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It is entitled:

Optical and Electrical Characterization of Single Semiconductor Nanowires

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Optical and Electrical Characterization of Single Semiconductor Nanowires

A dissertation submitted to the Graduate School of the University of Cincinnati in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Physics of the McMicken College of Arts and Sciences 2016

by

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Abstract

Strain distribution in the core and the shell of a semiconductor nanowire (NW) and its effect on band structures including carrier recombination dynamics of individual Wurtzite (WZ) In$_{1-x}$Ga$_x$As/InP and Zincblende (ZB) GaAs$_{1-x}$Sb$_x$/InP strained core-shell NWs are investigated using room temperature Raman scattering and transient Rayleigh scattering (TRS) optical spectroscopy techniques. In addition, the electrical transport properties of individual ZB InP NWs are explored using gate-dependent current-voltage (I-V) measurements.

Micro-Raman scattering from individual In$_{1-x}$Ga$_x$As NWs show InAs like TO and GaAs like TO modes with frequencies which are consistent with the 35% Ga concentration determined from the growth parameters. Calculations showed that the In$_{0.65}$Ga$_{0.35}$As core is under compressive strain of 0.26% while the InP shell is in tensile strain of 0.42% in In$_{0.65}$Ga$_{0.35}$As/InP NWs. TRS measurements of single NWs show clear evidence for a strong band resonance in the WZ In$_{0.65}$Ga$_{0.35}$As NW at 0.819 eV which is estimated to be a ~186 meV blue-shift with respect to bulk ZB In$_{0.65}$Ga$_{0.35}$As. Furthermore, both Raman scattering and TRS measurements are on excellent agreement with the band gap shift of In$_{0.65}$Ga$_{0.35}$As/InP core-shell NWs with respect to the core only NW by 46~48 meV which experimentally confirmed the InP shell induced compression of the core. The time decays of the resonance are observed to be long (~125 ps) for core-shell NWs while it is short (~31 ps) for core only NWs consistent with a larger nonradiative recombination rate.
Optical phonon modes of $\text{GaAs}_{1-x}\text{Sb}_x$ are observed to be red-shifted with increasing Antimony fraction in $\text{GaAs}_{1-x}\text{Sb}_x$ NWs which can be expected in an alloy with increasing concentration of a heavier atom in the lattice. Using TRS measurements, the $\text{GaAs}_{0.71}\text{Sb}_{0.29}$ band gap for the core-shell NW is observed to be reduced by 0.04 eV with respect to the core only NW because of the tensile strain in the core. Raman experiments show a blue-shift of the InP phonons and a red-shift of the $\text{GaAs}_{1-x}\text{Sb}_x$ phonons in individual $\text{GaAs}_{0.71}\text{Sb}_{0.29}/\text{InP}$ NWs, which is consistent with the tensile core strain inferred from TRS results. The recombination life times in $\text{GaAs}_{0.71}\text{Sb}_{0.29}$, $\text{GaAs}_{0.71}\text{Sb}_{0.29}/\text{InP}$ NWs are found to be 31 ps and 127 ps respectively reflecting the effectiveness of the InP shell surface passivation.

Individual InP NW field effect transistors are fabricated using photolithography to investigate the electrical transport properties of InP NWs. Gate-dependent I-V plots showed that the InP NWs are n-type and displayed typical non-Ohmic behavior due to the contact resistance between NW and metal electrodes. Carrier mobility determined for the InP NWs is as high as 655 cm$^2$/(V.s) for the carrier density of $4.08 \times 10^{17}$ cm$^{-3}$ which is comparable to n-type InP thin film materials with similar carrier densities and thus demonstrates the high quality of the NWs. An equivalent circuit model of the metal-semiconductor-metal structure is used to extract the carrier density and mobility of the NW as $1.00 \times 10^{17}$ cm$^{-3}$ and 511 cm$^2$/(V.s), This model makes it possible to determine the barrier heights of the NW device while providing a good agreement with the experimental results.
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Chapter 1

Introduction

The semiconductor industry has become a multibillion dollar industry in the world within the past few decades. The industry serves as a key driver for economic growth and indicator of technological progress. Indeed, semiconductors are the building blocks of most all consumer electronics, including cell phones, televisions, MP3 players, automobiles and computers, etc. in use every day use by individuals of every age.

1.1 Semiconductors and their Crystal Structures

1.1.1 Semiconductors

A semiconductor is a solid material whose electrical conductivity lies between a conductor and an insulator. Conductors, such as aluminum, have high conductivities, typically from $10^4 \, \Omega^{-1} \text{m}^{-1}$ to $10^7 \, \Omega^{-1} \text{m}^{-1}$ and insulators, such as glass, have very low conductivities, from $10^{-18} \, \Omega^{-1} \text{m}^{-1}$ to $10^{-8} \, \Omega^{-1} \text{m}^{-1}$. The conductivities of semiconductors are between these extremes.

Silicon (Si) is one of the most widely used semiconductor materials today because of its very low defect density and large abundance on the earth. However, certain other group IV elements of the periodic table (Germanium, Tin) as well as binary III-V compound semiconductors (GaAs, InP, GaN, InAs, etc.) are becoming more important in semiconductor industry because of their superior properties.
In addition, ternary compound semiconductors, from mixing the binaries (In$_x$Ga$_{1-x}$As, In$_x$Ga$_{1-x}$P, GaAs$_x$Sb$_{1-x}$, etc.) are technologically very important because of their adjustable lattice parameter and the energy gap by a suitable choice of composition. Figure 1 shows the band gap energies of most widely used binary semiconductors vary with their lattice constants. From mixing two binaries appropriately (e.g. 65% of InAs with 35% of GaAs), one can easily tune the band gap (or the lattice constant) of the ternary semiconductor (In$_{0.65}$Ga$_{0.35}$As). The band gap energy (or energy gap) of a semiconductor is described in more detail below.

![Figure 1: The graph of some commonly used binary semiconductors with their energy band gap versus the lattice constant and information about their band type [1]](image)

In electronics, the usefulness of semiconductors stems from the unique atomic structure that allows their conductivity to be controlled with an electric field, magnetic field, light or heat, or by the addition of impurities.
From the quantum mechanical description of solids, if N identical atoms are brought together to form a lattice, the discrete electronic energy levels of an isolated atom get split into a group of N distinct levels. For a macroscopic sample, N is so large ($\sim 10^{23}$) that the energy spacing between these levels is extremely small and the levels in a particular group are essentially continuous. The group is then called an energy band. The bands in solids may be filled, partially filled or empty according to their atomic levels. The lowest energy band that is not completely filled is called the conduction band (CB). The highest energy band that has at least one electron at absolute zero is the valence band (VB). These bands are separated by energy gap ($E_g$). Figure 2 shows the discrete energy level of a single atom (left diagram) and the band of energy levels for N atoms in a crystal (right diagram).

![Figure 2: Shell theory of an atom (left diagram) and band theory of a solid composed of N identical atoms (right diagram)](image)

In conductors, the valence band and the conduction band are the same. For insulators, the valence band is filled and the conduction band is separated from it by a relatively large energy gap. In semiconductors, the valence band is also filled, but the energy gap is small compared to
the insulators. Figure 3 shows the band structures of the three types of materials: conductor (metal), semiconductor and insulator.

Electrons in the conduction band can participate in the conduction process, because there are many unfilled energy levels nearby. Hence, the large number of mobile electrons in conductors causes their high conductivity. But, both semiconductors and insulators are quite poor conductors at absolute zero temperature, because they have empty conduction bands and filled valence bands. However, as the semiconducting materials exhibit moderate band-gaps (1 to 3 eV or less), it is possible to promote a valence band electron to the conduction band through thermal, optical or other suitable excitation process in the semiconductor material [2]. Once an electron is excited to the conduction band of the semiconductor, there is an electron vacancy in the valence band. This vacancy, known as a hole may be filled by a neighboring electron, which results in a shift of the hole from one crystal site to another. Hence, the current conduction in a semiconductor occurs via free electrons and holes, collectively known as charged carriers. In an intrinsic (pure)
semiconductor, there exist an equal number of free electrons and holes. Electrical conduction in intrinsic semiconductors is generally weak at room temperature.

1.1.2 Properties of Semiconductors

Semiconductors have a number of interesting and unique properties which makes them useful for many applications. Some of these properties are described below.

One can easily control the electrical conductivity of a semiconductor by a technique called doping. Doping a semiconductor with a small amount of impurity atoms greatly increases the number of mobile carriers within the semiconductor. Hence, it increases the electrical conductivity of the semiconductor. For example, the addition of about 10 atoms of boron (known as a dopant) per million atoms of silicon can increase its electrical conductivity a thousand fold \[3\]. By choosing a suitable dopant material (group III or group V element) one can make p-type or n-type semiconductors in a group IV material. Heterojunctions occur when two differently doped (p-doped and n-doped) semiconducting materials are joined together (p-n junction) \[4\]. This results in an exchange of electrons and holes between the differently doped semiconducting materials and ultimately makes an electric field near the junction. This phenomenon is utilized to make several electronic devices such as diodes, transistors and integrated circuits, etc.

When a semiconductor is illuminated with light, it can produce electron-hole pairs (Excitons), because of the excitation (promotion) of the valence band electrons to the conduction band by absorption of photons. The negatively charged electron and positively charged hole form a hydrogenic-like state by the Coulomb interaction to form an exciton, and it can transport energy by moving through the semiconductor. Using the equation for the relative motion of the exciton
as explained by N. Peyghambarian et al. [11] and P. Y. Yu et al. [12], the exciton Bohr radius \(\alpha^B\) and its binding energy \(E_b\) can be calculated.

\[
\alpha^B = \frac{\varepsilon \hbar^2}{m_e e^2} \quad \text{and} \quad E_b = \frac{\hbar^2}{2m_e (\alpha^B)^2}
\]

where, \(m_e\) is the electron-hole reduced mass and \(\varepsilon\) is the background dielectric constant.

When these excitons are created in a p-n junction the electrons and holes can be separated by the electric field and the charges collected at the electrodes and can be used to produce a current. Scientists used this property of semiconductors to develop solar cells and photodetectors [5].

![Energy band diagram of (a) direct band gap and (b) an indirect band gap semiconductor](image)

Figure 4: Energy band diagram of a (a) direct band gap and (b) an indirect band gap semiconductor [6]

Semiconductors can have a direct or indirect band gap. Figure 4 shows the energy band diagrams of a direct band gap and an indirect band gap semiconductor. As shown in the figure, the lowest energy of the CB and the highest energy of the VB are at the same position in k space for a direct
band gap semiconductor. Hence, when exciting an electron in the VB to the CB or recombining the excited electron in the CB with a hole in the VB (both carriers annihilating each other), the momentum of the electron remains the same. These electron transitions are known as direct transitions and it can absorb or emit photon (instead of producing heat via a phonon) upon excitation or recombination. This property had led towards the development of lasers, LEDs [5], fluorescent quantum dots [4] and many other applications.

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 have the same position in k space (momentum space). Hence, it is impossible to excite an electron from VB maximum to CB minimum or vice versa without changing its momentum. This kind of indirect transitions can only be possible with the absorption or emission of phonon (lattice vibration) to conserve the momentum. Figure 1 shows some commonly used direct and indirect band gap binary semiconductors.

1.1.3 Crystal Structures

Most of the semiconductors have cubic (diamond and Zincblende) or hexagonal (Wurtzite) crystal structures. Compound semiconductors such as GaAs, GaSb, InAs and InP have a crystal structure that is similar to that of diamond structure. Although this structure has tetrahedral coordination, each atom's nearest neighbors consist of four atoms of the opposite type positioned like the four vertices of a regular tetrahedron. This structure is referred to as the Zincblende (ZB) lattice. Figure 5 shows a Zincblende unit cell.
Figure 5: A Zincblende unit cell crustal structure [7]. Note that the yellow and blue spheres indicate two different types of atoms in the structure (e.g. yellow spheres are Indium atoms while the blue spheres are Phosphorus atoms in ZB InP crystal).

The third common crystal structure is the hexagonal structure also referred to as the Wurtzite (WZ) crystal structure. This structure is formed by two interpenetrating hexagonal close packed crystal structures with two different types of atoms (e.g. Gallium and Nitrogen hexagonal close packed crystal structures combine to form WZ GaN crystal).

Many II-VI compounds like ZnS occur in both the Wurtzite and Zincblende structures. In addition, AgI, ZnO, CdS, CdSe, GaN, AlN and BN [8] can be found in the WZ structure. In most of these compounds, Wurtzite is not the favored form of the bulk crystal, but the structure can be favored in some nanocrystal forms of the material [8]. For instance, InP NWs have recently been synthesized with both ZB and WZ structures [9, 10]. Figure 6 shows a Wurtzite unit cell and its crystal structure.
Figure 6: Left: Wurtzite unit cell. Right: Wurtzite crystal structure [8]. Note that the yellow and blue spheres indicate two different types of atoms in the structure (e.g. yellow spheres are Indium atoms while the blue spheres are Phosphorus atoms in WZ InP crystal).

1.1.4 Band Structures

The nanowire materials discussed in this dissertation are binary and ternary III-V semiconductors including Gallium-arsenide-antimonide (GaAs$_x$Sb$_{1-x}$), Indium-phosphide (InP) with ZB symmetry and Indium-gallium-arsenide (In$_x$Ga$_{1-x}$As), Indium-phosphide (InP) with WZ symmetry. All of these materials are direct-band gap semiconductors.

The details of the electronic band structure of a material can be explained as follows.

The electron in the conduction band of the material has s-type wave function which has total angular momentum, $J=\frac{1}{2}$ (orbital angular momentum $l=0$, spin momentum $s=\frac{1}{2}$ and $J= L+S$) resulting a two-fold degeneracy (spin angular momentum, $m_J = \pm 1/2$) at $k=0$. On the other hand, the valence bands are formed from the three atomic p orbitals. Due to the spin-orbit interaction,
the valence band splits into heavy hole and light hole bands as shown in Figure 7(a). As a result, one of the light hole bands is pushed to a higher energy level by an amount $E_{SO}$ (split-off band energy). For p-type wave function of the hole in the valence band has total angular momentum, $J=\frac{3}{2}$ and $\frac{1}{2}$ (orbital angular momentum $l=1$, spin momentum $s=\frac{1}{2}$ and $J=L+S$). For $J=3/2$, the spin angular momentum ($m_j$) can take $-3/2$, $-1/2$, $1/2$ and $3/2$. The heavy hole has spin angular momentum, $m_{j_{\text{hh}}} = \pm \frac{3}{2}$ and light hole has $m_{j_{\text{lh}}} = \pm \frac{1}{2}$ (corresponding to $J=3/2$) (Figure 7(a)). For $J=1/2$, the spin angular momentum ($m_j$) can take values of $-1/2$ and $1/2$. The split off band hole has spin angular momentum, $m_{j_{\text{so}}} = \pm \frac{1}{2}$ (corresponding to $J=1/2$).

Figure 7: The schematic diagram of the band structure of (a) InP with cubic ZB symmetry and (b) InP with hexagonal WZ symmetry at the center Brillion zone
As described in the previous section, since the WZ structure is formed by two interpenetrating hexagonal close packed crystal structures, the combination of hexagonal crystal field potential arising from the nearest neighbor atoms and spin orbit coupling, the valence band of the crystal structure is split into three different bands called A, B and C – hole bands at the \( \Gamma \) point. For instance, Figure 7(b) shows the schematic diagram of the band structure of InP with WZ symmetry at the zone center.

