blue) & weighted average absorption (black) in CdSe NPLs of (a) 2 ML (b) 4 ML (c) 6 ML (d) 8 ML. **Insets:** (i) Band-to-band absorption, $\alpha^c$; (ii) Excitonic bound state absorption, $\alpha^{ex,b}$. 
At any given energy, the CB DOS is higher for thinner NPLs.

The inter subband energy spacings are higher for thinner NPLs.

In a given energy span, thicker NPLs have more frequent subband steps.

Absorption follows DOS series of steps and is higher for thinner NPLs, and increases with photon energy.

**Fig. 55:** The density-of-states (DOS) of the CB and VB in CdSe NPLs of thickness (a) 2 ML (b) 4 ML (c) 6 ML (d) 8 ML.
Excitonic Absorption | Relative Absorption Peak Position/Intensity

**Fig. 56:** (a) Peak absorption position for HH, LH & SO peaks, (b) Peak intensity for HH, LH & SO peaks vs. the thickness of the CdSe NPLs.

<table>
<thead>
<tr>
<th>Thickness (ML)</th>
<th>HH position</th>
<th>LH position</th>
<th>SO position</th>
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<tr>
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<tr>
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</table>

<table>
<thead>
<tr>
<th>Thickness (ML)</th>
<th>TE HH intensity</th>
<th>TE LH intensity</th>
<th>TE SO intensity</th>
<th>TM LH intensity</th>
<th>TM SO intensity</th>
</tr>
</thead>
<tbody>
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<td>5</td>
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<td>10</td>
<td>5</td>
<td>2.5</td>
<td>2</td>
<td>1</td>
</tr>
</tbody>
</table>

**Fig. 57:** Comparison of avg. absorption of 2, 4, 6 & 8 ML CdSe NPLs. Inset: comparison of avg. absorption intensity for HH, LH & SO peaks.

- Avg. intrinsic is higher for thinner NPLs, ∴ e⁻ & h⁺ are closely packed, ∴ more excitons are created ⇒ higher intrinsic absorption
- Large $E_b^{ex}$ due to e⁻ & h⁺ being very close ⇒ orbits faster, more for lighter LH excitons than heavier HH excitons ⇒ LH peak > HH peak (in 2ML NPLs).
Excitonic Absorption | Experimental Verification

**Fig. 58:** Comparison of experimental absorption spectra measured by (a) Achtstein et al.,\(^44\) and (b) our group for 2 ML and 4 ML CdSe NPLs. In frame (a), *insets* (i) and (ii) show the building block and schematic of a typical NPL, grown along the [001] direction.

- **For 2 ML NPLs:** LH peak $>$ HH peak.
- Experimentally verified our theoretical findings by measuring the absorption spectra of 2 ML and 4 ML CdSe NPLs.
- Compared our measurements with that of Achtstein *et al.*\(^44\) for validation.

\(^44\) *J. Phys. Chem. C* **119** (34), 20156. Reprinted (adapted) with permission from American Chemical Society.
Excitonic Absorption | 2 ML CdSe NPL Characteristics

Fig. 59: (a) PL, (b) TRPL at 550 nm, (c) TRPL at 400 nm, (d) Absorption for varying size; and Relative absorption intensity of HH (∼393 nm) & LH/SO (∼372 nm) vs. (e) Avg. NPL area, and (f) NPL aspect ratio.

Fig. 60: TEM images of 2 ML CdSe NPLs of varying lateral sizes as indicated.

- Broad PL spectra (entire visible spectra). QY: >85% (solution), 70% (film).
- Reason: Deep surface trap states. $\tau_{\text{avg,peak}} = 100 \text{ ns}$ & $\tau_{\text{avg,edge}} = 0.14 \text{ ns}$.
- ↓ aspect ratio ⇒ ↑ surface trap state (major fraction of atoms are at surface).
- Trioctylamine (TOA) instead of Octadecene (ODE) ⇒ ↑ deep trap states QY.
- QR lateral size $\propto$ growth time after injecting Se precursor (TOP-Se).
Chapter Highlights

- Absorption spectra of NPLs has well recognized trend: higher intensity HH absorption peak and blue-shifted lower intensity LH absorption peak.
- But sub-nm 2 ML CdSe NPLs: absorption spectral properties: increased intrinsic absorption and inverted HH and LH relative peak intensities.
- Absorption spectra follows DOS step-like function (higher for thinner NPLs).
- Relative strength of HH and LH peaks depend on TE and TM TME strength, and ratio inverts with thickness.

Chapter Publications

Semiconductor Quantum Nanostructures for Optoelectronic Applications

1. Thesis Introduction, Motivation and Objective
2. Optoelectronic Theory of Semiconductors
3. II-VI CdSe/CdS Nanoplatelets & Quantum Ring
   - Dimension Effect
   - Temperature Effect
   - Alloying Effect
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4. Dilute-Nitride-Bismide III-V Quantum Dots & Wells
   - GaNBiAs/GaAs Quantum Dots
   - GaNBiAs/GaAs Quantum Wells
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   - InNBiSb/InSb Quantum Wells
5. Thesis Conclusion and Closing Remarks
**Research Problem and Objective**

- **QRs:** Topologically inverted type-I core/crown NPL heterostructure. Active material of lower $E_g$ laterally grown around barrier of higher $E_g$ (Ex: CdS/CdSe).

- **QRs vs. NPLs:** Emission window of QRs are extended over NPLs due to excitonic recombinations in QR crown (band alignment).

