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I, Bekele H Badada, hereby submit this original work as part of the requirements for the degree of Doctor of Philosophy in Physics.

It is entitled:
Probing Electronic Band Structure and Quantum Confined States in Single Semiconductor Nanowire Devices

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Probing Electronic Band Structure and Quantum Confined States in Single Semiconductor Nanowire Devices

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

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by

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Abstract

We have used electrical transport measurements, photocurrent spectroscopy (PC), photoluminescence (PL) and photoluminescence excitation spectroscopies (PLE) to investigate electronic band structure and quantum confined states in single (MOCVD) grown semiconductor nanowires. The nanowires used in this study include Zn$_2$As$_3$, GaAs, GaAsSb, GaAs/AlGaAs core-shell and GaAs/AlGaAs core-multishell (Quantum well tube (QWT)) nanowires. Single nanowire devices were fabricated using photolithography to deposit metal contacts on either end of the nanowire to allow optoelectronic measurements.

Electrical transport and photocurrent spectroscopy were used to characterize a novel II-V semiconductor nanowire device, Zn$_3$As$_2$, at room and low (10 K) temperature. Employing metal-semiconductor-metal modeling and self-consistent fitting, we have extracted relevant intrinsic semiconductor parameters from room temperature current-voltage characteristics. The extracted acceptor doping densities for nanowire and nanoplatelet devices are of $1.67 \times 10^{18} \text{cm}^{-3}$ and $7.41 \times 10^{18} \text{cm}^{-3}$ respectively. These values agree well with doping densities determined using transient Rayleigh scattering. The photocurrent spectra measurements reported here allow an estimation of the band gap of this material to be 1.13 eV which is in the near-infrared at 10 K.

The electronic band structure of single GaAs nanowires was also characterized using photocurrent spectroscopy at room and low (10 K) temperature. In bare 100 nm diameter GaAs nanowire devices we observed the non-linear dark current arising from back-to-back Schottky behavior. We observed saturation of photocurrent as we increased the bias for fixed photon energy above the band gap at room temperature. We attributed this saturation to the diffusion length of minority carriers resulting in the complete extraction of photogenerated carriers at high biases. Photocurrent spectra at 10 K exhibit a peak near the band edge of GaAs $\sim$1.5eV, in both bare GaAs core and
GaAs/AlGaAs core-shell nanowire devices. This peak is the signature of an excitonic resonance contributing to below band gap absorption. In addition, the GaAs/AlGaAs photocurrent spectra provide a clear estimation of the Al concentration in the barrier.

GaAsSb photocurrent spectra at 10 K were also measured which showed the onset of absorption at 0.9 eV. In addition, a peak observed at ~300meV above the band gap is related to the split off band consistent with a 40 %-45% Sb concentration found using EDX analysis.

We explored the nature of exciton localization in single GaAs/AlGaAs QWT devices using PC, combined with simultaneous PL and PLE measurements. Excitons confined to GaAs quantum well tubes of 8 and 4 nm widths embedded into an AlGaAs barrier were seen to ionize at high bias levels. Spectroscopic signatures of the ground and excited states confined to the QWT were seen in PL, PLE, and PC data and were consistent with simple numerical calculations. The demonstration of good electrical contact with the QWTs enabled the study of quantum confined Stark effect shifts in the sharp emission lines of excitons localized to quantum dot-like states within the QWT. Atomic resolution cross-sectional TEM measurements and an analysis of the quantum confined Stark effect of these dots provided insights into the nature of the exciton localization in these nanostructures.
To my parents
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Chapter-1. Introduction

1.1. Background

Semiconductor nanowires have been heavily studied for their potential use for future compact and efficient optoelectronic devices such as solar cells, light emitting diodes and field effect transistors. One of the many advantages of semiconductor nanowires is that it is possible to fabricate nanostructures from the bottom-up literally atom by atom. Such unprecedented control of the constituent materials allows one to create novel electronics and optoelectronic devices.

Since the invention of transistors in the second half of the 20 century, the electronics industry has experienced explosive growth, and demands for new technologies continue. Because of this, there has been a perpetual search for much faster, smaller, cheaper, and efficient electronic and optoelectronic devices, and so semiconductor physics remains an important area of research both in academia and industry. Over the past half a century, the transistor density of integrated circuits has been doubling every two years following Moore’s law. This trend of shrinking the size of transistors has nearly reached a limit beyond which traditional top-down fabrication using lithography cannot achieve. Moreover, controlling the device size on the nanoscale using lithography has been shown to result in a number of deleterious impacts such as increased leakage current, device-to-device variation of the on/off current, and other issues.

Some of these problems due to the smaller size of planar MOSFETs have been circumvented by designing a new architecture where the gates are wrapped around the channel, also known as FinFET. However, the cost of sophisticated lithography and decreasing yield rates, has the potential to create an economic barrier. Such size reductions of devices can alternatively be achieved by a bottom-up approach where the dimension of nanowires can be precisely controlled. In addition, one can grow core-shell heterostructured nanowires which have the potential to
provide superior advantages in quality and device architecture. Despite the current engineering challenges of integrating nanowires into working devices, the potential of solving both dimensional and architectural problems have been addressed by scientists around the globe. This is why semiconductor nanowires are considered essential components of the International Technology Roadmap for Semiconductors.\textsuperscript{11}

Another important driver for intense research in semiconductor nanowires is due to their interaction with light. This has opened up wide range of interesting applications as photovoltaic\textsuperscript{12-16} and light emitting diodes, \textsuperscript{17-22} single nanowire laser, \textsuperscript{23-29} and photo detectors.\textsuperscript{30-35}

Similar to integrated circuits, the nanowire growth and potential device architectures provide enormous flexibility to increase the existing photovoltaic efficiency or create new design of materials which are challenging to achieve in bulk devices. For example, single core-shell p-i-n nanowires where the core and shell are doped with p and n respectively will create a cylindrical p-i-n junction with much bigger surface area as compared to planar p-i-n junctions as shown in Fig.1.1. This increases the absorption surface area, dissociation rate of electron-hole pairs and reduces parasitic resistance and therefore carrier collection efficiency.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{comparison.png}
\caption{Illustration of comparison between planar p-i-n junction vs core-shell nanowire p-i-n junction.\textsuperscript{36}}
\end{figure}
Although Si and Ge are still dominant semiconductors in the integrated circuit electronics industry, optically they are not as efficient as group III-V semiconductors due to their indirect band gap. Group III-V semiconductors have clearly superior optical and electronic properties to serve as the basis for optoelectronic devices. Fig. 1.2 shows the comparison of direct and gap and indirect band gaps. In an indirect band gap material both absorption and luminescence involve a phonon to conserve momentum in optical transitions, which dramatically reduces the optical efficiency for light emission and absorption.

![Figure 1.2](image)

**Figure 1.2** a) band diagram of direct band gap the bottom conduction band and top of valence band are aligned at \( k=0 \) (b) band diagram of indirect band gap, the conduction band minimum occurs at different \( k \).

Most III-V semiconductors also have higher electron mobilities which makes them the best candidate for faster electronic devices.

Another unique and interesting property of III-V semiconductor nanowires is the possibility of alloying constituent elements to form a ternary alloy and so tune the optical and electrical properties over a wide range.\(^{37}\) This gives tremendous flexibility in the design of novel semiconductor devices.
In addition to providing an important basis for new technologies, semiconductor nanowires play an important role in understanding of fundamental physics on the nanometer scale. For example, the Majorana fermions, which have been theoretically predicted to exist in topological superconductors were first detected in Indium Antimoide nanowires.\textsuperscript{38} Spin injection and coherent spin transport on the nanoscale potentially open up new research areas to increase fundamental understanding of spins for quantum information technology.\textsuperscript{39}

1.2. Statement of the problem

In order to realize the potential of semiconductor nanowires, experiments to optimize growth technique and characterization of the resulting nanowires are critical for the design of new heterostructures. The fabrication of group III-V nanowires have been continuously improving in quality and diversity over the past decade.\textsuperscript{40-43} The research group led by Professor Chennupati Jagadish at Australian National University (ANU) is one of the pioneers of MOVCD growth techniques for growing a wide variety of III-V nanowires and nanowire heterostructures. The nanowires studied in this thesis were grown at ANU. After growth of the nanowires, different characterization techniques for both structural and optical properties are employed. Atomic resolution imaging techniques,\textsuperscript{44} X-ray diffraction and EDX\textsuperscript{45} techniques are used to study the quality of the nanowire crystal and estimate alloy concentration of constituent atoms along the nanowires. Extensive cross-sectional imaging is also implemented to investigate core-shell heterostructures nanowires.\textsuperscript{46}

In our group, photoluminescence and time resolved photoluminescence spectroscopies are primarily used to measure the band gap, optical quality and exciton lifetime in most GaAs and InP based nanowires.\textsuperscript{46-51} Recently, Shi \textit{et al.} has implemented photoluminescence imaging to spatially resolve the photoluminescence from a single nanowire.\textsuperscript{50,51} Micro-Raman spectroscopy is also
extensively used in order study the stress and strain of single nanowires. Strain and stress due to lattice mismatch of core shell nanowires are usually measured in order to understand the change in energy band structure as a result of different material interfaces.\textsuperscript{52}

Montazeri \textit{et al.} have developed polarization modulated Rayleigh scattering from a single nanowire to probe band gap and also measure the size of the nanowire.\textsuperscript{53} Furthermore, transient Rayleigh scattering has been used to measure the lifetime of photoexcited charge carrier recombination as well as carrier thermalization dynamics in single nanowires.\textsuperscript{54, 55}

The above-mentioned techniques are very powerful and accurate in characterizing single nanowires dispersed on a silicon substrate. Both photoluminescence and Rayleigh scattering are used to probe ground state transitions; however the electronic band structure of these semiconductor nanowires requires absorption spectra measurements. Absorption measurements on single nanowires is extremely challenging due to the size of the nanowires. Therefore it is important to carry out photocurrent spectroscopy which is proportional to the absorption in a single nanowire. Furthermore, electronic transport characterization is very crucial as these nanowires are to be used as building blocks of electronic and optoelectronic devices.

In this thesis, we investigate electronic band structure of select MOCVD grown GaAs based nanowires including bare GaAs, bare GaAsSb, GaAs/AlGaAs core-shell, GaAs/AlGaAs core-multishell or quantum well tube (QWT) and a group II-V, Zn\textsubscript{3}As\textsubscript{2} semiconductor nanowires. We primarily use transport and photocurrent spectroscopy techniques to measure the band structure of individual nanowires. We also combine both photoluminescence and photocurrent spectroscopies in later in chapter five in order to investigate the quantum confined Stark effect in quantum dot formed in quantum well tube nanowires. In all cases device fabrication was required.
1.3. Outline of the thesis

This thesis contains five chapters: In Chapter one (this chapter) we have introduced semiconductor nanowires and their motivation. We have discussed the historical context of evolution of nanowire growths and how it is important for future optoelectronic development as well as explores new physics in the nanometer scale.

In Chapter two, we will give a brief description of MOCVD method of nanowire using GaAs as an example. We also discuss single nanowire device fabrication processes using photolithography in detail and provide a description of all experimental techniques used in this research.

In chapter three, we introduce a novel Zn$_3$As$_2$ nanowire and its growth. We will also explain modeling of two probe nanowire devices as back-to-back Schottky diodes thus decoupling the contact effects so semiconductor nanowire parameters are extracted using a self-consistent fitting. We will also explain the photocurrent spectroscopy results.

In Chapter four, we investigate the band structure of binary and ternary GaAs based single nanowire devices. Namely, we investigate bare GaAs, GaAs/AlGaAs core-shell heterostructure and GaAsSb nanowire devices using transport and photocurrent spectroscopy techniques at both room and low (10 K) temperatures.

In Chapter five, we introduce core-multishell structures or quantum well tubes grown using MOCVD techniques. We also describe structural analysis of cross sections of the nanowires, as well as use a cylindrical approximation model to calculate confined energy eigenvalues and wave functions. We use simultaneous photocurrent (PC), photoluminescence (PL), and photoluminescence excitation (PLE) spectroscopy in single nanowire QWT devices to probe both the delocalized and localized states within the QWT. We will also describe the quantum confined
Stark effect observed in a semiconductor nanowire QWT where the well is narrow enough to result in exciton localization at low temperatures. The observed quantum dot-like emission in 4 nm quantum well tube were modeled using a truncated harmonic oscillator to estimate the quantum dot size and confining potential.

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Chapter-2. Experimental

2.1. Introduction

Interests in the reduced size, compact and efficient optoelectronic devices have grown over the years mainly due to the possibilities of growing nanostructure from bottom up which provides unprecedented control of compositions and size of the nanostructures for desired purposes. Over the last decade, many material scientists developed the possibility of growing electronic and optoelectronic devices using a bottom up approach. Group III-V and II-V semiconductor nanowires and heterostructures studied in this thesis were grown using MOCVD techniques at Australian National University, in the research group of Professor Jagadish. In this chapter, we briefly describe the growth of nanowires, detail of single nanowire devices fabrication, electrical characterization set up, and photocurrent spectroscopy measurement, Photoluminescence and Photoluminescence Excitation measurement.

2.2. Growth of Nanowires using MOCVD method

There are several techniques for growing group III-V nanowires. Gold-catalyzed Metal Organic Chemical Vapor Deposition is one of the most commonly used. Although there are a number of different binary and ternary III-V semiconductor materials, in this section we use GaAs as and AlGaAs as binary III-V and ternary III-V semiconductor respectively as examples to describe the MOVCD growth mechanism. Details of growth specific to each material in this thesis are outlined in each chapter.
The MOCVD mechanism involves a chemical reaction of carrier gas in a chamber where Ga and/or Al carrier and As carrier gas are introduced in a hydrogen environment. The group III elements, Ga and Al, are supplied as vapor phase organometallic precursor species: trimethylgallium (Ga(CH₃)₃, TMGa), and trimethylalumin (Al(CH₃)₃, TMAI) respectively. The group V element, As, is supplied as vapour phase hydrides: arsine (AsH₃). These reactants are carried into the reactor by ultra-high purity hydrogen gas, H₂. During growth, these precursors decompose to release group III and group V elements. Typically, the nanowires and growth substrates are the same III-V semiconductor materials. In our example, the GaAs (111B) substrate is used to grow the nanowires. The growth procedures are detailed in reference 6 and illustrated in Fig. 2.1. Au nanoparticles were deposited on the substrate surface as shown Fig 2.1a. The prepared substrate, hosting deposited Au nanoparticles, was placed into the reactor on a graphite susceptor. The substrate was heated to 600 °C and annealed in situ for 10 minutes to desorb surface contaminants, including the surface oxide. Annealing of the GaAs substrates was performed under group V over pressure, to prevent decomposition of the substrate. This group V overpressure was provided by an AsH₃ flow. After annealing, the substrate was cooled to growth temperature, typically
between 350 °C and 550 °C. The group V flow rate was adjusted for growth. Then group III precursors were fed to the reaction chamber to initiate growth. Growth times were generally between 30 s and 120 minutes, chosen according to the growth rate and the desired nanowire length. Upon completion of growth, each sample was cooled under group V overpressure (AsH₃ flow).