### 1.2 Nanoscale Semiconductor Devices and Nanostructures

Faster, cheaper and smaller semiconductors will be a benefit to all industries and will lead to technological innovation as well as new products, economic growth and productivity gains. Because of this great demand and competition of making more compact and powerful semiconductor devices, there is a growing interest in the development of nanoscale semiconductor devices that could enable new functions and greatly enhanced their performance. Among these nanoscale structures, one-dimensional (1D) nanostructures, such as nanowires (NWs) are ideal building blocks for nanoscale optoelectronic devices such as field effect transistors (FETs), nano infrared sensors, biosensors, nano lasers and solar cells, etc., because of their interesting optoelectronic properties and efficient charge transport.

The diameter of these semiconductor nanowires ranges from 20 nm to 200 nm while their length is several micrometers. As described in previous section, an exciton can transport energy through a semiconductor by moving through the material. In a bulk semiconductor, it can move freely in all three dimensions (X, Y and Z directions). But, in a NW, if the diameter of the NW is less than the exciton Bohr radius, the exciton can only move freely along the length of the NW (they are confined in the radial direction). In principle, this could change the energy band structure of the
nanowire and the quantum confinement effects could be observed in the emission or excitation spectrum. Although these confinement effects cannot be observed when the exciton Bohr radius ($a_B=11.3$ nm for GaAs [13][14]) is much less than the nanowire diameter, still the charge carriers are somewhat spatially restricted to move in the direction perpendicular to the NW axis, because of the huge surface-to-volume ratio of the nanowire. Therefore, the nanowire behavior is expected to be different from bulk materials. For example, absorption of light by a nanowire when it is excited parallel to the nanowire is different when it excited perpendicular to the NW long axis [15]. This polarization anisotropy of the nanowire will be discussed in more detail in Chapter 2 in the thesis. Also, the surface states, defects, structural inhomogeneities can strongly impact the optoelectronic properties of the nanowires.

1.3 Nanowires and their Heterostructures

1.3.1 Nanowire Growth

Semiconductor NWs are grown by both metal organic chemical vapor deposition (MOCVD) and molecular beam epitaxial (MBE) techniques. The NWs used for our experimental study are grown by our collaborators at Australian National University (Prof. C. Jagadish’s research group) by using the vapor-liquid-solid method in a MOCVD reactor. In this method gold catalyst nanoparticles are dispersed on the substrate and the semiconductor constituents are provided by metal-organic vapor-phase sources. Then the reactants (NW materials in the form of gas) form the liquid droplets with the metal catalyst nanoparticles and become supersaturated and a nucleation event occurs to initiate solid crystalline NW growth [16]. The size of the catalyst particle controls the diameter of the NW (Figure 9) and the length of the NW is proportional to
the growth time. Figure 8 shows the schematic diagram of the VLS growth process used for InP NW growth and the details of the growth technique are explained below.

![Figure 8: Schematic diagram of the VLS growth process used for InP NW growth](image)

An InP (111)B substrate is chosen as the growth substrate in order to grow the InP NWs perpendicularly to the substrate (along the (111) direction). First the gold catalyst nanoparticles are dispersed on the substrate and the substrate is heated to 600 ºC to remove any surface contaminants. Then the temperature is reduced to the growth temperature (400 ºC) and the semiconductor materials (Phosphine (PH₃) and Trimethylindium (TMIn)) are provided as gas phase into the chamber. When the gold nanoparticles are heated on the substrate, it could form a eutectic alloy with it, which would be Au-In. The most important growth parameters in this process are the growth temperature and the V/III ratio. Recent studies have shown that the higher V/III ratio leads to WZ dominant NWs and lower V/III ratios tends to grow ZB dominant NWs [17]. The V/III ratios used in this InP NW growth are 350 and 700 in order to grow ZB InP NWs and WZ InP NWs respectively [17].
With further precursor supply, the gold nanoparticle becomes supersaturated and starts precipitating material at the particle substrate interface [18]. The continued precipitation of III-V pairs at the interface with continued precursor supply ensures the nanowire growth as shown in Figure 8 (right). The growth rate of the NW can be controlled by the temperature and the amount of precursor gasses. Figure 9 shows the scanning electron micrograph (SEM) images of InP NWs grown by VLS technique with different V/III ratios and different catalyst sizes. The axial growth of the NW mainly arises from the precursors impinging on the Au particle. In addition, radial growth of the NW, which is a major disadvantage in the NW growth (tapered NWs - Figure 9 (c)) can be observed in this process. By supplying additional gasses like Silane (SiH₄) and Diethylzinc ((C₂H₅)₂Zn), it is possible to form doped n-type and p-type InP NWs respectively.

Figure 9: Scanning electron micrograph (SEM) images of InP NWs grown by VLS method as a function of V/III ratio and catalyst size. The scale bars are 2µm [17].
1.3.2 Nanowire Heterostructures

The development of NW growth technology has enabled scientists to control the materials at different locations along and across the NW. It is especially useful when fabricating nanoscale heterostructures (combination of two or more semiconductor materials within the same NW structure) during the synthesis. These heterostructures provide complex and functional building blocks for nanotechnology.

There are two basic heterostructures known as axial and radial heterostructures. In axial heterostructures, the heterointerface is perpendicular to the wire axis and in radial heterostructures (also known as core-shell heterostructures), the heterointerface is parallel to the wire axis. Figure 10 shows the schematic illustrations of (a) axial and (b) radial heterostructure NWs. Axial heterostructured NWs are fabricated by switching the precursor gas flows to the desired material. When fabricating the radial heterostructure NWs, the core is grown in usual way followed by the shell which is grown at a different temperature to facilitate surface growth. The details of the growth technique can be found elsewhere [19--21].

![Figure 10: Schematic illustrations of (a) axial and (b) radial heterostructured NWs. The dark blue and orange colors each represent a different type of III–V compound-semiconductor material (e.g. dark blue: GaAs and orange: InGaAs).](image)
There are a number of important reasons to focus on the radial heterostructured NWs. In particular, surface states can have a number of deleterious effects on device performance. These include [22],

(i) band bending induced by surface charge that could cause complete depletion of the NW;
(ii) a high density of surface states will mitigate the effect of an externally applied potential;
(iii) surface states can act as sinks for minority carriers, degrading the performance of optoelectronic devices and other minority carrier devices such as bipolar transistors;
(iv) the potential fluctuations associated with trapped charge at an interface can reduce carrier mobility.

Many of the above negative consequences can be avoided by passivating the nanowire surface at the time of synthesis, i.e. a core-shell heterostructured NW. In addition, because of the ability of controlling the band structure of the materials within the heterostructure, the optical and electronic properties of the NW can be adjusted according to the needs of the application. Hence, investigating the properties of the NW heterostructures will be profitable for future applications. In my research, properties of two of the core-shell heterostructure NWs (In$_x$Ga$_{1-x}$As/InP and GaAs$_x$Sb$_{1-x}$/InP NWs) were investigated and are discussed in more detail in Chapter 3 and Chapter 4 of the thesis.

1.4 Thesis Outline

This dissertation contains five chapters directed towards understanding the optical and electrical transport properties of single semiconductor NWs. We begin the first chapter (this chapter) with an introduction of bulk semiconductor materials by giving a brief summary of its properties,
electronic band structures and crystal structures. Then the NWs and their heterostructures are discussed with nanoscale semiconductor devices and NW growth techniques.

The second chapter is dedicated to our experimental techniques of investigating single semiconductor NWs. Specifically, the Raman and Transient Rayleigh scattering spectroscopy techniques and electrical characterization technique are described including the experimental setups, single NW device fabrication using photolithography and the circuit setup for studying transport properties of individual NW FETs.

In Chapter 3, we quantitatively study the hydrostatic strain of the core and the shell in the infrared WZ $\text{In}_{1-x}\text{Ga}_x\text{As}/\text{InP}$ strained core-shell NWs and its modified energy gap due to the shell-induced stress, using room temperature Raman and Transient Rayleigh scattering (TRS) spectroscopy techniques. These measurements provide a quantitative understanding of the band gap of WZ $\text{In}_{1-x}\text{Ga}_x\text{As}$ NWs which is still unclear to Physicists due to the technical limitations of doing research in the infrared wavelength region using the traditional spectroscopic techniques. The TRS spectroscopy technique which we used to probe the band structure of single NWs, uses the polarization anisotropy of the NW to optically probe the change in polarized reflectance of the NW due to the modulation of the dielectric function of the NW induced by a second strong laser beam (pump beam). Since the derivative like features can be observed at the energy states of its Rayleigh spectrum, TRS spectroscopy can directly probe the electronic band structure of single NWs. Furthermore, the experimental results from the two independent Raman scattering and TRS spectroscopy measurements are compared. In addition, the carrier life times of the $\text{In}_{1-x}\text{Ga}_x\text{As}$ NWs are studied.
Ga\textsubscript{x}As NWs are investigated from TRS measurements, since the Rayleigh spectrum in time after excitation reflects the dynamics of carriers of the NW.

Similarly, we have investigated the strain distribution, band gaps and carrier life times of the mid infrared ZB GaAs\textsubscript{1-x}Sb\textsubscript{x}/InP strained core-shell NWs using the Raman and TRS spectroscopy techniques in Chapter 4.

The last chapter of the thesis is devoted to characterizing the electrical transport properties of individual n-type InP (ZB) NWs. It introduces the basic transport theory for individual NW FETs such as the metal-semiconductor-metal (MSM) structure, controlling the gate in MSM structure and standard transistor expressions. Then the electrical characterization of InP NWs is studied by using the gate-dependent I-V measurements. Furthermore, the MSM modeling done by using Mathematica to fit the experimental dark current-voltage data is discussed to extract the electrical transport properties of the NWs such as carrier density, carrier mobility and Schottky barrier heights at the contacts of the device. Then these results from the theoretical MSM model are compared with the experimental gate-dependent I-V measurements.

The appendices include details of the Ammonium polysulfide etching process that we have been used in fabricating the NW FET devices, the Mathematica code used for the MSM model as well as the important parameters of the InP semiconductor crystals which we have used in the MSM model.
References:


[5] https://www.researchgate.net/post/What_are_the_most_basic_features_of_semiconductors


Rapid developments in techniques for growing semiconductor NWs in recent years have resulted in new methods for optimization of the growth of ternary semiconductor NW heterostructures. The control of composition and strain of these ternary semiconductor NW heterostructures provides a crucial means to control their optical and electronic properties which is essential for new applications.

In particular, the lattice mismatch between the two materials of the core and the shell in radial heterostuctured NWs, changes the band structure of its core due to the shell-induced stress (e.g. compressive stress) and likewise it changes the band structure of its shell due to the core-induced stress (tensile stress). Not only the lattice mismatch but also the geometrical parameters (core diameter and shell thickness) of the NW can be used to tune these strains inside the NW [1]. Investigating the strain engineering of the band structure of ternary semiconductor NW radial heterostructures is important to optimize them for a wide variety of novel nanodevices.

Therefore, one of the main objectives of our research is to study the strains in particular ternary semiconductor NW radial heterosstructures (In$_{1-x}$Ga$_x$As/InP and GaAs$_{1-x}$Sb$_x$/InP core-shell NWs) with a specific core diameter and shell thickness and examine the consequent modification of the electronic properties of these NWs due to the strains. Raman scattering spectroscopy measurements are used in our research to measure the strain and thus predict the change in the
The second objective of our research is to study the electrical transport properties of individual NWs (particularly, InP NWs) by fabricating NW Field Effect Transistors (FETs). In order to study these transport properties of single NWs, one has to fabricate metal contact pads at each end of the NW. Modern photolithography technique is used to fabricate these nanodevices and various important properties including carrier density, carrier mobility, Schottky barrier heights of the devices are studied. Obviously studying these electrical properties is crucial for NW characterization and electronic device applications.

2.1 Sample Preparation

A p-type Silicon substrate capped with 300 nm of silicon oxide layer is used as the sample substrate for our experiments. The oxide layer provides a perfect insulating layer for device fabrication and the conductive silicon is used as a back gate for the NW FETs.

It is very important to clean the substrate properly before dispersing the NWs on it. In order to remove any dust particles, organic and inorganic impurities on the substrate, it is cleaned by Acetone (2 min), Methanol (2 min) and Isopropyl alcohol (2 min) followed by a rinse using distilled water at room temperature. Then the substrate is dried using nitrogen gas.

In our Transient Rayleigh Scattering (TRS) experiment, the NWs are dispersed onto a patterned Silicon substrate. The Aluminium pattern on the Silicon substrate helps to locate a particular NW
when repeating measurements on the same nanowire. It is created on the Si substrate by using the photolithography process which is discussed in section 2.4.1.

For our Raman scattering measurements, NWs are dispersed to the center of a small half-sphere (8 mm in diameter) of high index glass (refractive index ~2) which is used as a Solid Immersion Lens (SIL). This eliminates the use of a Silicon substrate which removes the problem of interference between the Silicon and InP optic phonon energies which are both very close to 300 cm\(^{-1}\). Furthermore, the SIL enhances both the spatial resolution and numerical aperture of the optics. The same cleaning procedure which has described earlier is used to clean the SIL before dispersing the NWs. The SIL is placed face down into a vacuum chuck so that the wires being studied can be in either vacuum or nitrogen which eliminates the potential for photo-oxidation of the NWs which has been previously observed [2].

There are two methods for dispersing NWs onto the substrate. The first, mechanical dispersion, is done by gently sliding a piece of growth substrate (a small chip which has grown NWs) on top of the bare Si substrate. In the sonication method, a small growth substrate is placed in a small test tube with few (1 to 3) drops of clean methanol. Next, it is placed in an ultrasonic water bath for few (3 to 5) minutes. Then a small drop of the solution containing NWs is dispersed on the cleaned substrate using a micro pipette. Finally, the sample is dried using the nitrogen gun. Since this method results in a much lower density of NWs, the process may need to be repeated until some NWs are observed on the substrate. But this method is crucial in order to obtain isolated single NWs for device fabrication.
Mechanical dispersion method is used when making the samples for our TRS experiment while the sonication method is used to disperse the NWs underneath the SIL for Raman scattering experiment.

2.2 Raman Scattering Spectroscopy

2.2.1 Introduction

Atoms in a crystal vibrate due to their thermal energy and these vibrations are expressed in terms of a travelling wave solution because of the periodicity in the system. In fact, one can derive a dispersion curve (energy of vibration vs. wave vector) in a manner similar to the one used for band structure of electrons [3]. These lattice vibrations are known as phonons [3]. For instance, Figure 11 shows the phonon dispersion of GaAs, a III-V compound semiconductor material. Optical phonons have higher energies while the acoustic phonons have lower energies [4] as shown in Figure 11.

![Figure 11: The phonon dispersion bulk GaAs](image)
When photons from a laser are scattered from a crystal with an emission or absorption of phonons, the energy shifts of the photons are small. Usually the photon wave vectors are very small compared to the size of the Brillouin zone, so that the interactions are only with zone center phonons (acoustic or optical). Specifically, the interaction with optical phonons is called Raman scattering [5]. The frequency of the Raman signal (scattered photon) can be scattered to higher or lower frequencies known as anti-Stokes and Stokes shifts depending on the absorption or emission of a phonon.

These optical modes carry a polarization dipole moment and they include transverse optical (TO) modes and longitudinal optical (LO) modes depending on the direction of vibration. Since the Raman scattering spectroscopy directly couples to the polarization of the light, it provides a powerful technique to experimentally probe the frequency of phonons, crystal orientation, lattice (phonon) temperature and strain (or stress) of individual semiconductor NWs [6]. Further information regarding Raman spectroscopy can be found in standard text books and articles [5--8].