- **Recent report:** Type-I CdS/CdSe QRs have an emission range spanning from that of core CdS NPLs to that of core CdSe NPLs.

- **Properties:** High optical tunability and charge injection efficiency + Enhanced absorption range.

- **Chapter objective:** To study the optoelectronic properties of inverted Type-I CdS/CdSe core/crown QRs.

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45 S. Lamarre, et al., arXiv:1509.07793v2
We have studied inverted type-I core/crown CdS/CdSe QRs of 5 ML thickness.

Core and crown sizes (i.e. ring widths) are varied in range crown width : QR width $(d/a)$ of 0.10, 0.25 and 0.40

QR sizes are varied in range 10, 15 and 20 nm.

Fig. 61: (a) A 3D atom-by-atom view of a typical QR (ex: 3 ML CdS/CdSe QR). Red spheres are Cd atoms, yellow Se atoms and dark blue S atoms; and (b) Schematic of a typical core/crown CdS/CdSe QR of $a \times b \times t$ and crown width $d$. 
Semiconductor Quantum Nanostructures for Optoelectronic Applications  |  Sumanta Bose  |  sumanta001@e.ntu.edu.sg

Quantum Ring  |  Strain Profile Distribution

- Warmer (reddish) with shading ⇒ tensile strain.
- Cooler (greenish/bluish) without shading ⇒ compressive strain.
- For $\varepsilon_{xx}$ & $\varepsilon_{yy}$: compressive strain in CdS core, increases for thicker crowns as $(d/a)$ ratio rises.
- Magnitude of tensile (compressive) strain along [100] ([010]) at core/crown boundary depends on the $(d/a)$ ratio: higher for thinner crowns.
- At the core/crown boundary: abrupt change in the strain profile.
- $\varepsilon_{zz}$: predominantly compressive.

**Fig. 62:** Strain ($\varepsilon_{xx}$, $\varepsilon_{yy}$, $\varepsilon_{zz}$) in (001) plane at ($z = 0$) of CdS/CdSe QRs of size 15 nm & thickness 5 ML, with varying $(d/a) = 0.10$, 0.25 & 0.40.
**Quantum Ring | Energy & TME vs. Crown: QR width**

**Fig. 63:** (a) E1–H1 transition energy/wavelength, (b) TE mode TME vs. crown width: QR width \((d/a)\).

- As \((d/a)\) rises from 0 to 0.5, emission energy falls from 2.78 eV to 2.28 eV, ∴ QR transforms from pure CdS NPL \((d/a = 0)\) to pure CdSe NPL \((d/a = 0.5)\).
- Concavity due to optical bowing coefficient of CdS\(_x\)Se\(_{1-x}\) = 0.28.\(^{47}\)
- For QRs like pure CdS NPL \((d/a = 0)\) or pure CdSe NPL \((d/a = 0.5)\), TME values are higher, ∴ \(e^-\) & \(h^+\) wavefunction overlap is higher (localized within single material without leakage).
- For CdS/CdSe QR heterostructures, TMEs diminish, ∴ \(e^-\) & \(h^+\) wavefunction overlap is lower.

In CdS/CdSe QRs, $e^-$ and $h^+$ wavefunction tend to be localized in lower $E_g$ CdSe crown.

Extent of $e^-$ and $h^+$ wavefunction overlap dictates TME strength.

As $d/a$ increases, the $e^-$ and $h^+$ wavefunction overlap increases $\Rightarrow$ TME increases.

Most H states are $lh$ dominated.

Fig. 64: Spatial charge density distributions of the first 10 CB $e^-$ and VB $h^+$ of CdS/CdSe QR of size 15 nm and thickness 5 ML, with varying $d/a = 0.10, 0.25$ and $0.40$ (x-y plane at $z = 0$).
Quantum Ring | Band Energy/Mixing Probability

For a fixed \((d/a)\) ratio, as the size of the QR increases, \(E_{1}-H_{1}\) falls.

For QRs of same size, as \((d/a)\) increases, \(E_{1}-H_{1}\) follows a concave pattern (optical bowing coefficient).

For \((d/a) = 0.25\), \(E_{1}-H_{1}\) is \(\text{min}\). For \((d/a) = 0.10\), \(E_{1}-H_{1}\) rises by \(\sim 1100\) meV & for \((d/a) = 0.40\), \(E_{1}-H_{1}\) rises by only \(\sim 200\) meV.

\[ x = [1 - 2(d/a)]^2 \]

**Fig. 65:** Electronic bandstructure and band-mixing probability for 5 ML CdS/CdSe core/crown QRs of \((a) = 10, 15, 20\) nm (across); and \((d/a) = 0.40, 0.25, 0.10\) (down).
II-VI CdSe/CdS Nanoplatelets & Quantum Ring

Quantum Ring | Optical Gain Spectra

Optical gain factors:
- TME, carrier density,
- Fermi factor, QR dimensions, material,
- dephasing/scattering rate.

Higher carrier concentrations impose a larger gain with a blue-shift in the peak due to band-filling effect.

Increase in the QR size $\Rightarrow$ red-shift in emission wavelength.

Injection carrier density $\nabla$ of gain $> 0$ and $\nabla^2 < 0$ (Band filling effect).

