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Investigation of zincblende, wurtzite, and mixed phase InP nanowires by photocurrent, photoluminescence and time-resolved photoluminescence spectroscopies

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Investigation of Zincblende, Wurtzite and mixed phase InP nanowires by photocurrent, photoluminescence and time-resolved photoluminescence spectroscopies

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ABSTRACT

In this research, we use photocurrent, photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectroscopy to investigate the optical and electrical properties of single Zincblende (ZB), Wurtzite (WZ) and mixed phase ZB/WZ InP nanowires at low temperatures (10 K).

In this project, InP nanowires were grown by the vapor-liquid-solid method using 20nm and 50nm gold nanoparticles as catalyst at 400°C. The 50nm ZB nanowires, 50nm ZB/WZ mixed phase nanowires and 20nm WZ nanowires were grown at V/III ratios 350, 700 and 700 respectively. PL and TRPL spectroscopy of individual ZB, WZ and ZB/WZ mixed phase InP nanowires at 10ºK were studied by exciting single nanowires with a titanium Sapphire laser. From PL and TRPL spectroscopy, we have observed emission at the band edges of ZB and WZ InP at ~1.42eV and 1.504eV respectively, consistent with previous measurements.

For ZB/WZ mixed phase InP nanowires, we observe a change in PL emission energy from the ZB band edge to the WZ band edge as a function of excitation power, consistent with the nature of the mixed phase nanowires. TRPL measurements shows a dramatic increase of the recombination lifetime from 170ps for excitons in the continuum above the conduction and valence band barriers, to more than 8400ps for electrons confined in quantum potential wells defined by monolayer-scale ZB sections, and holes confined in quantum potential wells defined by the predominant WZ sections of the nanowire. Using detailed high-resolution transmission electron microscopy (HRTEM) measurements from a 657nm length of a single nanowire, we calculate a complete set of electrons and hole confined states using an eigenfunction expansion method. Analysis of the distribution of electron and hole confined states demonstrates that the
observed energy-dependent dynamics are consistent with the type II nature of the confined electron and hole wavefunctions.

In addition to PL and TRPL measurements of single InP ZB and WZ nanowires, photocurrent spectroscopy measurements in single InP nanowire devices have been carried out to investigate their electronic band structure. Photolithography techniques followed by etching with ammonium polysulfide are used to fabricate Ohmic Ti/Al metal contact pads separated by ~4 microns on several ZB or WZ InP nanowires. An SEM study of WZ nanowires dispersed on Si substrates shows that larger diameter nanowires are mixed with 20nm nanowires. I-V characteristics confirm highly photosensitive nanowire devices with Ohmic contacts. Using a monochromatic white light set up or a tunable (1.30 to 1.75 eV) CW laser, we obtain photocurrent at fixed bias voltage as a function of excitation energy by broad illumination of the InP nanowire device. At room temperature, we find that the photocurrent for all nanowire devices drops exponentially for photon energies below the fundamental band edge, showing evidence for an Urbach edge. We find that the WZ energy gap (~1.42eV) is ~70meV above the ZB energy gap (~1.35eV) at room temperature, consistent with previous photoluminescence measurements.

At low temperatures (10 K), the photocurrent spectrum for the ZB device shows strong evidence for two excitonic resonance peaks relevant to the band gap (1.425 eV) and split off band (1.539 eV) in the photocurrent spectrum. The measured spin orbit splitting energy of 114eV for ZB InP is consistent with the known spin orbit splitting of 110meV. The WZ nanowire device with larger diameter nanowires shows three excitonic peaks relevant to A (1.504eV), B (1.531eV) and C (1.655eV) valence bands at low temperature, consistent with recent PLE measurements. The crystal field energy (47meV) and the spin orbit splitting energy (127meV)
measured for a WZ InP nanowire device is consistent with recent PLE measurements for 100nm WZ InP nanowires and theoretical predictions. In some WZ InP nanowire devices with smaller diameter nanowires, A (~1.523eV), B (~1.565eV) and C (~1.675eV) excitonic peaks are observed at higher energies suggesting possible of quantum confinement in the 20nm WZ InP nanowires. These energy values are consistent with the theoretical calculation of transition energies from A, B and C hole bands to the conduction band by considering electron and holes as particles confined in an infinite cylindrical potential.

The polarized photocurrent spectroscopy measurement of a ZB InP nanowire device (~275nm) has been shown to have a negative polarization index which is consistent with theoretical calculations of InP nanowires with this diameter. Polarized photocurrent measurements of a WZ InP nanowire device having two nanowires of diameter ~26nm have a polarization index of about 95% which is consistent with theoretical calculations for smaller nanowires. In addition, the photoluminescence excitation (PLE) spectroscopy measurement for the same WZ nanowire device with the excitation parallel to the nanowire agrees very well with the polarized photocurrent measurements.
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Table of Contents

ABSTRACT ........................................................................................................................................ii

ACKNOWLEDGEMENTS ..................................................................................................................vi

LIST OF FIGURES ............................................................................................................................x

LIST OF TABLES ...............................................................................................................................xv

CHAPTER I ..........................................................................................................................................1

1. INTRODUCTION ............................................................................................................................2

1.1 Semiconductors ..........................................................................................................................2

1.1.1 Excitons in semiconductors .................................................................................................3

1.1.2 Photoluminescence .............................................................................................................7

1.2 Semiconductor Nanowires ........................................................................................................9

CHAPTER II ........................................................................................................................................13

2. InP NANOWIRES AND THEIR CRYSTAL STRUCTURE ..............................................................14

2.1 Energy Band Structure of Semiconductors .............................................................................14

2.1.1 ZB Crystal Structure .........................................................................................................17

2.1.2 WZ Crystal Structure .........................................................................................................18

2.2 Band structures and band parameters for InP ......................................................................19

2.2.1 ZB InP Band Structure .....................................................................................................19

2.2.2 WZ InP Band Structure .....................................................................................................21

2.3 Nanowire growth ......................................................................................................................23

CHAPTER III ......................................................................................................................................29

3. EXPERIMENTAL TECHNIQUES .................................................................................................30

3.1 Nanowire dispersion and mapping .........................................................................................30

3.2 Nanowire device fabrication ....................................................................................................31
3.2.1 Photolithography Fabrication................................................................. 33
3.2.2 Packaging and wire-bonding................................................................. 36
3.3 PL and TRPL Experimental Setup .......................................................... 39
  3.3.1 Spectrometers ................................................................................. 42
  3.3.2 CCD, APD and PMT Detectors ........................................................... 43
  3.3.3 Polarization Optics ........................................................................... 47
  3.3.4 Titanium–Sapphire Laser ................................................................. 49
  3.3.5 Optical Cryostat .............................................................................. 50
3.4 Dark Current measurement setup ............................................................. 51
3.5 Photocurrent Experiment setup ................................................................. 52
  3.5.1 Lock-in Amplifier ............................................................................. 55
CHAPTER IV ........................................................................................................ 58
4. PL & TRPL SPECTROSCOPY OF InP NANOWIRES ..................................... 59
  4.1 Introduction .......................................................................................... 59
  4.2 PL and TRPL experiments ................................................................... 59
  4.3 ZB, WZ and ZB/WZ mixed phase InP nanowires .................................... 60
  4.4 PL & TRPL Spectroscopy of single ZB and WZ InP nanowires ............... 63
    4.4.1 Photoluminescence (PL) Spectroscopy ........................................... 63
    4.4.2 Time Resolved Photoluminescence (TRPL) Spectroscopy ............... 65
  4.5 PL and TRPL spectroscopy of ZB/WZ mixed phase nanowires ............... 67
    4.5.1 ZB/WZ mixed Phase InP nanowires .............................................. 67
    4.5.2 Photoluminescence (PL) spectroscopy .......................................... 69
    4.5.3 Time-resolved Photoluminescence (TRPL) spectroscopy ............... 70
    4.5.4 Modeling recombination lifetimes ............................................... 74
  4.6 Summary .............................................................................................. 79
CHAPTER V .......................................................................................................... 83
5. PHOTOCURRENT SPECTROSCOPY OF InP OHMIC NANOWIRE DEVICES ...... 84
5.1 Introduction ........................................................................................................................................... 84
5.2 InP nanowire devices ............................................................................................................................... 85
5.3 Basis IV measurements and Ohmic behavior of nanowire devices ....................................................... 86
5.4 Lock-in IV measurements and photocurrent spectroscopy ................................................................. 87
5.5 Photocurrent spectroscopy of ZB and WZ InP nanowire devices at 300K ........................................... 88
5.6 Photocurrent measurements of ZB and WZ InP nanowire devices at 10K ......................................... 90
5.7 Quantum confinement of 20nm WZ InP nanowires ............................................................................. 92
5.8 Polarization photocurrent spectroscopy of ZB and WZ InP nanowires .............................................. 96
5.9 Summary ................................................................................................................................................ 102
APPENDICES .................................................................................................................................................. 106

A1. Eigenfunction expansion method ........................................................................................................ 106
A2. Quantum confinement in an infinite cylindrical well ........................................................................ 108
A3. Polarization anisotropy in nanowires .................................................................................................. 111

LIST OF FIGURES
Figure 1: Schematic diagram of the energy band diagram. The discrete energy states of Si atom (a) are replaced by the energy bands in a Si crystal (b). Since all electrons cannot have the same energy level, they form energy bands \(^2\) ................................................................................................................................. 2
Figure 2: Wannier-Mott exciton with much larger Bohr radius than the atomic spacing. .......... 5
Figure 3: Schematic diagram showing the energy of Wannier-Mott excitons (discrete and the continuum excitons) ......................................................................................................................... 6
Figure 4: Optical excitation, nonradioactive relaxation and luminescence process of a semiconductor .................................................................................................................................................. 7
Figure 5: Energy band diagram of (a) a direct band gap and (b) an indirect band gap semiconductor .............................................................................................................................................................. 15
Figure 6: Crystalline structure of ZB unit cell. Yellow spheres are Indium (In) atoms and grey spheres are phosphorus (P) atoms. ................................................................. 17

Figure 7: WZ unit cell (left) and WZ crystal structure (right). Yellow spheres are Indium (In) atoms and grey spheres are phosphorus (P) atoms. ................................................................. 18

Figure 8: Calculated ZB InP band structure by James R. Chelikowsky et al along with a schematic diagram of the band structure at the zone center (right). ................................................................. 19

Figure 9: Predicted WZ InP band structure by Craig E. Pryor et al along with a schematic diagram of the band structure at the zone center (right). ................................................................. 21

Figure 10: Vapor liquid solid (VLS) growth technique used for InP nanowire growth. The size of the nanoparticle defines the diameter of nanowires. ................................................................. 24

Figure 11: Scanning electron micrograph (SEM) images of InP nanowires grown by VLS method as functions of V/III ratio and catalyst size. The scale bars are 2µm. ............................................. 25

Figure 12: Nanowires dispersed on a patterned Si Substrate. The lithographically defined pattern on the Si substrate helps to find nanowires on the sample substrate. ......................................................... 30

Figure 13: Nanowire device fabrication process by micro-photo lithography techniques. .......... 31

Figure 14: (a) A schematic image of ultrasonic wedge bonding and (b) an optical image of a wire-bonding done with wedge bonding................................................................. 37

Figure 15: (a) Optical image and (b) Scanning electron microscopy (SEM) image of a nanowire device. (c) Nanowire device packaged on a chip carrier for measurements showing gold wire bonding from devices to the chip carrier. ................................................................. 38

Figure 16: Schematic display of the photoluminescence and time-resolved photoluminescence spectroscopy experimental set up. ................................................................. 40

Figure 17: Schematic diagram of (a) the Newport Spectrometer and (b) Spex spectrometer ...... 42
Figure 18: A schematic diagram of an avalanche photodiode (top) with an APD for single photon counting image of MPD (bottom) .......................................................... 44

Figure 19: Schematic illustration of a photo multiplier tube. ................................................. 45

Figure 20: (a) Schematic illustration of micro channel plate (MCP) and (b) its principle multiplication . .......................... 46

Figure 21: Schematic illustration of a Babinet-Soleil compensator. ................................. 47

Figure 22: Half-Wave Plates Rotate the Polarization Plane of Linearly Polarized Light .......... 48

Figure 23: Quarter-Wave plate makes the output polarization circular ................................. 48

Figure 24: Schematic diagram of a continuous flow liquid He cryostat ............................... 50

Figure 25: Schematic diagram of two probe DC measurement system ............................... 51

Figure 26: Schematic display of the Photocurrent spectroscopy experimental set up .......... 52

Figure 27: Example plots of (a) the DC current across a nanowire device, (b) the current across the device as a result of modulated excitation and DC current and (c) the current signal processed by the Lock-in amplifier as a function of time at fixed bias ........................................ 54

Figure 28: Dual phase SR800 (350W) Lock-in amplifier .................................................... 56

Figure 29: SEM (top row) and HRTEM (bottom row) images of (a, d) 50nm ZB InP nanowires, (b, e) 20nm WZ InP nanowires and (c, f) 50nm ZB/WZ mixed phase InP nanowires. Scale bars in the top row and the bottom row are 2µm and 5nm respectively. .......................... 61

Figure 30: Power-dependent CW PL spectra (a) 50nm ZB InP nanowires and (b) 20nm WZ InP nanowires. P is referred to an excitation power of 100 µW. Vertical blue and green lines represent the positions of band edges of ZB and WZ respectively ..................................... 63

Figure 31: Time-resolved spectral maps for a single (a) ZB InP nanowire and (b) WZ InP nanowire. White lines show WZ (1.504 eV) and ZB (1.42 eV) emission energies. Integrated PL
extracted from corresponding TRPL maps for (c) ZB and (d) WZ integrated for early time
(black) from 0-1ns and later time (red) from 3ns and later.......................................................... 65

Figure 32: (a) HRTEM of a ZB/WZ InP nanowire showing ZB inclusions in the nanowire; (b)
enlarge section of HRTEM image with ZB sections identified with white dashes and number of
atomic layers; (c) the band diagram and alignments corresponding to the image (b). ............... 67

Figure 33: (a) The normalized PL spectra showing the shift in PL peak position as excitation
power increases from \( P_0/2 \) to \( 2P_0 \) where \( P_0 = 100\mu W \). (b) Shows the PL peak position extracted
from (a) as a function of power........................................................................................................ 69

Figure 34: (a) Time resolved PL spectral map for a ZB/WZ mixed phase InP nanowire. The
white lines are the reference for the energies for ZB band edge (1.42eV), WZ band edge
(1.504eV) and energy related to the continuum (1.549eV). (b) PL extracted using individual time
slice of TRPL map showing the evolution of the spectra from 0.1 to 4.5 ns................................. 70

Figure 35: Time decays of photoluminescence for energies (a) near ZB band edge (b) near WZ
band edge and (c) near the continuum.......................................................... 72

Figure 36 : The energies of the bound states along the nanowire for electrons (a) and holes
(c).The width of the horizontal lines represents the spatial extend of these states for electron
(blue) and holes (red). (b) The variation bound state energy as a function of electrons (1 – 45)
and holes (1 - 150). .................................................................................................................. 74

Figure 37: Wave functions calculated for electron energy state number 18 along with hole states
with numbers 6, 32, 43, 47 and 65. The arrows point to the TEM image at the bottom to give an
indication of the special position of these states along the nanowire........................................... 76

Figure 38: The recombination lifetimes calculated from the model (Blue) and the TRPL
measurements (Red) as a function of emission energy................................................................. 78
Figure 39: IV characteristics of a ZB InP nanowire device in dark (black curves in (a) & (b)) and under white light illumination (red curve in (a)) at room temperature showing the Ohmic nature and the high photo sensitivity of the device.

Figure 40: Schematic diagram of photocurrent spectroscopy (a) where the nanowire is excited with light to create electron and holes in the CB and the VB in the semiconductor (b) as a result of photo excitation and the current is measured as a function of bias voltage and excitation energy.

Figure 41: Photocurrent spectra for ZB InP nanowire (blue dots) and WZ InP nanowire (red dots) devices at 300K where vertical axis represents the photocurrent in logarithmic scale. Dark lines represent the linear fits to the data below and above band edges showing changes of slopes at the band edge. Vertical dash lines represent the band edge for ZB and (blue) WZ (red).

Figure 42: Photocurrent spectra for ZB InP nanowire (blue) and WZ InP nanowire (red) devices at 10K. The arrows represent the positions of excitonic states correspond to transitions from CB to the degenerate heavy/ light hole band (HH/LH) and the split off band in the case of ZB and the A, B and C hole bands.

Figure 43: Comparison of photocurrent spectra for three different WZ InP nanowire devices D1, D2 and D3 at 10K. Three dash lines represents the energy positions of three hole bands A, B and C for the same WZ InP nanowire device (D1) shown in Figure 42. For D2, only B hole band is shifted to higher energy by ~30meV and the A and C hole bands are shifted by ~20meV while the position of B hole band is not clear for the device D3.

Figure 44: Scanning electron microscopy (SEM) images of two WZ InP nanowire devices (a) D2 having four nanowires and (b) D3 having two nanowires showing the bundling of nanowires. The scale bar on the top left of the images is 100nm.
Figure 45: Polarized photocurrent spectroscopy for (a) the ZB InP nanowire device and (b) the WZ InP nanowire device D3 at 10K. Excitation laser was polarized parallel/perpendicular to nanowire................................................................. 96

Figure 46: The theoretical polarization index (a) as a function of nanowire diameter calculated at excitation energy 1.55eV and (b) as a function of excitation energy for both 275 nm ZB (navy color line) and 26nm WZ InP nanowires (orange color line) along with the experimental polarization index measurements for both 275nm ZB InP nanowire device (blue dots) and the WZ InP nanowire device D3 (red dot)............................................................................................................ 99

Figure 47: Photoluminescence excitation measurement of the WZ InP nanowire device D3 measured with excitation parallel to the nanowire along with polarized photocurrent measurements for comparison. Black solid curve refers to the PL taken with excitation at 1.675eV .............................................................................................................................. 101

LIST OF TABLES
Table 2.1: Important band parameters of ZB InP calculated by James R. Chelikowsky et al\textsuperscript{[14]} along with experimental values ................................................................. 20
Table 2.2: Important band parameters of WZ InP calculated by E. Pryor et al\textsuperscript{[17]} ....................... 22
Table 5.1: Diameter measured for nanowires in two WZ InP nanowire devices D2 and D3 using SEM micrographs. .................................................................................................................. 94
Table 5.2: The energy shift of A, B and C excitonic states because of the quantum confinement of excitons................................................................. 95
CHAPTER I

INTRODUCTION
1. **INTRODUCTION**

1.1 **Semiconductors**

When we consider the electronic properties of solid state, we group them according to their electrical conductivity as conductors, semiconductors or insulators. The distinction between these materials is relative. All materials are conductive; some are more conductive than others. Our researches focus on semiconductor materials that have the conductivity in between that of both conductors and insulators. This conductivity is highly sensitive to illumination, temperature, magnetic field and electric field. This makes the semiconductor one of the most important materials in the electrical engineering community. Adding impurities to the semiconductor materials, known as doping, increases the number of charge carriers and as a result the conductivity of the semiconductor material. Doped semiconductors are called n-type or p-type depending on majority carrier type (electron or hole).