Due to the lattice mismatch between the two materials produces strain in the crystal which according to the deformation potential theory produces perturbation in the electronic states [9]. Therefore, Raman scattering by phonons can be used to quantify the strains (shell-induced strain and core-induced strain) and predict the change in electronic band structure using the deformation potential theory in radial heretosructured NWs. Further discussion can be found in Chapter 3.
2.2.2 Raman Scattering Experimental Setup

Figure 12 shows the micro-Raman scattering experiment setup which we used to map the phonon energies of individual radial heterostuctured NWs.

![Raman scattering experimental setup](image)

Figure 12: Raman scattering experimental setup

The continuous wave 514.5 nm Argon laser is used as the exciting source when analyzing the $\text{In}_{1-x}\text{Ga}_x\text{As} /\text{InP}$ core-shell NWs while a 632.8 nm He-Ne laser is used as the exciting source when analyzing the $\text{GaAs}_x\text{Sb}_{1-x}/\text{InP}$ core-shell NWs, ZB InP NWs and WZ InP NWs. In order to avoid any significant local heating of the sample, a low laser power of 300 $\mu$W is maintained during the experiment. As described in section 2.1, NWs are dispersed underneath the SIL. This SIL works as the window of the Nitrogen gas filled sample container. Therefore, the NWs are prevented from being oxidized. The sample container is mounted on a voltage-controlled translational stage to scan the NW with respect to the laser spot. A 100X microscopic objective
with numerical aperture 0.7 is used to locate the single NW with spot size ~1 μm. The backscattered light is collected by the same objective and dispersed onto a liquid nitrogen cooled CCD (charge-coupled device), through a DILOR XY spectrometer (1800l/mm, 800 mm focal length).

Since different optical phonon response intensities are predicted for different polarizations of the incident light and the scattered light [10], the Raman response from single NW at four different polarization configurations denoted as $X(z,z)\overline{X}$, $X(y,y)\overline{X}$, $X(z,y)\overline{X}$ and $X(y,z)\overline{X}$ is monitored in the experiment.

![Figure 13: A schematic diagram of the polarization configurations used for Raman scattering](image)

Figure 13 shows the schematic diagram of the sample geometry used in our experimental setup. The X, Y, and Z are the laboratory coordinates and x, y and z are the sample coordinates. The NW-long axis is along the z-axis as shown in Figure 13. The incoming laser beam is along X-axis and the scattered light direction is in the opposite direction ($\overline{X}$). The NW is thus perpendicular to the direction of the incident and scattered light. Polarizations of the incident and scattered light are measured with respect to the nanowire long axis. For instance, $X(z,z)\overline{X}$ means
both excitation laser and backscattered light have polarizations parallel to the NW long axis and $X(z,y)\bar{X}$ means that the excitation laser polarization is parallel to the nanowire and the backscattered light is polarized perpendicular to the NW long axis.

Polarizing optics, Glan-Thompson linear polarizers and a half wave plate play an important role in the experimental setup. The Glan-Thompson linear polarizer allows linearly polarized light (having a definite direction and orientation with respect to the optical axis) to pass through it. A half wave plate introduces a $\pi$ phase change between two orthogonal electric field components and rotates the linearly polarized light incident with an angle $\theta$ to its optical axis by twice as much.

The incident light polarization with respect to the NW long axis can be rotated in the YZ-plane by rotating the NW under microscope around the optical axis (X) while keeping the polarization of excitation as fixed by a linear polarizer. In order to control the polarization of the scattered light (Raman response) a half-wave plate (to rotate the polarization) and a linear polarizer (to filter the undesired polarizations) are employed in the scattered laser beam path (Figure 12). All the experiments are carried out at room temperature.

2.3 Transient Rayleigh Scattering Spectroscopy

Scientists have been using photoluminescence (PL) spectroscopy techniques to probe the ground state energies and photoluminescence excitation (PLE) and photocurrent techniques to probe the excited states which are coupled to the ground states in the band structure of NWs for decades. These techniques are powerful and applicable to the NWs whose ground state has an extremely
strong photoluminescence emission and whose excited states are strongly coupled to the ground state [11]. Because of these limitations as well as the technical limitations of performing the experiment in the infrared wavelength region using the traditional spectroscopic techniques, a new powerful technique which can directly probe the band structure of the NW is extremely important.

Reflectance and absorption measurements have been used to study the electronic band structure of bulk semiconductors for a long time. Since the complex index of refraction (or complex dielectric function) reflects the internal electronic structure of the material, the reflectance (depends on the real part of the complex index of refraction) or absorption spectra (depends on the imaginary part of the complex index of refraction) is used to probe the electronic states of the material. Unlike the bulk material, the scattering of light by the NW depends on both index of refraction as well as the absorption coefficient of the material. Also, it strongly depends on the polarization [12]. Using these unique characteristics of the scattering of light by the NW, a new powerful technique, Transient Rayleigh Scattering (TRS) spectroscopy is introduced to probe the electronic band structure of single semiconductor NWs [12]. In the TRS experiment, a laser excitation is used to pump carriers to the VB and CB. These photo-excited electrons and holes are thermalized by carrier-carrier scattering and lose energy by carrier-phonon scattering [13] and move down to the bottom of the CB. Then they recombine with the holes in the VB. In this process photons are emitted with approximately the same energy as band gap [14]. The TRS (pump-probe) measurement can directly probe the electronic band structure of single semiconductor NWs at both room and low temperatures with high energy resolution [11]. Furthermore, since the complex index of refraction is sensitive to carrier density and
temperature, TRS spectroscopy technique can be used to probe the carrier dynamics in single semiconductor NWs [12, 15].

In this thesis, we used TRS spectroscopy technique to directly probe the electronic band structure of individual radial heterostructured NWs.

2.3.1 Rayleigh Scattering

Since the diameter of the NW is much smaller than the wavelength of the incident light, the light scattering by the NW is in the Rayleigh scattering regime. As described in the introduction, Raleigh scattering is dependent on the complex index of refraction of equivalently the complex dielectric function. Further details of the Raleigh scattering can be found elsewhere [16--18].

More importantly, the one-dimensional nature of NWs means that in most cases they scatter light polarized parallel to the NW axis very efficiently because of the large dielectric contrast between the NW and the vacuum [11]. This polarization anisotropy is used to discriminate the small amount of light scattered by the NW from the huge background (unpolarized scattered light from the substrate) when obtaining the Rayleigh spectrum. As shown in Figure 15, a photo-elastic modulator (PEM) is used to modulate the polarization of the light incident on the NW between parallel and perpendicular to the NW long axis at a certain frequency. Therefore, a small AC signal corresponding to the backscattered light from the NW is superposed on top of a large DC signal (from background) can be obtained in the photocurrent signal of the detector. Using a lock-in amplifier referenced to the frequency of the PEM, the amplitude of the alternating current (AC) signal can be filtered out from the DC background with high sensitivity. Although, in principle, the Rayleigh scattering efficiency is sensitive to the internal electronic structure of
semiconductor NWs, it is buried in the noise in the experimental Rayleigh scattering intensity spectrum [11]. Therefore, photomodulation of the Rayleigh scattering cross section by a second intense laser beam (pump beam) is introduced to extract the electronic structure of single semiconductor NW in the spectrum. This intense pump beam modulates the dielectric function by injecting photo-carryers to the NW. Because of the modulation of the electronic energies, the resultant spectrum has derivative-like features around the electronic states of the semiconductor NW [11].

![Figure 14: Time evolution of the photo-excited carrier distribution after the pump beam is on](image)

When the incident photon energy (probe energy) is smaller than the band gap of the material, the VB electrons cannot be promoted to the CB states because the energy of the photon is not sufficient. Hence the absorption coefficient is zero. But, if the photon energy is larger than the energy gap, VB electrons can be excited to higher CB states and the absorption coefficient becomes positive. However, this absorption coefficient can become negative (gain), if the lower level occupation probability is smaller than the higher level. As shown in Figure 14, the occupation probability of the lower states of the CB is very small just after the pump beam is on (at $t = 0$), thus the absorption coefficient is negative near the band gap at $t = 0$. Therefore, the absorption coefficient can be negative or positive near the band edge as the pump beam is on or
off respectively. Since the TRS response from the NW is a function of absorption coefficient and the difference of Rayleigh scattering efficiency ($\Delta R'$) when the pump beam is on and off of the NW is measured, $\Delta R'$ is a direct reflection of the NW band structure. This derivative-like structure becomes very sharp at late times (at $t = t_2$) when the carrier densities are less at lower states of the CB (as shown in Figure 14). Furthermore, the zero crossing point of the TRS energy spectrum at late time is a direct measure of the direct band to band transition energy.

### 2.3.2 TRS Experimental Setup

![TRS Experimental Setup](image.png)

Figure 15: TRS Experimental Setup
Fianium supercontinuum laser with 20 MHz repetition rate is used as the exciting source in the TRS experiment. As described in section 2.1, NWs are dispersed on a small piece of patterned Si substrate (5 mm x 5 mm). Then the sample is mounted on a Copper sample holder using Silver-paste, in order to place it inside the optical cryostat. During the experiment the cryostat is maintained under high vacuum (~10\(^{-6}\) Torr) to prevent the NWs from being oxidized. In addition, a low probe beam power of 100 μW is maintained during the experiment to avoid any significant local heating of the sample.

As shown in Figure 15, the polarization of the probe pulse of 20 ps pulse width, tunable from 700 nm to 2200 nm is modulated by the PEM such that its polarization is parallel and perpendicular to the NW long axis at 100 kHz frequency. A reflective objective is used to focus the probe beam around the center of a single NW. The reflective objective is crucial in the experiment not only because of the zero chromatic aberration but also its remarkable throughput of the infrared laser. The backscattered light is collected by the same objective and its intensity is measured using a liquid Nitrogen cooled InSb detector which is sensitive from 800 nm to 5000 nm. The lock-in #1 amplifier is used to measure the polarized reflectance, R’ (the difference of Rayleigh scattering from NW when the probe polarization is parallel and perpendicular, \(R’ = R_\parallel - R_\perp\)) of the NW. Using the lock-in amplifiers are very important in the experiment because of their capability of extracting the extremely small signal from an extremely noisy environment [19]. As explained in section 2.3.1, another strong pump beam at 550 nm with 300 μW power is used to photomodulate the NW. The pump laser beam is also focused on the same spot around the center of the NW. A 600 nm Raman filter is used to block the scattered pump beam on the detector. The pump beam is modulated with a mechanical chopper at 771 Hz such that the lock-
in #2 amplifier referenced to the chopper frequency can measure the change in polarized reflectance, \( \Delta R' \) (difference of \( R' \) when the pump is on and off) of the NW. The relative change of the polarized reflectance, \( \Delta R'/R' \) can then be calculated using the lock-in #1 and lock-in #2 amplifier measurements.

Since the probe pulse time delay after the pump can be adjusted (0 ps to 2000 ps) using the time-delay line, \( \Delta R'/R' \) can be calculated as a function of both probe energy and probe delay time after the pump. All the experiments are done at room temperature.

### 2.4 Electrical Characterization Technique

The quasi-one dimensional nature of the NW is ideal for investigating how the electrical transport properties of nanostructures are changed because of dimensionality. Also, it is important to study the electrical transport properties of NWs for NW characterization and electronic device applications.

In order to study the electrical transport properties of NWs, we fabricated individual NW FETs using photolithography. Figure 16 shows a schematic view of the NW FET device structure.

![Figure 16: A schematic view of the NW FET device structure](image)
We used a p-type Silicon substrate capped with 300 nm of Silicon oxide layer as the device substrate. The underlying conductive Silicon layer acts as the back gate of the device while the oxide layer on the top of the Silicon substrate provides an excellent insulation for the NW FET device. Silane doped ZB InP NWs (100 nm in diameter and around 8μm in length) are used to fabricate the FETs. Source and drain electrodes of the device are defined by photolithography followed by metal evaporation of Ti/Al.

2.4.1 Device Fabrication

A standard photolithography technique is used to fabricate the electrodes of the FET device. In this optical lithography process, light (usually ultra-violet (UV)) is used to transfer a geometric pattern on a photo mask to a light-sensitive chemical (photoresist) on the substrate.

The Nanonex NX-2600 Nanoimprint lithography machine is used to align the photo mask with respect to the sample and expose the sample to UV light. The Nanoimprinter is capable of performing photolithography with sub-1 μm alignment accuracy [20]. The photo mask is made up of a Chromium film on a glass plate and various gaps between the contact pads are designed in the mask ranging from 2 μm to 5 μm. Since the length of the InP NWs which we use to fabricate the devices is 8 μm, a 4 μm gap between the contact pads is used in the mask.

A series of chemical processes is used to engrave the exposure pattern into the substrate underneath the photo resist. Then, an Ammonium poly-sulfide etching process is performed to etch off the natural oxide layer on the surface of the exposed NW and leaves a thin layer of unstable sulfur chains to prevent the NW from re-oxidization. This process is crucial in order to make Ohmic contacts between the metal-semiconductor interfaces. After that, the metals Ti (20
nm) and Al (500 nm) are deposited on the sample using an electron-beam thin film metal evaporator. Finally, the photoresist (with overlying metal film) is lifted off in Acetone to remove the unwanted metal portions which are deposited on the device. A schematic overview of the NW device fabrication process is shown in Figure 17. Below, the micro fabrication procedure is described in detail.

NW device fabrication Process:

1. Disperse the NWs on a small piece of clean Si/SiO$_2$ substrate (5 mm x 5 mm) using sonication method (more details can be found in section 2.1)
2. Deposit a thin layer of photo resist on the sample (Spin photo resist, Shipley 1818 at 6 krpm for 60 s using the spin coater)
3. Soft bake the sample on the hotplate at 115 °C for 60 s
4. Put the sample on the photolithographic mask aligner. Align the photo mask across a NW
5. Expose the sample to UV light through the photo mask for 5 s
6. Dip the sample in Chlorobenzene for 90 s and hard bake in conventional oven at 90°C for 3 min
7. Develop the exposed sample with developer 351:deionized (DI) water at 1:5 ratio solution for 15 s and clean it with DI water for 30 s (only the parts of the photo resist exposed to UV light is removed in this process (particularly the photo resist on the two ends of the NW))
8. Inspect under high magnifying microscope
9. Go through the Ammonium poly-sulfide etching process (more details can be found in Appendix A1 of the thesis)
10. Deposit metals Ti (20 nm) and Al (200 nm) on the sample using thin film metal evaporator
11. Immerse the sample in Acetone for 1 h and liftoff it in Acetone

An optical image of a NW device after the fabrication is shown in Figure 18.

![Figure 17: NW device fabrication process by micro photo lithography technique](image1)

![Figure 18: An optical image of a NW device](image2)

After the device fabrication process, it is essential to ensure that good electrical contacts are made between the NW and the metal pads. Therefore, the device is tested for dark current-voltage (I-V) measurements in a probe station at room temperature. Two sharp needle probes made up of tungsten are used to make the connection between the contact pads of the device and the external circuit in the probe station. A microscope with a 100X objective is used to image the device so that the probes can be positioned onto the metal pads of the device. An external voltage
source (lock-in amplifier) and an ammeter (a HP digital Multimeter) with a current amplifier (to measure small dark current in pA range) are used to supply a bias voltage across the device and measure the current through the NW respectively. The input voltage can be controlled automatically by the Lab View computer program via a general purpose interface bus (GPIB) interface and the I-V data is recorded using the program. A schematic diagram of the two probe DC measurement system in probe station is shown in Figure 19.