**Fig. 66:** Optical gain (cm$^{-1}$) of CdS/CdSe core/crown QRs of size ($a$) = 10, 15 and 20 nm (down); and ring width : QR width ($d/a$) = 0.40, 0.25 and 0.10 (across), and varying carrier density = 1, 3, 5, 7 $\times 10^{19}$ cm$^{-3}$. 

QR gain spectra for varying injection carrier conc. ($\times 10^{19}$ cm$^{-3}$).

- QR size: 10 nm; $d/a = 0.40$
  - Peak: 2.32 eV

- QR size: 10 nm; $d/a = 0.25$
  - Peak: 2.30 eV

- QR size: 10 nm; $d/a = 0.10$
  - Peak: 2.41 eV

- QR size: 15 nm; $d/a = 0.40$
  - Peak: 2.30 eV

- QR size: 15 nm; $d/a = 0.25$
  - Peak: 2.28 eV

- QR size: 15 nm; $d/a = 0.10$
  - Peak: 2.39 eV

- QR size: 20 nm; $d/a = 0.40$
  - Peak: 2.28 eV

- QR size: 20 nm; $d/a = 0.25$
  - Peak: 2.26 eV

- QR size: 20 nm; $d/a = 0.10$
  - Peak: 2.37 eV
Quantum Ring | Thin vs. Thick Crowns

Fig. 67: PL & absorption spectra of (i) thin & (ii) thick CdSe crown for square QRs.

- We study colloidally synthesized CdS/CdSe QRs of 3 ML & 30±10 nm.
- There is a redshift and fall in linewidth as ring width increases.
- Emission peak is tunable between that of 3 ML CdS NPL (382 nm) and 3 ML CdSe NPL (462 nm).

Fig. 68: Spatial charge density distributions of E1 & H1 for $d/a = 0.25$ (thick), 0.15 (medium), 0.05 (thin) CdSe crown for square QRs. Warmer (reddish): higher occupation probability over cooler (bluish).

Fig. 69: TEM image of CdS/CdSe QRs of thickness 3 ML & size 30±10 nm (scale: 200 nm)

- CdSe absorption:
  - E–HH: 460 nm (primary)
  - E–LH: 431 nm (secondary)

- CdS absorption:
  - E–HH: 382 nm (primary)
  - E–LH: 371 nm (secondary)
Quantum Ring | Maximum and Differential Gain

Fig. 70: (Top row) Maximum gain, and (Bottom row) Differential gain of CdS/CdSe core/crown QRs with carrier densities $1, 3, 5, 7 \times 10^{19}$ cm$^{-3}$, size ($a$) = 10, 15 and 20 nm, and ($d/a$) = 0.40, 0.25 and 0.10.

- Increase in carrier density $\Rightarrow$ maximum gain increases $\because$ more injected carriers causes increased radiative recombination.
- For fixed ($d/a$) ratio, maximum gain falls with rise in QR size.
- As the ($d/a$) ratio increases, the maximum gain increases, $\because$ greater fraction of active CdSe crown.
- At higher carrier densities, gain saturates.

As carrier density increases, differential gain falls for all ($d/a$) ratios.

Differential gain is higher for smaller QRs, and decreases as QR width increases.
Chapter Highlights

- Transition energy of core/crown CdS/CdSe QRs falls with increasing size, and increasing $d/a$ ratio (non-monotonically due to optical bowing effect).
- QRs transformed into pure NPLs have higher TMEs due to localized electron-hole wavefunction overlap in a single material.
- E and H states energy span rises as CdSe crown thickness falls, $\therefore m_{h,CdS}(0.98) > m_{h,CdSe}(0.62) \text{ and } m_{e,CdS}(0.25) > m_{h,CdSe}(0.12)$.
- $e^-$ and $h^+$ wavefunctions are localized in CdSe crown. As $d/a$ increases, wavefunction overlap increases $\Rightarrow$ TME increases.

Chapter Publications

Doping N & Bi reduces bandgap. N: tensile strain, Bi: compressive strain.

Lattice matching by ratio. Example: GaNBiAs (N:Bi = 0.58).

Dilute nitride: s-like N-resonant states coupling with CB → Band anticrossing (BAC).

Dilute bismide: p-like Bi-resonant states coupling with VB → Valence band anticrossing (VBAC).

Advantages: better e− and h+ quantum confinement, easy optical tunability, reduced CHSH Auger recombination.

Applications: near- and mid-infrared (2 – 5 µm) photonic devices.

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50 CHSH stands for Conduction-heavy hole-split off hole-heavy hole
InNBiSb/InSb QWs: Topological Insulators | Literature Review

- Simultaneously doping N & Bi: Quantum spin Hall (QSH) effect ⇒ Topological phase transitions.
- At critical QW thickness, electronic bandstructure switches from a normal to an inverted type ⇒ Topological insulators (TIs) can be realized.
- TIs: Material with bulk bandgap similar to ordinary insulator, but with topologically protected gapless conducting states on surface/edge.\(^{52}\)
- Properties: Time-reversal symmetry, spin texture w. Berry’s phase of \(\pi\), anti-nonmagnetic impurity scattering, counter-propagating and fully spin-polarized non-dissipative conduction channels.\(^{52}\)
- TIs in semiconductor: First QSH effect observed in HgTe/CdSe QWs.\(^{53}\)
- Applications: new electronic, spintronic and quantum computation memory and logic devices with low power dissipation – topotronics.\(^{54}\)

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Presentation Navigator

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5. Thesis Conclusion and Closing Remarks
Dilute-Nitride-Bismide III-V Quantum Dots & Wells

GaNBiAs/GaAs Quantum Dots

Research Problem and Objective

- **Current literature:** GaBiAs QWs using MBE,\(^{55}\) and band-edge characterization.\(^{56}\)

- **Theoretical studies:** 12-band VBAC model based effective mass Hamiltonian method by O’Reilly.\(^{57}\)

- However, not much progress has been made on the study of GaBiAs QDs.