### 2.2.1. Core-shell nanowire growth

The diameter at the tip of the nanowire is determined by the catalyst diameter. Other nanowire properties, such as height, morphology, crystal structure, crystallographic defects and impurity incorporation can be controlled by choosing appropriate growth parameters. These include growth time, temperature, pressure and the flow rates of group III and group V precursors. It has also been demonstrated that by changing growth temperature, the axial growth can be hindered while fostering radial growth. The ability to grow nanowires in a preferred direction allows the growth of core-shell nanowires and even more complex heterostructures which opens up opportunities to design novel optoelectronic devices. For instance the growth GaAs/AlₙGa₁₋ₙAs nanowire are grown by growing the GaAs core as described in previous section followed by

![Figure 2.2 Schematic representation of GaAs/AlGaAs core/shell nanowire growth.](image)
Al$_x$Ga$_{1-x}$As shell growth at higher temperature see Fig. 2.2. In Chapter five we will describe core-multishell nanowire grown by switching constituent elements alternatively during radial growth.

The nanowire core is grown first, by the Au nanoparticle-assisted mechanism. Then the precursor gases are changed and growth temperature is increased to promote radial growth. Fig.2.3 shows the SEM images of bare GaAs and GaAs/AlGaAs as grown nanowires.

![GaAs](image1.png) ![GaAs/AlGaAs](image2.png)

Figure 2.3 Scanning electron microscope (SEM) images of GaAs(left) and GaAs/AlGaAs core/shell (right) nanowires grown on (111)B GaAs substrate.
2.3. Device fabrication

Device fabrication involves several steps from cleaning the substrate to lift-off. The schematic of the process flow is shown in Fig 2.4. In this section, we present the description of experimental procedures and techniques in detail.

2.3.1. Substrate cleaning

We use a SiO₂/Si substrate where the thermally grown SiO₂ has a thickness of 300 nm and provides insulation from the heavily p-doped Si. To fabricate single nanowire devices, we begin with cleaning the substrate. The typical area of substrates size 5 mm X 5 mm. We clean the substrate with acetone, methanol, and isopropanol and DI water consecutively, and dry with nitrogen. The acetone removes organics contaminant such as oil. However, since acetone evaporates rapidly it re-deposits contaminant. Methanol removes the remaining contaminant and the isopropanol is known to be good rinsing agent. Rinsing with DI water and a dry blow with nitrogen completes the cleaning of the substrate.

Figure 2.4 Schematic of device fabrication process flow.
2.3.2. Dispersion of Nanowires

Nanowires were mechanically removed from the growth substrate by sonication in methanol. A few drops of the solution containing methanol and nanowires are transferred to the pre-cleaned SiO$_2$/Si substrates by micro pipette. After few minutes the methanol dries away, while a low number density of nanowire remain attached to the substrate due to Van Der Waals forces. Finally, the substrates are rinsed with methanol and isopropanol to remove contaminant or dirt particle deposited from the solution.

Figure 2.5 (a) High density of mechanically broken nanowires (b) low density after dispersion from solution.
2.3.3. Photolithography

The substrate with the dispersed nanowires are spin coated with S1818 photo resist at speed of 5 krpm for 30sec followed by soft baking to ensure evaporation of the remaining solvent. We use Nanonex 2600 optical mask aligner equipped with a 50X long working distance Mitutuyo objective (see Fig. 2.6). A specially designed photo-mask was used to mask the middle of the nanowires and expose the ends for UV exposure. Typically the UV exposure times are 5 sec. Several consecutive exposures are possible to make multiple devices on the same substrate. After UV exposure the substrates were soaked in chlorobenezene for 90 sec and hard baked for three minutes. Finally the exposed resist was developed in developer D-350: DI water at 1:5 ratio for 30 sec and rinsed with DI water dry blow with nitrogen. The developed samples are inspected under a microscope to determine whether the desired pattern is formed satisfactorily.

![Figure 2.6 Image of Nanonex 6200 Mask aligner](image)

2.3.4. Etching

This process is important to ensure the nanowire ends are clean and make good electrical contact with the metal. After development, the samples are transferred to a fume hood, where surface treatments are performed following the following recipe. To remove the native oxide from the exposed part of the nanowire, the samples were immersed in HCl (1): H₂O (1) for 8 seconds followed by DI water for 30 seconds. The last step of the surface treatment is passivation to avoid
re-oxidization by immersing in an ammonium polysulfide solution under 60W white light for half an hour and then rinsed with DI water.

2.3.5. Metal deposition and lift-off

Metal deposition is performed in high vacuum ($10^{-7}$ torr) using Temescal FC-1800 E-Beam Evaporator. In our devices we used 20 nm Ti and (300-500nm) Al consecutively as contacts. The last step is lift-off, by immersing the substrate after deposition in acetone for an hour and cleaning the sample. A typical SEM image of a nanowire device is shown Fig. 2.7.

Figure 2.7 SEM image of wire bonded device at different magnification (a) 35X, (b) 150X and (c) 25000X.

2.4. Electrical Measurements

Figure 2.8 shows the electrical measurement set up. At room temperature, dark I-V measurements of the nanowire devices were mostly performed on a probe station equipped with microscope and
tungsten probe needles. Standard two probe DC electrical characterization was performed where the bias was sourced from an SR830 lock-in output auxiliary and DC voltage is recorded using HP 34401A digital multimeter. Generally, the magnitude of electrical current from nanowire devices studied in research is very small (sub pA to µA) which requires amplification in order to be measured. We used an SR570 current pre-amplifier to amplify the current and produce a voltage. The maximum gain of the current amplifier is up 1pA/V.

2.4.1. Packaging Wire bonding

It is important to inspect the device both under a microscope and test electrical conduction using a probe station. After confirming their operation, the nanowire device substrates were glued to a gold-coated chip carrier using silver conductive paste. We used a 7476D model West bond Co. wire bonder and a very thin gold wire (with diameter of 25 µm) to connect the pin of the chip carrier to the pads contacted the ends of nanowire. See Fig. 2.7a.
2.4.2. Low temperature measurements

Low temperature optical and electrical measurements were performed on wire-bonded nanowire devices by mounting the chip carrier onto the cold figure of a JANIS Research Supertran ST-500 model optical cryostat. The low temperature ~ 10 K temperatures was maintained by continuous flow of liquid helium. The cryostat is equipped with Attocube (XY- piezo scanner) which allows precise positioning of the single nanowire under tightly focused laser light. It also has electrical feed-throughs for biasing the device and controlling the Attocube. The cryostat itself is mounted externally controlled peizo-electric stage for in z-direction for focusing or defocusing the illumination for both imaging and excitation of the device.

2.5. Photocurrent Spectroscopy

In order to study the band structure of semiconductor nanowires, absorption measurements are crucial. Measurement of the absorption of single nanowire is extremely challenging due to the size of the nanowires. For instance, absorption measurement using transmitted light and reflected light from individual nanowires are very difficult to detect. Therefore, an alternative and powerful method to study absorption (band structure) of a single nanowire is photocurrent spectroscopy.

![Photocurrent spectroscopy set up](image)

Figure 2.9 Photocurrent spectroscopy set up.
This technique involves photo excitation of electrons and holes in a semiconductor nanowire in the presence of applied bias across the nanowire device. The electric field in the nanowire separates the electrons and holes which contribute to the photocurrent in addition to drifting the carriers to their respective electrodes. Photocurrent measurements thus include both absorption and transport information. For a given bias across the nanowire, the light that is absorbed generates the photocurrent in the nanowire. Therefore the absorption of the nanowire is proportional to the measured photocurrent from single nanowire devices. By tuning the excitation energy of the laser light at a fixed bias we can essentially measure the energy band structure of single semiconducting nanowires.

The measurement set up of photocurrent is shown in the Fig.2.9. In this research we used different excitation sources such as a tunable Ti: Sapphire, Femto-white, and Fianium super continuum sources. Single nanowire devices were excited by the tightly focused laser light by 50X long distance working objective. The tunable excitation beam was chopped mechanically and the photocurrent measured at constant bias using lock-in detection. Fig. 2.9 shows a schematic of the photocurrent measurement set up.

2.6. Photoluminescence and Photoluminescence excitation

When a photon is absorbed by a semiconductor, electrons from the valence band are promoted to the conduction band leaving a hole in the valence band. In the absence of electric field, the electrons in the conduction band and holes in the valence band relax to the edge of their respective bands by emitting phonons. The electron and hole then eventually recombine emitting a photon with energy equal to the band gap of the semiconductor. Such photoluminescence is a very powerful tool to measure the band gap of a semiconductor and also the ground state transition in quantum well or quantum dots.
PLE spectroscopy is a technique which is used to measure excited states. It involves tuning of the excitation energy of photons and measuring the PL emitted by the ground state. If the absorption increases due to excited state and that stated is coupled to the emitting states, the PL intensity increases and PLE spectra shows the signature of the states as a peak. PLE is also an alternative to absorption or photocurrent spectroscopy in measuring excited states.

2.6.1. Simultaneous measurement of Photocurrent and Photoluminescence

By integrating the photoluminescence with photocurrent current set up (see Fig. 2.10), we were able to measure both photocurrent and luminescence from the same device at the same time. The photocurrent spectra and PLE spectra from the same nanowire device can be measured as complimentary measurements. In addition, this experimental set up allowed as to measure quantum confined Stark effect by allowing bias dependence PL measurements as detailed in Chapter 5.

2.7. Conclusion

In this chapter we described the experimental set ups used in this research. Short description of nanowire growth procedures are provided with references. Single nanowire device fabrication

Figure 2.10 (a) Illustration of photocurrent and photoluminescence from single nanowire device (b) Combined photocurrent and photoluminescence set up.
using photolithography and lift-off, packaging, and low temperature measurement set up are outlined. PL, PLE, electrical transport, photocurrent spectroscopy techniques are explained in detail including sources and detection instruments. Finally, a setup for simultaneous measurement of photocurrent and PL and PLE is presented.

2.8. References


Chapter-3. Electrical and optical characterization of Zn₃As₂

3.1. Introduction

Electronic and optoelectronic devices have continued to dominate the worlds technological development. As a result the search for new and efficient material that can replace the scarce earth elements is also pursued by many scientists across the globe. For instance, silicon is the most abundant and most widely used material in electronics industry. However, silicon has an indirect band gap which makes it optically inefficient compared to group III-V compound semiconductors which have direct band gap. Manufacturing of devices based on these III-V materials is not sustainable due to the rarity of some of the elements.

In an effort to look for alternative and abundant direct band gap materials, researchers have identified several promising II-V semiconductor as Zn₃P₂, CZTS. Recently, the research team at Australian National University has optimized growth of a group II-V, Zn₃As₂, nanowire. This material has direct band gap and has promise as a material for infrared photo detectors and photovoltaics. This unusual material has a direct band gap in the near-infrared spectral region. In this chapter we will describe the growth of these nanostructures and model transport properties in order to extract important semiconductor parameters and contact properties. Finally, we will use photocurrent spectroscopy to estimate the absorption at low temperature and estimate the band gap of Zn₃As₂ nanostructures.

3.2. Growth Nanowires and Nanoplatelets

Zn₃As₂ nanowires and nanoplatelets were grown via horizontal flow MOVPE (Aixtron 200/4) on semi-insulating GaAs (110), which had been pretreated with 50 nm, colloidal Au (Ted Pella, Inc.) Growth was performed at 400 °C and 10 kPa under a total flow of 15 standard liters per minute using the precursors AsH₃ and diethylzinc (DEZn) at molar fractions of $4.8 \times 10^{-3}$ and $4.8 \times 10^{-6}$,
respectively, to give a V/II ratio of approximately 1000. The growth time was 30 min. Subsequent investigation by both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) was performed utilizing a FEI Helios 600 NanoLab Dualbeam (FIB/SEM) see the Fig.3.1.

3.3. ZnAs nanowire devices and transport properties

Single nanowire devices were fabricated in order to realize the optoelectronic potential of our Zn$_3$As$_2$ nanostructures. The nanowire and nano platelet devices were fabricated photolithographically following the device fabrication process described in chapter two. The thickness of the metal contacts were Ti (20 nm)/Al (500nm). The room temperature I-V measurement for these devices are performed on a probe station and the devices were wire bonded into a chip carrier and mounted on the cold figure of optical cryostat for low temperature 10K photocurrent measurements. The low temperature was maintained by continuous flow of liquid helium.
3.3.1. I-V characteristics

Figure 3.2 shows typical current-voltage characteristics of \( \text{Zn}_3\text{As}_2 \) nanowire and nanoplatelet devices. Generally, the I-V characteristic of semiconductor nanowires depends on the intrinsic parameters such as mobility, doping density, and contact/behavior. When a semiconductor is in contact with a metal, depending on the relative difference between work function of the metal and conduction band edge of the semiconductor measured with respect to the vacuum, there is a built-in barrier as shown Fig. 3.3. The relative barriers heights at both contacts determine the current-voltage behavior of semiconductor nanowire devices. For heavily doped materials or if the barrier heights are negligible, the contacts are Ohmic and the I-V characteristics are linear which makes the extraction of intrinsic parameters of the semiconductor straightforward given the geometries of the contacts and nanowires. However, the I-V behavior, displayed in Fig.3.2, shows a non-linear behavior. This kind non-linearity is a typical characteristic of semiconductor nanowire contacts with metal. In order to understand this behavior it is essential to briefly review the behavior semiconductor metal contacts in general.
3.3.2. Metal semiconductor contacts

When a metal with a given work function $\phi_m$ comes in contact with n-type semiconductor (see Fig. 3.3), electrons in the conduction band of the semiconductor flow to the metal until the potential is built up to prevent further flow of electrons. When equilibrium is reached the Fermi level in both metal and semiconductor align as shown in Fig. 3.3 (b). Such phenomena create a barrier, $\phi_b$. This barrier at the junction of metal and semiconductor is called the Schottky barrier.