![Figure 19: A schematic diagram of the two probe DC measurement system](image)

If the metal pads of the device are making good contact with the NW, it is better to wire bond the device for measurements. In order to provide an electrical connection between the device contact pads, the fabricated device is mounted on a chip carrier using Silver-paste and wire bonded between metal contact pads and pin connections of chip career using gold wires. More effort had to be made when making the back gate connection of the FET. Because there is a native thin layer of SiO\(_2\) at the bottom of the Si layer a direct connection of the back gate is not possible. Therefore, as shown in Figure 20, silver paste is used to make the connection between the chip carrier and the Si layer. Then the back gate of the FET is electrically connected using another...
gold wire between the metal chip carrier and a pin on the chip career (because the chip carrier and the pins on it are electrically disconnected with each other). Figure 20 shows a schematic diagram of making the back gate connection and (inset) a NW FET packaged on a chip carrier for measurements.

Figure 20: A schematic diagram of making the back gate connection. (inset) A NW FET packaged on a chip carrier for measurements

Literature [21] suggests that etching the native oxide layer on the underlying Si would improve properties of the back gate contacts of the device. HF acid has the capability of etching away the SiO$_2$ layer on the back side of the substrate without removing the underlying Silicon. Hence, another effort of making a good back gate connection of the FET device was carried out separately. In this process, the Si substrate is immersed in the buffered oxide etch (BOE) solution (H$_2$O:NH$_4$F:HF=3:3:1 by volume) for 2 min and 45 s before dispersing the NWs on it [22, 23].
During the etching process, the upper SiO$_2$ layer is being kept safe by masking it with a thin layer of photo resist. Then the substrate is cleaned with DI water for 3 min and a thin metal layer of Ti/Al (20 nm/200 nm) is deposited on back gate in order to make Ohmic contact. After that, the photo resist is removed by cleaning the substrate in Acetone. Finally, the substrate is used to make the FET device as usual and wire bonded for measurements. However, a significant improvement of the back gate measurements after etching was not observed as expected.

The West Bond Co. model no. 7476D manual wire bonding machine is used to wire bond the device. It uses ultrasonic energy to bond wires on the contact pad for a 45$^\circ$ wire feed. High conductive and corrosion resistive gold wire (AU W-W1.0.001, 99.99% Au, 25 µm in diameter) is used in chip packaging. During this wedge bonding process, a clamped gold wire is brought in contact with the metal pad and ultrasonic energy is applied to the wire for a specific duration while being held down by a specific amount of force to form the first wedge bond between the wire and the metal pad. The wire is then run to the corresponding lead finger and pressed to form the second bond while applying ultrasonic energy to the wire. The wire is then broken off by clamping and movement of the wire. The thickness of the metal pads (> 200 µm), contact pad area (> 500 µm x 500 µm), sample temperature (120$^\circ$C), surface cleanness and mild etching of the device just before metal deposition always improve the wire bonding. It is not possible to guarantee the bonds will be contacted in same way with the metal pads in two FETs of the same material, because of irreproducibility of contact location with same conditions. Therefore, it is a basic disadvantage of this technique and really effects reproducing the measurements for several FETs.
After the NW FET device is packaged on a chip carrier, a special attention is paid to ensure no current leakage through back gate occurred. Therefore, a digital Multimeter is used to check if there’s an electrical connection between the source and the gate as well as the drain and the gate electrodes with each other.

### 2.4.2 Experimental Setup

![A schematic diagram of the InP NW FET device DC measurement system](image)

Figure 21: A schematic diagram of the InP NW FET device DC measurement system

Figure 21 shows the schematic view of the InP NW FET device which is ready for electrical transport measurements. Drain source voltage, $V_{ds}$ is applied across the NW device by using a voltage source (Lock-in amplifier) and the current through the NW device, $I_{ds}$ is measured using a HP digital Multimeter with a current amplifier. Another voltage source (Lock-in amplifier) is used to control the gate source voltage, $V_{gs}$ of the NW FET. The input voltages ($V_{ds}$ and $V_{gs}$) can be controlled automatically by the Lab View computer program via a GPIB interface.
The current through the NW, $I_{ds}$ vs. $V_{ds}$ and $I_{ds}$ vs. $V_{gs}$ are recorded using the computer program for the NW FET. All these electrical transport experiments are done at room temperature in a dark environment to avoid the influence of carriers induced by photon excitation.
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Chapter 3

InGaAs/InP Nanowire Characterization

3.1 Introduction

Researchers have been fabricating, optimizing and studying most of the binary III-V semiconductor NWs and their heterostructures for a long time. But, ternary III-V compound semiconductor NWs such as In_{1-x}Ga_xAs, In_{1-x}Ga_xP, GaAs_xP_{1-x} and GaAs_xSb_{1-x} have not yet been fully explored because of the significant challenges of growing them with homogeneous composition [1--4]. However, studying and improving the quality of these ternary III-V NWs are crucial because their lattice parameter and energy gaps can be tuned by a suitable choice of composition, which makes them valuable for future nanoscale device application.

In particular, the wide tunability of the band gap (~900 nm – 3500 nm) [5] of In_{1-x}Ga_xAs NWs and the high electron mobilities and tunable Schottky barrier heights [5,6] make these wires useful in various device applications such as solar cells [4], transistors [4], integrated photonics [5,6] and tunneling devices [6]. In_{1-x}Ga_xAs NWs can be grown in both Zincblende and Wurtzite symmetries which provides an opportunity for band structure engineering within only a single material. Details of the band structure of WZ In_{1-x}Ga_xAs NWs, however, are not understood because of the experimental difficulties of working in the infrared wavelength region [5]. Therefore, it is essential to investigate the band structure of WZ In_{1-x}Ga_xAs NWs for future band gap engineering.
In addition, In$_{1-x}$Ga$_x$As/InP core-shell NWs provide the ability to control the strain of the In$_{1-x}$Ga$_x$As core due to the lattice mismatch between the two materials of the core and the shell. This shell induced stress changes the band structure within the NW and provides the ability to tune the electronic and optical properties of the resulting NW. For instance, In$_{0.53}$Ga$_{0.47}$As/InP heterostructure is lattice matched to InP and its energy gap is close to the optimum wavelength for optical fiber communication [7].

Recently, our research collaborators at Australian National University, A. S. Ameruddin et al. [4] have synthesized high quality In$_{1-x}$Ga$_x$As/InP core-shell NWs on GaAs (111)B substrate using Au catalyst-assisted MOCVD technique with uniform composition. These hexagonal wurtzite NWs are ~30 nm in diameter and ~2 μm in length. The thickness of the InP shell is ~10 nm. Figure 22 shows the SEM image of these In$_{1-x}$Ga$_x$As/InP core-shell NWs and the cross-sectional high angle annular dark field (HAADF) images of the bare core and the core/shell structure.

Figure 22: (a) SEM image of the In$_{1-x}$Ga$_x$As/InP core-shell NWs and the cross-sectional HAADF images of the (b) bare core and the (c) core/shell structure [4]
Energy dispersive X-ray (EDX) images using scanning transmission electron microscope (STEM) cross-section mapping confirms that the Gallium concentration of the core is 35% [4]. The lattice mismatch between the two materials is about 0.79%. Since the lattice constant of $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}$ (5.92 Å) is greater than the lattice constant of InP (5.87 Å) [8], $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}$ core is under compressive stress while the InP shell is under tensile stress. Therefore, this shell induced stress changes the electronic band structure of the core of $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}/\text{InP}$ structure.

We use Raman scattering and TRS spectroscopy measurements to characterize the strain and band structure of these individual $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}/\text{InP}$ strained core-shell NWs and compared with $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}$ core only NWs.

### 3.2 Raman Scattering Spectroscopy Measurements

Raman scattering measurements of individual strained $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}/\text{InP}$ core-shell semiconductor NWs are made at room temperature. Raman scattering by phonons provides an insight into the state of stress/strain of the core and shell, because the phonon energies shift in a known way [9]. For instance, Figure 23 shows the Hydrostatic stress (pressure) dependence of GaAs phonon energy. As shown in the figure, the optical phonon energy of the material usually becomes larger when it is under compressive stress/strain and the phonon energy becomes smaller when it is under tensile stress/strain.
A theoretical model is needed to quantify the magnitude of the hydrostatic strains in the core-shell NW from the Raman shift measurements. The core of the NW is assumed to have a circular cross-section with a uniform averaged strain in the radial plane (without a strain gradient). The strain gradient in the core of the core-shell NW is expected to be modest since it is covered by the shell in all directions. Finite element calculations confirm this [12].

The symmetrized form of the strain tensor, $\epsilon$ which consists of two independent components can be used in the analysis because of the symmetry of the NW. We assume that the NW long axis is...
parallel to the [111] direction of the crystal. Because of the cylindrical geometry of the NW, the strain tensor should be invariant under any rotation angle $\Phi$ around the NW long axis. Hence,

$$A_{111}(\phi) \cdot \varepsilon \cdot A_{111}^T(\phi) = \varepsilon$$

(3.1)

where $A_{111}(\phi)$ is the rotation operator around [111] direction by angle $\Phi$.

Equation (3.1) can be solved for elements of the strain tensor for any rotation angle which results in the symmetrized strain tensor with equal diagonal components ($\varepsilon_{xx}$) as well as equal off-diagonal components ($\varepsilon_{xy}$) as follows.

$$\varepsilon = \begin{pmatrix} \varepsilon_{xx} & \varepsilon_{xy} & \varepsilon_{xy} \\ \varepsilon_{xy} & \varepsilon_{xx} & \varepsilon_{xy} \\ \varepsilon_{xy} & \varepsilon_{xy} & \varepsilon_{xx} \end{pmatrix}$$

(3.2)

Therefore, the magnitude of the $\varepsilon_{ii}$ components (the hydrostatic strain is proportional to the sum of the diagonal elements) in all directions (in xyz crystal coordinates) are equal and the shear strain components $\varepsilon_{xy}$ have the same magnitude in all planes.

Using a mass-spring model for the crystal and assuming a linear strain-induced change in the spring constant, the semi-classical dynamical problem can be reduced to a secular equation as follows [13--16].

$$\det \begin{bmatrix} p\varepsilon_{xx} + q(\varepsilon_{yy} + \varepsilon_{zz}) - \lambda & 2r\varepsilon_{xy} & 2r\varepsilon_{xz} \\ 2r\varepsilon_{xy} & p\varepsilon_{yy} + q(\varepsilon_{xx} + \varepsilon_{zz}) - \lambda & 2r\varepsilon_{yz} \\ 2r\varepsilon_{xz} & 2r\varepsilon_{yz} & p\varepsilon_{zz} + q(\varepsilon_{xx} + \varepsilon_{yy}) - \lambda \end{bmatrix} = 0$$

Here, $\lambda = \omega^2 - \omega_0^2$.

where $\omega$ and $\omega_0$ are the frequencies of the phonon in the unstrained material and strained material respectively. $p$, $q$ and $r$ are the phonon deformation potentials of the material.
The equation can be solved for the eigenvalues ($\lambda$) by replacing the strain tensor elements from the symmetrized tensor in equation (3.2).

$$\lambda_1 = \lambda_2 = -r\varepsilon_{xy} + (p + 2q)\varepsilon_{xx}$$  \hspace{1cm} (3.3)

$$\lambda_3 = 2r\varepsilon_{xy} + (p + 2q)\varepsilon_{xx}$$  \hspace{1cm} (3.4)

The eigenvectors provide the polarization of the phonons. Hence the eigenvector corresponding to $\lambda_3$ is parallel to the crystal [111] direction and the other two eigenvectors are perpendicular to this direction.

Since $\lambda = \omega^2 - \omega_0^2 \cdot \varepsilon_{xx} > 0$ and $\varepsilon_{xy} = 0$ (in the absence of the shear strain),

For the TO mode, $\omega_{\text{TO}}^2 - \omega_{\text{TO}_0}^2 = (p + 2q)_{\text{TO}}\varepsilon_{xx}$ \hspace{1cm} (3.5)

For the LO mode, $\omega_{\text{LO}}^2 - \omega_{\text{LO}_0}^2 = (p + 2q)_{\text{LO}}\varepsilon_{xx}$ \hspace{1cm} (3.6)

By simplifying equation (3.5), the hydrostatic strain can be found as follows:

$$(\varepsilon_{xx})_{\text{TO}} = \frac{\left(\frac{\omega_{\text{TO}}^2}{\omega_{\text{TO}_0}^2}\right)^2 - 1}{6(M)_{\text{TO}}}$$  \hspace{1cm} (3.7)

where $(M)_{\text{TO}} = \frac{(p+2q)_{\text{TO}}}{6\omega_{\text{TO}_0}^2}$.

Similarly, by simplifying equation (3.6),
\[(\varepsilon_{xx})_{LO} = \frac{(\omega_{LO}^2 - 1)}{6(M)_{LO}}\]  

(3.8)

where \((M)_{LO}\) and \((M)_{TO}\) are the mode Gruneisen parameters of the material for TO and LO modes respectively. Therefore, the phonon energies of the strained and unstrained materials can be used to estimate the hydrostatic strain of the core and the shell of \(\text{In}_{0.65}\text{Ga}_{0.35}\text{As/InP}\) core-shell NWs using the equations (3.7) and (3.8).

The electronic band structure of semiconductors is sensitive to the strain and is extensively discussed by F. H. Pollak \textit{et al.} [17] and M. E. Pistol \textit{et al.} [12]. The magnitude of the change in energy gap, \(\Delta E_g\), is proportional to the magnitude of the hydrostatic strain and can be quantified by the hydrostatic deformation potentials for the conduction band \((a_c)\) and the valence band \((a_v)\) of the material.

\[\Delta E_g = 3\varepsilon_{xx}|a_c - a_v|\]  

(3.9)

The hydrostatic strain calculated from Raman scattering spectroscopy measurements is used to estimate the change in energy gap of the core and the shell of \(\text{In}_{0.65}\text{Ga}_{0.35}\text{As/InP}\) NWs using equation (3.9). Furthermore, the estimated change in the energy gap of the core and the shell of \(\text{In}_{0.65}\text{Ga}_{0.35}\text{As/InP}\) NWs from Raman scattering spectroscopy are compared with the experimental TRS spectroscopy measurements of the same NWs.
3.2.1 Gallium Concentration in the InGaAs Core

Figure 24 shows the room temperature polarized Raman spectra of a single WZ In$_{1-x}$Ga$_x$As core only NW (there is no shell). The average energies of the InAs like TO and GaAs like TO modes of the single WZ In$_{1-x}$Ga$_x$As NW are measured for four different polarization configurations (X(z,z)$_X$, X(z,y)$_X$, X(y,z)$_X$ and X(y,y)$_X$) are used to estimate the Gallium concentration of the core. The schematic illustration of the optic modes found for In$_{1-x}$Ga$_x$As by Brodsky et al. [18] is used for the estimation as shown in Figure 25.
Figure 25: The average energies (black filled symbols) of InAs-like TO and GaAs-like TO modes of single WZ In$_{1-x}$Ga$_x$As NW at 300K, in the graph of phonon wave number vs. Ga content which was found by Brodsky et al. [18] for the optic modes in In$_{1-x}$Ga$_x$As. GaAs-like LO, GaAs-like TO, InAs-like LO and InAs-like TO modes are shown in pink, blue, red and green dashed lines respectively in the graph.