- **Chapter Objective:** To use an improved 16-band effective mass Hamiltonian to study GaN\(_x\)Bi\(_y\)As\(_{1-x-y}\)/GaAs pyramidal QDs for 1.3 – 1.55 \(\mu\)m range fiber technology applications.

---


We study GaNBiAs/GaAs QDs of size 12H, except for the size effect.

Height (H) & width (2H) are integer multiple of the lattice constant.

Impurity in the form of N and Bi are distributed uniformly.

8-band model is extended by 2 bands (s-like N-resonant states) and 6 bands (p-like Bi-resonant states) to construct 16-band $k \cdot p$ model.

**Fig. 71:** Side view geometry schematic of pyramidal QDs.

**Fig. 72:** (a) 3D atom-by-atom view and (b) Top view of a typical pyramidal QDs. Only anions are shown. Purple: As, Blue: N, Yellow: Bi.
Fig. 73: For GaN$_{0.64}$Bi$_{0.64}$As$_{0.872}$/GaAs QDs of $H = 12a$, $\epsilon_{xx} = +0.005$: (a) C1/V1 variation by VC, strain, BAC and VBAC, (b) Band mixing probabilities and energy bandstructure, (c) Charge densities of first 6 $e^-$ & $h^+$. 1st 2 rows: $x$–$y$ plane, 2nd 2 rows: $y$–$z$ plane. (d) Optical gain for carrier densities 2 to $10 \times 10^{18}$ cm$^{-3}$. $\Delta_{sp} = 95$ meV.

- Four contributing factors to bandedge characteristics: VC, strain, BAC and VBAC.
- BAC: lowers C1.
- VBAC: elevates V1.
- VC:
  \[
  \delta E_{VC}^{HH} = \kappa_{Nx} + \kappa_{By},
  \delta E_{VC}^{CB} = \alpha_{Nx} + \alpha_{By}.
  \]
- Strain:
  \[
  \delta E_{s}^{CB} = a_{c}(tr(\epsilon)),
  \delta E_{s}^{HH} = a_{v}(tr(\epsilon)).
  \]
- VBAC couples with HH ($LH$) as HH$_{Bi}$ ($LH_{Bi}$).
- Comp. of HH$_{Bi}$ $>$ ($<$) LH$_{Bi}$ when comp. of HH $>$ ($<$) LH.
- Gain peak at C1-V1, secondary peak at higher carrier density.
GaNBiAs/GaAs QDs | Characterization for $\epsilon_{xx} \simeq 0$

Fig. 74: For GaN$_{0.016}$Bi$_{0.027}$As$_{0.957}$/GaAs QDs of $H = 12a$, $\epsilon_{xx} \simeq 0.00$: (a) C1/V1 variation by VC, strain, BAC and VBAC, (b) Band mixing probabilities and energy bandstructure, (c) Charge densities of first 6 $e^-$ & $h^+$. 1st 2 rows: $x$–$y$ plane, 2nd 2 rows: $y$–$z$ plane. (d) Optical gain for carrier densities 2 to $10 \times 10^{18}$ cm$^{-3}$. $\Delta_{sp} = 62$ meV.

- Strain $\simeq 0$ has minimal effect on bandstructure.
- CB1: $s$-like, CB2 & CB3: $p$-like.
- $s$–$p$ splitting: $\Delta_{sp} = E_{CB2} - E_{CB1}$.
- $\Delta_{sp} = 62$ meV.
- Gain peak at C1-V1, secondary peak at higher carrier density.
Compressive strain increases the bandgap.

The wavefunctions distribution vary compared to Figs. 73 and 74. The peak of optical gain also moves.

$\delta E_{\text{strain}}^{\text{CB}} > 0$, while $\delta E_{\text{strain}}^{\text{HH}} < 0$ when the $\epsilon_{xx} < 0$, given when $a_c < 0$ and $a_v > 0$.

CB1: $s$-like, CB2 & CB3: $p$-like.

$s$-$p$ splitting: $\Delta_{sp} = E_{CB2} - E_{CB1}$.

$\Delta_{sp} = 69$ meV.

Gain peak at C1-V1, secondary peak at higher carrier density.

**Fig. 75:** For Ga$_{0.013}$Bi$_{0.064}$As$_{0.923}$/GaAs QDs of $H = 12a$, $\epsilon_{xx} = -0.005$: (a) C1/V1 variation by VC, strain, BAC and VBAC, (b) Band mixing probabilities and energy bandstructure, (c) Charge densities of first 6 $e^-$ & $h^+$. 1st 2 rows: $x$-$y$ plane, 2nd 2 rows: $y$-$z$ plane. (d) Optical gain for carrier densities 2 to $10 \times 10^{18}$ cm$^{-3}$. $\Delta_{sp} = 69$ meV.
GaNBiAs/GaAs QDs | Bandgap & Strain vs. Composition

**Fig. 76:** (a) and (b) Variation in CB1, VB1 and $E_g$ with the % of doped N and Bi. (c) Contour of the $E_g$ and strain with the composition of doped N and Bi.