3.3.2.1. Forward and reverse bias

Under forward bias conditions when a positive voltage is applied to the metal relative to the semiconductor the Fermi energy in the metal is lowered with respect Fermi energy of the semiconductor. Hence the barrier height is reduced which results in electron emission over the barrier from the semiconductor to the metal (see Fig 3.4a). This leads to a current through the junction which has an exponential relation with applied bias given by the equation: $^6$
$I(V_f, \phi_b) = AA^*T \exp \left( -\frac{\phi_b}{kT} \right) \exp \left( \frac{qV_f}{nkT} \right) \times \left\{ 1 - \exp \left( -\frac{qV_f}{nkT} \right) \right\}$, \hspace{1em} (3.1)

where $A$ is contact area, $A^* = 4\pi m^* q k^2 / h^3$ is Richardson’s constant, $V_f$ is the forward bias, $\phi_b$ is barrier height, $k$ is Boltzmann constant, $T$ is absolute temperature, $q$ is electronic charge and $n$ is the ideality factor of the Schottky diode.

When a negative bias is applied to the metal (see Fig 3.4b) the Fermi energy of the metal is raised with respect to the Fermi energy of the semiconductor. As a result, the electrons in the semiconductor see a larger barrier which restricts the flow of electrons which makes the flow due to electron emission over the barrier highly unlikely so that there is no current. The metal semiconductor junction therefore has a rectifying behavior, i.e. a large current exists under forward bias while almost no current exists under reverse bias. However, in the reverse bias case, there is a small current not due to emission of carriers over the barrier, but due to tunneling through the barrier. For the reverse applied bias, the tunneling current as a function of reverse bias $V_r$ and barrier height $\phi_b$ is given by $^6$

$$I(V_r, \phi_b) = I_{sr}(V_r, \phi_b) \times \exp \left[ V_r \left( \frac{q}{kT} - \frac{1}{E_0} \right) \right]$$ \hspace{1em} (3.2)

Where

$$I_{sr} = \frac{AA^*T(\pi q E_{00})^{1/2}}{k} \exp \left( -\frac{\phi_b}{qE_0} \right) \times \left\{ q(V_r - \xi) + \frac{\phi_b}{\cosh^2 \left( \frac{q \phi_b}{kT} \right)} \right\}$$ \hspace{1em} (3.3)

Here the $E_0$ and $E_{00}$ are given in terms of acceptor density and dielectric constant as follows
\[ E_0 = E_{00} \cot \left( \frac{qE_{00}}{kT} \right), \quad E_{00} = \frac{\hbar^2}{2} \left[ \frac{N_a}{m^* \varepsilon_0} \right]^{1/2} \]  

and other parameters are similar to the forward biased case, and \( \xi \) is the difference between Fermi energy and the bottom the conduction band.

### 3.4. Back-to-back Schottky model

Using these behaviors of Schottky contacts, we model our nanowire devices as back to back Schottky diodes as shown in Fig 3.5. The non-linearity in the I-V curves arises from the Schottky contact at both ends of the nanowires with different contact parameters such as barrier height, ideality factor and contact areas. Ideally the barrier height between the same metal and semiconductor is the same. However, in nanowire devices the contacts barrier heights might vary due to surface states of the nanowires and/or a thin insulating layer between the semiconductor and the metal despite the effort of etching to reduce these effects. Therefore we obtain the barrier potentials at both contacts doping concentration as a fitting parameter to the two probe I-V curve.

The back-to-back Schottky diode modeling of the I-V curves we have used was first proposed by Zhang.\(^5\) In this model when one of the diode is forward biased the other diode is reverse biased.

We treat the device as a three element equivalent circuit consisting of an Ohmic resistance in series with Schottky barriers described by thermionic emission under forward bias and thermionic field emission under reverse bias \(^7\) as shown in Fig. 3.4b.

In this approach, we exploit the fact that the current passing through the three sections of the circuit elements is the same, i.e.

\[ I(V) = I_1(V_1, \phi_{b1}) = I_2(V_2, \phi_{b2}) \]  

\[(3.5)\]
In addition, the sum of the voltage drop across each circuit elements shown in Fig. 3.5a is equal to the source drain voltage, \( V_{sd} = V_1 + V_2 + V_{NW} \). The voltage drop across the forward biased diode \( V_1 (I, \phi_1, n_1) \) is calculated by inverting current-voltage in Eqn. (3.1). Similarly the voltage dropped on the reverse biased contact, \( V_2 (I, \phi_2, n_2) \) can also be calculated by inverting the eqn (3.2). The voltage drop across the nanowire is given through Ohms law as \( V_{NW} = IR_{NW} \)

Implementing a self-consistent fit to the experimental I-V data was realized by taking the current through each contact and the NW to be equal to the source drain current and the sum of the voltage drops across each contact and the nanowire to be equal to the total source drain bias. Figure 3.6 a,b presents dark I–V characteristics of a single platelet device at room temperature and a single NW device at both room and low temperature with SEM images of the devices, respectively . Table 3.1 is the list of input spatial dimension for both nanowire and nanoplatelet devices used in this modeling. The spatial dimensions of the devices are obtained from SEM images. The material parameters of Zn₃As₂ i.e. relative permittivity (10)⁸ and effective mass of holes (0.36m₀) are taken from literature.⁹
Table 3.1: Spatial dimension estimated from SEM image

<table>
<thead>
<tr>
<th>Dimensions</th>
<th>Nanowire</th>
<th>Platelate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length (µm)</td>
<td>3.65</td>
<td>3.1</td>
</tr>
<tr>
<td>Diameter (nm)</td>
<td>92</td>
<td>255</td>
</tr>
<tr>
<td>Area (m²)</td>
<td>6.65 X 10⁻¹⁵</td>
<td>1.42 X 10⁻¹⁵</td>
</tr>
</tbody>
</table>

Using these input parameters, the fits to the I–V curves using this analysis are shown for the room temperature plots in Fig. 3.6. The symbols are the measured data and the lines correspond to the self-consistent fit described above. The extracted parameters from the analysis are displayed in Table 3.2. The extracted parameters such as ideality factors, and barrier heights in this analysis are effective values dependent upon the input parameters among which the geometry of the devices is significant. The background carrier concentration in the NW determined to be 1.67 × 10¹⁸ cm⁻³, and the platelet 7.41 × 10¹⁸ cm⁻³. The extracted carrier density values are consistent with previous studies, which have found Zn₃As₂ to possess a significant p-type background that has been related to shallow-level native defects. Compensation of this p-type character has previously been successfully achieved by doping with Indium. In the case of the related semiconductor material, Zn₃P₂, a similar p-type background has been related to the formation of charged phosphorus interstitial defects. Despite significant background hole concentrations, high room temperature hole mobilities of between 200 and 300 cm²/(V s) have previously been determined for Zn₃As₂.
Figure 3.6 a, b presents dark I–V characteristics of a single platelet device at room temperature and a single NW device at both room and low temperature, respectively. 3.2c and d show the SEM of platelet and nanowire devices respectively.

Table 3.2 Extracted parameters from the fitting

<table>
<thead>
<tr>
<th>Parameters</th>
<th>NW Device</th>
<th>Platelete Device</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_a$</td>
<td>$1.67 \times 10^{18}/cm^3$</td>
<td>$7.41 \times 10^{18}/cm^3$</td>
</tr>
<tr>
<td>$R$</td>
<td>$5.39 \times 10^7\Omega$</td>
<td>$5.32 \times 10^4\Omega$</td>
</tr>
<tr>
<td>$\phi_1$</td>
<td>$0.498, eV$</td>
<td>$0.361, eV$</td>
</tr>
<tr>
<td>$\phi_2$</td>
<td>$0.558, eV$</td>
<td>$0.399, eV$</td>
</tr>
<tr>
<td>$\xi$</td>
<td>$0.07, eV$</td>
<td>$0.07, eV$</td>
</tr>
<tr>
<td>$n_1$</td>
<td>$5.82$</td>
<td>$0.593, eV$</td>
</tr>
<tr>
<td>$n_2$</td>
<td>$4.5$</td>
<td>$0.799$</td>
</tr>
</tbody>
</table>
3.5. Photocurrent spectroscopy of Zn$_3$As$_2$ nanowire device

In order to investigate the band structure of the material we take advantage of light sensitivity of the nanowires to measure the absorption spectra of Zn$_3$As$_2$ nanowire. Figure 3.7 shows I-V measurements in dark and under illumination and demonstrates the photosensitivity of this material.

By exploiting this photosensitivity we measured the photocurrent at fixed bias. Photocurrent measurements were performed using a tunable pulsed light from a super continuum photonic crystal fiber. The laser light was focused onto the nanowire with 50×/0.5NA long working objective and a fixed bias of 5 V applied across the nanowire. We acquired the photocurrent data using a standard lock in technique involving chopping of the laser light. An InGaAs photodiode was used to monitor the intensity of the light incident on the nanowire devices. Cooling was provided by a continuous flow of liquid helium. The recorded photocurrent was normalized to the incident intensity. As shown in Figure 4c, the normalized photocurrent versus excitation energy at 10 K displays a clear onset at approximately 1.13 eV. This energy is consistent with the band gap
found by transient Rayleigh scattering (TRS) and extrapolation of the Varshni fit to the PL data. It also agrees well with previous measurements of the absorption edge at low temperature, which were assigned to a direct band gap transition.\(^{18-20}\)

Figure 3.8 Photocurrent normalized by incident power as a function of excitation energy for the single NW device imaged by SEM and illustrated schematically in panels d and e, respectively.

3.6. Conclusion

In this chapter we have demonstrated a novel II-V material as one of the earth abundant semiconductor for optoelectronics devices. We characterized both electrical and optical properties this material using two probe current voltage characteristics and photocurrent spectroscopy. Employing metal-semiconductor-metals modeling and self-consistent fitting we have extracted relevant intrinsic semiconductor parameters such as doping density of \(1.67 \times 10^{18} cm^{-3}\) and \(7.41 \times 10^{18} cm^{-3}\) for nanowire and nanoplatelet devices, respectively. This fitting method helps remove the effect of contacts in order to estimate other semiconductor parameters intrinsic to the
nanowire. The doping density obtained agrees very well with densities obtained using Rayleigh scattering measurements from free standing nanowires.\textsuperscript{5} Photocurrent spectra measurements also allowed estimating the band gap of this material to be 1.13 eV which is in near-infrared. This result is also consistent with bulk Zn\textsubscript{3}As\textsubscript{2} from the literature as well as different characterization techniques used on free standing nanowires of the same growth sample such as temperature dependent photoluminescence measurements and transient Rayleigh scattering measurements.\textsuperscript{5,22}

3.7. References


(8) Barbara Sujak-Cyrul, B. K., Jan Misiewicz, Janusz M. Pawlikowski J Phys Chem Solids 1982, 43, (11), 1045-1051


Chapter 4. Photocurrent Spectroscopy of Single GaAs, GaAsSb and GaAs/AlGaAs Heterostructure Nanowires

4.1. Introduction

GaAs is the most technologically important and most studied direct gap semiconductor material due to its high electron mobility and excellent optical properties. Many band structure parameters for GaAs are known with greater precision than for any other compound semiconductor as compiled by Vurgaftman et al. Such precise knowledge of band parameters provides guidance for low dimensional material growth and characterization. More importantly, the band gap of GaAs can be tuned substituting the Ga atoms with other group III elements such as In or Al, and the As atoms with other group V elements, such as P or Sb. The tuning of the band gap (and lattice constant) with ternary alloy concentrations can be tremendously advantageous in creating novel optoelectronic and electronic semiconductor devices. In this chapter we will investigate the band structure of MOCVD grown binary and ternary GaAs based single nanowire devices namely: bare GaAs, GaAs/AlGaAs core-shell heterostructure and GaAsSb nanowire devices using transport and photocurrent spectroscopy techniques at room and low (10 K) temperatures.

4.2. Band structure

In general, group III-V semiconductor nanowires have cubic zinc blende crystal symmetry. In some cases, particularly for nanowires, a hexagonal closed packed structure also known as Wurtzite crystal structure exists (see Fig. 4.1). Both structures involve the hexagonal closed packed structure where the stacking of III and V elements differ. Cubic zinc blende has ABC-ABC stacking of III and V elements while wurzite has ABAB type stacking. This difference results in different optical and electrical properties as well as band structures. During growth of nanowires, both zinc blende and wurzite structures can occur, because of stacking faults which
usually result in reducing the quality of the material. The crystal symmetry of solids in general determines the electronic band structure of a given material. Understanding the band structure is very critical in order to predict the optical and electrical properties of semiconductors.

The band structure of semiconductor is the dispersion relation i.e. the plot of electron energy vs. the momentum in the crystal. Due to the nature of the crystal symmetry the dispersion relation is different along different specific direction in momentum space (reciprocal lattice) denoted by the symbols \( \Gamma, \Delta, X, \Lambda, \text{ and } L \) as shown in Figure 4.2 a. The corresponding real space directions are for instance L is along [111] direction while X is along the [100] directions. Band gap of a semiconductor is defined by the energy difference between the maxima of the valence band and the minima of the conduction band (see Fig. 4.2c). In some semiconductors such as silicon and germanium the maxima of the valence band and the minima of conduction band occur at different points in momentum space. Such semiconductors are referred to as indirect gap semiconductors. Most group III-V semiconductor are direct band gap materials where the maxima of the valence band and the minima of conduction band are at the center of the Brillouin zones (the \( \Gamma \)- point) as shown in Fig. 4.2b.

Figure 4.1 (a) cubic zinc blende crystal structure of GaAs (b) Hexagonal close packed (Wurtzite) crystal structure of GaAs. Yellow spheres are Gallium (Ga) atoms and grey spheres are Arsenic (As) atoms.
The schematic band structures we show (eg. Fig. 4.2(c)) show the bands close to the Γ-point. In simplest form, the electrons in semiconductor behave like ‘free’ electrons with an effective mass $m^*$. The bottom of the conduction band and the plot of the dispersion relation follows a parabola $E = \frac{\hbar^2 k^2}{2m^*}$. Electrons in the conduction band have an s-type wave function which has a total angular momentum $J=1/2$: where the orbital angular momentum is zero and spin angular momentum, $s$ is $\pm 1/2$ resulting in two fold degeneracy.