From this analysis the frequency of the GaAs-like TO mode indicates a gallium concentration of 0.29, while the InAs-like TO mode indicates a gallium concentration of 0.37. The Gallium concentration of the core is therefore estimated to be 33% and it is consistent with the 35% Ga concentration determined from the growth parameters.
3.2.2 Strains and Change in Energy Gaps in InGaAs Core and InP Shell

Figure 26: Raman spectrum of single WZ In$_{0.65}$Ga$_{0.35}$As/InP strained core-shell NW (black solid line) compared to the Raman spectra of single WZ In$_{0.65}$Ga$_{0.35}$As unstrained (core only) NW (blue solid line) and WZ InP NW (green solid line) at X(z,z) polarization configuration (300 K). The Raman peaks are fitted by Lorentzian line shapes and plotted in the same graph. The coloured dashed vertical lines going through the Raman peaks of the unstrained WZ In$_{0.65}$Ga$_{0.35}$As NW and WZ InP NW are included as a guide to the eye for better comparison.

The room temperature Raman spectrum of single WZ In$_{0.65}$Ga$_{0.35}$As/InP strained core-shell NW is compared with the Raman spectra of a single WZ In$_{0.65}$Ga$_{0.35}$As unstrained NW and WZ InP NW for the X(z,z) polarization configuration in Figure 26. The Raman scattering spectrum of the In$_{0.65}$Ga$_{0.35}$As/InP core-shell NWs shows both the InAs-like TO and GaAs-like TO modes from the core-shell NW have energies about ~2 cm$^{-1}$ greater than measured in the unstrained...
core-only NW which indicates that they are under compression as expected from the lattice mismatch between the core and shell. The Raman response from the InP shell reveals TO and LO modes which have shifted about 5~6 cm$^{-1}$ to lower frequencies compared with an unstrained WZ InP NW which indicates that it is under tensile stress, again as expected.

The Raman peaks are fitted well by Lorentzian line shapes which are used to determine the frequencies of the TO and LO modes more precisely for calculations. As described in section 3.2, the hydrostatic strain of the core and the shell in In$_{0.65}$Ga$_{0.35}$As/InP strained core-shell structure can be calculated using the frequencies of the TO and LO modes of the In$_{0.65}$Ga$_{0.35}$As/InP strained and In$_{0.65}$Ga$_{0.35}$As unstrained NWs. Using equations (3.7) and (3.8), the magnitude of the hydrostatic strain of the core and the shell in In$_{0.65}$Ga$_{0.35}$As/InP strained core-shell NW are computed to be 0.26% and 0.42%, respectively. For this calculation, the mode Gruneisen parameters for the materials reported in the literature are used (see Table 3.1).

<table>
<thead>
<tr>
<th>Material</th>
<th>Mode Gruneisen parameter for TO mode</th>
<th>Mode Gruneisen parameter for LO mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>1.39</td>
<td>1.23</td>
</tr>
<tr>
<td>InAs</td>
<td>1.21</td>
<td>1.06</td>
</tr>
<tr>
<td>In$<em>{0.65}$Ga$</em>{0.35}$As</td>
<td>1.2730</td>
<td>1.1195</td>
</tr>
<tr>
<td>InP</td>
<td>1.44</td>
<td>1.24</td>
</tr>
</tbody>
</table>

Table 3.1: Mode Gruneisen parameters for the materials [9]. Mode Gruneisen parameter for the In$_{0.65}$Ga$_{0.35}$As material is estimated by using a linear interpolation.

These measured strains are expected to shift the band structure of both the In$_{1-x}$Ga$_x$As core and the InP shell. The hydrostatic deformation potentials for the In$_{1-x}$Ga$_x$As ternary compound
are determined from the known parameters for GaAs and InAs assuming a linear interpolation according to the known Ga concentration and are shown in Table 3.2. Using the equation 3.9 and these hydrostatic deformation potentials for the conduction band and valence band of the ternary material, the change in energy gap of the $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}$ core and the InP shell of the $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}/\text{InP}$ strained core-shell NW are computed to be 48 meV and -68 meV, respectively. The calculated results from the Raman spectroscopy measurements are summarized in Table 3.3.

<table>
<thead>
<tr>
<th>Material</th>
<th>$a_c$ (eV)</th>
<th>$a_v$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>-9.3</td>
<td>-0.7</td>
</tr>
<tr>
<td>InAs</td>
<td>-10.2</td>
<td>-5.2</td>
</tr>
<tr>
<td>$\text{In}<em>{0.65}\text{Ga}</em>{0.35}\text{As}$</td>
<td>-9.885</td>
<td>-3.625</td>
</tr>
<tr>
<td>InP</td>
<td>-6</td>
<td>-0.6</td>
</tr>
</tbody>
</table>

Table 3.2: Hydrostatic deformation potentials for conduction band ($a_c$) and valence band ($a_v$) of the materials [9, 19, 20]. The hydrostatic deformation potentials for conduction band and valence band of $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}$ material are estimated by using a linear interpolation.

<table>
<thead>
<tr>
<th>Material</th>
<th>Hydrostatic Strain %</th>
<th>Change in Energy Gap (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{In}<em>{0.65}\text{Ga}</em>{0.35}\text{As}$ core</td>
<td>0.26</td>
<td>48</td>
</tr>
<tr>
<td>InP shell</td>
<td>-0.42</td>
<td>-68</td>
</tr>
</tbody>
</table>

Table 3.3: Calculated hydrostatic strain and change in energy gap of $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}$ core and InP shell in $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}/\text{InP}$ strained core-shell NW from Raman spectroscopy measurements at room temperature.

To compare with these predicted values, in section 3.3 we present the band gap of the $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}/\text{InP}$ strained core-shell NWs as measured experimentally using TRS spectroscopy measurements.
3.3 TRS Spectroscopy Measurements

Transient Rayleigh scattering spectroscopy measurements of single $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}$ and $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}/\text{InP}$ strained core-shell NWs are used to study the electronic band structure of these materials.

3.3.1 Band Gap in InGaAs/InP NWs

The measured TRS energy spectra of single $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}$ unstrained NWs and $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}/\text{InP}$ strained core-shell NW at 300 K are shown in figure 28. The band gaps of these NWs can be directly extracted from the zero crossing point of the TRS energy spectra as discussed in section 2.3.1.

Our measurements show clear evidence for a strong band resonance in the unstrained $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}$ NW at 1514 nm (0.819 eV). This resonance moves up in energy in the core-shell NW to 1433 nm (0.865 eV), consistent with compressive strain. Therefore, $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}$ change in energy gap in core/shell structure is 46 meV which is also consistent with the calculated results in Raman scattering spectroscopy measurements in these NWs (see Table 3.3). In addition, another energy state at 1.238 eV for the core-shell NW and 1.176 eV for the core only NW is observed in the energy spectra (see Figure 27). This energy state cannot be the InP band gap since it appeared in core only NW. Our best guess is this state is related to optical transitions between the B or C valence bands and the conduction band of the structure, since these NWs have WZ symmetry.
Figure 27: The energy dependence of the relative change in polarized reflectance, $\Delta R'/R'$ at 0 ps delay time after the pump pulse for In$_{0.65}$Ga$_{0.35}$As unstrained NW (blue solid line) and In$_{0.65}$Ga$_{0.35}$As/InP strained NW (black solid line) at 300 K. The band gap of unstrained WZ InP (green dashed vertical line) at 300K with the expected change in energy gap of 68 meV (black dashed vertical line) in the core-shell structure due to core-induced tensile stress calculated from Raman scattering spectroscopy measurements are also marked in the graph.

### 3.3.2 Carrier Life Time in InGaAs/InP NWs

As shown in Figure 28, the time decay of the resonance in the In$_{0.65}$Ga$_{0.35}$As /InP core-shell NW is observed to be relatively long (~125 ps) at room temperature which is a measure of the electron and hole occupation as a function of time. In contrast, the lifetime of the equivalent resonance in the bare In$_{0.65}$Ga$_{0.35}$As core only NW is extremely short (~31 ps) consistent with a
larger non-radiative recombination rate. Indeed it clearly indicates that the passivation is required to suppress surface recombination.

Figure 28: The time decays of the relative change in polarized reflectance, $dR'/R'$ at 1.03 eV probe energy for $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}$ NW (blue solid line) and $\text{In}_{0.65}\text{Ga}_{0.35}\text{As}/\text{InP}$ NW (black solid line) at 300 K. The time decays are fitted by exponential decay line shape and plotted in the same graph.

3.4 Conclusion

In summary, we have investigated the electronic band structure, carrier recombination dynamics, composition and strain in the core and the shell of individual WZ $\text{In}_{1-x}\text{Ga}_x\text{As}/\text{InP}$ strained core-shell NWs with ~30 nm diameter core and ~10 nm thick shell grown via gold catalyst assisted MOCVD technique.
Micro-Raman scattering from individual In$_{1-x}$Ga$_x$As NWs show InAs like TO and GaAs like TO modes with frequencies which are consistent with the 35% Ga concentration determined from the growth parameters along with detailed EDX–STEM cross-section mapping measurements. Furthermore, the hydrostatic compressive strain in the In$_{0.65}$Ga$_{0.35}$As core is estimated to be 0.26% while the hydrostatic tensile strain in the InP shell is estimated to be 0.42% from room temperature Raman spectroscopy measurements.

![Figure 29: Measured band gap energy (red filled symbol) of the WZ In$_{1-x}$Ga$_x$As NW at 300 K as a function of Gallium composition (x). The expected band gap energy dependence of ZB In$_{1-x}$Ga$_x$As at 300 K [21] is shown in black solid line. The band gap energies (green filled symbols) of WZ/ZB mixed phase In$_{1-x}$Ga$_x$As (x = 0, 0.07, 0.19, 0.36) NW arrays at 4 K [5] as well as the band gap energies (blue filled symbols) of WZ In$_{1-x}$Ga$_x$As (x = 0.8, 0.84, 0.88) nanoneedles at 10 K [6] are also plotted in the graph. The well known band gap energies of WZ In$_{1-x}$Ga$_x$As (x = 0, 0.47, 1) at 300 K are plotted as pink filled symbols with a pink dashed line as a guide to the eye for better comparison.](image-url)
In order to provide a complete picture of the band gap energies of In\(_{1-x}\)Ga\(_x\)As material, the band gap energy which is found from our TRS spectroscopy measurements (0.819 eV) is plotted in the graph of energy gap vs. Gallium composition (Figure 29). The band gap energies of ZB In\(_{1-x}\)Ga\(_x\)As material at 300 K, WZ/ZB mixed phase In\(_{1-x}\)Ga\(_x\)As (x = 0, 0.07, 0.19, 0.36) NW arrays at 4 K, WZ In\(_{1-x}\)Ga\(_x\)As (x = 0.8, 0.84, 0.88) nanoneedles at 10 K and WZ In\(_{1-x}\)Ga\(_x\)As (x = 0, 0.47, 1) at 300 K are also plotted in the same graph for comparison. As shown in the figure, the band gap of WZ In\(_{0.65}\)Ga\(_{0.35}\)As is estimated to be ~186 meV higher in energy with respect to bulk ZB In\(_{0.65}\)Ga\(_{0.35}\)As. This finding provides an important insight into the band structure of WZ In\(_{1-x}\)Ga\(_x\)As which could be used for future applications.

The two independent Raman scattering and TRS spectroscopy measurements are both in excellent agreement with the band gap shift of strained In\(_{0.65}\)Ga\(_{0.35}\)As/InP core-shell NWs with respect to the core only NW by 46~48 meV at room temperature and thus experimentally confirmed the InP shell induced compression of the core. Furthermore, the passivation with the InP shell has enhanced the carrier lifetime (~125 ps) by more than four times larger than the bare In\(_{0.65}\)Ga\(_{0.35}\)As NWs (~31 ps) which proves the positive impact of the InP shell.

Indeed these results are important and useful for engineering the electronic properties of NWs for optimal design of NW devices by controlling the strain of the core and shell by varying the NW geometry.
References:


4.1 Introduction

In spite of the many growth related challenges (crystal structural perfection, composition homogeneity [1, 2]) of fabricating ternary III-V NWs, they are receiving a lot of attention due to their promise for advanced and efficient optoelectronic applications in the future. In particular, the GaAs$_{1-x}$Sb$_x$ ternary alloy is of interest for the fabrication of sources and detectors for near infrared optoelectronic applications such as photodiodes [3], photocathodes [4] and light-emitting diodes [5, 6] and also because of its high electron and hole mobilities [7] and band gap tunability over a large range of the spectrum from 870 nm to 1700 nm [8].

Not only by controlling the composition but also by using strain engineering, the band structure of these ternary alloys can be adjusted for device applications. For instance, GaAs$_{1-x}$Sb$_x$/InP radial heterostructure NWs provide the ability to tune the electronic and optical properties of the resulting NW due to the shell-induced stress of the core. Recently, R. Flückiger et al. [9] reported high frequency double heterostructure bipolar transistors (DHBT) made up of GaAs$_{1-x}$Sb$_x$/InP heterostructures with high quality performances. However, the real potential of using these GaAs$_{1-x}$Sb$_x$/InP NWs for nanoscale device applications has not yet been much explored.

In recent years, our research collaborators at Australian National University, X. Yuan et al. [8] have synthesized high crystal quality GaAs$_{1-x}$Sb$_x$/InP strained core-shell NWs on a WZ GaAs stem using Au catalyst-assisted MOCVD technique with uniform composition. These NWs are
~50 nm in diameter and ~4 μm in length. The thickness of the InP shell is ~12 nm. They have Zincblende (ZB) twin-free structures with two different Sb compositions: GaAs$_{0.71}$Sb$_{0.29}$/InP and GaAs$_{0.56}$Sb$_{0.44}$/InP. EDX measurements are used to confirm the Sb concentrations at the core of these GaAs$_{1-x}$Sb$_x$/InP structures [8]. Figure 30 shows the SEM images of these bare GaAs$_{1-x}$Sb$_x$ NWs, GaAs$_{1-x}$Sb$_x$/InP core-shell NWs and the cross-section of the core-shell structure.

![Figure 30: SEM images of the (a) GaAs$_{1-x}$Sb$_x$ NWs, showing the hexagonal cross section shape with \{110\} side facets, (b) GaAs$_{1-x}$Sb$_x$/InP core-shell NWs, showing the triangular cross section shape with \{112\} side facets and (c) top view of a GaAs$_{1-x}$Sb$_x$/InP core-shell NW. The GaAs$_{1-x}$Sb$_x$ NWs are grown along the [111]B direction [8].]

The lattice mismatch between the two materials of the core and the shell of GaAs$_{0.71}$Sb$_{0.29}$/InP and GaAs$_{0.56}$Sb$_{0.44}$/InP structures are about 1.55% and 0.38% respectively. Since the lattice constant of GaAs$_{0.71}$Sb$_{0.29}$ (5.78 Å) as well as GaAs$_{0.56}$Sb$_{0.44}$ (5.85 Å) are less than the lattice constant of InP (5.87 Å) [10], the GaAs$_{1-x}$Sb$_x$ core is under tensile stress while the InP shell is
under compressive stress. Therefore, this shell-induced stress changes the electronic band structure of the core of GaAs$_{1-x}$Sb$_x$/InP structure.

As previously for InGaAs/InP core-shell NWs, we use Raman scattering and TRS spectroscopy measurements in single unstrained bare and strained core-shell NWs to study the strain distribution in the GaAs$_{1-x}$Sb$_x$ core and the InP shell and its effect on band structure of GaAs$_{1-x}$Sb$_x$/InP NWs.