- As the N and Bi are doped uniformly, the composition of the two impurities are discrete.
- Variation in CB1 and VB1 for varying compositions is affected by the differences in BAC and VBAC.
- N:Bi ratio can be maintained for zero strain in GaNBiAs/GaAs.
GaNBiAs/GaAs QDs | Optical Gain Spectra

- Four different N and Bi compositions are shown.
- The red-shift in the first peak is due to reduced quantum confinement effect with increasing QD size.
- H = 12a has only 1 peak while, H = 16a has 2 peaks, and even 4 peaks for H = 20a.
- Large size of the QDs means smaller subband gap which is easier to be excited.

**Fig. 77:** Optical gain of GaNBiAs QDs of H = 12a, 16a and 20a, for carrier density = $6 \times 10^{18}$ cm$^{-3}$. 
Chapter Highlights

- The effective bandgap of GaN$_x$Bi$_y$As$_{1-x-y}$/GaAs pyramidal QDs can be tuned by varying the composition of N and Bi.

- The effective bandgap falls as we increase the composition of Nitrogen (N) and Bismuth (Bi).

- Factors affecting bandstructure and emission characteristics: virtual crystal (VC), strain profile, band anticrossing (BAC) and valence band anticrossing (VBAC).

- Emission wavelength can be tuned to span 1.3 – 1.55 µm, suitable for device applications in fiber technology.

Chapter Publication

Presentation Navigator

1. Thesis Introduction, Motivation and Objective
2. Optoelectronic Theory of Semiconductors
3. II-VI CdSe/CdS Nanoplatelets & Quantum Ring
   - Dimension Effect
   - Temperature Effect
   - Alloying Effect
   - Excitonic Absorption
   - Quantum Ring
4. Dilute-Nitride-Bismide III-V Quantum Dots & Wells
   - GaNBiAs/GaAs Quantum Dots
   - GaNBiAs/GaAs Quantum Wells
   - InNBiAs/InP Quantum Dots
   - InNBiSb/InSb Quantum Wells
5. Thesis Conclusion and Closing Remarks
A recent work by O’Reilly group has reported GaBiAs/GaAs QWs,\textsuperscript{58}.

Nasr \textit{et al.} have worked on GaNBiAs QWs, but not studied optical gain.\textsuperscript{59}

But here, we focus on GaNBiAs QWs, which has better $e^-$ confinement due to repulsion between N and the host material’s band edge.

We improve on the 12/14-band VBAC model based effective mass Hamiltonian method by O’Reilly.\textsuperscript{60} and use an improved 16-band model, capable of incorporating the effects of N and Bi doping effects.

\textbf{Chapter Objective:} To study lattice matched GaN$_x$Bi$_y$As$_{1-x-y}$/GaAs QWs for applications in 1.55 $\mu$m GaAs-based laser for optical fiber communication systems.


\textsuperscript{60} C. A. Broderick, \textit{et al.}, \textit{Semicond. Sci. Technol.}, \textbf{28}, 12, 125025 (2013)
We study lattice matched GaNBiAs/GaAs QWs of well width = 4, 4.8, 6.3 and 9.6 nm for 1.55 μm (0.80 eV) photon emission wavelength/energy.

**Fig. 78:** Variations in $E_g$ of GaNBiAs/GaAs at 300 K vs. N and Bi comp. (%) with lattice matching line.

- Doping N & Bi reduces bandgap. N: tensile strain, Bi: compressive strain.
- Lattice matching by ratio. Ex.: N:Bi = 0.58 for GaNBiAs (red line in Fig. 78.)
- With increasing QW width, N & Bi % falls (maintaining ratio). Thicker QW and lower N & Bi % → 1.55 μm emission maintained.

**Fig. 79:** Emission energy/wavelength vs. lattice matched GaNBiAs QWs width for varying N & Bi conc.

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GaNBiAs/GaAs QWs | Energy Dispersion Curves

**Fig. 80:** First 3 $e^-$ & 5 $h^+$ energy dispersion of lattice matched GaNBiAs QWs of width (a) 4 nm (b) 4.8 nm (c) 6.3 nm (d) 9.6 nm. $E = e^-$, HH (LH) = heavy (light) $h^+$. 

- $k$ is wavevector along [100] and [110] directions.
- The photon emission energy for all cases are $\sim 0.8$ eV (1.55 µm).
- As QW width increases, (N,Bi) comp. falls. The two counteract to ensure 1.55 µm emission.
- CB subbands: isotropic.
- VB subbands: anisotropic (more spread along [110] compared to [100]).
- Hole type sequence: HH1, LH1, HH2, HH3, LH2.
- Subband state gaps reduce with increasing QW width. $\Delta_{E1-E3}: 403$ to 222 meV. $\Delta_{HH1-LH2}: 234$ to 96 meV.
Fig. 81: TE mode optical gain of lattice matched GaNBiAs QWs (300 K) of width (a) 4 nm (b) 4.8 nm (c) 6.3 nm (d) 9.6 nm for varying carrier density = 2, 4, 6, 8 × 10^{18} \text{cm}^{-3}.