The valence band states are more complicated because of the origin of wave functions comes from the atomic p-orbitals, and so the orbital angular momentum, $l$, is 1. In this case, the total angular momentum therefore is the sum of orbital angular momentum, $l=1$ and spin, $s=\frac{1}{2}$. The total angular momentum therefore has two values; $J=3/2$ and $J=1/2$. These values results in two separate bands as shown in Figure 4.2.c. The $J=3/2$ is the valence band and the $J=1/2$ is referred to as the split-off band. The split-off band is a result of spin-orbit coupling. The $J=3/2$ valence band has two degenerate bands $k=0$ which splits when $k\neq 0$. Based on the value of the projection total angular momentum $J$ on the $z$-axis denoted by $m$, the bands are defined as heavy hole (hh) band when $(J, m) = (3/2, \pm 3/2)$ and light hole (lh) band for $(J, m)= (3/2, \pm 1/2)$ as shown in Fig. 4.2c. The description of electrons and holes in semiconductors using energy band diagrams is very powerful.

Figure 4.2 (a) First Brillion zone (b) Calculated electronic band structures along lines of high symmetry (c) band structure schematics of zinc-blende GaAs near k=0.
in characterizing semiconductor materials. The energy band gap, spin orbit energies, the effective masses of electrons and holes, are different for different materials and crystal symmetries. These parameters are the key to understanding the optical and electrical properties of semiconductors. Materials whose band gap is zero or half-filled are classified as metals whereas crystals with energy band gap are semiconductors (small band gap) and insulators (larger band gap). A simplified energy band diagram is shown in Fig 4.3.

### 4.2.1. Tuning the band gap in III-V semiconductors

The band gap of the III-V semiconductors depend on lattice parameters, constituent atoms and crystal structures. By alloying either group III, V or both it is possible to tune the band gap and hence the optical properties of III-V semiconductors. This flexibility makes III-V semiconductors superior for band gap engineering and novel opto-electronic materials. Figure 4.4 shows the band gap of III-V semiconductor possible alloys band gap vs. the lattice parameter. Some of the binary III-V semiconductors lattice constants are nearly equal while the band gap difference is significant. For instance the GaAs and AlAs lattice constants are nearly identical while their band gap difference is \( \sim 1.3 \) eV. By varying the aluminum concentration of the ternary alloy AlGaAs one can tune the band gap over a large range of energies without changing the lattice constant. In a layered
heterostructure such as GaAs/AlGaAs the aluminum concentration can be tuned over wide ranges without causing strain or stress.

In the next sections we focus on probing the electronic band structure of single GaAs and GaAsb nanowires as well as GaAs/AlGaAs core-shell nanowires by using photocurrent spectroscopy on single nanowire devices.

Figure 4.4 Direct Gamma-valley energy gap as a function of lattice constant for the zinc blende form of 12 III–V binary compound semiconductors points and some of their random ternary alloys curves at zero temperature.\(^1\)

### 4.3. GaAs Nanowires

The GaAs nanowires used in this study were grown by the gold-catalyzed MOCVD method on a (111-B) oriented GaAs substrate using a two temperature growth procedure that results in twin free cubic zinc blende nanowires 100 nm in diameter.\(^7\) Typical lengths of these nanowires is 5-8 µm long.

Single nanowire devices were fabricated from these nanowires using photolithography as described in Chapter-3 section 2.3. Figure 4.5a shows an SEM micrograph of a typical GaAs nanowires device.
4.3.1. I-V characteristics

The I-V behavior observed for a pure GaAs nanowire is shown in Fig. 4.4 b. The non-linear dark I-V curve (see inset in Fig 4.4) arises from back to back Schottky contact behavior. When a bias is applied across the nanowire, one of the contacts is forward biased and the other is reverse biased. For the forward biased contact, the I-V characteristic can be interpreted using the well-known thermionic emission over the barrier, where the applied bias reduces the Schottky barrier height for carriers to emit over the barrier. In the reverse biased case, the applied bias increases the barrier height and so tunneling current becomes dominant. The I-V characteristic of a nanowire device is therefore determined by the relative barrier height of both contacts. If the barrier heights are small and equal then the contacts become ohmic and the current is determined by the resistance of the nanowire. If the barrier heights are nearly equal and significantly larger, the I-V behavior will be symmetric and nonlinear. For relatively higher applied bias the I-V behavior approaches a linear nearly Ohmic behavior which is determined by the resistance of the nanowire. The observed I-V characteristics (shown in the inset of Fig.4.5 b.) are nonlinear for a smaller applied bias range (-3 V to 3 V) range and linear for larger biases. Using the Metal-Semiconductor-Metal model in Chapter 3 section 3.3.2, the measured I-V behavior is primarily a result of small Schottky barriers.
at both contacts. The fact that we observe significant dark current (~nA) indicates that free charge carriers in the nanowire contribute to the conductivity, presumably from unintentional doping of the nanowire during growth for the otherwise pure GaAs.

Under white light illumination, the I-V behavior of the nanowire changes to nearly Ohmic behavior because of the photo-doping and photo gating contribution. In addition, the photo current under moderate illumination intensity is about an order of magnitude larger than that of dark current, which dictates the Ohmic behavior under white light illumination. When a photon is absorbed in a semiconductor it creates a pair of an electron in the conduction band and a hole in the valence band. If there is no external field in the semiconductor the electron hole pairs will recombine either radiatively through band to band recombination or non-radiatively through defect and surface states. In the presence of bias the electrons and holes are driven apart by the electric field and contribute to the measured photocurrent.

4.3.2. Photocurrent spectroscopy

In order to measure the band structure of a single nanowire, several optical techniques have been employed such as photoluminescence, photoluminescence excitation (PLE), or photomodulated Rayleigh scattering. Measurement of the absorption of a single nanowire is challenging due to the size of the nanowires (the diameter is smaller than the wavelength of light). Photocurrent spectroscopy has been proven to be a powerful tool to measure the absorption of a single nanowire as a function of photon energy and thereby the band structure of single nanowires. The photocurrent signals are measured using a lock-in detection technique to remove the background conduction.
The plots in Fig. 4.6 show representative photocurrent responses as a function of applied bias for different excitation wavelengths. The photocurrent has a clear dependence on the wavelength with a maximum at 750 nm (1.65 eV) and negligible photocurrent at 950 nm (1.3 eV). For all photoexcitation wavelengths, the behavior of the photocurrent versus applied bias increases for small biases (less than 3 V) and tends to saturate at relatively higher biases.

Figure 4.6 Representative photocurrents as a function of applied bias across GaAs nanowire excited by photons of different wavelengths.

The saturation of the photocurrent for higher bias voltages in the GaAs nanowire presumably results from complete extraction of all the photogenerated carriers. For lower biases, the linear behavior may result from the lifetime of photogenerated carriers being shorter than the transit time across the nanowire. For a given mobility of charged carriers in the nanowire, if the product of electric field, mobility and carrier life times is less than the distance between the generation site to the contacts, increasing the electric field will linearly increase the photocurrent. The bare GaAs
nanowires usually have shorter carrier lifetimes of the order of several picoseconds which may explain the linear increase in the small bias region.\textsuperscript{18}

The photocurrent response as a function of excitation photon energy in a single GaAs nanowire device at 294 K (black square) and 10 K (red circles) is shown in Fig 4.7. The photocurrent shows an exponential increase for photon energies below the band gap before band to band absorption takes place. For photon energies above the band gap the photocurrent response follows a square root function which reflects the density of states of the electrons and holes as a function of energy. There are two major contributions to the below band gap absorption which will be described in the next section.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.7.png}
\caption{Semi logarithmic plots of photocurrent normalized to the incident power as a function of excitation photon energy at 294 K (black squares) and 10 K (red circles). The lines are the linear fit below the band gap for both temperatures. The measurements are taken at fixed bias of 10V. The inset is the linear plot of the same data set.}
\end{figure}
4.3.2.1. Defect state or dopant state contribution to absorptions

Due to the presence of the exponential tail below the gap in the photocurrent spectra, this indicates that the state distribution for non-ideal semiconductors, unintentionally doped or lightly doped semiconductor has absorption tails \(^{19,20}\)

\[ \alpha(E) \sim I_{pc} \propto \alpha_g e^{-\frac{E-E_g}{E_0}} \]

where the \(E_0\) is the Urbach disorder parameter and \(E_g\) is the optical band gap of the material. This exponential absorption tail is referred to as the Urbach tail characterized by \(E_0\). In bulk GaAs the measured Urbach parameter is \(~10\text{meV}\) at room temperature.\(^{21}\) Our measurement also show similar result where most of the contribution of the disorder is attributed to surface states in typical nanowires. Figure 4.7 shows the schematics of the density of states with exponential defect distributions.

4.3.2.2. Franz-Keldysh effect

Another important contribution to below band gap absorption is due to the applied electric field. An external electric field tilts the band edge allowing electrons and holes to tunnel into the band gap as shown in Fig. 4.8b. Photons with energy smaller than the band gap can excite these states which extend in to the gap resulting in a red shift in the onset of the absorption. The below band gap absorption due to Franz Keldysh effect is given by\(^{22}\):

\[ \alpha(E) \sim I_{ph}(E) \propto \exp\left\{\frac{-4\sqrt{2m^*}}{3\hbar F} \left(E_g - E\right)^{3/2}\right\} \]

Both of these contribution to the below band gap absorption or photocurrent follow an exponential dependence on the energy of the incident photons. The linear fits in the semi logarithmic plot Fig.4.7 show the below band to band absorption arises predominantly from the absorption of defect or impurity states in the nanowire crystal Evidence of the Franz Keldysh effect in the photocurrent
response is less clear. Unpassivated GaAs nanowires have higher a number of surface states which contributes significantly to the sub band gap absorption.²³ The estimated band gaps from the photocurrent at 294 K and 10 K are 1.42 eV and 1.52 eV respectively. These values are consistent with well-known bulk GaAs band gap values following Varshini's temperature dependence of band gap for GaAs.²⁴ ²⁵

\[
E_g (T) = 1.518 - \frac{\alpha T}{T+\beta}
\]

(3)

Where \( \alpha \) and \( \beta \) are phenomenological parameters whose values are \( 5.4e10^{-4} \) and 204 respectively.¹

At low temperature (10K), in addition to the band to band transition and defect absorption a peak appears near 1.5 eV. In order to understand this additional absorption we need take at a close look at the behavior of photoexcited carriers in semiconductors when the Coulomb interaction is considered.

Figure 4.8 Schematics of density of state of valence band and conduction band with exponential tail in to the band gap and (b) Schematics Franz-Keldysh effect: schematics adapted from: https://cms.uni-konstanz.de/en/physik/leitenstorfer/research/multi-terahertz-physics-and-technology/
4.3.2.3. Excitons

The optical excitation of semiconductors near the onset of absorption results in a transition of electrons from the top of valence band to the bottom of the conduction band creating an electron and hole pair. The electrons and holes form a quasi-particle due to the Coulomb interaction. Mathematically, the electron-hole pair is similar to hydrogen atom where the hole plays the role of the positively charged proton as shown in Fig. 4.9. Unlike the hydrogen atom, excitons have a shorter lifetime of the order of 1 ns. The Schrödinger equation describing the bound electron and hole in a semiconductor is known as the Wannier equation and the bound pair-state solutions are the Wannier exciton.

Generally, in direct bandgap semiconductors, electrons and holes near \( k = 0 \) act as free particles where the energy-momentum relation is quadratic and can be conveniently described within the effective mass approximation. The effective masses of both electron and hole are often lighter than the free electron mass in vacuum \( m_0 \). For example, in GaAs the electron effective mass is \( m_e = 0.067 m_0 \), while the heavy-hole mass is \( m_{hh} = 0.45 m_0 \).

The Hamiltonian for the exciton can be written in a form described by:  

\[
H_{ex} = H_e + H_h + H_{eh},
\]  

(4)
Where \( H_e \) and \( H_h \) are the Hamiltonians for the electron and hole and \( H_{eh} \) is the Columbic interaction Hamiltonian between electrons and holes. The solution of the Schrödinger equation provides similar wave functions and energy eigenvalues where the effective masses of electron and holes are substituted for the mass of electron and proton in the hydrogen atom respectively. Such solutions result in a Bohr radius, \( a_B = \frac{\hbar^2}{\mu \varepsilon} \), and binding energy of the ground state: \( E_B = \frac{\mu e^4}{2\hbar^2 \varepsilon^2} \) where \( \mu \) is reduced mass of electron and hole effective masses and \( \varepsilon \) is relative dielectric constant.\(^1\) Due to the smaller reduced mass \( \mu \) and the generally large dielectric constant, one can estimate that the exciton binding energy is about three orders of magnitude less than Rydberg constant. For example, the binding energy of the exciton in GaAs is 4.2 meV.\(^26\)

The inset in Fig.4.7 shows the photocurrent response plotted versus excitation photon energy on a linear scale. The peak observed near the onset of band to band absorption at 1.51 eV at 10K is a signature of an excitonic resonance. Similar excitonic peaks are seen in low temperature absorption spectra in a variety of different direct-gap semiconductors.\(^9\) The applied bias of 10 V can easily ionize the exciton with binding energy less than 5 meV which enabled the resolution of the exciton resonance using photocurrent measurement.