### 4.2 Raman Scattering Spectroscopy Measurements

Since the Raman scattering provides information on the vibrational properties of materials, it can be related to the composition and strain [7]. We present a qualitative study of the vibrational properties of GaAs$_{1-x}$Sb$_x$ NWs with two different Sb contents, 29% and 44%.

In addition, Raman scattering from individual GaAs$_{0.71}$Sb$_{0.29}$/InP core-shell NWs and the deviation of the Raman response from its unstrained GaAs$_{0.71}$Sb$_{0.29}$ NWs at room temperature are used to study the strain distribution in the GaAs$_{1-x}$Sb$_x$ core and the InP shell.

#### 4.2.1 Vibrational Properties of GaAsSb NWs

Micro-Raman scattering measurements are carried out at room temperature in the back-scattering configuration on the GaAs$_{1-x}$Sb$_x$ NWs. Figure 31 shows the Raman spectra of individual ZB GaAs$_{1-x}$Sb$_x$ NWs with two different Sb compositions, 29% and 44% which are confirmed from EDX measurements published previously [8].
Figure 31: Raman spectra of individual ZB GaAs$_{0.71}$Sb$_{0.29}$ NW (blue solid line) and ZB GaAs$_{0.56}$Sb$_{0.44}$ NW (red solid line) compared to the optical modes of unstrained ZB GaAs (green dashed line) at X(z,z) polarization configuration (300 K). The blue dashed vertical lines going through the Raman peaks of the ZB GaAs$_{0.71}$Sb$_{0.29}$ NW are included as a guide to the eye for better comparison.

The Raman phonon spectrum from the GaAs$_{1-x}$Sb$_x$ alloy show two sets of TO and LO optical phonon modes. They are classified as GaAs-like and GaSb-like with frequencies shifted from those for the GaAs and GaSb binary alloys respectively. For instance, the binary unstrained ZB GaAs is dominated by two TO and LO modes at 267 cm$^{-1}$ and 285 cm$^{-1}$ respectively [11]. It is clear from Figure 31 that the optical phonon modes of NWs containing Antimony (GaAs$_{1-x}$Sb$_x$ NWs) are quite different from that of unstrained GaAs. Basically, two sets of TO and LO phonon modes can be observed in the Raman spectra of GaAs$_{1-x}$Sb$_x$ NWs. Especially both the GaAs-like
TO and GaAs-like LO peaks of the Raman spectra of GaAs$_{1-x}$Sb$_x$ NWs can be observed to be shifted to lower frequencies with respect to the TO and LO modes of GaAs respectively. This behavior can be expected in an alloy with increasing concentration of a heavier atom (Antimony in place of Arsenic) in the lattice. Also, as expected, an increase of Sb fraction $x$ in the GaAs$_{1-x}$Sb$_x$ NWs results in a shift of the GaAs-like TO and GaAs-like LO modes towards lower energies.

In the case of the GaSb-like modes in the GaAs$_{1-x}$Sb$_x$ NWs, we are only able to detect the TO mode. Since the intensity of the LO mode is much lower than that of the TO mode [7], the LO mode here may not be very intense due to the relatively low concentration in Antimony in GaAs$_{1-x}$Sb$_x$ structures. Also, we can notice that the GaSb-like TO mode in the GaAs$_{1-x}$Sb$_x$ NWs is red-shifted with Antimony content. These results are in good agreement with values from the literature [6, 7].

4.2.2 Strains in GaAsSb Core and InP Shell

The room temperature Raman spectrum of single ZB GaAs$_{0.71}$Sb$_{0.29}$/InP strained core-shell NW is compared with the Raman spectra of single ZB GaAs$_{0.71}$Sb$_{0.29}$ unstrained NW and ZB InP NW in the X(z,z)$\overline{X}$ polarization configuration.

As shown in Figure 32, Raman scattering of GaAs$_{0.71}$Sb$_{0.29}$/InP core-shell NWs shows both the GaAs-like TO and GaSb-like TO modes from the core have energies about 5~6 cm$^{-1}$ less than measured in the unstrained core-only NWs which indicates that they are under tensile stress as expected from the lattice mismatch between the core and the shell. The Raman response from the
InP shell reveals TO and LO modes which have shifted about 2–5 cm\(^{-1}\) to higher frequencies compared with unstrained ZB InP NW which indicates that it is under compression.

Figure 32: Raman spectrum of single ZB GaAs\(_{0.71}\)Sb\(_{0.29}\)/InP strained core-shell NW (black solid line) compared to the Raman spectra of single ZB GaAs\(_{0.71}\)Sb\(_{0.29}\) unstrained (core only) NW (blue solid line) and ZB InP NW (green solid line) at X(z,z)\(\bar{X}\) polarization configuration (300 K). The coloured dashed vertical lines going through the Raman peaks of the unstrained ZB GaAs\(_{0.71}\)Sb\(_{0.29}\) NW and ZB InP NW are included as a guide to the eye for better comparison. GaAs-like LO mode appeared in GaAs\(_{0.71}\)Sb\(_{0.29}\) unstrained NW is marked by an asterisk.

4.3 TRS Spectroscopy Measurements

In order to characterize the fundamental carrier dynamics and band structure of GaAs\(_{1-x}\)Sb\(_{x}\) and GaAs\(_{1-x}\)Sb\(_{x}\)/InP core-shell NWs, room temperature TRS spectroscopy measurements of single GaAs\(_{0.71}\)Sb\(_{0.29}\) NWs and GaAs\(_{0.71}\)Sb\(_{0.29}\)/InP strained core-shell NWs are studied.
4.3.1 Band Gap and Carrier Life Time in GaAsSb/InP NWs

The previously measured TRS energy spectra and time decays of single GaAs$_{0.71}$Sb$_{0.29}$ unstrained NWs and GaAs$_{0.71}$Sb$_{0.29}$/InP strained core-shell NWs at 300 K are shown in Figure 33 [8].

![Figure 33](image)

Figure 33: (a) The energy dependence of the relative change in polarized reflectance, $dR'/R'$ at ~1000 ps delay time after the pump pulse for GaAs$_{0.71}$Sb$_{0.29}$ unstrained NW (red solid line) and GaAs$_{0.71}$Sb$_{0.29}$/InP strained core-shell NW (green solid line) at 300 K. (b) The time decays of the relative change in polarized reflectance, $dR'/R'$ at the low energy side of the band gap energy for GaAs$_{0.71}$Sb$_{0.29}$ NW (red solid line) and GaAs$_{0.71}$Sb$_{0.29}$/InP NW (green solid line) at 300 K. The time decays are fitted by exponential decay line shape and plotted in the same graph. Reprint with permission from ref. [8].

Using a simplified $\Delta R'/R'$ model based on Lorentz oscillator deduced dielectric function [12], the band gap of core-only GaAs$_{0.71}$Sb$_{0.29}$ NW and core-shell GaAs$_{0.71}$Sb$_{0.29}$/InP NW are extracted to be 0.99 eV and 0.95 eV respectively, as shown in Figure 33(a). The band gap of the GaAs$_{0.71}$Sb$_{0.29}$ core is observed to be red shifted by 40 meV in the GaAs$_{0.71}$Sb$_{0.29}$/InP core-shell structure, because of the tensile strain in the core caused by the InP shell. This tensile strain in the GaAs$_{0.71}$Sb$_{0.29}$ core is qualitatively confirmed by Raman measurements of these NWs (Figure 32).

Furthermore, the time decay of the resonance in the GaAs$_{0.71}$Sb$_{0.29}$ core-only NWs is observed to be extremely short (~31 ps) at room temperature (see Figure 33(b)) which is directly proportional
to the carrier density as a function of time. In contrast, the equivalent resonance in the GaAs$_{0.71}$Sb$_{0.29}$/InP core-shell NWs is substantially longer (~127 ps). This significant lifetime enhancement reflects the effectiveness of the InP shell surface passivation at reducing the non-radiative recombination centers at the GaAs$_{0.71}$Sb$_{0.29}$ surface.

4.4 Conclusion

In summary, we have investigated the electronic band structure, fundamental carrier dynamics and strain distribution in the core and the shell of individual ZB GaAs$_{1-x}$Sb$_x$/InP strained core-shell NWs with ~50 nm diameter core and ~12 nm thick shell grown via gold catalyst assisted MOCVD technique.

We have studied the vibrational properties of bare GaAs$_{1-x}$Sb$_x$ NWs with two different Antimony contents, 29% and 44% determined from detailed EDX measurements. Optical phonon modes of GaAs$_{1-x}$Sb$_x$ are observed to be red shifted with Antimony fraction, x in the NWs. This behavior can be expected in an alloy with increasing concentration of a heavier atom in the lattice. Furthermore, room temperature micro-Raman experiments show a blue-shift of the InP phonons and a red-shift of the GaAs$_{1-x}$Sb$_x$ phonons in individual GaAs$_{0.71}$Sb$_{0.29}$/InP strained core-shell NWs. It is a clear indication that the core is under tensile stress while the shell is under compression in the GaAs$_{0.71}$Sb$_{0.29}$/InP structure as expected from the lattice mismatch.

The room temperature TRS spectroscopy measurements confirmed that the band gap energy of GaAs$_{0.71}$Sb$_{0.29}$ core (0.99 eV) is red shifted by 40 meV after passivating it with InP shell and it is a clear evidence of the shell-induced tensile strain in the core. Hence, the Raman scattering and
TRS spectroscopy measurements are in qualitative agreement with each other. In addition, a significant lifetime enhancement (a factor of four) of the GaAs$_{0.71}$Sb$_{0.29}$ NWs is observed after passivating it with InP shell which makes them promising for nanoscale device applications in the near-infrared range.

Although this study should be continued to provide a detailed quantitative investigation of GaAs$_{1-x}$Sb$_x$/InP NWs in future, these findings provide an important base for structural studies on GaAs$_{1-x}$Sb$_x$ alloy and its usage in future device applications.
References:

Chapter 5

InP Nanowire Characterization

5.1 Introduction

Semiconductor NWs have gained a lot of interest in researchers because of their various nanoscale device applications including NW lasers [1--3], NW sensors [4--6], NW photovoltaics [7--9], photo detectors [10--12], single electron transistors [13--14], etc. In particular, InP binary III-V semiconductor NWs have excellent electrical and optical properties with high quantum efficiency and low sensitivity to surface defects [15--16]. Also, they have great potential in making nanoscale infrared detectors [17], since its band gap (1.34 eV [18]) lies in the near-infrared energy region at room temperature. InP is especially used in high power and high frequency semiconductor applications because of its excellent transport properties. Therefore, studying these electrical transport properties of InP NWs is crucial for NW characterization and future electronic device applications.

Here we use InP NW FETs fabricated by photolithography techniques to investigate the electrical transport properties of ZB InP NWs. These n-type (Si-doping concentration of ~10^{16} cm^{-3} [19]) ZB InP NWs, which are ~100 nm in diameter and ~8 µm in length are synthesized on an oriented InP (111) substrate using Au catalyst-assisted MOCVD technique by our research collaborators (Prof. C. Jagadish’s research group) at Australian National University. Detailed description of these InP NW synthesis and NW FET device fabrication can be found in sections 1.3.1 and 2.4.1 respectively.
Concisely, we used p-type Silicon substrate capped with 300 nm of Silicon oxide layer as the device substrate. The underlying conductive Silicon layer acts as the back gate of the device while the oxide layer on the top of the Silicon substrate provides an excellent insulation for the NW FET device. Source and drain electrodes of the device are defined by photolithography followed by metal evaporation of Ti/Al. A schematic view of the NW FET device structure and an optical image of a NW device can be found in Figure 16 and Figure 18 respectively.

For the most efficient FET performance with high electron mobility, both source and drain metal-semiconductor (MS) junctions should form Ohmic contacts with the NW. Therefore, in order to form Ohmic contacts and control the gate in a metal-semiconductor-metal (MSM) structure, it is best to understand the device operation of NW FET with the aid of band diagrams.

We use standard transistor expressions to probe the electrical transport properties of single InP NWs including carrier density and carrier mobility. Since these measured transport properties are dependent on the device geometry and the contact resistances of the NW FET, it is necessary to make a simple circuit model of the MSM structure of the NW device in order to clarify the effect of contact resistance and geometry for further experimental studies. Therefore, we propose an equivalent circuit model of the MSM structure of the InP NW device incorporating a pair of diodes in series with the NW resistance to model the measured mobility, carrier concentration and barrier heights of the NW device.

### 5.1.1 Metal Semiconductor Contact

When a metal is brought in contact with a semiconductor, it forms a Schottky barrier at the metal-semiconductor (MS) interface because of the different Fermi energies of the two materials.
It can form either a Schottky contact or Ohmic contact depending on the magnitude of the Schottky barrier formed at the MS interface. Hence, it is responsible for controlling current conduction through the junction.

Figure 34 shows the energy band diagrams of a metal and a n-type semiconductor which are not in contact. The quantity \((q\phi_M)\) is the metal work function which is the energy difference between vacuum level \((E_O)\) and the metal Fermi level \((E_F)\). And, it is defined as the energy required to move an electron from metal Fermi level to the vacuum state. Similarly, \((q\phi_n)\) is the semiconductor work function which is the energy difference between the vacuum level \((E_O)\) and the Fermi level \((E_F)\) of the semiconductor. \((q\chi)\) is the electron affinity of the semiconductor and it is defined as the energy difference between vacuum level \((E_O)\) and the bottom of the conduction band \((E_C)\). \(E_V\) is the valence band energy of the semiconductor.

![Energy band diagrams of a metal (on left) and a n-type semiconductor (on Right)](image)

The work function of the metal and the electron affinity of the semiconductor are intrinsic material properties. The Fermi level for n-type semiconductor lies above the middle of the gap.
between the conduction band and the valence band. If $\phi_M > \phi_n$, the Fermi level of the semiconductor lies above the Fermi level of the metal as shown in the figure. Because of this Fermi level difference, electrons in the conduction band of the semiconductor have higher energies than the electrons in the metal. Therefore, when the two materials are brought in contact with each other, the electrons flow from semiconductor to the metal until the Fermi levels are aligned with each other. This electron diffusion process forms a depletion layer in the junction. Hence, a built-in electric field as well as a built-in potential ($q\nu_0$) are generated inside the depletion layer of the MS junction. Electrons in the semiconductor will encounter this potential barrier, $q\nu_0 (= q\phi_M - q\phi_n)$ to flow from semiconductor to metal. On the other hand, the Schottky barrier height, $q\phi_B (= q\phi_M - q\chi)$ is formed for the electrons to flow from the metal to the semiconductor. Hence, after reaching the thermal equilibrium, the net flow of electrons through the MS junction is zero. Figure 35 shows the energy band structure of MS interface at thermal equilibrium.

![Energy band structure of MS interface at thermal equilibrium.](image)

Figure 35: Energy band structure of MS interface at thermal equilibrium. Note that the Fermi levels are aligned with each other at this equilibrium state and the bands are bent in the n-type semiconductor.
More interestingly, we can make the Schottky barrier height, $q\Phi_B$ very small by choosing a metal whose work function ($q\phi_M$) is very close to the electron affinity of the semiconductor ($q\chi$). Hence, the electrons can easily move from semiconductor to metal and metal to semiconductor. That means we can make Ohmic contact between metal and semiconductor by choosing a metal whose work function is very close to the electron affinity of the semiconductor.

When fabricating the NW FETs in our research, we choose Ti metal ($q\phi_M = 4.33$ eV) [20] to form an Ohmic contact with the InP ($q\chi = 4.38$ eV) [21] semiconductor NW.

It is very useful to understand the MS junction operation when some bias voltage is applied across it. Figure 36 and Figure 37 show the energy band diagrams of MS interface under forward bias and reverse bias states respectively.