- The peak emission position of all cases are \sim 0.8 \text{eV} (1.55 \mu\text{m}).
- The intraband relaxation time \(\tau\) was taken to be 0.1 ps.
- Band filling effect is more profound in thicker QWs compared to thinner QWs.
- Gain spectral width is higher for thicker QWs. \(e^- - h^+\) recombinations not only from E1-HH1, but also E1-LH1, E2-HH2, etc.
- Injection carrier density \(\nabla\) of gain \(> 0\) and \(\nabla^2 < 0\) (Band filling effect).
**Fig. 82:** (a) Maximum Optical Gain and (b) Differential Gain of lattice matched GaNBiAs QWs (300 K) of width (a) 4 nm (b) 4.8 nm (c) 6.3 nm (d) 9.6 nm vs. varying carrier density.

**Table 2:** Comparison of 4 GaNBiAs QW cases studied

<table>
<thead>
<tr>
<th>GaNBiAs QW Case</th>
<th>N : Bi : As ratio</th>
<th>Gain spectral width</th>
<th>Maximum gain</th>
<th>Transparency density</th>
<th>Differential gain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case A (4.0 nm)</td>
<td>3.50 : 6.03 : 90.47</td>
<td>✓</td>
<td>✗</td>
<td>✗</td>
<td>✗</td>
</tr>
<tr>
<td>Case B (4.8 nm)</td>
<td>3.25 : 5.60 : 91.15</td>
<td>✓</td>
<td>✗</td>
<td>✗</td>
<td>✗</td>
</tr>
<tr>
<td>Case C (6.3 nm)</td>
<td>3.00 : 5.17 : 91.83</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Case D (9.6 nm)</td>
<td>2.75 : 4.74 : 92.51</td>
<td>✗</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

- $\Delta F > E_1-H_1$ must hold for +ve gain.
- Maximum gain increases with carrier density.
- Max. gain pattern: Case D > C > B > A.
- Case C has higher and stable diff. gain across varying carrier densities.
**Fig. 83:** First 3 $e^-$ & 5 $h^+$ squared wavefunctions at $k = 0$ for GaNBiAs QWs of width (a) 4 nm (b) 4.8 nm (c) 6.3 nm (d) 9.6 nm vs. dist. from QW central plane along [001].
GaNBiAs/GaAs QWs | Chapter Highlights & Publication

Chapter Highlights

- GaNBiAs/GaAs QWs are excellent candidates for 1.55 $\mu$m optical applications.
- The QW thickness and (N:Bi) composition can be varied to tune optical performance.
- For our intended 1.55 $\mu$m (0.8 eV) GaAs-based fiber optic laser diode applications, the 6.3 nm thick GaN$_3$Bi$_{5.17}$As$_{91.83}$ lattice matched QWs give the best optical performance.

Chapter Publication

Semiconductor Quantum Nanostructures for Optoelectronic Applications  |  Sumanta Bose  |  sumanta001@e.ntu.edu.sg

Dilute-Nitride-Bismide III-V Quantum Dots & Wells

InNBiAs/InP Quantum Dots  |  Chapter Objective

Research Problem and Objective

- Theories and concepts of dilute nitride/bismide III-V semiconductors are not limited to GaNBiAs, but is also applicable to InAs, InSb, etc.

- Bulk InAs has a much lower RT $E_g$ of 0.354 eV compared to 1.424 eV of bulk GaAs\(^{62}\) ⇒ InAs based devices would have comparatively longer operating wavelengths.

- **Chapter objective**: To study $\text{InN}_x\text{Bi}_y\text{As}_{1-x-y}/\text{InP}$ QDs for achieving emission wavelength $\sim 2 - 5\mu\text{m}$ (250 - 650 meV) for mid-IR device applications.

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Semiconductor Quantum Nanostructures for Optoelectronic Applications | Sumanta Bose | sumanta001@e.ntu.edu.sg

Dilute-Nitride-Bismide III-V Quantum Dots & Wells

InNBiAs/InP Quantum Dots

InNBiAs/InP QDs | Schematic and Band Energy/Mixing

- We study InNBiAs/InP QDs of varying size (H).
- Height (H) & width (2H) are integer multiple of the lattice constant.
- Impurity in the form of N and Bi are distributed uniformly.
- 8-band model is extended by 2 bands (s-like N-resonant states) and 6 bands (p-like Bi-resonant states) to construct 16-band $k \cdot p$ model.

Fig. 84: Side view geometry schematic of pyramidal QDs.

Fig. 85: Electronic bandstructure and band-mixing probability. The concentration of N and Bi are 2.86% each and the height of QD is $H=12a$.

- CB majority: E. VB majority: HH.
- Coupling of the N/Bi-resonant states with CB/VB states (BAC/VBAC) $\rightarrow$ resonant N/Bi-state contributions in CB/VB states.
Fig. 86: Variations in CB1, VB1 and $E_g$ for InNBiAs/InP QDs of $H = 12a$, $16a$ and $20a$ for varying Bi conc. and fixed N conc. = 1.6%.

- With ↑ Bi conc. CB1 ↓ & VB1 ↑.
- Range of the CB1–VB1 (emission energy) is ~250 to 650 meV ⇒ InNBiAs/InP QDs are suitable for mid-IR (2–5 μm) applications.

Fig. 87: Variations in the $E_g$ of InNBiAs/InP QDs at 300 K vs. N and Bi conc. (%).

- Strain component $\varepsilon_{xx}$ is mentioned using isopotential lines.
- Doping N & Bi reduces bandgap. N: tensile strain, Bi: compressive strain.
- Lattice matching by N:Bi ratio.
InNbAs/InP Quantum Dots | Optical Gain Spectra

**Fig. 88:** TE and TM mode optical gain for InNbAs/InP QDs for varying carrier density from 1 to $5 \times 10^{18}$ cm$^{-3}$. Bi conc.: varied from 0.9% to 11.1%, while N conc.: fixed at 2.9%. QD height $H = 12\alpha$.