### 4.4. GaAs/AlGaAs Core shell nanowires

Despite the reduction in size and optimized growth conditions of GaAs nanowires, the luminescence efficiencies and conductivities are affected primarily by a high density of surface states. The surface recombination velocity is \( 10^6 \) cm/s which is 3 orders of magnitude higher than most other III–V semiconductors, so that nonradiative recombination usually dominates the electron-hole recombination.\(^27,28\) These problems are more significant in small diameter nanowires due to the high surface to volume ratio. To overcome the effect of surface states, an AlGaAs shell
can be grown around the GaAs core as a passivation layer. It has been shown that GaAs/AlGaAs core shell nanowires exhibit a two orders of magnitude increase in photoluminescence efficiency compared to bare GaAs.\textsuperscript{29-31} AlGaAs is a natural choice as passivation of GaAs for two reasons: 1) the lattice mismatch between GaAs and AlGaAs is very low, see Fig. 4.4, so there is no strain or stress to modify the band gap of the core or the shell. 2) AlGaAs has wider band gap with type-I band alignment which provides barriers to both electrons and holes in the GaAs core. Figure 4.10 shows a schematic conduction and valence band alignment of simplified GaAs/AlGaAs core-shell nanowire. The direct band gap of Al\textsubscript{x}Ga\textsubscript{1-x}As is a linear function of Al concentration, x, for x less than 0.45 as given by:\textsuperscript{32}

\[
E_g = (1.424 + 1.247x) \text{eV}
\]  
(5)

The conduction band edge discontinuity at the interface of GaAs/AlGaAs is given \( \Delta E_C = 0.79x \) for \( x < 0.41 \) and the valence band edge discontinuity is given by \( \Delta E_V = 0.46x \). Thus the band discontinuity can be tuned as desired.

![Schematic band structure of GaAs/AlGaAs core-shell nanowire.](image)

The GaAs/AlGaAs core-shell nanowires studied in this section were grown by the gold-catalyzed MOCVD method. The core is 60 nm in diameter the shell is nominally (7.5 nm) AlGaAs and 25 nm GaAs capping shell. A single nanowire device of a GaAs/AlGaAs nanowire was fabricated using photolithography as described in Chapter 2. The current voltage characteristic of
GaAs/AlGaAs nanowire devices shows strong photosensitivity. The I-V characteristics in such core-shell structures are more complicated as transport can occur through both the core and the shell.

Figure 4.11 shows photocurrent spectra of a GaAs/AlGaAs core-shell nanowire at 10K. We observe four distinct regions on the semi logarithmic plot shown in Fig.3 (a): the Urbach tail below the band gap of the core, core absorption (1.52 eV - 1.8 eV), an increase of absorption from (1.8 eV - 2 eV), and absorption of the AlGaAs shell. Near the band gap, we see a peak which corresponds to the excitonic resonance similar to the bare GaAs device shown in Fig 4.7. The increase in photocurrent (see the inset) near 1.8 eV comes from the contribution of the split-off valence band in the GaAs core, the deep defects from the AlGaAs shell and contribution from the band bending and other states formed at the interface of the core (GaAs) and the shell (AlGaAs). The nominal concentration of Al in these nanowires is expected to be 0.5. The direct band gap for this concentration is 2 eV. The clear peak at 1.95 eV may therefore be coming from the excitonic resonance in the AlGaAs shell.

The inset of Fig.4.11 depicts the photocurrent spectra of GaAs/AlGaAs nanowire devices plotted on a linear scale. Here we observe a clear on set of absorption starting at a photon energy less the split-off band of the core. Chen et al. have reported on the direct band edge discontinuity, for a lower aluminum concentration of 0.3. In our case, the concentration Al is nominally 0.5 which makes the onset of absorption of AlGaAs and the split-off band of the core overlap.
Figure 4.11 Photocurrent spectra normalized to the incident laser power of GaAs/AlGaAs core-shell nanowire device at 10K. The inset is the same spectra with linear scale- with additional plot of the 30X the signal around the core band gap.

An attempt to resolve the band gap discontinuity using PC spectroscopy is not precise. However, it can be qualitatively interpreted as the rapid increase of the photocurrent near 1.8 eV (see the inset of Fig. 4.11) as the resultant of absorption of AlGaAs defects and split off band from the core GaAs superimposed onto one another.

4.5. GaAs$_{1-x}$Sb$_x$ Nanowires

In the previous section we have realized the tuning of the band gap when Al from a group III atom partly substitutes for Ga in AlGaAs layers. In this section we will look at when a fraction of Arsenic atoms are replaced another group V atoms, in this case Antimony (Sb). Antimony-based ternary III-V nanowires allow a very wide band gap tunability. The direct band gap decreases as the fraction of antimony increases in the GaAsSb nanowires. The band gap of GaAsSb can be tuned
from the GaAs band gap (870 nm) to GaSb band gap (1700nm) at room temperature (see Fig. 4.4) which makes GaAsSb very important for optical telecommunication application, near infrared photodetectors and photovoltaic.\textsuperscript{34-37}

GaAs\textsubscript{1-x}Sb\textsubscript{x} nanowires were grown using MOCVD technique described in Chapter 2 and the references therein. The growth was initiated by 40 nm Au catalyst where subsequent the precursors for each element namely Trimethylgallium (TMGa) for Ga atoms, arsine (AsH\textsubscript{3}) for As and trimethyl-lantimony (TMSb) for Sb were introduced to the growth chamber at optimized growth condition detailed in reference.\textsuperscript{34, 38, 39} The grown nanowires were characterized by TEM and EDX to determine the morphology and composition of the nanowires as shown in Fig. 4.12 a and b.\textsuperscript{34}

We used I-V and photocurrent spectroscopy to investigate the band structure of GaAsSb. Single nanowires were contacted at either end by Ti/Au contacts using e-beam lithography.\textsuperscript{36} A typical SEM image of a device is shown in the inset of Fig. 4.12. Dark I-V characteristics show the devices to be Ohmic and highly photosensitive under illumination as shown in Fig. 4.12c.

After wire bonding into a ceramic package, the devices were mounted on the cold finger of the optical cryostat where low temperature (10K) was maintained by continuous flow of liquid helium. A narrow band of pulsed laser light tunable from 400 nm to 2400 nm was focused on the nanowire device by a 50X reflective objective. The photocurrent was recorded at fixed applied bias of 0.3 V using lock-in amplification techniques where the intensity of the excitation laser was modulated by a mechanical chopper. Figure 4.13 show photocurrent spectra, divided by the incident power at each wavelength, of GaAsSb and pure GaAs measured at 10 K. The GaAs data used for comparison here are the same data as shown in Fig. 4.7. As most of the ternary III-V
semiconductors, the band gap of GaAsSb depends on the concentration of Sb atoms. The band gap dependence on the fraction Sb concentration is empirically given by:

\[
E_g = (1 - x)E_g(GaAs) + xE_g(GaSb) - x(1 - x)C
\]

where the \(x\) is the fraction of Sb atoms and \(C\) is bowing parameter having a value of 1.4 for GaAsSb. From Fig. 4.13b, the band gap of GaAsSb is estimated to be 0.9 eV at 10 K. Such a band gap suggests the concentration of Sb to be in the range of 40% to 45% from Eqn. 6. This value is consistent with estimations of the Sb concentration using EDX. In addition to a clear absorption edge, the onset of band-to-band transition corresponding to the band gap, we also observe two distinct peaks in the photocurrent spectra. The band gap, \(E_{g}\), calculated using Eqn. 6 for GaAsSb, and \(E_g + \Delta_{SO}\) band are plotted as depicted in Fig. 4.13b, using the peak energy position we identify the first peak to be the split off band for a 0.45 concentration of Sb in the nanowire. This

Figure 4.12 (a) SEM image of as-grown GaAsSb NWs used in this work. The inset shows a magnified image of the NWs with the top Au particles clearly visible as indicated by arrows. (b) TEM image of a NW with the HRTEM image of a selected region (denoted by the rectangular mark) and diffraction pattern confirming the twin free ZB structure of the NW. EDX line scan results of the same NW show a uniform composition distribution along the NW. (c) Room temperature I-V characteristics in dark and under white light illumination. The insets in (c) are SEM image of the device and plot of dark I-V showing Ohmic behavior. Scale bars in the inset of (a) and TEM image in (b) are 100 nm and 1 \(\mu\)m, respectively.
identification of the split-off band further confirms the Sb concentration obtained using other techniques.

4.6. Conclusion

In this chapter we investigated the absorption spectra of single MOVCD-grown bare GaAs, GaAs/AlGaAs core shell heterostructure and bare GaAsSb nanowires. In the bare 100 nm diameter GaAs nanowire device we observed the non-linear dark current arising from back-to-back Schottky behavior. The saturation of the photocurrent as we increase bias is due to the diffusion length of minority carriers resulting in the complete extraction of photogenerated carriers at high biases. At 10 K, excitonic peak is resolved near the band edge of bare GaAs, in the GaAs core and the AlGaAs shell of core-shell nanowire. In addition the GaAs/AlGaAs photocurrent spectra provide a clear estimation of the Al concentration in the barrier. Photocurrent spectroscopy was also used to investigate the energy band structure of a GaAsSb nanowire device. The observed energy band gap at 10 K is consistent with the extrapolated estimation from the Varshni equation.

Figure 4.13 (a) Photocurrent spectra normalized to incident excitation powers of GaAsSb (blue) and GaAs (red) acquired at 10K with bias 0.3 V and 10V respectively. (b) Plot of band gap $E_g$ and $E_g + \Delta SO$ vs concentration of Sb. The horizontal lines are the observed peak positions in photocurrent spectra in (a).
fit of PL measurements and an analysis of EDX scan values. We also observe a peak corresponding to the split off band calculated using recommended bowing parameters from ref 1. In addition to measuring the band structure of single nanowires, photocurrent spectroscopy can be used to estimate the alloy concentration in ternary III-V semiconductor nanowires.

4.7. References


(22) Keldysh, L. V. Sov. Phys. JETP 1958, 6, 763.


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(32) http://www.ioffe.ru/SVA/NSM/Semicond/AlGaAs/bandstr.html


Chapter-5. Quantum Confined Stark Effect in GaAs/AlGaAs Nanowire

Quantum Well Tube Device

5.1. Introduction

Group III–V semiconductor nanowires have been extensively studied for their potential use for future compact and efficient optoelectronic devices ranging from solar cells to light-emitting diodes to field effect transistors.\textsuperscript{1–9} Strongly quantum confined electronic states in radial nanowire heterostructures are being explored particularly for accessing new one-dimensional geometries that are expected to be distinctively sensitive to external magnetic and electric fields.\textsuperscript{10,11} Such states with extremely high optical efficiency have been observed in GaAs quantum well tubes embedded inside an AlGaAs shell, along with a transition from delocalized one-dimensional states to zero-dimensional dot-like states with narrower well widths.\textsuperscript{10–15} Separately, quantum dots localized within the AlGaAs shell have been reported in MBE-grown QWT nanowires,\textsuperscript{16,17} along with the first attempts of modulation doping these structures.\textsuperscript{13,18}

In both self-assembled quantum dots,\textsuperscript{19–26} dots that are formed naturally through well-width fluctuations in 2D quantum wells\textsuperscript{27} and dots in nanowires defined by axial heterostructures,\textsuperscript{28,29} the application of electric fields laterally and vertically can provide important information on the potential profile and size of the quantum dots. In this chapter we describe experiments where this quantum confined Stark effect is observed in a semiconductor nanowire QWT where the well is narrow enough to result in exciton localization at low temperatures. In these experiments, a longitudinal electric field is applied along the length of the nanowire using metal contacts at either end. We use simultaneous photocurrent (PC), photoluminescence (PL), and photoluminescence excitation (PLE) spectroscopy in single nanowire QWT devices to probe both the delocalized and localized states within the QWT. Such measurements provide insights into the nature of the
localization observed in narrow QWTs and thus how these strongly quantum confined structures might be optimized in the future.

5.2. Quantum Well Tube Structure

A schematic of the cross sectional structure of the quantum well tube (QWT) and expected band structure is shown below in Fig. 5.1a. The QWT nanowires were grown using MOCVD. The core GaAs was first grown by a standard two-temperature technique using a 50 nm gold catalyst. After growth of the core, four layers of alternating AlGaAs and GaAs shells were grown resulting in a thick AlGaAs (90 nm) shell surrounding the core followed by a 4 or 8 nm GaAs quantum well, then an outer 25 nm AlGaAs shell and finally a 10 nm GaAs cap to prevent oxidation. The thin GaAs layer sandwiched between the two AlGaAs shells defines the quantum well tube. Figure 5.1b and c show cross-sectional HAADF-STEM images of the nominally 4 and 8 nm QWT nanowire samples respectively. In the images, the GaAs QWT are well-defined narrow stripes embedded within the AlGaAs barriers which surround the 50 nm GaAs core. These nanowires are typically 3-5 μm long.

Figure 5.1 (a) Schematic of a QWT nanowire (b) cross section and expected band diagram. (c) and (d) HAADF-STEM images for 4 and 8 nm QWTs.
Using the QWT widths obtained from the cross sections, we can calculate numerically the confined state eigenvalues of electrons and holes in the QWT by solving the Schrödinger equation for an equivalent cylindrical quantum well. The electron and holes in the QWT are free along the nanowire length and are radially confined to the thin GaAs embedded in between the thick AlGaAs shells. The cross section of the nanowire is approximated as a cylinder with radius of 144 nm and 148 nm for 4 nm and 8 nm QWTs respectively. A schematic of the cylindrical QWT and the energy diagram are shown in Figure 5.2.

![Figure 5.2. Schematics of cylindrical QWT nanowire structure and energy band diagram for 4 nm and 8 nm quantum well width](image)

### 5.3. Theoretical calculation of Confined state Eigenvalues and Eigenstates

The electrons and holes in these nanowires are free along the nanowire and are radially confined by potential barriers provided by the AlGaAs shells. The schematics of energy band profile as a function of radius the shown in Figure 5.2. The Schrödinger equation for such potential for cylindrical symmetry can be written as:

$$
-\frac{1}{\rho} \frac{\partial}{\partial \rho} \left( \rho \frac{\partial \chi(\rho)}{\partial \rho} \right) + \left[ \frac{m^2}{\rho^2} + k_z + V(\rho) - E \right] \chi(\rho) = 0 ,
$$
\[ V(\rho) =\begin{cases} 
0, & 0 \leq \rho \leq \rho_1 \\
V_0, & \rho_1 \leq \rho \leq \rho_2 \\
0, & \rho_2 \leq \rho \leq \rho_3 \\
V_0, & \rho_3 \leq \rho \leq \infty 
\end{cases}\]

Where \( V_0 \) is the conduction band offset which determines the confinement potential for the electrons, or the valence band offset which determines the confinement potential for the holes, \( k_z \) is kinetic energy along the z direction and \( m \) is the quantum number which determines the angular momentum.

Solving the Schrödinger equation for electrons and holes confined to such potential wells analytically is inherently difficult. A simple way to calculate the confined states is to expand the true eigenfunctions of electrons and holes in the potential wells using the eigenfunction of an infinite cylindrical potential well which has the same outer radius where the orbital angular momentum assumed to be zero as detailed in Fickenscher et al.\textsuperscript{12} Using the band offset of GaAs and AlGaAs for nominally 40% Al the electrons and holes barrier heights are set to 316 meV and 184 meV, respectively. Using the dimensions obtained from high resolution TEM images, the confined energy eigenvalues for ground state and first excited states for both 4 nm and 8 nm QWT are tabulated in Table1. The resulting eigenstate wavefunctions in all sections of the nanowire are shown in Fig. 5.3.
Energies are measured relative to the GaAs conduction and valence band edges. HH, LH and E refer to heavy holes, light hole and electrons respectively and n is the principal (radial) quantum number. All states are for zero orbital angular momentum.

Table 1. Energy eigenvalues of confined electron and hole states for 4 nm and 8 nm

<table>
<thead>
<tr>
<th></th>
<th>Principal Quantum number</th>
<th>8 nm QWT Eigenvalue (meV)</th>
<th>4 nm QWT Eigenvalue (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HH</td>
<td>n=1</td>
<td>9.2</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>n=2</td>
<td>41.6</td>
<td>151</td>
</tr>
<tr>
<td>LH</td>
<td>n=1</td>
<td>36.5</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>n=2</td>
<td>133.4</td>
<td>No such state</td>
</tr>
<tr>
<td>E</td>
<td>n=1</td>
<td>51.7</td>
<td>127.1</td>
</tr>
<tr>
<td></td>
<td>n=2</td>
<td>194.9</td>
<td>No such state</td>
</tr>
</tbody>
</table>

Energies are measured relative to the GaAs conduction and valence band edges. HH, LH and E refer to heavy holes, light hole and electrons respectively and n is the principal (radial) quantum number. All states are for zero orbital angular momentum.
The energy for optical transitions (ignoring any Coulomb effects between electrons and holes) can therefore be calculated as \( E = 1.518 \text{ eV} + E_n + H_n \), where \( E_n \) and \( H_n \) are the confinement energies listed in Table 1, and 1.518 is the GaAs energy gap at 10 K. Photoluminescence measurements only probe the ground state transition (\( E_1 \rightarrow HH_1 \)), which has an energy which is equivalent to the absorption (\( HH_1 \rightarrow E_1 \)). Excited states and other possible transitions from confined states to continuum can be measured using photocurrent and photoluminescence excitation (PLE) spectroscopies.

Figure 5.4. (a) Atomic resolution HAADF-STEM image of 4 nm QWT. (b) Cross-sectional Al concentration map with unit cell resolution. (c) Al concentration line profile across the GaAs quantum well, integrated across the width of the region indicated by the white rectangle in (c).

The 8 and 4 nm QWT widths were chosen to lie on either side of a transition from delocalized excitonic states (the 8 nm well) to localized states (the 4 nm well) at low temperatures.\(^{14}\) To understand the nature of the disorder responsible for this localization, we utilize an aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) using a Titan\(^3\) 80-300 standard Schottky field emission gun TEM/STEM operated at 300 keV to probe the morphology and composition of the cross-sectional quantum well tube. The aluminum concentration in a rectangular section within \( \sim3 \text{ nm} \) of either side of the GaAs quantum well is measured using a quantitative HAADF-STEM method.\(^{32}\)
The atomic resolution images show the extremely high crystalline quality of the NWs which is consistent with their high efficiency luminescence emission.\textsuperscript{12,14}

In this approach, the intensity distribution in the HAADF-STEM image is converted to a map of aluminum concentration via comparison with comprehensive frozen-phonon dynamical electron scattering calculations, incorporating all of the relevant electron-optical parameters (measured separately).\textsuperscript{33–36} This approach requires a much lower electron dose than spectroscopic methods, thus minimizing the risk of electron beam damage. Figure 5.4 shows an atomic resolution HAADFSTEM image of the QW and the surrounding AlGaAs barrier layer in the nominally 4 nm QW sample. The HAADF-STEM image was recorded with an electron beam semiconvergent angle of 16.2 mrad and detector collection angles from 46–200 mrad. The corresponding aluminum concentration map is shown in Fig. 5.4b. A typical composition line profile across the quantum well is shown in Fig. 5.4c. The average aluminum concentration in the neighboring barrier layer measured from the line profile “below” (0–3 nm region) and “above” (8–10 nm region) the QW is 39.9 ± 2.6%. The images and their analysis in this work were done at Monash University under the supervision of Professor Joanne Etheridge.

From such extremely high-resolution images, we see that the barrier/QW interfaces are not atomically sharp. The aluminum concentration transitions between AlGaAs to GaAs and back again are at least 1 nm in width, as well as some fluctuation in the QW width in the field of view.\textsuperscript{30} In addition, fluctuations of the aluminum concentration of up to ±3% are observed. These measurements provide accurate, high spatial resolution measurements of the Al composition across the cross-section of the wire, but only small volumes of the total nanowire can be sampled. Moreover, it is not yet known what the fluctuations in well width or aluminum composition are along the length of the wire.
5.4. Basic I-V and Photoluminescence of QWT Devices

5.4.1. I-V characteristics

To gain insight into this localization process using the quantum confined Stark effect, two terminal single QWT nanowire devices were fabricated photolithographically as described in Chapter 2.

Figure 5.5 (a) Schematic of experimental setup where the nanowires are excited with tunable laser and photoluminescence and the photocurrent are measured from the same device. (b) SEM images of typical QWT nanowire device and (c) The black (square + line) plot is the I-V measured in dark while the (red circle + line) is the current measured under illumination with 800 nm at room temperature.

Figure 5.3 depicts the schematics of spectral photoconductivity measurement and SEM image of typical QWT.. These devices were found to be extremely photosensitive with dark currents of a few picoamperes increasing by 4 orders of magnitude under 800 nm illumination see figure. Using
spectroscopic techniques described below, we show that these contacts are making excellent electrical contact with the QWT

5.4.2. Photoluminescence of QWT Nanowire Devices

Figure 5.6 shows the PL of both 8 nm and 4 nm QWT nanowire devices where the bias across the nanowires is 0V. The observed core emission at 10 K is at lower the GaAs emission at low temperature may due to carbon defect impurities. The 8nm quantum well tube nanowire shows intense luminescence at 1.56 eV while the 4 nm quantum well tube has intense broader luminescence centered at 1.67 eV above the core emission. The centers of the emission spectra are consistent with transition from E1 to HH1 in both 8 nm and 4 nm quantum well tubes. The 4 nm QWT PL shows sharp spectral lines in addition to the broad spectra centered at 1.67 eV. The observed sharp spectral lines coupled with the broad spectrum in 4 nm QWT nanowire devices will be discussed in more details in section 5.7.

Figure 5.6. PL spectra of single QWT nanowire devices with quantum well width of 8nm (black) and 4nm (red) at 10K.
5.5. Quenching of PL with applied Bias

Figure 5.7 shows photoluminescence (PL) spectra at 10 K of both the 8 and 4 nm QWT nanowire devices as a function of bias. The devices are photoexcited well above the AlGaAs barriers by 200 fs pulses at 590 nm with an average power of less than 4 μW and focused onto the NW to a 2 μm spot using a 50X long working length objective. The emission from the QWT dominates over the core emission at 10 K. Both NW devices exhibit weak emission from the core. The 8 nm quantum well tube nanowire shows intense luminescence at 1.56 eV that is 50 meV higher than the GaAs band edge (see Figure 5.7a), while the 4 nm quantum well tube has intense broader luminescence centered at 1.67 eV, 140 meV above the GaAs band edge (see Figure 5.7b). The

![Figure 5.7.](image)

Figure 5.7. (a,b) Photoluminescence spectra at different applied biases for 8 and 4 nm QWT, respectively. (c) Plot of integrated intensity versus the applied bias for the 8 nm QWT and (d) plot of PL integrated intensities for high energy side (>1.67 eV) and low energy side (<1.67 eV) for the 4 nm QWT device (see panel b).
centers of the emission spectra are consistent with optical transitions from E1 to HH1 calculated electron and hole ground states as described in theoretical modeling and tabulated in Table 1 in section 5.3. The emission from both the 8 and 4 nm QWT devices quench strongly with increased bias, as shown in Fig.5.7 a,b. This confirms that the device makes good electrical contact with the buried quantum well, because the excitons are expected to ionize as the internal electric field pulls the electrons and holes apart. The nature of luminescence quenching in these two devices is subtly different, however, as we will now describe.

As noted by Shi et al., excitons are strongly confined to the 8 nm QWT but delocalized along the length of the NW. When an external bias is applied across the 8 nm QWT nanowire device, the PL intensity is initially constant, but quenches rapidly as the bias is increased above 2 V (see Fig. 5.7a, c) and disappears completely for biases above 5 V. The PL quenching is observed to be symmetric for both positive and negative biases. With 2 μm between the contacts at a 2 V bias, the applied electric field is 10 000 V/cm. This means that the electric potential drop across the exciton Bohr radius (12 nm in GaAs) is 12 meV which is sufficient to ionize the exciton.

The 4 nm QWT PL (Fig. 5.7 b) shows sharp spectral lines distributed across a broad spectral background centered at 1.67 eV. The appearance of these sharp spectral emission lines is consistent with the localization of excitons to quantum dot-like potential minima due to nonuniformity of the quantum well tube width or barrier alloy composition. The quenching of the QD emissions that emit in the upper half of the PL spectra (1.67 eV) occurs at a lower bias than for QDs that emit in the lower half. Figure 5.7 d shows the integrated intensity versus bias for both the high energy and low energy emission bands. Clearly, the higher energy QDs quench at a lower applied bias (~1.3 V) than the lower energy QDs (~3 V). This suggests that modest electric fields can first delocalize the excitons by pulling them out of the QD potential, before the excitons ionize completely at
higher fields. This result suggests that the QDs on the high energy side of the PL band localize excitons more weakly than excitons localized to QDs on the low energy side. The 4 nm QWT emission appears to quench completely at biases above 6 V, which is slightly higher than what was observed in the 8 nm QWT. This may reflect an increased exciton binding energy in the smaller width QWTs.

5.6. Photocurrent Spectroscopy of QWT Devices

The ionization of excitons at low temperature in the QWT devices strongly suggests that the contacts are making good electrical contact to the quantum wells. To confirm this, we take photocurrent spectra from each device, which should enable the observation of the ground and excited states of the QWT. Figure 5.8 a shows a photocurrent spectrum from the 8 nm QWT nanowire device at 10 K and at an applied bias of −1 V (a voltage not sufficient to quench the exciton luminescence). The photocurrent (black solid line) in Fig. 5.8 a is normalized to the incident power. The sharp rise in the photocurrent response near 1.5 eV is due to the valence band to conduction band transition of the GaAs core. In addition to the core absorption, five prominent peaks (see Fig. 5.8 a) are observed in the photocurrent spectrum that are identified as optical transitions from confined states of the QWT, as well the band-to-band transition of the ∼40% AlGaAs shell. Using the numerical solutions described in section 5.3, we label the observed peaks according to transitions between the heavy- and light hole (HH and LH) and electron (E) confined states which have the same radial (principal) quantum number, n. For all transitions we assume the orbital angular momentum is zero.
Because the applied bias is relatively low, it is also possible to take PL (blue line) and PLE (red circles) spectra from the same device under the same conditions as displayed in Fig. 5.8a. The PL spectrum is dominated by the $E1 \rightarrow HH1$ transition between the electron and hole ground states. PLE spectra show the higher lying transitions between $HH2 \rightarrow E2$ and $LH2 \rightarrow E2$ are also observed in the PC spectrum in the 8 nm QWT NW devices. There is excellent correspondence between the PL and PLE spectra and the overall PC spectrum with both ground and excited state transitions observed and identified. In both the PLE and PC spectra a strong peak is observed which corresponds to the VB to CB continuum transition ($\sim 2.1$ eV) in the AlGaAs barrier. The arrows

Figure 5.8. (a) Black solid line is photocurrent spectrum, at an applied bias of $-1$ V, normalized to the excitation power. The blue solid line is the photoluminescence and the red (circle + line) is the photoluminescence excitation spectra with 0 V applied bias for the 8 nm QWT nanowire device. All measurements were done at 10 K. (b) The plots are the same as in (a) but for the 4 nm QWT device, and the applied bias for the photocurrent is $-5$ V.
show the energies of the indicated transitions that result from the eigenfunction expansion calculations, and close agreement between the calculation and optical measurements is observed.

Figure 5.8b shows equivalent PL, PLE, and PC spectra from the 4 nm QWT NW device at 10 K. Calculations (see section 5.3) show a number of confined states in the HH and LH bands but only a single radial quantum state is seen for electrons in the conduction band. The position of the PL emission peak corresponds closely to the expected \( E_1 \rightarrow \text{HH1} \) transition. A broad plateau is observed in the PC spectrum for the \( \text{HH1} \rightarrow E_1 \) transition, and a small peak at the \( \text{LH1} \rightarrow E_1 \) energy. Because our calculations predict no \( n=2 \) electron confined states, the peaks observed in the PLE and PC spectra correspond to bound-to-(AlGaAs) continuum transitions such as \( \text{VB} \rightarrow E_1 \), \( \text{LH1} \rightarrow \text{CB} \), \( \text{HH2} \rightarrow \text{CB} \), and the \( \text{VB} \rightarrow \text{CB} \) transition in the AlGaAs. Peaks in both the PLE and PC spectra are observed for these transitions and are consistent with simple cylindrically symmetric quantum calculations. All observed optical transition signatures in both 8 nm and 4 nm quantum well tube are listed in Table 2. Figure 5.9 shows a schematic of the optical transitions.

<table>
<thead>
<tr>
<th>Transition</th>
<th>8 nm (eV)</th>
<th>4 nm (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{GaAs (VB-CB)} )</td>
<td>1.518</td>
<td>1.518</td>
</tr>
<tr>
<td>( \text{HH1} \rightarrow E_1 )</td>
<td>1.578</td>
<td>1.681</td>
</tr>
<tr>
<td>( \text{LH1} \rightarrow E_1 )</td>
<td>1.606</td>
<td>1.729</td>
</tr>
<tr>
<td>( \text{HH2} \rightarrow E_2 )</td>
<td>1.754</td>
<td></td>
</tr>
<tr>
<td>( \text{LH2} \rightarrow E_2 )</td>
<td>1.846</td>
<td></td>
</tr>
<tr>
<td>( \text{VB} \rightarrow E_1 )</td>
<td></td>
<td>1.829</td>
</tr>
<tr>
<td>( \text{LH1} \rightarrow \text{CB} )</td>
<td></td>
<td>1.918</td>
</tr>
<tr>
<td>( \text{HH2} \rightarrow \text{CB} )</td>
<td></td>
<td>1.985</td>
</tr>
<tr>
<td>( \text{AlGaAs (VB-CB)} )</td>
<td>2.017</td>
<td>2.017</td>
</tr>
</tbody>
</table>
Comparison between the PC, PL, and PLE spectra and theoretical calculations of the quantum confined states show that we understand in detail the energy structure of these single NW devices. The differences in the peaks observed in PL, PLE, and PC spectra and the calculated energies are much smaller than the confinement energy in every case. As was noted previously, in the 4 nm QWT device sharp peaks are observed in the PL spectra that indicate that the ground state excitons are indeed localized in the narrow quantum well. In order to understand the nature of this localization, we now probe these states by observing the quantum confined Stark effect.

![Figure 5.9. Schematic of optical transitions observed in PL and PC measurements](image)

5.7. QD Confinement Probed Using the Quantum Confined Stark Effect

The photoluminescence in the 4 nm QWT shows sharp quantum dot-like emission superimposed on the broader spectrum centered at approximately 1.67 eV. The center of the spectra, nearly 140 meV above the emission of the core GaAs, is consistent with $E_1 \rightarrow HH1$ transition calculated using both cylindrically symmetric eigenfunction expansion model and a hexagonally symmetric finite element calculation. As seen in the previous high-resolution TEM images (Fig. 5.4 b,c), these quantum dot-like emissions likely result from exciton localization due to either quantum well width fluctuations or alloy concentration fluctuations along the length of the NW or around the perimeter, or both.
In the QWT 4 nm NW device, the sharp PL peaks disappear as the bias increases along the length of the NW with the QD-like peaks on the high energy side disappearing more rapidly than those on the low energy side. However, because of the Stark effect, before the PL is completely quenched the QD emissions are shifted to lower energy with applied electric field. As we will show, the shift to lower energy combined with the electric field where quenching occurs can be used to determine simultaneously the size of the QDs and the depth of the confining potential.

Figure 5.10. Quantum confined Stark effect: (a) low energy side PL intensity at zero applied bias across the 4 nm QWT device; (b) false color map of PL intensity versus applied bias (electric field) and (c) enlarged plots of the rectangular region in false color map (b). The two peaks clearly show a Stark shift with electric field. The symbols are the peak positions for each applied bias obtained by Gaussian fit. The solid lines are the quadratic fit of energy shift versus applied electric field. (d–f) Similar plots as (a–c), respectively, for the high energy side of the spectra defined in Figure 5.7. All measurements were carried out at 10 K.
In Fig. 5.10a normalized PL intensity at zero applied field (bias) of the low energy side is displayed. Figure 5.10b is a false color plot that shows the PL intensity versus applied external field. The two prominent peaks in Fig. 5.10a correspond to the marked rectangular box in Fig. 5.10b where a visible shift to lower energy is seen for both positive and negative bias. Such a shift to lower energy is clear evidence for the quantum confined Stark effect. The fact that the shift is symmetric around zero bias suggests that there is no built-in dipole for excitons confined to the dot-like potential.\(^1\)

![Figure 5.11. (a) Schematics of truncated harmonic confining potential (b) modified barrier along the direction of externally applied electric field F.](image)

We now utilize the two phenomena we have observed, namely the bias dependence of the photoluminescence intensity (quenching) and the Stark shift of the quantum dot emission, to provide insight on the nature of the quantum dot-like states in these QWT nanowires. We will determine both the size of the dots and the depth of the confinement potential. The fact that Shi et al. showed that the dot PL quenches around 100 K suggests that the localization potential is of order 10 meV.\(^1\) The size of the dots should be of order the exciton Bohr diameter in GaAs or 24 nm. In self-assembled quantum dots, the quenching of the PL has been modeled as due to quantum tunneling through a triangular barrier, while the quantum confined Stark effect (QCSE) has been modeled as a displaced harmonic oscillator.\(^37\)–\(^39\) If one assumes that the electrons and holes are confined to a truncated parabolic potential,\(^37\)–\(^39\) as shown in Fig. 5.11, the depth of the potential...
is $V_0 = (1/8)m\omega^2L^2$, where $L$ is the diameter of the quantum dot and $\omega$ is the oscillation angular frequency of the harmonic oscillator. The tunneling rate through the barrier with electric field can be estimated using the WKB approximation as an attempt frequency $(\omega/2\pi)$ times the tunneling probability$^{40,41}$

$$R = \frac{\omega}{2\pi} \exp\left[\frac{-4}{3\hbar F\sqrt{2m^*V_0^3}}\right]$$

where $F$ is the electric field, $V_0$ is the depth of the potential well, and $\omega$ is the angular frequency of the oscillator. As discussed by Fry et al., the PL quenches when the tunneling rate equals the recombination rate of the excitons.$^{40}$ The QCSE for a simple harmonic oscillator potential in an electric field, $F$, is just$^{37-39}$

$$\Delta E = -\frac{F^2}{2m^*\omega^2}$$

Figure 5.12: Time-resolved PL spectra of a single 4 nm QWT nanowire dispersed on a silicon substrate at 10 K.
For each localized state we determine the parabolic shift of the emission energy with field (see data of Fig. 5.10) and so determine $m^*\omega^2$ (the curvature of the confining potential) for that state using Eqn. 2. Once $\omega$ for a state is determined, the depth of the confining potential, $V_0$, can be

![Figure 5.13](image)

Figure 5.13. (a) Plot of estimated diameter from the quadratic fit of the Stark effect for different quantum QD emission energies at zero bias, $E_0$. (b) Confining potential, $V_0$, versus $E_0$. Error bars for $L$ and $V_0$ determined by parabolic fit to data as in Figure 5.8 and ±5% change in quenching field as determined in Figure 5.7. (c) Change in confinement energy as a function of change in Al concentration (blue curve) and fractional change in the well width. The horizontal black dashed line show a 15 meV change in the confinement energy. The red dashed arrow shows the fractional well width change (±0.5 nm) required to provide a $\sim 15$ meV change in confinement energy. The blue dashed arrow shows the change in Al concentration (±8%) required to provide a 15 meV change in the confinement energy.
calculated using Eqn.1 by setting the tunneling rate $R = 1/\tau_r$ (the exciton recombination lifetime).

From $V_0$, the size of the dot can be determined using $V_0 = (1/8) m*\omega^2 L^2$.

To determine the recombination lifetime, we measured a full time-resolved spectrum from a single 4 nm QWT NW as shown in Fig. 5.12. One can see the characteristic sharp emission lines which persist out to 6 ns. By fitting each emission line to a single exponential decay one can show that the recombination lifetime ranges from 200 ps on the high energy side to 600 ps on the low energy side. From the quenching data shown in Fig. 2 we find that the high energy PL quenches at a field of 5.8 kV/cm while the low energy PL quenches at 16 kV/cm. Thus, for each emission line we can measure (1) the emission energy and QCSE shifts (Fig. 5.10), (2) the quenching fields (Fig. 5.7), and (3) the recombination lifetime (Figure 5.12). We use the procedure described above to determine both the size and depth of the localization potential for each QD emission line. Fig. 5.13 displays the QD size and the depth of the potential as a function of QD emission energy. The errors are determined by fits to the parabolic QCSE shifts (Fig. 5.10), and ±5% changes in the quenching field (Fig. 5.7). One can see that the dots on the low energy side are 32 meV deep and approximately 35 nm in diameter. On the other hand, for QD emission on the high energy side the localization potential is a smaller 15 meV in depth and a smaller diameter of 18 nm. The fact that the localization potential for the dots on the high energy side is 15 meV is consistent with the observation by Shi et al.\textsuperscript{14} that these dots persist to temperatures of around 100 K. This localization potential might be caused by either well width fluctuations or alloy concentration fluctuations in the barrier. To estimate the magnitude of these fluctuations, we use our eigenfunction expansion calculations to show what change in the well width or alloy concentration would yield such a 15 meV change in the confinement energy within the well. As shown in Fig. 5.13c, a 15 meV change in confinement energy can be caused by only a ±0.5 nm change in the well width or a ±8% local...
change in the AlGaAs alloy concentration in the barrier. Such a small change in the well width is consistent with the roughness seen in the HRTEM cross sections shown in Fig. 5.4. The concentration fluctuation is quite a bit larger than the ±3% estimated from the HRTEM analysis in Fig. 5.4 but substantially smaller than observed in recent atom probe tomography results in MBE-prepared GaAs/AlGaAs nanowires.\textsuperscript{42,43} Clearly the presence of the QD-like emissions points to disorder effects in the growth that may need to be better controlled in the future.

5.8. Conclusions

Photocurrent spectroscopy is used to probe the quantum confined states of single GaAs/AlGaAs QWT nanowire devices. The observed peaks in the photocurrent spectra were matched with theoretically predicted transitions in the QWTs consistent with their respective thicknesses. In addition, PLE measurements closely correspond to the photocurrent spectra measurements. We observed a strong quenching of the photoluminescence when a bias was applied, as expected. Finally, a quantum confined Stark effect was observed in the quantum dot emissions superimposed on the broader spectrum of the 4 nm QWT emissions. From an analysis of the Stark shifts of the quantum dot-like emissions, we estimate both the confinement energies (∼15 meV) and diameters (∼20 nm) of the quantum dots associated with the 4 nm QWT that are formed due to variations in the QWT width or Al concentration along the quantum well tube. This result is consistent with alloy and well-width disorder seen in high resolution cross-sectional TEM measurements. Understanding the nature of exciton localization in these QWT devices is a necessary first step in imagining and implementing real device structures.

5.9. References


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Chapter 6 Summary and future directions

We have investigated the optical and electrical properties of single semiconductor nanowires using transport measurements, photocurrent, photoluminescence and photoluminescence excitation spectroscopies. The nanowires studied in this work are all grown using MOCVD techniques. The variety of nanowires includes Zn$_2$As$_3$, bare GaAs, GaAs/AlGaAs core-shell, bare GaAsSb, and GaAs/AlGaAs quantum well tube nanowires.

The nanowire wire devices were fabricated using photolithography to define contacts on either end of the nanowires. The devices are wire bonded to allow low temperature measurement in an optical cryostat. Room temperature transport measurements were used for estimation of semiconductor parameters such as doping densities of $1.67 \times 10^{18} cm^{-3}$ and $7.41 \times 10^{18} cm^{-3}$ for Zn$_2$As$_3$ nanowire and nanoplatelet devices, respectively. These results were obtained by employing a simple metal-semiconductor-metal model and self-consistent fitting. The doping densities obtained from the fitting using the model agree very well with densities obtained using transient Rayleigh scattering measurements.

Absorption spectra of single nanowires were measured by photocurrent spectroscopy at 10 K. Exciton resonances were resolved in both bare GaAs and GaAs/AlGaAs core-shell heterostructure nanowires near the band edge of GaAs. In addition, photocurrent spectra of the core-shell nanowires exhibited a clear onset of absorption of the shell as well as the core which provides an estimation of Al concentration in the shell of the nanowire. Photocurrent spectroscopy was also used to characterize the band structure of GaAsSb nanowire devices. The observed spectra show the clear onset of absorption corresponding to the band gap and also a signature of the split-off band. Using an empirical equation of band gap dependence on the concentration of Sb atoms in
the nanowire, we estimated the concentration of the Sb 40-45% which is consistent with EDX measurements.

Photocurrent spectroscopy was also used to probe quantum confined states in single GaAs/AlGaAs QWT nanowire devices. The observed spectral signatures in the photocurrent spectra were matched with theoretical predictions for respective thicknesses of the quantum well tubes. Photoluminescence excitation spectroscopy performed on the same devices closely corresponds with the photocurrent spectra. We observed a strong quenching of the photoluminescence when a bias was applied, as expected.

Finally, a strong quantum confined Stark effect was observed in the quantum dot emissions superimposed on the broader spectrum of the 4 nm QWT emissions. From an analysis of the Stark shifts of the quantum dot-like emissions, we estimate both the confinement energies (∼15 meV) and diameters (∼20 nm) of the quantum dots associated with the 4 nm QWT that are formed due to variations in the QWT width or Al concentration along the quantum well tube. This result is consistent with alloy and well-width disorder seen in high resolution cross-sectional TEM measurements. Understanding the nature of exciton localization in these QWT devices is a necessary first step in imagining and implementing real device structures.

6.1 Future Directions

The photocurrent we used in this work is time-integrated PC spectra; a pulsed white light super continuum source is filtered using a prism-based pulse shaper which provides narrow bandwidth (~3 nm) tunable excitation from 600nm to 2400nm. The tunable excitation beam was chopped mechanically and the photocurrent measured at constant bias using lock-in detection. We have demonstrated PC spectroscopy is powerful in probing the band structure quantum confined in state
in quantum well tube. The next logical step is to use time-resolved photocurrent spectroscopy to investigate the dynamic photoexcited carriers in single nanowire devices.

We have developed an experimental setup for time-resolved photocurrent and measured preliminary data. The experimental set up and preliminary time resolved photocurrent signal at a single probe energy are shown in Fig. 6.1. A 550 nm pump pulse was used to excite the NW devices at $t = 0$. Using a mechanical delay line, a delayed tunable probe pulse also excited the NW device. The photocurrent created by the probe pulse is measured using a lock-in tuned to the chopper frequency which modulates the delayed probe beam. The pump beam is unchopped, and so the probe response is measured as a function of the relative delay of the probe pulse keeping the device bias constant. For fixed probe energy we observed strong quenching of the photocurrent when $t_d=0$ and a semi exponential rise until it reaches a plateau. We attribute the quenching of the photocurrent to the band filling which inhibits further excitation by the probe. By tuning the probe energy one can map out the dynamic response of the device at different energies. Spectral signatures are observed both at early and late times after the pump pulse which can be assigned to particular energies associated with the specific NW being measured. The response clearly involves both carrier filling of the bands as well as transport of the electrons and holes. The development of a model and of a modified experimental set-up is future work.
Figure 6.0.1 (a) Time-resolved photocurrent set up. (b) time-resolved photocurrent signal at 10 K, pump wavelength~550nm, probe wavelength~700nm and applied bias~3V measured on 4 nm QWT.
Appendices

A. Mathematica code for back-to-back Schottky model

\[
\begin{align*}
k &= 1.38 \times 10^{-23}; \\
h &= 6.63 \times 10^{-34} / (2 \pi); \\
h &= 6.63 \times 10^{-34}; \\
\rho &= 0.36 \times 9.1 \times 10^{-11}; \\
\epsilon_r &= 12 \times 8.85 \times 10^{-12}; \\
\epsilon_0 &= 8.85 \times 10^{-12}; \\
q &= 1.6 \times 10^{-19}; \\
T &= 294; \\
A &= (4 \pi \rho q k^2) / (h^3); \\
S_1 &= 20 \times 10^{-12}; \\
\mathcal{E}_0 &= (\hbar \alpha / 2) \left( \frac{N_d}{\mu \epsilon \sigma \epsilon_c} \right)^{1/2}; \\
\mathcal{E} &= \mathcal{E}_0 \cdot \text{Cosh} \left( \frac{q \cdot \mathcal{E}_0}{k \cdot T} \right); \\
S &= 3.14 \times 25 \times (10^{-4})^2 \\
7.85 \times 10^{-16}
\end{align*}
\]

\[
data = \text{Import["C:\Documents and Settings\Bekele\Desktop\DarkIVD2.txt", "Table"]};
\]

\[
v11[I1\_\_, n1\_\_, x\_\_] := v1 /., \text{FindRoot}[I1 \cdot \text{Exp}[39.4 \cdot v1 / n1] \cdot (1 - \text{Exp}[39.4 \cdot v1]) - x, \{v1, 0.1}\]
\]

\[
v11[1.3 \cdot 10^{-7}, 3, \text{data}[[12, 2]]]
0.00478404
\]

\[
v22[I2\_\_, c0\_\_, x\_\_] := v2 /., \text{FindRoot}[I2 \cdot \text{Exp}[v2 (39.4 - 1/c0)] - x, \{v2, 0.1}\]
\]

\[
v22[1.3 \cdot 10^{-9}, 0.7, \text{data}[[12, 2]]]
0.0765452
\]

\[
\text{vff}[I1\_\_, I2\_\_, n1\_\_, c0\_\_, x\_\_] := \text{v11}[I1, n1, x] + v22[I2, c0, x]
\]

\[
\text{vff}[1.3 \cdot 10^{-7}, 1.3 \cdot 10^{-9}, 3, 0.7, \text{data}[[12, 2]]]
0.0815293
\]

\[
v33[I3\_\_, n2\_\_, x\_\_] := -v1 /., \text{FindRoot}[I3 \cdot \text{Exp}[39.4 (v1) / n2] \cdot (1 - \text{Exp}[39.4 \cdot v1]) + x, \{v1, 0.3}\]
\]

\[
v33[1.3 \cdot 10^{-7}, 3, \text{data}[[4, 2]]]
-0.158406
\]

\[
v44[I4\_\_, c0\_\_, x\_\_] := -v2 /., \text{FindRoot}[I4 \cdot \text{Exp}[v2 (39.4 - 1/c0)] + x, \{v2, 0.3}\]
\]

\[
v44[1.3 \cdot 10^{-9}, 0.7, \text{data}[[4, 2]]]
\]
-0.176017

\[ vrr[Is_3, Is_4, n_2, e_0, x_] := v33[Is_3, n_2, x] + v44[Is_4, e_0, x] \]
\[ vrr[1.3 \times 10^{-7}, 1.3 \times 10^{-9}, 3, 0.7, data[[4, 2]]] \]
-0.334423

\[ vtotal[Is_1, Is_2, n_1, Is_3, n_3, e_0, x_] := \{ vrr[Is_3, Is_4, n_2, e_0, x] \ x < 0 \ vff[Is_1, Is_2, n_1, e_0, x] \ x \geq 0 \}
\[ vtotal[1.3 \times 10^{-7}, 1 \times 10^{-9}, 3, 2 \times 10^{-7}, 1.4 \times 10^{-5}, 3, 0.07, data[[2, 2]]] \]
-0.480074

\[ vtl[Is_{11}, Is_{21}, n_{11}, Is_{31}, n_{21}, e_{01}, x_] := \{ v33[Is_{31}, n_{21}, x] + v44[Is_{41}, e_{01}, x] \ x \leq 0 \ v11[Is_{11}, n_{11}, x] + v22[Is_{21}, e_{01}, x] \ x > 0 \}
\[ vtl[1.3 \times 10^{-7}, 1 \times 10^{-9}, 3, 2 \times 10^{-7}, 1.4 \times 10^{-9}, 3, 0.07, data[[2, 2]]] \]
-0.480074

\[ v33[2 \times 10^{-7}, 3, data[[2, 2]]] - v44[1.4 \times 10^{-5}, 0.07, data[[2, 2]]] \]
-0.480074

\[ vtt[Is_1, Is_2, n_1, Is_3, Is_4, n_2, e_0, x_] := \]
\[ v1 /. \text{FindRoot}[Is_3*\text{Exp}[39.4 (v1)/n_2] \ (1 - \text{Exp}[-39.4 v1]) - x, \{v1, 0.3\}] \ v2 /. \ x < 0 \]
\[ \text{FindRoot}[Is_4*\text{Exp}[v2 (39.4 - 1/e_0)] + x, \{v2, 0.3\}] \]
\[ v11[Is_{11}, n_{11}, x] + v22[Is_{21}, e_{01}, x] \ x \geq 0 \]

\[ x^2 = \text{Sum}[\text{data[[1, 1]]} - vtotal[Is_1, Is_2, n_1, Is_3, Is_4, n_2, e_0, data[[1, 2]]] - R*data[[1, 2]]]^2, \{i, 1, \text{Length[data], 1}\} ; \]
\[ \text{ans} = \text{FindMinimum}\{x^2, \{Is_1, 2 \times 10^{-6}\}, \{Is_2, 2 \times 10^{-9}\}, \{n_1, 3\}, \{Is_3, 2 \times 10^{-9}\}, \{Is_4, 2 \times 10^{-9}\}, \{n_2, 1.8\}, \{e_0, 0.04\}, \{R, 1000000\}\} ; \]
\[ 0.00523053, \{Is_1 \rightarrow 1.74987 \times 10^{-7}, Is_2 \rightarrow 1.36584 \times 10^{-5}, n_1 \rightarrow 5.19194, Is_3 \rightarrow 1.69379 \times 10^{-4}, Is_4 \rightarrow 7.06458 \times 10^{-5}, n_2 \rightarrow 2.8302, e_0 \rightarrow 0.0688723, R \rightarrow 57991.2\} \]

\[ \text{fitbias} = \]
\[ \text{Table}[vtotal[\text{ans[[2, 1, 2]]}, \text{ans[[2, 2, 2]]}, \text{ans[[2, 3, 2]]}, \text{ans[[2, 4, 2]]}, \text{ans[[2, 5, 2]]}, \text{ans[[2, 6, 2]]}, \text{ans[[2, 7, 2]]}, \text{data[[1, 2]]}] + \text{ans[[2, 0, 2]]}*\text{data[[1, 2]]}, \{i, 1, \text{Length[data], 1}\}] \]
\[ \{-0.511617, -0.717082, -0.627955, -0.556541, -0.476572, -0.400327, -0.324699, -0.247037, -0.165711, -0.0686201, -0.051717, 0.120417, 0.177232, 0.235877, 0.316976, 0.403692, 0.488731, 0.563963, 0.641981, 0.71708, 0.796348\} \]

95
```math
bias = Table[Part[data[[i]], 1], {i, 1, Length[data], 1}]
{-0.8, -0.72, -0.64, -0.56, -0.48, -0.4, -0.32, -0.24, -0.16, 0.08, 0.08, 0.16, 0.24, 0.32, 0.4, 0.48, 0.56, 0.64, 0.72, 0.8}
current = Table[Part[data[[i]], 2], {i, 1, Length[data], 1}]
ListPlot[Transpose[{bias, fitbias}]]

Show[ListPlot[Transpose[{current, bias}], PlotStyle -> {Black, PointSize[0.01]}], ListLinePlot[Transpose[{current, fitbias}], PlotStyle -> Red]]

data1 = Import["C:\Documents and Settings\Bekalc\Desktop\CrydarkIV.txt", "Table"];
ax2 = Sum[(data1[[i, 1]] - vt1[Is1, Is2, n1, Is3, Is4, n2, e0, data1[[i, 2]]] - R*data1[[i, 2]])^2, {i, 1, Length[data1], 1}];
ans1 = FindMinimum[{ax2, [[Is1, 9*10^-13], [Is2, 2*10^-10], [n1, 19], [Is3, 2*10^-10], [Is4, 2*10^-9], [n2, 16.5], [e0, 0.07], [R, 1.000000]]}
{2.44824, [Is1 = 4.31377*10^-12, Is2 = 2.74767*10^-10, n1 = 10.996, Is3 = 1.31318*10^-11, Is4 = 2.28904*10^-22, n2 = 16.7044, e0 = 0.0708071, R = 1.43853*10^6]}
```
fitbias1 = Table[vtotal, {ans1[[2, 1, 2]], ans1[[2, 2, 2]], ans1[[2, 3, 2]], ans1[[2, 4, 2]], ans1[[2, 5, 2]], ans1[[2, 6, 2]], ans1[[2, 7, 2]], data1[[1, 2]]}]

bias1 = Table[Part[data1, {1, 1}, {1, 1, Length[data1], 1}];

current1 = Table[Part[data1, {1, 2}, {1, 1, Length[data1], 1}];

Show[ListPlot[Transpose[{current1, bias1}], PlotStyle -> {Black, PointSize[0.01]}],
ListLinePlot[Transpose[{current1, fitbias1}], PlotStyle -> Red]]

ListPlot[Transpose[{bias1, fitbias1}]]

ans2 = FindMinimum[x2, {{1, 4.3*10^{-12}}, {1, 2.7*10^{-12}}, {1, 9.1*10^{-11}}, {1, 2.9*10^{-23}}, {1, 19.5}, {1, 0.07}, {1, 9.1*10^8}}]
{1.69503, {1.42996*10^{-12}, 2.7*10^{-10}, 9.1*10^{-11}, 2.9*10^{-23}, 19.5, 0.07, 9.1*10^8}}

fitbias2 = Table[vtotal, {ans1[[2, 1, 2]], ans1[[2, 2, 2]], ans1[[2, 3, 2]], ans1[[2, 4, 2]], ans1[[2, 5, 2]], ans1[[2, 6, 2]], ans1[[2, 7, 2]], data1[[1, 2]]}]
{-4.71192, -4.32799, -4.00735, -3.62359, -3.15165, -2.71329, -2.20359, -1.66588, -1.00369, -0.77133, 0.6804, -0.046825, 0.960365, 1.7132, 2.28792, 2.7233, 3.11121, 3.42839, 3.76738, 4.15599, 4.5292}
\begin{verbatim}
Show[ListPlot[Transpose[{current1, bias1}], PlotStyle -> {Black, PointSize[0.01]}],
ListLinePlot[Transpose[{current1, fitbias1}], PlotStyle -> Red]]

diff = Transpose[{current1, fitbias12}]

[[{\ -1.50232\times 10^{-8}, \ -4.71192}, {\ -8.21668\times 10^{-9}, \ -4.32799}],
{\ -2.42786\times 10^{-9}, \ -3.62388}, {\ -1.02779\times 10^{-9}, \ -3.15168}],
{\ -4.73712\times 10^{-10}, \ -2.71329},
{\ -1.7706\times 10^{-10}, \ -2.20359}, {\ -6.48985\times 10^{-11}, \ -1.66588}],
{\ -1.8814\times 10^{-11}, \ -1.00369}],
{\ -4.2755\times 10^{-12}, \ -0.771131}, {\ -8.07794\times 10^{-13}, \ -0.6804}],
{\ -.5.3595\times 10^{-12}, \ -0.045893},
{\ -4.1403\times 10^{-13}, \ 0.960365}, {\ 1.88005\times 10^{-19}, \ 1.7132}],
{\ 5.9363\times 10^{-10}, \ 2.28792}],
{\ -1.40549\times 10^{-6}, \ 2.7233}, {\ 2.98268\times 10^{-9}, \ 3.11121}],
{\ 5.36159\times 10^{-9}, \ 3.42388}],
{\ 9.86717\times 10^{-9}, \ 3.76738}], {\ 1.86645\times 10^{-9}, \ 4.15599}],
{\ 3.11219\times 10^{-9}, \ 4.5292}]

Export["diff.xls", diff, "XLS"]

Extraction of parameter

\[ \phi_\text{phi} = \frac{k \times T}{q \times \text{area}} \times \log \left[ \frac{T_s}{\text{area} \times \lambda \times T} \right] \]

\[ \phi_{\text{phi1}} = \phi_k \left[ 4.3 \times 10^{-12}, \ 3.14 \times 10^{-11} \right] \]
0.492445

\[ \phi_{\text{phi2}} = \phi_k \left[ 1.3 \times 10^{-11}, \ 3.14 \times 10^{-11} \right] \]
0.644392

\[ m0 = s / \text{FindRoot} \left[ s \times \text{Cosh} \left[ \frac{q \times s}{k \times T} \right] = 0.0688, \{s, 100\} \right] \]
0.0681666

\[ \phi_{\text{phi1}} = \phi_k \left[ 1.7 \times 10^{-3}, \ 3.14 \times 10^{-11} \right] \]
0.224038

\[ \phi_{\text{phi2}} = \phi_k \left[ 1.7 \times 10^{-3}, \ 3.14 \times 10^{-11} \right] \]
0.282426

FindRoot::mnumr: The function value \((\approx -0.0433414[0.01])\) is not a list of numbers with dimensions \((1)\) that
FindRoot::xroot: One or more of the given \((\approx 100)\) variables \(\{x\}\) are not correctly used

\[ \text{Density} = \rho \times \frac{2 \times m0}{\pi} \]
5.80771 \times 10^{24} \]
\end{verbatim}
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Quantum Confined Stark Effect in a GaAs/AlGaAs Nanowire
Probing Exciton Localization
Author: Bekele H. Badara, Teng Shi, Howard E. Jackson, et al
Publication: Nano Letters
Publisher: American Chemical Society
Date: Dec 1, 2015
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