![Figure 36](image)

Figure 36: Energy band diagram of MS interface under forward bias state. Note that the positive voltage is applied at metal with respect to the n-type semiconductor.
As shown in Figure 36, when a positive bias is applied to the metal with respect to the semiconductor (forward bias state), the applied voltage $V$ reduces the built-in potential $qV_0$ by $qV$. Therefore, the entire band system moves up in the semiconductor by $qV$ allowing more electrons to diffuse from semiconductor to metal. Since the Schottky barrier height stays constant, a net current starts to flow from the metal to the semiconductor through the MS junction.

![Energy band diagram of MS interface under reverse bias state. Note that the negative voltage is applied at metal with respect to the n-type semiconductor.](image)

For the reverse bias state (Figure 37), when a negative bias is applied to the metal with respect to the semiconductor, the applied voltage $V_R$ enhances the built-in potential by $(qV_R)$. Therefore, the entire band system moves down by $(qV_R)$ in the semiconductor creating a huge built-in potential $q(v_0+V_R)$ for the electrons in the semiconductor. On the other hand, the Schottky barrier height which is independent of the applied voltage stays unchanged and limits the flow of
electrons from metal to semiconductor. Hence the current is blocked when the MS junction is in the reversed bias state. Here, we neglect the tunneling of electrons from metal to semiconductor. This will be discussed in more detail in section 5.1.2 under thermionic field emission theory.

This interesting rectifying behavior of the MS junction (i.e. It conducts current under forward bias state and blocks current transport under reverse bias state) is similar to the behavior of a Schottky diode.

5.1.2 MSM Structure and its Electronic Model

Since the NW device has two metal contacts across the NW, it can be considered as a MSM device which has series combination of two MS junctions or two Schottky diodes facing in opposite direction as shown in Figure 38. Because the MS junction behaves as a rectifier it can be replaced by a Schottky diode in its electronic model.

![Figure 38: MSM structure and its electronic model. Note that V is an applied voltage on the MSM device. The bias voltages on Schottky contact 1, the NW and Schottky contact 2 are denoted as $V_1$, $V_{NW}$, and $V_2$ respectively.](image)
When the NW device is biased with some voltage as shown in the figure, one MS junction becomes forward biased and other MS junction becomes reverse biased. Hence, no current transport can be expected through the NW because of the reverse biased MS junction. Thermionic field emission theory is used to explain the reverse current in MS junction which predicts the tunneling of electron from metal to semiconductor at higher electric fields. Thermionic emission theory is used to explain the electrical transport phenomena in forward biased MS junction. Therefore, we can explain the electrical transport in two terminal MSM device using thermionic emission theory and thermionic field emission theory.

**Thermionic emission Theory:**

Basically, thermionic emission theory assumes that electrons with energies greater than the top of the barrier will cross the barrier and contribute to current transport. Therefore, the current transport through the forward biased MS junction can be successfully explained from this theory. There are many electrons with energy greater than the modified built in potential, \( q(v_0-V) \) in the conduction band of the semiconductor which will diffuse to the metal and contribute to current transport at forward bias state of the MS junction. Therefore, the thermionic emission current through the MS junction depends solely on the barrier height. At high temperature and low field, the thermionic emission over the barrier dominates and the temperature dependence of the carrier density distribution function is mainly responsible for the emitted current [22, 23].

The current density (\( J \)) through the forward biased MS junction is given by the following formula [22, 24],

\[
J(V, \Phi_b) = A^*T^2 \exp \left(-\frac{\Phi_b}{kT}\right) \exp \left(\frac{qV}{kT}\right) \times \left\{ 1 - \exp \left(-\frac{qV}{kT}\right) \right\}
\]  

5.1
where \( A^* \) is the Richardson constant of the semiconductor, \( \Phi_b \) is the Schottky barrier height, \( k \) is the Boltzmann constant, \( q \) is the magnitude of electronic charge, \( T \) is the absolute temperature and \( V \) is the applied bias voltage across the MS junction.

However, this thermionic emission theory predicts zero current through the reverse biased MS junction. But, when we are studying electrical transport in NW devices, the tunneling current at reverse bias state of the MS junction cannot be neglected, since it is comparable to the forward biased current of the MS junction which is in the order of picoamperes.

**Thermionic Field Emission Theory:**

Thermionic field emission theory explains the tunneling of electrons from metal to semiconductor when the MS junction is under reverse bias. Since one MS junction remains under reverse bias with respect to the other in an MSM NW device, the tunneling current dominates the transport through the NW device. According to theory, the width of Schottky barrier reduces significantly when under reverse bias which causes tunneling or leakage current from metal to semiconductor through the MS interface. A detailed description of thermionic field emission theory can be found elsewhere [22].

The current density, \( J \) from metal to semiconductor across MS junction is given by [22, 25, 26],

\[
J(V, \Phi_b) = -J_{tr}(V, \Phi_b) \times \exp \left[ V \left( \frac{q}{kT} - \frac{1}{E_0} \right) \right]
\]

where \( J_{tr} = \frac{A^* T (\pi q E_{00})^2}{k} \exp \left( -\frac{\Phi_b}{q E_0} \right) \times \left\{ q (V - \zeta) + \frac{\Phi_b}{\cosh^2 (q E_{00}/kT)} \right\}^{1/2} \) and

\[
E_0 = E_{00} \coth \left( \frac{q E_{00}}{kT} \right)
\]

and

\[
E_{00} = \frac{\hbar}{2} \left[ \frac{N_d}{m^* \epsilon_s \epsilon_0} \right]^{1/2}
\]
where $N_d$ is the donor density at the metal-semiconductor interface, $m_e^*$ is the effective mass of electron in the semiconductor, $\zeta$ is the distance between the Fermi level and the bottom of the conduction band, $\varepsilon_s$ is the relative permittivity of the semiconductor and $\varepsilon_0$ is the permittivity of free space.

As explained above, the MSM structure of the InP NW device can be modeled as a combination of two MS Schottky diodes connected back to back in series with the NW resistance $R$ (Figure 38). When a certain voltage is applied across the NW device, one contact will be forward biased and other contact will be reverse biased. At low bias state, both barriers in series with semiconductor NW will resist current flow. But, when the bias voltage increases, the Schottky barrier on the forward biased contact nearly vanishes while the barrier height on the reverse biased contact is increased (though it becomes narrower). The decreased barrier width in the reverse biased contact allows electrons to tunnel. Hence, current transport through the NW can be observed at moderately high biases.

For the numerical MSM modeling, we use the Mathematica programming language (Mathematica code for the MSM model and the parameters of InP semiconductor crystal used in the model can be found in Appendix A2 and Appendix A3 of the thesis respectively). The basic concept of the MSM modeling which we used to fit the measured I-V characteristics of the NW device can be described as follows.

Suppose a negative voltage $V$ is applied on the right electrode of the MSM structure and a current $I$ is passing through the NW (see Figure 39). At this state, Schottky contact 1 is forward
biased and Schottky contact 2 is reverse biased. Denoting the bias voltages on contact 1, the NW, and contact 2 as $V_1$, $V_{NW} (= IR)$ and $V_2$ respectively, the total voltage $V = V_1 + V_{NW} + V_2$. On the other hand, the current through the NW, and the reverse and forward-biased contacts must be the same. The current density through the forward biased Schottky contact 1 can be modeled by the thermionic emission equation 5.1. For the reverse biased contact 2, the current density can be modeled by thermionic field emission equation 5.2.

By fitting the measured I-V characteristics of the NW device using the model, the electrical transport properties of single InP NWs including carrier concentration, carrier mobility and Schottky barrier heights at the contacts of the NW can be extracted.

5.1.3 Controlling the Gate in MSM Structure

One can understand the gate operation of the NW FET with the aid of a band diagram. More importantly, the change in the gate voltage produces variations in the electrostatic potential of the NW, and hence modulates the carrier concentration and conductance of the NW.

Suppose we apply a positive gate voltage $V_{gs}$ to the NW FET. The applied voltage drops across the insulator and the semiconductor of the NW FET. Therefore, the electrostatic potential of the semiconductor $qv_0$ is increased from its equilibrium value to $q(v_0 + V_{gs})$. Then the bands are lowered towards the Fermi level which leads to an accumulation of electrons in the n-type NW and enhances the conductivity. Conversely, a negative back gate voltage raises the bands and decreases the conductivity of the n-type NW. Figure 39 shows schematically the effect of $V_{gs}$ on the electrostatic potential for n-type semiconductor NW.
As for a conventional MS interface, the p-type semiconductor NW bands bend up to bring the NW Fermi level in line with that of the metal contacts at thermal equilibrium state. When the applied gate voltage is positive, the bands are lowered (away from the Fermi level) which depletes the holes in the NW and suppresses conductivity. Conversely, for a negative gate voltage, the bands will raise and increase the conductivity of p-type NW. Hence, by mapping the dependence of the conductance on the gate bias, it is possible to determine the doping type of the NW. In addition, the electron carrier density and carrier mobility of the individual NW can be estimated using the gate dependent I-V measurements of the NW FET. Section 5.1.4 discusses the standard transistor formulas which we used to estimate the NW capacitance, electron carrier density and carrier mobility of individual NW FETs.
5.1.4 Standard Transistor Formulas

The geometry of the NW FET device leads to a formation of a capacitance between the conductive back gate electrode and the conductive channel in the NW, separated by insulating Silicon Dioxide (Figure 40). The NW capacitance can be calculated by using the standard model of a “metallic cylinder on an infinite metal plate”. The metallic cylinder represents the surface of the semiconductor NW, while the metal plate represents the back-gate electrode.

Figure 40: A schematic diagram of the InP NW cross section. Note that the red lines represent electrical field in back-gate capacitor.

Assuming a floating conducting tube above the gate electrode, the capacitance $C$ of the NW is given by [27, 28],

$$ C \approx \frac{2\pi\varepsilon\varepsilon_0 L}{\ln\left(\frac{2h}{r}\right)} $$

where $\varepsilon$ is the dielectric constant of SiO$_2$, $L$ is the active length of the NW, $r$ is the radius of the NW and $h$ is the thickness of the SiO$_2$ dielectric.
When deriving equation 5.3, we assume that the NW has a circular cross section and it has a high carrier concentration. Furthermore, we assume that the thickness of the insulator is very much smaller than the length of the NW and all the electric field lines are only passing through SiO$_2$ medium. But as shown in Figure 40, the NW is not totally surrounded by SiO$_2$ (it consists of the ambient air around the NW), and hence instead of using 3.9 for the dielectric constant of SiO$_2$, an effective dielectric constant of 2.25 as obtained from the best fit from a finite element calculation [29, 30] is used for the calculation.

Since the volume of the NW is given by $(\pi r^2 L)$, the total charge in the NW, $Q$, can be given as $(ne_e)(\pi r^2 L)$.

where $n_e$ is the carrier concentration of the NW and $e$ is the magnitude of electronic charge.

Also, we can write $Q = C (V_{th} - V_{gs})$ for the capacitor, if the threshold voltage of the NW FET device is denoted by $V_{th}$.

When gate-source voltage is zero, $V_{gs} = 0$, the carrier concentration ($n_e$) can be written as [27],

$$n_e = \frac{V_{th}C}{e\pi (r)^2 L} \quad 5.4$$

The mobility of the carriers ($\mu$) can be estimated from transconductance of the FET. The transconductance of the FET is given by [27, 28],

$$\frac{dI_{ds}}{dV_{gs}} = \frac{\mu C}{(L)^2} V_{ds} \quad 5.5$$
Hence, from the slope of the graph of transconductance vs. bias voltage ($V_{ds}$), the carrier mobility can be calculated. However, most real NW FET devices show typical non-Ohmic I-V characteristics because of the influence of contact resistance between the NW and the metal electrodes. Therefore, the effect of contact resistance should be considered when estimating the carrier mobility of the NW. Equation 5.5 is valid only if the MS contacts are Ohmic. Hence, if the contact resistance is considered, the carrier mobility can be estimated from the modified equation [27],

$$\frac{g_d}{\sqrt{g_m}} \sqrt{\frac{L V_{ds}}{d C_i}} = \sqrt{\mu} (V_{gs} - V_{th})$$

where $g_d$ is the differential conductance ($\frac{\partial I_{ds}}{\partial V_{ds}}$), $g_m$ is the transconductance ($\frac{\partial I_{ds}}{\partial V_{gs}}$), $d$ is the diameter of the NW and $C_i$ is the capacitance of the SiO$_2$ layer per unit area.

### 5.2 Electrical Transport Measurements

Many InP NW FET devices are fabricated under the same conditions. But, the I-V characteristics of each of them are observed to be different from one another depending upon the surface condition of the NW, contact area, material resistance and the varying conditions in which devices were fabricated. However, these NW FET devices are all highly photosensitive under white light. The current is observed to be increased by three orders of magnitude (especially the undoped InP NWs) with white light illumination.

Current ($I_{ds}$) vs drain-source voltage ($V_{ds}$) and $I_{ds}$ vs. gate-source voltage ($V_{gs}$) are recorded for the NW-FET to characterize its electrical properties.
5.2.1 Gate-Dependent I-V Measurements

Figure 4 shows a set of current vs. drain-source voltage ($V_{ds}$) data obtained from a single InP NW-FET at different gate-source voltages ($V_{gs}$). The two-terminal I-V curve at $V_{gs}=0$ V is non-linear, thus indicating that the metal electrodes make non-Ohmic (Schottky) contacts with the InP NW.

Figure 41: Measured gate-dependent I-V characteristics of a doped InP NW FET at room temperature. The gate voltages for each I-V curve are indicated.

In addition, the gate-dependence of the I-V curves shows that the InP NWs are n-type that is, the conductance of the NW increases (decreases) with increasingly positive (negative) $V_{gs}$.
5.2.2 Carrier Density and Carrier Mobility of InP NWs

The transport characteristics of the InP NW FETs have also been examined. The $I_{ds}$ vs $V_{gs}$ curves for the InP NW FET recorded at different $V_{ds}$ are shown in Figure 42.

![Figure 42: I-V_{gs} data recorded for values of V_{ds} (0.5 V to 2.5 V) of the doped InP NW FET at room temperature. Note that the linear fit of I-V_{gs} at V_{ds} = 0.5 V is used to obtain V_{th} for analyzing the data.](image)

As shown in the figure, the linear fit of $I_{ds}$ vs $V_{gs}$ at $V_{ds} = 0.5$ V is used to obtain the threshold voltage, $V_{th}$ (-10.18 V) of the InP NW FET. The conductance ($C$) and carrier concentration ($n_e$) are thus found to be $2.01 \times 10^{-16}$ F, $4.08 \times 10^{17}$ cm$^{-3}$ respectively using the equations 5.3 and 5.4 for InP FET devices. Since the source and drain metal pads are 4 μm apart, it is used as the active length of the NW in calculations.
From the slope of $(dI_{ds}/dV_{gs})$ vs. $V_{ds}$ graph (Figure 43), the carrier mobility $\mu$ is estimated to be $1.06 \times 10^2$ cm$^2$/V.s using the equation 5.5 for the n-type InP NWs.