- Gain increases with increasing carrier density. TM gain < TE gain (relatively).
- Injection carrier density $\nabla$ of gain $> 0$ and $\nabla^2 < 0$ (**Band filling effect**).
- With ↑ Bi conc. $E_g$ ↓ ⇒ red-shift in gain peak.
**Chapter Highlights**

- The effective bandgap of InN$_x$Bi$_y$As$_{1-x-y}$/InP pyramidal QDs can be tuned by varying the composition of N and Bi.
- The effective bandgap falls as we increase the composition of Nitrogen (N) and Bismuth (Bi).
- Factors affecting bandstructure and emission characteristics: virtual crystal (VC), strain profile, band anticrossing (BAC) and valence band anticrossing (VBAC).
- Emission wavelength can be tuned to span 2–5 µm (∼250 to 650 meV) for mid-IR applications.

**Chapter Publication**

Presentation Navigator

1. Thesis Introduction, Motivation and Objective
2. Optoelectronic Theory of Semiconductors
3. II-VI CdSe/CdS Nanoplatelets & Quantum Ring
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   - GaNBiAs/GaAs Quantum Dots
   - GaNBiAs/GaAs Quantum Wells
   - InNBiAs/InP Quantum Dots
   - InNBiSb/InSb Quantum Wells
5. Thesis Conclusion and Closing Remarks
Simultaneously doping N & Bi: Quantum spin Hall (QSH) effect ⇒ Topological phase transitions.

At critical QW thickness, electronic bandstructure switches from a normal to an inverted type ⇒ Topological insulators (TIs) can be realized.

TIs: Material with bulk bandgap similar to ordinary insulator, but with topologically protected gapless conducting states on surface/edge.\(^{63}\)

TIs in semiconductor: First QSH effect observed in HgTe/CdSe QWs.\(^{64}\)

Others: InAs/GaSb/AlSb,\(^{65}\) Bi\(_2\)Se\(_3\),\(^{66}\) InN/GaN,\(^{67}\) Ge/GaAs,\(^{68}\) etc.

Chapter objective: To propose and verify that InN\(_x\)Bi\(_y\)Sb\(_{1-x-y}\)/InSb QWs can realize QSH effect and topological phase transition.

---


Effective Hamiltonian

For projecting into low energy sub-space

\[ H = H(0, 0, -i \frac{\partial}{\partial z}) + H' (k_x, k_y, -i \frac{\partial}{\partial z}) \]

Here first term is non-perturbative, second term is perturbative. Now, effective Hamiltonian a/c to Lowding perturbation method is

\[ H_{\text{eff}}^{mm'} = E_m \delta_{mm'} + H'_{mm'} + \frac{1}{2} \sum_l H'_{ml} H'_{lm'} \left( \frac{1}{E_m - E_l} + \frac{1}{E_m' - E_l} \right) \]

Two-terminal conductance

Green’s function:

\[ G = \frac{e^2}{\hbar} \text{Tr} \left[ \Gamma_S G^r \Gamma_D G^a \right] \]

---

InNBiSb/InSb QWs | Bandstructure & $E_g$ Phase Diagram

Fig. 89: Bandstructure around Γ–point of InNBiSb/InSb QWs of width (a) 7 nm (b) 7.7 nm (c) 8.2 nm and barrier width = 7 nm. In QW, N conc. = 2.4%; Bi conc. = 3.2% ⇒ 0.48% tensile strain. (d) Phase diagram of $E_g$ vs. width of well and barrier.

- QWs < critical thickness (7.7 nm in our case) ⇒ normal electronic structure, and QWs > critical thickness ⇒ inverted electronic structure.
- normal: zero edge state conductance, and inverted: edge channel transport conductance.
- Phase diagram has two phases: $E_g > 0$ ⇒ trivial phase, and $E_g < 0$ ⇒ non-trivial phase.
Fig. 90: For Fig. 89 (c): electron (E), heavy-hole (HH), light-hole (LH) and split-off hole (SO) band mixing probability of (a) CB1 and (b) VB1.

- Around Γ point, majority of CB1 is LH dominated, while majority of VB1 is E dominated.
- This directly confirms band-inversion.
- VB1 is LH dominated due to induced tensile strain.
InNbSb/InSb Quantum Wells | Topological Edge States

Proof of topological edge states:

- CB/VB inversion in ribbon bandstructure.
- Ribbon wavefunctions having localized distribution at edges and edge-state spin-momentum locking ⇒ 2D TI.\(^{71}\)
- Magnitude of RSS\(^{72}\) > 1 meV for LH. Such huge splitting enables spintronics application.\(^{73}\)

---


\(^{72}\) RSS (Rashba Spin-Splitting) is a momentum-dependent splitting of spin bands in semiconductor heterostructures.

We study two-terminal conductance of rectangular superlattice sample of $L \times N$.

The non-zero conductance ($G$) indicates the presence of topological edge states.

Even when the Fermi energy lies in the $E_g$ window, the conductance, $G \neq 0$, but has a finite value (here $G = 2e^2/h$).

It exhibits edge channel transport conductance independent of the QW thickness (expected in QSH insulator) $\Rightarrow$ they're are edge-states driven.

Fig. 92: (a) Schematic of the two-terminal sample. Red shade: central region, green shade: external infinite leads. (b) The two-terminal conductance, $G$ of a finite sample as a function of Fermi energy.
**Fig. 93:** Laudau levels (LLs) fan figure for InNBiSb/InSb QWs (well-width = 8.2 nm; barrier-width = 7.0 nm).

- **Topological phase:** has crossing point between zero-mode LLs; **Normal phase:** has no such crossing point.\(^7\)

- Crossing point bw. 2 LLs (red curves) ⇒ existence of topological band inversion at zero magnetic field.

---

**Fig. 94:** \(E_g\) phase diagram for the topological phase transitions in InNBiSb/InSb QWs (well-width = 8.2 nm; barrier-width = 7.0 nm).

- Phase diagram has two phases: \(E_g > 0 \Rightarrow \) trivial phase, and \(E_g < 0 \Rightarrow\) non-trivial phase.

- The magnitude of -ve \(E_g > 60\) meV. This is essential for practical implementation of TIs.

---

Chapter Highlights

- Proposed and verified that InN<sub>x</sub>Bi<sub>y</sub>Sb<sub>1−x−y</sub>/InSb QWs can realize QSH effect and topological phase transition.

- We have confirmed:
  - band-inversion when QW thickness > critical thickness.
  - topologically protected edge-states.
  - edge-localized wavefunctions distribution and spin-momentum locking.
  - two-terminal conductance ≠ 0 even when \( E_F \) ∈ \( E_g \) window.
  - zero-mode LL crossover points without magnetic field.
  - large RSS in external electric field.

Chapter Publication

Presentation Navigator

1. Thesis Introduction, Motivation and Objective
2. Optoelectronic Theory of Semiconductors
3. II-VI CdSe/CdS Nanoplatelets & Quantum Ring
   - Dimension Effect
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   - InNBiSb/InSb Quantum Wells
5. Thesis Conclusion and Closing Remarks


**Thesis Contributions and Novelty**

**II-VI NPLs & QRs**

**Dimension Effect:** Showed that both thickness and lateral size significantly affect NPL characteristics.

**Temperature Effect:** Characterized, experimentally verified and deduced parameters of NPLs at high temperature.

**Excitonic Absorption:** Studied polarization dependent absorption of NPLs and justified anomalous properties for 2 ML NPLs.

**Quantum Ring:** Characterized type-I QRs based on crown : core ratio and size; Studied effect of thin/thick crown.

**Dilute Nitride/Bismide III-V QDs/QWs**

**KdotPSoft:** Developed in-house GUI software simulation platform to model and simulate semiconductor quantum nanostructure.

**GaNBiAs/GaAs QDs:** Used improved 16-band model to study optoelectronic properties for 1.3 – 1.55 µm applications.

**GaNBiAs/GaAs QWs:** Maintained lattice matching N : Bi ratio to study bandstructure and gain for 1.55 µm applications.

**InNBiAs/InP QDs:** Used improved 16-band model to characterize optoelectronic properties for 2 – 5 µm applications.
Thesis Conclusion and Future Works

**Thesis Conclusion**

- Characterized, simulated, studied new optoelectronic properties of:
  1. NPLs and QRs of II-VI semiconductors/alloys.
  2. QDs and QWs of dilute nitride/bismide III-V semiconductors.
- Application: visible and mid-IR (LEDs, lasers, solar cells).
- **KdotPSoft**: Developed in-house GUI software simulation platform to model and simulate semiconductor quantum nanostructure.
- Can design experiments & predict optoelectronic characteristics to tune reiterations parameters (reduce device production time/cost).

**Future Works**

- Study novel nanostructure systems: Dot-in-rod, Graded core-shell QD.
- Study optoelectronic properties under electric/magnetic field effect.
- Extend the $k \cdot p$ model for perovskite materials.
KdotPSoft | Modeling Quantum Nanostructure

**Step 1:** Nanostructure shape setup.

- Pyramid
- Lens
- Semiellipsoid

**Step 2:** Nanostructure alloy profile setup.

- Linear
- Trumpet
- Inverted pyramidal

**Step 3:** Nanostructure atomic structure setup.

**Step 4:** Calculation of strain tensor profile.

**Step 5:** Calculation of electronic potential profile.

**Step 6:** Calculation of electron/hole wavefunctions.
KdotPSoft | Working and Software Setup

- User-friendly GUI with built-in semiconductor parameters to study DOS, TME, gain, emission rate, charge density, etc of arbitrary material’s QDs/QWs/NPLs.\(^7\)

![Flowchart showing the working flow of the KdotPsoft software.](image)

**Fig. 95:** Flowchart showing the working flow of the KdotPsoft software.

- Can be used in academia or industry to design experiments and predict optoelectronic characteristics. More info: kdotpsoft.com

![Setup of KdotPsoft software for experiments and fabrication.](image)

**Fig. 96:** The setup of KdotPsoft software for experiments and fabrication.

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\(^7\) Published as S. Bose, et al., “KdotPsoft: Modelling and Simulation of Semiconductors and Device Physics”, 9\(^{th}\) Intl. Conf. on Materials for Advanced Technologies, Singapore (2017)
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<th>Author and Paper Details</th>
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Author’s Publications (2/2) | Conferences


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- TUBA-GEBIP.
Thank You (Base) Image Courtesy: https://www.pinterest.com/pin/200410252144981142/