![Energy Band Diagram](image)

**Figure 1**: Schematic diagram of the energy band diagram. The discrete energy states of Si atom (a) are replaced by the energy bands in a Si crystal (b). Since all electrons cannot have the same energy level, they form energy bands [2].
We also can characterize these materials according to their band structures. Figure 1 shows the energy band diagram of Si which is the most widely used semiconductor material because it’s the second most abundance material on earth. The electrons in an atom occupy discrete energy levels as shown in Figure 1(a). If two atoms are brought together, each energy level will split into two due to the Pauli Exclusion Principle. When many atoms ($\sim 10^{23}$) are brought together to make a solid, the discrete energy levels are replaced with energy bands as shown in Figure 1 (b). Normally, the electrons fill up the low energy bands first, only one electron per state because of the Pauli Exclusion Principle. The uppermost fully occupied band in an insulator or semiconductor is called the valance band (VB) and the lowest, almost unoccupied band is called the conduction band (CB) \cite{1, 2, 3}. In metals, the VB is partially filled regardless of temperature; therefore they have very high conductivity. The difference between insulators and semiconductors is only that the forbidden band gap between the VB and CB is larger in an insulator. The electrons can be excited from VB to the CB through thermal or optical excitation \cite{4}. The electron in the VB can jump in to the CB by absorbing a photon (light) of energy $E$ greater than the band gap ($E_g$). In this thesis, we discuss the use of photocurrent, Photoluminescence and time-resolved photoluminescence spectroscopies of these photoexcited carriers, to study the band structure of semiconductor materials.

1.1.1. Excitons in semiconductors

When an electron is excited from the VB to the CB, the process leaves a vacancy in the sea of electrons in the VB called a hole. A hole acts as a positively charged particle which is similar to the proton in the nucleus of the Hydrogen atom, except with a much smaller mass. An exciton is a bound state of the electron and hole which are attached to each other because of the electrostatic Coulomb interaction. An exciton is an electrically neutral quasiparticle that exists in
semiconductors, insulators and in some liquids. The exciton has slightly less energy than the unbound electron and hole. The wave function of the exciton is said to be like hydrogenic, however the binding energy is much smaller and the particle size is much larger than a hydrogen atom because of (1) the small masses of the electron and hole, and (2) the dielectric constant of the material which reduces the coulomb force between the electron and hole. Solving the Hydrogen-like Hamiltonian \[^{5,6}\] for the exciton, one can find the binding energy and the Bohr radius of the excitons.

\[
E_b = \frac{\hbar^2}{2\mu(a^0)^2} \quad (1.1)
\]

\[
a_B = \frac{\varepsilon \hbar^2}{\mu \varepsilon} \quad (1.2)
\]

Equations 1.1 and 1.2 represent the binding energy and Bohr radius of an exciton respectively. \(\mu\) is the effective mass of the exciton and \(\varepsilon\) is the dielectric constant of the material. There are two types of excitons; Frenkel excitons and Warnnier-Mott excitons depending on their size and binding energy because of the difference in dielectric constant.

In materials with a small dielectric constant, the coulomb interaction between the electron and the hole is strong and the exciton size is thus small of the same order of the unit cell. This Frenkel exciton, named after Yakov Frenkel, has a typical binding energy of 0.1 to 1 eV. Frenkel excitons are typically found in alkalihalid crystals and in organic molecular crystals.
In semiconductor materials, the dielectric constant is generally large (~12.9 for GaAs & 12.5 for InP) and as a result the Coulomb interaction between the electron and the hole is small. Figure 2 shows a Wannier-Mott exciton\cite{7}, named after Gregory Wannier and Nevill Francis Mott, which has a larger radius than lattice spacing and small binding energy typically in the order of 10meV. The exciton binding energy of InP is \( \sim 5\text{meV} \); 4.8meV\cite{8} for ZB InP and 5.1meV\cite{9} for WZ InP and the Bohr radius is 12nm\cite{10,11,12}. The binding energy of the WZ InP (5.1meV) by Mishra et al\cite{9} has been measured using temperature dependence photoluminescence (PL) measurements. These types of excitons are typically found in semiconductor crystals with small energy gaps and high dielectric constants, but have also been identified in liquids such as liquid Xenon.

The total energy of the exciton is given by the equation;

\[
E_n = E_g + \frac{K^2 h^2}{2M} - \frac{h^2}{2\mu (a^R)^2} \frac{1}{n^2} \tag{1.3}
\]
where $M$ is the total mass of the electron-hole pair and $K$ is the center of mass wave vector of the exciton and $E_g$ is the band gap of the semiconductor.

![Figure 3: Schematic diagram showing the energy of Wannier-Mott excitons (discrete and the continuum excitons).](image)

Figure 3 shows a schematic diagram showing the excitons energy levels of Wannier-Mott exciton with respect to the center of mass wave vector. As the quantum number $n$ increases the spacing between the energy levels decreases and becomes a continuous band for very large $n$. These are called bound states ($n = 1, 2, 3\ldots$) and the continuum state. In the continuum, the excitons (electron–hole pairs) are considered to be ionized into free electrons and free holes.
1.1.2. Photoluminescence

Figure 4: Optical excitation, nonradioactive relaxation and luminescence process of a semiconductor

Figure 4 shows a possible optical excitation and emission process of a direct band gap semiconductor. Electrons in the VB can be excited into the CB by absorbing a photon of energy $h\nu_1 \geq E_g$ leaving a vacancy of electron namely hole in the VB by photo-excitation. Eventually the photo-excited electron will recombine with the hole after nonradioactive relaxation process by emitting photons. In the nonradioactive relaxation process, the excited electrons relax in to the minimum possible energy in the CB by emitting phonons (lattice vibration). The electron and hole in the band minima then form a bound state called an exciton as discussed above. Then the electron in the CB minimum recombines with the hole in the VB maximum (the bottom of the hole band) by emitting a photon with energy $h\nu_2$. The photon emission as a result of this recombination is called photoluminescence. Similarly luminescence can be observed in the recombination process by using different excitation sources; for example, if an electric current is used, the luminescence is called electroluminescence.

Electric current can flow only when the electrons populate the conduction band leaving a vacancy of an electron in the valence band called a hole. The electrons can be excited from VB
to the CB through thermal or optical excitation. The current flow as a result of photoexcited carriers is called a photocurrent. The electron in the VB can jump in to the CB by absorbing a photon (light) of energy $h\nu$ greater than the band gap ($E_g$). The density of states $N(h\nu)$ is the number of electron in the CB (holes in the VB) as a function of the photon energy $E$ given by

$$N(h\nu) = A (h\nu - E_g)^{1/2}$$

(1.4)

where $A$ is called the absorption coefficient. Therefore, the photocurrent through the nanowire at a particular bias voltage is a measure of the density of states, $N(h\nu)$ of both electron and holes. In a pure semiconductor, since the electron density in the CB (hole density in the VB) becomes zero when the photon energy is less than or equal to $E_g$, the absorption coefficient and thus the photocurrent will drop very sharply when the photon energy drops below $E_g$. In a real semiconductor, the presence of impurities and defects result in electronic states below the fundamental energy gap which results in an exponential decay of the absorption coefficient and also the photocurrent for photon energies below $E_g$.

$$N(h\nu) = A \exp \left( \frac{h\nu - E_g}{E_u} \right)$$

(1.5)

The equation 1.5 represent the behavior of the density of states or the absorption coefficient below the band gap where $E_u$ is known as urbach energy which is a measure of the defect and impurity density in a real semiconductor\textsuperscript{[13,14]}. In the photocurrent study discussed in chapter V, we observe an exponential tail of the photocurrent spectra below the band edge of the semiconductor both at room temperature and low temperature.

In Chapter III, we discuss the experimental methods and experimental setup for both photoluminescence and photocurrent measurements. Detailed experimental measurement done
using photoluminescence and time-resolved photoluminescence spectroscopies on InP nanowires used in this research will be discussed in chapter IV and In Chapter V, we discuss the photocurrent spectroscopy of InP nanowires.

1.2 Semiconductor Nanowires

With the development of Nanotechnology, scientists have developed new methods for fabrication of one dimensional nanowires from semiconductors, our research goal is to investigate how electronic band structure of semiconductor nanowires changes according to material structure. The recently grown nanowires using III-V and II-IV semiconductors show either the expected ZB (cubic) structure or the more unusual WZ (hexagonal) structure which is not usually seen in bulk InP materials. These semiconductor nanowires show significant promise for bottom-up fabrication of novel semiconductor devices [15,16,17,18,19,20]. Scientists have observed the existence of both ZB and WZ structures in the same nanowire for InP and have observed a band gap difference of 80 meV between pure ZB and WZ nanowires [21,22,23,24]. In addition, the phase (ZB or WZ) of InP nanowires can be controlled by changing the growth condition: temperature and V/III ratio [25].

The InP nanowires we used in this research were grown using the most common method of one dimensional nanowire growth; namely vapor liquid solid (VLS) technique. In this method a catalyst (usually gold nano particle) is dispersed on the growth substrate. Then the nanowire materials in the form of gas is introduced selectively, which from the liquid droplet with catalyst and becomes supersaturated and nucleation occurs with a solid crystalline nanowire growth depending on the growth parameters. The diameter of the nanowire is defined by the size of the catalyst nano particle. A more detailed discussion of the nanowire growth technique, crystal structures and the energy band structure is explained in Chapter II.
The interaction of polarized light with nanowires is completely different compared with
the bulk materials. Absorption of polarized light by a nanowire when it is excited parallel to the
nanowire is different when it polarized light excites the nanowire perpendicular to the long axis.
This polarization dependence of nanowires has been analyzed by H.E. Ruda et al\textsuperscript{[26]}, who
showed that while nanowires are polarized along the nanowire axis for smaller diameter
nanowires they can be polarized perpendicular to larger diameter nanowires. The effect of
polarized light on the nanowire can vary both as a function of energy as well as the diameter of
the nanowire. We will discuss how light interact with nanowires in chapter V in more detail.
Reference:


CHAPTER II

InP NANOWIRES AND THEIR CRYSTAL STRUCTURE
2. InP NANOWIRES AND THEIR CRYSTAL STRUCTURE

2.1 Energy Band Structure of Semiconductors

As discussed briefly in Chapter I, semiconductors have different optical and electronic properties compared with metals and insulators. In solid state physics, the band theory that we discussed in chapter I is used to explain the optical and electronic properties of semiconductor materials. The energy band structure is usually indicated by plotting the electrons energy for different values of $k$ in the Brillouin zone because of the translational invariance of the lattice. The crystal potential is different in different directions because of the difference in the atomic spacing. As a result, the electron energy depends both on the magnitude and direction of $k$ and makes energy bands. The uppermost fully occupied band is called the valance band (VB) and the lowest, almost unoccupied band is called the conduction band (CB). The gap between the bottom of the CB and the top of the VB is known as the band gap ($E_g$). For insulators, the band gap is large making excitations of an electron in the VB to the CB quite difficult, making the conductivity low. For semiconductors, the gap is not so large so that electrons in the valence band can easily be excited thermally or through optical excitation into the conduction band. In solid state physics, materials can be characterized as metals, semiconductors or insulators using the band theory. The band gap plays an important role in determining the optical and electronic properties of semiconductors. In semiconductor physics, the band gap of a semiconductor is always one of two types a direct band gap and an indirect band gap.
Figure 5: Energy band diagram of (a) a direct band gap and (b) an indirect band gap semiconductor.

Figure 5 shows the energy band diagram of a direct and an indirect band gap semiconductor. As shown in Figure 5 (a) if the lowest energy of the CB and the highest energy of the VB is at the same position in k space, we called it a direct band gap semiconductor where a excited electron in the CB can recombine with a hole in the VB or one can excite an electron in the VB to the CB without changing its momentum. This is because the momentum of the associated photon is very small compared to the crystal momentum of the electron in the CB and the VB. Such transitions are known as direct transitions. On the other hand in an indirect band gap semiconductor the highest energy of the VB and the lowest energy of the CB do not occur at the same position in k space making it is impossible to excite an electron from VB maximum to CB minimum or vice versa without changing its momentum. These types of transitions are called indirect transitions and can only be possible with the absorption or emission of phonon (lattice vibration) to conserve the momentum. Because such a transition involves a three body interaction, the efficiency can be very small. Because a direct transition only involves the initial
and final electron states, optical processes can occur with very high efficiency in direct band gap semiconductors.

Indium Phosphide (InP) is a direct band gap semiconductor used in high power and high frequency applications because of its excellent transport properties. It has been used as a building block in many optoelectronic devices such as field effect transistors, light emitting diodes, sensors etc.\[^{1,2,3,4,5,6}\] InP has a band gap of 1.344eV at room temperature\[^{7,8}\].

Most semiconductors have either cubic (diamond and Zincblende) or hexagonal (wurtzite) crystal structures\[^{8,9}\]. InP is a semiconductor which has a Zincblende (ZB) structure in the bulk, while InP nanowires can exist in both ZB or wurtzite (WZ) phases. The most common crystal structure used in semiconductor physics is the diamond lattice where each atom in the diamond lattice has four nearest neighbor atoms which together form a tetrahedron. The space lattice is face centered cubic with pairs of atoms at \((0, 0, 0)\) and \((1/4, 1/4, 1/4)\) forming a pattern unit cell. The diamond lattice therefore is a face-centered-cubic lattice with a basis containing two identical atoms. Silicon or Germanium semiconductors exist in the diamond structure. On the other hand, binary semiconductors such as GaAs and InP have a crystal structure that is similar to that of diamond, however with two different types of atoms in the lattice. Each atom still has four nearest neighbors of the other type. This structure is known as the Zincblende (ZB) lattice structure, named after the Zincblende crystal (ZnS). The third common crystal structure is the hexagonal crystal structure also known as the wurtzite (WZ) crystal structure, which is the hexagonal form of zinc sulfide (ZnS).
2.1.1 ZB Crystal Structure

Figure 6: Crystalline structure of ZB unit cell. Yellow spheres are Indium (In) atoms and grey spheres are phosphorus (P) atoms.

InP is a direct band gap III-V semiconductor crystal. While bulk InP only crystallizes in a cubic Zincblende (ZB), InP nanowires have recently been synthesized with both cubic ZB and hexagonal wurtzite (WZ) structures. Figure 6 shows the crystalline structure of ZB unit cell. In the zinc blende type InP structure, the space lattice is face centered cubic (fcc) where there are two such fcc lattices separated by 1/4 of the body diagonal of the unit cube. One lattice is occupied by Indium atoms shown by yellow spheres and the other by Phosphorus atoms (grey spheres). Each atom has 4 nearest neighbors of the opposite kind and is bound to these 4 atoms arranged at the corners of the surrounding tetrahedron with covalent bindings.
2.1.2 WZ Crystal Structure

![WZ Unit Cell and WZ Crystal Structure](image)

*Figure 7:* WZ unit cell (left) and WZ crystal structure (right). Yellow spheres are Indium (In) atoms and grey spheres are phosphorus (P) atoms.

Zinc sulfide crystalizes in two different forms: Wurtzite (WZ) and Zincblende (ZB). If the sulfide ions originally crystalize in a hexagonal close packed structure, the ZnS crystal is WZ. If sulfide ions originally crystalize in a cubic structure, the ZnS crystal is ZB. Similarly InP can be synthesized in WZ structure in the form of nanowires similar to the ZnS WZ structure even though InP crystalizes only in the ZB structure in bulk. Figure 7 shows the WZ crystal unit cell and WZ structure of WZ InP nanowires. The hexagonal WZ nanowire grows along the c-axis (or [001] direction) with In and P atoms are stacked in an ABABAB…. pattern hexagonal closed packed (HCP) layers while the cubic ZB nanowires grows along the diagonal (or [111]) direction of the unit cell with In and P atoms are stacked in an ABCABC…. pattern.
2.2 Band structures and band parameters for InP

2.2.1 ZB InP Band Structure

Figure 8: Calculated ZB InP band structure by James R. Chelikowsky et al.\textsuperscript{[14]} along with a schematic diagram of the band structure at the zone center (right).

Figure 8 shows the electronic band structure of ZB InP calculated by an empirical nonlocal pseudopotential method by James R. Chelikowsky et al.\textsuperscript{[14]} along with the band structure of ZB InP at the center of the Brillouin zone shown by the blue dotted rectangle. The fundamental absorption edge of ZB InP is corresponds to the direct transitions form the highest VB to the lowest CB at the $\Gamma$ point ($\Gamma^6 \rightarrow \Gamma^6$). These transitions are dominated by free excitons which are particularly evident at low temperatures.\textsuperscript{[15]} The excitonic transitions energy is 5meV less than the band gap $E_g$. This is not the case at room temperature because the excitons become free electrons and free holes because of the thermal energy. The second lowest inter band transition corresponds to the direct transition from the spin-orbit split off VB to the lowest CB at
the \( \Gamma \) point \((\Gamma^7 \rightarrow \Gamma^6)\). In the split-off valence band, one of the light hole band is pushed to a higher energy by the spin-orbit energy \((\Delta E_{SO})\), which is 110meV for the ZB InP structure\(^7\).

The electron in the CB is an s-type wavefunction which has a net angular momentum of \(J=1/2\); orbital angular momentum of \(l=0\) and spin momentum of \(s=1/2\) resulting two fold degeneracy at \(k=0\). The electronic states become more complicated in the VB because of the spin- orbit interaction splitting the VB into heavy hole \((hh)\) and light hole \((lh)\) bands. The holes in the VB have p-type wavefunction with a net angular momentum of \(J=3/2\); orbital angular momentum of \(l=1\) and spin momentum of \(s=1/2\). The heavy hole \((hh)\) has spin angular momentum of \(m_J = \pm 3/2\) and the light hole \((lh)\) has \(m_J = \pm 1/2\). When an electron in the CB recombines with a hole in the VB, the net momentum has to be conserved. The net angular momentum of the electron hole pair, namely the exciton has to be equal to spin of photon \((\pm 1)\); providing four possible recombination, \(|\frac{3}{2}, \frac{1}{2}\rangle, |\frac{3}{2}, -\frac{1}{2}\rangle, |\frac{1}{2}, \frac{1}{2}\rangle, |\frac{1}{2}, -\frac{1}{2}\rangle\). There is a possibility of creating an electron-hole pair with a total angular momentum of either 0 or \(\pm 2\). This kind of exciton is known as a dark exciton since it cannot be recombined optically as the total angular momentum (0 or \(\pm 2\)) is not equal to the spin of a photon \((\pm 1)\).

Table 2.1: Important band parameters of ZB InP calculated by James R. Chelikowsky et al\(^{14}\) along with experimental values

<table>
<thead>
<tr>
<th>Zone center State</th>
<th>Energy (eV)</th>
<th>Experimental Values (eV)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma^6 )</td>
<td>1.50</td>
<td>1.42(^{[12,13,16]})</td>
<td>Bottom of the CB</td>
</tr>
<tr>
<td>( \Gamma^8 )</td>
<td>0.00</td>
<td>0.00</td>
<td>Top of the VB</td>
</tr>
<tr>
<td>( \Gamma^7 )</td>
<td>-0.21</td>
<td>-0.11(^{[7]})</td>
<td>Spin Orbital Splitting</td>
</tr>
</tbody>
</table>
Table 2.1 states the band structure positions of the CB ($\Gamma^6$), $hh/lh$ band ($\Gamma^8$) and the split off band ($\Gamma^7$) in the VB of ZB InP along with experimental measurements. In the next section of this chapter, we discuss the electronic band structure of WZ InP nanowires.

Figure 9: Predicted WZ InP band structure by Craig E. Pryor et al\cite{17} along with a schematic diagram of the band structure at the zone center (right).

Figure 9 shows the predicted electronic band structure of WZ InP by Craig E. Pryor et al\cite{17} along with the band structure near the zone center as indicated by the red dashed rectangle. The important difference between the potential that an electron experiences in a WZ lattice compared to a ZB lattice is the small difference in crystal field due to sites beyond the next nearest neighbors. As a result of the crystal field and the spin orbit interactions, the VB of the WZ structure splits into three bands A, B and C with $\Gamma^9$, $\Gamma^7$ and $\Gamma^6$ symmetries respectively as shown in Figure 9 (right) at the $\Gamma$ point. According to the calculation by Craig E. Pryor et al\cite{17}, there is also a second higher conduction band just 238meV above the lowest conduction band.
which has the $\Gamma^8$ symmetry, which results from zone folding of the L-valley to zone center.

Table 2.2 below displays some important band parameters for Zone center states, their energies and effective masses for the WZ InP structure as predicted by Craig E. Pryor [17]. More information about ZB and WZ band structure can be found in the book “Properties of Group III-V and II-VI semiconductors” [8].

Table 2.2: Important band parameters of WZ InP calculated by E. Pryor et al[17].

<table>
<thead>
<tr>
<th>Zone center State</th>
<th>Energy (eV)</th>
<th>$m\parallel$</th>
<th>$m\perp$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma^8$</td>
<td>1.712</td>
<td>1.094</td>
<td>0.132</td>
</tr>
<tr>
<td>$\Gamma^7$</td>
<td>1.474</td>
<td>0.105</td>
<td>0.088</td>
</tr>
<tr>
<td>$\Gamma^9$</td>
<td>0.000</td>
<td>1.273</td>
<td>0.158</td>
</tr>
<tr>
<td>$\Gamma^7$</td>
<td>-0.063</td>
<td>0.839</td>
<td>0.169</td>
</tr>
<tr>
<td>$\Gamma^7$</td>
<td>-0.348</td>
<td>0.097</td>
<td>1.205</td>
</tr>
<tr>
<td>$\Gamma^9$</td>
<td>-0.849</td>
<td>1.894</td>
<td>0.230</td>
</tr>
</tbody>
</table>

The WZ type crystals have $C_{6v}$ point-group symmetry [8,13]. At the $\Gamma$ point, the CB has $I^7$ (s-like) symmetry and the A, B and C valance bands have $I^6$, $I^\tilde{7}$ and $I^\tilde{7}$ (p- like) symmetries respectively. The polarization vectors $E \perp c$ and $E \parallel c$ belongs to $I^5$ and $I^d$ symmetries respectively. The direct products for the transitions from the A, B and C valance bands to the CB1,

\[ I^6 \rightarrow I^7 \text{ (A \rightarrow CB1):} \quad I^6 \times I^7 = I^6 + I^6 \]

\[ I^7 \rightarrow I^7 \text{ (B, C \rightarrow CB1):} \quad I^7 \times I^7 = I^d + I^2 + I^6 \]

2.1

2.2
The direct product of the transition; \( I^7 \rightarrow I^7 \) (B, C \( \rightarrow \) CB1) contains the representations for both \( E \downarrow c \) and \( E \parallel c \), but the transition; \( I^0 \rightarrow I^7 \) (A \( \rightarrow \) CB1) contains only the representation for \( E \downarrow c \). This means that for \( E \parallel c \), the optical transition between the A valance band and the CB is forbidden, while for \( E \downarrow c \), all the optical transitions are possible \(^{[8, 13]}\). We will discuss the experimental polarization photocurrent spectroscopy for WZ InP nanowires in Chapter V.

### 2.3 Nanowire growth

There are two basic approaches to synthesizing nanowires; top-down and bottom-up. A top-down approach reduces a large piece of material to small pieces by using various processes such as lithography, etching or electrophoresis while the bottom up approach synthesizes the nanowire by combining constituent ad atoms. The most common nanowire synthesis techniques use the bottom up approach. Nanowire production uses several common laboratory techniques, including suspension, electrochemical deposition, vapor deposition, or vapor liquid solid (VLS) growth. The InP nanowires we used for this research work were grown by the vapor-liquid-solid (VLS) method at the Australian National University by our research collaborators. The nanowires were grown using a horizontal flow metalorganic chemical vapor deposition (MOCVD) reactor operating at 100mbar with hydrogen as the carrier gas. We can vary the growth parameters to control the growth process of the desired material. The most important growth parameters are the growth temperature, and the V/III ratio. Au nano-particles of 50nm and 20nm were used as catalyst for the growth of ZB, WZ and ZB/WZ mixed phase InP nanowires used for this research. The V/III ratio of phosphine (PH\(_3\)) to trimethlindium (TMIn) was 350 for ZB InP growth and 700 for WZ and ZB/WZ mixed phase InP nanowire growths and the nanowires were grown at a temperature of 400\(^\circ\)C for 20 min. Recent studies has shown that the higher V/III ratio leads to WZ dominant nanowires and lower V/III ratios tends to grow ZB
dominant nanowires, with some twins and stacking faults present as determined by high-resolution transmission electron microscopy imaging\cite{12}. Nanowires grown with smaller nanoparticles as catalyst favor WZ structure while nanowires grown with larger nanoparticles favor ZB structure\cite{12}.

**Figure 10:** Vapor liquid solid (VLS) growth technique used for InP nanowire growth. The size of the nanoparticle defines the diameter of nanowires.

The MOCVD method used to grow the InP nanowires we used in this research is very similar to the VLS method described by *Wagner and Ellis*\cite{18}. Figure 10 shows the schematic picture of the VLS growth process used in this nanowire growth. For InP nanowire growth, a InP (111)B substrate is used as the growth substrate because the nanowires grow along the (111) direction. As a result, the nanowires will be aligned perpendicular to the substrate as they grow. The gold catalyst is dispersed on the substrate first and the growth substrate is heated to 600 °C to remove any surface contaminants. The nanowire growth was then carried out at 400 °C for 20min. The V/III ratio, i.e. the total flow of phosphine (PH3) over trimethylindium (TMIn), was varied by changing PH3 flow rate between 1339 to 8527 μmol min\(^{-1}\), while keeping the TMIn flow rate constant at 12.14 μmol min\(^{-1}\). The V/III ratios used in this InP nanowire growth are 350 for ZB growths and 700 for WZ growths.
When the gold nanoparticle becomes super-saturated with InP, the InP crystalizes underneath the Au particle and pushes the Au particle upward as the nanowire grows epitaxially as shown in Figure 10 (right). This axial growth mainly arises from the precursors impinging on the Au particle. The size of the Au nanoparticle determines the diameter of the nanowire. The diffusion of atoms on the growth surface and on the sidewall of the nanowire towards the Au particle give rise to radial as well as axial growth of the Nanowire. As a result of this radial growth, the nanowires get tapered. This is a major disadvantage in this nanowire growth.

![Figure 11: Scanning electron micrograph (SEM) images of InP nanowires grown by VLS method as functions of V/III ratio and catalyst size. The scale bars are 2µm.](image)

Figure 11 shows the SEM images of InP nanowires grown at 400 °C with different V/III ratios and different sized Au catalysts using the VLS method. The top row shows 20 nm nanowires while the bottom row shows 50 nm nanowires. The V/III ratio has a significant effect
on the nanowire growth, which changes from irregular shapes to long and straight vertically aligned nanowires with increasing V/III ratios. Clear tapering can be observed in some nanowires as in Figure 11 (c), where the base of the nanowire is much bigger than the tip of the nanowire. More detail discussion about the nanowires used in this research will be discussed in Chapter IV.
Reference:


CHAPTER III

EXPERIMENTAL TECHNIQUES
3. EXPERIMENTAL TECHNIQUES

3.1 Nanowire dispersion and mapping

![Figure 12: Nanowires dispersed on a patterned Si Substrate. The lithographically defined pattern on the Si substrate helps to find nanowires on the sample substrate.](image)

Figure 12 shows an optical image of nanowires which are dispersed onto a patterned Si Substrate. The patterned Si substrate helps us locate single nanowires (e.g. NW1, NW2, NW3, …….) for repeated measurements. The patterning on the Si substrate is done using a photolithography process similar to one discussed in section 3.2. The distance between two nearest L-shaped patterns is 10μm. The patterned Si substrates are cleaned to prevent contaminations from the substrates before dispersing the nanowire. The patterned Si substrates are separately rinsed with Acetone, Methanol, Isopropyl Alcohol and distilled water for two minutes each at room temperature respectively. The substrate is then dried by blowing with dry N2 on the substrate. There are two main techniques for dispersing nanowires onto the substrates. The first method is called mechanical dispersion where the nanowire growth substrate is gently
slid onto the patterned Si substrate. In this method, many nanowires are dispersed on the substrate and form clusters of nanowires most of the time. Careful rinsing of the mechanically dispersed nanowire substrate with Methanol can reduce the density of nanowires on the substrate. In the second method, a small piece of nanowire growth substrate is sonicated in Methanol solution in a glass vial. Using a micro-pipette, a small drop of the sonicated nanowire-Methanol solution is transferred on to the patterned Si substrate and then the Methanol is allowed to evaporate. In this method, the nanowire density on the substrate is very small and as a result, single nanowires can be obtained. The nanowire dispersed Si substrate is then observed under a microscope and the positions of single nanowires that can be used for experimental studies are located. The nanowire substrate is mounted onto a copper holder using Silver-paste and the copper sample holder is mounted onto the cold finger of a low temperature optical cryostat for photoluminescence and time-resolved photoluminescence measurements.

3.2 Nanowire device fabrication

![Nanowire device fabrication process](image)

Figure 13: Nanowire device fabrication process by micro-photo lithography techniques.

Modern photolithographic and e-beam lithographic techniques have enabled scientists and engineers to fabricate nanowire devices which allow us to study various important physical
properties including quantum effects in such nanowire devices. Here we discuss the fabrication process we used to fabricate single nanowire devices. Figure 13 shows the complete sequence of steps in the nanowire fabrication process by Micro photolithography. The process requires the dispersion of nanowires onto the substrate, photoresist spin, aligning the photo mask and UV exposure, photoresist development, Ammonium poly-sulfide etching, metal deposition followed by liftoff. Each step will be described in more detail below. For this research, we fabricate nanowire device from ZB and WZ InP nanowires. These nanowires are 50nm, 20nm in diameter respectively and around 10μm long.

We used a Si substrate capped with a thermally grown 300nm thick SiO$_2$ layer as the device substrate. The oxide layer provides a very good insulation between the nanowire device and the Si substrate. Typical resistance of the nanowires are in the scale of 100’s of Giga Ohms and the SiO2 layer on the top of the Si substrate provides an excellent insulation which is even higher. We used standard photolithography technique to fabricate our nanowire devices $^{[1,2]}$. Photolithography is a micro fabrication process of semiconductor devices which uses light usually ultra – violet (UV) light to transfer a pattern from a photo mask to a light sensitive chemical called photo resist on the substrate. A series of chemical processes then removes only the parts of the resist exposed to light, so that only portions of the samples are exposed for further processing. All modern semiconductor devices such as complex integrated circuit of computer processor and other optoelectronic devices are fabricated using advanced photolithography lithography methods. Most famous semiconductor device companies like Intel cooperation and IBM use the photolithography techniques to fabricate more complex electronics like computer processing chips consisting billions of logic transistors on single chips.
3.2.1 Photolithography Fabrication

The Si/SiO\textsubscript{2} substrate is cleaned to prevent contaminations using the same procedure discussed above in section 3.1. To isolate single nanowires from growth substrate, nanowires are first mechanically transferred onto a small piece of Si substrate which is then sonicated into a methanol solution to create a very dilute distribution of nanowires. Using a micro-pipette a droplet containing these nanowires is dispersed onto small piece (~ 5mm×5mm) of the Si/SiO\textsubscript{2} substrate for fabrication of the nanowire devices. The dispersed substrate is then observed under a microscope to find single long nanowires for fabrication. The Si substrate is then spun with a light sensitive chemical called photoresist, and after curing in an oven, is then positioned under an optical mask having large 200µm openings separated by 1 - 5µm protrusions. By observing through the large openings in the mask, a nanowire can be positioned so that contacts windows can be exposed with UV light using a Karl Suss MJB3 mask aligner where the maximum resolution is about 1µm. This means we can fabricate any device down to the 1µm scale. Then we develop the exposed substrate by deep rinsing of the substrate in a diluted developer solution. The development process removes all areas of the photoresist which is exposed to UV light, in particular the two ends of the InP nanowire. After development, the substrate is immersed in an Ammonium Polysulfide solution under a 60W white light for a half an hour to etch off the natural oxide layer on the surfaces of the nanowire which is exposed. The purpose of ammonium polysulfide etching is to etch away the native oxide layer and leave a thin layer of unstable sulfur chains to help prevent re-oxidization of the nanowire. This helps to make the Ohmic contact between the metal-semiconductor interfaces. Similar techniques have been used by several groups to make Ohmic contact with semiconductor materials like InAs, GaAs and AlGaAs\textsuperscript{[3,4,5,6]}. 
Standard metal deposition and lift off techniques are then used to fabricate 200nm Ti/Al contact pads across the nanowire separated by a $\sim 4 \mu m$ gap.

Here is the micro fabrication process to make an Ohmic single nanowire device:

**Device fabrication Process**

a. Clean the substrate in Acetone, Methanol, Isopropyl Alcohol and rinse in DI water.

b. Spin photo resist (Shipley 1818) at 6 krpm for 60 sec.

c. Soft bake on the hotplate at 115°C for 60 sec.

d. Put the sample on the photolithographic mask aligner. Align the photo-mask across a nanowire (gap ranging from 2um to 5um).

e. Expose with UV light at power = 12mW for 10sec.

f. Dip the sample in chlorobenzene for about 90 sec and then hard bake at 90°C in conventional oven for 3 minutes.

g. Develop the exposed sample with developer 350: DI water at 1:5 ratio for 30 sec and then in DI water for 60sec.

h. Inspect under high magnifying microscope.

i. Etch with diluted ammonium poly-sulfide solution as discussed below.

j. Deposit metals Ti (20 nm) and Al (200 nm) in thin film metal evaporator.

   Liftoff in Acetone. Inspect the device under microscope until the nanowire has contact pads at the end with clear gap.
Making Ammonium Poly-sulfide Solution

Making the solution is very straightforward. The basic process requires saturating Ammonium sulfide with sulfur such that the dissolved sulfur will polymerize and create chains. It is these sulfur chains that are left on surface that help slow the oxidization process of the material.

Note: The final product is photosensitive and should be placed in a dark bottle and properly stored.

a. Place 20mL of ammonium sulfide ((NH₄)₂S) into a beaker with a stir rod.

b. Turn on the stir plate and adjust the speed so that the liquid does not splash.

c. Gradually add the Sulfur powder making sure that there are no clumps.

d. Once no more Sulfur can be added, allow the solution to continue to mix for ~30 min.

e. Pour the Solution into a Dark (amber bottle) container so that it is not exposed to light.

f. Label the container and place into the corrosive cabinet.

Note: There will be some sulfur powder remaining at the end. As it floats on the surface of the liquid, this is not a problem and Ammonium poly-sulfide solution can be drawn using a pipette from the center of the container.

Ammonium poly-sulfide Etching

The purpose of this process is to etch away the native oxide layer and leave a thin layer of unstable sulfur chains to help prevent re-oxidization of the nanowire.

After developing the resist and just before metal deposition in the device fabrication process,

a. Mix Ammonium polysulfide solution with DI water (1: 500 ratio by volume).
Note: be sure to pipet far enough below the surface of the solution in order to avoid the sulfur powder.

b. Place the device in the diluted solution and place on a hotplate set to 60°C

c. Place it under a 60 watt light bulb.

d. The etch lasts for 1/2 an hour.

e. Rinse thoroughly with DI water.

f. Blow-dry with nitrogen

g. Put in vacuum for metal deposition

Note: Make sure to wear protective clothing as this is a corrosive solution and it will burn.

3.2.2 Packaging and wire-bonding

Wire-bonding is the primary method of making interconnections between the semiconductor nanowire device (device in this research) and the chip carrier during semiconductor device fabrication process using very fine bonding wires. The chip carrier contains large wires which can easily be soldered to for making connections to the outside world. Wire-bonding is the process where very thin gold (Au), Aluminum (Al) or Copper (Cu) wire is bonded between the small nanodevice and the larger wires on the chip carrier. Wire diameters start at 15μm and can be up to several hundred micrometers for high powered applications. In this research, we use a gold (Au) wire with diameter of 25μm. There are two common wire-bond processes: Au ball bonding and Al wedge bonding. Ball bonding is usually restricted to gold and copper wire and usually requires heat. Wedge bonding can use both gold and aluminum wires, with only the gold wires requiring heat.

We used West Bond Co. model no 7476D wire-bonding machine that uses Al wedge bonding tool. This wire-bonder requires that the diameter of the tool be 1/16”at the length of the
tool, for 45° wire feed, should be 0.75” and it uses ultrasonic energy to bond the thin wire onto the contact pad. The wedge bond is formed through a combination of ultrasonic action and slight force of the bonding tool to the metal surface of the metal pads on the device or the pin connections on the chip carrier. It should be noted that while the wedge bonding can be made at room temperature (with aluminum wires on Al metal pads), the most reliable wire bonding will come from the optimal combinations of parameters (time, temperature, force and ultrasonic power).

**Figure 14:** (a) A schematic image of ultrasonic wedge bonding and (b) an optical image of a wire-bonding done with wedge bonding.

Figure 14 shows a schematic image of the ultrasonic wedge bonding along with an optical image of a wire-bonding being done on a metal pad. The first bond is made to the corresponding gold pin on the chip carrier and second bond is made to the corresponding metal contact pad of the device by applying ultrasonic power which presses the wire against the bonding surface. During the second bond, the wire is broken off by clamping and movement of the wire against the contact pads because of the ultrasonic vibrations of the bonding tool.

The wedge bonding technique can be used with both aluminum and gold wires. The main difference between the two is that the aluminum bonding can be made at room temperature
whereas the gold wire bonding can be performed through an ultrasonic bonding process only with the device heated up to 150°C. In this research, the most of the wire bonding are done using gold wire on aluminum metal contacts at 100-120°C.

Figure 15: (a) Optical image and (b) Scanning electron microscopy (SEM) image of a nanowire device. (c) Nanowire device packaged on a chip carrier for measurements showing gold wire bonding from devices to the chip carrier.

Figure 15 shows (a) an optical image and scanning electron micrograph (SEM) of one the nanowire device used in this research where the nanowire can be identified easily in the two images. The gap between two metal contacts is about 4μm. Figure 15 (c) shows the device substrate (having device) placed on a chip carrier where the gold wire bonds are visible from devices (three devices on this substrate) to the external contacts on the chip carriers.

A considerable advantage of wedge bonding is that it can be used to make wiring between the chip carrier to the very small dimensions of the nanodevice down to a 50μm area. Even though we used gold ultrasonic wedge bonding in this research, aluminum wedge bonding
is the most common wedge bonding process because of the low cost and low working temperature. The main advantage for gold wire wedge bonding is the possibility to avoid the need of enclosed packaging after bonding due to the attractive properties of the gold like high conductivity, corrosion resistance and lack of oxidation.

3.3 PL and TRPL Experimental Setup

Photoluminescence (PL) is a process in which a material absorbs photons and then re-emits photons. This can be describe quantum mechanically as an excitation to a higher energy state by absorption of a photon and then return to a lower energy state by emission of a photon. The time period between the absorption and the emission is typical extremely short in the order of nanoseconds for a direct gap semiconductor. In semiconductor materials, the electrons are excited from the VB to the CB which leaves a hole in the VB by absorbing a photon of energy higher than the band gap of the semiconductor. The excited electrons have significant kinetic energy and relax to the minimum possible energy in the CB by emitting phonons (lattice vibrations). This process is known as non-radiative relaxation which is very fast. The electron stays there for some time known as recombination lifetime before it recombines with the hole in the VB by emitting a photon which is the photoluminescence. Here we discuss the experimental procedure of measuring the photoluminescence and the recombination life times.
Figure 16: Schematic display of the photoluminescence and time-resolved photoluminescence spectroscopy experimental set up.

Figure 16 shows a schematic diagram of the photoluminescence (PL) and time-resolved photoluminescence (TRPL) experimental set up. A titanium- Sapphire (Ti:S) laser was used as the excitation light source in this research. For PL measurements, the continuous wave (CW) mode of the laser was used while for TRPL experiment the mode-locked pulse mode of the laser was used. The polarization of the incoming laser beam was controlled by using a matched set of Glann-Thomson linear polarizers and Babinet Soleil compensators for both the incident laser and also for the collected photoluminescence. As shown in the Figure 16, the collimated laser was directed towards the nanowire sample using a beam splitter and a convergent lens. The laser was focused onto a single nanowire on the sample substrate using a 50X/0.5-Numerical-Aperture (N.A.) long working distance microscope objective. The emitted photoluminescence is collected through the same microscope objective and directed through the similar polarizing optics by using the back scattering geometry. The photoluminescence signal was focused onto the slit of
the spectrometer using a converging lens and the dispersed photoluminescence by the spectrometer was detected using a CCD (charge coupled device) detector.

For TRPL experiments, the mode-locked pulsed mode of the Ti:S laser is used instead of the CW laser and a reference beam of the laser is focused onto a fast photodiode which produces a reference current pulse of the laser. A selected band of emitted photoluminescence dispersed by the spectrometer is then directed to the APD (avalanche photo diode) or the MCP-PMT (micro channel plate-photo multiplier tube). The APD (or PMT) produces a current pulse for the each single photon it detects from the dispersed PL signal and therefore the number of pulses is directly proportional to the number of photons detected by APD (or PMT) at that instant. This weak signal is amplified by using a preamplifier before send it to a Constant Fraction Discriminator (CFD). The CFD converts the APD current signal to a standard NIM logic pulse while compensating for the variances which occur in the pulse height in the current pulse produced by APD or PMT. The output logic pulse from the discriminator is then sent to the TAC (Time-to-Amplitude Converter) act as a ‘stop’ signal to the photon counting system. The fast photodiode reference signal is discriminated by a second discriminator and the NIM logic pulse is used as the "start" signal to the TAC. The TAC converts the time interval between the start and stop signal to a voltage difference which is proportional to the time difference between creation of an electron-hole pair to an annihilation of the pair. By accumulating many thousands of events, this generates a histogram of number of photons counted as a function of time after the laser pulse for selected emission energy as shown in the figure where one can measure the recombination life time of the semiconductor material. A detailed discussion about the Time-correlated photon counting can be found in the review article “photoluminescence spectroscopy of crystalline semiconductors” by G. D. Gilliland[7].
3.3.1 Spectrometers

Figure 17: Schematic diagram of (a) the Newport Spectrometer and (b) Spex spectrometer

Figure 17 shows a schematic illustration of the two spectrometers we used in this research. The Newport spectrometer was used for both PL and TRPL experiments while the Spex spectrometer was used only for TRPL experiment in this research. These spectrometers use the asymmetric in plane Czerny-Turner optical geometry. In the Newport MS260i spectrometer, there are two gratings (1200 and 300 groves/mm) mounted on a rotating stage which helps to interchange gratings. The 300 groves/mm grating was used to investigate a PL spectrum over a wide range of wavelengths while the 1200 groves/mm grating was used to investigate a narrow spectral range but at significantly higher resolution. For most of the PL measurements discussed in this research, 300 groves/mm grating was used because of the broad PL emission. A PMT is mounted by the side of the spectrometer as shown in Figure 17 (a) for the TRPL experiment.

The Spex spectrometer shown in Figure 17 (b) uses two concave mirrors with long focal lengths of 1m and a 1200 groves/mm grating which is interchangeable and for a slit width of 25µm, it has a maximum theoretical resolution of 2nm. The exit port of this spectrometer was changed from its original configuration to accommodate a Silicon APD which is used in TRPL measurements.
3.3.2 CCD, APD and PMT Detectors

CCD (Charge Coupled Device)

The CCD is a major technology for digital imaging which was invented in 1969 by Willard Boyle and George E. Smith. In a CCD camera, pixels are represented by capacitors. The Silicon CCD camera we used in this research has 2000 pixels in the horizontal direction and 800 pixels in the vertical direction. The photoluminescence dispersed from the grating of a spectrometer will be directed onto the CCD camera at different horizontal positions referring to wavelengths which differ from each other. In addition, photoluminescence originate from different vertical position on the sample will be directed to the CCD camera at different vertical pixels. When a photon strikes on a particular pixel, the corresponding capacitor charged due to the photoelectric effect and transfers into the CCD interface which develops a 2D image of the charges collected from both horizontal and vertical pixels. The vertical position on the CCD corresponds to the position of the photoluminescence focused onto the entrance slit while the horizontal position corresponds to the wavelength of the photoluminescence. Ultimately one can map these positions to the corresponding positions on the nanowire sample where these photons originated from as well as the energy of the photon which is emitted as a result of a particular decay process. The photoluminescence spectrum which is a plot of intensity versus energy can be obtained by integrating the intensity by adding the charges in all vertical pixels as a function of energy.
**APD (Avalanche Photo-Diode)**

An avalanche photodiode (APD) is a highly sensitive semiconductor electronic device that uses the photoelectric effect to convert light to electricity. An APD can be thought of a photo detector that provides a built-in first stage of gain through avalanche multiplication.

![Schematic diagram of an avalanche photodiode](image)

**Figure 18:** A schematic diagram of an avalanche photodiode (top) with an APD for single photon counting image of MPD (bottom).

Figure 18 shows a schematic illustration of a Silicon APD along with an image of a commercially available APD for single photon counting MPD. In an APD, as with any other photodiode, incoming photons produce electron hole pairs; however the APD is operated with a large reverse bias (up to 2 kV), which accelerates the photon-generated electrons that collide with the atomic lattice releasing additional electrons via secondary ionization. These secondary electrons are also accelerated, which results in an avalanche of carriers. An APD is a small, easy to operate device having high internal gain that operates at a high light levels and over a broad
range of wavelength. The APD uses a thermo-electric cooler to reduce the dark count level. The APD used in our research delivers a time resolution of ~50ps.

**MCP-PMT (Micro Channel Plate-Photo Multiplier Tube)**

Photo multiplier tubes (PMT) are extremely sensitive detectors of light in the ultraviolet, visible, near infrared ranges of the electromagnetic spectrum. These detectors multiply the current produced by incident light by as much as 100 million times in multiple dynode stages. This enables us to detect individual photons even when the intensity of the incident light is very low. The combination of properties like high gain, low noise, ultra-fast response and large area of collection of the PMT enable scientist to use it in variety of research studies.

![Figure 19: Schematic illustration of a photo multiplier tube.](image)

Figure 19 shows a schematic diagram of a photo multiplier tube. Incident photons strike the photocathode which is present as a thin deposit on the entry window, with electrons being produces as a result of the photoelectric effect. These electrons are directed by a focusing electrode toward the electron multiplier known as a dynode where electrons are multiplied by the process of secondary emission. There are number of dynodes as shown in Figure 19 where each dynode is held at a higher positive voltage than the previous one. Because of the electric field between the photocathode and the dynodes, the electrons accelerate and hit the next dynode with
more energy giving more and more electrons. Because of this repeated process large number of electrons is collected on the anode and the signal from the anode is directed to the discriminator for TRPL measurements. The MCP-PMT also has the same working principle but it uses a Micro Channel Plate (MCP) instead of Dynodes.

![Diagram of MCP-PMT](image)

**Figure 20**: (a) Schematic illustration of micro channel plate (MCP) and (b) its principle multiplication. 

Figure 20 (a) illustrates the schematic structure of a MCP along with its principle of multiplication. The MCP consists of a great number of glass calipers (channels) bundled together in parallel to form a disk. These glass channels are 6 to 20μm in diameter with inner walls processed to have the proper electrical resistance and the secondary emission. When an electron is impact on the inner wall of a channel, secondary electrons are emitted. The accelerated electrons as a result of the electric field across the two side walls of the MCP strike the channel wall again and again to produce more and more secondary electrons. This process repeats many times to release large number of electrons at the output end. Large number of secondary electrons ($10^5$–$10^6$) will result in a fast response time (~50ps) in the operation of the MCP-PMT. The MCP-PMT model we used in this research was the Hamamatsu R2809U-11 which operates at a high voltage (2900V) and it must be cooled down to -45°C by using liquid nitrogen to reduce the dark count rate to a manageable ~100 counts per second.
3.3.3 Polarization Optics

Polarizing optics consisting of two sets of Glan-Thompson linear polarizers and Babinet soleil compensators play an important role in the optical experiments in this research. A polarizer is an optical filter that passes light of a specific polarization and blocks waves of other polarization. Linear polarizers allow linearly polarized light to pass through which has a definite direction and orientation with respect to the optical axis.

![Figure 21: Schematic illustration of a Babinet-Soleil compensator.](image)

Figure 21: Schematic illustration of a Babinet-Soleil compensator.

Figure 21 shows a schematic diagram of a Babinet-Soleil compensator which is a continuously variable, zero order retarder that consists of two birefringent wedges which is movable on each other which is fixed to a compensator plate. It can change circularly or elliptically polarized light into linearly polarized light or vice versa by acting as a half wave plate or quarter wave plate.
Figure 22 shows a schematic illustration of how a half wave plate works. A half wave plate introduces a $\pi$ phase change between two orthogonal electric field components which rotate the linearly polarized light incident at an angle $\theta$ to its optical axis by an angle $2\theta$.

Figure 23 shows a schematic illustration how a quarter wave plate changes linearly polarized light in to circularly polarized light. The polarization of the incident linearly polarized light is sent at an angle of $\pm 45^\circ$ with the optical axis of the quarter wave plate. Depending on the sign of the angle of the alignment of linearly polarized light with the optical axis, the quarter wave plate produces right or left circularly polarized light as the output.
3.3.4 Titanium–Sapphire Laser

Titanium: Sapphire (Ti:S) lasers are tunable lasers which emit red and near infrared light in the range from 650nm to 1100nm. These lasers are mainly used in scientific research because of their tunability and their ability to generate ultra-short pulses. The Ti:S laser (model : Mira 900) used as the excitation light source in this research can emits light in the wavelength range between 700nm to 1000nm in both continuous wave (CW) and mode locked pulsed configurations. Ti:S refers to the lasing medium, a sapphire (Al₂O₃) crystal that is doped with titanium ions. A 5W 532nm CW laser output of a solid state Coherent Verdi laser was used as the pump source of the Ti: laser to excite titanium sapphire crystal. Ti:S lasers operate most efficiently at wavelength near 800nm. In the pulse mode, Ti:S laser generates laser pulse with 200fs pulse width with a repetition rate of 76MHz. The laser rod of the laser was cooled using a continuous water cooling system at 19°C where the gain is maximum and a minimum of 0.8 gal/min flow rate should be maintained. For efficient mode-locking operation at specific wavelengths the laser cavity should be purged with dry nitrogen gas to eliminate water absorption lines. More detailed explanations about Ti:S lasers can be found in the article “Spectroscopic and laser characteristics of Ti:Al₂O₃” by P.F. Moulton[9]. Further technical detail and working principles of model Mire 900 laser can be found in the operator’s manual for the Ti:S laser[10]. For PL and TRPL experiments we used the Ti:S laser at 780nm (1.589eV) while we tune the laser manually from 700nm to 1000nm for our photocurrent spectroscopy measurements which takes a long time because of the constant tuning and realignment of the laser during the experiment.

In addition to the Ti:S laser, we used a white light setup to excite our nanowire devices. Here we used a car light which emits light in the white light spectrum. The white light can be
filtered using a monochrometer (Oriel 74000) similar to the Newport spectrometer which provides a rapidly tunable monochromatic light source. This set up was specially used for our photocurrent measurements in our nanowire devices. This setup enables us to study many nanowire devices within a relatively small time period. Because of the large wavelength range of the white light, this can be used to study semiconductors such as InAs which has a small band gap that no laser is available for resonant excitation. The disadvantage of this set up over the Ti:S laser is that the power density of the output monochromatic light is very low.

### 3.3.5 Optical Cryostat

![Schematic diagram of a continuous flow liquid He cryostat.](image)

Figure 24 shows a schematic illustration of the optical cryostat used in this research. The cryostat was originally manufactured by the Janis Company and has undergone several modifications for the needs of the experiments described here. In addition, there is an internal wiring of the cryostat for electric measurements of nanowire devices. The cryostat is maintained at high vacuum (~10^{-6} torr) during experiments to help keep the sample at low temperature and to eliminate heat loss because of the convection. A cold radiation shield also significantly helps reduce heat transfer from radiation. The cryostat is cooled using a continuous flow of liquid helium and the temperature can be controlled using a temperature controller if necessary to any
desired temperature between 6 and 300°K. The heater coil is used to increase and maintain the desired temperature. There are two temperature sensors, one near the sample holder and another near the heater coil which is used to measure the temperature of the sample and to help control the temperature. The sample is mounted on a Cu sample holder which is attached to the cold finger that transfers the heat from the cold finger to the liquid helium flow. We kept the temperature at 10-15°K in the low temperature experiments in this research.

3.4 Dark Current measurement setup

After fabricating nanowire devices, they need to be first checked by doing electrical transport measurements to check the contacts between the nanowires and the metal contacts before wire bonding them for photocurrent measurements.

![Figure 25: Schematic diagram of two probe DC measurement system.](image)

Figure 25 shows a schematic illustration of the DC current measurement of a nanowire device. Usually DC measurements of nanowire devices are done at room temperature under a probe station. We have a probe station which is capable of probing electronic devices by using its sharp tungsten probes. Electrical connection from the DC current circuit is given by
contacting these probes on the contact pads of the devices. The current is amplified using an amplifier which is then measured using a digital HP multimeter. The input voltage and the digital multimeter are controlled automatically by a Labview computer program through a GPIB interface. The probe station is placed under a microscope where one can find and make contacts to a nanowire device easily for DC current measurements.

### 3.5 Photocurrent Experiment setup

![Schematic display of the Photocurrent spectroscopy experimental set up.](image)

**Figure 26:** Schematic display of the Photocurrent spectroscopy experimental set up.

For photocurrent measurements we excite the nanowire with CW Ti:S laser or the monochromatic white light setup discussed above in section 3.3.4. Figure 26 shows a schematic illustration of the photocurrent measurement setup used in this research. Using a 10X (or 50X) objective lens, the whole area of the nanowire device is illuminated with light and the current-voltage (IV) measurements were taken at a number of wavelengths by changing the excitation wavelength of the laser from 700nm to 1000nm. The power of the laser was kept approximately
constant using density filters throughout the experiment. The polarization of the incoming laser beam was controlled by using a Glann-Thomson linear polarizers followed by a Babinet Soleil compensator. In this experiment, a wire bonded nanowire device mounted to a chip carrier is mounted inside the cryostat and a voltage bias V is applied across the nanowire device by using a voltage source (voltage output from the Lock-in amplifier). The current through the nanowire device is measured using a Lock-in amplifier as a function of voltage bias.

The current flowing through the nanowire device contains two parts; the current produced as a result of thermally excited free carriers in the nanowire and the current produced as a result of photo excited carriers. Since we need to measure the current resulting only from photo excited carriers, we chop the incoming laser with a mechanical chopper with a desired frequency (137Hz) and the current is measured with a Lock-in amplifier. The chopping frequency is optimized to separate the modulated photocurrent signal from the background noise (predominantly at 60 Hz).
Figure 27: Example plots of (a) the DC current across a nanowire device, (b) the current across the device as a result of modulated excitation and DC current and (c) the current signal processed by the Lock-in amplifier as a function of time at fixed bias.

Figure 27 shows some example current – time plots of (a) the current without excitation (DC current), (b) the total current with the modulated excitation provided by the chopped laser with background noise. Figure 27 (c) shows the photocurrent; the current resulting only because of the photoexcited carriers processed by a Lock-in amplifier. In DC signal, there can be both low and high frequency noise coming from the background and variety of effects such as impurities, thermal carriers that can interfere with measuring the photocurrent produced by the laser. A lock-in amplifier filters out the noise coming from the DC signal and the background and the current is measured as the average of the voltage difference between the on/off intervals of the signal.
### 3.5.1. Lock-in Amplifier

A lock-in amplifier, also known as a phase sensitive detector,\[^{11,12}\] is a type of amplifier that can extract a signal from a known current signal from an extremely noisy environment\[^{13}\]. It is a homodyne detector followed by a steep low pass filter. Recovering signals at low signal-to-noise ratios requires a strong, clean reference signal with the same frequency as the received signal.

Operation of a lock-in amplifier depends on the orthogonality of sinusoidal functions. When two sinusoidal functions of frequencies $f_1$ and $f_2$ are multiplied together and integrate over a time much longer than the periods of two functions, the result is zero if $f_1 \neq f_2$ and half of the product of the amplitudes if $f_1 = f_2$.

A lock-in amplifier follows the same concept that multiplies the reference signal with the input signal and integrates it over a specified time in the order of milliseconds to a few seconds giving a DC signal as the result. The contribution from any signal that is not at the same frequency as the reference signal is attenuated to zero as well as any out of phase signal that has the same frequency as the reference because of the orthogonality of a cosine function with a sine function with the same frequency. This is a reason why a Lock-in is a phase sensitive detector in electric measurements.

For a reference sine signal and an input wave form $U_{in}(t)$, the DC output signal $U_{out}(t)$ can be calculated for an analog Lock-in amplifier by:

$$U_{out}(t) = \frac{1}{T} \int_{t-T}^{t} S \left[ 2\pi f_{ref.} s + \theta \right] U_{in}(s) \, ds$$

where $\theta$ is a phase that can be set on the Lock-in (set to zero by default).
Practically, many applications of the Lock-in only require recovering the amplitude of the signal rather than the relative phase. For this purpose, Lock-in measures two components; \( X = V_{\text{sig}} \cos \alpha \) and \( Y = V_{\text{sig}} \sin \alpha \) where \( \alpha \) is the phase difference between the input signal and the reference signal. \( X \) is called the in-phase component and \( Y \) is the quadrature component. By taking \( \sqrt{X^2 + Y^2} \) of the signal components, the phase dependency can be removed.

![Dual phase SR800 (350W) Lock-in amplifier](image)

**Figure 28:** Dual phase SR800 (350W) Lock-in amplifier

Figure 28 shows an image of a SRS lock in amplifier (model number SR 830 (350W)) which can measure both in phase (X) and out of phase signal (Y) simultaneously.
Reference:

1 Stephan A. Campbell. "The Science and Engineering of Microelectronic Fabrication."


CHAPTER IV

PL TRPL SPECTROSCOPY OF InP NANOWIRES
4. PL & TRPL SPECTROSCOPY OF InP NANOWIRES

4.1 Introduction

Semiconductor nanowires are one-dimensional structures having excellent electrical and optical properties that can be used as building blocks in designing nanoscale devices such as field-effect transistors, single-electron transistors, light-emitting diodes and sensors\[1, 2, 3, 4]. Indium Phosphide (InP) is a III/V semiconductor having excellent electrical and optical properties with high quantum efficiency and low sensitivity to surface defects. In bulk, InP can be observed only in the cubic ZB crystal structure. In contrast, InP nanowires can be synthesized in either the cubic ZB or hexagonal WZ crystal phases, and also with controlled and uncontrolled ZB/WZ mixed phase homostructures \[5, 6, 7, 8]. Previous studies on InP ZB and WZ nanowires show that they have \sim 80\text{meV} difference of the band gaps and \sim 45\text{meV} off set of the band alignment in the VB in the case of mixed phase structure \[5, 6, 7, 8, 9, 10], which has significant interference on symmetry of the band structure and electronics and optical transitions. To understand the band structure of semiconductor materials, photoluminescence (PL) and time-resolved photoluminescence (TRPL) play major roles in semiconductor characterization techniques. In this chapter, we study the electronic band structure of ZB, WZ and ZB/WZ mixed phase nanowires using PL and TRPL spectroscopies.

4.2 PL and TRPL experiments

Photoluminescence (PL) is the emission of light or photons from a material under optical excitation. Studying the PL spectrum provides important information on the electronic band structure of materials. We measure the PL using the experimental setup shown in the schematic diagram shown in section 3.3. We remove nanowires from the growth substrate and deposit them onto a patterned Si substrate as discussed in section 3.1. The sample is then mounted inside the
Cryostat onto a copper cold finger. Throughout our experiment, we maintain the cryostat temperature at about 10°K. A Titanium Sapphire laser of 780nm (~1.589eV) was used to excite the nanowire sample and the photoluminescence was detected using a CCD camera attached to the spectrometer. For the time-resolved photoluminescence (TRPL) experiment, the laser was used in its pulsed mode while for PL experiments we used the continuous wave (CW) laser. The laser beam was collimated and focused onto the sample using a 50x microscope objective combined with beam splitters, lenses and mirrors. The PL emitted from the sample was collimated and focused on to the entrance slit of the spectrometer. Then the beam of PL is dispersed and detected using a CCD camera. For TRPL measurements, the PL was detected using an avalanche photo diode (APD). A reference beam of the pulse laser was to excite a fast photo diode to provide the reference signal for time-resolved experiment. The reference signal and the PL signal were discriminated using a constant fraction discriminator and a TRPL spectrum was obtained as described in section 3.3.

4.3 ZB, WZ and ZB/WZ mixed phase InP nanowires

The InP nanowires were grown using a horizontal flow metalorganic chemical vapor deposition (MOCVD) reactor operating at 100mbar with hydrogen as the carrier gas. Au nanoparticles of 50nm and 20nm were used as catalyst for the growth of ZB and WZ nanowires respectively. For ZB/WZ mixed phase nanowire growth, 50nm Au nano-particles were used as the catalyst. The V/III ratio of phosphine (PH\textsubscript{3}) to trimethylindium (TMIn) was 350 for single phase ZB InP growth and 700 for single phase WZ and mixed phase ZB/WZ InP nanowire growths and the nanowires were grown under a temperature of 400°C for 20 min. These nanowires were grown by our collaborators in Australian National University. Recent studies have shown that the higher V/III ratio leads to WZ dominant nanowires and lower V/III ratios.
tends to grow ZB dominant nanowires, with some twins and stacking faults present as determined by high-resolution transmission electron microscopy imaging [11].

**Figure 29:** SEM (top row) and HRTEM (bottom row) images of (a, d) 50nm ZB InP nanowires, (b, e) 20nm WZ InP nanowires and (c, f) 50nm ZB/WZ mixed phase InP nanowires. Scale bars in the top row and the bottom row are 2µm and 5nm respectively [11].

PL and TRPL measurements of these nanowires have confirmed that the 50nm wires are predominantly ZB and 20nm wires are predominantly WZ [6, 8].

Figure 29: shows scanning electron microscopy (SEM) (top row) and high resolution transmission electron microscopy (HRTEM) (bottom row) images of (a, d) 50nm ZB InP nanowires, (b, e) 20nm WZ InP nanowires and (c, f) 50nm ZB/WZ mixed phase InP nanowires. ZB InP nanowires are grown with V/III ratio of 350 while WZ and ZB.WZ mixed phase nanowires are grown with V/III ration of 700. SEM images of these nanowires shows that these
nanowires are around 8-10μm long. In addition, the WZ nanowires are tapered compared to the ZB and mixed phase nanowires. ZB and mixed phase InP nanowires are uniform and long compared to WZ InP nanowires. A more detailed picture of crystal structure can be obtained from the HRTEM images shown in the bottom row of Figure 29. This shows that these nanowires consist of rotational twins and mixed phase structures. 20nm InP WZ nanowires (Figure 29. (e)) shows a clear WZ structure (about 90% WZ) [11] with few ZB segments. The HRTEM image of mixed phase InP nanowire shows some ZB inclusions of the WZ dominant nanowire which will be discussed in more details later in this chapter. To study how the crystal structure of these nanowires affects their optical properties, the PL and TRPL spectroscopy of single nanowires was carried out which will be discussed in the following section.
4.4 PL & TRPL Spectroscopy of single ZB and WZ InP nanowires

4.4.1 Photoluminescence (PL) Spectroscopy

Figure 30: Power-dependent CW PL spectra (a) 50nm ZB InP nanowires and (b) 20nm WZ InP nanowires. $P$ is referred to an excitation power of 100 µW. Vertical blue and green lines represent the positions of band edges of ZB and WZ respectively.
As discussed in section 3.1, the nanowires from growth substrate were transferred to a patterned Si substrate and then mapped to identify the positions of single nanowires for repeated measurements. The nanowire samples are then mounted inside a Helium flow cryostat and cooled down to 10K. As explained in section 3.3, single nanowires are photoexcited using a 780nm (1.589eV) CW laser and the photoluminescence emitted from the NW is focused on the slit of a spectrometer to collect PL spectra using a CCD detector. Figure 30: shows the PL spectra measured from single (a) ZB and (b) WZ InP nanowires as a function of excitation power ranging from 0.2 mW to 3 mW. Previous studies\cite{12, 6} have shown that ZB InP nanowires have the free exciton line at 1.42eV while the excitons in WZ InP nanowires emit at 1.49-1.50eV, both are consistence with other band gap measurements\cite{7, 13}. The PL spectra taken from the InP ZB nanowire shows an exciton emission line near 1.42eV and the position of the ZB exciton emission line remains the same for the whole excitation power range showing the nanowire is predominantly ZB. On the other hand, the WZ InP nanowire emits a broad PL at energies nearly 50meV higher than ZB at around 1.47eV which is around 30meV below the expected band gap of WZ InP nanowires and shows no significant dependence on the excitation power. A previous study by Bao et al\cite{5} showed that in ZB/WZ mixed-phase NWs the peak position of the PL spectra moves to higher energy with excitation power because of the band filling to the states resulting from the twining effect in InP nanowire. We will observe the similar behavior from the ZB/WZ mixed phase nanowires which will be discussed later on this chapter. Since there is no dependence on the excitation power of the PL for both ZB and WZ InP nanowires, We can assume that these nanowires are dominantly ZB and WZ respectively. Similar measurements have been observed for at least two nanowires from each ZB and WZ InP nanowires. Because of the WZ PL emission line is about 30meV below the expected band gap, TRPL is used to study
more closely the structure of these WZ InP nanowires as will be discussed in the following section.

### 4.4.2 Time Resolved Photoluminescence (TRPL) Spectroscopy

For TRPL spectroscopy, a pulsed laser (200fs pulse width) of wavelength 780nm (1.589eV) is used to excite single nanowires and the PL was detected using an avalanche photodiode (APD) as discussed in more details in section 3.3.

![Figure 31: Time-resolved spectral maps for a single (a) ZB InP nanowire and (b) WZ InP nanowire. White lines show WZ (1.504 eV) and ZB (1.42 eV) emission energies. Integrated PL extracted from corresponding TRPL maps for (c) ZB and (d) WZ integrated for early time (black) from 0-1ns and later time (red) from 3ns and later.](image-url)
Figure 31(top row): shows false color image spectral maps of (a) a ZB InP nanowire and (b) a WZ InP nanowire, where the vertical axis shows time after the laser excitation pulse and the horizontal axis is the emission energy of the collected PL. Color mapping is on a logarithmic scale where intensity increases from dark to light colors. Two white lines show the position of band gap for the ZB and WZ InP structures. Figure 31(bottom row): shows the normalized integrated PL spectra extracted from the corresponding time-resolved map in the top row, integrated in early times (black) and later times (red) on a linear scale for both single (c) ZB and (d) WZ InP nanowires. Time integrated for early time (0 ns – 1 ns) and later time (> 3ns) is shown by two double pointed arrows in between two TRPL maps. The WZ InP nanowire shows an intense emissions from the WZ band edge (∼1.50 eV) which relaxes rapidly (700ps at 1.50 eV) to a lower energy state assumed to be a defect state which is around 1.47 eV which decays with longer life time (3000 ps). The integrated PL for the WZ InP nanowire at early times show an emission line at 1.50eV which corresponds to the band edge of WZ InP and at later times, the integrated PL shows an emission line at 1.47 eV which is likely related to a defect state. The TRPL map of ZB InP nanowire shows a short lived (300ps life time) emission centered around ZB InP band gap. Both early time and later time integrated PL spectra show well matched emission lines at ∼1.42 eV relevant to ZB InP band edge. PL and TRPL spectroscopy of both ZB and WZ InP nanowires suggest that these nanowires are ZB and WZ dominant nanowires consistent with previous measurements [6, 7, 11]. We will study the band structure of both ZB and WZ InP nanowires using photocurrent spectroscopy in more detail in next chapter. In the next section of the thesis, we study PL and TRPL spectroscopy of ZB/WZ mixed phase nanowires.
4.5 PL and TRPL spectroscopy of ZB/WZ mixed phase nanowires

4.5.1 ZB/WZ mixed Phase InP nanowires

Figure 32: (a) HRTEM of a ZB/WZ InP nanowire showing ZB inclusions in the nanowire; (b) enlarge section of HRTEM image with ZB sections identified with white dashes and number of atomic layers; (c) the band diagram and alignments corresponding to the image (b).
Figure 32 (a) shows a high resolution transmission electron microscopy (HRTEM) image of the end of a ZB/WZ mixed phase InP nanowire where part of the gold catalyst can be seen on far right; showing dominantly WZ InP nanowire with 2 – 10 atomic monolayers of ZB inclusions along the nanowire. Figure 32 (b) shows a magnified section of the HRTEM image (a) where atomic planes of both ZB and WZ structures of the nanowire can be identified. Figure 32 (c) shows the conduction band (CB) and the valance band (VB) structure of the nanowire consistent with the structure observed in the magnified HRTEM image (b). Because of the band off sets \[7, 9, 14\] of 45 meV in the VB and 129 meV in CB, the electrons are confined in narrow deep potential wells relevant to ZB inclusions while the holes are confined to the wide potential wells relevant to the WZ sections; allowing confined electrons and holes to make type II transitions as shown in the figure. In addition, one can consider the transitions of energy 1.549 eV or higher between the unconfined electrons and holes which lie above the top of the barriers in the CB and VB respectively. This defines the energy above which there are no confined states, namely the continuum. The information from similar HRTEM images of a 660nm section of the mixed phase InP nanowire enable us to calculate energy eigenstates for this nanowire which will be discussed in more detail later in this chapter. The type II alignment of ZB and WZ sections of the nanowire and the continuum should have a dramatic impact on the optical properties of ZB/WZ mixed phase InP nanowire. In the next section, we discuss the photoluminescence spectroscopy done on ZB/WZ mixed phase InP nanowires.
4.5.2 Photoluminescence (PL) spectroscopy

![Normalized PL spectra and peak position graph](image)

**Figure 33:** (a) The normalized PL spectra showing the shift in PL peak position as excitation power increases from \( P_0/2 \) to \( 22P_0 \) where \( P_0 = 100 \mu \text{W} \). (b) Shows the PL peak position extracted from (a) as a function of power.

Using a Ti:S laser of wavelength 780nm (~1.59eV), a single InP nanowire is excited and the PL spectra at different excitation powers are taken using the spectrometer as discussed in section 4.4.1. Figure 33 (a) shows the normalized PL spectra showing the rapid shift in the PL spectrum with excitation power from 50µW to 2.2mW. At low powers the peak position of the emission line is very close to the ZB band edge while at high powers, the peak position of the emission shifts closer to the WZ band edge. A similar observation was made by Bao et al.\(^5\) for InP ZB nanowires having many rotational twins. This strong power dependence of the PL is not observed for InP nanowires which exhibits only single phase ZB or WZ structure\(^5, 15\) as in Figure 30. Figure 33 (b) shows the peak position of the emission as a function of excitation power determined from the spectra in (a). The shift in the PL is caused by band filling of lower energy states occurring at high power where the photo excited electron-hole density is large. A more detailed picture of these type II transitions can be understood by using time-resolved
spectroscopy where the lifetime of the photo excited electron-hole pairs varies with the degree of overlap between the electron and hole wavefunctions.

### 4.5.3 Time-resolved Photoluminescence (TRPL) spectroscopy

![TRPL Spectrogram](image)

**Figure 34:** (a) Time resolved PL spectral map for a ZB/WZ mixed phase InP nanowire. The white lines are the reference for the energies for ZB band edge (1.42eV), WZ band edge (1.504eV) and energy related to the continuum (1.549eV). (b) PL extracted using individual time slice of TRPL map showing the evolution of the spectra from 0.1 to 4.5 ns.

Figure 34 (a) shows the time resolved spectral map of a ZB/WZ mixed phase InP where the vertical axis shows time after the laser excitation pulse and the horizontal axis is the emission energy of the collected PL. The color mapping is on a logarithmic scale where intensity increases from dark to light colors. Three white lines show the energy positions of the ZB and WZ InP
band gaps and the continuum. At early times the PL emission is near to the continuum and the WZ band edge and decays very fast. At later times, the PL emission energy is close to the ZB band edge, with much longer decay times. Longer decay times for emission near ZB band edge is because of type II transitions between the confined electron and holes. Figure 34 (b) shows single normalized PL spectra extracted from the time-resolved map from 0.1ns to 4.5ns in a linear scale. The normalized PL emission line moves near to the ZB band edge from the continuum as a function of time displaying a remarkable spectral. At the earliest times, the emissions is near the continuum (1.549 eV), nearly 45meV above the WZ band edge consistent with the energy of the continuum. The position of the emission peak moves within the first nanosecond to just below the WZ band edge and then gradually falls to higher energies near 1.43eV with time progress. During the lifetime of the exciton, the spectral peak energy moves by more than 100meV.

This remarkable shift in the emission energy with time is a direct evidence of a dramatic change in the exciton dynamics with energy in these ZB/WZ mixed phase InP nanowires. Figure 35 shows a series of time decays measured from a different nanowire than shown in Figure 34 at different energies with PMT. All measured mixed phase InP nanowires showed a similar behavior as in Figure 34 and Figure 35.
Figure 35: Time decays of photoluminescence for energies (a) near ZB band edge (b) near WZ band edge and (c) near the continuum.
Figure 35 shows the time decays measured for excitons with energy (a) near the ZB band edge at 1.42eV, (b) near the WZ band edge at 1.504eV and (c) near the continuum at 1.549eV corresponding to the band alignments shown in Figure 32 (c) in logarithmic vertical scale; where we see quite different behavior in time decays in these three regions. Near the continuum, Figure 35 (c), the time decays are single exponential with recombination lifetimes of 175ps at 1.56eV, increases to 220ps at 1.54eV. Near the WZ band edge, Figure 35 (b), the time decays are distorted in early times because of filling of carriers from higher energy states since early time decays is slower than the time decays observed at later times. Nonetheless, the later times decays are single exponential, with decay times increasing to 680ps near WZ band edge of 1.504eV and increases further more to 1300ps at 1.485eV. Near ZB band edge, Figure 35(a), no significant state filling is observed as in (b), but the time decays are non-exponential at early times; fast decays in early time followed by longer decays at later times. At later times, the time decays become single exponential with lifetimes increases rapidly with energy up to 8400ps at 1.433eV. Comparing the time decays observed near the continuum (~175ps) to the longest observed time decays (~10ns) near the ZB band edge, we see that the recombination lifetime increases dramatically by a factor 50. For a single phase ZB nanowire, the time decays are single exponential with recombination lifetime of exciton of ~1ns\textsuperscript{[15]} as shown in Figure 31 (a). The fact that the lifetimes are much longer in lower energy states compared to that of higher energies is because of the confinement of elections and holes in specially separated potential wells in the CB and the VB in the ZB and WZ phases in the mixed phase InP nanowire respectively. To understand the recombination dynamic, one can model the quantum dynamic of electron and holes in a ZB/WZ mixed phase InP nanowire. In the following section, we discuss the model done by Dr. Richard Gass to study the exciton dynamic of these nanowires.
4.5.4 Modeling recombination lifetimes

Using the HRTEM image (Figure 32 (a)) of the 657nm long section of a ZB/WZ mixed phase InP nanowire taken from the same part of the substrate as the nanowire measured here, we identified the ZB and WZ sections and then measured the positions and widths of these sections to identify the potentials. The nanowire was predominantly a WZ structure with over 150 sections of ZB inclusions ranging from 2 to 10 monolayers occurring individually or in clusters.

Figure 36: The energies of the bound states along the nanowire for electrons (a) and holes (c). The width of the horizontal lines represents the spatial extend of these states for electron (blue) and holes (red). (b) The variation bound state energy as a function of electrons (1 – 45) and holes (1 - 150).
The one dimensional potential related to the nanowire is used in solving the Schrödinger’s equation using the method of eigenfunction expansion discussed in appendix A1. Because of unknown effective masses for electron and holes in InP WZ structure, the known effective masses of bulk InP (ZB structure) (0.58\textit{m}_e for the heavy holes and 0.073\textit{m}_e for the electrons) were used as the uniform effective masses in this calculation for both ZB and WZ InP sections of the nanowire. The problem was solved by considering the potential profile inside an infinite 657nm one dimensional wide quantum well. The wave functions are assumed to be a sum of 400 particles in a box wave functions. The solution for the actual potential distribution is determined by finding the eigenvalue and eigenvectors of the resulting 400 × 400 matrix for the electrons and a similar one for the holes. We found that there are 45 bound states for electrons and 150 bound states for holes. Figure 36(b) shows the variation of bound state energy for the electrons and holes as a function of quantum number. Figure 36 (a) and (c) shows the positions and energy of these bound states on two dimensional plots for electron and holes respectively. The vertical position of a state refers to the energy of the electron or hole within the potential well of depth of 129eV for electrons and 45eV for holes. The horizontal width of each bound state represents the spatial extend of the state. The lowest ground state for electrons is about 50meV above from the bottom of the 129meV potential wells in the CB and for the holes the lowest ground state is only 2meV (for the widest WZ section of 8.4nm) above the bottom of the 45meV potential wells in the VB with many closely packed higher energy states. This is because of the width of the potential wells is narrow (few monolayer) in the case of electrons which are localized in ZB inclusions along the nanowire and the small electron effective mass. In the case of holes, potential wells in the VB are wider and the large hole effective mass. For narrow WZ
sections, the hole bound states are much higher than the top of the VB. At lower energies, electron and hole are quite localized and becomes much less at higher energies.

Figure 37: Wave functions calculated for electron energy state number 18 along with hole states with numbers 6, 32, 43, 47 and 65. The arrows point to the TEM image at the bottom to give an indication of the special position of these states along the nanowire.

Figure 37 shows the wave functions calculated for a specific electron bound state shown by a blue box in Figure 36 (a); 18th electronic bound state (blue) along with several hole bound states (red) having some overlap with 18th electronic state which is strongly localized to a section of around 5 separate ZB inclusions.
To calculate the recombination lifetimes for all possible emission energies, all possible overlap integrals between electron and hole wave functions need to be calculated. To do this it is not necessary to consider all possible hole states, but only those which show significant overlap with the 18th electron state. To do this we have calculated the 9600 squared overlap integrals, $\langle \Psi_e | \Psi_h \rangle^2$, between all 45 electron bound states and 129 hole bound states where each wavefunction is properly normalized so that $\langle \Psi_e | \Psi_h \rangle = 1$. Considering the overlap of hole states with the 18th electron state, we observe an increased overlap of the electron and hole wave functions as we go to higher energies, which results in lower the recombination lifetimes. The red plots in Figure 37 show several of these overlapped hole states, in order of their energy, which happen on either side of the ZB section with localized electrons. These same hole states are colored in black in Figure 36 (c). For a selected electron state, the emission energy is reduced for more confined hole states. Thus lower energy states make less overlap of wave functions and thus longer lifetimes.

To calculate the recombination lifetimes, we assume that the overlap integral squared is proportional to recombination rate:

$$\langle \Psi_e | \Psi_h \rangle^2 \propto \frac{1}{\tau}$$  \hspace{1cm} (4.1)

To compute the appropriate lifetime from the distribution of all possible electron and hole bound states, the average of the overlap integral squared:

$$\tau(\varepsilon) \propto \frac{1}{\sum \langle \Psi_e | \Psi_h \rangle^2 / N}$$ \hspace{1cm} (4.2)

is considered for all electron hole pair within the particular energy range where $N$ is the number of electron – hole pair states within the energy range centered at $\varepsilon$. The proportionality constant was adjusted by best fitting the data with the calculated lifetimes. At higher energies than 1.5 eV,
this model does not work because of the rapid oscillation of hole wavefunction to calculate the overlap with localized electrons without the inclusion of Coulomb interaction.

![Graph showing recombination lifetimes](image)

**Figure 38**: The recombination lifetimes calculated from the model (Blue) and the TRPL measurements (Red) as a function of emission energy.

Figure 38 shows the comparison of lifetimes calculated using this model (blue) with the lifetimes measured from the time decays using time resolved measurements (red) as shown in Figure 35. The measured lifetimes increase exponentially at lower energies showing a dramatic increase of the lifetimes from ~200ps (at higher energies) to ~10ns (for lower energies). There is good agreement between our experimental lifetimes with lifetimes calculated from the simple model. Emission in the energy range 1.42eV to 1.504eV is mainly because of the recombination of bound electrons and bound holes which are trapped in the potential well structure in these nanowires. The lifetime near the ZB band edge (1.42eV) is much larger because of this spatially separated wave functions of localized electrons and holes. The lifetimes of excitons with energy higher than 1.549eV is very small (~200ps), because of the rapid recombination of unconfined electron and hole pairs and rapid relaxation of excitons into confine electron and hole states by
optical phonon emission. Since we have more bound hole states than electrons, once the electron states are saturated there will be some hole states still available. The remaining hole states will then be filled with holes leaving the electrons in the continuum and recombine the free electron with somewhat bound hole states which we see as a feeding phenomenon observed in Figure 35 (b). Very fast recombination is observed near continuum as seen in Figure 35 (c), because of the fast filling of unconfined holes in the continuum into vacant hole bound states.

4.6 Summary

We use photoluminescence and time-resolved photoluminescence spectroscopy to investigate the band structure and exciton dynamics of ZB, WZ and ZB/WZ mixed phase InP nanowires. The nanowires were synthesized using Au catalyst assisted MOCVD growth at 400°C growth temperature for 20min. The V/III ratio was 350 for ZB InP growth and 700 for WZ and ZB/WZ mixed phase InP nanowire growths. 50nm Au nanoparticles were used as the catalyst for ZB and ZB/WZ mixed phase nanowire growths while 20nm Au nanowire particles were used for WZ growth. The SEM and HRTEM study of these nanowires show nanowires of ~10µm length with some twinning and stacking faults. All ZB nanowires showed a PL emission line at the expected band gap of 1.42eV consistent with the TRPL measurements. PL from all WZ nanowires showed a dominant defect line at ~ 1.47eV and because of that emission from the band edge (1.504eV) could not be observed. But spectra extracted from TRPL study of WZ nanowires shows an emission line at the band edge at early times and evolve in to the defect line at 1.47eV at later times.

PL spectra from the ZB/WZ mixed phase InP nanowires shows a strong excitation power dependence of the emission line as a result of band filling from lower energy states to higher energy states consistent with the TRPL spectroscopy. A detailed study of the TRPL spectroscopy
and time decays exhibits a dramatical increase of life times of excitons at lower energy is observed. The modeling of the exciton dynamics associated with the potential well structure of the mixed phase nanowire showed a very good agreement with the data. We have shown that the exciton dynamics are strongly affected by type II nature of the ZB/WZ band off sets of InP. Clear evidence of confined electrons and holes was observed showing higher recombination rate at higher energies and slow recombination at lower energies where the electrons and holes are strongly confined. In additions, feeding of excitons from higher energy states to the lower energy states was observed as a result of the type II nature of these mixed phase nanowires.
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CHAPTER V

PHOTOCURRENT SPECTROSCOPY OF InP OHMIC NANOWIRE DEVICES
5. PHOTOCURRENT SPECTROSCOPY OF InP OHMIC NANOWIRE DEVICES

5.1 Introduction

The photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra provide information about the electronic band structure and recombination dynamics of excitons, as discussed in chapter IV for ZB, WZ and ZB/WZ mixed phase InP nanowires. From PL and TRPL spectroscopy of ZB and WZ InP nanowires, we observe the nature of ZB and WZ structure of these nanowires even though the HRTEM study shows some twinning and stacking faults in these nanowires. As discussed in section 4.4, the nanowires grown using 50nm Au nanoparticles as the catalyst and V/III ratio of 350 at 400 °C show an exciton emission line near the known ZB band edge 1.42eV using both PL and TRPL spectroscopy. Early time recombination study of nanowires grown with 20nm Au particles and V/III ration of 700 at 400 °C shows an exciton emission line near the WZ band edge 1.504eV from TRPL spectroscopy even though PL and later time TRPL spectroscopy shows a emission near 1.47eV which recognized as a defect emission.

Most of the band parameters of ZB InP structure are well known, but only a few studies for WZ InP structure can be found in the literature. The band parameters relevant to the valance band structure have been studied recently by photoluminescence excitation (PLE) measurements \(^1,2\) of WZ InP nanowires. Recently, Craig E. Pryor et al\(^3\) has also theoretically predicted the band structure for III/V WZ semiconductors where energy positions of A, B and C bands as discussed in section 2.1.2 have been predicted. Here we use photocurrent spectroscopy to probe the band structure of the InP ZB and WZ nanowires. Room temperature photocurrent spectroscopy was used recently by Amir Maharjan et al\(^4\) to probe the standard band gaps of
both ZB and WZ InP NW. In this chapter, we study the band structure of both ZB and WZ InP nanowires using the photocurrent spectroscopy at low temperatures (10 K).

5.2 InP nanowire devices

As discussed in section 2.3, InP nanowires are grown using the Vapor-Liquid-Solid method using 20nm and 50nm gold nanoparticles as catalyst at 400°C using metal-organic chemical-vapor deposition. 50nm ZB nanowires are grown with V/III ratio of 350 while 20nm WZ wires are grown with V/III ratio 700. Recent studies has shown that the higher V/III ratio leads to WZ dominant nanowires and lower V/III ratios tends to grow ZB dominant nanowires, with some twins and stacking faults present as determined by high-resolution transmission electron microscopy imaging\textsuperscript{[5]}. CW and time resolved photoluminescence measurements of these nanowires has shown that the 50nm wires are predominantly ZB while 20nm wires are predominantly WZ, as discussed in section 4.4. The ZB and WZ InP nanowire devices are fabricated using photolithographic techniques followed by Ammonium polysulfide etching to make Ti/Al Ohmic metal contacts to the nanowire as discussed in section 3.2. The similar techniques have been used by several other groups to make Ohmic contact with III-V semiconductor materials like InAs, GaAs and AlGaAs\textsuperscript{[6, 7, 8, 9]}. The standard metal deposition and lift off techniques are then used to fabricate 200nm Ti/Al contact pads across the nanowire separated by a ~4 µm gap. Thin gold wires are used to wire bond external connections to the large metal pads of the nanowire device after mounting on a chip carrier, using a West Bond 7476D manual wire-bonder. Before making photocurrent spectroscopy measurements of these devices, we measure basic IV characteristics of these nanowire devices; which are discussed in detail in the next section of the thesis.
5.3 Basis IV measurements and Ohmic behavior of nanowire devices

![Graph showing IV characteristics of a ZB InP nanowire device in dark and under white light illumination.]

Figure 39: IV characteristics of a ZB InP nanowire device in dark (black curves in (a) & (b)) and under white light illumination (red curve in (a)) at room temperature showing the Ohmic nature and the high photo sensitivity of the device.

Before making detailed photocurrent spectroscopy measurements, the nanowire devices are characterized electronically in both the dark and under white light illumination at room temperature. Figure 39 shows the IV characteristics of a ZB InP nanowire device in the dark (black curve in (a) & (b)) and under white light illumination (red in (a)) at room temperature. The linear behavior of the dark IV characteristic in Figure 39 (b) implies that the device has Ohmic contacts. Under the illumination of white light, the current increases by 3 or more orders of magnitude (5 orders of magnitude for this device) compared to the dark current showing these nanowires are highly photo sensitive. The photocurrent saturates for higher biases (>1 V for this device), perhaps because of the saturation of the drift velocity of the photoexcited carriers. We have observed the similar IV characteristics for most of our ZB and WZ InP nanowire devices. In the next section of this chapter, we discuss the photocurrent IV measurement and photocurrent spectroscopy.

86
5.4 Lock-in IV measurements and photocurrent spectroscopy

Photocurrent spectroscopy is an excitation spectroscopy techniques which can be used to study the band gap, excitonic states, defects and disorders where the current resulting from photo excited carriers is measured as a function of excitation energy at fixed bias.

![Schematic diagram of photocurrent spectroscopy](image)

*Figure 40:* Schematic diagram of photocurrent spectroscopy (a) where the nanowire is excited with light to create electron and holes in the CB and the VB in the semiconductor (b) as a result of photo excitation and the current is measured as a function of bias voltage and excitation energy.

Figure 40 (a) shows a schematic diagram of how the photocurrent is measured from a nanowire device. The exciton, the bound state of the photoexcited electron and hole in the CB and the VB respectively as shown in Figure 40(b) is created through photoexcitation. Once the exciton is created, the electrons and holes are separated by applying a bias V across the nanowire and the resulting current (photocurrent) through the circuit is measured. The current contains two parts, the photocurrent plus the dark current. So the laser is chopped with a known frequency and a lock-in amplifier is tuned to that frequency to measure directly only the current flowing through the circuit which was created through photoexcitation by the laser. To measure the photocurrent spectrum, the photocurrent is measured as a function of bias voltage (lock-in IV) and the
excitation energy. In the next section of this chapter, we discuss the room temperature photocurrent spectroscopy data from ZB and WZ InP nanowires.

5.5 Photocurrent spectroscopy of ZB and WZ InP nanowire devices at 300K

The nanowire device is mounted to the cold finger of a continuous flow liquid He cryostat, and the device is observed through a thin window using a long working distance 10X/50X microscope objective. The nanowire is broadly illuminated with a CW Ti-Sapphire tunable (700nm-1000nm) laser (or white light setup) chopped at a 137Hz frequency to induce a photocurrent. In these measurements, the laser is circularly polarized to excite all the linearly polarized electronic states with the same probability.

![Photocurrent spectra](image)

Figure 41: Photocurrent spectra for ZB InP nanowire (blue dots) and WZ InP nanowire (red dots) devices at 300K where vertical axis represents the photocurrent in logarithmic scale. Dark lines represent the linear fits to the data below and above band edges showing changes of slopes at the band edge. Vertical dash lines represent the band edge for ZB and (blue) WZ (red).

The photocurrent is measured using a digital lock-in amplifier after amplification of the signal by a preamplifier at both room temperature and low temperature. Figure 41 show the photocurrent spectra of ZB (blue dot) and WZ (red dot) InP nanowire devices at room temperature measured.
with a monochromatic white light set up. The vertical axis is the photocurrent on a logarithmic scale while the horizontal axis shows the excitation energy. Black solid lines represent linear fits to the data below and above the band edges showing a discontinuity in slope at the band edge. The photocurrent drops exponentially by about 3 orders of magnitude below the band edge. Vertical dash lines represents the band edge of ZB (blue) at 1.353eV and WZ (red) at 1.421eV InP nanowires at room temperature, consistent with previous room temperature photocurrent measurements done by Maharjan et al\textsuperscript{[4]} . The slope of the sub gap photocurrent energy distribution (Urbach energy of 27meV for ZB and 58meV for WZ InP) is in reasonable agreement with the urbach parameter for bulk InP\textsuperscript{[4,10]}. A larger Urbach parameter for WZ InP nanowire indicate the presence of more defects and disorders. The observed separation of the WZ and ZB band edges of 80meV agrees very well with the energy difference measured using PL and TRPL measurements at low temperatures as discussed above in section 4.4 and other optical measurements\textsuperscript{[5,11,12,13,14]}. In the next section of this chapter, we discuss the photocurrent spectroscopy measurements of ZB and WZ InP nanowires at low temperatures (10\textdegree K).
5.6 Photocurrent measurements of ZB and WZ InP nanowire devices at 10K

Figure 42: Photocurrent spectra for ZB InP nanowire (blue) and WZ InP nanowire (red) devices at 10K. The arrows represent the positions of excitonic states correspond to transitions from CB to the degenerate heavy/ light hole band (HH/LH) and the split off band in the case of ZB and the A, B and C hole bands.

Figure 42 shows the photocurrent spectra measured for a ZB InP nanowire device (blue) and a WZ nanowire device (red) at 10K. SEM study of the ZB nanowire device shows a nanowire of diameter ~275nm even though the ZB nanowires used in these devices were grown using 50nm gold nanoparticles as catalyst. The SEM micrographs suggest that the WZ InP nanowires get bundled during the dispersing procedure. In addition, the nanowires with different diameters ranging from 20nm -100nm have been observed even though 20nm Au nano particles were used in the growth of these InP WZ nanowires. These larger diameter nanowires may be a result of the Au nanoparticles agglomerating to make larger gold nano particles during the pre-growth process. For the ZB InP nanowire, the photocurrent spectrum shows two excitonic-like peaks, one associated with the band edge (~1.425eV, comparable with PL measurements from similar ZB InP nanowires as shown in Figure 30 (a) and Figure 31 (a & c)) and another peak at 1.539eV.
corresponds to the transition between the split off hole band and the CB of the ZB InP nanowire at 10K. The measured spin orbit splitting energy of 114meV is comparable with the known spin orbit splitting of bulk ZB InP (110meV) [15]. The Photocurrent spectrum for the WZ InP nanowire device shows three excitonic like peaks related to the valance bands of WZ InP: A (heavy hole band), B (light hole band) and C (split off band). The energies of these A, B and C bands are at ~1.504eV, ~1.531eV and ~1.653eV respectively, are consistent with recent PLE measurements on 100nm InP WZ nanowires [1]. From our photocurrent data for the WZ InP nanowire device shown in Figure 42, we determine the energy splitting between A and B hole bands ($E_{BA}$) as 27 meV and the energy splitting between A and C hole bands ($E_{CA}$) as 149 meV consistent with recent measurements and theoretical predictions [1,2,16]. Using the quasi-cubic approximation, we can estimate values for spin-orbit coupling ($\Delta_{SO}$) and crystal field splitting ($\Delta_{CR}$) [22,15].

\[
E_{CA} = \frac{\Delta_{SO} + \Delta_{CR}}{2} + \sqrt{\left(\frac{\Delta_{SO} + \Delta_{CR}}{2}\right)^2 - \frac{2}{3}\Delta_{SO}\Delta_{CR}} 
\]

\[
E_{BA} = \frac{\Delta_{SO} + \Delta_{CR}}{2} - \sqrt{\left(\frac{\Delta_{SO} + \Delta_{CR}}{2}\right)^2 - \frac{2}{3}\Delta_{SO}\Delta_{CR}} 
\]

From our measurements, we calculate a crystal field energy, $\Delta_{CR}$=47 meV, and a spin-orbit energy, $\Delta_{SO}$=129 meV, using equations (5.1) and (5.2). These values are consistent with recent PLE measurements for 100nm WZ InP nanowires and theoretical predictions [1,17]. In addition, we have observed the positions of A, B and C hole bands at different positions for other WZ InP devices (D2 & D3) compared to the InP WZ nanowire device (D1) shown in Figure 42, which might be a evidence of quantum confinement in the 20nm WZ InP nanowires that we discuss in the next section.
5.7 Quantum confinement of 20nm WZ InP nanowires

Figure 43: Comparison of photocurrent spectra for three different WZ InP nanowire devices D1, D2 and D3 at 10K. Three dash lines represents the energy positions of three hole bands A, B and C for the same WZ InP nanowire device (D1) shown in Figure 42. For D2, only B hole band is shifted to higher energy by ~30meV and the A and C hole bands are shifted by ~20meV while the position of B hole band is not clear for the device D3.

Figure 43 shows a comparison of three photocurrent spectra measured for three WZ InP nanowire devices at 10 K: (a) D1 (the same InP WZ nanowire device as shown in Figure 42), (b) D2 and (c) D3. These spectra shows three excitonic like peaks relevant to the valence bands of WZ InP, A, B and C. The arrows show the theoretically calculated energy shifts with respect to A, B and C energies of nanowire device D1. The energy positions of these A, B and C for the InP WZ nanowire device D1 (a) is consistent with recent PLE measurement of a 100nm diameter InP WZ nanowire [1]. For the WZ InP nanowire device D3 (c) the position of A, B and C excitonic like peaks have shifted to higher energy: ~20meV for A and C while the exact position
of B cannot be resolved because of the very weak signal from the device. For the WZ InP nanowire device D2 (b), only the position of B is shifted to higher energy by ~30meV while a significant shift cannot be observed for A and C. To address the energy difference in these photocurrent spectra, we have done some SEM studies on these InP WZ nanowire devices. The SEM micrographs suggest that these InP nanowires get bundled during the dispersing procedure. In addition, the nanowires with different diameters ranging from 20nm -100nm have been observed even though 20nm Au nano particles were used in the growth of these InP WZ nanowires. These larger diameter nanowires may be a result of getting 20nm Au nano particles together to make larger nano particles during the pre-growth process.

Figure 44: Scanning electron microscopy (SEM) images of two WZ InP nanowire devices (a) D2 having four nanowires and (b) D3 having two nanowires showing the bundling of nanowires. The scale bar on the top left of the images is 100nm.

Figure 44 shows the SEM micrographs of WZ InP nanowire devices (a) D2 having four nanowires (three ~25nm nanowires and one ~75nm nanowire bundle) and (b) D3 having two nanowires of diameter ~25nm. The metal contact pads of the nanowire devises are visible in the bottom for D2 and on the right for D3. Actual measured diameters of nanowires in these two devices using SEM study are shown in Table 5.1. From the measured diameters of these nanowires, the average diameter for the smaller nanowires is 26nm.
Table 5.1: Diameter measured for nanowires in two WZ InP nanowire devices D2 and D3 using SEM micrographs.

<table>
<thead>
<tr>
<th>Device</th>
<th>W1</th>
<th>W2</th>
<th>W3</th>
<th>W4</th>
</tr>
</thead>
<tbody>
<tr>
<td>D2</td>
<td>27 ± 2 nm</td>
<td>25 ± 2 nm</td>
<td>28 ± 2 nm</td>
<td>77 ± 2 nm</td>
</tr>
<tr>
<td>D3</td>
<td>27 ± 2 nm</td>
<td>24 ± 2 nm</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

We believe that the device D1 contains one or two larger diameter nanowires since it shows consistency with PLE measurement done with 100nm diameter WZ InP nanowire. This suggests that the shifts for A, B and C hole bands between photocurrent spectra of devices D2 and D3 compared with D1 suggests possible quantum confinement in smaller diameter WZ InP nanowires.

To study these confined states, one can solve the Schrödinger’s equation for particles (electrons and holes) confined in an infinitely long cylinder in cylindrical coordinate [18] and obtain wave functions

$$\Psi_{k,m,l}(\rho, \alpha, z) = N e^{ikz} e^{ima} J_m \left( \rho \frac{x_{ml}}{a} \right)$$

and the energy eigenvalues

$$E_{k,nl} = E_0 + \frac{1}{2\mu} \left( \frac{x_{ml}}{a} \right)^2$$

where $x_{ml}$ is $i^{th}$ zero of the Bessel function $J_m(x)$, $\mu$ mass of the particle, $a$ is the radius of the nanowire and $E_0$ is the band gap. The energy shift of the confined states for excitons is the sum of the energy shifts of confined electrons and holes;
\[ \Delta E_{k,ni} = \frac{1}{2m_e} \left( \frac{x_{mi}}{a} \right)^2 + \frac{1}{2m_h} \left( \frac{x_{mi}}{a} \right)^2 \]  

(5.5),

where \( m_e^* \) and \( m_h^* \) are the effective mass of the electron and the hole respectively. In this model, the coulomb interaction between electron and hole has not been considered.

**Table 5.2**: The energy shift of A, B and C excitonic states because of the quantum confinement of excitons.

<table>
<thead>
<tr>
<th></th>
<th>( \Delta A ) (meV)</th>
<th>( \Delta B ) (meV)</th>
<th>( \Delta C ) (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D2</td>
<td>-</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>D3</td>
<td>19</td>
<td>30 - 40</td>
<td>23</td>
</tr>
<tr>
<td>Model for ( d = 26nm )</td>
<td>18.5</td>
<td>30.9</td>
<td>23.9</td>
</tr>
<tr>
<td>Model for ( d = 20nm )</td>
<td>31.2</td>
<td>52.3</td>
<td>40.5</td>
</tr>
</tbody>
</table>

Table 5.2 shows the energy shifts of A, B and C excitons for WZ InP nanowire devises D2 and D3 and calculated ground state energy shifts of A, B and C for nanowires with diameter \( d = 26nm \) and \( d = 20nm \). For this calculation the effective masses of the electrons, the heavy holes, light holes and holes in the split off band were assumed to be the known effective masses of bulk ZB InP. The experimental energy shifts measured from WZ InP nanowire devices D2 and D3 are consistent with the theoretical calculation done for a nanowire with diameter of 26nm using equation (5.5) as shown by black arrows in Figure 43. The calculated energy shifts of the A, B and C excitonic states for a nanowire with diameter of 20nm is much higher compared to the experimental shifts.
5.8 Polarization photocurrent spectroscopy of ZB and WZ InP nanowires

Figure 45: Polarized photocurrent spectroscopy for (a) the ZB InP nanowire device and (b) the WZ InP nanowire device D3 at 10K. Excitation laser was polarized parallel/perpendicular to nanowire.

Figure 45 shows the polarized photocurrent spectra for (a) the same ZB InP nanowire device shown in Figure 42 and (b) the WZ InP nanowire device D3 at 10K. The left vertical axis of (b) refers to the photocurrent measured with light polarized along the nanowire while the right vertical axis refers to perpendicular polarization. To measure the polarization response of these InP nanowires, the photocurrent spectrum is measured exciting with a linearly-polarized laser oriented parallel or perpendicular to the nanowire. Dash vertical lines refer the energy positions of the excitation from (a) the heavy/light hole band and the split off band and (b) A, B and C hole bands to the conduction band. For ZB InP nanowire the photocurrent measured with excitation parallel to the nanowire axis is higher than that with excitation perpendicular to the nanowire axis. For the WZ InP nanowire device D3, the photocurrent measured with excitation parallel to the nanowire is about two orders of magnitude higher than the photocurrent even though the excitonic peak A is more clear with perpendicular polarization. Previously A. Mishra et al. [11] used photoluminescence spectroscopy to show that ZB InP nanowires are polarized
along the nanowire while the WZ InP nanowires are polarized normal to the nanowire axis. In
the polarization shown in Figure 45, the ZB InP nanowire is more polarized perpendicular to the
nanowire axis and WZ nanowire is more polarized along the nanowire. This is surprising
because the optical selection rules for excitation of electrons and holes for InP with ZB
symmetry are completely isotropic and also the dielectric contrast almost always results in laser
excitation more efficient for the laser polarized along the nanowire axis for diameters of less than
100 nm. In contrast, a hexagonal WZ crystal structure exhibits a completely different symmetry.
When WZ nanowire is excited with light polarized perpendicular to the nanowire, All excitations
from A (Γ⁹), B (Γ⁷) and C (Γ⁷) hole bands to the conduction band (Γ⁷) are allowed while
excitations from A (Γ⁹) hole band to the conduction band (Γ⁷) are forbidden when excited with
light polarized parallel to the nanowire as discussed in section 2.2.2. The excitonic peak A is
more prominent when excited with light polarized perpendicular to the nanowire consistent with
the selection rule even though nanowire is more polarized along the nanowire because of the
dielectric contrast of smaller diameter nanowires. The excitonic peak C is clear for both parallel
and perpendicular excitation even if the peak B is not clear. This experimental polarization
results are consistent with the selection rules for the excitation even if the WZ InP nanowire is
more polarized along the nanowire because of the dielectric contrast. SEM micrographs of the
ZB InP nanowire device show that the diameter of this nanowire is ~275nm while the WZ InP
nanowire device D3 has two nanowires with diameters ~ 26nm. The polarization dependence of
thick nanowires has been studied by H.E. Ruda et al[19], who showed that while nanowires are
polarized along the nanowire axis for smaller diameter nanowires they can be polarized
perpendicular to larger diameter nanowires. The polarization of the nanowire can vary both as a
function of both the diameter of the nanowire and the excitation energy.
To more closely investigate the polarization phenomena in a nanowire device, one can solve the Helmholtz equation;

\[
\frac{1}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial F}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial^2 F}{\partial \alpha^2} + \frac{\partial^2 F}{\partial z^2} + \frac{\epsilon}{c^2} \omega^2 F = 0
\]  \hspace{1cm} (5.6)

(in cylindrical coordinates) to find the electric field (magnetic field) of the form;

\[
F_Z(\rho, \alpha) = F_0 \sum_{m=-\infty}^{\infty} i^m A_m J_m^{(1)}(k \rho) e^{i m \alpha} e^{-i \omega t}
\]  \hspace{1cm} (5.7)

inside and

\[
F_Z(\rho, \alpha) = F_0 \sum_{m=-\infty}^{\infty} i^m (J_m^{(1)}(k \rho) - B_m H_m^{(2)}(k \rho)) e^{i m \alpha} e^{-i \omega t}
\]  \hspace{1cm} (5.8)

outside an infinitely long dielectric cylinder, corresponding to light polarized along (perpendicular to) the cylinder axis \(^{[20]}\). Even though the approximation of infinite cylinder breaks down for 275nm ZB nanowire because the ratios; length/radius and length/wavelength are very small, this classical model agrees quite well with the experimental result. Applying the boundary conditions for the electric field (magnetic field) at the surface of the cylinder, the coefficients \(A_m\) and \(B_m\) can be found. In case of the photocurrent spectroscopy, the photocurrent is a measure of absorption, so the absorption efficiency for a long cylinder \(Q_{abs}\) is given by

\[
Q_{abs} = \frac{2}{\kappa a} \sum_{m=-\infty}^{\infty} (Re\{B_m\} - |B_m|^2)
\]  \hspace{1cm} (5.9),

where the coefficient \(B_m\) is given by

\[
B_m = \begin{cases} 
\frac{n J_m^{(1)}(n \kappa a) J_m(n \kappa a) - J_m^{(1)}(n \kappa a) J_m^{(1)}(n \kappa a)}{n J_m^{(1)}(n \kappa a) H_m^{(2)}(n \kappa a) - J_m^{(1)}(n \kappa a) H_m^{(2)}(n \kappa a)} & \text{for E field } // z \text{ - axis} \\
\frac{J_m^{(1)}(n \kappa a) J_m(n \kappa a) - n J_m(n \kappa a) J_m^{(1)}(n \kappa a)}{n J_m^{(1)}(n \kappa a) H_m^{(2)}(n \kappa a) - J_m^{(1)}(n \kappa a) H_m^{(2)}(n \kappa a)} & \text{for E field } \perp z \text{ - axis}
\end{cases}
\]  \hspace{1cm} (5.10),
where $k$ is the light wave vector in vacuum, $a$ is the radius of the cylinder and $n$ is refractive index of the dielectric material\textsuperscript{[20]}. $J_m(x)$ and $H_m^{(2)}(x)$ are the Bessel functions of first kind and the Henkel functions of second kind, respectively, and the prime denotes the derivatives with respect to $x$. In this calculation, the complex dielectric function ($\varepsilon = n^2$) of the nanowire is assumed to be equal to the constant background dielectric constant with a Lorentzian oscillator at the fundamental absorption edge (band gap) of ZB InP and WZ InP\textsuperscript{[21,22]}. The polarization index defined as

$$P_{\text{abs}} = \frac{Q_{\parallel}^{\text{abs}} - Q_{\perp}^{\text{abs}}}{Q_{\parallel}^{\text{abs}} + Q_{\perp}^{\text{abs}}}$$

(5.11)

characterizes the polarization dependence of absorbed light, where $Q_{\parallel}^{\text{abs}}$ and $Q_{\perp}^{\text{abs}}$ represent the absorption efficiency relevant to excitation light polarized parallel and perpendicular to the nanowire respectively.

Figure 46: The theoretical polarization index (a) as a function of nanowire diameter calculated at excitation energy 1.55eV and (b) as a function of excitation energy for both 275 nm ZB (navy color line) and 26nm WZ InP nanowires (orange color line) along with the experimental polarization index measurements for both 275nm ZB InP nanowire device (blue dots) and the WZ InP nanowire device D3 (red dot).
Figure 46 shows the theoretical polarization index (a) as a function of nanowire diameter calculated at excitation energy 1.55eV and (b) as a function of excitation energy for both 275 nm ZB (navy color line) and 26nm WZ InP nanowires (orange color line) along with the experimental polarization index measured using photocurrent measurements in Figure 45 for both 275nm ZB InP nanowire device (blue dots) and the WZ InP nanowire device D3 (red dot). In Figure 46 (a), the polarization index is nearly one for nanowires with diameter less than ~75 nm and for nanowires with diameter higher than ~75nm, the polarization index decreases and become negative for nanowires with diameters from ~240nm to ~290nm. This variation of polarization index also changes as a function of excitation energy. In Figure 46 (b), the dark blue line shows the polarization index calculated from the model for a ZB InP nanowire of diameter 275nm, showing the positive index for excitation with energy less than ~1.35eV and excitation with energy higher than ~1.65eV and negative polarization index for excitations with energy in the region from ~1.35eV – 1.65eV. The orange line in Figure 46 (b) shows the polarization index calculated from the model for a 26nm WZ InP nanowire, showing the polarization index close to 95% throughout the whole energy range. Similar calculation has been done by H.E. Ruda et al \[19\], where the dependence of dielectric function with excitation energy has not been considered. The experimental polarization index calculated from the photocurrent measurements for both ZB and WZ nanowire devices agrees very well with the theoretical calculation as seen in Figure 46 (b).

In addition to the polarized photocurrent measurements, the photoluminescence excitation (PLE) is measured for the WZ InP nanowire device D3 at 0 V bias with excitation light polarized along the nanowire. For PLE measurement, the photoluminescence (PL) of the nanowire is measured as a function of excitation energy using same photoluminescence
experimental set up discussed in section 4.2. The PL signal is very weak even at very high excitation power (2mW) that we cannot obtain PL from the device polarized perpendicular to the nanowire; PL is measured only exciting the nanowire with light polarized along the nanowire long axis.

![Graph](image)

**Figure 47:** Photoluminescence excitation measurement of the WZ InP nanowire device D3 measured with excitation parallel to the nanowire along with polarized photocurrent measurements for comparison. Black solid curve refers to the PL taken with excitation at 1.675eV.

Figure 47 shows the PLE spectrum measured for the WZ InP nanowire device D3 with excitation laser parallel to the nanowire along with polarized photocurrent data for comparison. Black solid curve refers to the PL spectrum measured with excitation energy at 1.675eV, where we have the peak photocurrent and PL intensity. We use a 830nm (1.494eV) low pass Raman filter to cut off the laser line as it is tuned to higher energies so that only the defect emission is detected from the PL. To measure the PLE of the WZ InP nanowire device D3, we integrate the filtered defect emission over all energies as the laser is tuned to higher excitation energies. As the laser is tuned to higher energies, only excitonic resonance for the C hole band is observed.
The excitonic resonances for A and B hole bands cannot be resolved because of the weak PL signal from the nanowire and the observed C excitonic resonance is consistent with the photocurrent measurements.

**5.9 Summary**

We have used photocurrent spectroscopy to study InP nanowire Ohmic devices having either zinc-blende (ZB) or wurtzite (WZ) crystal structures at temperatures 300°K and 10°K. Dark IV measurements of most of the InP nanowire devices shows linear Ohmic behavior and the current increases by 3 or more orders of magnitude with light excitation showing high photosensitivity of these nanowires. At room temperature, we have found that the energy band gap (1.421eV) of WZ InP nanowires has ~70meV higher energy than the band gap energy (1.353eV) of ZB InP nanowires which is consistent with previous measurements \[4, 5, 11, 12, 14\].

At low temperatures (10K), we have observed the excitonic resonance of excitons relevant to heavy hole/light hole band (1.425eV) and the spin-orbit band (1.539eV) for ZB nanowire and the exciton resonance of excitons relevant to A, B and C hole band of WZ nanowire devices which is consistent with recent PLE studies\[1\]. The spin orbit splitting energy of 114eV for ZB InP is consistent with the known spin orbit splitting of 110meV\[15\] while the crystal field energy (47meV) and the spin orbit splitting energy (127meV) measured for a WZ InP nanowire device is consistent with recent PLE measurements for 100nm WZ InP nanowires and theoretical predictions\[1,2,3\]. In some WZ nanowire devices with smaller diameter nanowires, A (~1.523eV), B (~1.565eV) and C (~1.675eV) excitonic peaks are observed at higher energies suggesting possible quantum confinement of the electrons and holes in the 20nm WZ InP nanowires consistent with the theoretical model of confined electrons and holes in an infinite cylindrical potential.
The polarized photocurrent measurements of a ZB InP nanowire device has shown to have negative polarization index which is consistent with the theoretical calculations done using classical electrodynamics. Polarized photocurrent measurements of the WZ InP nanowire device having two nanowires of diameter ~26nm has shown to have a polarization index about 95% which is consistent with theoretical calculation. In addition, the PLE spectroscopy measurement for the same WZ nanowire device with the excitation parallel to the nanowire agrees very well with the polarized photocurrent measurements.
Reference:


18 R. W. Robinett, “*Visualizing the solutions for the circularly infinite well in quantum and classical mechanics*”, *American Association of Physics teachers*, 1996


APPENDICES

A1. Eigenfunction expansion method

The method of eigenfunction expansion is a powerful approach of solving problems in quantum mechanics that we used to model the recombination life times for excitons in a type II InP homostructures discussed in chapter IV.

To implement the eigenfunction expansion method, a state wavefunction $\Psi(x)$ can be expanded in some complete set of wavefunctions $\{\varphi_n(x)\}$ as

$$\Psi(x) = \sum_n C_n \varphi_n(x)$$

where the coefficient;

$$C_n = \langle \varphi_n(x) | \Psi(x) \rangle = \int_{-\infty}^{\infty} \varphi_n^*(x) \Psi(x) dx$$

for all n. The complete set of wavefunctions $\{\varphi_n(x)\}$ is assumed to include only normalizable state vectors ($\langle \varphi_n(x) | \varphi_n(x) \rangle = 1$). In any eigenfunction expansion, we must include all of the eigenfunctions except those whose coefficients are zero.

In the calculation of modeling the recombination lifetimes for excitons trapped in type II homostructures, the wavefunction of the complete set is assumed to be the wavefunction of the Hamiltonian for an infinite potential well of the well width of $L$ (length of the nanowire);

$$\varphi_n(x) = \sqrt{\frac{2}{L}} \sin \left( \frac{n\pi x}{L} \right)$$

To find the wavefunctions; $\Psi(x)$ satisfying the Hamiltonian;

$$H \Psi(x) = \left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right\} \Psi(x) = E \Psi(x)$$
where $V(x)$ is the potential well structure along the nanowire defined by ZB section for electrons and predominant WZ sections for holes similar to one shown in Figure 32(c) in chapter IV.

Now considering

$$\langle \varphi_n(x) | H | \Psi(x) \rangle = -\frac{\hbar^2}{2m} \langle \varphi_n(x) | \frac{d^2}{dx^2} | \Psi(x) \rangle + \langle \varphi_n(x) | V(x) | \Psi(x) \rangle$$  A1.5

$$E \ C_n = -\frac{\hbar^2}{2m} \langle \varphi_n(x) | \frac{d^2}{dx^2} | \Psi(x) \rangle + \langle \varphi_n(x) | V(x) | \Psi(x) \rangle$$  A1.6

The first term of the right hand side (RHS) of A1.6

$$-\frac{\hbar^2}{2m} \langle \varphi_n(x) | \frac{d^2}{dx^2} | \Psi(x) \rangle = -\frac{n^2 \pi^2 \hbar^2}{2ml^2} \ C_n$$  A1.7

Since our potential is either zero or a constant $\alpha$, the second term of the RHS reduced to a sum of two terms; one with coefficient $C_j$ where $j \neq n$ and the other with coefficient $C_n$ that sums over the entire potential well in the structure.

So at the end, we will arrive at a recursion expression of $C_n$'s, that can be used to find the coefficients and then the wavefunctions.
A2. Quantum confinement in an infinite cylindrical well

Solving the Schrödinger’s equation for a particle confined in an infinitely long cylinder in cylindrical coordinate and obtains the wavefunction

\[ \Psi_{k,m,i}(\rho, \alpha, z) = N e^{ikz} e^{ima} J_m \left( \frac{\rho x_{mi}}{a} \right) \]  \hspace{1cm} (A2.1)

and the energy eigenvalues

\[ E_{k,ni} = E_0 + \frac{1}{2\mu} \left( \frac{x_{mi}}{a} \right)^2 \]  \hspace{1cm} (A2.2)

where \( x_{mi} \) is \( i^{th} \) zero of the Bessel function \( J_m(x) \), \( \mu \) mass of the particle, \( a \) is the radius of the cylinder and \( E_0 \) is a constant (background energy).

In the case of exciton confined in a nanowire, the total energy of the exciton;

\[ E_{k,ni} = E_0 + \frac{1}{2m_e} \left( \frac{x_{mi}}{a} \right)^2 + \frac{1}{2m_h} \left( \frac{x_{mi}}{a} \right)^2 \]  \hspace{1cm} (A2.3)

Where \( E_0 \) is the unconfined energy of the exciton and \( m_e^* \) and \( m_h^* \) are the effective mass of the electron and the hole respectively. In this model, the coulomb interaction between electron and hole has not been considered.

We used “Mathematica” to calculate the excitonic states confined in an InP nanowire.

To find the zeros of the Bessel functions

\[ \text{bessel}\{Z = \text{Table}[N[\text{Bessel}J_n(m, i)], \{m, 0,6\}, \{i, 1,10\}] \]
Parameters used in this calculation

\[ me = 0.08; \]
\[ mlh = 0.089; \]
\[ mh = 0.6; \]
\[ mso = 0.17; \]
\[ a = d/2; \]
\[ d = 26; \]

To find energies of the confined states relevant to transitions from the A (heavy hole), B (light hole) and C (holes in the split-off band) to the electron in the CB respectively

\[ E_{hh} = \text{Table}[[\{m, i, 1.504 + \frac{1239.8^2}{4\pi^2 20.511 \times 10^6} \left( \frac{1}{me} + \frac{1}{mh} \right) \text{bessel}Z[[m + 1, i]] \right)^2}, \{i, 1, 2\}, \{m, 0, 2\}] \]
\[ E_{lh} = \text{Table}[[\{m, i, 1.531 + \frac{1239.8^2}{4\pi^2 20.511 \times 10^6} \left( \frac{1}{me} + \frac{1}{mlh} \right) \text{bessel}Z[[m + 1, i]] \right)^2}, \{i, 1, 2\}, \{m, 0, 2\}] \]
\[ E_{so} = \text{Table}[[\{m, i, 1.653 + \frac{1239.8^2}{4\pi^2 20.511 \times 10^6} \left( \frac{1}{me} + \frac{1}{mso} \right) \text{bessel}Z[[m + 1, i]] \right)^2}, \{i, 1, 2\}, \{m, 0, 2\}] \]

The resulting energy positions of the A, B and C excitons

\[ E_A = \{\{0, 1, 1.522\}, \{1, 1, 1.551\}\}, \{\{0, 2, 1.601\}, \{1, 2, 1.661\}\}\} \]
\[ E_B = \{\{0, 1, 1.562\}, \{1, 1, 1.610\}\}, \{\{0, 2, 1.694\}, \{1, 2, 1.794\}\}\} \]
\[ E_C = \{\{0, 1, 1.677\}, \{1, 1, 1.714\}\}, \{\{0, 2, 1.779\}, \{1, 2, 1.857\}\}\} \]

In this calculation, the transitions were considered only in-between electron and holes with same quantum numbers \(m\) and \(i\). The unconfined energy positions of A, B and C excitons are assumed to be 1.504eV, 1,531eV and 1.653eV respectively as discussed in chapter V.
The radial parts of the wavefunction of electrons and holes;

\[ \frac{\text{bessel}}{1} Z\{1, f\} x, \{x, 0, 1\}, \text{PlotRange} \rightarrow \text{All}, \{f, 1, 5\} \]

In the calculation of this wavefunction, the radius of the nanowire was assumed to be 1.
A3. Polarization anisotropy in nanowires

As discussed in chapter V, the absorption efficiency for a long cylinder \( Q^{abs} \) is given by

\[
Q^{abs} = \frac{2}{ka} \sum_{m=-\infty}^{\infty} (\text{Re}\{B_m\} - |B_m|^2)
\]

(A3.1), where the coefficient \( B_m \) is given by

\[
B_m = \begin{cases} 
\frac{n'_m(nka)f_m(ka)-f_m(nka)f'_m(ka)}{n'_m(nka)H^{(2)}_m(ka)-f_m(nka)H^{(2)}_m(ka)} & \text{for E field } \parallel z - \text{axis} \\
\frac{n'_m(nka)f_m(ka)-f_m(nka)f'_m(ka)}{n'_m(nka)H^{(2)}_m(ka)-f_m(nka)H^{(2)}_m(ka)} & \text{for E field } \perp z - \text{axis}
\end{cases}
\]

(A3.2), where \( k \) is the light wave vector in vacuum, \( a \) is the radius of the cylinder and \( n \) is refractive index of the dielectric material. \( f_m(x) \) and \( H^{(2)}_m(x) \) are the Bessel functions of first kind and the Henkel functions of second kind, respectively, and the prime denotes the derivatives with respect to \( x \).

The polarization index defined as

\[
P^{abs} = \frac{Q^{abs}_{\parallel}-Q^{abs}_{\perp}}{Q^{abs}_{\parallel}+Q^{abs}_{\perp}}
\]

(A3.3)

First we need to calculate the complete dielectric function of the semiconductor. Here we do the calculation only for ZB InP nanowires. Here we use “Mathematica” to model the polarization of light in nanowire.

Parameters used in the calculation of dielectric function
To compute the dielectric function of ZB InP at low temperatures

\[ f(x) := \frac{1}{x^2} (2 - (1 + x)^{1/2} - (1 - x)^{1/2}) ; \]

\[ \chi_0 = (\epsilon + \Delta \Gamma) / E_0 ; \]
\[ \chi_0 s = (\epsilon + \Delta \Gamma) / (E_0 + \Delta) ; \]
\[ \chi_1 = (\epsilon + \Delta \Gamma) / E_1 ; \]
\[ \chi_1 s = (\epsilon + \Delta \Gamma) / (E_1 + \Delta) ; \]
\[ \chi_2 = \epsilon / E_2 ; \]
\[ E_0 A = E_0 ; \]
\[ E_0 B = E_0 ; \]
\[ E_0 C = E_0 + \Delta ; \]
\[ a_0 = 5.869 ; \]
\[ Z_0 = 1 ; \]
\[ x_{B1} = \frac{44 (E_1 + \Delta)}{a_0 E_1^2} ; \]
\[ x_{B2} = \frac{44 (E_1 + 2 \Delta)}{a_0 (E_1 + \Delta)^2} ; \]

\[ \text{Dielectric1}(\epsilon) = A E_0^{1.5} \left( f(x) + \frac{1}{2} \left( \frac{E_0}{E_0 + \Delta} \right)^{1.5} f(x_0 s) \right) - B_2 \chi_1 s^2 \log(1 - \chi_1^2) - B_2 \chi_1 s^2 \log(1 - \chi_1^2) - \frac{C_1}{(1 - x^2) - \Delta^2} \cdot \epsilon \omega ; \]

Plot[Re[Dielectric1[\epsilon]], \{\epsilon, 0, 6\}, PlotRange -> All, AxesOrigin -> {1.2, -0.1}, AxesLabel -> {"E (eV)", "\epsilon"}, PlotStyle -> (Black, Thick)]

LogPlot[Im[Dielectric1[\epsilon]], \{\epsilon, 1, 6\}, PlotRange -> All, AxesOrigin -> {1.2, -0.1}, AxesLabel -> {"E (eV)", "\epsilon"}, PlotStyle -> (Black, Thick)]

\[ \epsilon_{MD} [\epsilon] := \text{Dielectric1}[\epsilon] ; \]
Real part of the dielectric function

![Graph of real part of the dielectric function]

Imaginary part of the Dielectric function

![Graph of imaginary part of the dielectric function]
Define functions $A_n$, $B_n$, $Q^{abs}$ and $P^{abs}$ (here $A_n$, $B_n$ are functions $B_n$ above for perpendicular and parallel respectively.)

\[
\begin{align*}
\text{hc} &= 1239.8; \\
\alpha &= .01; \\
\varepsilon_{\text{BG}}[\varepsilon_{\gamma}] &= 12.9; \\
\varepsilon_{\text{SHO}}[\varepsilon_{\gamma}, 0, \gamma] &= \varepsilon_{\text{MDF}}[\varepsilon] - \frac{0.008}{\varepsilon} - \frac{\varepsilon \alpha - 1}{\varepsilon}; \\
m[\varepsilon_{\gamma}, 0, \gamma] &= \text{Sqrt}[\varepsilon_{\text{SHO}}[\varepsilon, 0, \gamma]]; \\
b[n, m, x] &= (m \times \text{BesselJ}[n, x] \times \text{BesselJ}[n - 1, m \times x] - \text{BesselJ}[n - 1, x] \times \text{BesselJ}[n, m \times x]) / (m \times \text{HankelH2}[n, x] \times \text{BesselJ}[n - 1, m \times x] - \text{HankelH2}[n - 1, x] \times \text{BesselJ}[n, m \times x]); \\
a[n, m, x] &= (\text{BesselJ}[n, x] \times (\text{BesselJ}[n - 1, m \times x] - \text{BesselJ}[n + 1, m \times x]) + m \times (\text{BesselJ}[n + 1, x] - \text{BesselJ}[n - 1, x] \times \text{BesselJ}[n, m \times x])) / (2 \times m \times \text{HankelH2}[n, x] \times ((m^2 - 1) \times n \times \text{BesselJ}[n, m \times x]) / (m \times x) \times \text{BesselJ}[n - 1, m \times x]) - 2 \times m \times \text{HankelH2}[n - 1, x] \times \text{BesselJ}[n, m \times x]); \\
Q^{abs}_{\text{Par}}[m, x, NN] &= \text{Abs} \left[ \frac{2}{\pi} \sum_{x} \text{Re}[b[n, m, x]] - \text{Abs}[b[n, m, x]]^2, \{n, -NN, NN, 1]\right] \\
Q^{abs}_{\text{Per}}[m, x, NN] &= \text{Abs} \left[ \frac{2}{\pi} \sum_{x} \text{Re}[a[n, m, x]] - \text{Abs}[a[n, m, x]]^2, \{n, -NN, NN, 1]\right] \\
P^{\text{Index}}[m, x, NN] &= \frac{Q^{abs}_{\text{Par}}[m, x, NN] - Q^{abs}_{\text{Per}}[m, x, NN]}{Q^{abs}_{\text{Par}}[m, x, NN] + Q^{abs}_{\text{Per}}[m, x, NN]}
\end{align*}
\]
To compute absorption efficiencies and polarization index as a function of diameter at excitation energy of 1.55eV.

$$\begin{align*}
\text{NN} &= 5; \\
\varepsilon_0 &= 1.42; \\
\gamma &= 0.025; \\
R_0 &= 25; \\
x_1 &= \frac{hc}{1000}; \\
x_2 &= \frac{hc}{700}; \\
\varepsilon_1 &= 1.55; \\
\text{Plot}\left[\left\{\text{QabsPar} \left[ m[\varepsilon_1, \varepsilon_0, \gamma], \frac{2 \pi}{hc} \frac{\varepsilon_1 d}{2}, \text{NN} \right], \text{QabsPer} \left[ m[\varepsilon_1, \varepsilon_0, \gamma], \frac{2 \pi}{hc} \frac{\varepsilon_1 d}{2}, \text{NN} \right]\right\}, \{d, 0, 340\}, \text{PlotStyle} \to \{(\text{Red, Thick}), (\text{Blue, Thick})\}, \text{AxesOrigin} \to \{x_1, 0\}, \\
\text{AxesLabel} \to \{"\text{Absorption efficiency @ 1.55eV}"\}, \text{AxesLabel} \to \{"\text{d (nm)}", "\text{Ia}"\}, \\
\text{AxesStyle} \to \{(\text{Black, Thick}), (\text{Black, Thick})\}, \text{Ticks} \to \{\{0, 100, 200, 300\}, \text{Automatic}\}\right]\]
\text{Plot}\left[\left\{\text{PIndex} \left[ m[\varepsilon_1, \varepsilon_0, \gamma], \frac{2 \pi}{hc} \frac{\varepsilon_1 d}{2}, \text{NN} \right], \{d, 0, 340\}, \text{PlotStyle} \to \{\text{Black, Thick}\}, \\
\text{AxesOrigin} \to \text{Automatic}, \text{AxesLabel} \to \{"\text{Polarization index @ 1.55eV}"\}, \\
\text{AxesLabel} \to \{"\text{d (nm)}", "\text{Pa}"\}, \text{AxesStyle} \to \{\text{Black, Thick}\}, (\text{Black, Thick})\}, \\
\text{Ticks} \to \{\{0, 100, 200, 300\}, \text{Automatic}\}\right]\]
\text{MM} = \text{Table}\left[\left\{d, \text{PIndex} \left[ m[\varepsilon_1, \varepsilon_0, \gamma], \frac{2 \pi}{hc} \frac{\varepsilon_1 d}{2}, \text{NN} \right]\right\}, \{d, 1, 340, 1\}\right]; \\
\text{Export["PInvd.xls", MM, "XLS"]}
\text{ListLinePlot[MM]}
\end{align*}$$

The diameter dependence of absorption efficiency for a nanowire at excitation energy of 1.55eV;
The diameter dependence of polarization index absorption for a nanowire at excitation energy of 1.55eV;

![Graph showing polarization index as a function of nanowire diameter.](image)

To compute absorption efficiencies and polarization index of absorption as a function of energy for a nanowire with diameter of 275nm.

```math
\text{NN} = 5;
\varepsilon_0 = 1.42;
\gamma = 0.025;
d_0 = 275;
R_0 = d_0 / 2;
x_1 = \hbar c / 1000;
x_2 = \hbar c / 700;
Plot\left[\left\{\text{QabsPar}[m[\varepsilon, \varepsilon_0, \gamma], \frac{2\pi}{\hbar c} e R_0, \text{NN}], \text{QabsPer}[m[\varepsilon, \varepsilon_0, \gamma], \frac{2\pi}{\hbar c} e R_0, \text{NN}]\right\}, \{\varepsilon, x_1, x_2\},\right.
\text{PlotStyle} \rightarrow \{\{\text{Red, Thick}\}, \{\text{Blue, Thick}\}\}, \text{AxesOrigin} \rightarrow \{x_1, 0\},
\text{PlotLabel} \rightarrow 2 R_0 \text{ "nm dia.; Absorption efficiency"}, \text{AxesStyle} \rightarrow \{\{\text{Black, Thick}\}, \{\text{Black, Thick}\}\},
\text{AxesLabel} \rightarrow \{\"\varepsilon \ (\text{eV})", \"P_{\text{abs}}"\}\]
Plot\left[\left\{\text{PIndex}[m[\varepsilon, \varepsilon_0, \gamma], \frac{2\pi}{\hbar c} e R_0, \text{NN}], \{\varepsilon, x_1, x_2\}, \text{PlotStyle} \rightarrow \{\text{Black, Thick}\},\right\}
\text{AxesOrigin} \rightarrow \text{Automatic}, \text{PlotLabel} \rightarrow 2 R_0 \text{ "nm dia.; Polarization index"},
\text{AxesStyle} \rightarrow \{\{\text{Black, Thick}\}, \{\text{Black, Thick}\}\}, \text{AxesLabel} \rightarrow \{\"\varepsilon \ (\text{eV})", \"P_{\text{pa}}"\}\]
\text{KK} = \text{Table}\left[\{\varepsilon, \text{PIndex}[m[\varepsilon, \varepsilon_0, \gamma], \frac{2\pi}{\hbar c} e R_0, \text{NN}]\}, \{\varepsilon, x_1, x_2, 0.01\}\right];
\text{Export["PvsE.xls", KK, "XLS"}]
```
The absorption efficiency for a nanowire with diameter of 275nm;

The polarization index of absorption for a nanowire with diameter of 275nm;