As shown in Figure 41, the InP NW FET device has typical non-Ohmic I-V characteristics because of the influence of contact resistance between NW and metal electrodes. If the contact resistance is considered, the carrier mobility is estimated to be $6.55 \times 10^2$ cm$^2$/V.s using the modified equation 5.6. Therefore, it is clearly observed that the calculated carrier mobility is about six times larger than the mobility obtained from equation 5.5 and it confirms the influence of the contact resistance towards the calculation of mobility. Also, the estimated carrier mobility for n-type InP NWs is comparable with literature values [31].
5.3 Theoretical MSM Model

As discussed in section 5.1.2, we used an equivalent circuit model of the MSM structure of the InP NW device incorporating a back to back diodes in series with the NW resistance to model the measured mobility and carrier concentration of the NW device. Since, the estimated carrier concentration and mobility are depended on the device geometry and the contact resistances, it is relevant to use the electronic model of the MSM structure of the NW device to calculate the transport properties of the NW. Details of the MSM model including the basic concepts of the model which we used to fit the measured I-V characteristics of the NW device can be found in section 5.1.2.

![Figure 44: Modeling of the InP NW FET. The experimental data points are plotted as blue filled symbols while the I-V MSM fitting model is plotted as red line in the same graph. The numbers inside the plot indicate the carrier density \( n_e \), carrier mobility \( \mu \), Schottky barrier heights \( \phi_{b1} \) and \( \phi_{b2} \) of the NW FET extracted from the fitting model.](image)

Figure 44 shows the fitted curve with the measured experimental I-V data of the InP NW device. The model is observed to be well fitted with the experimental I-V characteristics of the MSM structure. Not only the transport properties of the InP NWs, but also information about each of
the contacts is extracted using the MSM model. The values for the carrier concentration and mobility are extracted as $1.00 \times 10^{17} \text{cm}^{-3}$ and $5.11 \times 10^2 \text{cm}^2/(\text{V.s})$. These values approximately agree with the experimental values using the FET analysis and the model is also helpful in finding the barrier heights of the NW device as 0.15 eV and 0.08 eV. Both sides of contacts are fabricated at the same time and different barrier heights are due to different surface conditions. Also, the asymmetry of the observed dark I-V curve (Figure 41) indicates that the Schottky diodes on each ends of the NW are not identical which is in good agreement with the extracted different barrier heights from the model.

5.4 Conclusion

Single InP NW field effect transistors are fabricated using n-type InP NWs with ~100 nm diameter and ~8 μm length grown by Au catalyst-assisted MOCVD. Gate-dependent electrical transport measurements showed that the InP NWs are n-type. Current-voltage plots display typical non-Ohmic behavior due to the contact resistance between NW and metal electrodes, which was identified by comparison between the estimated carrier mobility including the contact resistance and excluding the contact resistance. Carrier mobility determined for the InP NWs is as high as $655 \text{cm}^2/(\text{V.s})$ for the carrier density of $4.08 \times 10^{17} \text{cm}^{-3}$. This mobility is comparable to n-type InP NWs with similar carrier density and thus demonstrates the high quality of these NW building blocks and their potential for nanoscale electronics. In addition, an equivalent circuit model of the MSM structure is used for quantitatively analyzing the experimental two-terminal I-V curve of InP NWs at $V_{gs}= 0 \text{V}$ and extracting the carrier density and mobility of the NW as $1.00 \times 10^{17} \text{cm}^{-3}$ and $511 \text{cm}^2/(\text{V.s})$. While providing a good agreement with the FET
experimental results, this model makes it possible to determine the barrier heights of the NW device.

These results provide important feedback to crystal growers in order to optimize the quality of NWs and prove the potential of using InP NWs for future nanoscale device applications.
References:


Appendices

A1: Ammonium poly-Sulfide Etching Process

Making Ammonium poly-Sulfide solution

Saturating Ammonium Sulfide with Sulfur is required for the process such that the dissolved Sulfur will polymerize and create chains. These Sulfur chains that are left on surface help slow the oxidization process of the material. Making the solution can be described as follows in detail.

a. 20 ml of Ammonium Sulfide ((NH₄)₂S) is placed into a beaker with a stir rod.

b. Next the stir plate is turned on and the speed is adjusted. So that, the liquid does not splash.

c. Then the Sulfur powder is added gradually into the breaker while making sure that there are no clumps.

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

e. After that, the solution is poured into a dark container, since it is photosensitive.

f. Finally, the container is labeled and placed in the corrosive cabinet.

Note: There may be some Sulfur powder floated on the surface of the solution. Therefore, Ammonium poly-Sulfide solution can be drawn using a pipette from the center of the container.

Ammonium poly-Sulfide etching

Ammonium poly-Sulfide etching process is used to etch away the native oxide layer of the NW and leave a thin layer of unstable Sulfur chains to help prevent it from re-oxidization. It is
performed just before the metal deposition in the device fabrication process. The process can be described as follows in detail.

a. Ammonium polysulfide solution is mixed with DI water (1:500 ratio by volume).

b. Next, the device is placed in the diluted solution which is on a hotplate at 60° C.

c. A 60 W light bulb is set up above the solution.

d. The etching process will be lasted for 1/2 an hour.

e. Then the devices are rinsed thoroughly with DI water.

f. After that, they are blow-dried with nitrogen.

g. Finally the devices are put in a vacuum for metal deposition.
A2: Mathematica Code for the MSM Model

Define the values for the parameters

\[ k = 1.38065 \times 10^{-23}; \]
\[ \hbar = 6.626 \times 10^{-34} / (2 \times \pi); \]
\[ h = 6.626 \times 10^{-34}; \]
\[ mn = 0.078 \times 9.1 \times 10^{-31}; \]
\[ es = 12.4; \]
\[ e = 8.854 \times 10^{-12}; \]
\[ q = 1.602 \times 10^{-19}; \]
\[ T = 294; \]
\[ A = (4 \times \pi \times mn \times q \times k ^ 2) / (h ^ 3); \]
\[ S = N[\pi \times (50 \times 10 ^ {-9}) ^ 2]; \]
\[ \zeta = 0.24; \]

Here S, \( mn \), \( \zeta \), A, es, e and q are the cross-sectional area of the NW, the effective mass of an electron in the semiconductor, the distance between the Fermi level and the bottom of the conduction band, Richardson constant, relative permittivity of the semiconductor, permittivity of free space and the magnitude of electronic charge respectively.

Data Import

\texttt{expdata = Import["C:\Users\Nadeeka\Desktop\aa.txt", "Table"];}

Table Generation

\texttt{bias = Table[Part[expdata[[i]], 1], \{i, 1, Length[expdata], 1\}]
\{-2.5, -2, -1.5, -1, -0.5, 0, 0.5, 1, 1.5, 2, 2.5\}}
\texttt{current = Table[Part[expdata[[i]], 2], \{i, 1, Length[expdata], 1\};}
Define the voltage functions

\[ v_{I1} \equiv n_{I1} \cdot L_{I1} = v_1 \parallel \text{FindRoot}\left[ b_{I1} \cdot \exp\left(39.4 \cdot v_1 / n_{I1}\right) \times (1 - \exp(-39.4 \cdot v_1)) - I_1 \right, (v_1, 0.1) \right] \]

\[ v_{I2} \equiv n_{I2} \cdot e_0 \cdot I_{I2} = v_2 \parallel \text{FindRoot}\left[ b_{I2} \cdot \exp\left(39.4 \cdot v_2 / (0.4 - 1 / e_0)\right) - I_2 \right, (v_2, 0.1) \right] \]

\[ v_{Ib} \equiv n_{Ib} \cdot e_0 \cdot I_{Ib} = v_I \parallel \text{FindRoot}\left[ b_{Ib} \cdot \exp\left(39.4 \cdot v_I / (0.4 - 1/e_0)\right) - I \right, (v_I, 0.3) \right] \]

\[ v_{Iv} \equiv n_{Iv} \cdot e_0 \cdot I_{Iv} = v_v \parallel \text{FindRoot}\left[ b_{Iv} \cdot \exp\left(39.4 \cdot v_v / (0.4 - 1/e_0)\right) - I \right, (v_v, 0.3) \right] \]

\[ v_{I0} \equiv n_{I0} \cdot e_0 \cdot I_{I0} = v_0 \parallel \text{FindRoot}\left[ b_{I0} \cdot \exp\left(39.4 \cdot v_0 / (0.4 - 1/e_0)\right) - I \right, (v_0, 0.3) \right] \]

\[ v_{total} \equiv n_{total} \cdot e_0 \cdot I_{total} = \begin{cases} v_{Ib} \parallel b_{Ib} \cdot e_0 \cdot I_{Ib} & I < 0 \\ v_{Iv} \parallel b_{Iv} \cdot e_0 \cdot I_{Iv} & I \geq 0 \end{cases} \]

Fitting

\[ \chi^2 = \text{Sum}\left[\expdata[[i, 1]] - v_{total}[[i, 1, 1], 1, 4, 6, 2, 0, 0.026, 8, 8, 10^5]]\right] \]

\[ \{0.0075327, \{1s_1 \rightarrow 2.79995 \times 10^{-6}, 1s_2 \rightarrow 1.9561 \times 10^{-6}, n_1 \rightarrow 15.9032, 1s_3 \rightarrow 1.429494 \times 10^{-7}, 1s_4 \rightarrow 3.98562 \times 10^{-8}, n_2 \rightarrow 27.5282, e_0 \rightarrow 0.027064, R \rightarrow 618.746 \} \]

\[ \text{Show[ListPlot[Transpose[[\text{bias, current} / 10^{10}]], PlotStyle \rightarrow \text{Blue}, PointSize[0.02]], PlotLegends \rightarrow \{ \text{V Exp}, \text{AxesLabel} \rightarrow \{"Bias Voltage (V)", "Dark Current (\mu A)\}"}, \text{ListLinePlot[Transpose[[\text{finalv, current} / 10^{10}]], PlotStyle \rightarrow \text{Red}, PlotLegends \rightarrow \{ \text{V Fit}, \text{AxesLabel} \rightarrow \{"Bias Voltage (V)", "Dark Current (\mu A)\}"}]\]

![Graph showing exponential fit vs. V]
Define the fitting parameters

\[
\text{Is4}[\phi_{ib2}, N_d, v_2] := \frac{-S \ast \mathcal{A} \ast T \ast (\pi \ast q \ast e_{00} [N_d])^{1/2}}{k} \ast \exp \left[ \frac{-\phi_{ib2} \ast q}{q \ast e_{00} [N_d]} \right] \ast \exp \left[ \left( \frac{\phi_{ib2} \ast q}{k} \ast \frac{\phi_{ib1} \ast q}{e_{00} [N_d]} \right)^{1/2} \right] \ast \frac{q \ast (v_2 - \zeta) + \frac{\phi_{ib2} \ast q}{(\cosh \left[ \frac{e_{00} [N_d]}{k} \ast T \right])^2}}{1/2}
\]

\[
\text{Is2}[\phi_{ib1}, N_d, v_2] := \frac{-S \ast \mathcal{A} \ast T \ast (\pi \ast q \ast e_{00} [N_d])^{1/2}}{k} \ast \exp \left[ \frac{-\phi_{ib1} \ast q}{q \ast e_{00} [N_d]} \right] \ast \exp \left[ \left( \frac{\phi_{ib2} \ast q}{k} \ast \frac{\phi_{ib1} \ast q}{e_{00} [N_d]} \right)^{1/2} \right] \ast \frac{q \ast (v_2 - \zeta) + \frac{\phi_{ib1} \ast q}{(\cosh \left[ \frac{e_{00} [N_d]}{k} \ast T \right])^2}}{1/2}
\]

\[
\text{Is1}[\phi_{ib2}] := S \ast \mathcal{A} \ast T \ast 2 \ast \exp \left[ \frac{-\phi_{ib2} \ast q}{k \ast T} \right]
\]

\[
\text{Is3}[\phi_{ib1}] := S \ast \mathcal{A} \ast T \ast 2 \ast \exp \left[ \frac{-\phi_{ib1} \ast q}{k \ast T} \right]
\]

Extract the barrier heights from the model

\[
\text{Solve}\left\{ \text{Is3} = S \ast \mathcal{A} \ast T \ast 2 \ast \exp \left[ \frac{-\phi_{ib2} \ast q}{k \ast T} \right] \& \& \text{Is3} = 1.4249351570813517 \ast 10^{-7}, \{\text{Is3, phi1}\} \right\}
\]

\[
\text{Solve}\left\{ \text{Is1} = S \ast \mathcal{A} \ast T \ast 2 \ast \exp \left[ \frac{-\phi_{ib2} \ast q}{k \ast T} \right] \& \& \text{Is1} = 2.799948327302957 \ast 10^{-6}, \{\text{Is1, phi2}\} \right\}
\]

Extract the transport properties from the model

\[
e_{00}[N_d] := (\frac{\hbar}{2}) \ast (N_d / (mn \ast es \ast e))^{1/2};
\]

\[
7.79287 \times 10^{-42}
\]

\[
e_{0}[N_d] := (\frac{\hbar}{2}) \ast (N_d / (7.7928 \ast 10^{-42}))^{1/2} \ast N[\cosh[39.4 \ast (\frac{\hbar}{2}) \ast (N_d / (7.7928 \ast 10^{-42}))^{1/2}]];
\]

\[
e_{0}[1.00527 \ast 10^{23}]
0.02585
\]
\[ v_{33}^{t} \text{[\sigma_\theta]} := \frac{N_d}{\beta} \text{FindRoot}\left[ \left( \frac{\sigma_\theta}{2} \right) = \frac{N_d}{(7.7928 \times 10^{-6} - 42)^{1/2}} \times \text{N} \left[ \text{Coth} \left[ \frac{39.4 \times \left( \frac{\sigma_\theta}{2} \right) \times (N_d/(7.7928 \times 10^{-6} - 42))^{1/2}}{N_d} \right] \right] \right] = \sigma_\theta, (N_d, 10^{-21}) \]

\[ v_{33}^{0.02585} \]

1.00527 \times 10^{23}

Here, \( N_d \) is the carrier density of the NW

\[
\text{Since conductivity (sigma)} = \frac{L}{R \cdot S},
\]

\[
\text{sigma} = 4 \times 10^{-6}/(6.19 \times 10^{-5} \cdot S)
\]

822.772

\[
\text{Mobility} = \frac{\text{conductivity}}{(N_d \cdot q)}
\]

\[
\text{mobility} = \frac{\text{sigma}}{1.0052696187119611 \times 10^{-23} \cdot q}
\]

0.0510898
### A3: InP Material Properties

Some important parameters of InP semiconductor crystal [1--3] used in the MSM model in Chapter 5:

<table>
<thead>
<tr>
<th>Parameter of the material</th>
<th>Remark</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band gap</td>
<td>At room temperature</td>
<td>1.34 eV (Zincblende)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.42 eV (Wurtzite)</td>
</tr>
<tr>
<td>Effective mass of electron</td>
<td>$m_o$ is the free electron mass</td>
<td>0.078$m_o$</td>
</tr>
<tr>
<td>Effective mass of hole</td>
<td>$m_o$ is the free electron mass</td>
<td>0.6$m_o$</td>
</tr>
<tr>
<td>Lattice constant</td>
<td>cubic lattice</td>
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<tr>
<td>Electron affinity</td>
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<td>4.38 eV</td>
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<tr>
<td>Intrinsic carrier concentration</td>
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<td>$1.3 \times 10^7$ cm$^3$</td>
</tr>
<tr>
<td>Density</td>
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<td>4.81 g/cm$^3$</td>
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<tr>
<td>Relative permittivity</td>
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<td>12.4</td>
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<tr>
<td>Effective conduction band density of states</td>
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<td>$\sim 10^{17}$ cm$^3$</td>
</tr>
<tr>
<td>Effective valence band density of states</td>
<td></td>
<td>$\sim 10^{19}$ cm$^3$</td>
</tr>
</tbody>
</table>
References:


