Thang Ba Hoang

I, __________________________, hereby submit this work as part of the requirements for the degree of:

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in:

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Investigation of Single Semiconductor Nanowire Heterostructures

Using Polarized Imaging Spectroscopy

This work and its defense approved by:

Chair: Professor Leigh M. Smith

Professor Mark S. Jarrell

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Investigation of Single Semiconductor Nanowire Heterostructures Using Polarized Imaging Spectroscopy

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by

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Abstract

In this work, we use optical spectroscopic techniques including micro-photoluminescence (PL), spatially-resolved PL imaging, time-resolved PL, PL polarization measurements to investigate the optical and electronic properties of single CdS and core-shell GaAs/AlGaAs nanowires (NWs) at both room and low temperatures.

CdS nanowires grown by the Vapor-Liquid-Solid (VLS) method show variation in morphology ranging from straight and uniform, to extremely irregular with bends, kinks, and irregular shaped clusters of material aggregating locally on the nanowires. At room temperature we observe that all nanowires, regardless of size and shape, emit PL with a single broad peak with Full Width at Half Maximum (FWHM) ~ 70 meV at energy below the band gap energy of bulk CdS (2.51 eV). The emission is often referred as the Near Band Edge (NBE) emission. At low temperature, PL emission from these nanowires are significantly different: PL from uniform wires still display a broad peak near 2.54 eV (FWHM ~32 meV) but irregular wires show a broad band with a high energy shoulder near ~2.54 eV and a number of sharp emission lines are observed on the lower energy side of the broad band. Spatially resolved PL imaging and temperature dependent PL measurements reveal that these sharp emission lines originate from specific positions along the nanowire and are completely quenched by 80-90K. Time-resolved measurements show that the decay times of the emission from the high energy shoulder (or near band edge) is very short (< 50 ps) while it is significantly longer for the sharp lines (500-1000 ps). We conclude that the sharp emission lines result from defect or surface related electron states.
For single core-shell GaAs/AlGaAs nanowires, we observe an order-of-magnitude higher quantum efficiency for emission than for bare GaAs nanowires. This results from passivation of the GaAs surface with AlGaAs, reducing non-radiative surface recombination. Non-equilibrium spin distributions in single GaAs/AlGaAs core-shell nanowires are excited using resonant polarized excitation at low temperature (6 K). The large dielectric mismatch between the semiconductor nanowire ($\varepsilon = 12$ for GaAs and AlGaAs in this case) and the surrounding vacuum ($\varepsilon = 1$) results in significant polarization anisotropy of both excitation and emission at all excitation energies. We observe a significant increase in PL intensity (by a factor of \~70) occurs when the exciting laser is polarized along the nanowire versus perpendicular to it. The suppression of the electromagnetic (photon) field in these nanowires results directly in a corresponding suppression of the radiative rate for excitonic dipoles aligned perpendicularly to the nanowire. We observe two strong resonances at 1-LO and 2-LO phonons of GaAs and a third resonance likely from electronic states of the AlGaAs shell. More interestingly, we observe that the polarization of the PL emission is strongly enhanced as the excitation energy comes closer to resonance with the exciton emission. This strong polarization enhancement indicates that resonant excitation creates non-equilibrium exciton spin distributions near resonance. Rate equation modeling allows us to estimate the spin relaxation times which range from \~5 ps at high energies to \~50ps at energies close to resonance.

Our results suggest the use of polarization measurements, spatially- and temporally-resolved optical spectroscopies are important tools for rapidly characterizing nanowire growth for the optimization of future applications in nano devices.
To My Parents
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I. Introduction

As part of the rapid development of nanotechnology, semiconductor nanowires (NWs) have become essential building block components for future “nano-devices”. Nanowire based photo-detectors, [1,2] bio-sensors, [3] lasers, [4,5], field effect transistors, [6,7] optical switches [8] have been demonstrated. Recent efforts in the studies of semiconductor nanowires have also revealed numbers of interesting properties such as polarization sensitivity, [9-14] size-dependent photoluminescence,[15] quantum dots in nanowires for single photon LED (Light Emitting Diode),[16] or single hybrid nanowires for photonic crystals,[17] etc.. These new properties and applications of semiconductor nanowires have attracted both scientific and industrial communities. [18-30]

In a semiconductor nanowire, the huge surface to volume ratio (~$10^8$ m$^{-1}$ for nanowires compared to ~$10^2$ m$^{-1}$ for bulk materials) results in strong sensitivity of the excitons to surface states as well as defects and structural inhomogeneities. Understanding the optical and electronic properties in a single nanowire is extremely important in order to understand in detail how the electronic states are modified by such effects in this nearly one dimensional structure. Detailed study will potentially level the nature of nanowire fabrication processes, and lead to the optimization for specific nanowire devices.

This thesis is devoted to the optical characterization of single semiconductor nanowires (CdS and core-shell GaAs/AlGaAs) using polarized imaging spectroscopy. While single nanowire spectroscopy presents significant experimental challenges, such information is essential for understanding the optical properties of these structures, since
the physical size, shape and composition vary significantly from wire to wire and has a strong effect on their physical properties. This thesis describes the experimental techniques used for the study of single semiconductor nanowires along with our major results and conclusions.

The thesis is composed of five parts. The Introduction (Part I) being the first. Part II is devoted to a brief introduction of general aspects of CdS and GaAs semiconductors and their nanowire structures. Also in this Part, nanowire growth and several related issues such as twin defects, polarization sensitivity will be discussed. Part III will describe our experimental approaches to the spectroscopic studies of single nanostructures. The last two parts (IV and V) correspond to two different materials of nanowires: Part IV deals with photoluminescence spectroscopy of single CdS nanowires both at room temperature and low temperature. Near band edge, defect related emissions, time-resolved, spatially-resolved photoluminescence of single CdS nanowire are discussed. Part V describes our results on single core-shell GaAs/AlGaAs nanowires including: general photoluminescence properties, resonant polarized excitation, imaging and temperature dependent of photoluminescence. Non-equilibrium spin distribution and rate equations for spin relaxation are also discussed.

*Cincinnati, Ohio, February 2008*

Thang Ba Hoang
References


[2] C. Lieber et al., Core/Multishell nanowire heterostructures as multicolor high-efficiency light-emitting diodes, NanoLetter 5 2287 2005


[10] H. Ruda et al., Polarization-sensitive optical phenomena in semiconducting and metallic nanowires, PRB 72 115308 2005
Highly polarized photoluminescence and photodetection from single InP nanowires,
Science 293 1455 2001

[12] Thang Ba Hoang, Lyubov V. Titova, Jan M. Yarrison-Rice, Howard E. Jackson,
Alexandre O. Govorov, Y. Kim, H. J. Joyce, H.H. Tan, C. Jagadish and Leigh M.
Smith., Resonant Excitation and Imaging of Nonequilibrium Exciton Spins in Single

[13] C. Shan et al., PL polarization in individual CdSe nanowires., PRB 74 153402 2006:

[14] L. Samuelson et al., Growth and optical properties of strained GaAs-Ga\textsubscript{x}In\textsubscript{1-x}P core-


[16] V. Zwiller et al., Optically bright quantum dots in single nanowires, NanoLett. 5
1439 2005

Structures, NanoLett. 6 11-15 2006

[18] C Lieber et al., Nanowire electronic and optoelectronic devices, Mat. Today. 9 18-
27


[20] C. Lieber et al., Detection, Stimulation, and Inhibition of Neuronal Signals with
High-Density Nanowire Transistor Arrays, Science 313 1100-1104 2006

[21] C. Lieber., Dopant-Free GaN/AlN/AlGaN Radial Nanowire Heterostructures as
High Electron Mobility Transistors., NanoLett. 6 1468-1473 2006


Part II

CdS, GaAs semiconductors and their nanowire structures
II.1 Semiconductor electronic band structures

Electronic band structures

In solid state physics, the electronic band structure is described with a diagram which plots the energy of electron $E$ as a function of its wave-vector $k$. The wave-vector is allowed to take any possible values, however due to the translational invariance of the lattice, the band structure can always be reduced to the first Brillouin zone. There are often gaps between energy bands, which referred as band gaps, and the completely occupied highest energy band is called the valence band (VB), the next higher band of states is called the conduction band (CB). Based on these band gaps, solid state physics has successfully sorted out different types of materials including insulator, conductor (metals) and semiconductor. Many calculation techniques have been developed to calculate the band structures of semiconductors, and interestingly, each semiconductor has its own unique band structure which can be associated with the particular physical properties.

Band structure, especially the band gap, plays an important role in understanding optical properties of a semiconductor. A direct band gap semiconductor (a semiconductor that has both extrema of the valence band and the conduction band at $k=0$) has much higher quantum efficiency than that of an indirect band gap semiconductor. This happens because optical transitions mostly happen around the zero value of the wave-vector $k=0$ (or the center of the Brillouin zone) where the momentum selection rule is satisfied (describe in detail below). This is the main reason that most of the materials for opto-electronic devices are direct band gap semiconductors. As an example, Figure II.1.1 below shows the band structure of the direct band gap GaAs semiconductor.[1]
**Figure II.1.1-** Band structure of zinc-blend GaAs. [1]

The red rectangle indicates the region where optical transitions mostly occur.

**Figure II.1.2-** Band structure of a zinc-blend direct band gap semiconductor near the center of the Brillouin zone

*Figure (II.1.2)* illustrates the band structure of a zinc-blend direct band gap semiconductor at the center of the Brillouin zone in a simplest case where we assume
energy surfaces are spherical shells. The electron in the conduction band has an s-type
wave function which has total angular momentum \( \frac{1}{2} \) (orbital angular momentum \( l=0 \) and
spin momentum \( s=\frac{1}{2} \)) and it results a two-fold degeneracy at \( k=0 \). In the valence band,
the electronic states become more complicated due to the spin-orbit interaction (recall the
spin-orbit interaction term \( \hat{L} \cdot \hat{S} \) in the Hamiltonian). The spin-orbit interaction splits the
valence band into heavy hole (hh) and light hole (lh) bands. As a result, one of the light
hole band is pushed to a higher energy level by an amount \( E_{SO} \) (split-off band energy)
(see Figure II.1.2). The holes in the valence band have p-type wave functions with total
angular momentum \( \frac{3}{2} \) (\( l=1 \) and \( s=\frac{1}{2} \)). The heavy hole (hh) has spin angular momentum
\( m_j = \pm \frac{3}{2} \) and light hole (lh) has \( m_j = \pm \frac{1}{2} \).

In a radiative recombination process (the process that an electron from the
conduction band recombinates with a hole in the valance band and photons are produced),
the condition that total momentum has to be conserved requires that total angular
momentum has to be equal to spin of photon (\( \pm 1 \)). It follows that there are only four
possible recombination possibilities, in term of spin conservation:
\[ \begin{align*}
\left| \frac{3}{2}, \frac{1}{2} \right>, & \quad \left| -\frac{3}{2}, -\frac{1}{2} \right>, \\
\left| \frac{1}{2}, -\frac{1}{2} \right>, & \quad \left| -\frac{1}{2}, \frac{1}{2} \right>.
\end{align*} \]

There are three other different states with total spin 0 and \( \pm 2 \) called
dark states (radiative recombination forbidden) and are not directly observable in optical
spectroscopy. Also, due to the large spin-orbit coupling off-set energy (for example \( E_{SO} \approx 68 \) meV for CdS and around 340 meV for GaAs), the recombination processes between
electron and the light hole in the split-off band are often ignored because they are not thermally populated.

**Temperature dependence of band gap**

It has long been understood that as temperature varies, the energy of band gap can be described by the empirical Varshni equation [2]

\[ E_g = E_0 - \frac{\alpha T^2}{\beta + T} \]

where \( \alpha \) and \( \beta \) are fitting parameters, \( E_0 \) is the band gap at 0K. However, recently Cardona et al., [3] has revisited this problem and by using general thermodynamic argument observed that the appropriate temperature dependence at low temperatures should be \( T^4 \) rather than \( T^2 \). An extended version of the above Varshni’s equation can therefore be written as [4]

\[ E_g = E_0 - \frac{\alpha_1 T^4}{\beta_1 + T^3} \]

At low temperature (\( T \to 0 \)) the energy gap \( E_g \) varies as \( T^4 \) while at high temperature \( E_g \) should vary linearly with \( T \). Our results of temperature dependent photoluminescence from single CdS and core-shell GaAs/AlGaAs nanowires are consistent with this \( T^4 \) dependence law (Sections IV.4 and V.2)

**II.2 Excitons in semiconductors**

In a semiconductor, when a negatively charged electron is promoted from the valence band to the higher energy conduction band, a positively charged hole (vacancy) is created in the valence band. The Coulomb interaction between the negatively charged
electron and the positively charged hole \((e-h)\) causes their motion to be correlated. As a result, a hydrogen-like bound state is formed which is called an exciton.

Depending on the coupling between the electron and hole, excitons are classified into two different types: Mott-Wannier and Frenkel for weak and strong couplings, respectively. There is no clear line between these two types of excitons. However, the general rule is that the Mott-Wannier exciton has an \(e-h\) separation much larger than lattice spacing and its binding energy is much smaller than that of a hydrogen atom. As we will see below, excitons in CdS and GaAs semiconductors are of the Mott-Wannier type, due to the large dielectric constants and small effective masses in these semiconductors.

Like any other two-body system, the exciton effective mass \(m_{ex}\) is given by the reduced mass:

\[
\frac{1}{m_{ex}} = \frac{1}{m_e} + \frac{1}{m_h}
\]

where \(m_e\) and \(m_h\) are electron and hole masses, respectively. As in a hydrogen atom, the exciton binding energy \(E_{ex}\) of the \(n^{th}\) quantum state is

\[
E_{ex} = \frac{\left(\frac{e^2}{\epsilon}\right)}{2a_{ex-h}n^2} = \frac{e^4 m_{ex}^2}{2 \epsilon^2 \hbar^2 n^2}
\]

with the electron charge square \(e^2\) is replaced by \(\frac{e^2}{\epsilon}\), \(\epsilon\) is the dielectric constant. The exciton Bohr radius \(a_{ex-B}\) is given by

\[
a_{ex-B} = \frac{\hbar^2 \epsilon}{m_{ex} e^2}
\]
Semiconductors like CdS, GaAs have large dielectric constants (~10) and small effective masses (~1/10 of a bare electron) so one can estimate that the exciton binding energy $E_{ex}$ is of order $1/1000$ of the hydrogen binding energy, and so the exciton Bohr radius can extend over many unit cells (~100 times larger) (see Figure II.2.1).

Figure II.2.1- Mott-Wannier exciton is a weak bound state between an electron and a hole with Bohr radius extends over many lattice spacing.

The ground state of a semiconductor is where the valence band is completely filled with electrons and the conduction band is empty. The exciton is an excited state where electron is promoted to the conduction band and a vacancy (hole) is left in the valence band. Consider an electron at the bottom of the conduction band and a hole at the top of valence band. Let $k_e$, $k_h$ be the wavevectors of electron and hole in the single particle picture and $K = k_e + k_h$ the exciton wavevector in the two-particle picture. As described by P. Yu and M. Cardona, [5] in the two-particle representation, the total energy of the exciton can be represented as
\[ E = E_g + \frac{K^2}{2m_{ex}} - E_{ex} \]

where \( E_g \) is the energy band gap. Figure II.2.2 below shows a typical exciton energy diagram in the two-particle picture with \( n = 1 \) and 2.

*Figure II.2.2- Exciton energy states \( n=1 \) and \( 2 \) in the two-particle picture*

As an example (and for further references in this thesis), Table 2.1.1 below shows the exciton binding energies and exciton Bohr radii of CdS and GaAs.

*Table II.2.1- Exciton binding energies and Bohr radii of CdS and GaAs [5]*

<table>
<thead>
<tr>
<th>Semiconductors</th>
<th>Exciton binding energies (meV)</th>
<th>Bohr radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS</td>
<td>27</td>
<td>23</td>
</tr>
<tr>
<td>GaAs</td>
<td>4.9</td>
<td>112</td>
</tr>
</tbody>
</table>
II.3 Cds semiconductor

II.3.1 Crystal structures

Cds is a II-VI semiconductor. It comes with two different crystal structures: hexagonal and cubic. For the samples investigated in this thesis, Cds nanowires have hexagonal structure. Figure II.3.1 shows a unit cell (first Brillouin zone) in the reciprocal lattice of the hexagonal Cds. More about lattice parameters of hexagonal Cds can be found in [6].

![Brillouin zone of the hexagonal lattice](image)

*Figure II.3.1- Brillouin zone of the hexagonal lattice [6].*

II.3.2 Band structure

Hexagonal Cds is a direct band gap semiconductor with the smallest band gap at the center (Γ point) of the Brillouin zone [6]. Band structures of hexagonal Cds have been calculated by several authors [for example see 7-9]. In hexagonal Cds, due to the crystal field and spin-orbit coupling, the highest valence band Γ₁₅ is split into three different band Γ₉, Γ₇, and Γ₇ (see Figure II.3.2 below).
At room temperature, the band gap energy ($E_g$) between the lowest conduction band and the highest valence band is 2.485 eV. [5] The split-off band energies $\Delta E_{CF}$ (due to crystal field) and $\Delta E_{SO}$ (due to spin-orbit coupling) have been calculated and measured by several authors.[8-11] For example, Thomas and Hopfield [11] have used the exciton reflectance method to obtain $\Delta E_{CF} \sim 0.028$ eV and $\Delta E_{SO} \sim 0.068$ eV. Because of the splitting of the valence band, the exciton states formed between holes from these valence bands with electrons in the conduction band are A, B and C excitons, respectively. In the two-particle picture, the exciton band structure of hexagonal CdS is illustrated as in Figure II.3.3 below:
Figure II.3.3-Exciton states A, B and C of hexagonal CdS in the two-particle picture

Exciton states A, B and C have been observed by different methods. [10, 11]

II.3.3 Some important parameters

At low frequency, hexagonal CdS has dielectric constants 8.45 and 9.12 along the $a$ and $c$ axes, respectively. Also, the effective masses of electron and hole are different in different crystal directions (see Table II.3.1 below). These differences will eventually make changes in a number of physical quantities such as polarization sensitivity or electron-hole Coulomb interaction is screened differently when measured along the $a$ and $c$ axes.

For convenience, some physical parameters of CdS are listed in the following Table II.3.1 (these parameters can be found in Landolt-Bornstein [6], for example).
### Table II.3.1 - Some physical parameters of CdS

<table>
<thead>
<tr>
<th>CdS</th>
<th>Values</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constants (A)</td>
<td>(4.14, 6.7)</td>
<td>Along $a$ and $c$ (Hex.)</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>2.485</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Dielectric constants</td>
<td>(8.45, 9.12)</td>
<td>Low frequency ($a,c$)</td>
</tr>
<tr>
<td></td>
<td>(5.32, 5.32)</td>
<td>High frequency ($a,c$)</td>
</tr>
<tr>
<td>Effective masses</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Here A, B and C indexes represent A, B and C bands, respectively. $\perp$ and $\parallel$ represent perpendicular and parallel to the c-axis)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Room temperature (by cyclotron resonance)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrons:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$m_{e\perp}^A$</td>
<td>0.159 m$_o$</td>
<td></td>
</tr>
<tr>
<td>$m_{e\parallel}^A$</td>
<td>0.168 m$_o$</td>
<td></td>
</tr>
<tr>
<td>Holes:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$m_{h\perp}^A$</td>
<td>0.43 m$_o$</td>
<td></td>
</tr>
<tr>
<td>$m_{h\parallel}^A$</td>
<td>1.96 m$_o$</td>
<td></td>
</tr>
<tr>
<td>$m_{h\perp}^B$</td>
<td>0.70 m$_o$</td>
<td></td>
</tr>
<tr>
<td>$m_{h\parallel}^B$</td>
<td>0.43 m$_o$</td>
<td></td>
</tr>
<tr>
<td>$m_{h\perp}^C$</td>
<td>0.79 m$_o$</td>
<td></td>
</tr>
<tr>
<td>$m_{h\parallel}^C$</td>
<td>0.37 m$_o$</td>
<td></td>
</tr>
<tr>
<td>dEg/dT (meV/K)</td>
<td>-0.41</td>
<td></td>
</tr>
<tr>
<td>(Eg-band gap energy)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dEg/dP (meV/K)</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>(Eg-band gap energy)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>(W/cm.K)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk modulus (GPa)</td>
<td>61.5</td>
<td></td>
</tr>
</tbody>
</table>
II.4 GaAs semiconductor

II.4.1 Crystal structure

GaAs semiconductor compound belong to the III-V group. It has cubic (zincblende) crystal structure type with a lattice spacing constant of 5.64 Å. *Figure II.4.1* shows a unit cell (first Brillouin zone) in the reciprocal lattice of GaAs.

*Figure II.4.1- Brillouin zone of the GaAs cubic lattice [12].*

GaAs has very similar lattice parameters with the lattice parameters of AlGaAs (lattice constant of 5.65 Å – varies linearly with Al composition), which is one of the reasons that the GaAs/AlGaAs heterostructures have been widely used in research and industrial applications because they can be grown strain-free.
II.4.2 Band structure

GaAs is a direct band gap semiconductor with minimum band gap at the center (Γ point) of Brillouin zone. Figure II.4.2 shows band structure of cubic GaAs at room temperature as calculated by Chelikowski, J. R., Cohen, M. L. [1].

![Band structure of GaAs](image)

Figure II.4.2- Band structure of GaAs obtained by a non-local pseudopotential calculation [1].

The minimum of the lowest conduction band Γ₆, as well as the higher sets of minima at L₆ and near X₆ (about 10% away from zone boundary [14]) are important for optical as well as transport properties [1].
At the highest point of the valence bands ($\Gamma_8$), the energy levels are degenerate. There are two bands corresponding to heavy the hole (spin 3/2) and light hole (spin 1/2). There is also another valence band ($\Gamma_7$) which has light hole mass which lies at higher energy due to spin-orbit coupling. At room temperature, the band gap between the $\Gamma_8$ valence band and $\Gamma_6$ conduction band is 1.43 eV [5]. The dependency of the energy band gap of GaAs on temperature was also calculated by several authors.[For example, see 15-18] Detail band structure of GaAs near the Brillouin zone is very similar to the discussion in Section II.1 above.

II.4.3 Some other important physical parameters for GaAs

GaAs has dielectric constants of 12.8 (for example, see [19]) at low frequency and 11.6 (measured by reflection, absorption and film interference methods) at high frequency. Dielectric constants of GaAs are important for determining the polarization of excitonic dipoles in a GaAs nanowire. This problem will be discussed in depth in Section II.11.

Table II.4.1 below gives a summary of physical parameters of GaAs as obtained from Landolt-Börnstein. [12]

Table II.4.1- Some physical parameters of GaAs.

<table>
<thead>
<tr>
<th>GaAs</th>
<th>Values</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice constants (Å)</td>
<td>5.64</td>
<td>Cubic</td>
</tr>
<tr>
<td>Band gap (eV)</td>
<td>1.43</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Dielectric constants</td>
<td>12.8</td>
<td>Low frequency</td>
</tr>
<tr>
<td></td>
<td>11.6</td>
<td>High frequency</td>
</tr>
<tr>
<td>--------------------------</td>
<td>------</td>
<td>----------------</td>
</tr>
</tbody>
</table>
| Effective masses (where $m_o$ denote the bare electron mass, and the numbers in [ ] indicate the crystal direction) | Electron: 0.0635 $m_o$  
Heavy hole: 0.33$m_o$ [100]  
0.78 $m_o$ [111]  
Light hole: 0.090$m_o$ [100]  
0.077 $m_o$ [111] | Room temperature (PL)  
(By band mass method) |
| $dE_g/dT$ (meV/K)        | -0.395 |                |
| $dE_g/dP$ (meV/K)        | 115   |                |
| Thermal conductivity (W/cm.K) | 0.54 |                |
| Bulk modulus (GPa)       | 75.4  |                |
II.5 From bulk materials to nanowires

Semiconductor nanowires (NWs) are one dimensional structures whose diameter vary from ~30 nm to 150 nm with lengths of several micrometers. The diameter of these nanowires is quite larger than the exciton Bohr radius (for example the Bohr exciton radius is 2.3 nm for CdS, ~ 10 nm for GaAs), one would expects only negligible quantum confinement of the exciton electronic states. Because of this, the electronic band structure of a nanowire is similar to that of the bulk material.

However, in a semiconductor NW, due to the huge surface-to-volume ratio (~$10^8$ - $10^9$ m$^{-1}$ in NW compare to ~$10^2$ m$^{-1}$ in bulk material); excitons are somewhat spatially restricted to move in the direction perpendicular to the NW axis, and as a result their behavior is expected to be very different from bulk materials. Surface states, structural inhomogeneities and defects also have strong effects on the optical and transport properties of these nanostructures.

In the next sections we present some nanowire growth techniques and descriptions of the semiconductor nanowires investigated in this thesis.
II.6 Nanowire growth

Recent advances in knowledge and technologies have enabled scientists to fabricate nanowires with significant precision and flexibility. In fact, nanowires with different sizes, shapes have been grown by various mechanisms and methods.[20-23] Most importantly, besides controlling the size and shape of a nanowire, scientists can also control the materials in different locations along or across a nanowire (nanowire superlattice) (see Figure II.6.1). This is especially helpful when one needs to develop nano-heterostructures or hybrid nano devices (such as a single quantum dot embedded inside a p-n junction to create a single photon LED). [24]

Figure II.6.1-Nanowire heterostructures a) a quantum dot (InAsP) embedded in a p-n junction InP nanowire and b) a core-shell GaAs/AlGaAs nanowire

As an example, a nano-tree sample (a complex of nanowires) grown by the Metal-Organic Vapor Phase Epitaxy (MOVPE) method with controlled height, diameter and compositions is shown in Figure II.6.2.[20]
Figure II.6.2- a) GaP and b) GaP-GaAsP nanotrees [20]

Figure II.6.2-a shows a TEM (Transmission Electron Microscope) image of a GaP nanotree with five branches in different growth directions. In Figure II.6.2-b, a GaP-GaAsP nanowire heterostructures with four branches, and the compositions of each element in the main tree and branches are well controlled.

In general, the strategy of growing nanowires is to force crystallization to develop along one dimension (the nanowire’s axis). There exists several growth mechanisms which have been described in details by P. Yang.[21,25] One of the most popular mechanisms used for growing nanowires is the Vapor-Liquid-Solid (VLS) mechanism. In the VLS method, nano-particles catalysts (usually gold is used) on a substrate at elevated temperature form a eutectic solid solution with vapor reactants, which then diffuse to form solid nanowires in the vertical direction towards the substrate (see Figure II.6.3a). Figure II.6.3b shows the composition and phase changes during the nanowire growth process. [25]
Figure II.6.3- a) Schematic illustration of the nanowire growth using the Vapor-Liquid-Solid mechanism and b) evolution of phase and composition during the growth process [25]

The VLS mechanism was first developed by Wagner and Ellis in 1964 tried to produce whiskers.[26] In recent years, this mechanism has been extensively used by many groups and in fact the CdS and core-shell GaAs/AlGaAs nanowire samples studied in this thesis were grown by this mechanism. The VLS technique has many advantages because the nanowire diameter can be easily controlled through the size of the catalyst seeds, while the length and wire composition can also be easily controlled by changing growth time or the gases. Several issues remain still with VLS technique include the twinning defects, tapered nanowire shape, and surface passivation. These problems
determine the performance of nanowire based devices, and so it is important to understand and control. In the next section (II.7), we will briefly discuss the twin defects and recent improvements made by our collaborators.

**II.7 Twin defects in nanowires**

Twin defects in III-V semiconductor nanowires are crystalline imperfections which occur along the growth direction (<111>B-oriented) and have been reported by various research groups.[27-30] Twin defects play an important role in the performance of nanowire based devices. Unfortunately, in most popular nanowire growth methods such as VLS (or MOCVD), the most favorable growth direction is <111>B.[31]

In zincblende semiconductor nanowires, such as GaAs, twin defects are referred as twin planes that are normal to the growth direction. As it was explained by Jonas Johansson *et al.* [31] and Brian A. Korgel [32], in III-V zincblende crystals, the buck between twin planes (between two {111} facets which are perpendicular to the <111>B growth direction) is of octahedral shape. Twin planes are formed due to a $60^\circ$ turn of an octahedral around the growth direction (see *Figures II.7.1*).

Authors in [31] have observed that the twin spacing was not periodic and not sensitively correlated to the nanowire diameter. They also found that the higher nanowire growth temperature, the higher twin defect density. One of the possibilities could lead to the formation of the twin defects are the strain and surface energy at the gold-nanowire edge where the nanowire nucleation occur.
Figure II.7.1- Octahedral model of GaP nanowires. Twin defects are caused by a 60 degrees turn of an octahedral around the growth direction [31]

Figure II.7.2- a) HRTEM images of a GaP nanowire growth along <111>B direction. b) shows a closer look at the area indicated by the rectangle in a; c,d and e are power spectra which indicate the zincblende crystal structure of the nanowire [31]
Figures II.7.2 shows a HRTEM (High Resolution Transmission Electron Microscope) image of a GaP nanowire fabricated by MOVPE method. The nanowire has a hexagonal cross section and the twin planes are clearly visible (see figure caption for details). [31]

It has been reported that the twin defects can be reduced by lowering the growth temperature. In a recent work by Hannah J. Joyce et al.,[23] it is shown that twin defect free, uniform GaAs nanowires can be grown by MOCVD method using two temperatures procedure. First, they nucleate the wire by growing briefly (1 minute) at temperature of 450°C. Then the temperature is rapidly decreased to 390°C for the remainder of the nanowire growth. TEM (Transmission Electron Microscope) images in Figures II.7.3 below show the comparison of GaAs nanowires grown by one and two temperatures procedures.[23]

Figures II.7.3- a) and b) TEM images of GaAs nanowires grown by single temperature (450°C) procedure (the arrows in a) show the twin planes); c) and d) by two temperatures (390°C and 450°C) procedure [23].

In these TEM images, we can clearly see in Figure II.7.3-a,b, grown by single temperature procedure, there are twin planes (as indicated by arrows in a, for example).
However, in Figure II.7.3-c,d, grown by two temperature procedure, no indications of twin defects appear.

**II.8 CdS nanowires**

CdS NWs measured in this thesis were grown using the vapor-liquid-solid (VLS) method using colloidal gold catalysts. The schematics of the growth process is illustrated as in the figure below.

![Vapor-Liquid-Solid growth](http://www.nunanoalliance.org)

**Figure II.8.1-Illustration of the CdS nanowire growth**

(Source: Lauhon Lincoln lab – Northwestern University, http://www.nunanoalliance.org)

Nanowires were grown with the CdS single-source precursor placed at the upstream end of a quartz tube furnace. For nanowires investigated in our experiments, two different sizes of gold catalysts were used: 50 nm and 20nm. For the 50 nm gold catalysts, the growth substrate held at 525°C, was placed downstream of the precursor, which was held at ~200°C. The 20 nm nanowires were grown at the same substrate temperature, but the precursor was heated in a separate chamber to ~230°C and delivered to the reactor with a hydrogen carrier gas flow. Independent heating of the CdS precursor
resulted in better control over NW morphology. The 20 nm nanowires were straight, uniform, and 3.5 - 5 µm in length, while the 50 nm nanowires were on average three times longer (12 – 15 µm) and displayed more morphological variations. TEM images show that nanowires were grown along the c-axis of the single CdS crystal. A detailed description about this growth method can be found in [33]. Because the exciton Bohr radius is only 2.8 nm in CdS, neither set of wires are expected to show any quantum confinement effects.

Shown below is a SEM (Scanning Electron Microscope) image of a CdS nanowire sample which was grown on a Silicon substrate. It is clearly that majority of nanowires are straight and uniform but few have significant irregularities.

Figure II.8.2- CdS nanowire sample grown on a Silicon substrate

In order to investigate a single nanowire from a high density sample, nanowires were transferred from the grown substrate into a solution and then deposited onto a marked Si substrate. Figure II.8.3 below shows an example (an AFM image) of a single CdS nanowire on a Si substrate. This particular nanowire will be discussed in detail latter in Part IV.
Figure II.8.3- AFM image of a single nanowire on a Si substrate

Individual nanowires are ~30-150 nm in diameter, depending on the seed catalysts, and ~5-15 μm long.

**II.9 Core-shell GaAs-AlGaAs nanowires**

GaAs/AlGaAs nanowire samples were fabricated by the Vapor - Liquid - Solid (VLS) method. Undoped GaAs (111)B substrates were functionalized by dipping in 0.1% poly-L-lysine (PLL) solution for 1 minute. After rinsing and drying, 30 nm diameter gold (Au) nanoparticles were dispersed on the substrate surface. Negatively charged Au nanoparticles were attracted to positively charged PLL layer. GaAs nanowires were grown by horizontal flow MOCVD at a pressure of 100 mbar. The total flow rate of H₂ carrier gas in the reactor cell was 15 standard liters / min. Prior to nanowire formation, the substrate was annealed in-situ at 600 °C under AsH₃ ambient for 10 min to desorb surface contaminants and form a eutectic alloy between the Au nanoparticle and Ga from the substrate. After cooling down to the growth temperature at 450 °C, trimethylgallium (TMG) source gases were switched on to initiate nanowire growth. The approximately
40 nm diameter GaAs nanowires were grown along the (111)B axis. The molar flow rates of trimethylgallium (TMG) and AsH₃ were $1.2 \times 10^{-5}$ mol/min and $5.4 \times 10^{-4}$ mol/min, respectively. Growth time was 30 minutes. After switching off Ga source, the growth temperature was increased to 650 °C, shell growth was initiated by switching on trimethylgallium (TMG) and trimethylaluminum (TMA) sources simultaneously. The vapor aluminum composition was 0.26 and the shell growth time was 15 min. The growth processes are illustrated as in the Figure II.9.1 below.

![Figure II.9.1 – Illustration of core-shell GaAs-AlGaAs nanowire growth](image)

Shown below is a FESEM (Field Emission Scanning Electron Microscope) image of the nanowire sample which we have been investigated. One can see clearly that the nanowires grow vertically on the substrate but have a tapered shape.
Figure II.9.2 – FESEM (Field Emission Electron Microscope) image of a GaAs-
AlGaAs core-shell nanowire sample investigated in this thesis

As will be shown in the following section, the AlGaAs cap layer around the core
GaAs nanowire reduces the affects of non-radiative surface recombination.

In order to investigate a single nanowire, nanowires were transferred from the
grown substrate into methanol solution and then deposited onto marked Si substrate.
Figure II.9.3 below shows an AFM (Atomic Force Microscope) image of a single
nanowire on a Si substrate.

Figure II.9.3- AFM image of a single nanowire on a Si substrate
Individual GaAs/AlGaAs nanowires are around 6-8 µm long, with the core
diameter of ~40 nm and total diameter of around 80 nm. The Bohr exciton radius in
GaAs is ~11 nm and is quite smaller than the wire’s diameter so no significant quantum
confinement effects are expected in these nanostructures.

II.10 Core-shell GaAs/AlGaAs nanowires vs. bare GaAs

The reason that one chooses core-shell GaAs/AlGaAs nanowires over bare (or
uncoated) GaAs nanowires is that bare GaAs nanowires have low quantum efficiency due
to non-radiative recombination at the surface.[34,35] Core-shell GaAs-AlGaAs
nanowires have much a higher quantum efficiency (over an order of magnitude higher)
compared to the quantum efficiency of bare GaAs nanowires. The shell AlGaAs is
chosen because AlGaAs and GaAs have similar lattice constants. This is especially
helpful for a strain-free nanowire structure.

![Figure II.10.1- A schematic illustration of a bare GaAs nanowire (left) and a core-shell GaAs/AlGaAs nanowire (right)](image-url)
Figure II.10.2 below shows an example of PL spectra from a core-shell nanowire and the most intense bare nanowire recorded at identical excitation conditions. The enhancement of the low-temperature PL efficiency by passivating the GaAs surface with AlGaAs is comparable to that previously reported in room temperature PL measurements on similar core-shell structures grown by selective-area metalorganic vapor phase epitaxy.\[36\]

![Figure II.10.2 - Photoluminescence emissions from a single bare GaAs and a core-shell nanowires at 10K](image)

Figure II.10.2 - Photoluminescence emissions from a single bare GaAs and a core-shell nanowires at 10K

On the other hand, time-resolved measurements (not shown here) have indicated that the recombination lifetime of excitons in both the bare and core-shell GaAs/AlGaAs nanowires at 10 K is less than 80 ps, which is the system response time of our time-correlated photon counting system. Even in the core-shell GaAs/AlGaAs structures such
a lifetime is more than an order of magnitude less than the lifetime observed in high quality GaAs double heterostructures.[37] This reduced lifetime may result from defects within the GaAs nanowire core, or at the GaAs-AlGaAs interface. TEM studies (not shown here) of bare GaAs nanowire have shown the existence of twinning defects, which are known to adversely affect the optical and electronic properties of semiconductors.[38,39] This suggests that there is still significant room for improvement in optimizing the luminescence efficiency of these core-shell nanowires.

II.11 Photoluminescence polarization in semiconductor nanowires

Nanowires are inherently anisotropic structures, and it is not surprising that their optical properties are anisotropic as well, with optical absorption and emission for different polarization being significantly different. In fact, this anisotropy has already been utilized for device applications.[40] There are several factors that determine the polarization properties of nanowires including crystal structures and dielectric mismatch which we will be now discuss in details.

In a semiconductor NW with large dielectric constant, the large dielectric mismatch between the NW and surrounding air results in a strong suppression of an electromagnetic field perpendicular to the nanowire axis. Consider a single NW as a perfect, infinitely long cylinder with dielectric constant $\varepsilon$ embedded in a surrounding environment of dielectric constant of $\varepsilon_0 < \varepsilon$. In terms of classical electrodynamics, there exists certain degrees of polarization for both absorption and emission of the NW [41, 42]. If the wavelength of the incident field is much larger than the wire’s diameter, then for an
incident field polarized parallel to the NW $E_{||0}$, the transmitted laser field inside the NW is still the same i.e. $E_{||} = E_{||0}$. However, if the incident laser field is polarized perpendicular to the NW $E_{\perp 0}$ then the transmitted field is reduced as (see Figure II.11.1):

$$E_{\perp} = \frac{2\varepsilon_0}{\varepsilon + \varepsilon_0} E_{\perp 0} \quad (1)$$

![Figure II.11.1- Illustration of the suppression of a perpendicularly polarized incident electromagnetic field](image)

On the other hand, if we assume that there are equal numbers of parallel and perpendicular polarized photons are created inside the NW, the ratio between intensities of parallel and perpendicular emitted photons is (see Figure II.11.2):

$$\frac{I_{||}}{I_{\perp}} = \frac{(\varepsilon + \varepsilon_0)^2 + 2\varepsilon_0^2}{6\varepsilon_0^2} \quad (2)$$

where $I_{||}$ and $I_{\perp}$ are the intensities of parallel and perpendicular polarized photons, respectively.
If we define a degree of polarization as:

\[ P = \frac{I_\parallel - I_\perp}{I_\parallel + I_\perp} \quad (3) \]

then for GaAs \( \varepsilon = 12.5 \) and surrounding \( \varepsilon_0 = 1 \) one would expect a degree of polarization \( P \sim 93\% \) of the emission.

The above argument is only valid for nanowires with zincblende (ZB) crystal structure (such as GaAs, InGaAs or InP grown at certain temperatures) since in ZB materials, the s-like electrons in the conduction band have \( \Gamma^6 \) symmetry while p-like light and heavy holes in the valence band have \( \Gamma^8 \) symmetry (\( \Gamma^7 \) band is excluded because of large spin-orbit coupling). The emission from recombination \( \Gamma^6 \rightarrow \Gamma^8 \) is completely unpolarized [43, 44] and in this case the dielectric contrast between the nanowires and surrounding is mainly responsible for the PL polarization.

In nanowires with wurtzite crystal structure (such as CdS, or InP grown at certain temperatures), however, the situation is different. In a wurtzite material, the s-like electrons of the conduction band have \( \Gamma^7 \) symmetry and p-like holes in the valence band split into three bands (called A, B and C where A band has the lowest energy and C band the highest) due to the spin-orbit coupling and crystal field splitting. [43, 44] Band A has
Γ⁹ symmetry while bands B and C have Γ⁷ symmetry. The lowest energy recombination Γ⁷ -> Γ⁹ is dipole allowed only if E field is perpendicular to the c-axis and forbidden if E parallel to the c-axis.[43, 44] Most of semiconductor nanowires with wurtzite crystal structure are grown along [0001] direction which means that the c-axis is parallel to the nanowire axis. In other words, in a nanowire with wurtzite crystal structure, the lowest energy transition (Γ⁷ -> Γ⁹) is strongly polarized perpendicular to the nanowire axis. [45]

References


[23] Hannah J. Joyce, Qiang Gao, H. Hoe Tan, Chennupati Jagadish, Yong Kim, Xin Zhang, Yanan Guo, and Jin Zou, Nano Letter 7, 921-926, 2007

[24] V. Zwiller et al., Optically bright quantum dots in single nanowires, NanoLett. 5 1439 2005


Part III

Experimental techniques for Studying Single Nanostructures
**III.1 Photoluminescence spectroscopy study of single nanowires**

### III.1.1 Introduction

Photoluminescence (PL) spectroscopy is a powerful method which has long been used to non-destructively study physical properties and dynamical processes of a variety of materials. This is a particularly important technique for studying semiconductors. In optical spectroscopy, photons (with energies greater than the band gap of the semiconductor) are used to excite electrons to the conduction band, leaving holes in the valence band. The Coulomb interaction between a pair of an electron (negatively charged) and a hole (positively charged) causes their motion to be correlated and a hydrogen-like bound state is formed: an exciton (discussed earlier in Section II.2).

![Schematic diagram shows excitation and emission of excitons in a photoluminescence measurement](image)

*Figure III.1.1 Schematic diagram shows excitation and emission of excitons in a photoluminescence measurement*
An electron and a hole can either recombine non-radiatively by emitting phonons (or transferring energy to other particles) or radiatively by emitting photons (Figure III.1.1). In the later case, by using spectroscopy to analyze the emitted photons (or photoluminescence), we can extract information about the electron energy levels, including their spin alignment at the time of recombination. In a time-resolved measurement, one can also obtain dynamical information such as the lifetime of the excitons.

There are different ways in which an electron from the conduction band can radiatively recombine with a hole in the valence band. For example in a band-to-band recombination process where the electron and hole may go through several scattering processes (with optical phonons, for example) and relax to the bottoms of the conduction band and the valence band before recombining (see Figure III.1.1). In another recombination process the electron and hole may recombine before they relax to the bottoms of the bands, resulting a broad emission spectrum (the electron and hole are referred as hot carriers in this case).

*Figure III.1.2 Electron-hole binding energy lowers the free exciton emission band*
When the electron and hole are correlated (exciton), the electron-hole binding energy will lower the energy of the emitted photon, which results in a free exciton emission band below the band gap (Figure III.1.2).

An excellent review of photoluminescence spectroscopy of crystalline semiconductors has been given by G.D. Gilliland.[1]

III.1.2 The micro-photoluminescence experimental setup

In order to investigate the optical properties of a single nanostructure such as a single nanowire, micro-photoluminescence methods are used. A schematic diagram describing the equipment used in this method is shown below.

Figure III.1.3 Schematic illustration of the confocal setup for a micro-photoluminescence measurement
In this confocal microscopic set up, a laser source (Argon or Ti:Sapphire) is used for excitation. The laser is manipulated by polarizing optics (a matched set of Glan-Thomson linear polarizers and Babinet-Soleil compensators - see discussion in Section III.1.4), a Beam Splitter (BS) and focused onto the sample through a 50X/0.5NA long working distance (10.6 mm) microscope objective. The sample, which is a Si substrate with the dispersed nanowires, is placed onto the cold finger of a variable temperature continuous-flow helium cryostat. PL emission from a single NW is collected by the same microscope objective (backward scattering), spatially filtered by a pinhole, and analyzed by a second set of polarizing optics before being focused on the entrance slit of the spectrometer. In a PL imaging experiment, a Dove prism is used to rotate the PL image of the NW so that it will lie along the entrance slit of the spectrometer. This allows one to obtain a spatial profile of PL emission along a nanowire. The PL is then dispersed by the spectrometer and detected by the detector (CCD camera, MCP-PMT or APD).

The working principles of the several optical components including lasers, polarizing optics, the cryostat, spectrometers and detectors will now be described in detail.

**III.1.3 The lasers.**

In a non-resonant excitation experiment, electrons and holes are excited with significant excess energy which must be lost due to multiple scattering events before recombination. For such a measurement, we use a laser with a fixed wavelength and the energy of photon is larger than the band gap. For the CdS nanowires (band gap $E_g=2.53\text{eV}$), the 458 nm line (which corresponds to 2.71eV) of an Ar+ laser was used as an excitation source. For the GaAs nanowires (band gap $E_g\sim1.52\text{ eV}$) an excitation of 780 nm ($E \sim 1.59\text{eV}$) from a continuous Ti:Sapphire laser was used.
For a resonant excitation measurement, the wavelength of the excitation laser is tuned so that electrons and holes are pumped directly into well defined electronic states (excited states) or closely coupled to the vibronic states (such as optical phonons). Such resonant excitation make it possible to study directly the electronic and vibronic structures of semiconductor nanostructures. In our resonant excitation measurements with core-shell GaAs-AlGaAs nanowires, the excitation wavelength of a Ti:Sapphire laser was scanned from 700 nm up to 808 nm. These wavelengths have enough energy to reach several orders of LO (Longitudinal Optical) phonon in GaAs or the gap of AlGaAs barrier.

![Image of a typical laser pulse with decay time measured <80 ps](image)

*Figure III.1.4 Example of a typical laser pulse: decay time measured <80 ps limited by the resolution*

For time-resolved measurements of CdS nanowires, a mode locked (pulsed) 864 nm Ti:Sapphire (200 fs wide laser pulses at a repetition rate of 76 MHz or 13.6 nm between pulses) laser line was frequency doubled by the use of β-barium borate (BBO) non-linear optical crystal to create 432 nm laser pulses. Such pulses have an energy larger
than the CdS band gap, and can excite electrons from the valence band to the conduction band. For GaAs-AlGaAs nanowires, we use 780 nm Ti:Sapphire laser pulses to excite the nanowires. Figure III.1.4 above shows an example of a laser pulse measured at 418 nm. The measured decay time was less than 80 ps, which was limited by the resolution. There were couple of peaks at longer times which were caused by electronic equipment. In Section III.2, we will discuss in detail how a time-resolved measurement is conducted.

### III.1.4 The polarizing optics

In order to conduct a photoluminescence polarization measurement, polarizing optics are required. The polarizing optics used here includes Glan-Thompson (GT) linear polarizers and Babinet-Soleil (BS) compensators. These optical components are used to manipulate the polarization of laser excitation and to analyze the polarization of photoluminescence. The principle of the GT and BS are illustrated in the following diagram.

*Figure III.1.5 An illustration of polarizing optics setup*

The first Glan-Thompson (GT₁) (see figure above) ensures that the laser is purely linearly polarized. This linearly polarized wave then goes through the first Babinet-Soleil
compensator BS. If BS is set as a half-wave plate and at an angle \( \alpha \) (relative to the vertical axis) then the outgoing laser is still linearly polarized but rotated by an angle of \( 2\alpha \). This is especially helpful when one would like to linearly excite a nanowire with the laser linearly polarized at any angle relative to the nanowire axis. If BS is set as a quarter-wave plate (an angle of 45 or -45 degrees, relative to the linearly polarized laser, is chosen in order to have the same amplitudes and phases of the ordinary and extraordinary laser components) then the outgoing laser will be circularly polarized with a phase difference of \( \pi/2 \) between the two components. To have a better idea of how the polarizing optics works, one can analyze the optics using the Jones vectors and matrices. Consider a plane wave which propagates in the z-direction with electric field of the form

\[
\vec{E} = \begin{bmatrix} E_x(z,t) \\ E_y(z,t) \end{bmatrix} = \begin{bmatrix} E_{0x} e^{i\phi_x} \\ E_{0y} e^{i\phi_y} \end{bmatrix}
\]

with some phases \( \phi_x \) and \( \phi_y \). For simplicity we assume that \( E_{0x} = E_{0y} \). The wave is linear polarized if \( \phi_x = \phi_y \pm n\pi \) or circular polarized if \( \phi_x = \phi_y \pm \frac{\pi}{2} \). We then define the Jones vectors as follow: [2]

For P-state:

- horizontal: \( \vec{E}_h = \begin{bmatrix} e^{i\phi_x} \\ 0 \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \end{bmatrix} \)
- vertical: \( \vec{E}_v = \begin{bmatrix} 0 \\ e^{i\phi_y} \end{bmatrix} = \begin{bmatrix} 0 \\ 1 \end{bmatrix} \)

and for R-, L – states (normalized)
We can easily verify that

\[ E_h + E_v = \begin{bmatrix} 1 \\ 1 \end{bmatrix} = E_{\pi/4} \]

and

\[ E_R + E_L = \sqrt{2} E_h \]

which means that the sum of two linearly polarized waves gives a linearly polarized wave and the sum of left and right circular waves also gives a linearly polarized wave. In general, any polarization can be described as a linear combination of the basic states \( E_h, E_v \) or \( E_R, E_L \). It is also easy to verify that the Jones vectors satisfy the orthogonal conditions.

Suppose an electric filed \( E \) passes through an optical element and changes to \( E' \).
between $E$ and $E'$ (Figure III.1.6) there exists a relation $\vec{E}' = J \vec{E}$ where $J$ is a 2x2 matrix known as the Jones matrix. In the case of a plane wave propagating along the $z$-direction we have, for example:

$$
\begin{bmatrix}
E'_x \\
E'_y
\end{bmatrix}
= \begin{bmatrix}
a_{11} & a_{12} \\
a_{21} & a_{22}
\end{bmatrix}
\begin{bmatrix}
E_x \\
E_y
\end{bmatrix}
$$

where $a_{ij} (i, j = 1, 2)$ are complex constants. The following list shows the Jones matrices for several simple polarizing optical elements.[2]

$$
\begin{bmatrix}
1 & 0 \\
0 & 0
\end{bmatrix}
\quad \quad \quad \quad \quad
\begin{bmatrix}
1 & -1 \\
-1 & 1
\end{bmatrix}
\quad \quad \quad \quad \quad
\begin{bmatrix}
1 & i \\
-1 & 1
\end{bmatrix}
\quad \quad \quad \quad \quad
\begin{bmatrix}
1 & i \\
i & 1
\end{bmatrix}
$$

*Figure III.1.7 Jones matrices of several simple polarizing optics: horizontal, vertical, 45°, -45°, right and left circular polarizations.*[2]
In general, the Jones matrix elements are functions of some rotation angle $\theta$ (see Figure III.1.8). We have: $J_{\theta}^h = R_{\theta}^{-1} J_h R_{\theta}$ where $R_{\theta}$ is a 2x2 rotational matrix and $J_h$ is the Jones matrix corresponding to the horizontal state.

In order to analyze the exciton spin alignments in a single nanowire, a second set of Babinet-Soleil and Glan-Thompson (BS$_2$ - GT$_2$ see Figure III.1.5) is used. Assuming that the signal from the sample is circularly polarized, the BS$_2$ is set to introduce a phase delay of $\pm \pi/2$ (an angle of 45 or -45 degrees is chosen) which therefore converting the circularly polarized light to vertically linearly polarized light. The GT$_2$ (always set to select only vertically polarized light) will then select either right or left circular polarization which will be dispersed by the spectrometer and detected by a detector.

**III.1.5 The optical cryostat**

Usually, photoluminescence measurements are conducted at low temperatures (10 K). At low temperatures, we will have higher quantum efficiency, lower thermal effects and reduced scattering with phonons. Photoluminescence measurements at low temperature use an optical cryostat shown schematic in Figure III.1.9 below.
The optical cryostat is constructed from a standard made by the Janis company. However, several modifications have been made. For example, the cold finger and the vacuum jacket were redesigned so to fit in the bore of a superconducting magnet (working in the Faraday geometry, up to 4T). A different design is optimized to hold more samples and for better temperature control in temperature dependent measurements. The cryostat is maintained at a vacuum of $10^{-6}$ Torr (to remove conductive heat transfer between the cold finger and the room temperature shield). The temperature can be varied from 4 to 300K using a heater attached to the cold finger. The temperature is controlled using a temperature controller which monitors the temperature using a temperature sensor attached to the cold finger. This optical cryostat has a large solid angle for luminescence collection.

![Figure III.1.9 Schematic illustration of continuous cryostat (Janis)](image)

III.1.6 The Dove prism

The Dove prism, or image rotator, has a very interesting feature: it can rotate an image around its optical axis. Unlike usual prism (which disperses light with different
wavelengths at different angles), the Dove prism rotates an image twice the angle that it rotates through. The figure below shows how a Dove prism works. [3]

Figure III.1.10 A Dove prism rotates an image (image courtesy of Edmund optics [3])

In our imaging measurements of photoluminescence from single nanowires, we use an uncoated Dove prism to rotate the photoluminescence image of a nanowire so that the image will be parallel to the vertical slit of the spectrometer and detected by a CCD camera. In this way, we can study the photoluminescence emission from particular positions along the nanowires. The diagram below illustrates how a Dove prism is used in an actual experiment.

Figure III.1.11 Dove prism rotates NW - PL image along vertical slit of spectrometer
III.1.7 The spectrometers

III.1.7.a Triple Dilor spectrometer

Figure III.1.12 below illustrates the configuration of mirrors, gratings, slits of the triple Dilor spectrometer which has been employed to take data from single CdS nanowires. In this spectrometer, $S_1$ and $S_3$ - corresponding to entrance and exit slits of the subtractive double stages - strongly affect the spatial resolution. In our experiment, these slits are set at 200 $\mu$m which corresponds to 0.9 $\mu$m on the sample. This is smaller than the system spatial resolution (1.5 $\mu$m).

![Schematic illustration of the Dilor triple spectrometer working in the subtractive mode.](image-url)

Figure III.1.12 Schematic illustration of the Dilor triple spectrometer working in the subtractive mode.
The triple grating Dilor spectrometer has excellent spectral resolution (~70 µeV). The total system response gives spatial resolution ~1.5 µm. These features are especially helpful when used to image defect related states in single nanowires (CdS, for example). However, the holographic gratings of this spectrometer are only efficient at wavelengths between 400 and 700 nm, so in order to investigate optical properties of GaAs nanowires (which emit photons with wavelength at ~820 nm) other spectrometers (MS260i Newport spectrograph and SPEX) are used.

III.1.7.b MS260i ¼ m spectrometer (Oriel-Newport)

![Image](image.png)

*Figure III.1.13 Schematic illustration of the MS260i 1/4m (image courtesy of Newport [4])*

The MS260i spectrometer uses an asymmetric in-plane Czerny-Turner optical configuration with an input F/number of 3.9 and a resolution of 0.10 nm. The
spectrometer can use either of two gratings: 1200 grooves and 300 grooves/mm. This is very convenient for measuring photoluminescence over a wide range of wavelength since the gratings can be rapidly changed. The GaAs/AlGaAs core-shell nanowire data presented in this thesis was taken by this spectrometer. One disadvantage of this single grating spectrometer is that it cannot reject the laser properly for near resonant experiments. To get around with this problem, a sharp laser filter is used to block the laser from entering the entrance slit.

**III.1.7.c SPEX 1m spectrometer**

A third spectrometer, the SPEX 1m, has been employed to investigate the optical properties of III-V semiconductor nanowires.

![SPEX 1m spectrometer using Czerny-Turner configuration](image)

*Figure III.1.14 SPEX 1m spectrometer using Czerny-Turner configuration*

The SPEX spectrometer can archive high dispersion (~0.1 nm resolution) and yet its grating is changeable, easy to access and align. For GaAs-AlGaAs and InP nanowires
which emit PL near 820-860 nm, we use the 2nd order of a grating with 600 grooves/mm and which is blazed at 1600 nm.

**III.1.8 Luminescence detection: CCD camera, MCP-PMT and APD**

The final and most important task in an optical spectroscopy measurement is to sensitively detect luminescence (or the scattered light, e.g. Raman) from the sample. Depending on the nature of the experiment and the physical properties of the sample, different detectors are used. We use Silicon CCD (Charge Coupled Device) camera to detect photoluminescence spectrum (intensity vs. wavelength) of a sample that have emission wavelengths in the range of 400-1000 nm. To measure the decay time of excitons we use a MCP-PMT (Micro Channel Plate – Photomultiplier Tube) or an APD (Avalanche Photo-Diode) depending on the emission wavelengths of the sample. These detectors have the capability of detecting single photons at a time and can provide a temporal (or decay) spectrum (intensity vs time). Here we briefly describe the principle of these instruments and their uses.

**III.1.8.a CCD camera**

A CCD camera contains an array of capacitors, each capacitor called a pixel. The Silicon CCD camera we use most often has 2000 pixels in the horizontal and 800 pixels vertical. The luminescence, or photons, dispersed from the grating of a spectrometer will impinge on the CCD camera at different horizontal positions as their wavelengths differ from each other. In addition, photons originate from different vertical position on the sample will impinge the CCD camera at different vertical pixels. This can be seen from
Figure III.1.14 in the description of the spectrometer (Section III.1.7.c). Figure III.1.15 below shows a schematic diagram of a CCD camera and corresponding read out spectrum.

When a photon strikes on a pixel, a charge will arise from the photoelectric effect. After an exposure (time between the open and close of the spectrometer shutter), the accumulated charge of a pixel is transferred to the interface unit connected to the CCD. In this way the number of photons, or the light intensity, will be recorded at every single pixel of the camera. At this point, depending on what kind of data one desires, a spectrum (intensity vs wavelength) or a 2D image (spatial vs wavelength) can be obtained. To get a spectrum, the intensities of every pixel in each column will be added and plotted as a function of wavelength. To obtain a 2D CCD image, the intensity at each pixel will be kept separately and a map with 2000 pixels horizontal and 800 pixels vertical will be
created. The intensity of each pixel in this map will be proportional to the number of photons detected by each pixel on the CCD camera.

III.1.8.b MCP-PMT and APD

MCP-PMT (Micro Channel Plate Photo-Multiplier Tube) and APD (Avalanche Photo-Diode) are used in a time-resolved experiment where photons are detected according to the time they arrive at the detectors.

A MCP-PMT has three main components: the photocathode, the electron multiplier and the anode. When a photon impinges on the photocathode, it creates photoelectrons via photoelectric effect. These photoelectrons are then accelerated toward the electron multiplier which is, in this case, a Micro Channel Plate (MCP). A MCP consists of a bundle of metal coated hollow glass fibers which acts as different channels. The glass fibers are fused together in the form of a thin disk and each channel serves as an independent electron multiplier. With each incident electron, the electron multiplier (the MCP) generates $10^5$-$10^6$ secondary electrons. The anode collects these secondary electrons and provides an output signal which can be detected by a constant fraction discriminator (discuss in detail in the next section). Figure III.1.16 below shows a diagram of how the PMT works (and as just discussed above, the electron multiplier in our case is a MCP instead of dynodes as indicated).
Figure III.1.16 Schematic of a PMT showing multiplication of secondary electrons [5]

The MCP-PMT used in our lab was made by the Hamamatsu company (model *Hamamatsu R2809U-11*). It operates at voltage 2700V and temperature -45°C (using a liquid nitrogen PMT housing made by Product for Research model TE335TSRF). At this voltage and temperature, the MCP-PMT has low dark count rate (~100 counts per second). The MCP-PMT provides a fast response (~50 ps) and has been used to study the exciton dynamics in single CdS nanowires which have emission wavelength at ~490 nm and decay time ranges from ~80 ps up to several hundred pico-seconds.

The MCP-PMT described above only effectively works in a certain range of wavelengths (~400-800nm). When the emission wavelength is in the infrared range (>800 nm) (as in the case of GaAs nanowires, for example) an Avalanche Photo Diode (APD) is used. An APD uses epitaxial silicon Single Photon Avalanche Diodes (SPAD) based on the principle that a semiconductor under illumination by photons will generate a current. Figures below show an APD made by the Micro Photon Devices (MPD) Company [6] and its detection quantum efficiency as a function of wavelength.
An APD has many advantages over the MCP-PMT: it is small, easy to operate, has high internal gain, operates at a high light levels and over a broad range of wavelength. It uses thermo-electric cooler which reduces the dark count level. The APD used in our lab provides a 50 ps time resolution. One disadvantage of the APD is the very small size of the active area (around 100 $\mu$m$^2$) where photons can be detected. This
requires a lot of attention when one aligns the set up for the measurement. Another issue of the APD is its Instrument Response Function (IRF). The instrument response causes a long decay below the first decade (10 in the logarithm scale) which appears as a shoulder in a time-resolved spectrum. However, this is not a significant problem since our signal is usually at the order of the second or third decades.

**III.2 Time-Resolved measurements: single photon counting**

Time-resolved PL spectroscopy is used to study exciton dynamics in semiconductors. In time-resolved PL spectroscopy, photons from a short laser pulse are used to excite electrons and holes in one instant, which then form excitons. As an electron and a hole recombine, time-resolved spectroscopy allows one to measure the lifetime of the exciton, i.e. the time since it was created until it is annihilated. The following diagram illustrates the principle of the time-correlated single photon counting method.

*Figure III.2.1 Schematic diagram for a single photon measurement setup.*

Pulses from a mode locked Ti-Sapphire laser are split into two different beams. One of the beams is sent to sample to create exciton which then emit photon. The emitted
photon is analyzed by a spectrometer and detected by either a MCP-PMT or an APD. The APD has its own amplifier and discriminator, which can provide logic pulses as the output, while the signal (electron current) from the MCP-PMT is amplified by the Preamplifier and discriminated by a CFD (Constant Fractional Discriminator). A CFD internally compensates timing-jitter due to the fluctuation of the pulse height and converts current pulse to a NIM logic pulse. The output pulse from the CFD (or APD) serves as the “stop” signal of a Time-to-Amplitude-Converter (TAC). Pulses from the other laser beam are detected by a fast photodiode (not shown in the figure) and sent directly to a second CFD. The output logic pulse of this second CFD will serves as a “start” signal of the TAC. The TAC produces a pulse with a voltage proportional to the time between “start” and “stop” pulses. A Multi Channel Analyzer (MCA) board in the computer bins the output pulse voltages from the TAC into various channels, which correspond to different times. In this way, the MCA can record each photon arriving at the MCP-PMT at a particular time. The number of output pulses from the MCP-PMT is directly proportional to the number of incident photons. Averaging over millions of photons, the measurement creates a histogram which shows how long excitons “live” after being created by the laser pulse.

Below, we list the instruments which were used in our time-resolved measurements of CdS and GaAs/AlGaAs nanowires

*Table III.2.1: List of instruments for time-resolved measurement*

<table>
<thead>
<tr>
<th>Name</th>
<th>Manufacturer/ Model</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti:Sapphire laser</td>
<td>Spectra Physics/ 2030</td>
<td>5 and 10W, 200fs pulse width, 76MHz,</td>
</tr>
</tbody>
</table>
use self focusing Kerr-Lens effect, wavelength tunable from 700 to 900 nm

<table>
<thead>
<tr>
<th>Component</th>
<th>Manufacturer/ Model</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dilor/SPEX spectrometer</td>
<td>Dilor /SPEX</td>
<td>25 cm, triple spectrometer, 70 µeV resolution</td>
</tr>
<tr>
<td>MCP-PMT (Micro Channel Plate Photo-Multiplier Tube)</td>
<td>Hamamatsu/ R2809U-11</td>
<td>50s respond, operating at 2.7 kV, working at -45°C, gain ~10^5</td>
</tr>
<tr>
<td>PMT (Photo-Multiplier Tube) housing</td>
<td>Research product/ TE335TSRF</td>
<td>Provides temperature down to -50°C</td>
</tr>
<tr>
<td>CFD (Constant Fractional Discriminator)</td>
<td>Tennelec quad-CFD/ TC455 and Ortec 9307</td>
<td></td>
</tr>
<tr>
<td>TAC (Time-to-Amplitude-Converter)</td>
<td>Tennelec TAC/ TC864 and Ortec 566</td>
<td></td>
</tr>
<tr>
<td>MCA (Multi Channel Analyzer)</td>
<td>Data Translation/ DT2890</td>
<td></td>
</tr>
<tr>
<td>Pre-amplifier</td>
<td>Avantek/ UTC 10-223-6</td>
<td></td>
</tr>
<tr>
<td>APD (Avalanche Photo Diode)</td>
<td>PDM series by Micro Photon Devices</td>
<td>50 ps resolution</td>
</tr>
</tbody>
</table>

Overall, the time response of this system is around 50-80 ps
III.3 Resonant excitation measurements

In resonant excitation measurements, the laser wavelength is tuned so that at particular excitation energies, the laser might excite electron-hole pairs directly at some excited states. These resonances can be either related to optical phonons (vibronic) coupled to the exciton states or some other electronic or defect related states. In our resonant excitation measurements with core-shell GaAs-AlGaAs nanowires, the excitation wavelength of a Ti:Sapphire laser was scanned from 700 nm up to 808 nm. This wavelength range is broad enough in order to cover energy of several orders of LO phonon in GaAs (where the first order is known to be ~36 meV above free exciton emission line) and possibly to the bottom of the conduction band of the AlGaAs barrier. Recall that in a core-shell NW structure like GaAs-AlGaAs, there are conduction and valence bands corresponding to the core GaAs and the shell AlGaAs. The band gap of AlGaAs is dependent on the concentration of Al. So, in principle, resonant states may originate from both GaAs and AlGaAs. Figure III.3.1 below shows a schematic diagram of the core-shell GaAs-AlGaAs nanowire, its band structures in real space, the exciton bands in momentum space, and several possible of resonant states.
Figure III.3.1 Schematic diagram of a core-shell GaAs-AlGaAs nanowire, its band structures in the real space, exciton band in momentum space and several possibilities of resonant states.

As the laser wavelength was tuned from 700 nm up to 808 nm, the integrated intensity of the emission photoluminescence was recorded as function of laser energy. The PL intensity vs. excitation energy results in photoluminescence excitation (PLE) spectrum. In addition, to remove the scattered laser light, we used a Raman razor filter.

**III.4 Spatially-Resolved photoluminescence imaging of single nanowires**

In order to study spatial distributions of exciton, defects or surface related states along single nanowires, spatially-resolved photoluminescence imaging is employed. In a spatially-resolved imaging measurement, the photoluminescence image of a nanowire is rotated (by using a Dove prism (see Section III.1.6) if needed) so it stays parallel to the
slit of a spectrometer. The data is collected in the form of a 2-dimensional CCD image: spatial vs. wavelength. In other word, the vertical dimension of the CCD image corresponds to emission along the wire, while the horizontal dimension corresponds to emission energy (Figure III.4.1).

![Figure III.4.1 Schematic of how a 2D CCD image of PL from a nanowire is taken](image)

With our micro-photoluminescence experimental setup presented in Section III.1.2, a spatial resolution of 1.5 µm along the vertical direction is obtained.

References


Part IV

Optical characterizations of single CdS nanowires
IV.1 Photoluminescence from single CdS nanowires

Both high resolution SEM (Scanning Electron Microscope) images as well as AFM measurements show that the CdS nanowires measured in this thesis display a range of diameters (30-200 nm). In addition, their morphologies range from straight and uniform, to extremely irregular with bends, kinks, and irregularly shaped clusters of material aggregating locally on the nanowire (see Figure II.8.2, Part II for an example). These morphological flaws may originate either during the growth of the nanowires, or during the deposition of the nanowires onto the Silicon substrate for single nanowire study.

Figure IV.1 below shows PL spectra of several single CdS nanowires at room temperature. We can see that at room temperature the PLs from all NWs exhibit a single broad peak (FWHM ~70 meV), regardless the wire’s morphology, at energies below the room temperature band gap energy of bulk CdS (~ 2.51 eV). This emission close in proximity to the emission of bound exciton complexes in CdS such as acceptor and donor bound excitons [1] and is often referred to as the Near Band-edge Emission (NBE). This suggests that the emission originates from impurity-bound excitons or perhaps defects. We note also that there is a small variation in the emission energy from wire to wire. This indicates that there may exist non-uniform strain, diameter or compositional variation between wires.
Figure IV.1 - PLs from several single CdS nanowires measured at room temperature show emission below the band gap of bulk CdS.

In contrast to the PL measurements at room temperature, the low-temperature emissions from these nanowires differ dramatically. In Figure IV.2 we show the PL spectra at T = 10K of several uniform (left) and irregular (right) wires. We can see that the PLs from uniform wires display a broad peak (FWHM of 32 meV) which is ~30 meV below the low temperature free exciton (FX) energy at 2.551 eV and energies blue-shifted in comparison with room temperature case. In contrast, the PLs from the irregular...
wires consist of a broad band with a high energy shoulder near ~2.54 eV. On the lower energy side of the broad band, a number of sharp emission lines are observed. Clearly, quantum confinement of carriers is not important in these CdS nanowires, since the diameter of the nanowires is significantly larger than the exciton Bohr radius (2.8nm).

**Uniform wires**

**Irregular-shaped wires**

![Graphs showing PL spectra of uniform and irregular nanowires](image)

**Figure IV.2** At low temperature (10K) PL spectrum of uniform, straight nanowires and irregular shape nanowires are dramatically different. (FX- free exciton emission energy)

In order to understand of the nature of the NBE and these sharp, narrow line emissions, we have conducted a series of measurements including spatially-resolved photoluminescence imaging, time-resolved photoluminescence imaging, temperature and catalyst size dependent photoluminescence. In the following Sections, we will present the results of these experiments and will mainly focus our discussion on two representative
single CdS nanowires (except Section IV.3) whose AMF images are shown in Figure IV.3 below. One of these wires (wire 1, left) is seen to be relatively straight and uniform while wire 2 (right) displays significant morphological irregularities. From the height of the line scans across the wires, we see that the diameter of wire 1 is 45-50 nm, while the diameter of wire 2 ranges from 120 nm in the straight region to nearly 200 nm in the irregularly shaped regions.

Figure IV.3 - AFM images of two representative CdS nanowires: wire 1 (left) is straight and uniform, wire 2 (right) is extremely irregular with bends, kinks. The scale bars in the two top images are 3 µm.

The room temperature PL spectra of these two wires (1 and 2) are alike and consist of a single broad band (FWHM ~ 70 meV) with the peak energy below the bulk CdS band gap (Eg = 2.51 eV). As before, we label this peak the near band edge (NBE) emission (Figure IV.4 left).
Figure IV.4 - Room temperature (left) and low temperature (right) PL spectra of two different wires (1 and 2): wire 1 is straight and uniform while wire 2 has significant morphological irregularities

However, the low temperature PL spectra 10 K of these single nanowires differ significantly (Figure IV.4 right). The uniform wire 1 continues to emit a single NBE peak at an energy of 2.52 eV, which is comparable to the excitonic emission from bulk CdS at low temperature. While the PL spectra from the irregularly shaped nanowire 2 exhibits a series of narrow lines at about 30-60 meV lower in energy than the broad NBE emission. For this wire, the NBE emission appears only as a high energy shoulder to the PL emission band. Correlation of the detailed spatially resolved photoluminescence studies
with atomic force microscopy imaging (section below) indicates that the narrow lines in the low temperature PL spectrum is emitted at spatially distinct positions along the nanowire length and can be associated with the presence of morphological irregularities such as kinks or lobes in CdS nanowires.

**IV.2 Spatially – resolved PL imaging of single CdS nanowires**

To gain further insight into the origin of the NBE and sharp, narrow emissions, we performed micro-PL imaging on two particular nanowires shown in *Figure IV.3*. A two-dimensional (2D) PL map of wire 2 is displayed in *Figure IV.5 a*). In this image, the vertical axis denotes the spatial position along the nanowire, while the horizontal axis corresponds to the emission energy. The laser is defocused so it can illuminate the entire length of the nanowire. The atomic force microscopy AFM image of wire 2 is displayed to the right of the PL image and shows that wire 2 is particularly non-uniform with many kinks, bends, and lobes. Spectra at horizontal cross sections of the CCD image taken at four different positions A, B, C, and D along the nanowire are shown in *Figure I.5 b*). In this way, one can see that each sharp spectral feature is associated with a particular position along the wire. The spectral map identifies clearly that the lower energy emission observed in PL spectrum of wire 2 appears in the form of sharp spectral peaks, originating from specific localized points along the nanowire, superimposed on a broad background. Moreover, the different emission energies of each line must also reflect differences in the local confining potentials. The NBE emission, while significantly less pronounced under continuous-wave excitation compared to the pulsed excitation, appears as a high energy shoulder in the emission spectrum.
Figure IV.5 - Photoluminescence imaging of the wire 2 at 10 K: a) 2D map of the wire 2 emission b) PL spectra extracted from the 2D map at the positions specified by the circles in a) and c) schematic description of the experiment: PL image of the nanowire aligned along the slit of the spectrometer.
Figure IV.6 - Photoluminescence imaging of the wire 1 at 10 K: a) 2D PL emission map of the wire 1 b) PL spectra extracted from the 2D map at the positions specified by the lines in a c) schematic description of the experiment image of the spectrometer slit superimposed on the AFM micrograph of the wire.
In contrast to wire 2, the 2D PL image of wire 1 in Figure IV.6 a) shows no evidence of localized states. As can be seen in the AFM image displayed in Figure IV.6 c), wire 1 is largely uniform and straight, and thus its spectra are dominated by the NBE broad emission peak. The intensity of the PL emission from this nanowire varies by almost an order of magnitude at different positions along the 14 µm length of the wire. More importantly, one can clearly see in the spatially resolved spectra extracted from the image in Figure IV.6 b) that the PL peak position also varies significantly by nearly 10 meV. The variations in emission intensity and energy are possibly related to non-uniform strain or compositional variation along the length of these nanowires.

From comparisons of nanowires of different structural qualities, we conclude that emission of the spatially localized states which emit at lower energies results from structural imperfections. The emission energies of these states vary from line to line and do not precisely coincide with the known emission energies of excitons bound to bulk impurities (such as donor-acceptor pair, neutral donor-acceptor etc.). On the other hand, their recombination lifetimes (will discuss in Section IV.4), ranging from 300 ps to 1 ns, are similar to those observed for bound exciton complexes in bulk CdS. [1,2] Thus we tentatively assign these states to excitons which are bound to structural defects and aggregates on the surface of the nanowires. Energies and electron-hole overlaps, and hence lifetimes of these states, are determined by the local confinement potential of the defects and therefore can vary significantly from position to position along the wire.

**IV.3 3D PL imaging**

Three dimensional photoluminescence images (which have two spatial dimensions and the third dimension is emission energy) of single nanowires were
collected by scanning the region of the sample containing the nanowire with 400 nm steps across the spectrometer slit and collecting the CCD images at each step. A detail description of this imaging method was described by Hewaparakrama et al in [3]. These three dimensional photoluminescence images contain the spatial positions (X and Y), as well as the spectral information. With this, we are able to exactly identify the locations along the wire where various spectral features originate.

A three dimensional data set allows one to create a map upon which one can clearly distinguish several individual lines (localized states) along the wire. These are spectrally sharp and spatially distinct from one another. In Figure IV.7 a), contour intensity maps corresponding to six of those localized states (labeled A, B, C, D, E, F) are depicted over a grey background. This grey background is, in fact, the outline of the room temperature photoluminescence map and provides the image of the nanowire. The contour intensity maps show which locations along the nanowire emit light at a given wavelength, as well as the intensity of the emission at the chosen wavelength at those locations. Figure IV.7 b) shows the corresponding individual spectra of six localized states. Note that lines B and C are emitted from two closely spaced positions (~1.5µm apart from each other which is about our optical resolution), and their emission wavelengths are very close as well (of 0.2 nm from each other). In addition, lines A and F have some spectrally similar peaks, but are located at opposite sides of the nanowire.
As we have seen in the previous section, these narrow lines originate from defect or surface related states. This 3D PL imaging method gives complete details of spatial and spectral information of the localized states.

In another example, Figure IV.8 below shows a PL image (left) of a single nanowire and its integrated emission spectrum (right). The PL spectrum was taken with a
defocused laser beam, so the entire nanowire was excited. In this emission spectrum we can clearly see a series of sharp, narrow lines on the low energy side of a broad emission band. These sharp, narrow lines, denoted as A, A’, B, C and D, are emitted from different locations along the wire as indicated on the PL image on the left. We observe that the emissions from A and A’ positions (at the two end of the nanowire) have the same emission energy (or very close energies which cannot be resolved in this experiment). Also, the two narrow peaks (denoted as C) on the emission spectrum are associated with one position C on the PL image. There is a possibility that these two peaks are emitted from two different spatial positions and in this case the two positions must be less than 1.5 µm apart (limited by the spatial resolution).

Figure IV.8 – Low temperature PL image of a single CdS nanowire (left) and its integrated emission spectrum (right). Several emission peaks show up at different locations along the wire.
As we discussed in Part I, the as grown nanowire sample was sonicated and dispersed into solution and then deposited onto a Silicon substrate for single nanowire study. During this process, some nanowires may have been broken into small pieces and randomly distributed on the substrate surface. These small pieces could show up on the PL image when one scans the sample and, as a result, the peak F in the PL spectrum (Figure IV.8 right) is emitted from such a small piece of CdS material on the substrate.

**IV.4 Time-resolved PL imaging**

Time-Resolved Photoluminescence (TRPL) measurements can provide insights into the nature of electronic states in nanowires and reveal dominant recombination mechanisms. Low-temperature band edge PL of bulk CdS, for instance, displays bound exciton complex emission, or free exciton emission, with lifetimes ranging from 500 to 1000 ps, reflecting the different electron-hole overlaps for different excitonic states.[1,2] Since the size of the nanowires studied here is large compared to the exciton Bohr radius in CdS (2.8 nm), quantum confinement effects are not significant, and one would expect low temperature nanowire emission to exhibit similar properties to the bulk. However, the interesting feature is the sensitivity to the presence of a surface or non-radiative defects. TRPL and micro-PL measurements were conducted on ten different CdS nanowires. Here we present a detailed discussion the two representative nanowires chosen above (Section IV.1). These wires were selected to demonstrate the range of observed behavior.

In Figure IV.9 a) and b) we show TRPL images from these two wires, (1 and 2) as false-color images (a logarithmic intensity scale) where the vertical axis corresponds to the time after the laser pulse, while the horizontal axis corresponds to the emission
energy (with ~5 meV resolution). Wire 1 (Figure IV.9 a)) shows a single broad band at an energy of 2.525 eV which decays rapidly. The energy of this peak is comparable to that of the excitonic emission from bulk CdS, but the measured exciton recombination lifetime (Figure IV.9 c)) is only 80 ps (limited by our system response), nearly an order of magnitude shorter than observed in bulk CdS.

Figure IV.9 - a) time-resolved PL map from nanowires 1 and b) from wire 2 at 10 K. Intensity (in logarithmic scale) is shown as a color scale c) nanowire 1, decay spectrum taken at NBE emission energy, 2.525 eV d) nanowire 2, decays taken at NBE emission energy, 2.525 eV (bottom curve) and two energies (~2.472 eV and 2.486 eV) in the defect-related band (top and middle curves).
In contrast, while the TRPL image from wire 2 (*Figure IV.9 b*) shows the same intense, but short-lived, NBE emission at early times, it also exhibits a series of sharp peaks at lower energy which persist to much longer times after the laser pulse. This can be seen in the corresponding time-decays displayed in *Figure V.9 d*). The recombination lifetime of the NBE emission at 2.525 eV from wire 2 is again only 80 ps. However, time-decays taken at two positions in the lower energy range (2.472 eV and 2.486 eV respectively) show distinctly longer recombination lifetimes of 355 and 620 ps.

The short (<80 ps) lifetime of the NBE emission displayed by all nanowires is likely to be caused by the close proximity of the non-radiative surface states due to the large surface-to-volume ratio of the nanowires. Optical emission of the strongly ionic materials such as CdS is known to be strongly affected by the dark trap states formed by the dangling bonds at the surfaces,[17] as well as by the surface states associated with any adsorbed impurities.[18] While the diameter of the nanowires is significantly larger than the exciton Bohr radius, the exciton diffusion length of around 1 µm at 7K [19] suggests that the excitons are likely to interact with the nanowire surfaces many times during their lifetimes, and are thus susceptible to annihilation at surface trap states.

The results of TRPL measurements are in excellent agreement with results from previous sections where we have seen spatially-resolved measurements of the near band edge and defect related emissions. These results are also in excellent agreement with the temperature dependent photoluminescence measurements which we will present in the next section.
**IV.5 Temperature dependence PL from single CdS nanowires**

In order to provide some further insight into these defect-related states, we show in *Figure IV.10* the PL emission from wire 2 at a number of different temperatures from 5 to 295 K. All spectra have been normalized for clarity. At low temperatures (5-20 K), the imperfection related sharp lines are prominent, while the NBE emission appears only as a high energy shoulder. As the temperature increases, the sharp lines exhibit a marked decrease in intensity starting around 30 K and are completely quenched by 80-90 K. As the temperature increases further, only a single NBE emission peak is observed. The center of the NBE peak redshifts, as expected, above 90 K and persists up to room temperature.

*Figure IV.10 - Temperature dependent PL of wire 2 (PL spectra have been normalized and offset for clarity)*
Figure IV.11 - Energies of NBE as well as several localized state emissions (as denoted in Figure IV.10) as function of temperature. Temperature dependence of band gap of bulk CdS is shown for reference. [11]

The temperature dependence of the NBE peak energy as well as the energies of several of the narrow lines from nanowire 2 are shown in Figure IV.11. For comparison, we show the temperature dependence of the band edge for bulk CdS single crystals as measured by Imada et al. [11] The temperature dependence of both the bulk CdS band edge and the nanowire NBE energy was fitted to the extended phenomenological Varshni equation. [12]

\[ E_g = E_0 - \frac{\alpha T^4}{\beta + T^3} \]

This form of the Varshni equation is consistent with the recent result by Cardona et al. [13] who used general thermodynamic arguments to show that the appropriate energy
gap temperature dependence in the low temperature regime as \( T \) goes to 0 should be \( T^4 \) rather than \( T^2 \).

Good fits to the nanowire NBE data were obtained using the fitting parameters \( E_0 = 2.535 \text{ eV} \), \( \alpha = 0.00028 \), and \( \beta = 4.2 \times 10^6 \), while the bulk fitting parameters were \( \alpha = 0.00033 \) and \( \beta = 7.7 \times 10^6 \). The slight variation between the nanowire and bulk Varshni parameters likely results from an intrinsic difference between nanowire and bulk crystal structure and the particular sensitivity of the nanowires to the surface properties and strain due to their small size and large surface to volume ratio (\( \sim 10^8 \text{ m}^{-1} \)).

The energies of the defect related sharp lines 1 - 4 in Figure IV.10 follow the NBE peak closely as temperature increases until they are quenched. This suggests that the narrow lines are not related to deep levels (which do not follow the band gap as temperature increases) and implies that the defect-related emission is excitonic in nature. This conclusion is in agreement with the time-resolved measurements (discussed in the previous section) on this nanowire which showed that the recombination lifetimes of these states are 300–1000 ps [14] and are comparable to excitonic lifetimes measured in bulk CdS.[15]

To further study the rapid quenching of the sharp spectral features, we plot the integrated intensities of the PL as a function of temperature Figure IV.12. The temperature dependence of the integrated intensities (labeled as NBE) of PL emitted from the nanowire as a whole is plotted in Figure IV.12 (top) and shows that the overall PL efficiency decreases somewhat as the temperature increases from 10 to 150 K, but it remains fairly constant from 150K up to room temperature. The integrated intensity of the defect-related PL lines is obtained through subtraction of the background and
integration of the isolated peak (see inset to Figure IV.12 bottom). The results from this procedure are plotted for three spectral lines and shown in Figure IV.12 (bottom).

Figure IV.12 - Intensities of NBE as well as several localized state emissions as a function of temperature. Inset: temperature progression of one of the localized state emissions (line 1) as a function of temperature from 5 to 100 K.

The temperature dependent intensities of these three lines show unique
temperature dependencies which quench at different temperatures. However, all defect-related PL lines completely disappear by 90 K. One might conclude that excitons are only weakly bound to these defects by 4 - 8 meV, which is not consistent with the fact that these lines emit nearly 30-60 eV below the exciton complexes near the band edge. Clearly, some configuration of the defect, perhaps a charge state, is only stable at low temperature. Excitons are only localized at defects with this configuration. Moreover, the low temperature (10K) time-resolved PL measurements of these states also show recombination lifetimes ranging from 300 to 1000 ps.[14]

In summary, the temperature dependent measurements have shown that the room-temperature PL of single CdS nanowires is not sensitive to the structure of or defects within each nanowire. Indeed, both straight, uniform nanowires and nanowires with significant morphological irregularities emit a single peak near the band edge at room temperature (Section IV.1). In strong contrast, low temperature PL emission is extremely sensitive to the nanowire morphology. We find that the low temperature 20 K PL spectra of single nanowires exhibit two bands: one which is observed in all studies of nanowires regardless of morphological quality and is associated with bound excitons at the band edge, and the other which is associated with excitons localized to morphological defects along the nanowires. These defect-related states manifest themselves as narrow emission lines at a variety of lower energies, which track with the temperature dependence of the band edge, but exhibit unique quenching behaviors with temperature. As we showed in the previous section, each defect line exhibits a unique recombination lifetime. This rather remarkable variability strongly suggests that nanowire defects are sensitive to the local properties or structure of the nanowire. All such defect lines disappear by 90 K,
leaving the near band edge emission which persists up to room temperature. The
temperature dependent PL results suggest that the sharp, narrow lines result from exciton
localization to defects with emission energies, quenching behavior, and lifetimes which
vary significantly, possibly due to varying local properties or structure of the nanowire
near the defect site. Because of the sensitivity to the nanowire surface and morphology,
we have shown that low temperature PL measurements of single nanowires are absolutely
essential for understanding the properties of defects in these structures.

**IV.6 Catalyst size dependent photoluminescence**

In order to see how the size of the gold nano-particle catalysts will affect the
photoluminescence of individual NWs (recall that the sizes of these catalysts determine
the diameters of the NWs), we have investigated several NWs grown using both 20 nm
and 50 nm gold catalysts. The detailed description of the growth conditions of these
nanowires was given in *Section II.8, Part II*.

*Figure IV.13* displays the representative PL spectra at 295 K of several nanowires
with 20 nm and 50 nm catalyst sizes, it is clear that the room temperature optical
properties of all nanowires of either type are similar. At room temperature all nanowires
of either type show a broad (FWHM ~ 75 meV) emission line centered near 2.45 eV.
Figure IV.13 - PL spectra of comparing emission from single 20 nm catalyst wires (top 2 spectra) with the 50 nm catalyst wires (other two spectra) taken at 295 K.

Figure IV.14 - PL spectra of a) set 20 nm NWs and (b) set 50 NWs taken at 7 K.
On the other hand, at low temperature significant differences between the two sets of nanowires can be seen (Figure IV.14). Each sets of wires shows two features, near-band-edge (NBE) emission from 2.52 to 2.54 eV, and a broad defect emission band extending from 2.43 to 2.5 eV which is most likely related to defect or impurity luminescence in the wires. However, the 20 nm catalyst NWs generally show dominant NBE emission with weaker defect band emission. In contrast, the 50 nm catalyst NWs generally show defect band emission which can be as strong, or stronger than, the NBE emission. Moreover, the longer 50 nm catalyst NWs also occasionally show a number of sharp emission lines localized to the sites of morphological defects along the nanowires [14]. Remarkably, the defects and structural irregularities manifest themselves only in low temperature PL spectra, while the room temperature spectra are unaffected by them.

Through such surveys of single NWs, it becomes possible to select wires from both growths which show no defect band emission or morphological defects (sharp lines) and emit a single featureless NBE line. To gain more detailed comparisons between these types of wires, we use spatially resolved direct PL imaging, temperature dependent and time-resolved measurements of single nanowires, which have been described in detail in the previous sections.

**IV.7 Conclusions: single CdS nanowires**

In this chapter, we presented our recent results of optical spectroscopic studies of single CdS nanowires. CdS NWs grown by the vapor-liquid-solid (VLS) method using colloidal gold catalysts may result in a range of diameters as well as morphologies going from straight and uniform, to extremely irregular with bends, kinks, and irregular shaped clusters of material aggregating locally on the nanowire. We found that at room
temperature the PL spectra of all nanowires are alike, regardless their morphologies, which contain a broad peak below the band gap of bulk CdS. However, at low temperature (10K), the PL spectra from regular, straight, uniform nanowires and irregular with bends, kinks are dramatically different. While PL from regular, straight, uniform nanowires show a single broad peak (with peak energy blue shifted in comparison with room temperature), PL spectra from irregular nanowires with bends, kinks show a broad band with a high energy shoulder near ~2.54 eV and a number of sharp emission lines on the low energy side. By taking 2D (spatial vs. energy) and 3D (X vs. Y vs. energy) images, we found that these sharp emission lines originate from different locations along nanowires. These imaging results suggest that the sharp, narrow lines are related to defects or surface states. We also performed the time-resolved measurements on these nanowires and found that the decay times of excitons with energies corresponding to the energies of the sharp lines are much longer (about 2 orders of magnitude) than that of excitons with energy corresponding to the broad shoulder. By taking the temperature dependent photoluminescence, we observed that the energies of the sharp lines decrease consistently with the band gap and the intensity completely quenches at around 90K. This again confirms that the narrow, sharp emission lines are related to defects or surface states, not deep levels. Finally, by studying the PL properties of CdS nanowires grown with different catalyst sizes, we found that the irregular nanowires featured with bends and kinks occur most often with large catalyst diameter (~40 nm and up).

The results suggest the use of spatially and temporally-resolved optical spectroscopic measurements are important for rapidly characterizing CdS nanowires growth for the optimization of future applications in nano-devices.
References


Lensch, & L. J., Temperature dependent photoluminescence of single CdS nanowires,


Lensch and L. J. Lauhon., Low-Temperature Optical Characterization of Single CdS 
Volume **1**, 17-20 June 2006 Page(s): 123 – 125

Lensch, L.J. Lauhon, Y. Kim, H. J. Joyce and C. Jagadish., Spatially-resolved
Photoluminescence Imaging of CdS and GaAs/AlGaAs Nanowires., 28th
Part V

Optical characterizations of single core-shell

GaAs-AlGaAs nanowires
V.1 General properties of the PL emission from single core-shell GaAs-AlGaAs nanowires

As we have mentioned in Section II.10 (Part II), PL emission from single core-shell GaAs/AlGaAs nanowires has much higher (over an order of magnitude higher) quantum efficiency than that of bare GaAs indicating the non-radiative surface recombination in this nanostructure. More interestingly, it has been observed that the PL emission from single core-shell GaAs/AlGaAs exhibits a much broader energy range than does of bulk GaAs.

Figure V.1 - PL emission from a single core-shell GaAs/AlGaAs nanowire (top) and from GaAs epilayers (bottom).[1]
Figure V.1 (top) above shows a typical PL spectrum from a single core-shell GaAs/AlGaAs nanowire which is featured by a single broad peak with line width (FWHM) \( \sim 20 \text{meV} \). This is much broader in comparison with typical emission from GaAs epilayers (bottom).[1] As noted in the top panel, all of the emissions from a high purity epilayer are within the energy range denoted by the two vertical dashed lines. In contrast to a single broad peak emission with no structure of the NW, the PL emission spectrum from the epilayer shows clear electronic structures with free exciton (FX) emission peaks \((n=1, 2)\) and several other donor and acceptor related emissions. The reason that makes these differences between the PL emission of a core-shell GaAs/AlGaAs NW and GaAs epilayer is still unclear. One possibility is due to the fluctuations in the surface charge density and local fields in the low dimensional structures.[4] Some authors have associated the broadening of the NW PL emission to the band filling effect of the photoexcited carriers in the nanowires.[6]

Because nanowires are relatively thick, they do not exhibit quantum confinement effects, but the dielectric contrast between the nanowire and its surroundings results in significant polarization anisotropy.[7,19] (also discussed in detail in Section II. 11 of this thesis) This is true also for core-shell GaAs/AlGaAs nanowires \((\varepsilon = 12.5)\). We have observed that a significant increase in PL intensity (by a factor of \( \sim 70 \)) occurs when the exciting laser is polarized along the nanowire versus perpendicular to it. We have also observed that the suppression of the electromagnetic (photon) field in these nanowires results directly in a corresponding suppression of the radiative rate for excitonic dipoles aligned perpendicularly to the nanowire. Figure V.2 shows an example of PL emissions
spectra from a single core-shell GaAs/AlGaAs nanowire when detected parallel and perpendicular to the nanowire. In this measurement laser was circularly polarized.

![Emission polarization](image)

\[ P = \frac{|I_{pa}|}{|I_{pa}| + |I_{pe}|} \]

\[ \approx 82\% \]

**Figure V.2 - PL emission spectra detected parallel and perpendicular relative to the nanowires axis**

Strongly polarized PL emission from semiconductor nanowires has been reported by many groups. [7-11] An extensive description of polarized PL emissions from single core-shell GaAs/AlGaAs nanowires will be presented in the later Section V.4 of this Chapter.

### V.2 Temperature dependent photoluminescence of single core-shell GaAs-AlGaAs nanowires

A series of PL emission spectra from a single core-shell GaAs-AlGaAs nanowire as a function of temperature from 10 K to 140 K are shown in **Figure V.3**. As the
temperature increases, the nanowire emission broadens and redshifts, and is strongly quenched at temperatures above 140 K.

Figure V.3 - PL spectra from one of the nanowires (wire A) at different temperatures from 10 to 140 K

Figure V.4 - Temperature dependence of the PL emission peak energy of several nanowires as well as bulk GaAs band gap temperature dependence from Ref. [12]; solid lines show fits to these data using the modified Varshni equation.[13,14]
The temperature dependence of the peak emission energy of several nanowires is shown in Figure V.4 along with the bulk GaAs epilayer temperature-dependent band gap.[12]

Fits to these data were carried out using a modified form of the Varshni equation which varies as $T^4$ at low temperatures and becomes linear at higher temperatures. As we have mentioned in Section IV.5, Cardona et al. [13] have argued that this is a thermodynamically correct form for the variation of the energy gap as a function of temperature in contrast to the phenomenological form used by Varshni which varies quadratically at low temperatures. While the GaAs/AlGaAs nanowires emit approximately at the same energy as bulk GaAs, the fits to the modified Varshni equation are significantly different from that for the bulk semiconductor. In particular, the linear slope of the curve at higher temperatures is significantly shallower than observed in the bulk. The reason for this behavior is not clear at this moment, but may be due to different phonon response for nanowires or the appearance of strain as the temperature is raised.

The PL of the nanowires quenches above 140 K. In order to observe the activation energies associated with this behavior, we plot the $I/I_0 - 1$ where $I_0$ is a parameter which reflects the intensity of the PL line at zero temperature, and $I$ is the intensity of the PL line at a temperature $T$. If one plots this expression as a function of $1/T$ the activation energy is given by the slope of the line fit to the data.[15] (Figure V.5)
Figure V.5 - Temperature-dependent quenching of the PL emissions from three nanowires (A, B and C); $I_0$ is a fitting parameter of the PL intensity at $T=0$, while $I$ is the PL intensity at temperature $T$. The symbols show experimental data while the lines are linear fits in the low- and high-temperature regions showing activation energy.

We find that while the intensity of the PL changes dramatically around 50 K it is not possible to observe a change in slope and thus the $\sim$4 meV activation energy expected for ionization of excitons in GaAs. This is probably because the emission lines are wide enough that we are not able to distinguish spectrally the transition from exciton emission to emission from an electron-hole plasma which should occur at temperatures above 50K. Moreover, the nanowire PL strongly quenches with an activation energy of 17 meV, which is probably associated with the presence of non-radiative centers, possibly at the uncovered ends of the nanowire (which was originally in contact with the substrate before ultrasonication). In contrast, in high quality AlGaAs/GaAs double heterostructures
where surface recombination is extremely small, PL emission can be observed all the way to room temperature.[16]

**V.3 Spatially-resolved PL imaging of single core-shell GaAs-AlGaAs nanowires**

As it was mentioned in the Part III (Section III.4) a 2D CCD spectral image has an advantage that it can provide spatially-resolved photoluminescence. In this experiment, the laser is defocused in such a way that it can illuminate the entire nanowire, and the nanowire is oriented along the entrance slit of the spectrometer. The vertical axis of the CCD image shows the spatial position along the wire while the horizontal axis shows the emission energy. *Figure V.6* below shows a complete PL image of a NW at zeroth order of the grating and temperature $T=10K$. At zeroth order, the grating acts like a mirror and there is no dispersion so the entire surface can be imaged. The large circle represents the defocused laser beam which is covering the entire NW. The NW is oriented along the vertical entrance slit of the spectrometer (Y axis). From the image, it is clear that the wire emits PL more intensely at one end, possibly reflecting the wider taper (and thus larger amount of GaAs material) of the NW at one end. Since our optical resolution is only 1.5 $\mu$m, we are unable to resolve the taper of the nanowire.
Figure V.6 - 2D PL image of a nanowire at zeroth order of the grating. The large circle represents the defocused laser beam.

Figure V.7 a) below shows a 2D spectral image of a single nanowire. In this image, the vertical axis corresponds to the spatial position along the nanowire, and the horizontal axis denotes the emission energy. An AFM image of the wire shown to the right of the PL image indicates that the wire is ~7 µm long, morphologically uniform and slightly tapered. The 2D map of the intensity of the PL emission varies substantially along the nanowire, with a particularly bright spot close to the middle of the nanowire. In Figure V.7 b), we extract spectra collected at two different points along the nanowire (indicated by AA’ and BB’ in Figure V.7 a) which shows that the emission energy and line-shape are remarkably uniform at different positions along the nanowire. Moreover, the PL spectrum obtained by integrating the PL from the entire nanowire is very similar. Each of these PL spectra exhibit a single broad (FWHM ~25 meV) peak at 1.518 eV.
which corresponds to energy of excitonic emission in bulk GaAs epilayers, and a lower energy shoulder which can be attributed to defect-related luminescence.

Figure V.7- Photoluminescence imaging of a single core-shell GaAs-AlGaAs NW at 10 K: a) 2D map of the wire emission; on the right – AFM image of the wire (~7.4 µm long, with average diameter of 120 nm) and b) PL spectra extracted from the 2D map at the positions specified by the lines in a) and integrated PL spectrum from entire nanowire.
V.4 Polarization measurements of single core-shell GaAs-AlGaAs nanowires

As discussed in Section II.11 above, in the case of core-shell GaAs-AlGaAs nanowires, the large dielectric mismatch between GaAs ($\varepsilon = 12$) and surrounding vacuum ($\varepsilon_0 = 1$) results in strong polarization of in both the excitation efficiency and photoluminescence emission.

Figure V.8 – Linearly polarization of excitation (top) and of emission (bottom) of a single nanowire

Figure V.8 (top) shows spatially integrated PL of a single nanowire when it is excited with laser fields polarized parallel and perpendicular to the wire. A large degree of
polarization \( P = \frac{I_\parallel - I_\perp}{I_\parallel + I_\perp} = 96\% \) was observed. Figure V.8 (bottom) shows spatially integrated PL spectra of the same NW for circularly polarized excitation and luminescence was collected along and perpendicular to the wire. In this case we observed a smaller degree of polarization 82\% than the estimated theoretical value \( P = \frac{I_\parallel - I_\perp}{I_\parallel + I_\perp} = 93\% \), resulted from \( \frac{I_\parallel}{I_\perp} = \frac{(\varepsilon + \varepsilon_0)^2 + 2\varepsilon_0^2}{6\varepsilon_0^2} \), see Part I- Section II.1). The reason is because the investigated NW is not an infinitely long cylinder (it is tapered) and also has surface imperfection, so the boundary conditions are not as for the perfect case.

![Figure V.9](image)

**Figure V.9** - a) PL intensity as a function of linearly polarized excitation angles: absorption is strongly polarized along the wire, b) PL intensity as a function of linearly polarized detection angles: emission is strongly polarized along the wire (angles are relative to the nanowire axis)
Figure V.9 a) above shows the spatially integrated intensity of the PL emission from a single nanowire as a function of the linear polarization angle while the laser is circularly polarized. The emitted PL is clearly polarized in the direction along the NW axis (note that 0° is along the NW axis). In Figure V.9 b), the emission is analyzed for circular polarization, while the integrated intensity of the PL emission is plotted as a function of the linear polarization direction of the laser. For maximum PL intensity, the laser polarization has a preferential direction for polarization along the nanowire axis. In these figures the solid circles (squares) are experimental data and the solid curves are fits to \( \cos^2 \theta \), where \( \theta \) is the angle of the analyzer.

It is also possible to spatially resolve the NW PL polarization as shown Figure V.10. Figure V.10 a) shows a 2D CCD image of a nanowire where the parallel (to the NW axis) polarization of photoluminescence is collected. Figure V.10 b) shows a similar map but selected for the perpendicular polarization. It is clear that the parallel polarization luminescence intensity is much stronger than that of perpendicular polarization. Figure V.10 c) shows a polarization map which is calculated from Figures V.10 a) and b) using the formula \( P = \frac{I_\parallel - I_\perp}{I_\parallel + I_\perp} \) on every pixel to pixel of each map. Figure V.10 d) shows a histogram of the degree of polarization which is constructed from the portion of the map indicated by a box in Figure V.10 c). This histogram indicates that the degree of polarization is mostly peaked at 82% which is in agreement with results shown in Figure V.8 (bottom) above.
Figure V.10 - a) parallel emission, b) perpendicular emission c) polarization and d) histogram of wire selected area in c)
**V.5 Resonant excitation study of single core-shell nanowires**

Resonant excitation is one of the most powerful methods in optical spectroscopy which allows us to probe directly the electronic and vibronic properties of materials. A detailed description of resonant excitation is described in the *Section III.3*.

In these measurements, the wavelength of the continuous Ti:Sapphire excitation laser was tuned from 700 nm up to 808 nm and the integrated intensity of the emission photoluminescence was recorded as function of laser energy. The PL intensity vs. excitation energy relation results in a photoluminescence excitation (PLE) spectrum. A sharp Raman razor filter was used to eliminate the scattered light.

![Figure V.11 - a) PL and b) PLE of two nanowires A and B](image)

*Figure V.11 - a) PL and b) PLE of two nanowires A and B*
Figures V.11 a) and b) show PL and PLE spectra of two nanowires, named NWs A (bottom) and B (top). There are clear resonances at ~36 meV, ~73 meV and ~135 meV above the free exciton emission line in the PLE spectra of both wires A and B. Resonances at ~ 36 and ~73 meV can be interpreted as 1-LO and 2-LO phonons, respectively, of the core GaAs. The resonance at ~135 meV is unlikely to be the 3-LO or 4-LO phonon since it is not in the right energy positions. We tentatively assign this peak to the resonant excitation of exciton carriers into the AlGaAs shell, followed by capture and radiative recombination in the GaAs core. The energy of this resonance corresponds to an AlGaAs band gap with 10-13% Al composition which is smaller than the intended growth value of 26%. This result is not unexpected since the 26% value was calibrated using the growth of epilayers so for NWs one could expect a difference. Another possibility of this resonance is AlGaAs defect related electronic state rather than vibronic state. Further measurements to high energy or direct emission from the AlGaAs shell would confirm this assumption.

V.6 Polarized resonant excitation study of single nanowires

Because the laser polarization is directly related to the symmetry of the excited exciton, a natural question is whether the polarization of the emitted PL changes with excitation energy. In this Section we present the results of resonant excitation dependent degree of polarization. Figures V.12 below shows the PL and PLE spectra from wires A and B, and the degree of polarization of the emission as the laser energy is tuned.
Figure V.12 - Photoluminescence excitation spectroscopy. (A) PL (solid line) and PLE (solid line with symbols) for wire A; (B) PL (solid line) and PLE (solid line with symbols) for wire 2; Solid line fits to PLE spectra are to 3 Gaussians. Top: degree of linear polarization of PL emission as a function of excitation laser energy for wire A (solid circles) and wire B (solid squares).

It is clear that (Figure V.12 – top) the degree of polarization changes with excitation energy for both wires: For the laser polarized parallel (∥) to wire A (solid circles) and wire B (solid squares), the degree of emission polarization decreases with
increasing laser energy. For the laser polarized perpendicular (⊥) to wire B (open squares) the degree of polarization increases with increasing laser energy. From Figure V.12 (top) we see that when the parallel polarized excitation energy decreases from the 135 meV resonance down to the 36 meV resonance, the degree of polarization increases from ~84 % to ~95% for wire A while from ~76% to ~94 % for wire B. The difference in the dependency of the degree of polarization on the excitation energy between wires may be related to morphological difference between the two wires. The AFM image of wire A (as shown on the right of Figure V.7 a) indicates that this wire is quite straight, smooth in a tapered shape. Unfortunately we do not have similar AFM image of wire B but its optical image (not shown) suggests that this wire is not as smooth or uniform.

When the incident laser is polarized parallel to the nanowire, it excites exciton quantum states with dipoles aligned parallel to the nanowire. It is important to note that even for equal populations of excitons with dipoles aligned parallel and perpendicular to the nanowire, the PL emission is expected to be strongly polarized. Several groups have calculated classically that for an infinitely long and cylindrically symmetric nanowire with a dielectric constant of 12, the emission should have a polarization of 92%. [7,9,19] Note that at the highest excitation energies the emission polarizations from wires A and B are significantly smaller than this value, and moreover are quite different from each other: 84% versus 76%. However, for both wires the degree of polarization increases as the excitation laser comes closer to resonance with the PL emission band. Because the emission energy does not change as the excitation laser is scanned, we do not expect the classical degree of polarization expected for equal exciton distributions to change either.

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We therefore attribute the increasing emission polarization to a corresponding development of increasingly non-equilibrium exciton distributions.

These non-equilibrium polarized exciton distributions can also be seen for wire B where the excitons are excited into the nanowire with the laser polarized perpendicular to the nanowire. For this case, the exciton dipoles are excited by the laser perpendicular to the nanowire. While much less efficient [11] (by a factor of 70) than the previous case, with much longer averaging times (10 minutes compared with 1 minute) we can observe the emission polarization. We find that at the lowest energies, the emission is still polarized parallel to the nanowire, because even the small density of excitons parallel to the nanowire emit much more efficiently than those with dipoles aligned perpendicular to the nanowire. Remarkably, as the laser is tuned to higher energies, the emission polarization increases. At higher energies the excitons scatter more, depolarizing the exciton distributions into the radiatively efficient exciton dipoles aligned parallel to the nanowire. The fact that at the highest energies the emission polarization is approximately the same for parallel and perpendicular pumping indicates that the densities of the excitons are approaching thermal equilibrium, or equal densities. The dynamics of exciton recombination as well as the spin scattering times are intimately involved in understanding this data as we will now discuss.

**V.7 Exciton decay rate in single core-shell nanowires**

In a nanowire, due to the large surface to volume ratio (~$10^8$/m) the surface plays an important role in the electronic and optical properties of the nanostructure. In GaAs nanowires, the surface become a more sensitive matter because of its very high surface recombination velocity $s \sim 10^6$ cm/s.[20, 21] (which is, for example, nearly a 1000 times
higher than that of undoped epilayers in InP with $s \sim 10^3$ cm/s,\cite{22, 23}). Such a high surface recombination velocity would have a dramatic impact on the non-radiative lifetime in GaAs nanowires. Even in core-shell GaAs-AlGaAs nanowires, where the purpose of AlGaAs the shell is to reduce this surface recombination, the non-radiative lifetime was found to be less than 80 ps (limited by system the response). Figure V.13 below shows a time decay (PL intensity vs lifetime) of the emission from a single core-shell nanowire.

![Figure V.13 - A typical decay spectrum from a single core-shell GaAs-AlGaAs nanowire which shows decay time less than 80 ps (limited by the system response)](image-url)
V.8 Rate equations: A model for spin relaxation in single core-shell GAAAs-AlGaAs nanowires

The dielectric mismatch of the nanowire in air results in strongly linearly polarized emission from even thick (~40-100 nm) semiconductor nanowires where no quantum confinement is possible. [7,9,19] Since there is no quantum confinement possible in these 40 nm nanowires, the exciton wavefunctions are spherically symmetric, and the optically active exciton state wavefunctions can be written as $|x\rangle$, $|y\rangle$, and $|z\rangle$, where the index $\alpha = x, y, z$ specifies a dipole moment direction of a particular state. (The relationship between these eigenstates and the standard spherically symmetry ones are shown in the supplementary materials – Appendix A1). The direction $y$ corresponds to the NW axis and the lens collects photons propagating from the NW within the angle $\theta_0$ around the $z$-axis (see Figure V.14). Note that while the light polarizer selects photons either with $\parallel$ or $\perp$ polarizations that correspond to the x and y directions in our system of coordinates, the finite collection angle of the microscope objective (with numerical aperture 0.5) means that each exciton state ($x, y, z$) potentially contributes to the observed polarized luminescence. Thus, the intensity of light (photons/sec) emitted from recombination of a population density excitons of three types, $n_\alpha$, is just determined by the probabilities $W_{\alpha \rightarrow \parallel}$ and $W_{\alpha \rightarrow \perp}$:

$$I_\perp = \sum_{\alpha=x,y,z} W_{\alpha \rightarrow \perp} \cdot n_\alpha, \quad I_\parallel = \sum_{\alpha=x,y,z} W_{\alpha \rightarrow \parallel} \cdot n_\alpha.$$

(V.1)
Since we observe $I_{\parallel} > I_{\perp}$ and $\theta_0 = \pi / 6 \ll \pi$ (the collecting system catches mostly photons with $k \parallel z$), we expect that $|y\rangle$ excitons will dominate the PL signal. Simultaneously, the $|x\rangle$ and $|z\rangle$ exciton emissions are suppressed due to the dielectric properties of the NW.[7,9,19] The contribution of $|z\rangle$ is suppressed further because of the small collection angle $\theta_0$. We next provide a more quantitative discussion of these observations.

In the following, we consider a NW in a vacuum and ignore the effect of the silicon substrate. In addition, we will treat a single exciton as a two-level system. The
radiative lifetimes of the excitons inside the NW can be calculated using the methods of quantum optics [24] and the approach used recently in [25]. A quantum state of photons is given by two vectors \((\mathbf{k}, \mathbf{e}_\beta)\), where the two polarization vectors \(\mathbf{e}_\beta\) should be orthogonal to the photon wave vector, \(\mathbf{k}\). The light-matter interaction is described by the operator \(\hat{V}_{\text{int}} = -\hat{d} \cdot \hat{E}\), where \(\hat{d}\) and \(\hat{E}\) are the exciton dipole moment and photon electric field. Inside the nanowire, the electric field becomes partially screened: \(\hat{E}_{x,z} = \hat{E}^0_{x,z} \frac{2}{1 + \varepsilon_s}\) and \(\hat{E}_y = \hat{E}^0_y\) [26], where \(\hat{E}^0_{\alpha}\) are the field components in vacuum and \(\varepsilon_s\) is the relative dielectric constant of a semiconductor. The above equation is valid for a narrow wire, \(r_{NW} / \lambda << 1\), where \(r_{NW}\) and \(\lambda\) are the NW radius and the wavelength of the emitted photons, respectively; this inequality is well satisfied in our experiments. Then, using Fermi’s golden rule, we obtain the exciton lifetimes:

\[
\tau_{x,z} = \tau_y \left(1 + \frac{\varepsilon_s}{2}\right)^2, \quad \tau_y = \tau_{\text{vac}} = \frac{3\pi \varepsilon_0 \hbar c^3}{\omega_{\text{exc}} d_{\text{exc}}^2},
\]

(V.2)

where \(\tau_{\text{vac}}\) is the lifetime of excited two-level system in vacuum [24], \(d_{\text{exc}}\) and \(\omega_{\text{exc}} = c_0 k\) are the inter-band dipole moment of exciton and its frequency; \(\varepsilon_0\) is the permittivity of vacuum. Since \(\varepsilon_s = 12.5\), \(\tau_{x,z} >> \tau_y\). We have seen above for wire 2, for instance, that the emission is strongly polarized parallel to the wire even while the excitation laser is polarized perpendicular to the wire directly. This result reflects this difference in radiative lifetimes for excitons oriented parallel and perpendicular to the wire, as reflected in equation V.2.
To compute the probabilities $W_{\alpha \rightarrow \parallel}$ and $W_{\alpha \rightarrow \perp}$, we have to integrate over the vectors $\mathbf{k}$ only within the cone $0 < \theta < \theta_0$ and also take into account the geometry of the experiment (see Figure V.14). Since the NW in our system can be treated as a point source, it is convenient to use spherical coordinates and introduce three unit orthogonal vectors $(\mathbf{r}, \phi, \theta)$. Then, one possible choice of emitted photon polarizations is $\mathbf{e}_\phi = \mathbf{\varphi}$ and $\mathbf{e}_\theta = \mathbf{\theta}$. Due to the cylindrical symmetry of the lens, the photons $\mathbf{e}_\phi$ and $\mathbf{e}_\theta$ become transformed into photons with polarizations $\mathbf{a}_\phi = -\sin \phi \cdot \mathbf{x} + \cos \phi \cdot \mathbf{y}$ and $\mathbf{a}_\theta = -\cos \phi \cdot \mathbf{x} - \sin \phi \cdot \mathbf{y}$, respectively. The polarizer selects either $\parallel (\mathbf{y})$ photons or $\perp (\mathbf{x})$ photons and the corresponding photonic states can be represented as $\mathbf{e}_\perp = \mathbf{e}_x = \sin \phi \cdot \mathbf{a}_\phi + \cos \phi \cdot \mathbf{a}_\theta$ and $\mathbf{e}_\parallel = \mathbf{e}_y = \cos \phi \cdot \mathbf{a}_\phi - \sin \phi \cdot \mathbf{a}_\theta$. This result can be used to define new orthogonal photonic polarizations $\mathbf{b}_\perp = \phi \sin \phi + \theta \cos \phi$ and $\mathbf{b}_\parallel = \phi \cos \phi - \theta \sin \phi$. These photon polarizations have the convenient property that the lens provides the mapping $\mathbf{b}_\perp \rightarrow \mathbf{e}_x$ and $\mathbf{b}_\parallel \rightarrow \mathbf{e}_y$ where the photon states $\mathbf{b}_\perp (\mathbf{||})$ are defined before entering the lens and $\mathbf{e}_x(y)$ are the photon states after passing the lens.

For example, the $x$-polarizer will transmit the photons $\mathbf{b}_\perp$ and completely block the photons $\mathbf{b}_\parallel$. The emission probabilities are then easily expressed as

$$W_{\alpha \rightarrow \perp} = \frac{2 \pi \lambda_{\text{e}}^2 (\hbar \omega_{\text{exc}})^2}{4 \hbar \epsilon_0} \sum_{\mathbf{k}, 0 < \theta < \theta_0} R_{\alpha} (\mathbf{b}_\perp \cdot \mathbf{a})^2 \delta (\hbar \omega_{\text{exc}} - \hbar c_0 k), \quad (V.3)$$

$$W_{\alpha \rightarrow \parallel} = \frac{2 \pi \lambda_{\text{e}}^2 (\hbar \omega_{\text{exc}})^2}{4 \hbar \epsilon_0} \sum_{\mathbf{k}, 0 < \theta < \theta_0} R_{\alpha} (\mathbf{b}_\parallel \cdot \mathbf{a})^2 \delta (\hbar \omega_{\text{exc}} - \hbar c_0 k),$$
where \( R_{x(z)} = R = \left( \frac{2}{1 + \varepsilon_x} \right)^2 \) and \( R_y = 1 \) are the screening factors. This factor appears only next to the \( x \)- and \( y \)- components of the polarization vectors \( \mathbf{b}_{\perp(\parallel)} \). By integration over the collecting cone in \( k \)-space we derive the collection probabilities \( W_{\alpha \rightarrow \perp(\parallel)}(\theta_0) \). This procedure can be seen in the supplementary materials (\textit{Appendix A1})

In our resonant excitation experiments we have found that as the laser (polarized \( \parallel \) to the wire) moves closer and closer to resonance with the emission line, the degree of polarization strongly increases (see \textit{Figure V.12}). As we will show this occurs because the exciton populations must be out of equilibrium with \( n_y > n_x = n_z \). At higher excitation energies, however, the excitons must rapidly thermalize through exciton-exciton scattering and the emission of optic and acoustic phonons which depolarizes the exciton spin states. Thus at higher excitation energies the emitting exciton population must be close to thermal equilibrium with \( n_x = n_y = n_z \). In this case, the intensity ratio,

\[
\gamma(\theta_0) = \frac{I_\perp}{I_\parallel} = \frac{\sum_{\alpha=x,y,z} W_{\alpha \rightarrow \perp}}{\sum_{\alpha=x,y,z} W_{\alpha \rightarrow \parallel}}, \tag{V.4}
\]

can be computed. Detailed calculations and plot of \( \gamma \) is shown in \textit{Appendix A1}. From \textit{Figure V.14} we can see that \( \gamma(\theta_0) \) strongly increases with the collection angle \( \theta_0 \). The reason is that for small \( \theta_0 \), only \( x \)-excitons with \( k \parallel z \) contribute to the signal \( I_\perp \). Since these excitons have reduced interaction with vacuum photons due to dielectric screening, their emission is suppressed; \( \gamma(\theta_0 \rightarrow 0) = R \approx 0.022 \). For large \( \theta_0 \), the unscreened, bright \( y \)-excitons contribute to the signal \( I_\perp \) and the ratio \( \gamma(\theta_0) \) strongly grows. For our
experimental geometry, $\gamma(\theta_0 = 30^0) \approx 0.025$. Figure V.12 (top) shows the polarization,

$$P = \frac{I_\parallel - I_\perp}{I_\parallel + I_\perp},$$

for both wires A and B as a function of the relative energy $\Delta \omega = \omega_{\text{laser}} - \omega_{\text{exc}}$. For high $\Delta \omega$, $P \to 0.88$ and 0.75 for wires A and B, respectively. With the above numbers ($\gamma(\theta_0 = 30^0) \approx 0.025$), our model gives $P = 0.95$. The discrepancy between experiment and theory might be attributed to NW defects and roughness; it is clear from Figure V.12 (top) that $P$ is sample dependent.

To model these experiments further we now consider optically-created excitons, which can then recombine radiatively or non-radiatively, or scatter between the states, as shown in Figure V.15.

*Figure V.15 - Schematic diagram of exciton basis states and transitions between them.*

*Suppose that the exciton is pumped with laser polarized along the nanowire axis (y-axis).*
Because we have found that the recombination lifetime for excitons in the GaAs/AlGaAs nanowire is less than 80 ps, it is clear that the excitons are dominated by non-radiative recombination.[11] Moreover, since we observe a significant nonthermal population of spins, the spin scattering rate must be comparable to the nonradiative lifetime. Thus we consider a hierarchy of scattering times: \( \tau_{x,z} \gg \tau_y \gg \tau_{nr}, \tau_s \). We consider the case where all times are constants, while the spin scattering time changes with the laser excitation energy. The coupled rate equations are thus:

\[
\begin{align*}
\frac{dn_x}{dt} &= G_\perp - \frac{n_x}{\tau_\perp} - \frac{n_x}{\tau_{nr}} - 2\frac{n_x}{\tau_y} + \frac{n_y}{\tau_s} + \frac{n_z}{\tau_s}, \\
\frac{dn_y}{dt} &= G_\parallel - \frac{n_y}{\tau_\parallel} - \frac{n_y}{\tau_{nr}} - 2\frac{n_y}{\tau_y} + \frac{n_x}{\tau_s} + \frac{n_z}{\tau_s}, \\
\frac{dn_z}{dt} &= -\frac{n_y}{\tau_\perp} - \frac{n_y}{\tau_{nr}} - 2\frac{n_y}{\tau_y} + \frac{n_x}{\tau_s} + \frac{n_z}{\tau_s},
\end{align*}
\]

where \( \tau_\perp = \tau_{x(z)}, \tau_\parallel = \tau_y \), and \( G_\perp \) and \( G_\parallel \) are the pumping rates for the excitation beams with \( \perp \) and \( \parallel \) polarizations, respectively. We solve these coupled equations in steady state (\( dn_\alpha / dt = 0 \)) neglecting the radiative recombination rate for all exciton populations.

In addition, we simplify equations \( V.1: I_\parallel \approx W_{x \rightarrow \perp} \cdot n_x, \quad I_\parallel \approx W_{y \rightarrow \parallel} \cdot n_y \). This simplification is valid for small collection angles (\( \theta_0 \ll \pi \)). Then, we obtain the result:

\[
P = \frac{I_\parallel - I_\perp}{I_\parallel + I_\perp} = \frac{1 - \frac{n_x}{n_y} \gamma_1}{1 + \frac{n_x}{n_y} \gamma_1} = \frac{1}{1 + \frac{n_x}{n_y} \gamma_1} \left( \frac{\tau_s}{\tau_{nr}} - \gamma_1 \right), \quad (G_\perp = 0, \quad G_\parallel \neq 0) \quad \text{“parallel pumping”}
\]

\[
P = \frac{\gamma_1}{1 + \frac{\tau_s}{\tau_{nr}}}, \quad (G_\perp \neq 0, \quad G_\parallel = 0) \quad \text{“perpendicular” pumping}
\]

(V.6)
where \( \gamma_1 = W_{x\rightarrow\perp} / W_{y\rightarrow\parallel} \). If we assume that the polarization at the highest energy for \( G_{\parallel} \neq 0 \) occurs when \( n_z = n_y = n_x \) this sets the ratio \( \gamma_1 \) which is equal to 1/16 for wire A and 1/7 for wire B, which results in polarizations of 88% and 75%, respectively. Using equations V.6, we obtain ratio \( \frac{\tau_s}{\tau_{nr}} = \gamma_1 \left( \frac{1 + P}{1 - P} \right) - 1 \) for parallel pumping and

\[
\frac{\tau_s}{\tau_{nr}} = \frac{1}{\gamma_1} \left( \frac{1 - P}{1 + P} \right) - 1
\]

for perpendicular pumping. In this way we can extract the ratio \( \tau_s/\tau_{nr} \) directly for all the data in Figure V.12. The results of this analysis are displayed in Figure V.16.

![Figure V.16 - Ratio of spin scattering time to non-radiative lifetimes as a function of excitation energy for both wires and also for different pumping (wire B). The symbol notations are identical to those in Figure V.12.](image)

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Remarkably, all data for both wires and different excitation polarizations in Figure V.16 group well on one line with a negative derivative. From this we can say that the ratio $\tau_s/\tau_{nr}$ ranges from 0.1 at the highest energies to 1 as the laser comes close to resonance. Assuming that the nonradiative recombination lifetime is 50 ps, this means that the spin scattering rate varies from approximately 5 ps at high energies to greater than 50 ps at lower energies. Moreover, it is clear from this analysis that the reason we are able to see this effect is that the large nonradiative recombination rate means that the excitons do not live long enough to randomize their spin profiles.

We also can make our model more complex by involving dark excitons. It is interesting that the results of equation V.4 will hold even in the presence of dark excitons for the limit $\tau_{\perp,\parallel} \gg \tau_{nr}, \tau_s$. Strictly speaking, the approach of the two-level system used in this paper is valid for localized excitons with spherical symmetry. However, for the 3D free excitons confined inside the NW, the results in equations V.4 and V.6 and displayed in Figure V.14 c) remain valid. To account for the free exciton distribution, we should add the Boltzmann factor $e^{-\frac{\hbar^2k_z^2(\theta,\phi)}{2m_e k_s T}}$ to the functions inside the sums in equations V.3.

This approach assumes that the photon with $\mathbf{k} = (k_x, k_y, k_z)$ is created by the exciton with $\hbar \mathbf{k} = (0, \hbar k_y, 0)$ i.e. only the $y$-component is conserved and $r_{NW}/\lambda << 1$. Since the photon wavelength is so long, the exponent is very small ($\frac{\hbar^2k_z^2(\theta,\phi)}{2m_e k_s T} \leq 0.01$) and the Boltzmann factor does not make any difference. We assume here a typical temperature of 4 K and exciton mass of $0.5m_0$.
In conclusion, we have shown that one can use polarized optical spectroscopy to investigate the exciton spin relaxation in single core-shell GaAs-AlGaAs nanowires. We observed that in core-shell GaAs-AlGaAs nanowires, the quantum efficiency is much higher (~20-100 times) than of bare (uncoated) GaAs nanowires due to the non-radiative surface recombination is suppressed. The PL emission from a single GaAs-AlGaAs nanowire typically shows a single broad peak, which has energy close to the free exciton line of bulk GaAs (~1.515 eV at low temperature) but with much larger line width (~20 meV). The broadening of the spectrum in GaAs-AlGaAs nanowires is probably due to the band gap renormalization or the diffusion of excitons along the length of the nanowires. Furthermore, 2D imaging results show the uniformity of the PL emission along a single nanowire, indicating the good quality nanowire growth.

GaAs (and AlGaAs) has cubic crystal structure and large dielectric constant (12) which result in strong excitation and emission polarization of photoluminescence. The theoretical polarization of the emission photoluminescence 92 % is very close to our experiment results (~90% near resonant). The difference between the experimental and theoretical values is easy to understand since the theoretical value is calculated for a perfect cylinder while the real nanowires are not. Using the resonant excitation method, we observed striking 1-LO and 2-LO resonances of these nanowires. A third resonant (~135 meV above free exciton line), probably related to the AlGaAs shell, was also observed. More interestingly, using polarized resonant excitation, we observed that the polarization of the photoluminescence emission is strongly enhanced as the excitation
energy comes closer to resonance with the free exciton emission. This indicates that resonant excitation creates non-equilibrium exciton spin distributions near resonance. Using rate equation modeling we estimate the spin relaxation times in these single GaAs/AlGaAs nanowires around 50 ps.

GaAs is an important material for optoelectronic devices and GaAs nanowires are promising candidates for photonic nano-devices. We have shown that the quantum efficiency of these nanowires can be improved by coating the GaAs core with an AlGaAs shell. The results of polarized resonant photoluminescence studies provide a deeper understanding of the optical properties and electronic structure in single nanowires and therefore benefit further development and optimization of future nano-devices.

References


VI. Appendices

A1. Calculation of $\gamma(\theta_0)$ (equation V.4, Section V.8)

(We would like to thank Prof. A. O. Govorov from Ohio University for his collaboration in this part as well as in Section V.8)

The probabilities

$$W_{\alpha \rightarrow \perp} = \frac{2\pi d^2_{\text{exc}} (\hbar \omega_{\text{exc}})^2}{4\hbar \varepsilon_0} \sum_{k, 0 < \theta < \theta_0} R_{\alpha} (b_{\perp} \cdot a)^2 \delta(\hbar \omega_{\text{exc}} - \hbar c_0 k)$$

and

$$W_{\alpha \rightarrow \parallel} = \frac{2\pi d^2_{\text{exc}} (\hbar \omega_{\text{exc}})^2}{4\hbar \varepsilon_0} \sum_{k, 0 < \theta < \theta_0} R_{\alpha} (b_{\parallel} \cdot a)^2 \delta(\hbar \omega_{\text{exc}} - \hbar c_0 k)$$

contain sums over photonic states ($\alpha = x, y, z$). These sums should be replaced with integrals. The results are:

$$W_{x \rightarrow \perp} = \frac{1}{4} \pi R (11 + 4 \cos \theta_0 + \cos 2\theta_0) \sin^2 \frac{\theta_0}{2}$$

$$W_{y \rightarrow \perp} = \frac{2}{3} \pi R \sin^6 \frac{\theta_0}{2}$$

$$W_{z \rightarrow \perp} = \frac{4}{3} \pi R (2 + \cos \theta_0) \sin^4 \frac{\theta_0}{2}$$

$$W_{x \rightarrow \parallel} = \frac{2}{3} \pi R \sin^6 \frac{\theta_0}{2}$$

$$W_{y \rightarrow \parallel} = \frac{1}{4} \pi R (11 + 4 \cos \theta_0 + \cos 2\theta_0) \sin^2 \frac{\theta_0}{2}$$

$$W_{z \rightarrow \parallel} = \frac{4}{3} \pi R (2 + \cos \theta_0) \sin^4 \frac{\theta_0}{2}$$

where the indexes $\parallel$ and $\perp$ mean parallel and perpendicular relatively to the nanowire axis (y) and $R = \left(\frac{2}{1 + \varepsilon_s}\right)^2$ is the screening factor. The factor $\gamma(\theta_0)$ (equation V.4) in the Section V.8 becomes:
\[ \gamma(\theta_0) = \frac{W_r}{W_\parallel}, \]

where

\[ W_\parallel = -\frac{1}{4} \pi (-11 - 5R + 4(R - 1)\cos \theta_0 + (R - 1)\cos 2\theta_0)\sin^2 \frac{\theta_0}{2}, \]

\[ W_\perp = \frac{1}{12} \pi (3 + 45R + 4(R - 1)\cos \theta_0 - (R - 1)\cos 2\theta_0)\sin^2 \frac{\theta_0}{2}, \]

A Mathematica routine to compute \( \gamma(\theta_0) \) is as follow:

```mathematica
In[1]:= nw[\[Theta], \[Epsilon]] := (
   r = (2 / (1 + \[Epsilon]))^2;
   wpar =
     -0.25 Pi *
     (-11 - 5 \* r + 4 \* (r - 1) \* Cos[\[Theta] Pi / 180] +
       (r - 1) \* Cos[2 \* \[Theta] Pi / 180]) \* (Sin[\[Theta] Pi / 180 / 2])^2;
   wper = 0.0833333 Pi *
     (3 + 45 \* r + 4 \* (r - 1) \* Cos[\[Theta] Pi / 180] -
       (r - 1) \* Cos[2 \* \[Theta] Pi / 180]) \* (Sin[\[Theta] Pi / 180 / 2])^2;
   N[wper / wpar])

In[2]:= nw[45, 12.5]
Out[2]= 0.0293372

In[3]:= Plot[nw[\[Theta], 12.5], \{\[Theta], 0, 180\}, AxesLabel -> \{\[Theta][degree], \[Gamma][\[Theta]]\}]
```

![Figure A1.1 – Plot of the function \( \gamma(\theta_0) \) (Figure V.13c)](image-url)
A2. LabView programs

Implementing the experiments and analysis in this thesis requires extensive use of computer programs. The LabView programming language has excellent capabilities for both data acquisition and data analysis. Listed below are some representative programs I wrote and have been employed frequently in the lab for acquisition and analysis of data.

1. LabView program to control SPEX spectrometer using CY545 stepper motor controller and Data Translation board DT335-50

The principle of this low-level controlling software is as follows:

Figure A.2.1 - Control diagram of the Spectrometer using computer

In a snapshot, the program shows up on the computer screen as follows:
Figure A.2.2 - A snapshot of program “SPEX-Control.vi” which is used to control SPEX spectrometer.

The program, named “SPEX-Control.vi”, allows users to move the grating of the SPEX-spectrometer to the desired wavelength position. The program first reads the current position of the spectrometer (stored in memory of the computer), gets the new position input from users, and then calculates the distance needed to be moved (in steps of the stepper motor) and then move the spectrometer. It also allows user to calibrate the spectrometer in case there is an error in the wavelength. An acceptable error of the program is ~0.1 nm.

2. **Spectroscopy data acquisition, a LabView program to acquire data from JY CCD3000 camera. Mainly for photoluminescence and Raman experiments, (2005)**

This is a medium level program which employs some low-level routines provided by the JY Company to acquire data from a JY CCD3000 camera controller. This program
allows users to acquire photoluminescence and Raman data. It is also possible to perform a photoluminescence imaging acquisition with this program. The principle of the program flow is as follow:

*Figure A.2.3 - Control flow diagram of the “SPEX.vi” program*

The graphic user interface of the “SPEX.vi” program appears as follows in “Spectrum mode”:

*Figure A.2.4 - A snapshot of program “SPEX.vi” which is used to acquire data from JYCCD 3000 camera.*
Note that, for convenience, the “SPEX-Control.vi” discussed in 1) is embedded in this “SPEX.vi” so it is easy for users to control the SPEX spectrometer while taking data.

3. Optical image scanner: a LabView code to spatially scan a photoluminescence image (with ~100 nm spatial resolution) through the slit of a spectrometer for an exciton transport measurement.

This program controls a micro-stepper motor through a Parker Compumotor Controller. This is part of the progress I made toward my summer project which was funded by the University Research Council (URC) – 2007

![ParkeR Control](image)

Figure A.2.5 a snapshot of “ParkeR-Control.vi” program which is used to scan a PL image from single nanowires across the entrance slit of a spectrometer.
4. **LabView programs to analyze data:** I have written many LabView programs to analyze data obtained either in Binary or ASCII types. The data often derived in the form of a spectrum (1-D) or an 2D image (wavelength vs. spatial) or a 3D image (X - Y - wavelength). Following are routines that frequently used:

- Convert multi binary data files into ASCII data files – “Convert-PLs.vi”. This program allows users to convert up to 250 binary files to ACII files at a time.

- 1D analysis – Deal with 1D data type: file name “1D-FFT.vi”

- 2D analysis – Deal with 2D data type: file name “2D-FFT.vi”

- 3D analysis – Deal with 3D data type: file name “3D-FFT.vi”

- Polarization data analysis - analyze different polarized components of photoluminescence: file name “PLs-polarization.vi”

- FFT signal processing - a series of LabView programs which employ Fast Fourier Transform method to analyze 1-D, 2-D (image) and 3-D data types)

- Time-resolved data analysis: file name “Time-resolve-t.vi”

These programs are stored in most computers in the lab under directory \LabView\Analysis\Pl-map-FFT

These programs have the following coding procedures:
As an example, shown below is a program which deals with time-resolved data type: the data was taken in the form of a 2D image (time vs emission wavelength). This 2D image is shown on the upper left corner. The upper right figure shows decay at a particular wavelength of the 2D image in the upper left. The lower left figure shows PL spectrum (intensity vs wavelength) at a particular time from the 2D image. The lower right plot is the calculated decay time as a function of emission wavelength.
A3. Mathematica programs

I find it useful to write some small codes to calculate certain quantities such as exciton diffusion length, donor-acceptor binding energy, least square fit, Jones vectors etc … These routines are of convenience for everyday use so one will not have to look into a reference book for some parameters or constants. Following are some Mathematica codes.
1. Polarization and Jones matrices

Jones matrices of polarization

Define Jones matrices:

\[
\begin{align*}
\mathbf{J}_{\text{ver}} &= \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}; \\
\mathbf{J}_{\text{hor}} &= \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}; \\
\mathbf{J}_{45} &= \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix}; \\
\mathbf{J}_{\text{neg45}} &= \frac{1}{2} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}; \\
\mathbf{J}_{\text{r}} &= \frac{1}{2} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix}; \\
\mathbf{J}_{\text{l}} &= \frac{1}{2} \begin{pmatrix} 1 & -1 \\ 1 & 1 \end{pmatrix}; \\
\mathbf{J}_{\uparrow} &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}; \\
\mathbf{J}_{\downarrow} &= \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}; \\
\mathbf{J}_{0} &= \begin{pmatrix} 0.7 & 0 \\ 0 & 0.3 \end{pmatrix};
\end{align*}
\]

Define Jones vectors:

\[
\begin{align*}
\mathbf{E}_{\text{h}} &= \begin{pmatrix} 1 \\ 0 \end{pmatrix}; \\
\mathbf{E}_{\text{v}} &= \begin{pmatrix} 0 \\ 1 \end{pmatrix}; \\
\mathbf{E}_{45} &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}; \\
\mathbf{E}_{\text{r}} &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix}; \\
\mathbf{E}_{\text{l}} &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix};
\end{align*}
\]

\[
\mathbf{E}_{\text{r}} + \mathbf{E}_{\text{l}} \quad \text{// MatrixForm} \quad \text{// Simplify}
\]

\[
\begin{pmatrix} \sqrt{2} \\ 0 \end{pmatrix}
\]
Define rotation matrix:

\[ r[\theta] = \begin{pmatrix} \cos(\theta) & \sin(\theta) \\ -\sin(\theta) & \cos(\theta) \end{pmatrix}; \]

\[ \text{rinverse} = \text{Inverse}[r[\theta]] // \text{MatrixForm} // \text{Simplify} \]
\[ \begin{pmatrix} \cos(\theta) & -\sin(\theta) \\ \sin(\theta) & \cos(\theta) \end{pmatrix} \]

\[ N[r[\pi/4]] // \text{MatrixForm} \]
\[ \begin{pmatrix} 0.707107 & 0.707107 \\ -0.707107 & 0.707107 \end{pmatrix} \]

\[ r[\theta].\text{Inverse}[r[\theta]] // \text{MatrixForm} // \text{Simplify} \]
\[ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \]

\[ r_{h} = \text{Inverse}[r[\theta]].jh.r[\theta] // \text{MatrixForm} // \text{FullSimplify}; \]

\[ r_{g} = \text{Inverse}[r[\theta]].jg.r[\theta] // \text{MatrixForm} // \text{FullSimplify}; \]

Example: Vertical length comes in, going through a half-wave plate set at 45 degree and then another half-wave plate set at -45 degree

\[ \theta_{1} = \pi/4; \]
\[ c_{1} = \text{ch}; \]
\[ e_{1} = \text{Inverse}[r[\theta_{1}]].jh.r[\theta_{1}].c_{1} // \text{MatrixForm} \]

\[ \text{Inverse}[r[\theta_{1}]].jh.r[\theta_{1}] // \text{MatrixForm} \]
\[ \begin{pmatrix} 0 \\ 1 \\ 0 \\ 1 \end{pmatrix} \]

\[ \theta_{2} = \pi/2; \]
\[ c_{2} = \text{ch}; \]
\[ e_{2} = \text{Inverse}[r[\theta_{2}]].jh.r[\theta_{2}].c_{2} // \text{MatrixForm} \]
\[ \begin{pmatrix} -1 \\ 0 \end{pmatrix} \]
2. Exciton-diffusion length

This calculates the exciton diffusion length

Exciton diffusion length:
\[ L = \sqrt{D \times \tau_E} \]

where \( D \) the diffusion coefficient, \( \tau_E \) the exciton recombination time

\[ D = \frac{k_bT}{m^*} \tau_\text{sc} = \frac{k_bT}{e} \mu \] (for example see PRB 47 3582)

where \( \tau_\text{sc} \) the exciton scattering time,
\[ m^* = m_h + m_e \text{ since } m_h >> m_e \text{ then here we can take } m^* \approx m_h \]
\( \mu \) the mobility
\[ L = \sqrt{\frac{k_bT}{m^*} \times \tau_E \text{ sc}} \]

Einstein relation
\[ \mu = \frac{\tau_\text{sc}}{\tau_e} \]

Knowing the exciton lifetime \( \tau_E \), mobility \( \mu \),
one can estimate the exciton scattering time \( \tau_\text{sc} \),
exciton diffusion length \( L \), diffusion coefficient \( D \).

In the following, \( L \) and \( D \) are built as functions of \( \tau_E \),
\( m^* \text{ and } T \). \( L \) has unit of meter, \( \tau_E \) in second, mass in kilogram,
\( m_0 \) the mass of bare electron, \( \mu \text{ in cm}^2/\text{V.s}, D \text{ in cm}^2/\text{s} \)

```python
L[\tau_e, T, m, \mu] := {
    kbt = 0.0258 * T / 300;
    mo = 9.109 * 10^-31;
    \tau_\text{sc} = \mu * m * 0.572 * 10^-15;
    evperkg = 1.782 * 10^-36 * (2.99 * 10^8) ^ 2;
    Sqrt[kbt * evperkg * \tau_e * \tau_\text{sc} / m / mo]}
```

The scattering time [s]

```python
Scat[\mu, m] := {
    mo = 9.109 * 10^-31;
    \mu * m * 0.572 * 10^-15)
```

The diffusion coefficient[cm^2/s]

```python
Dif[T, m, \mu] := {
    kbt1 = 0.0258 * T / 300;
    mo1 = 9.109 * 10^-31;
    \tau_\text{sc} = \mu * m * 0.572 * 10^-15;
    evperkg1 = 1.782 * 10^-36 * (2.99 * 10^8) ^ 2;
    \tau_\text{sc} = kbt1 * evperkg1 / m / mo1}
```
In case of CdS nanowires, $n^d = 0.4 - n^o$ (along c axis),
$t = 50 \text{ ps} = 50 \times 10^{-12} \text{ s at 10 K (Near Band Edge emission)}$

$L[0.5 \times 10^{(-10)}, 10, 0.40]$

$9.69569 \times 10^{-7}$

which is in order of $1 \mu$m

$D[0.5 \times 10^{(-10)}, 10, 0.40]$

$0.0160013$

or $D = 18 \text{ cm}^2/\text{s}$

$\text{Plot}[L[.5 \times 10^{(-10)}, T, 0.40], \{T, 5, 100\}]$

--- Graphics ---

3. **Donor-acceptor pair**

**Donor-Acceptor pair in II-VI semiconductors**

The spectral position of zero-phonon transition of a DAP recombination

$$E_p = E_g - (E_A + E_L) + \frac{e^2}{4\pi\varepsilon_0\varepsilon r}$$

$r$ distance between donor and acceptor

$$\left[ \frac{e^2}{\varepsilon r} \right] \approx eV, \text{ then } \left[ \frac{e^2}{4\pi\varepsilon_0\varepsilon r} \right] \approx eV$$

in the following distance has unit of nm, energy has unit of eV

$$\hbar c = 197.327 \times 10^4 \times (6) + 10^5 (-6) + eV + \text{nm}$$

$$\frac{e^2}{4\pi\varepsilon_0\hbar c} = \frac{1}{137.035}$$

$$\frac{e^2}{4\pi\varepsilon_0} = \frac{\hbar c}{137.035} = \frac{197.327 \times 10^4 \times (6) + 10^5 (-6) + eV \times \text{nm}}{137.035} = 1.43990 \text{ eV nm}$$

$$E_p = E_g - (E_A + E_L) + \frac{e^2}{4\pi\varepsilon_0\varepsilon r} \rightarrow hv =$$

$$E_g - (E_A + E_L) = \frac{1.43990 \times eV \times \text{nm}}{e \times 10^5 (9) \times \text{nm}} = Eg - (E_A + E_L) = \frac{1.43990 \times 10^5 (-2) \text{ eV}}{e \times \varepsilon}$$

\[
\begin{align*}
E_b &= E_g - (E_a + E_d) + E_c; \\
E_c &= e^2 / \varepsilon; \\
E_g &= 2.5826 \text{eV}; \\
E_a &= 170 \text{meV}; \\
E_d &= 30.5 \text{meV}; \\
\varepsilon &= 10.33 \\
\end{align*}
\]

\[
\begin{align*}
ed &= 3.05 \times 10^{-3}; \\
es &= 23.6 \times 10^{-3}; \\
\varepsilon &= 10.33; \\
e_c &= ed - es; \\
r &= 12.7 \times 10^{-9}; \\
const &= ec \times r; \\
a &= 1.3843 \times 10^{-10}; \\
ap &= a \times \varepsilon / 8.67; \\
r1 &= a / ec = 0.0069 \\
8.763 \times 10^{-11} \\
1.3843 \times 10^{-10} \\
1.64934 \times 10^{-10} \\
2.00623 \times 10^{-9} \\
\end{align*}
\]


\[
\begin{align*}
ed &= 0.0316 \text{eV}; \\
ea &= 0.1675 \text{eV}; \\
E_g &= 2.580 \text{eV}; \\
\varepsilon &= 8.67; \\
\text{and believe or not } e^2 / \varepsilon &= 1.64934 \times 10^{-10} \text{eV nm.}
\end{align*}
\]
Now we calculate distance between donor and acceptor as a function of emission energy (or vice versa)

\[ \text{dap}[\text{ep}, \text{ed}, \text{ea}, \text{eg}] = \left( \begin{align*}
\text{ed} &= 0.0316; \\
\text{ea} &= 0.1675; \\
\text{eg} &= 2.582; \\
\text{c} &= 1.64943 \times 10^{-10}; \\
\text{c} / (\text{ep} + \text{ed} + \text{ea} - \text{eg}) \times 10^{-9}
\end{align*} \right) \]

\[ \text{dap}[2.42807] \\
3.65161 \]

\[ \text{p1} = \text{Plot} [\text{dap}[\text{ep}], \{\text{ep}, 2.395, 2.6\}, \text{PlotStyle} \to \text{RGBColor}[1, 0, 0], \text{AxesLabel} \to \{"E[eV]", "r[\text{nm}]"\}, \text{PlotRange} \to \{(2.38, 2.6), (0, 15)\}] \]

\[ r [\text{nm}] \]
\[ \begin{array}{c}
14 \\
12 \\
10 \\
8 \\
6 \\
4 \\
2 \\
\text{E [eV]} \\
\end{array} \]
\[ \begin{array}{c}
2.45 \\
2.5 \\
2.55 \\
2.6 \\
\end{array} \]

- Graphics -

**Decay rate:**

\[ W(r) = Wo^*\text{Exp}[ -2^*r/a] \]

where \( r \) - the distance between 2 impurities, \( a \) - the Bohr radius (2.8nm), \( Wo \) the initial decay rate (estimated \( 2^*10^8 \)). This turns out \( \text{Ln} [W(r)/Wo]=-2^*r/a \).
4. Fast Fourier Transform (FFT) of 1D and 2D data types

Data Processing

This code is a modified version of Image Processing code written by Dr. Richard Gass
(https://support.yourwebsite.com). The earlier version aimed to remove noise from original data (image) by going into Fourier space and remove frequency with small amplitude and then go back to real space. This version tries to remove unwanted frequencies (in Fourier space) by using LowPassFrequency, HighPassFrequency, and BandPassFrequency. H. E. T. H. Oct, 2005

Exit

Clear[amplitude, z, data]
amplitude[data_List] := Module[{},
  z = Drop[Fourier[data], Apply[Sequence, Map[(Floor[#/2] + 1, #) & Dimensions[data]]],
    z = Abs[z];
    z / Max[z];
    z]

Clear[SpectrumPlot]
SpectrumPlot[data_?VectorQ, options___] :=
  ListPlot[Transpose[{Range[0, Floor[Length[data]/2 - 1]], amplitude[data]}], options];
SpectrumPlot[data_?MatrixQ, options___] := ListPlot3D[amplitude[data], options];

This RemoveNoise function removes small noises:

RemoveNoise[data_List, ε_] := Module[{cleanData},
  cleanData = Chop[Abs[Fourier[data]]/Max[Abs[Fourier[data]]], ε];
  Chop[InverseFourier[ReplacePart[Fourier[data], 0, Position[cleanData, 0]]]]}
These deal with one dimensional data

This LowPassFrequency function allows only low frequencies:

\[
\text{LowPassFrequency}[\text{data}_{\text{List}}, 1] := \text{Module}[\{\text{lowData}\}, \\
\text{lowData} = \\
\quad \text{Fourier}[\text{data}] - \text{UnitStep}[1 - \text{Table}[i, \{i, -\text{Length[}\text{data}] / 2, \text{Floor[}\text{Length[}\text{data}] / 2\}]]) \ast \\
\quad \text{UnitStep}[1 + \text{Table}[i, \{i, -\text{Length[}\text{data}] / 2, \text{Floor[}\text{Length[}\text{data}] / 2\}]]) \ast \\
\quad \text{Fourier}[\text{data}]; \\
\quad \text{Chop}[\text{InverseFourier[}\text{lowData}]]
\]

This HighPassFrequency function allows only high frequencies:

\[
\text{HighPassFrequency}[\text{data}_{\text{List}}, \_] := \text{Module}[\{\text{highData}\}, \\
\text{highData} = \text{UnitStep}[\text{h - Table}[i, \{i, -\text{Length[}\text{data}] / 2, \text{Floor[}\text{Length[}\text{data}] / 2\}]])] \ast \\
\quad \text{UnitStep}[\text{h + Table}[i, \{i, -\text{Length[}\text{data}] / 2, \text{Floor[}\text{Length[}\text{data}] / 2\}]])] \ast \text{Fourier}[\text{data}]; \\
\quad \text{Chop}[\text{InverseFourier[}\text{highData}]]
\]

This BandPassFrequency function works only with f = \text{\_\_} due to symmetry reason:

\[
\text{BandPassFrequency}[\text{data}_{\text{List}}, a, h] := \text{Module}[\{\text{bandData}\}, \\
\text{bandData} = \text{UnitStep}[a - \text{Table}[i, \{i, -\text{Length[}\text{data}] / 2, \text{Floor[}\text{Length[}\text{data}] / 2 - 1\}]])] \ast \\
\quad \text{UnitStep}[-h + \text{Table}[i, \{i, -\text{Length[}\text{data}] / 2, \text{Floor[}\text{Length[}\text{data}] / 2 - 1\}]])] \ast \text{Fourier}[\text{data}]; \\
\quad \text{Chop}[\text{InverseFourier[}\text{bandData}]]
\]

These deal with two dimensional data

This LowPass2DFrequency function allows only low frequencies (It takes all frequencies within a circle radius \( \sqrt{i^2 + j^2} \))

\[
\text{LowPass2DFrequency}[\text{data}_{\text{List}}, 11, 12] := \text{Module}[\{\text{low2DData}\}, \\
\text{low2DData} = \\
\quad \text{Fourier}[\text{data}] - \\
\quad \text{UnitStep}[\text{Sqrt[}\text{11}^2 + \text{12}^2] - \text{Table}[\text{Sqrt[i}^2 + \text{j}^2], \\
\quad \{i, -\text{First[}\text{Dimensions[}\text{data}] / 2, \text{Floor[}\text{First[}\text{Dimensions[}\text{data}] / 2 - 1\}]}, \\
\quad \{j, -\text{Last[}\text{Dimensions[}\text{data}] / 2, \text{Floor[}\text{Last[}\text{Dimensions[}\text{data}] / 2 - 1\}]}) \ast \\
\quad \text{UnitStep}[\text{Sqrt[}\text{11}^2 + \text{12}^2] + \text{Table}[\text{Sqrt[i}^2 + \text{j}^2], \\
\quad \{i, -\text{First[}\text{Dimensions[}\text{data}] / 2, \text{Floor[}\text{First[}\text{Dimensions[}\text{data}] / 2 - 1\}]}, \\
\quad \{j, -\text{Last[}\text{Dimensions[}\text{data}] / 2, \text{Floor[}\text{Last[}\text{Dimensions[}\text{data}] / 2 - 1\}]}) \ast \\
\quad \text{Fourier}[\text{data}]; \\
\quad \text{Chop}[\text{InverseFourier[}\text{low2DData}]]
\]

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This HighPass2DFrequency function allows only high frequencies (It takes all frequencies outside a circle radius $\sqrt{h_1^2 + h_2^2}$)

\[
\text{HighPass2DFrequency}[\text{data}_\text{List}, h_1, h_2] := \text{Module}[\{\text{high2DData}\},
\begin{align*}
\text{high2DData} &= \text{UnitStep}[\text{Sqrt}[h_1^2 + h_2^2]] - \text{Table}[\text{Sqrt}[i^2 + j^2],
\{i, \text{-First[Dimensions[\text{data}]]/2, \text{Floor[First[Dimensions[\text{data}]]/2 - 1]}\},
\{j, \text{-Last[Dimensions[\text{data}]]/2, \text{Floor[Last[Dimensions[\text{data}]]/2 - 1]}\}]\} \times \\
\text{UnitStep}[\text{Sqrt}[h_1^2 + h_2^2]] - \text{Table}[\text{Sqrt}[i^2 + j^2],
\{i, \text{-First[Dimensions[\text{data}]]/2, \text{Floor[First[Dimensions[\text{data}]]/2 - 1]}\},
\{j, \text{-Last[Dimensions[\text{data}]]/2, \text{Floor[Last[Dimensions[\text{data}]]/2 - 1]}\}]\} \times \\
\text{Fourier[\text{data}]};
\text{Chop[InverseFourier[\text{high2DData}]]}
\end{align*}
\]

This to import file (data)

\[
\text{ImportSTMData[filename\_String]} := \text{Module}[\{\text{importdata}\},
\begin{align*}
\text{importdata} &= \text{Import[filename]};
\text{Map[ToExpression, Drop[Drop[\text{importdata}, -1], 1]]}
\end{align*}
\]

This tests one dimensional data (in this case, a Photoluminescence spectrum)

\[
data\ = \text{ImportSTMData["Z:\\Thang\pl1.csv"]};
data1 = \text{Import["Z:\\Thang\pl1.csv", "List"]};
\]

This is the original data:

\[
\text{plot1} = \text{ListPlot[Table[data1], PlotJoined -> True, PlotStyle -> RGBColor[0, 0, 1]]}
\]
This passes only high frequencies (sharp peaks):

```math
\begin{align*}
\text{plot3} &= \text{ListPlot} \left[ \text{HighPassFrequency} \left[ \text{Table} \left[ \text{data1}, 997 \right], 997 \right] + 1000, \ 	ext{PlotJoined} \rightarrow \text{True}, \\
&\quad \text{PlotRange} \rightarrow \text{All}, \ 	ext{PlotStyle} \rightarrow \text{RGBColor}[0, 1, 0] \right];
\end{align*}
```

---

5. Least Square Fit

This is to calibrate the SPEX spectrometer

The dispersion relation of a CCD camera (with 2000 horizontal pixels) is represented as

\[ \lambda = \lambda_{\text{center}} + \beta (p - 1000) + \gamma (p - 1000)^2, \]

where \( p \) is the \( p \)th pixel along the horizontal dimension

\[ \beta = \beta_0, \ \beta_1, \ \beta_2, \ \beta_3 = \beta_0 + \beta_1 + \beta_2 + \beta_3, \gamma = \gamma_0, \ \gamma_1, \ \gamma_2 = \gamma_0 + \gamma_1 + \gamma_2, \]

with \( \beta_0, \ \beta_1, \ \beta_2, \ \gamma_0, \ \gamma_1, \gamma_2 \) are numerical constants we need to find for each CCD camera so the error is minimum

---

\text{data} =

Import[
  "F:\Thang\Routines\SpeX\SubVIs\calibrating\SPEX-dispersion-reduce-second-order.csv"], {List}];

\text{Length[data]}

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\( \phi[\beta_0, \beta_1, \beta_2, x] := \beta_0 + \beta_1 x + \beta_2 x x; \)

\( \chi[y_0, y_1, x] := y_0, y_1 x; \)

\( \lambda[\lambda_{\text{center}}, \text{pixel}, \beta_0, \beta_1, \beta_2, \gamma_0, \gamma_1] := \lambda_{\text{center}} + \beta \{ \beta_0, \beta_1, \beta_2, \lambda_{\text{center}} \} (\text{pixel} - 1000) + \gamma \{ y_0, y_1, \lambda_{\text{center}} \} (\text{pixel} - 1000) \)

\( \chi_1[\text{data}, \beta_0, \beta_1, \beta_2, \gamma_0, \gamma_1] := \sqrt{\frac{1}{\text{Length[data]}} \text{Sum} \left[ (\lambda[\text{data}[\{i, 2\}], \text{data}[\{i, 3\}], \beta_0, \beta_1, \beta_2, \gamma_0, \gamma_1] - \text{data}[\{i, 1\}] )^2, \{i, 1, \text{Length[data]}\} \right]} \)
The histogram plot below shows that the error of the SPEX spectrometer is around 0.1 nm.

![Histogram plot of the error of the SPEX spectrometer](image)

Figure A.3.1 - Histogram plot of the error of the SPEX spectrometer