CARRIER TRANSPORT AND SENSING IN COMPOUND SEMICONDUCTOR NANOWIRES

by

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University of Toronto

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Abstract

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Experiments and analysis in this thesis advance the understanding of critical issues in the carrier transport properties of InAs and InAs/GaAs core/shell heterostructure nanowires (diameter 30-60 nm) grown by molecular beam epitaxy. Effects of robust sub-band quantization structure on the gate-voltage dependence of conductance are observed up to 77 K in a single InAs nanowire with diameter 34±2 nm. Electronic field effect mobility at 300 K and 30 K are typically 2000-4000 cm²V⁻¹s⁻¹ and 10000-20000 cm²V⁻¹s⁻¹.

Strain induced by lattice mismatch in epitaxial core/shell InAs/GaAs heterostructure nanowires is found to relax by formation of dislocations, correlated with nearly one order of magnitude suppression of room temperature field effect mobility compared with bare InAs nanowires. The carrier transport properties of Mn-doped ZnO nanowires were also investigated, where despite the large bandgap, conductivity is not thermally activated, and carrier mobility is consistent with strong degeneracy of the electron gas at 10 K.

A novel method was developed providing the first experimental characterization of the quasi-equilibrium gate-voltage dependent surface potential in nanowire field-effect transistors, based on statistics of charging/discharging of a single Coulomb impurity evident in a random telegraph signal, which succeeds in nanostructures with tiny (attofarad) gate capacitance, where similar capacitance-voltage methods are challenging or impossible. We find that the evolution of channel potential with gate voltage is suppressed in the transistor’s accumulation regime due to the screening effects of surface states with
\[ D_{ss} = 1 - 2 \times 10^{12} \text{ cm}^{-2} \text{eV}^{-1}. \]

The gate voltage dependence of the random telegraph signals were used as a novel probe to spectroscopically study strong carrier reflection by single Coulomb impurities in nanowires. Reflection probabilities \( R = 0.98 - 0.999 \) approach unity for an electron gas with density \( n = 30 - 10 / \mu \text{m} \) in 30 nm diameter, 1 \( \mu \text{m} \) long InAs nanowires at 30 K. Results were compared with microscopic theory of electron scattering by Coulomb impurities in nanowires with dielectric confinement, \( \text{i.e.} \) low dielectric constant surroundings. The latter, which is known to enhance the bare Coulomb interaction and excitonic binding energy, is an essential ingredient for the strong scattering in this regime, and in small diameter nanowires causes a breakdown in linear screening.

Extending this, we show that InAs nanowires can operate is extremely sensitive charge sensors with sensitivity 60 \( \mu \text{eHz}^{-1/2} \) at high temperatures (200 K), a combination of characteristics that is not achieved by existing technology. Strong electrostatic coupling of a single charge to the conducting electron gas in the nanowire is enabled by miniaturization of nanowire diameter, operation in a regime of carrier density where the electronic screening length exceeds the nanowire diameter, and dielectric confinement.

Finally, single ZnSe nanowire photodetectors are fabricated and studied. Peak responsivity at 2.0 V bias is 20 A/W at room temperature, similar to that of the best epitaxial ZnSe photodetectors. The high responsivity is due to a photoconductive gain \( g \approx 500 \), the ratio of carrier lifetime to carrier transit time. The former is enhanced at room temperature due to rapid selective trapping of one species of excited carriers by surface states.
Dedication

To My Parents and Melissa
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nanowires presented in this thesis, and its correlation with their transport properties.

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Nanostructured semiconductors, where carriers are confined at the nanometer scale along one or more directions, are of both scientific and technological interest, since the carrier confinement can lead to modified or completely different behaviour compared with bulk semiconductors where electrons and holes are free to move in three dimensions. Semiconductors in which carriers are confined to motion in two dimensions, realized by growth of thin films or multilayers on planar substrates by so-called crystal hetero-epitaxy, have been studied the most extensively. Methods for crystal hetero-epitaxy have sufficient maturity[3] that several commercialized technological applications exist, some of which are discussed below. There is also a strong scientific interest in semiconductors whose carriers are confined to motion along a line or in all three dimensions, but to some extent these scientific research efforts and potential technological applications are still hampered by a lack of methods for controlled fabrication that produce nanostructures with the desired properties on the desired substrates. A brief, bird’s eye perspective on the landscape of fabrication, characterization, and (potential) technological applications of nanostructures is included to serve as an introduction to more specialized topic of
Chapter 1. Introduction, Objectives, and Background

nanowires, which in turn will provide the necessary backdrop to define the objectives of this thesis.

Perhaps the most well studied two-dimensional carrier systems are the Si inversion layer and the AlGaAs/GaAs/AlGaAs heterostructured quantum wells. In the former, electrons or holes in Silicon can be confined by electric fields to within approximately 10 nm the interface with SiO$_2$, while in the latter, electrons and/or holes are confined to the a thin (10 nm or so) GaAs layer by the surrounding AlGaAs material having a type-I heterostructure band alignment\[4\]. Today, Silicon inversion layers are the backbone of the complementary metal-oxide-semiconductor (CMOS) field effect transistors (FETs)\[5\] upon which modern integrated circuit technology is based, and were the first system in which what is now called the Integer Quantum Hall Effect (IQHE) was observed\[6\]. The modulation-doped\[7\] AlGaAs/GaAs/GaAs quantum wells are known for their exceptionally high electron mobility at cryogenic temperatures\[8\]. Applications of two dimensional semiconductor heterostructure quantum-wells and super-lattices include the high electron mobility transistors (HEMTs) from which radio-frequency and microwave circuits are designed\[9\], and quantum cascade lasers from which coherent sources of mid-infrared\[10\] and terahertz radiation\[11\] have been constructed. Modulation doped structures were instrumental in the discovery of the Fractional Quantum Hall Effect (FQHE)\[12\] which continues to generate new riddles in physics\[13\]. Recently, graphene has emerged as a remarkable new two dimensional system with its relativistic, semi-metallic dispersion and host of touted applications\[14\].

Research interest in the fundamental properties and potential applications for zero-dimensional and one-dimensional structures, where carriers are confined in two or three dimensions, respectively, have also flourished. The very first experimental demonstration of fully quantized electronic states in zero-dimensional structures, the so-called quantum dots, was reported in reference\[15\]. Later, the dramatic size-dependence of their electronic structure and, therefore, optical absorption spectrum, attracted considerable
interest[16, 17]. Experiments on transport through quantum dots eventually progressed to the level where the number of electrons in such systems could be controlled down to the last few, where atomic shell-filling effects, symmetries, and magnetic-field-induced single-triplet splitting were observed[18], strengthening the analogy between quantum dots and atoms systems. Later, electrical control of electronic level filling down to the last electron was accomplished in electrostatic gate-defined quantum dots[19]. Following theoretical proposals that coupled quantum dots could be used as the technological underpinnings for quantum information processing[20], control and manipulation of spins in quantum dots and other solid-state systems has progressed rapidly[21, 22].

Moving to the one-dimensional semiconducting structures, among the first important scientific discoveries was the observation of ballistic (scattering-free) electron transport through quasi-one-dimensional systems, and its hallmark quantization of conductance in units $e^2/h$ per electronic sub-band, in electrostatically gated “quantum point contacts” (QPCs) of modulation doped two-dimensional electron systems in GaAs/AlGaAs heterostructures[23]. Besides QPCs, other incarnations of these so-called quantum wires have been realized by clever modification of GaAs/AlGaAs modulation doped structures. Single-walled carbon nanotubes with diameter $\approx 1$ nm later emerged as extreme examples of model one-dimensional systems with metallic, semiconducting, or insulating behaviour depending on their chirality[24], long mean-free paths[25] and low temperature electrical properties consistent with predictions of the behaviour of one-dimensional correlated electron systems[26]. More recently, signatures of strong electron-electron interactions have been observed in these and other one-dimensional systems[27]. However, prospects for nanoelectronic devices based on carbon nanotubes are presently limited by difficulty in controlling both their placement and electronic structure[28]. For the majority of GaAs/AlGaAs heterostructure-based quantum wires, the “in plane confinement” is relatively weak, limiting the expression of their one-dimensionality to liquid Helium temperatures.
A recent addition to the menagerie of quasi-one-dimensional systems are the semiconductor nanowires grown by the metal-catalyzed vapour-liquid-solid (VLS) method. These methods, which stem from the first demonstration by Wagner and Ellis[29], are noteworthy for their applicability to a truly wide variety of materials[30] and for sophisticated control over geometry, composition (heteroepitaxy[31] and crystal polytypes[32]), and accurate placement and orientation[33] of large numbers of nanowires, not to mention promising electronic properties[34]. In semiconductor nanowires with sufficiently miniaturized diameter (the necessary diameter depends on the material) we may also hope for quasi-one-dimensional behaviour at room temperature.

Among the potential technological applications of zero and one-dimensional systems are information technology, renewable energy, and life sciences, and due to nanostructure’s small size and sensitivity to their environment, a host of sensing applications. Advanced Micro Devices (AMD) and Intel’s miniaturization of the channel length of Silicon CMOS transistors is rapidly converging to 10 nm[35, 36]. Devices at this length scale include ballistic and coherent effects not present in their larger counterparts. The challenges and opportunities for data storage and manipulation emerging from the quantum mechanical underpinnings of such small devices, including gate leakage and subthreshold conduction, are apparent, and a glance at the International Technology Roadmap for Semiconductors (ITRS) reveals that the FinFET[37] and other new nanowire and nanostructure-based devices are emerging as strong candidates for digital processing and information storage[38]. One obvious deficiency of existing Silicon-based technology is the difficulty in realizing any devices that can emit light. Direct-bandgap nanostructured compound-semiconductor materials are more suitable for light emitters[39], detectors[40] capable of sensing a wider variety of wavelengths of electromagnetic radiation, and photovoltaics[41], as progress on their integration onto Silicon or other cheap substrates is made.
1.1 Semiconductor Nanowires

Semiconductor nanowires grown by the VLS mechanism have attracted considerable worldwide research efforts evidenced today on the ISI Web of Knowledge[42] by the continued exponential growth of both technologically and scientifically oriented studies of these structures. The VLS mechanism for growth of nanowires is a bottom-up approach where precursors in (V)apour phase impinge on and are subsequently incorporated into a (L)iquid catalyst particle, often Au, on a substrate heated to an appropriate temperature. When the concentration of precursors incorporated into the liquid catalyst reaches a critical value of saturation, (S)olid precipitation of precursors occurs at the interface between the catalyst and the substrate, resulting in nanowire growth. This process is illustrated schematically, left to right in Figure 1.1a, starting with liquid metal droplets exposed to flux of precursors and resulting in nanowire growth. Considerable research efforts on VLS and the related vapour-solid-solid (VSS) method for nanowire growth has demonstrated several unique and useful characteristics, summarized below.

- **Control of geometry of nanowires**: The diameter of nanowires grown by VLS or VSS is related to the diameter of the catalyst particle, and the orientation of the nanowire with respect to the substrate’s normal vector is related to the substrate’s crystallographic orientation. See reference [33] for a review.

- **Degree of miniaturization**: It is possible grow nanowires with diameter down to 5 nm or even smaller, and length of at least several hundred nm, in a controlled fashion. See, for example, references [33, 43].

- **Control of position of nanowires on a substrate**: Top-down lithographic processing[44] or bottom-up methods[45] have been used to pattern catalyst particles at well-defined positions on a substrate, permitting control over the exact location of nanowire growth. Therefore it is not necessary to build devices from randomly dispersed nanostructures. See reference [33] for a review.
• **Control of composition of nanowires**: Well-controlled growth of heterostructure nanowires can be accomplished by modulating the composition of precursors. Both axial (along the length) and radial heterostructures are possible. See reference [46] for a review.

• **Strain accommodation in heterostructures**: In nanowire heterostructures, defect free heteroepitaxy can occur between two materials with a larger lattice-mismatch compared with planar growth, due to cylindrical nanowire geometry. This provides additional flexibility for defect-free heteroepitaxy of strained nanostructures not possible in planar systems. See reference [46] for a review.

• **Choice of substrate**: Several groups have demonstrated growth of compound-semiconductor nanowires on elemental semiconductor substrates such as Germanium and Silicon. See references [47, 48] for a review.

• **No etch damage**: An automatic consequence of the bottom-up VLS growth strategy is that semiconductor nanostructures with the above characteristics are defined without the need for wet or dry etching processes, which often degrade the properties of semiconductor surfaces.

Figure 1.1b is a scanning electron microscope (SEM) image of an array of InP nanowires grown from Au catalysts that were patterned by nano-imprint lithography process followed by physical vapour deposition and liftoff, as described by Mårtensson *et. al* from University of Lund[1]. Nanowires shown were obtained by loading the sample with pre-patterned catalysts into a metal-organic vapour-phase epitaxy (MOVPE)[3] reactor and subjecting it to a flux of precursors used for epitaxy of InP planar substrates. Nanowires approximately 1.5 microns long with base diameter 290 nm grown from the position of the pre-patterned catalyst.

Modulating the precursor flux to different combinations of chemicals offers the possibility to change the composition of the material precipitating from the catalyst, that
Figure 1.1: (a) Schematic of growth process, left to right, with liquid droplets on a substrate, subsequent collection of vapour phase precursors, and precipitation of nanowires. (b) SEM image array of InP nanowires grown at Au catalysts defined by electron beam lithography. Dark field TEM images (scale: 20 nm) of InAs nanowire with two inserted InP segments (c) 100 nm apart and (d) 20 nm apart. (b) is reprinted with permission from reference [1], and (c) and (d) are reprinted with permission from reference [2], Copyright 2004 American Chemical Society.
is, modulate the composition of the nanowire along its length. Well-defined, dislocation-free heterostructured growth of InP segments within InAs nanowires with corresponding lattice mismatch of $\approx 3\%$[49], were obtained by chemical beam epitaxy (CBE)[50] by Bjork et. al. at Lund University in references[31]. This was extended for growth of few nm length InP segments surrounding 100 nm and 20 nm long segments of InAs, shown in Figure 1.1c and 1.1d[2]. Growth of thin films with similar lattice mismatch on planar substrates only proceeds for a few monolayers before surface roughening (nano-island formation) begins[51, 52], and eventually, dislocation formation[53]. Much of the interest in heterostructured nanowires grown by VLS is due to expectation, backed up by theoretical predictions[54, 55], that for a given lattice mismatch, nanowires can tolerate a greater thickness of axial or radially deposited material before generation of dislocations, thereby opening up the possibility to explore new and interesting materials combinations and strain effects not previously possible due in conventional planar epitaxy. Indeed, defect free heteroepitaxy has been demonstrated in many material systems where planar growth is heavily restricted. In particular, controlled growth of direct-bandgap compound semiconductor nanostructures in selected locations on Silicon substrates is extremely attractive for sources and detectors in nanowire-based Silicon-integrated photonics[47] and for incorporation of nanoscale transistors with narrow bandgap III-V channels, which have considerably higher electron mobility than elemental semiconductors. Despite large lattice mismatch, recent progress towards integration of III-V nanowire materials on Silicon substrates by VLS is encouraging[47, 48].

The advantages provided by these unique aspects of VLS growth are beginning to be exploited for demonstration of novel electronic device prototypes. Coaxial-gated vertical-nanowire field-effect transistors[56] and sensors based vertical nanowires[57] are some of the first prototype electronic and sensing devices to benefit from grown of nanowires by VLS at selected sites on pre-patterned catalysts. Passive[44] and very recently active[58] photonic-crystal based optical devices have been demonstrated based on periodic arrays of
nanowires grown by site-selective patterning of catalysts. Meanwhile, controlled transfer of nanowires to mm² areas of wafer scale substrates has been demonstrated by several research groups. Notably, Fan et al. have developed a reliable procedure in reference [59] that was later employed in reference [60] for printing nanowire circuits onto flexible substrates.

1.2 Objectives and Overview

Compound semiconductor nanowires, with their approximately cylindrical cross-section of nanometer scale diameter and controllable composition have unique structural and electronic properties compared with planar devices. The bottom-up VLS fabrication method has been shown in permit precise control over geometry and positioning of nanowires, as well as growth of heterostructure nanowires when implemented by methods allowing precise, time-dependent control of precursor fluxes. This sophistication combined with impressive progress on controlled integration of compound semiconductor nanowires onto Silicon substrates gives them tremendous potential for realization of commercializable semiconductor devices compared with carbon nanotubes and solution processed nanorods and nanocrystals. Among the III-V semiconductor nanowires, InAs is distinguished by its native electron accumulation layer, relatively low effective mass, and correspondingly large electronic mean free path and sub-band quantization energies in nanostructures. Combined with its large Landé g-factor and strong spin-orbit coupling, InAs nanowires are extremely interesting for nano-electronic and nano-spintronic devices. Despite this promise, the effect of sub-band quantization and electronic transport has so far remained elusive, especially for small diameter nanowires where electronic quantization is expected to be large but where disorder is also expected to play a crucial role. Meanwhile, II-VI semiconductors with their large direct band-gap and efficient optical emission traditionally find applications in light emitting and detecting devices. More recently, wide bandgap
semiconductors GaN and ZnO have attracted considerable interest due to the theoretical prediction of hole-mediated ferromagnetism at room temperature\cite{61} and subsequent experimental observation of magnetic hysteresis at room temperature in Zn$_{x}$Mn$_{1-x}$O with $x \approx 0.95$\cite{62}.

This thesis focuses on the electronic and carrier transport properties of compound semiconductor nanowires grown by the VLS method, and the related question of how these nanostructures can be used to design high-performance electronic and opto-electronic devices. First, a set of experimental findings is presented considering the related themes of carrier transport and electronic structure in nanowires, electronic screening and scattering by single impurities in nanowires, electrostatic properties of nanowire transistors, and finally, the structure-property relationship between strain relaxation and carrier mobility in strained core/shell heterostructure nanowires with dislocations. We find evidence, through temperature-dependent differential conductance measurements, of gate-voltage controlled filling of robustly quantized electronic sub-bands in $\approx 30$ nm diameter InAs nanowires grown by MBE. We also demonstrate two novel methods for characterization of single-InAs-nanowire field effect transistors in this regime, based on stochastic fluctuation of the electronic occupation of a single trap state (Coulomb impurity), which produces a “random telegraph signal” in conductance. These signals, so-named due to their resemblance to signals present on the electrical lines of early telecommunications systems, appear as a stochastic switching of conductance between two well defined discrete levels, under fixed bias conditions. A novel method was developed providing the first experimental characterization of the quasi-equilibrium gate-voltage dependent surface potential in nanowire field-effect transistors, based on the temporal statistics of the random telegraph signal. This method succeeds in nanostructures where standard capacitance-voltage methods are hampered by the tiny gate capacitance of nanowires. Random telegraph signals are also used to spectroscopically study carrier back-reflection by a single Coulomb impurity in these one dimensional structures, where we show that
in addition to electronic size effects, size effects related to electronic screening play a critical role in enhancing the reflection probability. Finally, we studied the carrier transport mechanism in Mn-doped ZnO nanowires exhibiting room temperature ferromagnetism, a material with much promise for potential spin-based electronics technology. We found that these nanowires are n-type with degenerate electron conduction limited in band-like states limited by impurity scattering.

The observed strong back-reflection probability by localized charges in the small diameter InAs nanowires provides ample motivation to study their performance as single-nanowire charge detectors. The measured charge sensitivity \( dQ \approx 20 - 60 \, \mu\text{eHz}^{-1/2} \) of InAs single-nanowire field effect transistors to localized charge in the temperature range 30 K – 200 K is orders of magnitude higher than planar field effect transistors at 1 K[63], and similar to that of state of the art single-electron-transistor (SET) electrometers that require cooling to 4 K[64]. Ultra-sensitive electrometers at room temperature would eliminate the need for complex and expensive cryogenic apparatus needed by SETs and could pave the way for applications including ultra-low power single or few electron memories and fast single molecule detection, to mention a few. Finally, we characterize the electrical contacts to individual ZnSe nanowires and study their performance as UV photodetectors. We find high peak responsivity of 20 A/W, implying an internal gain of \( g \approx 500 \) electrons collected at the terminals per incident photon at only 2.0V bias. The thesis topics are summarized in Figure 1.2, which reflects the dual focus of the underlying physical properties of nanowires and novel and high-performance nanowire-based devices.

The first step in fabrication of all of the devices studied in this thesis involves transfer of free-standing nanowires from parent substrates on which they were grown, to host substrates coated with a thin layer of SiO\(_2\). Individual nanowires were located on the host substrates, and planar processing by electron beam lithography was carried out to define electrical contact structures. Meanwhile, several research groups have now
succeeded in fabricating devices directly on the substrates where nanowire growth was carried out by VLS at pre-defined locations. Among the first such devices fabricated include vertically oriented single[65] and multi-nanowire field effect transistors[56] with coaxial (wrap) gates. While the latter approach is undoubtedly preferable for large-scale fabrication of nanowire-based devices, the scheme employed in this thesis is justified since it reduces the complexity of fabrication without any sacrifice in the objectives.

This thesis is organized into seven chapters. The remainder of the first Chapter introduces the necessary theoretical background on the properties of semiconductor nanostructures employed in Chapters 2−7 after a discussion of the pertinent nanowire device fabrication and experimental methodology. Chapter 2 addresses the transport properties of free carriers in InAs nanowires, which are studied by electrical measurements of nanowire-based field effect transistors. Cryogenic temperatures in the range 10 to 300 K are employed in order to elucidate both the electronic structure of nanowires and physics of carrier scattering. Electrons in 30 nm diameter InAs nanowires exhibit evidence gate-voltage controlled filling of robust electronic sub-bands, which has been observed at a temperature as high as 77 K. The significance vis-á-vis technological applications of nanowires is manifold. First, robust one-dimensional quantization imparts exceptional negative differential resistance in nanowire-based resonant tunneling diodes[31], and is a pre-requisite for long-wavelength optical devices utilizing radiative intersub-band transitions. Second, electronic sub-band quantization is a signature of relatively weak disorder approaching the ballistic limit, where the highest transconductance, speed, lowest power, and lowest noise[66] field effect transistors are obtained. Moreover, fully ballistic transport is a property upon which novel spintronic and electronic devices have been proposed[67, 68]. We also compare the electronic properties of InAs nanowires and InAs/GaAs core/shell heterostructure nanowires with diameter between roughly 30 and 60 nm. Despite the nanowire’s higher tolerance for lattice mismatch heteroepitaxy compared with planar structures, significant strain relaxation by dislocations is observed in
Figure 1.2: Tasks, phenomena, and applications studied are in small boxes, and larger boxes surrounding them denote nanowire materials considered in these studies. Conceptual flow follows thick arrows from sample fabrication and development of measurement methodology (top), to experiments performed (bottom left), to phenomena and properties studied (bottom middle), and finally, applications considered (bottom right). Tasks in unshaded boxes were performed by other individuals at the institution denoted within parentheses.
InAs/GaAs core/shell nanowires with < 5 nm thick shells and core diameters \( \approx 20 \) nm. Consequently, electrons confined to the InAs core of core/shell nanowires have suppressed electronic carrier mobility compared with bare InAs nanowires.

The electronic and carrier transport properties of Mn-doped ZnO nanowires is included as a supplementary material in Appendix A. Incorporation of \( \approx 1 \) atomic % Mn imparts ferromagnetic behaviour on these nanowires with a Curie temperature exceeding room temperature[69]. We identify the carrier polarity and density in Mn-doped ZnO nanowires exhibiting room temperature ferromagnetism, two parameters of importance with respect to both their electrical and magnetic properties. Impurity scattering dominates the electrical properties of their carriers, which behave semiclassically.

Chapter 3 describes random telegraph signals which are observed in electrical measurements of about one-third of electrically measured InAs nanowires. We establish that these signals, characterized by stochastic switching of the nanowire’s conductance between two well-defined values, arise due to capture and emission of a single electron from a single trap in on the surface of the nanowire. Chapter 4 builds on this basic observation to quantitatively extract, from the detailed balance of charging and discharging events, the quasi-equilibrium relationship between surface potential and gate potential of InAs nanowires. This method could have special relevance since traditional capacitance-voltage (CV) measurements of the gate electrode of nanowire field effect transistors, which provides similar information are difficult due to their tiny gate capacitance, are often very difficult to carry out. Typically, CV measurements on nanowires require sophisticated electronics[70, 71, 72], and either special measurement apparatus or fabrication of specialized test structures[71, 72, 73]. The electronic properties of the defects response for random telegraph signals, capture cross section, activation energy, were also extracted from the trapping dynamics, and quantitatively interpreted in terms of a multiphonon emission model to obtain lattice distortion energy upon trapping of an electron.

Electron transport through the nanowire occurs on a much faster timescale compared
to the typical timescale \( \gtrsim 1 - 10 \text{ ms} \) of observed random telegraph signals. Exploiting this fact, we analyze the gate-voltage dependence of random telegraph signals to extract the carrier energy dependent scattering probability due to a single Coulomb impurity in \( \approx 30 \text{ nm} \) diameter InAs nanowires, in Chapter 5. The reflection probability for impurities becomes exponentially close to unity for low carrier densities varying from \( n \approx 30 - 10 / \mu \text{m} \) where the diameter of the nanowires is similar to the electronic screening length. These results are compared with theoretical scattering calculations showing that the low permittivity dielectric surroundings for the nanowire dramatically enhance the interaction between conducting carriers and the fixed charge. We demonstrate failure of both the Born approximation and linear (Lindhard) screening of the impurities by the conducting electrons, two commonly invoked approximations, as a consequence of the enhanced Coulomb interaction. Consequently, screening of the impurity is further weakened, and the scattering rate is dramatically enhanced compared with the case of dielectric surroundings that are matched to the nanowire’s permittivity.

Single-nanowire electrometers and photodetectors are considered in Chapters 6 and 7, respectively. The strong scattering by repulsive charges in dielectric confined nanowires discussed in Chapter 5 makes them excellent candidates for high sensitivity electrometry. The equivalent charge sensitivity of nanowire field-effect transistors was obtained by measuring both the change in conductance due to single charges, and the background high frequency white noise obtained by Fourier analysis of the random telegraph signal waveforms. The charge sensitivity \( dQ \approx 20 - 60 \mu \text{eHz}^{-1/2} \) of InAs single-nanowire field effect transistors between 30 K and 200 K is orders of magnitude higher than planar field effect transistors, and similar to that of state of the art single-electron-transistor-based electrometers that require cooling to 4 K[64]. This work demonstrates the feasibility of nanowire-based single-electron memories[74], and illustrates a physical process of potential relevance for high performance gas and chemical sensors[75, 76]. The charge state detection capability we demonstrate makes nanowires a promising host system for impu-
rities with potential long spin lifetimes[77].

In Chapter 7 we characterize the electrical contacts and photocurrent spectral responsivity of a high sensitivity single ZnSe nanowire photodetector, which are $\rho_c = 0.025 \, \Omega\text{-cm}^2$ and $R \approx 20 \, \text{A/W}$. The high responsivity implies a photoconductive gain of $g \approx 500$ carriers collected per photon absorbed, and the lifetime of carriers exceeds their transit time through the device by the same amount. This gain is obtained using a bias of only $V = 2.0 \, \text{V}$ across the 10 micron long nanowire, excluding the possibility of the gain being a result of an avalanche effect. Supported by the device’s slow transient response, the high gain is ascribed to fast and selective excess carrier trapping, confirming the important role of carrier trapping in nanowires and nanowire-based nanosensors. The achievement of a gain of $g \sim 500$ at an operating voltage of $V = 2.0 \, \text{V}$ compares favourably with avalanche diodes which normally require voltages exceeding 50 V to obtain a similar gain.

Within each of the scientific and engineering themes explored in this thesis, an original and significant research contribution has been made. A concise statement of my work and the contributions of others upon which this work was contingent follows. Initial development and successive refinement of the fabrication process and cryogenic setup for electrical measurements was carried out solely at the University of Toronto by the author of this thesis, as were all device fabrication, experiments, data analysis, and theoretical modeling presented in Chapters 2–7, with the exception of analysis of strain in Section 2.3 that was carried out jointly with Prof. Kavanagh and Dr. Savelyev with feedback from Dr. Blumin and Prof. Harry Ruda. The ZnO:Mn and ZnSe nanowires studied in this thesis were synthesized by Dr. Usha Philipose, who also provided data for structural and magnetic characterization of the former that is briefly summarized in a few paragraphs spanning Sections A.2 – A.3. Growth of InAs and InAs/GaAs core/shell nanowires described in Section 2.2 was performed by Dr. Igor Savelyev and Dr. Marina Blumin. The transmission electron microscopy of core/shell nanowires in Section 2.3 was performed at Simon Fraser University by Prof. Karen Kavanagh. Appendix A lists peer-
reviewed publications, manuscripts in preparation, and contributed talks and posters completed under the supervision of my thesis advisor Prof. Harry Ruda. Research projects beyond the scope of this thesis were carried out, resulting in additional peer-reviewed publications listed in Appendix B.

1.3 Methods

This section is intended to serve as a brief background of methods for nanowire growth, single-nanowire device fabrication, and single-nanowire electrical measurements common to Chapters 2 – 7. Supplemental details are provided in each Chapter, where appropriate.

1.3.1 Nanowire Growth

Semiconductor nanowires studied in this thesis were produced by metal-catalyzed VLS growth in either a closed quartz tube furnace using powder sources, or in the ultra-high vacuum (UHV) environment of a molecular beam epitaxy (MBE) system[3]. Figure 1.3a is a schematic diagram of a quartz tube furnace, where a carrier gas such as Argon is used to carry vapours evaporating from source powder(s) at a temperature $T_S$ in a suitable boat, to a heated target boat holding a growth substrate with gold droplets like those in Figure 1.1a, at a temperature $T_G$. After loading source and target boats, the quartz tube was purged with Argon gas for 1 hour and ramped to the final temperature using resistive heating elements in close proximity to the quartz tube. After nanowire growth for a specified time, carrier gas flow is maintained until the furnace cools sufficiently to safely remove the target and/or source boats.

The MBE method used for nanowire growth affords independent and precise control of fluxes of molecular beams with partial pressure $10^{-6} - 10^{-8}$ mbar, which are essentially non-interacting due to the background chamber pressure which is at a level of $10^{-9} - 10^{-10}$ mbar or lower, i.e., UHV. Figure 1.3b is a schematic diagram of a modified
Figure 1.3: Schematic diagram of (a) chemical vapour deposition in quartz tube furnace and (b) ultra-high vacuum chamber for MBE.
commercial MBE system (ATC-EP3) housed in the facilities for the Centre for Advanced Nanotechnology at University of Toronto. Six of the eight effusion cells are shown, each with an independently controllable shutter, oriented towards a central, rotatable substrate holder held at a temperature $T_G$. Ultra high purity solid sources of Arsenic, Aluminum, Indium, Gallium, Silicon, Gold, Beryllium, in effusion cells with independent, programmable, feedback control of source temperature and shutter position, were available for nanowire growth. During growth, cryoshield panels are cooled by flowing liquid Nitrogen to 77 K to condense residual gas-phase contaminants in the ion-pumped UHV system. Composition of the background pressure before and during growth is monitored in real time by a mass spectrometer. Catalyst deposition and nanowire growth were performed in the same chamber. Reflection high energy electron diffraction capabilities are present, though they were not used during actual nanowire growth.

1.3.2 Device Fabrication

Heavily-doped p+ Silicon wafers (resistivity $\rho \approx 0.002 - 0.005 \, \Omega\cdot\text{cm}$) were thermally oxidized using a standard dry thermal process to produce 100 nm thick SiO$_2$ on their surface, and were cut up to square target substrates $\approx 13 \, \text{mm} \times 13 \, \text{mm}$ in size. The target substrates had a grid of metallic markers deposited on them. Nanowires were transferred to the surface of the SiO$_2$ layer on the pre-patterned target substrate, by gently touching the face of the growth substrate to the SiO$_2$ surface of the target substrate. Doing this without transferring too many or too few nanowires, not breaking the nanowires into small pieces, and not compromising the insulating properties of the SiO$_2$ on the target substrate is not terribly difficult; the only prerequisite is patience. Just prior to the nanowire deposition step, substrates were cleaned at 60 °C for ten minutes in a N-Methyl-Pyrrolidinone (NMP-based) organic stripper to remove resist residue from marker deposition, followed by a standard solvent cleaning step consisting of immersion in heated (60 °C) acetone and isopropanol (IPA) for 120 seconds and de-ionized (DI)
Single-nanowire transistors were fabricated using the process summarized in Figure 1.4. Target substrates were first transferred to a commercial electron beam lithography (EBL) system with a nanometer precision laser interferometric stage (RAITH Elphy Plus), and coordinates of selected nanowires were recorded with respect to the pre-defined marker grid. A Poly-Methyl-Methacrylate (PMMA)-based resist was deposited by spin-coating and the target substrate was re-loaded into the EBL chamber for exposure of electrode openings of appropriate size, shape, and location, over nanowires. A copolymer underlayer, which provides a retrograde resist profile, was sometimes used to enhance yield for the liftoff process following metal deposition. To prevent nanowires from moving during spin-coating, and thereby invalidating the recorded coordinates, substrates were baked at 120 °C for 10 minutes immediately after nanowire transfer described in the preceding paragraph. Openings for wirebonding pads 200 × 200 micron in size, and 10 micron wide traces connecting the electrodes and pads were also exposed. Afterwards, samples were developed in methyl-isobutyl-ketone (MIBK) and IPA (1:3), producing a pattern similar to the one shown in Figure 1.4b for each selected nanowire. Descumming of patterns to lower contact resistance and improve liftoff was performed in a home-built system, with samples downstream of an Oxygen plasma generated by a commercial McCarroll cavity (Opthos Instruments) operating at 2.45 GHz supplied with Oxygen gas.
by a precision mass-flow controller (MKS Instruments), and pumped by a turbomolecular
pump. This system was built by the author with assistance from Dr. Carlos Fernandes
at the Centre for Advanced Nanotechnology (CAN).

InAs and InAs/GaAs nanowires were subjected to surface treatments described in
more detail in Chapter 2, with the goal of providing a sulfur-terminated surface (Figure
1.5c). Evaporation of metallic contacts was performed in a custom-built physical vapour
deposition system with thermal sources (MDC Vacuum model Re-vap 900) that can pro-
vide a vacuum of $\approx 10^{-7}$ mbar in about 20 minutes of pumping time. It was modified
during the course of this thesis to include a four pocket mini electron-beam evapora-
tor (Oxford Applied Instruments model EGN4) with Ni and Ti crucibles. Liftoff was
performed in acetone to realize patterns illustrated in Figure 1.4d. The liftoff process
in acetone was followed by immersion in NMP resist stripper at 60 °C for ten min-
utes to remove residual resist, acetone and IPA for another two minutes, and rinsing in
DI water. Rapid thermal annealing of Ti/Au electrical contacts to ZnO:Mn and ZnSe
nanowires, described in Chapter 2 and 7 was carried under flowing N$_2$ gas in a home-
built Quartz-tube rapid annealing furnace surrounded by six symmetrically positioned
1000 Watt tungsten-halogen bulbs (Ushio P120V1000W FSH) providing radiation heat-
ing to the sample surface under feedback control by a commercial temperature controller
(Eurotherm model 808).

An SEM image of Ti/Au electrodes fabricated on InAs nanowires is shown in Figure
1.5a. Large 200 $\times$ 200 micron pads, connected to the small electrodes by 10 micron
wide traces, are shown in the optical micrograph in Figure 1.5b. For about half of the
measurements in this thesis, substrates were mounted in custom designed copper dual-
inline-package (DIP) chip carriers with 18 pins. These chip carriers were fragile, difficult
to work with, and wirebonading the 200 $\times$ 200 micron pads on the substrates to the chip
carrier leads proved tedious and time-consuming. Later, ceramic 28-pin leadless-chip-
carriers (LCCs) were employed, since the latter are small, cheap, mechanically robust,
Figure 1.5: (a) SEM micrograph of two Ni/Au electrodes on an InAs nanowire (scale: 1 micron), (b) optical micrograph of traces and pads (scale: 200 microns), (c) wedge-bonder operation connecting on-chip pads to LCC chip-carrier pads and (d) chip carrier in cryostat chip holder.
provide good thermal anchoring even below 4 Kelvin, and were found to be suitable for wirebonding using a commercial wedge-bonder (Kulicke and Soffa model 4526). A partially wirebonded chip carrier is shown mounted in the wedge-bonder in Figure 1.5c. A wire-bonded LCC chip carrier is shown placed inside a custom built copper hip holder on the copper coldfinger of a closed-cycle He cryostat in Figure 1.5d. The LCC chip is held in place at the top by a copper plate (not shown), and at the bottom by individually spring loaded contact pins which, besides providing electrical contact, press the LCC chip against the copper top plate for thermal anchoring.

1.3.3 Electrical Measurements and Cryogenic Apparatus

Electrical measurements of ZnO:Mn and ZnSe nanowires described in Chapters 2 and 7 were carried out using an electrometer-style DC pico-ammeter and DC voltage sources, schematically illustrated in the equivalent circuit diagram in Figure 1.6a. Networks on the terminals of the transistor were simple series resistors, in the case of the source and drain, 2 kΩ resistors, and for the gate, 1 MΩ. Figure 1.6b is an equivalent circuit diagram of differential conductance and time-resolved conductance measurements of InAs nanowires in Chapter 2 and 3-6 respectively, using a low-noise current preamplifier (Ithaco Instruments model DL1211 or FEMTO model DLPCA). For the former an AC bias $dV_{DS} \cos(2\pi ft)$, attenuated by either 1/100 or 1/1000 using a resistor-divider network, was inductively coupled using a magnetically shielded signal transformer (Triad Magnetics) onto the DC source $V_{DS}$ which was also sometimes attenuated by a divider network. In both differential conductance and time-resolved electrical measurements, current signals were obtained using a low-frequency (100 kHz) lock-in (Stanford Research Instruments SR830). For the time-resolved measurements, this approach requires that the post-mixing filter of the lock-in is set to a bandwidth $1/\tau$ that passes the frequencies of interest. In this case the measurement’s output bandwidth of $1/\tau$ requires a total circuit bandwidth of $\approx f + 1/\tau$, which exceeds the circuit measurement bandwidth $1/\tau$.
required if the bias is not modulated. For this reason, a direct approach not using the
lock-in is sometimes preferable, but otherwise the two approaches are equivalent and give
the same results. Details are provided as needed in the appropriate chapters.

With the exception of the Coulomb blockade measurements discussed in Chapter 2,
low temperature measurements performed in Chapters 2–6 were performed in a closed
cycle He cryostat (Advanced Research Systems model ARS DE 202) with a temperature
range of 7 – 350 K and 12 low frequency twisted pairs (24 wires total) with bandwidth
practically limited to approximately 50 kHz by wiring capacitance, and a commercial
temperature controller (Lakeshore model 330) with two temperature sensors. Coulomb
blockade measurements were carried out in top-loading dilution refrigerator (Oxford In-
struments, Kelvinox TLM 400) with RuO$_2$ temperature sensors for the mixing chamber
and a 9 Tesla superconducting magnet, using a similar differential conductance mea-
surement setup. In this case, filtering networks at device inputs are 1 kΩ resistors in
series with PI filters (1.5 nF capacitance, Spectrum Control, Inc). Circuits were placed
inside a shielded, RF-tight electrical breakout box that also provides translation of the
vacuum electrical feedthrough (24 pin Fisher) to coaxial connectors required for electrical
instrumentation such as preamps and voltage sources, etc. The length of electrical ca-
bles carrying sensitive signals was minimized to minimize interference from stray signals
and maximize circuit bandwidth, and such cables were also double-shielded to further
minimize interference from stray signals. The grounding of instrumentation and cir-
cuits was optimized to remove loops that couple stray AC magnetic fields, permitting
measurements of current and current noise with high spectral purity. The particularly
troublesome low frequency components at 60 Hz were eliminated by troubleshooting us-
ing a digital sampling oscilloscope (Agilent model Infinium 54845a). The sample space
of this cryostat was always evacuated to a pressure of less than 10$^{-5}$ mbar for at least
10 hours prior to measurement of InAs nanowires. This was found to be necessary to
stabilize their room-temperature transistor characteristics and ensure minimal hysteresis,
Figure 1.6: (a) DC gate-source and drain-source voltage sources $V_{GS}$ and $V_{DS}$ connected to gate and source terminals of back-gated nanowire, and DC ammeter for reading current through nanowire. (b) DC gate-source and drain-source voltage sources $V_{GS}$ and $V_{DS}$, the latter superimposed with a resistor-divider attenuated AC voltage source $dV_{DS}$ by an AC transformer. A current preamplifier is attached to the opposite terminal, from which both differential current and average current can be obtained. The grounded resistor in the divider network must have a resistance much less than the sample resistance otherwise the attenuation will be sample-dependent. (c) Breakout box converting electrical wiring at vacuum feedthrough of the cryogenic apparatus to coaxial connectors, through switchable grounding resistors that can be used at any time to ground instrumentation and/or device pins.

reflecting the sensitivity of nanowire characteristics to ambient.

Wirebonded chip carriers containing single-nanowire devices can only be handled by electrically grounded individuals to avoid hazards of electro-static discharge (ESD) that in our experience can vapourize and/or melt the nanowires. Insertion of a chip into electrical test apparatus with floating pins (such as those of a voltmeter) or incorrectly zeroed input offset voltage (such as that of a feedback ammeter) can destroy nanowires, as can transient voltages/currents generated by electrical equipment that is allowed to auto-range. Therefore, toggle switches permitting independent grounding and ungrounding of instrument terminals and LCC pins, through 10 MΩ resistors, were inserted into the electrical breakout box, as depicted in Figure 1.6c. A custom LCC chip holder was assembled for the wirebonder providing a resistance of 50 kΩ to ground for each pin.
Taking these precautions, the yield of measurable nanowire transistors exceeds 80%.

1.4 Background

Some aspects of the theory of semiconductor nanostructures and their physical properties are now reviewed to furnish the discussions in subsequent chapters. First we review the basic Hamiltonian governing the behaviour of electrons in the potential constructed by the average position of ions in a solid. From here, we further discuss the Hartree and Fock terms in the mean-field treatment of electron-electron interactions used throughout the analysis presented in this thesis, and commenting on the electron-density dependence of relative contributions of kinetic energy and mutual Coulomb interactions, for electrons in solids. The remainder of the discussion is specialized to the topic of semiconductor nanostructures, and their electron transport properties. The envelope function approximation for semiconductor heterostructures is introduced, and the sub-band electronic structure of size-quantized InAs nanowires is considered taking into account conduction band non-parabolicity, relevant for Chapters 2–6. The phenomenology of semiconductor surfaces is introduced for Chapters 2–4, and finally, topics in mesoscopic electron transport of particular relevance to Chapters 2–6 are reviewed.

Although the charged constituent particles (electrons, nuclei) comprising semiconductor nanostructures obey the same dynamical equations of motion (Quantum Mechanics) as those in bulk solids, their physical properties including electrical and thermal conductance and optical absorption spectrum, among others, can differ significantly from those of bulk semiconductors as a consequence of the limited geometrical freedom of their electrons. In both the bulk solids[78] and nanostructured solids[79], the difficulty of solving for their electronic properties, even when the vibrational properties are decoupled from the electronic properties by the Born-Oppenheimer approximation, is that the inter-electronic repulsion in the non-relativistic N-electron Hamiltonian in Equation 1.1
prevents tractable solution of even the static N-electron problem (1.2)

\[
\hat{H} = \sum_i \frac{\hat{p}_i^2}{2m} + \sum_{i,j} V_{ei}(\mathbf{r}_i - \mathbf{R}_j) + \sum_{i<j} \frac{e^2}{4\pi\varepsilon_0|\mathbf{r}_i - \mathbf{r}_j|},
\]

(1.1)

\[
\hat{H}\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = E\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N),
\]

(1.2)

where \(\hat{p} = -i\hbar \nabla_r\) is position representation of the momentum operator, \(V_{ei}(\mathbf{r} - \mathbf{R})\) is the interaction between an electron at \(\mathbf{r}\) and a lattice ion with average position \(\mathbf{R}\), and the third term describes the Coulombic electron-electron interactions. The electronic wavefunction \(\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)\) has the additional constraint that it must be anti-symmetric under exchange of particle coordinates. We note for completeness that in the presence of an electromagnetic field described by a vector magnetic potential \(\mathbf{A}(\mathbf{r})\), the non-relativistic Hamiltonian is obtained by making the replacement[80]

\[
\hat{p} \rightarrow \hat{p} - e\mathbf{A}(\mathbf{r}).
\]

(1.3)

### 1.4.1 Hartree and Hartree-Fock

An approximate solution to the problem of Equations 1.1-1.2 can be obtained by assuming the total electronic wavefunction has the form of a Slater determinant of single particle wavefunctions \(\psi_i(\mathbf{r})\),

\[
\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \ldots & \psi_1(\mathbf{r}_N) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & \ldots & \psi_2(\mathbf{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\mathbf{r}_1) & \psi_N(\mathbf{r}_2) & \ldots & \psi_N(\mathbf{r}_N) \end{vmatrix},
\]

(1.4)

which is automatically antisymmetric under any permutation \(\mathbf{r}_i \leftrightarrow \mathbf{r}_j\). Assuming this form for the wavefunction and minimizing the total energy \(\langle \Psi_0 | H | \Psi_0 \rangle\) of the N-electron ground state \(\Psi_0\) via the method of Lagrange multipliers, leads to the Hartree-Fock
equations[81],
\[
\left[ -\frac{\hbar^2}{2m} \nabla^2 + \left( \sum_j V_{ei}(r - R_j) \right) + \sum_j \int \frac{d^3r'}{4\pi\epsilon_0|\mathbf{r}' - \mathbf{r}|} e^2 |\psi_j(r')|^2 \right] \psi_i(r) \\
- \sum_j \delta_{\sigma_i\sigma_j} \int d^3r' \frac{e^2 \psi_j^*(r')\psi_i(r')}{4\pi\epsilon_0|\mathbf{r}' - \mathbf{r}|} \psi_j(r) = \epsilon_i \psi_i(r),
\]
for single particle orbitals \(\psi_i(r)\). The first and second terms in the operator on the left hand side are the kinetic energy and electron-ion interaction, respectively. As a consequence of the rather constraining assumption that the ground state is a Slater determinant of single particle states, direct Coulomb interactions, represented by the third, “Hartree” term on the left hand side, take place between the orbital \(\psi_i(r)\) and the spatially averaged position of the electron density \(|\psi_j(r)|^2\) of electrons in other orbitals.

The fourth and final term on the left hand side is the “Fock” term which is a discount to the Coulomb energy of electrons of the same spin state (when \(\delta_{\sigma_i\sigma_j} = 1\), which owing to the Pauli principle, are in different orbital states and therefore have less Coulomb interaction compared to electrons of opposite spin which could be in the same orbital state. This leads to an effectively attractive interaction between electrons of like spin, and a depletion of electrons of same spin in the neighbourhood of any particular spin, the so-called “exchange hole”. The energy \(\epsilon_i\) represents energy required to add (remove) a particle to a previously unoccupied (unoccupied) orbital \(\psi_i(r)\).

These equations, termed a mean-field approach to electron-electron interactions for obvious reasons, can be solved iteratively and constitute a major simplification of the original N-electron problem. While the exchange interaction is conceptually important for magnetism, its inclusion in the Fock term gives unusual properties to the low-energy excitations at the Fermi surface[78, 79]. This is due to absence of correlation effects which are also an important in both magnetic and non-magnetic metals. Conceptually the simplest scheme to include correlations is the configuration interaction (CI) method, where the N-electron state is represented as a linear superposition of an infinite set of Slater determinants, which produces a computational problem of considerably increased
difficulty and cannot practically be applied to nanostructures or solids[79].

### 1.4.2 Interacting Electron Gas

In the Hartree-Fock approach, the Coulomb interaction is treated approximately, by construction of the electronic wavefunction as a Slater determinant. The relative importance of kinetic energy and electron-electron interactions can be interpreted within the scheme of Wigner and Seitz[82] which divides a solid into many cells each containing a single ion and $Z$ electrons. The cell is the volume enclosed by planes that bisect lines connecting an ion to its nearest neighbours. overall, and due to its electrical neutrality, each cell can be treated independently. Kinetic and potential energies are calculated in terms of a dimensionless parameter,

$$r_s = \left( \frac{3}{4\pi} \right)^{1/3} \frac{1}{n^{1/3}a_0}, \quad (1.6)$$

the ratio of the average inter-electron spacing for an electron gas with density $n_e$ and the Bohr radius $a_0$. The kinetic energy $\epsilon_{\text{kin}}$ per electron of a three dimensional free (uniform) electron gas with the same electron density is

$$\epsilon_{\text{kin}} = \frac{3}{5} \epsilon_F$$

$$= \frac{2.21}{r_s^2} \text{Ry}, \quad (1.7)$$

where Ry $\approx 13.6$ eV is the Rydberg energy. Approximating each neutral cell as a sphere of radius $r_e$, the mean-field Coulomb energy of mutual electron repulsion $\epsilon_{\text{coul}}$ for the same uniform electron gas is approximated, inside the cell, as

$$\epsilon_{\text{coul}} = \int_0^{r_e} \text{d}^3r \frac{e^2}{4\pi\epsilon_0r} n_e \times n(r)$$

$$= \frac{1.2}{r_s} \text{Ry} \quad (1.10)$$

where $n(r) = 4\pi r^3 n_e/3$ is the number of electrons enclosed in a sphere of radius $r$. Two observations are important. First, the kinetic energy scales as $r_s^{-2}$ compared with the Coulomb energy which scales as $r_s^{-1}$. Second, for densities $r_s \approx 1$ the kinetic and
Coulomb energies are comparable, and in the regime $r_s \gtrsim 1$ when Coulomb energy is similar to or greater than the kinetic energy, the Hartree and Hartree-Fock (mean-field) approach could be problematic, and correlations could become important. Incidentally, Wigner observed that for low enough electron density (high enough $r_s$), the electronic sub-system is essentially dominated by Coulomb repulsion, and the lowest energy state is an ordered array of electrons[83]. The values of $r_s$ where these transitions occur depends on the dimensionality of the system[84, 85, 86].

### 1.4.3 Semiconductor Nanostructures

An infinite crystal lattice free of imperfections has a crystal potential $V_{cr}(r)$ that is periodic in three dimensions and therefore invariant upon translation by a vector $R = ia_1 + ja_2 + ka_3$, where $i$, $j$ and $k$ are integers, and $a_i$ are the lattice basis vectors. This periodic potential opens energy gaps where there are no extended states in the crystal momentum-dependent ($k$-dependent) quasi-continuous energy spectrum of states $E(k)$. A pure semiconductor is characterized at zero temperature by a completely filled valence band with maximum energy $E_v$, separated from a completely empty conduction band minimum $E_c$ by an energy gap $E_g$[81]. In this situation, the semiconductor is an electrical insulator, since extended states in completely filled and empty bands do not electrically conduct. Optical or thermal excitation of an electron from the valence band across the bandgap $E_g$ into the conduction band also leaves behind a hole in the valence band. The effective mass $m^*$ of a carrier in a locally isotropic energy band with energy dispersion $E(k)$ is defined as $m^* = \hbar^2/(\partial^2 E(k)/\partial k^2)$. Doping, introduction of donor (acceptor) impurities into the semiconductor lattice whose ionization introduces an electron (hole) into the conduction (valence) band, is a way to controllably introduce carriers into the bands of semiconductors, thereby permitting engineering of their electrical properties.

In semiconductor nanostructures, the carriers in the conduction and/or valence bands
are confined to regions of space of the order of roughly 10 nm typically by either externally applied electric fields or discontinuities in electronic band structure at heterointerfaces, \emph{i.e.}, changes in the electron-ion potential $V_{ei}(\mathbf{r})$. This confinement leads to changes to the energy spectrum $E(k)$ including both an increase in the band gap and discretization of the crystal momentum along directions of confinement. This generates two and one-dimensional sub-bands in the energy spectrum of carriers whose motion is confined to sheets and wires, and fully discretized states for carriers confined to boxes. Despite the confinement, carriers still experience a local crystal potential that is not dramatically different from that of the bulk crystal. This is the motivation for the most popular and computationally simple theory for the electronic properties of nanostructures, the Envelope Function Approximation (EFA), which is considered next.

**Single Band Envelope Function Approximation**

In the envelope function approach (EFA), discontinuities in band structure and effective mass at hetero-interfaces and surfaces are incorporated into an applied potential $V(\mathbf{r})$ and effective mass $m^*(\mathbf{r})$ whose values take on the position dependent bulk band edges and effective masses of the materials making up the heterostructure. The single band approximation, which most readily applies to the conduction band of direct gap semiconductor nanostructures, consists of assuming that the combination of the discontinuous potentials, discontinuous masses, and any externally applied potentials, do not mix the bulk bands, and that the single particle wavefunction takes approximately the form[87]

\[
\psi(\mathbf{r}) = \sum_{\mathbf{k}} F'(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}) u_{n0}(\mathbf{r}) = u_{n0}(\mathbf{r}) F(\mathbf{r}).
\]

Here, $u_{n0}(\mathbf{r})$ is the Bloch wavefunction at the minimum of the bulk conduction band edge, and $F_n(\mathbf{r}) = \sum_{\mathbf{k}} F(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r})$ is the envelope wavefunction, which in the simplest case
of non-interacting electrons, can be shown to satisfy an effective mass equation\[87\]

\[
\left(-\frac{\hbar^2}{2} \nabla \frac{1}{m^*(\mathbf{r})} \nabla + V_a(\mathbf{r})\right) F(\mathbf{r}) = E F(\mathbf{r}). \tag{1.13}
\]

This is obviously a tremendous simplification for obtaining single electron wavefunctions \(\psi(\mathbf{r})\) and energies \(E\), since only the few occupied states in the conduction band are described, and the electron ion interaction is effectively replaced by the effective mass \(m^*\) that is determined empirically. Since it is based on effective mass, the theory has the downside that it only can be justified for electrons near band extrema and does not produce accurate electronic structure for wavevectors in the entire Brillouin Zone (BZ). In nanostructures with confined, interacting electrons, the single band envelope function approximation can still be used. This is accomplished by zeroing \(V_{ei}\) and replacing the free electron mass \(m\) with the effective mass \(m^*\) of the conduction band in Equation 1.1, and introducing \(V_a(\mathbf{r})\) to include the effects of band offsets and applied potentials\[79\], such that the ideas discussed in Sections 1.4.1 and 1.4.2 remain valid in the EFA. The stationary states can be improved by including Bloch states \(u_{nk}(\mathbf{r})\) from other bands in \(\psi(\mathbf{r})\)[87]. While empirical tight binding (ETB) and empirical pseudopotentials (EPM) produce superior electronic spectrum \(E(\mathbf{k})\) valid throughout the entire BZ\[88, 79\], it is at the expense of significantly greater computational complexity. Typically, use of EFA is justified by its conceptual and computational simplicity and good reasonable results for carriers near band extrema.

**InAs Nanowires with Cylindrical Cross-section**

Sub-band energy quantization, sub-band dispersions, and carrier densities at the onset of beginning to populate higher sub-bands of InAs nanowires are calculated using the envelope function approximation for the cylindrical hard wall potential with \(V(x, y, z) = 0\) for \(r^2 = x^2 + y^2 < R^2\) and \(V(x, y, z) \rightarrow \infty\) for \(r^2 = x^2 + y^2 > R^2\), where \(R\) is the radius of the nanowire. Band structure parameters used are those of cubic InAs due to the lack of availability of parameters for Wurtzite InAs. To overcome some limitations
of the parabolic single-band EFA, the Kane model electronic dispersion[89] is employed to include nonparabolicity in the subband quantization energies and dispersions, for a cylindrical hard wall potential. The starting point is $E(k) = E'(k) + \frac{\hbar^2 k^2}{2m_0}$ where $E'(k)$ is given by the following implicit relationship

$$E'(k)(E'(k) - E_G)(E'(k) + \Delta) = \frac{\hbar^2 k^2}{2m_0}.$$  \hfill (1.14)

Here, $E_P$ is the Kane parameter, $\Delta$ is the spin-orbit splitting, $E_G$ is the bulk band-gap, and $m_0$ is the free electron mass. Since the Kane dispersion $E(k)$ is an even function of $k$ it can be expanded in powers of $k^2$, and therefore the parabolic Hamiltonian $H_{\text{para}}(\hat{k}) = \frac{\hbar^2 k^2}{2m_e}$ and the effective Kane model Hamiltonian $H_{\text{kane}} = E(\hat{k})$ share the same eigenfunctions, which go to zero at $r = R$ due to the cylindrical hard wall potential. These eigenfunctions, which are readily determined for $H_{\text{para}}$, are $\psi_{n,l,k_z}(r,\phi,z) = \varphi_{n,l}(r,\phi) \exp(-ik_z z)$, where $\varphi_{n,l}(r,\phi) = C_{n,l} J_{|l|}(\kappa_{n,l} r) \exp(\pm il\phi)$, $J_{l}(\xi)$ is the cylindrical Bessel function of the first kind, $\xi_{n,l} = \kappa_{n,l} R$ is the $n^{th}$ root of $J_{l}(\xi)$, $k_z$ is the wavevector along the axis of the NW, and $C_{n,l} = (\sqrt{\pi R} J_{|l+1|}(\kappa_0 R))^{-1}$ is a constant of normalization. There is a different dispersion $E_{n,l}(k_z)$ for each sub-band with quantum numbers $n$ and $l$. The sub-band dispersions can be exactly evaluated by noting that $\hat{k}^2 \psi_{n,l}(r,\phi,z) = (\kappa_{n,l}^2 + k_z^2) \psi_{n,l}(r,\phi,z)$. We obtain

$$E_{n,l}(k_z) \equiv \langle \psi_{n,l,k_z} | H | \psi_{n,l,k_z} \rangle = E \left( \sqrt{\kappa_{n,l}^2 + k_z^2} \right).$$  \hfill (1.15)

A comparison between the Kane dispersion for cubic InAs with $E_G = 0.42$ eV, $\Delta = 0.39$ eV and $E_P = 22$ eV[90] and the parabolic approximation for the same set of parameters with

$$\frac{m_e}{m_0} = \left( 1 + \frac{2E_P}{3E_G} + \frac{E_P}{3(E_G + \Delta)} \right)^{-1} = 0.022$$  \hfill (1.16)

is shown in Figure 1.7a. There is a noticeable deviation of the Kane dispersion (solid line) from the simple parabolic approximation (dashed line) for energies 100 meV or more above the band edge, but the Kane dispersion is still in good agreement with
Figure 1.7: (a) Kane model dispersion for InAs (solid line) corresponding to parameters $\Delta$, $E_p$, and $E_G$ for cubic InAs (dashed line). (b) Dispersions for first three sub-bands of $d = 30$ nm nanowire with hard-wall confinement energy based on bulk Kane dispersion (solid) and parabolic approximation (dashed) lines.

The energy dispersion of the first three sub-bands is plotted for $d = 30$ nm InAs nanowire in Figure 1.7b alongside the dispersions predicted for parabolic bands (dashed line). Low energy carriers in the first sub-band are well represented by the parabolic approximation, but nonparabolicity is noticeably more important for the second and third sub-bands.

The one dimensional carrier density at the onset of filling the second and third sub-bands, denoted $n_{0,1}$ and $n_{0,2}$, are obtained under the conditions $E_F = E_{0,1}(0)$ and $E_F = E_{0,2}(0)$, respectively. Evaluation of $n_{0,1}$ and $n_{0,2}$ is easily carried out in reciprocal space. When a sub-band $i$ is degenerate, it contributes carrier density of $n_i \approx D_i (2/\pi) k_{i,F}$, where $k_{i,F}$ and $D_i$ are the Fermi wavevector and orbital degeneracy of the $i^{th}$ sub-band,
Table 1.1: Calculated sub-band edges $E_{0,0}$, $E_{0,1}$, $E_{0,2}$, and carrier densities $n_{0,1}$ and $n_{0,2}$ at onset of filling the second and third sub-bands for 30 and 60 nm diameter NWs with cylindrical hard wall potential using the Kane dispersion. Sub-band edges calculated using the parabolic dispersion are in parentheses.

<table>
<thead>
<tr>
<th>Diameter (nm)</th>
<th>$E_{0,0}(k_z = 0)$ (meV)</th>
<th>$E_{0,1}(k_z = 0)$ (meV)</th>
<th>$E_{0,2}(k_z = 0)$ (meV)</th>
<th>$n_{0,1}$ (10$^6$ cm$^{-1}$)</th>
<th>$n_{0,2}$ (10$^6$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 (NW2)</td>
<td>41 (45)</td>
<td>94 (113)</td>
<td>155 (204)</td>
<td>1.3</td>
<td>4.8</td>
</tr>
<tr>
<td>60 (NW3)</td>
<td>11 (12)</td>
<td>27 (29)</td>
<td>46 (52)</td>
<td>0.6</td>
<td>2.4</td>
</tr>
</tbody>
</table>

To evaluate the sum, we need $k_{i,F}$ for each occupied sub-band and sub-band orbital degeneracies $D_i$ which for the first three bands are $D_{0,0} = 1$, $D_{0,1} = 2$ and $D_{0,2} = 2$. From Figure 1.7b is evident that we can re-write the condition $E_F = E_{0,1}(0)$ as $E_{0,0}(k_{0,0,F}) = E_{0,1}(0)$. Using the previous result $E_{n,l}(k_z) = E \left( \sqrt{\kappa_{n,l}^2 + k_z^2} \right)$ we obtain $E \left( \sqrt{\kappa_{0,0}^2 + k_{0,0,F}^2} \right) = E \left( \sqrt{\kappa_{0,1}^2} \right)$, i.e. $k_{0,0,F}^2 = \kappa_{0,1}^2 - \kappa_{0,0}^2$. Similarly the density $n_{0,2}$ is found by setting $E_F = E_{0,2}(k_z = 0)$ which gives $k_{0,0,F}^2 = \kappa_{0,2}^2 - \kappa_{0,0}^2$ and $k_{0,1,F}^2 = \kappa_{0,2}^2 - \kappa_{0,1}^2$. Since the density of states of a one dimensional sub-band is constant in reciprocal space, the carrier density at the onset of filling of the second and third sub-bands does not depend on the details of the dispersion, only the radius of the NW through the transverse wavevectors $\kappa_i$ of the different sub-bands. Values for $n_{0,1}$ and $n_{0,2}$ are given in Table 1.1, along with minimum and maximum carrier densities estimated from $n = C(V_{GS} - V_T)/(eL)$ in the range of gate voltages in the experiments.

The EFA-based approach for describing electronic sub-band structure will be of use in Chapter 2 which describes InAs semiconductor nanowires in a regime where electronic sub-band effects are important. A more detailed model incorporating self-consistent electron-electron interactions at the Hartree level will be employed for theoretical de-
scription of the variation of surface potential with gate voltage in both Chapters 4 and 5.

1.4.4 Semiconductor Surface and Interfaces

Localized, midgap states may be present on clean semiconductor surfaces, oxidized semiconductor surfaces and heterointerfaces, alike. The simplest effect of surface states in bulk semiconductors is the thermal equilibrium depletion of carriers near the surface, and generation of the associated surface electric field and surface band-bending[91]. The width of the surface depletion layer of an n-type semiconductor is approximated by the simple relation

\[ z_{\text{dep}} = \frac{|Q_{\text{sc}}|}{eN_{d(a)}} \]  

(1.18)

where \( Q_{\text{sc}} \) is the surface charge density per unit area and \( N_{d(a)} \) is the ionized donor (acceptor) density in the bulk. The former satisfies

\[ Q_{\text{sc}} = e \int \text{d}E \left[ D_{sd}(E)(1 - f_{0d}(E - E_F)) - D_{sa}(E)f_{0a}(E - E_F) \right] , \]  

(1.19)

where \( D_{sd}(E) \) and \( D_{sa}(E) \) are the donor and acceptor surface state densities, and \( f_{0d}(E - E_F) \) and \( f_{0a}(E - E_F) \) are the donor and acceptor distribution functions, respectively[91]. These surface state distributions are approximately characterized by a surface charge neutrality energy \( E_{\text{CNL}} \) in the midgap, above which there are predominantly acceptors and below which their are predominantly donors[91]. When \( E_F = E_{\text{CNL}} \) the surface is overall neutral, but for \( E_{\text{CNL}} \) in the midgap anywhere but \( E_F \), the surface will be depleted of the majority carrier. One notable exception is the clean InAs surface where \( E_{\text{CNL}} \) is above the conduction band edge, creating a “native” electron accumulation layer[92].

These surface and interface states modify the electronic properties of bulk semiconductors near their surfaces. For example, charged surface states generally reduce carrier mobility near the surface, and surface states also usually act as efficient recombination centres that reduce radiative efficiency and excess carrier lifetime. In steady state, ef-
icient recombination at the surface of a semiconductor leads to a diffusion current of excess carriers to the surface. This diffusion current can be characterized by the effective surface velocity $s^*$,

$$s^* = U_s/\Delta p^*,$$

(1.20)

where $U_s$ is the steady-state recombination rate per unit area and $\Delta p^*$ is the steady-state excess hole density at the inner edge of the depletion region[91]. Surface states have additional implications for carrier transport in nanowires. Localized charges at semiconductor surfaces can increase scattering of carriers that are nearby enough to the surface to experience the associated Coulomb potential. This leads to the definition of surface mobility for electrons and holes respectively, are generally suppressed compared with bulk mobilities.

These states also generally degrade the performance of semiconductor devices. Both the on and off-state performance of field effect transistors that operate by controlling the electron density near a semiconductor/oxide interface are degraded by interface states. Not only do they reduce carrier mobility, but they also screen the applied field of the gate[93]. Reduction of carrier lifetime due to surface and interface states reduces excess carrier lifetime and can reduce brightness of light-emitting diodes and increase threshold current for diode lasers. The influence of surface states on device properties is generally more pronounced as device size shrinks, making them a critical issue in semiconductor nanostructures. Electronic passivation, a special terminal of dangling bonds at the semiconductor surface that modifies the density of donor and/or acceptor-like surface states $D_{sd}(E)$ and $D_{sa}(E)$, can be used to control or reduce surface depletion, surface recombination, and improve surface and field effect mobility.

Effects related to these states that are expressed in measurements presented Chapters 2–5 of this thesis are manifold. First, the distribution of donor-like surface states expected to be present above the conduction band edge in InAs nanowires appears to provide a significant fraction of the non-thermally-activated carriers observed in measure-
ments. Second and third, measured non-ideal subthreshold characteristics and variation of surface potential with gate voltage in Chapter 4 are consistent with a donor surface state of density \( \approx 10^{12} \text{cm}^2\text{eV}^{-1} \) \textit{in electrical communication with the conducting electrons}. Fourth, random telegraph signals which are used as a tool to study various phenomena in this thesis arise due to capture and emission from electron trapping surface states. We study the microscopic mechanism (multi-phonon emission) and dynamics of capture and emission in Chapter 4, Section 4.5. Finally, it is highly likely that the long-lived selective traps that provide high photocurrent spectral responsivity and gain are likely, though not conclusively proven to be, surface states.

### 1.4.5 Mesoscopic Electron Transport in Narrow Wires

Mesoscopic systems are systems with size and properties intermediate between those of bulk crystals and molecules. When some characteristic length or related energy scale of a mesoscopic system approaches a critical value, the physical properties of the mesoscopic system differ from those of the corresponding bulk system. Length scales related to electronic structure and carrier transport in mesoscopic wires with length \( L \) and diameter \( d \) are summarized in Table 1.2. When the diameter \( d \) inside which both carriers are confined falls below either the Bohr exciton radius \( a_B \), the bound state of an electron (hole) will feel addition confinement beyond that which is generated by its oppositely charged particle, leading to a modification of absorption and emission spectrum. When the diameter falls below that of the Fermi wavelength \( \lambda_F \), electronic structure is expected to be quantized as described in Section 1.4.3. When diameter of a low dimensional system falls below the electronic screening length, the screening phenomena are weakened. Length scales related to scattering play an important role in carrier transport. When carriers are accelerated by an applied field the net momentum (and also kinetic energy) of the collection of carriers increase. Scattering events with \( e.g. \), impurities or phonons randomize momentum and limit the electronic mean free path \( L_{MFP} \), retarding
### Table 1.2: Some length and energy scales of interest in mesoscopic electron transport.

<table>
<thead>
<tr>
<th>Scale</th>
<th>Symbol</th>
<th>Ineq.</th>
<th>Critical Length Scale</th>
<th>Symbol</th>
<th>Physical Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter</td>
<td>$d$</td>
<td>$&lt;$</td>
<td>Bohr-Exciton radius</td>
<td>$a_B$</td>
<td>Confined exciton</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$&lt;$ Fermi wavelength</td>
<td>$\lambda_F$</td>
<td>Sub-band quantization</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$&lt;$ Screening length</td>
<td>$\lambda_S$</td>
<td>Weakened screening</td>
</tr>
<tr>
<td>Length</td>
<td>$L$</td>
<td>$&lt;$</td>
<td>Mean free path</td>
<td>$L_{MF}$</td>
<td>Ballistic transport</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$&lt;$ Coherence length</td>
<td>$L_\phi$</td>
<td>Phase coherent transport</td>
</tr>
<tr>
<td>Thermal Energy</td>
<td>$k_B T$</td>
<td>$&lt;$</td>
<td>Charging Energy</td>
<td>$E_C$</td>
<td>Coulomb blockade</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$&lt;$ Quantization Energy</td>
<td>$\Delta E$</td>
<td>Sub-band quantization</td>
</tr>
</tbody>
</table>

The flow of carriers. In electronic quantized one dimensional systems, the phase space of final states available for scattering are fewer compared with bulk systems, which modifies momentum relaxation and therefore, carrier transport, compared with bulk systems. When the electronic mean free path $L_{MF}$ exceeds the wire length $L$, the so-called ballistic transport is obtained, and conductance is quantized in units $2e^2/h$ per occupied sub-band. Yet another important transport length scale is the distance $L_\phi$ that carriers travel before their quantum mechanical phase is randomized by interaction with their environment. When $L_\phi \gtrsim L$, electron interference phenomena such as weak localization, Aharonov-Bohm effect, and universal conductance fluctuations begin to manifest themselves in the conductance\cite{94}. Ohms law (classical behaviour) is obtained when three conditions are met, $L_{MF} \ll L$, $L_\phi \ll L$, and $\lambda_F \ll d$\cite{95}. The charging energy scale $E_C$ will also be important as the length of the structure shrinks to $\approx 100$ nm or smaller, and the phenomena of Coulomb blockade and Kondo effect can be observed when tunneling resistances to the structure satisfy $R_T \gg e^2/h$ and $R_T \lesssim e^2/h$, respectively\cite{94}. The semiconductor nanowires studied in this thesis have dimensions/energy scales satisfying several of the conditions listed in Table 1.2, and in this case, signatures of non-classical
behaviour are obtained. Beyond this, however, one of the aims of this thesis is to obtain and study structures whose size is small enough that these effects can be of practical use in devices that operate as close as possible to room temperature.

**Landauer Formula and Quantized Conductance**

When carriers are confined on a length scale similar to their Fermi wavelength, their electronic structure is quantized into electronic sub-bands as illustrated schematically in Figure 1.8a. In this situation, elastic (energy-conserving) scattering of carriers in a single sub-band is related to the linear conductance using concepts introduced by Landauer. In the simplest picture the current through a two-terminal conductor with only a single sub-band occupied is the sum of right and left-moving currents from the left and right reservoirs with chemical potentials \( \mu_L \) and \( \mu_R \) and carrier distributions \( f_L(k) \) and \( f_R(k) \),

\[
I = \frac{e}{L} \left( \sum_{k>0,\sigma} T(k)v(k)f_L(k) - \sum_{k<0,\sigma} T(k)v(k)f_R(k) \right),
\]

(1.21)

where \( T(k) \) is the transmission probability for a wavevector \( k \) incident on a scatterer, and \( v(k) \) is the velocity of the carrier. Assuming spin degeneracy, the sum over one-dimensional wavevectors \( k \) and spin \( \sigma \) is converted to an integral over energies by \( \sum_{k,\sigma} \). The carrier velocity is given by \( v(k) = 1/\hbar(\partial E/\partial k) \), giving

\[
I = \frac{2e}{\hbar} \left( \int dE T(E)(f_L(E) - f_R(E)) \right).
\]

(1.22)

In the linear conductance regime where \( eV = \mu_R - \mu_L \ll k_B T \), the conductance \( G = I/V \) follows from the Taylor expansion \( f_L(E) - f_R(E) \approx (\mu_L - \mu_R)\partial f / \partial E \),

\[
G = \frac{2e^2}{\hbar} \int dE T(E) \left( -\frac{\partial f}{\partial E} \right),
\]

(1.23)

which is readily adapted to the case of multiple electronic sub-bands by introducing transmission probabilities \( T_{ij}(E) \) for scattering of carriers of energy \( E \) in sub-band \( j \) from sub-band \( i \),

\[
G = \frac{2e^2}{\hbar} \sum_i \int dE \left( \sum_j T_{ij}(E) \right) \left( -\frac{\partial f}{\partial E} \right).
\]

(1.24)
When the transmission probability of $M$ modes are unity, the conductance is still a finite value $\frac{2e^2}{h} M$. This minimum resistance was interpreted by Imry\cite{97} as a contact resistance to the one dimensional conductor arising from the interface between the one-dimensional channel and the reservoirs, where current is carried by a relatively large number of modes. This theory was generalized to the case of applied magnetic fields and multiterminal devices by Büttiker\cite{98}.

The most common one-dimensional system where full transmission $T_{ij} = \delta_{ij}$ is observed is the quantum point contact (QPC) formed by a constriction of a remotely doped two dimensional electron gas in a AlGaAs-GaAs-AlGaAs structure. In this case, a saddle potential is formed and the number of modes that can be transmitted through the constriction is controlled by gate voltages $V_{G1}$ and $V_{G2}$ in Figure 1.8c. Metallic carbon nanotubes with conductance approaching the value $4e^2/h$ for full transmission through their (twice orbitally degenerate) semi-metallic dispersion have been observed by several authors, as summarized in reference\cite{25}. The connection between carrier scattering by a single Coulomb impurity in an InAs semiconductor nanowire to the effective single Coulomb impurity “resistance” experimentally inferred from a random telegraph signal.
and calculated as described above from microscopic theory of Coulomb impurity screening. The strong carrier scattering observed in experiments depend strongly on nanowire diameter and dielectric confinement. Similar ideas will also be employed in Chapter 2.

**Coulomb Blockade and Quantum Dots**

When a finite-size island is coupled weakly by a tunneling barrier to a comparatively large reservoirs of electrons, such that there is a well defined number of electrons on the island, charge transfer from the reservoir to the island can only take place if electrons in the reservoir have sufficient energy to overcome the charging energy $E_C$ of the island. When there are two such tunneling barriers connected to the island and the charging energy $E_C$, which can be several tens of meV for nanometer scale islands, exceeds greatly the thermal broadening $k_BT$ of the carrier distributions of the two reservoirs, the current-voltage characteristics from one reservoir to another are qualitatively modified from the description of the previous section by the Coulomb interaction. The system is in a state of Coulomb blockade where no current can flows from one reservoir when they are biased such that the electrochemical potential difference between them is less than $k_BT$.

In semiconductor nanowires, electrons/holes are automatically confined along two directions to a length scale of nanometers. Coulomb blockade can be obtained by introducing at least two barriers along the length of the nanowire, which can be created either by local gates, or by heterostructures such as those shown in Figure 1.1d and e. Quite a few aspects of the transport behaviour can understood within the constant interaction model, which was reviewed for semiconductor quantum dots in reference [99]. The situation is illustrated in Figure 1.9a, where a central island is capacitively coupled to a gate electrode by capacitance $C_G$, and coupled by tunneling barriers of resistance $R_{R(L)}$ and capacitance $C_{R(L)}$ to the right (left) lead. The ground state energy $U(N)$ of the unbiased ($\mu_L = \mu_R$) system of $N$ electrons is assumed to be the sum of the electrostatic energy of the gate capacitance $C_G$, left ($C_L$) and right ($C_R$) tunneling capacitances, and
Figure 1.9: (a) Schematic diagram of single electron transistor source, drain, gate and island with tunneling resistors and capacitors on source and drain terminals, and gate capacitor, (b) elastic electron tunneling onto island with $n$ electrons from left lead, (c) situation with $n+1$ electrons on island, and (d) elastic electron tunneling from island to the right lead, and (e) charge stability diagram of quantum dot in Coulomb blockade regime.
the single-particle energies $E_i$ of electrons on the island,

$$U(N) = \left[ eN - C_G V_{GS} \right]^2 / 2C_\Sigma + \sum E_i,$$  \hspace{1cm} (1.25)

where $C_\Sigma = C_L + C_R + C_G$ is the total capacitance. The chemical potential for this $N$-electron ground state is defined as the difference between the $N$ and $N-1$ electron ground state

$$\mu_{\text{dot}}(N) = U(N) - U(N-1) = E_C(N - 1/2) - e(C_G/C_\Sigma)V_{GS} + E_N$$  \hspace{1cm} (1.26)

where $E_C = e^2/C_\Sigma$ is the charging energy. When the electron number in the QD is fixed, a change in gate voltage $\Delta V_{GS}$ induces a change in chemical potential of $\Delta \mu = -e(C_G/C_\Sigma)\Delta V_{GS}$, where $\alpha = C_G/C_\Sigma$ is often called the lever arm in the literature. In the linear regime of bias when $-eV = \mu_L - \mu_R \ll k_B T$, $\mu_{\text{dot}}(N) - \mu_{\text{dot}}(N-1)$, current flows by sequential tunneling when $\mu_{\text{dot}}(N)$ lines up with the chemical potential of the leads, as shown in Figure 1.9b-d. The addition energy $\Delta \mu_{\text{dot}}(N)$ is defined as the additional energy required to fill the $N$ electron ground state, compared to the $N-1$ electron ground state, and is given by

$$\Delta \mu_{\text{dot}}(N) = \mu_{\text{dot}}(N) - \mu_{\text{dot}}(N-1) = E_C + E_N - E_{N-1}$$  \hspace{1cm} (1.27)

In the linear regime of conductance satisfying $eV = \mu_R - \mu_L \ll k_B T$, $G = I/V$ oscillates between zero and a finite value as the gate voltage is varied, corresponding to the situation when a level in the quantum dot is not or is lined up with the leads, respectively. The relationship between the addition energy and the gate voltage of the N$^{\text{th}}$ and (N-1)$^{\text{th}}$ peaks in the linear conductance is given by $\Delta \mu(N) = e\alpha (V_G^N - V_G^{N-1})$.

When the bias voltage applied to the reservoirs is increased, the conditions for degeneracy and current flow by sequential tunneling is modified. The differential conductance $G = \partial I/\partial V$ is appreciable along lines of degeneracy between the Fermi energy of the source lead and quantum dot, in the dependence of this quantity on $V$ and $V_{GS}$. Lines of nonzero differential conductance due to sequential tunneling are shown as solid and
dashed lines in the charge stability diagram of Figure 1.9e. Regions in the schematic stability diagram marked 0,1,2,..., bounded by diamond shapes, denote bias conditions where the number of electrons on the quantum dot is fixed. The solid top border line of an N-electron diamond (labeled ■) is the bias condition where the chemical potential of the left (right) reservoir lines up with the \( N + 1 \) electron ground state, when \( V > 0 \) (\( V < 0 \)). Increasing the bias slightly, the chemical potential of the left (right) reservoir lines up with an excited \( N + 1 \) electron state, when \( V < 0 \) (\( V < 0 \)). The bottom border (labeled □) is the bias condition when the \( N \) electron ground state is emptied by a lead.

Current at the onset of sequential tunneling through an \( N \)-electron ground state with energy \( E_{N}^{0} \), represented by the solid lines in Figure 1.9e, can also be supplemented by sequential tunneling (the dashed line of non-zero differential conductance) through the \( N \)-electron excited state with energy \( E_{N}^{1} \) by a bias increase that brings this level in line with the chemical potential of the source lead of electrons.

InAs nanowires cooled below 1 K in Chapter 2 exhibit Coulomb blockade, and the theory presented herein cements the interpretation that the Coulomb blockade oscillations occur due to tunneling from the leads into the nanowire, and that the entire 1 micron length of the nanowire acts as a Coulomb island. In contrast, another study in reference [100] demonstrated that presence of stacking faults in InAs nanowires produce multiple tunnel junctions (MTJ), that in nanowires manifest multiple island Coulomb blockade phenomena. Finally, the nanowire field-effect-transistor based electrometer proposed in Chapter 6 is contrasted with traditional single-electron-transistor based electrometers whose principle of operation is that of Coulomb blockade. With a sound theoretical backdrop, we now turn to the main results of the thesis organized in Chapters 2–6.
Chapter 2

Carrier Transport in InAs and InAs/GaAs Core/Shell Heterostructure Nanowires

2.1 Introduction

Bolstered by recent improvements in control over InAs nanowire growth by the VLS method[32, 101], the small bandgap, low electronic effective mass \( m_e = 0.023m_0 \)[49], long electronic mean free path, and high carrier saturation velocity of InAs relative to other semiconductors make InAs nanowires attractive candidates for high speed nano-electronic and nano-spintronic devices and infrared nano-opto-electronic devices. Relative to GaAs, InN and InP, InAs is also an interesting material for studies of charge and spin transport in nanowires due to its relatively large sub-band quantization energies and stronger spin-orbit coupling. Such potential is enhanced by the potential for axial and radial heteroepitaxy during VLS nanowire growth, and the associated opportunities for band-structure engineering. Making this even more interesting is the fact that equilibrium strain analysis predicts that critical thickness for (dislocation-free) axial or radial
Chapter 2. Carrier Transport in InAs Nanowires

heteroepitaxy is enhanced in semiconductor nanowires due to their small size\cite{54, 55}, since both materials in the heterostructure can deform to share the interfacial strain. The material system InAs/GaAs, which forms a type-I heterointerface confining both electrons and holes in the InAs\cite{90}, is a very interesting one for exploring the limits of coherent epitaxy and strain in nanowires due to the large lattice mismatch $f = \Delta a/a_{\text{GaAs}} \approx 7.1\%$\cite{49}. During planar growth of InAs on GaAs, the large lattice mismatch results in island formation after only two monolayers of InAs deposition \cite{51}.

In this chapter we study the structure and electronic transport properties of InAs nanowires prepared by Au-catalyzed MBE-VLS growth at different temperatures between 10 K and 300 K, and compare their room temperature transport properties to InAs/GaAs core/shell nanowires grown by the same method. InAs nanowires with length $L = 1000$ nm between electrodes are found to have field effect mobility $\mu_{\text{FE}} = 2000 - 4000$ cm$^2$V$^{-1}$s$^{-1}$ at room temperature, increasing to $\mu_{\text{FE}} = 10000 - 20000$ cm$^2$V$^{-1}$s$^{-1}$ at 30 K, and room temperature free electron density of $\approx 10^{17}$ cm$^{-3}$. These values are similar to the highest reported field effect mobility $\approx 4000$ cm$^2$V$^{-1}$s$^{-1}$\cite{102} in single-wall carbon nanotube field-effect transistors with comparable channel length ($L \approx 3$ \mu m). Step-like signatures of sub-band quantization were observed in the gate-voltage dependence of differential conductance measurements of $\approx 30$ nm diameter InAs nanowires, at temperatures as high as 77 K. The gate-voltage spacing of the plateaus is consistent with predicted quantization energies predicted in Chapter 1, and shows that it is possible to get effects of clean carrier transport even in relatively long InAs nanowires. Below 4 K, the gate-voltage dependence of the zero bias differential conductance of InAs nanowires with $L = 1000$ nm between contacts exhibit Coulomb oscillations. The stability diagram, revealed by mapping of the gate and drain-bias dependence of differential conductance, confirms single-island Coulomb blockade demonstrating the excellent structural and electronic homogeneity of InAs nanowires.

Microstructural analysis by TEM revealed significant strain relaxation by dislocations
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in InAs/GaAs core/shell nanowires with InAs core radii 11 – 26 nm and shell thickness > 2.5 nm. Axial strain relaxation varies from 54 ± 5 % to full (100 %) relaxation, and is smallest in nanowires with the smallest diameter core. While the thinnest nanowires had undetectably small radial relaxation, the larger nanowires had almost complete radial relaxation. A novel process for depositing electrical contacts on the InAs core of InAs/GaAs core/shell nanowires was developed, based on chemical and site selective etching of GaAs shells underneath the metal electrode. Field-effect-mobility of 500 – 1000 cm²/V.s is extracted for core/shell InAs/GaAs nanowires, suppressed compared with bare InAs nanowires.

2.2 Nanowire Growth and Structural Characterization

InAs and InAs/GaAs Core/Shell nanowires were grown by Au-catalyzed molecular beam epitaxy (MBE) with solid sources, on GaAs (100) substrates. Once inside the MBE growth chamber, substrates were baked at 590 °C for 30 minutes to desorb the native oxide, and an undoped GaAs buffer layer was grown at a temperature of 480 °C. Gold catalysts were prepared by deposition of an Au film at 580 °C with an average thickness of 0.5 nm, which, upon annealing for 5 minutes, forms a droplet structure on the GaAs buffer layer. InAs nanowires were grown via the Au catalyst by MBE deposition of InAs at 410 °C. A typical InAs nanowire grown by 200 nm equivalent deposition is shown in Figure 2.1a. Growth of InAs/GaAs core/shell nanowires is accomplished by the same steps with an additional deposition of 10-20 nm equivalent planar thickness of GaAs, at the same temperature. Nanowires with clear collar shape near the tip are obtained, as shown in Figure 2.1b. Post-growth elemental analysis by EDXS reveals that both axial and radial growth occur during GaAs deposition, suggesting that the diffusion length of Ga adatoms on the InAs nanowire surface is similar to the 2-3 micron length
Figure 2.1: SEM image of (a) InAs nanowire grown by InAs deposition with 200 nm equivalent planar thickness, (b) InAs/GaAs nanowire grown by sequential deposition of InAs (100 nm) and GaAs (15 nm).

Figure 2.2: (a) STEM image of InAs/GaAs Core/Shell nanowire and (b) EDXS element mapping for Indium core (solid points) and Gallium shell (open points) and lines depicting least squares fit to model described in main text.

of the InAs core at the indicated growth conditions[103]. These InAs/GaAs core/shell heterostructures and others grown by solid source MBE [104, 105, 106] contrast CBE growth of pure axial nanowires heterostructure with InAs and GaAs, as demonstrated in e.g. reference[107] using organometallic group III and group V sources carried at 465 °C.

Both InAs and InAs/GaAs core/shell nanowires were transferred onto carbon coated Cu grids for HRTEM and spatially resolved EDXS in a scanning TEM. Elemental mapping for an InAs/GaAs core/shell nanowire grown by sequential deposition of InAs (130 nm) and GaAs (20 nm) at 410 °C, along the line depicted in the dark field TEM of Figure 2.2a, is shown in Figure 2.2b. The spatial dependence of the x-ray counts for Gallium
and Indium were fit to the following theoretical expressions, obtained by assuming spatially uniform but not necessarily equal x-ray generation rates from Ga and In atoms in concentric outer GaAs and inner InAs lattices with radii \( R_G \) and \( R_I \), respectively.

\[
C_G = 2\alpha \sqrt{R_G^2 - (x - x_G)^2} - 2\alpha_G \sqrt{R_I^2 - (x - x_I)^2} \tag{2.1}
\]

and

\[
C_I = 2\alpha \sqrt{R_I^2 - (x - x_I)^2} \tag{2.2}
\]

Results of the curve fitting yield \( R_G = 27.0 \pm 0.2 \) nm, \( R_I = 19.9 \pm 0.2 \) nm, and \( x_G - x_I = 0.1 \pm 0.3 \) nm, the projected difference in the centre of mass of the InAs core and GaAs shell. The total thickness of the GaAs shell is \( R_G - R_I = 7.0 \pm 0.3 \) nm, typical for nanowires grown by the indicated MBE deposition sequence. These expressions neglect both the possibility of intermixing or alloying that would grade the InAs/GaAs heterojunction, and the finite spatial broadening \( \sim 1 \) nm of the 200 kV electron beam in the TEM.

### 2.3 Crystal Structure of InAs and InAs/GaAs Nanowires

The crystal structure of InAs and InAs/GaAs Core/Shell nanowires grown as described in Section 2.2 were characterized by transmission electron microscopy (TEM). The radial boundary between InAs material and vacuum is shown in the lattice-fringe HRTEM image in Figure 2.3a. A lower magnification bright field TEM image of the same InAs nanowire is shown in the inset Figure 2.3a. The dark region where the InAs nanowire terminates at the bottom-left of the inset is the Au catalyst tip, and there is a region within \( \approx 100 - 200 \) nm of the tip where some extended defects can be seen. Beside these defects near the tip, extended defects are absent from the bare InAs nanowires. Diffraction patterns such as the one shown in Figure 2.3a were examined to determine the crystallinity of the InAs nanowires which were found to grow predominantly in the Wurtzite crystal structure with [0001] growth direction from the GaAs [001] substrates,
consistent with the literature\cite{108}. In contrast, InAs crystals like most III-V materials adopt cubic Zincblende structure in bulk form\cite{109}.

Figure 2.4a is a bright field TEM image of a WZ [0001] oriented InAs/GaAs nanowire, viewed perpendicular to a [21\bar{1}0] direction. The total nanowire diameter is $71 \pm 2$ nm with InAs core radius 25 nm visible from Moiré fringe diffraction contrast with period $6.2 \pm 0.5$ nm. The GaAs shell appears thicker on the concave side of the nanowire. Tilting the nanowire away from the [21\bar{1}0], strong diffraction from (0002) planes is obtained, as shown in Figure 2.4b. The matching dark field (0002) TEM image is shown in Figure 2.4c. The positions of the bright inner and outer most spots in Figure 2.4b correspond to diffraction from planes of the InAs and GaAs respectively, and are assigned distances $r_{\text{InAs}}^{hklj}$ and $r_{\text{GaAs}}^{hklj}$ respectively, from the centre spot.

A dark field (0110) TEM image and diffraction pattern for a [21\bar{1}0] zone axis direction are shown in Figure 2.4c and 2.4d, respectively. The diffraction pattern reveals streaks parallel to the [0002] direction, consistent with dislocations that are visible in the shell and faintly visible in the core region. A double-spot in the diffraction pattern for plane $(hklj)$ confirmed by Moiré fringes in the dark field TEM image for the same plane indicates relaxation of strain near the interface between the InAs and GaAs. The amount of strain relaxation for planes $(hklj)$ can be quantified using

$$R_{hklj} = 2 \left( \frac{r_{\text{InAs}}^{hklj} - r_{\text{GaAs}}^{hklj}}{r_{\text{InAs}}^{hklj} + r_{\text{GaAs}}^{hklj}} \right) / 0.072 \quad (2.3)$$

where $R = 100\%$ indicates total relaxation of strain, and $0\%$ indicates the opposite condition, complete absence of strain relaxation such that the interplanar spacing in the core and shell match exactly.

The axial relaxation $R_{0002}$ and radial relaxation $R_{01\bar{1}0}$ were obtained from analysis of diffraction patterns for a collection of several InAs/GaAs core/shell nanowires with core radii $R_{\text{InAs}} = 11 - 26$ nm and shell thicknesses $2.5 - 15$ nm. The average strain relaxation $R_{hklj}$ for planes $(hklj)$ is given by Equation 2.3, the ratio of the difference in their spot spaces $r_{hklj}$ to their average spot position, normalized to the maximum value, which for
Figure 2.3: (a) Lattice fringe HRTEM image of Wurtzite InAs nanowire (scale: 10 nm) and inset, Bright field TEM image of Au tip region for the same InAs nanowire (scale: 20 nm) (b) Diffraction pattern taken at lower magnification along [2110] pole. Arrow corresponds axial vector of nanowire, which is identified as [0002] crystal direction.
Figure 2.4: (a) Low magnification bright field TEM of curved InAs/GaAs Core/Shell nanowire viewed close to a [21\bar{1}0] direction (b) Selected area diffraction pattern tilted away from [21\bar{1}0] pole (c) Dark field (0002) image (d) Dark field (01\bar{1}0) image (e) Selected area diffraction pattern when looking down [21\bar{1}0] pole.
Figure 2.5: (a) Plot of axial and radial strain relaxation (closed and open circles, respectively) as a function of ratio of shell thickness to core radius of individual InAs/GaAs Core/Shell nanowires. (b) Dark field TEM of thinner shell side of an InAs/GaAs nanowire in (01\(\overline{1}0\)) and (c) (0002) diffraction conditions.

InAs-GaAs is 0.072.

Axial relaxation, plotted as filled data points in Figure 2.5a, is observed in wires with even the smallest shell to core ratio. Radial relaxation, plotted on the same set of axes as open data points, was absent in some of the wires with smaller shell thickness (and hence, smaller shell thickness to core radius ratio). Dislocations, which are known to relax strain at mismatched heterointerfaces, were directly imaged at the heterointerface between InAs and GaAs in dark field (01\(\overline{1}0\)) diffraction contrast in Figure 2.5b and for (0002) diffraction contrast in Figure 2.5c. The smallest shell thickness investigated (1.5 and 2.5 nm on either side) had an axial relaxation of 58 \%, still quite appreciable, and edge dislocations with an average spacing of 8 nm were observed. Splitting in the the radial diffraction spots was not visible indicating no detectable radial relaxation.
Figure 2.6: Schematic of process starting with (a) patterned resist, (b) etching in NH$_4$OH:H$_2$O$_2$:H$_2$O (1:1:100) and either (c) resist removal, or (d) deposition of metallic electrodes and liftoff.

2.4 Field-Effect Transistor Fabrication

Nanowires on parent GaAs (001) substrates, grown as described in Section 2.2, were transferred to p+ degenerately doped Si “host” substrates coated with 100 nm of SiO$_2$ by mechanically touching the host and parent substrates together. Coordinates of selected nanowires were measured relative to pre-defined markers on the host substrate, using an electron beam lithography system. After spin-coating a Copolymer/PMMA resist mask on the host substrates, two to four electrode patterns per nanowire with length (along direction parallel to wire) of $L_C \approx 500$ nm, spaced typically $L = 1000$ nm apart, were written by electron beam lithography and developed.

Substrates with InAs nanowires were dipped in a solution of 0.3 % by wt ammonium polysulfide in deionized water for ten minutes to remove native oxide of InAs nanowires and terminate their surface with Sulfur atoms[110]. This process was found to be essential for formation of low resistance metallic contacts to the InAs nanowires. After the treatment, samples were briefly rinsed in DI water, blow dried, and immediately loaded into a vacuum chamber for deposition of Ni (10 nm)/Au (100 nm) contacts at a base pressure of $2 \times 10^{-7}$ mbar. Rapid thermal annealing was not employed, as InAs readily forms ohmic contacts owing to the well known native electron accumulation at InAs surfaces[111] and semiconductor-metal interfaces[112].
Fabrication of electrical contacts to InAs/GaAs nanowires followed a different fabrication process depicted in Figure 2.6a-d, in which metal junctions were fabricated directly to the InAs core after selective removal of the GaAs shell directly underneath the contact. Similar to InAs nanowires, patterns with openings for two to four electrodes, each like the one shown in Figure 2.6a, were written in a Copolymer/PMMA resist mask. After development but prior to metal deposition, host substrates with patterned Copolymer/PMMA resist were dipped in NH$_4$OH:H$_2$O$_2$:H$_2$O (1:1:100 by volume), an etchant with 50 times selectivity in etching rate for GaAs and In$_{0.1}$Ga$_{0.9}$As[113], for 7 seconds to remove the GaAs shell in the electrode region. The etch rate for this solution was estimated to be 5 nm per second at 22 °C. A seven second etch terminated by dipping the sample in DI water was used to ensure complete removal of the 5-10 nm thick GaAs shell in the open region of the mask, as shown schematically in Figure 2.6b. SEM inspection of selected patterns revealed under etching depicted in Figure 2.6c by an amount of $L_u \approx 20 - 50$ nm. Metal deposition was performed through the same resist mask after passivation of the now exposed InAs surface using the same ammonium polysulfide solution using on bare InAs nanowires. After rinsing in DI water and drying, the patterned host substrate was immediately transferred to a thermal evaporator where Ni (10 nm)/Au (100 nm) were sequentially deposited, producing metal-semiconductor junctions between the Ni/Au electrodes and the InAs core (Figure 2.6d). SEM images of finished InAs and InAs/GaAs nanowire devices are shown in Figure 2.7a and b, respectively. After processing, host substrates were diced and mounted in cryogenic chip carriers. The Ni/Au pads and the back-gate of the patterned host substrate were wirebonded to pads on the chip carrier.
Figure 2.7: SEM images of (a) two Ni/Au contacts on InAs nanowire (scale: 300 nm) and (b) four Ni/Au contacts on InAs/GaAs core/shell heterostructure nanowire with visible under etch (scale: 200 nm), fabricated as described in the main text.

2.5 InAs and InAs/GaAs Core/Shell FETs

Wirebonded chip carriers were loaded into a closed-cycle He cryostat with the sample in vacuum at a pressure $\approx 10^{-5}$ mbar obtained by pumping using a turbo molecular pump. Current-gate voltage characteristics were measured using a standard lock-in setup with a small AC bias with RMS amplitude $\delta V_{DS} = 0.3$ mV at a frequency $f = 1470$ Hz applied to one terminal, and the current $\partial I_{DS}$ was measured at an opposing terminal using a low-noise current preamplifier. The gate-voltage dependence of the linear conductance $G = \partial I_{DS}/\partial V_{DS}$ of a typical InAs and InAs/GaAs nanowire are shown in Figure 2.8a and 2.8b respectively, at several temperatures. Conductance is plotted in units $2e^2/h$, the maximum linear conductance of a single spin-degenerate subband of a ballistic quantum wire[96], to highlight the fact that electrons in the 1000 nm long nanowires are not transported fully ballistically from source to drain. Two essentially indistinguishable curves are shown for each temperature corresponding to increasing and decreasing gate voltage, showing that gate hysteresis and associated slow charging effects are negligible.

At any given temperature, the conductance $G$ of both bare InAs and InAs/GaAs core/shell nanowires increases with increasing gate voltage, acting as depletion mode transistors and demonstrating that both are naturally n-type with no gate bias applied.
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Figure 2.8: Temperature dependence of linear conductance $G$ on gate voltage for (a) InAs nanowire with diameter $d = 40 \pm 2$ nm (b) InAs/GaAs core/shell nanowire with core diameter $d = 30 \pm 2$ nm.

The main difference between the InAs and InAs/GaAs nanowires is that for any fixed temperature $T$, InAs nanowires consistently have higher transconductance $\partial I_{DS}/\partial V_{GS}$. For InAs nanowires, peak transconductance, and therefore, peak field effect mobility, increases with decreasing temperature. Threshold voltages $V_T$ of InAs nanowires of diameter $\approx 30 – 60$ nm, interpreted in the charge control model (Equations A.1a - A.1b), yield an equivalent electron density $n_0 \approx 10^{17} – 10^{18}$ cm$^{-3}$ at room temperature. When converted to equivalent surface units, the densities bunch around $1 – 2 \times 10^{12}$ cm$^{-2}$, suggesting that donor-like surface states above the conduction band, like those responsible for electron accumulation in planar InAs surfaces[111], are at least partially responsible for the carrier gas in InAs nanowires. The gate voltage dependent field-effect mobility $\mu_{FE} = \partial G/\partial V_{GS}L^2/C$ for nanowires with a distribution of diameters on two chips, one containing InAs nanowires and the other InAs/GaAs nanowires was estimated using an analytical expression for the gate capacitance of a cylinder separated from a conducting plane by a dielectric slab of thickness $t_{ox} = 100$ nm $C = 2\pi\varepsilon_0\varepsilon_{eff}L/\text{arccosh}((t_{ox} + R)/R)$. Here, $L$ is the patterned length between electrodes, $R$ is nanowire radius measured by a field emission SEM, and $\varepsilon_{eff}$ is an effective gate dielectric constant taking the inhomoge-
neous dielectric surroundings of the nanowire into account[114]. The quantity $\partial G/\partial V_{GS}$ was obtained by numerical differentiation of the measured $G - V_{GS}$ characteristic.

The peak field effect mobility, which occurs close to the threshold voltage $V_T$, was plotted in Figure 2.9a for the InAs (solid data points) and InAs/GaAs core/shell nanowires (open data points). Vertical error bars on this plot represent uncertainty introduced by the numerical derivative. For bare InAs wires it is typical for the room temperature field effect mobility to increase with increasing diameter, in this case $\approx 2300 \pm 100$ to $\approx 3100 \pm 100$ cm$^2$/V.s for radii increasing from $\approx 20$ to $30$ nm. Recently, diameter-dependent mobility of InAs nanowires was reported[115] which the authors attributed to surface roughness scattering. Although the surface roughness scattering-limited electron mobility in quantum wires is consistent with this trend[116], the scattering rate due to charged surface or bulk states also decreases in strength as diameter increases[117]. Peak field effect mobility is plotted versus temperature in Figure 2.9b for two InAs nanowires. The same general trend shown here applies to all InAs nanowires; increasing peak field effect mobility with decreasing temperature. Hall mobility of carriers in three dimensional (bulk) and two-dimensional systems generally increase with decreasing temperature, due to the decrease in the population of polar optical phonons with decreasing temperature[118]. Thermal effects of carrier distribution are also expected to play a role for gate voltages just above $V_T$.

In comparison, the electron mobility of InAs-GaAs core-shell nanowires with shells $\approx 5 - 10$ nm thick is in the range $500 - 1000$ cm$^2$/V.s and lacks any discernible correlation to the diameter of the InAs core, which was measured at the under etched region near the ohmic contact. Carrier density estimated from the charge control model is $\approx 10^{18}$ cm$^{-3}$ at room temperature, similar to what is observed for bare InAs. Dislocations generated at the InAs/GaAs interface, which appear to be the leading mechanism for strain relaxation in the core/shell nanowires, are expected to introduce two additional sources of carrier scattering. First, an inhomogeneous deformation potential will accompany the
locally varying microscopic strain associated with dislocations. Second, traps containing fixed charge are likely to exist on the dislocations, introducing additional Coulomb impurity scattering. The latter is thought to be dominant in two-dimensional InGaAs/GaAs quantum wells\[119\]. We cannot rule out the possibility that the capacitive coupling to the conducting electrons has been weakened compared to InAs nanowires, by gate-induced modulation of charge at a larger population of trap states at the Fermi energy in InAs-GaAs nanowires. This effect would further reduce the field-effect mobility\[120\].

More accurate calculations taking into account the (i) finite electronic density of states and (ii) realistic spatial distribution of electronic charge in nanowires explained in further detail in Chapter 4 show that the geometrical capacitance is uniformly about 20 % larger than the total gate capacitance, for nanowires in the diameter range studied. Field effect mobilities $\mu_{FE} = \partial I_{DS}/\partial V_{GS} L^2 / CV_{DS}$ shown in 2.9a, obtained from measured $I_{DS} - V_{GS}$ characteristics and numerical estimates of the geometrical capacitance, can therefore be understood to be approximately 20 % smaller than the true field effect mobilities of the
InAs and InAs/GaAs nanowires. Nevertheless, Figure 2.9a is still expected to provide a reliable estimate of the field effect mobility and its trends with respect to nanowire diameter. A large collection of InAs nanowires have been measured, and typical values for field effect mobility fall in the range $2000–4000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. We comment that this is similar to the highest field effect mobility $\approx 4000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$[102] in semiconducting carbon nanotube field-effect transistors with similar channel length ($L \approx 3 \text{ \mu m}$). While single wall carbon nanotubes with length $L \approx 300 \text{ \mu m}$ can have extremely large room temperature field effect mobility $\mu_{\text{FE}} \approx 100,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$[121], the disparity with shorter semiconducting nanotubes has been explained as due to enhanced role of carrier scattering at the contact interface and fundamental, mode mismatch related contact resistance[102].

Some of the longer InAs/GaAs nanowires had electrodes deposited on the GaAs, between two terminals deposited directly on the core, after passivation of the GaAs surface by ammonium polysulfide. Two and three terminal measurements on these nanowires established that resistance of contacts deposited on 5-15 nm thick GaAs shells has negligible temperature dependence and is at least a factor of 10 more than the two terminal resistance between the two outer electrodes deposited directly on the InAs core. Therefore, the GaAs shell acts as a barrier for tunneling of electrons from the Fermi energy of the electrode into the conduction band of the InAs core, which remains conductive down to 10 K and below. From this we conclude that there is no current flow in the GaAs shell, consistent with type-I band-alignment, and the conducting carrier gas in the InAs core is not thermally activated.

### 2.6 Sulfur Passivation

Sulfur passivation treatment is always employed during ohmic contact deposition on InAs nanowires. To clarify the effect of sulfur passivation, two separate chips with InAs nanowires were fabricated using the usual process, but just prior to loading into the
cryostat, the clean ceramic LCC chip carrier with freshly prepared, mounted, and wire-bonded InAs nanowire devices was dipped in 0.3 % ammonium sulfide for 5 minutes, rinsed in de-ionized water, and briefly dried with compressed air. As usual, the cryostat was pumped to a vacuum of 10\(^{-5}\) mbar using a turbomolecular pump. Electrical measurements showed that the two-terminal resistance of these nanowires with \(L = 1000\) nm between their contacts, \(R \approx 5 \sim 10\) kΩ, was typically lower than unpassivated InAs nanowires. More significantly, nanowires with sulfur terminated surfaces were essentially impossible to fully deplete electrically, even for \(V_{GS} < -20\) V, at 10 K. In comparison, InAs and InAs/GaAs nanowires would typically be fully depleted for \(V_{GS}\) below \(-1\) to \(-2\) V at 10 K. It is concluded that the Fermi energy of the sulfur terminated InAs nanowires is pinned higher above the conduction band edge compared to the InAs nanowires covered with native oxide, increasing electron accumulation. This is consistent with studies of sulfur termination of planar InAs surfaces, where increased electron accumulation was observed[110]. While it is not clear how physical vapour deposition of Ti/Au contacts influences the electronic structure of sulfur passivated InAs nanowire surface, local electron accumulation is certainly advantageous for ohmic contact formation to n-type InAs nanowires[122].

### 2.7 Evidence of Sub-band Quantization in InAs nanowires

Plateau structures have been observed in the gate-voltage dependence of the differential conductance \(G = \partial I_{DS}/\partial V_{DS}\) of some InAs nanowires. For one such InAs nanowire with 34 nm diameter and a field effect mobility \(\mu_{FE} \approx 4000\) cm\(^2\)V\(^{-1}\)s\(^{-1}\), the dependence of \(G\) on the DC source-drain bias \(V_{DS}\) is shown in Figure 2.10a at 30 K, for several fixed gate voltages \(V_{GS}\). There is a bunching of differential conductance curves at \(G \approx 0.15 \times (2e^2/h)\) in the gate voltage ranges \(-0.75\) V < \(V_{GS}\) < \(-0.5\) V, and at \(G \approx 0.3 \times (2e^2/h)\) in the gate voltage ranges \(-0.25\) V < \(V_{GS}\) < \(0.25\) V. The dependence of the these plateau-like features
Figure 2.10: (a) Differential conductance versus DC bias $V_{DS}$ for gate voltages $V_{GS}$ between $−1.15$ V to 0.5 V for an InAs nanowire at 30 K, (b) Differential conductance versus gate voltage $V_{GS}$ for selected $V_{DS} = 0.0, 2.5, 5.0, 7.5, 10.0, 12.5, 15.0$ mV, and (c) Dependence of differential conductance on $V_{DS}$ and $V_{GS}$ displayed as intensity map, for data in (a).
in the differential conductance is shown for several fixed DC source drain biases between 0 and 15 mV in Figure 2.10b. Here, the difference in gate voltages between the adjacent plateaus is clearly identified as ≈ 0.75 V. The model discussed in Section 1.4.3 predicts ≈ 55 meV splitting between the first and second subband in a 30 nm InAs nanowire, which translates to $\Delta V_{GS} \approx 0.55$ V, since $\partial \Phi / \partial V_{GS} \approx 0.1$ for our particular the back-gate geometry (see Chapter 4). The full differential conductance map is shown in colour in Figure 2.10c, which clearly shows oscillatory behaviour of differential conductance with gate voltage. These oscillations, which are also visible in Figure 2.10b, shift to smaller gate voltages for larger drain-source voltages $V_{DS}$, as the associated resonances enter the increasing bias window of accessible states. The oscillations are spaced 0.20 V apart in gate voltage, and therefore, approximately 20 meV apart in energy, which is far too large to be due to an electronic Fabry-Perot resonance over the full $L = 1000$ nm length of the nanowire.

This can be seen as follows. The change in linear electron density $n'$ with gate voltage $V_{GS}$ satisfies $\Delta n' = \Delta V_{GS} C'/e$, where $C'$ is the gate capacitance per unit length, and $\Delta V_{GS}$ is the difference in gate voltage between adjacent Fabry-Perot peaks. But, increasing the gate voltage sufficiently to transmit electrons through the next Fabry-Perot resonance changes the electron density by $\Delta n' = 2/L$. Solving for $L$ we obtain $L = 2e/(C'\Delta V_{GS}) \approx 300$ nm as the effective length of the Fabry-Perot cavity. This could be explained by the presence of a scatterer such as a point defect located $\approx 300$ nm away from a contact. Very recently, such resonances were reported in the two terminal measurements of suspended InAs nanowires with 300 nm between contacts, except at a much lower temperature of 0.3 K[123]. Gate-voltage dependent measurements of the differential conductance at $V_{DS} = 0$ and several fixed temperatures show that the observed plateau structure is still discernible at 77 K ($k_B T \approx 7$ meV). Since the conductance does not reach $G_0$ on each plateau, some electron scattering processes prevent full transmission of electrons from the source to the drain, i.e., transport from source to drain is not
ballistic. Rather, transmission is limited by scattering events in the channel and/or metal-semiconductor junction. Regardless, the step structure is compelling evidence for electronic sub-band structure in the InAs nanowires, and this is a significant finding since precious little evidence for sub-band quantization has been observed in InAs nanowires studied in the literature. Moreover, the temperature up to which the apparent sub-band quantization persists is higher than previous studies in Ge/Si core/shell nanowires, where the same effects were observed up to \( \approx 10 - 20 \) K\[124]\.

### 2.8 Coulomb Blockade in InAs Nanowires at Ultra-Low Temperatures

Three InAs nanowires with two terminals spaced \( L = 1000 \) nm apart were cooled to \( \approx 100 \) mK in a dilution refrigerator, where oscillations of zero-bias differential conductance with period \( \Delta V_{GS} \approx 3.0 - 3.3 \) mV could be seen. A few periods of approximately 350 conductance oscillations observed between gate voltages \( V_{GS} = 0.3 - 1.4 \) V are shown in Figure 2.12a for an InAs nanowire.
Differential conductance spectroscopy for different DC gate voltages $V_{GS}$ and drain-source voltages $V_{DS}$, shown in Figure 2.12b, reveals prominent Coulomb-diamond patterns. No noticeable even-odd effects were observed in adjacent Coulomb oscillations, so the quantization of electronic states along with length of the nanowire is negligible compared to the Coulomb repulsion. In this regime, the gate capacitance is $C_G \approx e/\Delta V_{GS} = 50 \pm 2$ aF. The charging energy is obtained from the half height $\Delta V_{DS} = 1.1 \pm 0.05$ mV of the Coulomb diamond is $E_C = e\Delta V_{DS} = 1.1 \pm 0.05$ meV. The total island capacitance is given by $C_\Sigma = C_L + C_R + C_G = e^2/E_C \approx 145 \pm 5$ aF, where $C_L$ and $C_R$ are the capacitances of the tunneling junctions, which sum to $C_L + C_R = C_\Sigma - C_G = 95 \pm 5$ aF.

The geometrical capacitance per unit length discussed in Section 2.5 is $C_G = 55$ aF per micron for a 60 nm diameter InAs nanowire on $t_{ox} = 100$ nm of thermal SiO$_2$. Therefore, the Coulomb island, with $C_G = 50 \pm 2$ aF, is nearly the full length of the nanowire, with the metal-semiconductor junctions acting as tunneling barriers to the nanowire island below 1 K.
2.9 Conclusions

Back-gated, single nanowire field effect transistors were fabricated with InAs and InAs/GaAs core/shell nanowires. Evidence of robust quantization of free electrons into one-dimensional sub-bands was observed in the gate-voltage dependence of differential conductance for an InAs nanowire with channel length $L = 1000$ nm and diameter $34 \pm 2$ nm, up to 77 K, well above temperature that reported in Ge/Si core/shell nanowires by Lieber and coworkers[124]. Steps separating the plateaus occur at a gate voltage separation consistent with expected sub-band quantization energy of a 30 nm diameter cylindrical nanowire, and electrostatics of the back-gated device. Both InAs and strained InAs/GaAs heterostructure nanowires were found to be n-type with the former having higher electron mobility of typically $\mu_{\text{FE}} = 2000 - 4000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature and $\mu_{\text{FE}} = 10000 - 20000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at 30 K. Below 1 K, Coulomb blockade was observed in all InAs nanowires measured, with entire $L = 1000$ nm length of the InAs nanowire acting as a single Coulomb island. Sulfur termination of the InAs nanowire surface by passivation in ammonium polysulfide is found to increase electron accumulation, consistent with studies on planar surfaces.

Significant strain relaxation and dislocations were found at the interface of core/shell InAs/GaAs nanowires due to large lattice mismatch, consistent with predictions from equilibrium elasticity theory. These dislocations introduce scattering centres which suppress significantly the electronic field effect mobility of InAs/GaAs nanowires to the range of $500 - 1000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. Further reduction in nanowire core diameter or reduction in strain by e.g. deposition of an alloyed shell, is likely required to produce dislocation-free structures. Such coherently strained heterostructures could have enhanced electronic mean free path.
3.1 Introduction

As the size of electronic devices shrink, fluctuations in current flowing through them become more noticeable in comparison with the mean value of the current flowing from one terminal to another. Besides the Johnson-Nyquist noise and the shot noise, which arise, respectively, from thermal fluctuations of the current-carrying states, and the discreteness of the charge of electrical carriers[66, 125], the current $I(t)$ flowing through almost any electrical conductor exhibits fluctuations whose autospectral density

$$S_{II}(f) = \int_{-\infty}^{\infty} d\tau \exp(-2\pi i f \tau) \left( \int_{-\infty}^{\infty} dt I(t)I(t-\tau) \right)$$  \hspace{1cm} (3.1)

is inversely proportional to frequency[125]. Due to its signature power spectral density $S_{II}(f) \propto 1/f^{\alpha}$, this noise is called $1/f$ noise. Empirically it is found that the normalized autospectral power density of current flowing through a wide variety of biased electrical conductors satisfies

$$\frac{S_{II}(f)}{\langle I \rangle^2} = \frac{\alpha_H}{N} \frac{1}{f}$$  \hspace{1cm} (3.2)
when $N$, the number of electrical carriers in the system, is much larger than unity[125]. Here, $\alpha_H$ is a characteristic of the conductor, and $\langle I \rangle$ is the average current flowing. While this empirical relationship can not be expected to be preserved exactly as $N$ is made arbitrarily small (by e.g. reducing the size of the conductor to nanometer scale), it is nevertheless important that the fluctuations scale roughly in inverse proportion to $N$.

The microscopic process producing this noise in metal-oxide-semiconductor field effect transistors (MOSFETs) was considerably elucidated by Ralls et. al.[126] not long after it became possible to fabricate planar, silicon MOSFETs of submicron scale. The authors observed random sequences of transitions between two discrete levels of current flowing through them under fixed bias conditions. The term random telegraph signals (RTS) was adopted to describe these waveforms of conductance versus time, due to their resemblance to signals present on the electrical lines of early telecommunications systems. From the temperature and gate-voltage dependence of the temporal statistics of these RTS, it was established that they are the result of stochastic capture and emission of a single electron from a single trap at the Si/SiO$_2$ interface[126]. Many such traps fluctuating with an ensemble of different time constants, as would be reasonably expected for a set of traps influenced by disorder of the semiconductor-insulator interface in larger devices, produces a noise power spectrum that is a sum of many Lorentzians in the frequency domain[127]. When there are sufficiently many such traps number of interface traps, their superposition of Lorentzians essentially converges to the classical $1/f$ shape of macroscopic field effect transistors.

Approximately $1/3$ of the InAs nanowire FETs described in Chapter 2 exhibit random switching of their conductance between two well defined values, in some window of temperature or gate voltage. In this chapter we describe the basic features of these RTSs, including the gate-voltage and temperature-dependence of the statistics of intervals of time spent in either state, the relationship between these quantities and the energy level of the trap, and the conductance of the two states. Discussion of the temporal statistics
of the signals provide a basic understanding of the mechanism producing RTS, and a context for the more advanced discussion of Chapter 4 in which the temporal characteristics of RTS are used to extract the gate-voltage dependence of the surface electrostatic potential of nanowires. Two additional observations are made with relevance to Chapter 5. The first is that the low conductance state is always statistically favoured for larger gate voltages, and second, that the timescale of discrete fluctuations of the charge state is nearly ten orders of magnitude slower than the momentum relaxation rate of charge carriers. Therefore, the two conductance states of a RTS in a represent the averaged properties of electron scattering in a system whose Coulombic disorder configuration changes by a single localized charge, the minimum possible amount.

### 3.2 Random Telegraph Signals

An example of this behaviour is shown in the waveforms of Figure 3.1a-c for a 60 nm diameter InAs nanowire FET cooled to $T = 43$ K, for three different gate voltages, top to bottom, (a) $V_{GS} - V_T = 0.200$ V, (b) $V_{GS} - V_T = 0.275$ V, and (c) $V_{GS} - V_T = 0.350$ V. The waveforms, which have a bandwidth of 300 Hz and were sampled at 1 kS/s, exhibit a qualitative trend where switching events are apparently randomly distributed but favour the low conductance state as gate voltage increases. Moreover, when such random telegraph signals were found, they always persisted for the entire course of the experiment; days to two weeks. The statistical distribution of conductances in sampled waveforms shown in Figure 3.2a-c are bimodal, confirming that the conductance is bistable, and fit well to a sum of two Gaussians. The quantities $G_H$ and $G_L$ are defined as the mean conductance of the high and low conductance states, respectively. The ratio of areas under the peaks in Figure 3.2a-c, corresponding to $G_H$ and $G_L$, must also reflect the statistical trend where the low conductance state is favoured for higher gate voltages.

The measured, bistable conductance reflects the state of a bistable two-level system
within the nanowire, and the apparent randomness of the conductance waveforms reflects the stochastic time sequence of quantum mechanical transitions between these states. Indeed, these are the so-called random telegraph signals (RTSs) first observed in Silicon inversion layers by Ralls et. al.[126]. The charging and discharging manifests itself in the conductance of the nanowire through a change in electron number and increase in electron scattering rate. Another familiar example of similar jumping behaviour is the blinking noise of fluorescence exhibited by individual semiconductor nanocrystals[128].
Figure 3.2: Histograms of conductance and fitting to sum of two Gaussians, corresponding to waveforms in 3.1 for gate voltages (a) $V_{GS} - V_T = 0.200$ V, (b) $V_{GS} - V_T = 0.275$ V, and (c) $V_{GS} - V_T = 0.350$ V.

3.3 Statistical Properties of RTS

Further investigation of the basic properties of RTS waveforms taken at fixed gate voltages and temperatures was carried out. For this purpose, waveforms with approximately one thousand or more transitions were obtained by sampling the conductance for an appropriate time interval, and sequences of consecutive intervals of time $t_H$ and $t_L$ spent in the states $G_H$ and $G_L$, respectively, were determined. In most cases, the difference in mean conductances $G_H$ and $G_L$ was large compared to the broadening of their distributions due to other noise sources. These includes unwanted interference from stray electric and magnetic fields, which were carefully eliminated by successive refinements to the measurement setup, electrical noise originating from the preamplifiers, and other electrical noise sources from the nanowire. Electrical noise in the nanowire includes most prominently the $1/f$ background noise of fluctuators that only couple weakly to the conductance, but also includes intrinsic shot noise and thermal noise[120]. The former are invariably present, but are distinguished from the defect producing the random telegraph signal in that they do not strongly scatter carriers. Three algorithms for determining sequences of times $t_H$ and $t_L$ were investigated:
1. Threshold detection: Compare a sample of conductance (or a sample of the conductance filtered by a finite impulse response (FIR) filter) to a threshold conductance, \( G_t = 1/2(G_H + G_L) \), to determine if the nanowire is in the low conductance or high conductance state.

2. Edge detection: Compare a sample of the first time derivative of conductance (again subjected to a finite impulse response filter) to a threshold to identify transitions between the two states, as described by Giusi et al.[129].

3. Hidden Markov model (HMM) detection: Assume of hidden Markov model for the two-state system, and use a MATLAB based maximum likelihood estimator based on the Viterbi algorithm[130] to reconstruct the sequence of times spent in the two states.

All algorithms were implemented in MATLAB using sampled data imported from experiments. A freely available hidden Markov model library[131] was employed to implement the third algorithm. The first two algorithms require choice of FIR filters and thresholds to produce results where no spurious transitions are detected, but this approach is relatively straightforward. The threshold algorithm has a tendency to generate a spurious transitions in situations similar to Figure 3.1, when the slow 1/f-like conductance fluctuations approach in magnitude \( \Delta G = G_H - G_L \). The edge detection and HMM methods were preferred, and always produced the same distributions.

Once the transitions were identified, the statistical ensemble of times \( t_H \) and \( t_L \) spent in the high and low conductance states were obtained. Results for \( t_H \) and \( t_L \) are shown as squares and diamonds, respectively, in Figure 3.4a-c for conditions identical to Figure 3.1a-c.

How should these times \( t_H \) and \( t_L \), which correspond to waiting times before a transition to the other state, be distributed? Considering that statistical means of times \( \langle t_H \rangle \) and \( \langle t_L \rangle \) do not change appreciably with time, it is reasonable to tentatively assume
Figure 3.3: (a) Conductance waveform exhibiting RTS and for $V_{GS} - V_T = 0.275$ V. (b) Extraction of state (high or low) using edge detection algorithm.

Figure 3.4: Distribution of times $t_H$ (squares) and $t_L$ (triangles) spent in the high and low conductance states and fit to Poisson statistics (lines) for (a) $V_{GS} - V_T = 0.200$ V, (b) $V_{GS} - V_T = 0.275$ V, and (c) $V_{GS} - V_T = 0.350$ V.
that the probability per unit time of a transition, defined as \(1/\tau\), does not change over
the observation interval for the entire waveform. Then, the probability of transition in
the time interval \(dt\) between \(t\) and \(t + dt\) is \(p(t)dt = P_0(t)dt/\tau\), where \(P_0(t)\) is the prob-
bility that no transition has occurred up to time \(t\). The probability of no transition
has occurred up to a time \(t + dt\) is obtained by subtracting the probability of transition
during the interval \(dt\), i.e., \(P_0(t + dt) = P_0(t) - P_0(t)dt/\tau\). Dividing this expression by
\(dt\), re-arranging, and taking the limit \(t \to 0\), \(dP_0(t)/dt = -P_0(t)/\tau\) is obtained. This first
order differential equation is readily solved to obtain \(P_0(t) = P_0(0) \exp(-t/\tau)\), where
\(P_0(0) = 1\). Therefore, the probability that a transition occurs between time \(t\) and \(t + dt\)
is \(p(t)dt = 1/\tau \exp(-t/\tau) dt\). Then, the probability of transition in the time interval \(dt\)
between \(t\) and \(t + dt\) is \(p(t)dt = P_0(t)dt/\tau\), where \(P_0(t)\) is the probability that no transi-
tion has occurred up to time \(t\). The probability of no transition has occurred up to a time
\(t + dt\) is obtained by subtracting the probability of transition during the interval \(dt\), i.e.
\(P_0(t + dt) = P_0(t) - P_0(t)dt/\tau\). Dividing this expression by \(dt\), re-arranging, and taking
the limit \(t \to 0\), \(dP_0(t)/dt = -P_0(t)/\tau\) is obtained. This first order differential equation
is readily solved to obtain \(P_0(t) = P_0(0) \exp(-t/\tau)\), where \(P_0(0) = 1\). Therefore, the
probability that a transition occurs between time \(t\) and \(t + dt\) is \(p(t)dt = 1/\tau \exp(-t/\tau) dt\).

This is the so-called Poisson distribution of events for a stationary process, whose
events are distributed such that their mean \(\langle t \rangle\) and variance \(\sqrt{\langle (t) - \bar{t} \rangle^2}\) are both \(\tau\), the
probability of transition per unit time. Like RTS observed in the conductance of silicon
inversion layers[126, 132], distributions of times \(t_H\) and \(t_L\) for InAs nanowires fit very
well a Poisson process. Least squares fits of the distributions are shown in Figure 3.4a-b.
This contrasts the statistics of fluorescence intermittancy (blinking) of semiconductor
nanocrystals, which normally follows a power law distribution[133] indicative of complex
processes such as spectral diffusion, as reviewed by Stefani et. al.[134]. Here, we see
evidence for the qualitative trend that the relative time spent in the state of high con-
ductance, \(\langle t_H \rangle / \langle t_L \rangle\), decreases with increasing gate voltage, since \(\langle t_H \rangle / \langle t_L \rangle = 14\) for
When experimental conditions, gate voltage, temperature, and bias, are kept constant, all of the two-level telegraph signals studied in about a dozen InAs nanowires fit very well the bi-modal Gaussian distributions for the distributions of conductance, and have single time-constants for both capture and emission. Moreover, the statistics and mean conductances exhibit systematic trends with gate voltage common to all wires and active defects.

3.4 Dependence on gate voltage and temperature

One trend that appears prominently in the RTS in Figure 3.1 is that switching events are arranged so that the mean time spent in the low conductance state is favoured as gate voltage increases. Figure 3.5a is a plot of the dependence of $\langle t_H \rangle$ (open points), $\langle t_L \rangle$ (solid points) for four different nanowires with measured diameters $59 \pm 2$ nm (squares, at $T = 43$ K), $36 \pm 2$ nm (inverted triangles, at $T = 53$ K), $33 \pm 2$ nm (circles, at $T = 31$ K), and $28 \pm 2$ nm (triangles, $T = 25$ K). The gate voltage can be seen to influence mainly $t_H$, which decreases exponentially with increasing gate voltage. The time spent in the low conductance state $t_L$ increases slightly with increasing gate voltage.

The ratio $\langle t_H \rangle / \langle t_L \rangle$, shown in Figure 3.5b, is the physically meaningful quantity in the context of the grand canonical ensemble[135], in which the RTS is produced by electron exchange of a single electron between the defect’s electronic orbital subsystem and electrons occupying conducting electronic states in the nanowire. Within this ensemble, the probability $p(N)$ of an $N$ electron state of the defect is $p(N) \propto \gamma(N) \exp(-\beta(E(N) - NE_F))$, where $E_F$ and $\beta = 1/k_B T$ are the common Fermi energy and inverse temperature for the nanowire and defect subsystem, and $\gamma(N)$ and $E(N)$ are the degeneracy and energy of the $N$ electron state of the defect. Since
Figure 3.5: Gate voltage dependence of (a) $\langle t_H \rangle$ (open points), $\langle t_L \rangle$ (solid points) and (b) $\langle t_H \rangle / \langle t_L \rangle$ for four different nanowires with measured diameters 59 ± 2 nm (squares, at $T = 43$ K), 36 ± 2 nm (inverted triangles, at $T = 53$ K), 33 ± 2 nm (circles, at $T = 31$ K), and 28 ± 2 nm (triangles, $T = 25$ K). Lines are b-spline fits to the measured data, provided only as a guide to the eye for understanding the qualitative trends.
Figure 3.6: Simplified energy diagram showing trap energy $E_{T1}$ within a few $k_B T$ of Fermi energy $E_F$, and $E_{T2}$ outside of energy window in which charging/discharging of this level is energetically probable, as defined by the Fermi-Dirac distribution of occupied conducting states in the nanowire.

\[
\langle t_H \rangle / \langle t_L \rangle = \frac{p(n-1)}{p(n)}\]

We have

\[
\frac{\langle t_H \rangle}{\langle t_L \rangle} = \frac{1}{g} \exp(\beta(E_T - E_F))
\]

(3.3) 

where $g = \gamma(n)/\gamma(n-1)$ and $E_T = E(n) - E(n-1)$ are the degeneracy and energy of the trap level, respectively. With this result and the help of the simplified energy diagram in Figure 3.6, the trend of Figure 3.5b can be readily understood. As $V_{GS}$ increases, the difference between the Fermi energy $E_F$ increases relative to the both the conduction band edge $E_C$ and the trap energy $E_T$, and the probability of trap occupancy increases. This implies that the low conductance state $G_L$ is produced by charging the defect with one additional electron, and conversely, the high conductance state $G_H$ corresponds to when this electron is emitted.

A level $E_{T2}$ associated with another charge state of this defect or simply another defect altogether, that is not within at least a few $k_B T$, has a very low relative probability of being occupied. In other words, the energy window of $\pm \approx 2k_B T$ about $E_F$ defines the defect states which can participate in charge exchange with the InAs nanowire’s conduction electrons. In measurements of current versus gate voltage, this may appear as shown in Figure 3.7a when the measurement and data capture rate is faster than the
average capture and emission rates. In the region $V_{GS} < 0.0$ V there is minimal current switching, and in the region $0.0$ V $< V_{GS} < 1.0$ V, the time spent in the high conductance state gradually diminishes.

Consider the possibility to charge a single defect site’s two levels $E_{T1}$ and $E_{T2}$. Even if the orbital state corresponding to $E_{T1}$ can hold an electron of either spin, twice filling this orbital with opposite spins requires an additional energy to overcome the Coulomb repulsion $U$ of the two electrons. This renders observation of two charge transitions $n - 1 \rightarrow n$ and $n \rightarrow n + 1$ on the same defect highly unlikely. Indeed, three-level random telegraph signals were not observed. A single four-level RTS was observed due to switching of two defects, which is discussed in detail in Chapter 4.

In addition to the strong gate voltage dependence of times $\langle t_H \rangle$ and $\langle t_L \rangle$, temperature-dependent measurements demonstrate that both $\langle t_H \rangle$ and $\langle t_L \rangle$ depend exponentially on temperature with $\langle t_H \rangle^{-1} \propto \sigma_{c,\infty} \exp(-\beta E_B)$ and $\langle t_L \rangle^{-1} \propto \sigma_{e,\infty} \exp(-\beta E_X)$. Here, $E_B$ and $E_X$ are the capture and emission activation energies, respectively, which are plotted.
for the same conditions in Figure 3.1-3.7 in Figure 3.8. We infer that the microscopic process responsible for capture and emission is a thermally activated multiphonon emission process relevant for deep levels in semiconductors\cite{136, 137}, and later identified as the mechanism responsible for random telegraph signals in Silicon inversion layers\cite{126}. The barriers $E_B$ and $E_X$ are signatures of lattice perturbation associated with the localized nature of the captured electron\cite{126, 138, 139}. Cascade capture and Auger assisted trapping can be ruled out, since their rates exhibit weak power-law dependence on temperature\cite{140}. The microscopic origins of the capture activation energies, will be discussed further in Chapter 4, Section 4.5.

Consequently, a good strategy for finding random telegraph signals that will be used to study channel potential in Chapter 4 and carrier scattering by single Coulomb impurities in Chapter 5, is to start measurements at room temperature, and successively cool down the sample to lower and lower temperatures, performing a scan of conductance versus gate voltage at each temperature, looking for ranges of $V_{GS}$ where conductance exhibits the characteristic switching shown in Figure 3.7.
3.5 Conclusions

Random telegraph signals\[126\] with clearly resolvable high and low conductance states were observed in n-type InAs single nanowire field effect transistors fabricated as described in Chapter 2. Procedures for extracting the times spent in in either state, and their conductances, were described. Telegraph signals have Poisson distribution of capture and emission times, and mean capture and emission rates that depend monotonically on gate voltage. The high conductance state is statistically more likely for smaller gate voltages, indicating that the low conductance state is obtained when a trap state is filled. The capture and emission rates are thermally activated, consistent with multiphonon emission. Chapter 4 details with interpretation of the statistics and rates of the telegraph signals, in terms of the electrostatic potential of the nanowire field effect transistor. Chapter 5 considers the absolute values of conductances in the random telegraph signal, corresponding to disorder potentials that differ in by a single charged impurity.
Chapter 4

Probing the Gate-Voltage Dependence of the Surface Potential of Individual Nanowires by Sensing the Charge Occupation of a Single Defect

4.1 Introduction

The essential property of metal-insulator-semiconductor (MIS) and metal-semiconductor (MS) structures that makes them of both technological and scientific interest is that an applied potential (voltage) on the metal (M) electrode can be used to control the surface potential (voltage) of the semiconductor (S). Consequently, the gate voltage either depletes or accumulates free carriers near the semiconductor surface, depending on whether or not the applied potential is repulsive or attractive, respectively. In studies of carrier transport physics, the gate electrode acts as a convenient parameter for tuning the carrier
density and populating electronic states such as the set of electronic sub-bands of one or two-dimensional electronic systems. In field-effect transistors and high-electron-mobility transistors, gate control over the semiconductor’s surface potential provides control of the electrical characteristics of the semiconductor between two terminals, the source and drain. In technological applications, the gate voltage also provides the basic mechanism for controlling the conductance of a nanostructure, a prerequisite for logic, storage, and sensing applications. Gate control enables the MIS or MS structure to act as a switching device in the case of digital logic, or an amplifier of electrical signals in the case of analog circuitry.

Among the methods that have been used in the past to provide invaluable information about the fundamental properties of two-dimensional carriers systems, the electric field effect on conductance, the Hall effect, and capacitance-voltage spectroscopy continue to play an important role[4]. These techniques also provide significant diagnostic information for material quality and device characterization, and technological development of Silicon MOSFETs benefited considerably from these three methods[141]. The dependence of gate capacitance on gate voltage can provide indirect information about surface potential, and related methodology can be used for accurate determination of interface state distribution. The Hall effect can be used to extract gate-voltage dependent mobility and carrier concentration. As will be argued in Section 4.1.1, only the field-effect experiment is straightforwardly carried out in one-dimensional systems, especially those fabricated by bottom-up techniques.

In this chapter a novel method for extraction of the gate-voltage dependence of the surface potential of individual nanowires is presented. It is based on the statistical probability of occupation of a single defect site on the nanowire’s surface. The time-sequence of electron capture and emission at the defect site is determined from a random telegraph signal, from which the occupation of the defect can be inferred at any given moment, and the occupation probability of the trap, averaged over many transitions,
can be obtained. The average occupation probability of the trap observed over many transitions is used to directly obtain the trap energy, and therefore, surface potential energy, relative to the Fermi energy. Put another way, the statistics of time sequences of stochastic fluctuations of charge on a single defect, which is read out by measuring the nanowire’s conductance, act as a voltmeter. The results reinforce the important notion that fluctuations in nanoscale systems are not “just noise”. Rather, they can provide important quantitative information about physical properties. In this case, the effect of electrostatic coupling that is extremely difficult to measure capacitively is observed in the gate-voltage dependence of surface potential in a back-gated nanowire. The notion of the usefulness of fluctuations is particularly compelling in nanostructures, where the amplitude of measured fluctuations, e.g., the Universal Conductance Fluctuations (UCF), and the Blinking Noise of photoluminescence, can be of the same order of magnitude as the mean value.

An analytic relationship between gate voltage and surface potential in a coaxial-gate nanowire is derived, and extended by numerical calculations to the case of a back-gated nanowire. Compared to the coaxial gate case, an appreciable radial asymmetry develops in the potential of the back-gated nanowires, primarily due to the planar sheet of charge on the back-gate. Results of the numerical calculations are compared with measured surface potentials for three InAs nanowires: NWa (59 ± 2 nm diameter at $T = 40$ K), NWb (28 ± 2 nm at $T = 25$ K), and NWc (49 ± 2 nm at $T = 77$ K). NWa and NWb both have a single defect capturing and emitting a single electron, producing RTS of the kind described in detail in Section 3 of Chapter 3. NWc has an RTS with four stable levels of conductance, due to two switching defects. Detailed analysis reveals that the two defects are essentially uncorrelated with negligible mutual electrostatic interaction.

Comparison with a self-consistent theoretical model shows that surface potential variation is retarded in the conducting regime due to screening by surface states. For NWc, calculations reproduce the measured gate-voltage dependence of trap energy when the
gate modulates charge in surface states with density \( D_{ss} = (1.05 \pm 0.2) \times 10^{12} \text{ cm}^{-2} \text{eV}^{-1} \), in the linear regime. Similarly, \( D_{ss} \approx 10^{12} \text{ cm}^{-2} \text{eV}^{-1} \) is consistent with measured trap energy in both NWa and NWb. Results are discussed in terms of a recent report on capacitance-voltage spectroscopy on long, locally gated InAs nanowires[115].

The temperature and gate-voltage dependent dynamics for electron capture and emission at the defect are well captured by a theoretical model for multiphonon emission. The lattice distortion energy and cross section[137] associated with capturing an electron on the trap site are extracted for NWa, \( Sh\omega = 187 \pm 15 \text{ meV} \) and \( \sigma_{\infty} \approx 3 \times 10^{-19} \text{ cm}^2 \) respectively. Another defect studied in NWa has \( \sigma_{\infty} \approx 2 \times 10^{-17} \text{ cm}^2 \). The small capture cross sections support the notion that RTS occurs due to capture and emission of carriers from traps probably residing at the border or just inside the 2-3 nm native oxide of the nanowire.

### 4.1.1 Hall Effect and Capacitance-Voltage Spectroscopy

The classical version of the Hall effect which permits extraction of carrier mobility and densities is essentially ill-defined in one-dimensional semiconductors. The main problem is the requirement that opposite edges of the system under study, from which the Hall voltage must be sampled, should be many mean free paths apart[142]. This criteria does not hold in anything that can be reasonably called one-dimensional or quasi-one-dimensional. Another problem that is not so subtle is that it will be difficult to sample potential by depositing some type of leads on a nanowire which could be 30 nm or less in diameter. The integer and fractional versions of the Hall effect, which are accompanied by the Shubnikov-de Haas (SdH) magnetoconductance oscillations, require that lateral dimensions of the sample are larger than the effective cyclotron radius, and that the mean free path is several magnetic lengths. This normally only holds in samples with the longest carrier mean free paths, at low temperatures similar to 4 K.

Capacitance-voltage methodology, while still meaningful for semiconductor nanowires
and nanotubes, is very difficult to carry out in the common circumstance of extremely low (attofarad) gate capacitance. The geometrical capacitance, calculated by replacing the gate and semiconductor with a perfect electrical conductor, provides an upper bound for the total gate capacitance [143]. It can be relatively easily estimated for the two most important gate geometries. The first geometry is the coaxial gate shown in Figure 4.1(a), below. Here, a coaxial gate of radius $R + t_{ox}$ surrounds a nanowire of radius $R$ and permittivity $\epsilon_s$, separated from it by a gate dielectric with permittivity $\epsilon_{ox}$. The geometrical capacitance per unit length of nanowire $C'_G$ is easily calculated by integrating the Laplace equation in cylindrical coordinates between the nanowire and gate boundaries, yielding

$$C'_G = \frac{2\pi\epsilon_{ox}}{\ln\left(\frac{R + t_{ox}}{R}\right)}.$$  

(4.1)

The geometrical capacitance of the back-gated nanowire shown in Figure 4.1b with radius $R$ dielectric permittivity and thickness of $t_{ox}$ and $\epsilon_{ox}$ respectively, and ambient permittivity $\epsilon_a$. When $\epsilon_a = \epsilon_{ox}$ the geometrical capacitance per unit length $C'_G = C_G/L$ is straightforward [114],

$$C'_G = \frac{2\pi\epsilon_{ox}}{\text{arccosh}\left(\frac{R + t_{ox}}{R}\right)}.$$  

(4.2)

Figure 4.2a is a plot of the geometrical capacitance of the dependence of the geometrical capacitance of the coaxial gate and back-gate for different values of $(R + t_{ox})/R$ and $\epsilon_{ox} = 3.9\epsilon_0$, the static dielectric constant of thermally oxidized SiO$_2$. The ambient dielectric constant in the back-gated case is taken as $\epsilon_a = \epsilon_0$ to be consistent with InAs nanowires studied in this thesis. The quantity $\epsilon_{ox}$ in Equation (4.2) is replaced with an effective dielectric constant $\epsilon_{ox} = 2.2\epsilon_0$ valid for SiO$_2$ in the range $2 < (t_{ox} + R)/R < 100$, as shown by Wunnicke [114]. The geometrical capacitance of the coaxial gate is approx $3 - 4$ times higher than the back-gate capacitance. Take for instance a $R = 15$ nm diameter nanowire with a coaxial gate $t_{ox} = R$, and a length $L = 1000$ nm. The geometrical capacitance of this relatively long channel transistor is only $C_G \approx 300$ aF. Back-gated
Figure 4.1: (a) Coaxial gate at radius $R + t_{ox}$, gate dielectric with static permittivity $\epsilon_{ox}$ surrounding a nanowire of radius $R$ and static dielectric permittivity $\epsilon_s$. (b) Planar back-gate separated from nanowire of radius $R$ by planar dielectric with thickness $t_{ox}$.

Figure 4.2: (a) Geometrical capacitance of coaxially gated capacitance (black squares) and back-gated (red circles) nanowires with radius $R$ and dielectric thickness $t_{ox}$ for SiO2 gate dielectric with $\epsilon_{ax} = 3.9\epsilon_0$. 
Chapter 4. Gate-Voltage Dependence of Surface Potential

nanowires fabricated and measured in this thesis have $t_{ox} = 100$ nm and $R = 10 - 30$ nm, corresponding to $C_G = 42 - 55$ aF for nanowire length $L = 1000$ nm. These geometrical capacitances, which are upper bounds on the total gate capacitance, are similar to or below the precision of standard capacitance meters.

As such, there are only a handful of studies of the gate capacitance of individual one dimensional semiconductors such as carbon nanotubes or semiconductor nanowires[115, 71, 70, 72, 73]. Even then state-of-the-art, high-cost capacitance instrumentation and either long ($\approx 3 - 10 \, \mu$m) gate lengths[115, 71, 70, 72] or multiple-nanowire devices have been employed[73]. Capacitance-voltage measurements on back-gated nanowires like those fabricated in this thesis can probably be eliminated outright as a possibility due to the high stray capacitance of the gate to the source and drain pads which is easily 5-6 orders of magnitude larger than the gate capacitance and can be expected to vary at least slightly, with gate voltage. This situation however can be remedied by use of a local gates, though special shielding for the gate terminal is sometimes also employed[71]. The strict requirement of high performance capacitance instrumentation arises since $C = 30 - 300$ aF produces $dI = 2\pi f C dV = 3.6 - 36$ fA of displacement current using a modulation voltage $dV = 10$ mV alternating at $f = 1$ kHz, and only $dI = 2\pi f e = 1$ fA of displacement current per electron.

Alternative methods are desirable for characterization of quasi-equilibrium carrier concentration and surface potential. Among them, the scanned-probe, force-based techniques such as scanning capacitance microscopy[144] (SCM) and scanning kelvin probe microscopy[145] (SKPM) are interesting candidates. The latter is a method for spatially resolving the contact potential of a material and makes visible the built-in potential at a semiconductor P-N junction[145] or the band-bending in a field-effect transistor[146]. Application to semiconductor nanowires is limited however to imaging spatial dependence of the static contact potential produced by doping[147] or built-in potentials at Schottky contacts[148].
4.2 Trap Energy

Interpretation of the statistics of trap occupation is possible in the context of statistical mechanics, as outlined in Chapter 3, Section 3, with the caveat of a change in perspective from ensemble averages to time averages. Herein we present the assumptions for our model for trap statistics, and connect the gate voltage dependence of these statistics with the gate-voltage dependence of the electrostatic potential in the nanowire.

4.2.1 Ensemble Theory for Systems with Small Numbers of Particles

The microscopic description of statistical mechanics produces specific predictions about the ensemble average values of observable quantities and reproduces macroscopic thermodynamics in the limit of large numbers of particles[135]. This limit is not appropriate to describe experimental observations of, evidently, a single electron charging/discharging from a trap in a nanowire, i.e., an RTS. Statistical treatment of an RTS necessitates a change of perspective from the ensemble average properties of a large number of identical systems are predicted, to time averages. Systems which are equivalent under this change of perspective in statistical mechanics are called ergodic[135], and the experimentally observed stability of telegraph signals and Poisson distribution of times $t_H$ and $t_L$ justifies invoking ergodicity in our case. The situation for electron exchange between the nanowire and trap and nanowire and leads is shown in Figure 4.3. The common temperature $T = (\delta S/\delta E)^{-1}$ of the defect and nanowire, where $S$ is the entropy and $E$ is the energy, holds independent of the size of the ensemble[135], and their common Fermi Energy is defined by $E_F$. Under these assumptions, the validity of the grand canonical ensemble is sure to hold since the number of electrons in the trap, $N$, is much less than the total number of conducting electrons in the nanowire, $N_e$, not the mention the electrons in the source and drain, which the nanowire is free to exchange electrons with[135].
Figure 4.3: Nanowire with $N_e$ conducting electrons coupled to trap with $N$ electrons with common temperature $T$ and Fermi Energy $E_F$.

4.2.2 Trap Energy

Recall that the trapping energy $E_T$ in Equation (3.3), $\langle t_H \rangle / \langle t_L \rangle = 1/g \exp(-\beta (E_T - E_F))$, was defined as $E_T = E(N) - E(N-1)$, the difference in energy the definition between the energies $E(N)$ and $E(N-1)$ of the $N$ and $N-1$ electron states of the defect which correspond to the low and high conductance states of the nanowire, respectively. This difference is broken up into two terms.

1. Energy $E_T^0$ shown in Figure 4.4a that includes both the ionic interaction energy of the lattice distortion created when the localized trap level is filled, and the electronic level produced by the deep electron-ion potential of the trap, that is independent of gate voltage.

2. An electrostatic potential $\Phi(r, \phi_d)$ shown in Figure 4.4a accounting for the combination of the charge on the electrostatic gate the charge induced in the nanowire, which depend on gate voltage $V_{GS}$.

The relationship between the trap energy and electrostatic potential described in item 2 is $E_T = E_T^0 - e\Phi(r_d)$ where $r_d$ is the position of the defect on the nanowire’s surface,
and is governed by the Poisson equation

\[ \nabla \cdot (\epsilon(r) \nabla \Phi(r)) = \rho(r) = e(N_D - n(r)) + \rho_s \]  

where \( \epsilon(r) \) is a position-dependent dielectric permittivity of the system and \( \rho(r) \) is a charge density comprised of a uniform background density \( N_D \) of ionized donors, the free electron density \( n(r) \) and a surface charge density \( \rho_s \) at radial coordinate \( r = R \).

Besides this, the Fermi energy \( E_F \) increases with respect to the band edge \( E_1 \) and trap energy \( E_T \) both in the classical (non-degenerate carrier statistics) and quantum-mechanical (degenerate carrier statistics) case. In the case of degenerate carrier statistics \((E_F/k_BT > 1)\), this is due to the Pauli principle and finite nature of the thermally broadened density of states. In metals, which have even stronger degeneracy \((E_F/k_BT \gg 1)\), and large density of states, this effect is negligible. Indeed in the perfect electric conductor approximation, which is equivalent to assumption an infinite density of states, this effect is completely neglected\[143, 149, 150\].
The relationship between Fermi energy and one dimensional carrier density for the $i^{th}$ sub-band, shown in Figure 4.4a, is obtained by integrating the density of states in the sub-band over phase space, which gives

$$n_i'(E_F + e\Phi(0) - E_i, T) = 2(2\pi m_e k_B T / h^2)^{1/2} F_{-1/2}(\beta (E_F + e\Phi(0) - E_i))$$

where $F_j(\eta) = 1/\Gamma(j + 1) \int_0^\infty du u^j (1 + \exp(u - \eta))^{-1}$ is the complete Fermi-Dirac integral of order $j$ and $\Gamma(x)$ is the gamma function. The total three-dimensional electron density is given by adding up the contributions of each band

$$n(r) = \sum_i n_i'(E_F + e\Phi(0) - E_i, T) |\varphi_i(r, \phi)|^2$$

where $\varphi_i(r, \phi)$ is the electronic wavefunction for the $i^{th}$ sub-band. Given sub-band energies $E_i$ and wavefunctions $\varphi_i(r, \phi)$, the model comprising Equations (4.3) - (4.5) describes the potential inside the uniform region in that is roughly one or two screening lengths away from both the source and drain electrodes shown in Figure 4.4b. Translational invariance along $z$ in this region effectively reduces the solution domain from three dimensions to one dimension in the case of the coaxial gate (Figure 4.1a) and two dimensions in the case of the planar back gate (Figure 4.1b), dramatically reducing the complexity of their analytic and numerical solutions, respectively. This approach also neglects the gate-voltage dependence of the trapped electron’s self-energy, the electrostatic interaction between the electron in the trap and the perturbation to electron density in the nanowire arising from screening (see Chapter 5).

Experimentally measured trap statistics $\langle t_H \rangle / \langle t_L \rangle$ in Figure 3.5 are therefore converted into trap energies by equation (3.3). The exact value of the degeneracy factor $g$ appearing in this equation, which includes both spin and orbital degeneracies, is not known with certainty for these defects. For both shallow donors in conduction bands with $\Gamma_6$ symmetry and deep levels there is no orbital degeneracy so $g = 2$. For shallow acceptors in bulk semiconductors $g = 4$ due to the degeneracy of the light and heavy holes around the $\Gamma$-point. The trap levels in experiments are deep in the sense
that the wavefunction is sufficiently localized to produce significant lattice-related activation barriers. Charge transfer is correspondingly slow, preventing significant hybridization with bands, pointing to $g = 2$ as the correct degeneracy factor. For certain, the term $k_B T \ln(g) \approx k_B T$ is small, but more importantly, it is independent of gate voltage. For the purpose of studying the gate voltage dependence of the channel potential, $E_T - E_F - k_B T \ln(g) = k_B T \ln(\langle t_H / t_L \rangle)$ is sufficient. The right hand side of this equation is plotted in Figure 4.5 for the same set of measurements corresponding to Figure 3.5.

The condition of $\langle t_H \rangle / \langle t_L \rangle = 1$, which is equivalent to $E_T = E_F$, occurs for gate voltage $V_{GS}$ exceeding $V_T$ by 50 mV to more than 300 mV. Trap levels are therefore above the conduction band edge.

### 4.3 Analytic Results: Coaxially gated Nanowires

An illustrative special case of the above trap model is the coaxial gate with radius $R + t_{ox}$ separated from a nanowire with radius $R$ by a gate dielectric with permittivity $\epsilon_{ox}$, as
shown in Figure 4.4. For the moment, zero surface charge density is assumed $\rho_s = 0$. The radially symmetric electrostatic potential is obtained by integrating the Poisson equation in cylindrical coordinates along the radial direction. The result at $r = R$ is

$$
\Phi (R) - \Phi(0) = -\frac{e R^2 N_D}{4 \epsilon_s} + \frac{e}{\epsilon_s} \sum_i F_i n'_i (E_F + e\Phi(0) - E_i, T), \quad (4.6)
$$

where $F_i = \int_0^R \frac{dz}{r_2} \int_0^{r_2} dr_1 r_1 |\varphi_i (r_1)|^2$ is a dimensionless constant, and $\epsilon_s$ is the dielectric constant for the semiconductor nanowire. Substituting $E_T = E_T^0 - e\Phi(R)$ from our trap model in Section 4.2.2, the variation of trap energy with respect to the Fermi energy is obtained, parameterized in terms of $E_F + e\Phi(0)$

$$
E_T - E_F = E_T^0 + \frac{e^2 R^2 N_D}{4 \epsilon_s} - \frac{e^2}{\epsilon_s} \sum_i F_i n'_i (E_F + e\Phi(0) - E_i, T) - (E_F + e\Phi(0)) \quad (4.7)
$$

In experiments, $V_{GS}$ controls the surface potential $\Phi(R)$, and the relationship between $V_{GS}$ and $E_F + e\Phi(0)$ is obtained by integration of the Poisson equation to the gate boundary, giving

$$
\Phi (R + t_{ox}) = \Phi(R) + R d\Phi/dr|_{r\rightarrow R^+} \ln \left(\frac{(R + t_{ox})}{R}\right). \quad (4.8)
$$

Employing boundary conditions for continuity of the electric field ($\rho_s = 0$),

$$
d\Phi/dr|_{r\rightarrow R^+} = \epsilon_s/\epsilon_{ox} d\Phi/dr|_{r\rightarrow R^-} = -e/(2\pi \epsilon_{ox} R) \sum_i n'_i (E_F + e\Phi(0) - E_i) \quad (4.9)
$$

and continuity of the potential,

$$
- e\Phi(R + t_{ox}) = E_F - eV_{GS} \quad (4.10)
$$

we obtain $V_{GS}$ is terms of $E_F + e\Phi(0)$

$$
V_{GS} = -\frac{E_T - E_F}{e} + \frac{en'}{C'_G} \quad (4.11)
$$

where $n' = \sum_i n'_i (E_F + e\Phi(0) - E_i, T)$ and $C'_G = 2\pi \epsilon_{ox} / \ln \left((R + t_{ox})/R\right)$ are the electron density and geometrical gate capacitance per unit length, respectively.
The value of Equations (4.7) and (4.11) is that they permit direct evaluation of the trap energy and gate voltage in terms of a single parameter $E_F + e\Phi(0)$, if the geometrical parameters of the nanowire are known, along with the electronic structure. The latter is assumed to be quasi-one-dimensional but an arbitrary number of sub bands can be included. This treatment applies only to the situation when only a small source to drain bias $V_{DS}$ is applied to the nanowire, as in the case of experiments. If a large $V_{DS}$ is applied, which could be sufficient for the field-effect transistor to enter the saturation regime, the trap energy will be modified.

### 4.3.1 Capacitive Formulation of Trap Energy

It is possible to combine equations Equations (4.7) and (4.11) together in a capacitive formulation of the trap energy. Let $\alpha(V_{GS}) = \partial(E_T - E_F)/\partial V_{GS}$ be the partial derivative of the trap energy with respect to gate voltage. Taking the partial derivative of Equation (4.11) with respect to gate voltage $V_{GS}$, $\alpha(V_{GS}) = eC'(C_G^{-1} - C^{-1})$ is obtained, where $C' = e\partial n'/\partial V_{GS}$ is the total gate capacitance. In the single sub band case of Equation (4.7), $C' \approx (F_1/\epsilon_s + C'_{Q}^{-1} + C'_{Q}^{-1})^{-1}$, where $C'_Q = e^2 \partial n'/\partial E_F$ is the quantum capacitance[143]. The main insight provided by these analytical results is that, provided the geometrical capacitance $C'_{G}$ is small compared to the other capacitances in $C'$, $\alpha(V_{GS}) \approx -eC'_G(C'_Q^{-1} + F_1/\epsilon_s)$ provides information on the sum of electronic density of states ($C'_{Q}$) and electrostatics ($F_1$). If $C'_G$ significantly exceeds the quantum capacitance and $\epsilon_1/F_1$, then $\alpha(V_{GS}) \approx -e$. Neglecting the surface electrostatic potential produced by charges in the nanowire, the standard expression for total gate capacitance derived by Luryi in reference [143] is recovered $C' = (C'_{G}^{-1} + C'_{Q}^{-1})^{-1}$.

An equivalent circuit shown in Figure 4.6 summarizes the individual contributions $C'_Q$, $\epsilon_s/F_1$, and $C'_G$ to the total gate capacitance per unit length, $C' = e\partial n'/\partial V_{GS}$. Radial coordinates bounding physical regions corresponding to these equivalent capacitors are shown, along with the electrostatic potential energy relative to the Fermi energy. The
4.4 Back-gated Nanowires: Theory and Experiment

The planar back-gate, shown in Figure 4.1b, of the fabricated nanowire field-effect transistors breaks the radial symmetry of electrostatic potential in the nanowire FET. The trapped electron samples the electrostatic potential $\Phi(r)$ over a small volume similar to the size of its spatially localized electronic wavefunction. Consequently, the radial asymmetry is expected to play a role and has to be taken into account for quantitative comparison of the dependence of $E_T - E_F$ on gate voltage $V_{GS}$ between theory and experiments.

Calculation of Equation (4.3) was performed in the sub domain shown in Figure 4.7 with Neumann boundary conditions top, left, and right boundaries in the cross section, and a Dirichlet condition for $V_{GS}$. Measured nanowire radii $R$ and gate dielectric thickness $t_{ox}$ are taken into account in Equation 4.3, along with realistic static dielectric constants.

![Figure 4.6: Equivalent circuit diagram for total gate capacitance $C'$ in terms of quantum capacitance $C'_Q$, geometrical capacitance $C'_G$, and the electrostatic contribution $\epsilon_s/F_1$.](image)

additional capacitance $C''_E = \epsilon_s/F_1$ appearing in Figure 4.6 originates from the fact that the uncertainty principle in quantum mechanics prevents charge from approaching arbitrarily close to the semiconductor/dielectric interface. Rather, the charge in the first sub-band spread out spatially due to the uncertainty principle.
Figure 4.7: (a) Electrostatic potential $\Phi(r)$ calculated for $V_{GS} = -0.05$ V for $R = 15$ nm radius nanowire with $V_T = -0.2$ V, showing Neumann and Dirichlet boundary conditions and (b)-(e) Lateral variation of electron density $|\varphi_{m,l}(r,\phi)|^2$ for $\{m,l\} = \{1,0\}, \{1,1\}, \{1,2\}$, and $\{2,0\}$.

for InAs ($\epsilon_s = 15.5\epsilon_0$) and SiO$_2$ ($\epsilon_{ox} = 3.9\epsilon_0$), where $\epsilon_0$ is the vacuum permittivity. Subband energies corresponding to an infinite cylindrical well, $E_{m,l}^0 = \hbar^2 \xi_{m,l}^2/(2m_e R^2)$, are corrected to leading order in $\Phi$, giving

$$E_{m,l} = E_{m,l}^0 + \langle m, l | -e\Phi(r,\phi) | m, l \rangle,$$  \hspace{1cm} (4.12)

with wavefunctions proportional to the cylindrical Bessel functions $J_{|l|}(\xi)$

$$\varphi_{m,l}(r,\phi) = J_{|l|}(\xi_{m,l} r/R) \exp(-il\phi)/(\sqrt{\pi R} J_{|l|+1}(\xi_{m,l})),$$  \hspace{1cm} (4.13)

where $l = 0, \pm 1, \pm 2, \ldots$. Electron densities $|\varphi_{m,l}(r,\phi)|^2$ corresponding to the four lowest energy sub-bands are shown in Figure 4.7b-e. The one-dimensional electron density $n'_{m,l}$
for each sub-band is obtained by integrating over phase space,

\[ n'_{m,l} = 2 \left( 2\pi m_e k_B T / h^2 \right)^{1/2} \mathcal{F}_{-1/2} (\eta_{m,l}), \]

(4.14)

where \( \eta_{m,l} = \beta (E_F - E_{m,l}) \), \( \mathcal{F}_j (\eta) = 1/\Gamma (j+1) \int_0^\infty du u^j (1+\exp (u-\eta))^{-1} \) is the complete Fermi-Dirac integral of order \( j \), and \( \Gamma (x) \) is the gamma function. The effective mass \( m_e \) of electrons is taken from bulk band structure of Zincblende InAs, and \( \xi_{m,l} \) is the \( m \)th root of \( J(|l|) (\xi) \). This approach is justified since only one or two sub-bands should be occupied in the regime of gate voltages and temperatures corresponding to Figure 4.5. Further details are given in Sections 4.4.1 and 4.4.2. Charging of surface states is included using a simple model employing a spatially continuous surface state density with a uniform energy distribution. Here, surface charge density is \( \rho_s = e k_B T D_{ss} \mathcal{F}_{0d} (\eta_s) \) where \( D_{ss} \) is the density of surface states, \( \mathcal{F}_{0d} (\eta_s) = \int_0^\infty du (1+2\exp (u-\eta_s))^{-1} \) describes donor occupation, \( \eta_s = \beta (E_{CNL} - e \Phi (R,\phi) - E_F) \), and \( E_{CNL} \) is a surface charge neutrality level[91, 151].

Although the number of parameters in the theoretical model appears to be large, several of them are fixed by the geometry of the measured sample, and others are fixed using known material parameters for InAs and SiO\(_2\), including band-structure. Essentially, \( D_{ss} \) is the only parameter that tunes \( \alpha (V_{GS}) \). The charge neutrality level \( E_{CNL} \) and fixed background ionized donor concentration \( N_D \) determine only the predicted threshold voltage. [152].

### 4.4.1 Single Switching Defect

Consider the dependence of trap energy on gate voltage for NWa, with diameter=59 ± 2 nm, at \( T = 40 \) K, as shown in Figure 4.5 (squares). A least squares linear fit of trap energy variation gives \( \alpha (V_{GS}) = -0.095\pm0.005 \) eV/V, quite far away from the limit of \( \alpha = -1 \) eV/V corresponding to the situation where the geometrical capacitance dominates. The theoretically calculated variation of trap energy with gate voltage is plotted along
selected angles $\phi$ for NWa in Figure 4.8, together with experimentally extracted trap energy and thermally broadened density of states $\partial n'/\partial E_F$. The planar back-gate has induced significant radial asymmetry in the calculated surface potential in the nanowire for $D_{ss} = 0$, bounding $\alpha$ in the range $-0.165 \text{ eV/V} < \alpha < -0.065 \text{ eV/V}$ for $\phi$ in the full range of $-\pi/2 < \phi < \pi/2$. As expected, trap energies towards the bottom of the nanowire ($\phi = -\pi/2$) vary more rapidly with gate voltage than those on the top ($\phi = \pi/2$), due to the closer proximity to the gate electrode. Nevertheless, the measured trap energy fits well the calculated surface potential when $D_{ss} = 0$ is assumed in the calculation, with slope decreasing as gate voltage increases, in accordance with the increasing density of states. However, the experimentally extracted $\alpha(V_{GS})$ matches the theoretically calculated quantity for a range of surface state densities $0 < D_{ss} < 2 \times 10^{12}$ cm$^{-2}$eV$^{-1}$ corresponding to angles $-\pi/8 > \phi > \pi/2$. The larger surface state densities in this range correspond to the larger angles $\phi$, that is, trap locations towards the top of the nanowire.
The thermally broadened density is obtained by differentiating Equation (4.4) with respect to Fermi energy, giving

\[
\frac{\partial n'}{\partial E_F} = \sum_{m,l} \frac{\partial n'_{m,l}}{\partial E_F} \tag{4.15}
\]

and

\[
\frac{\partial n'_{m,l}}{\partial E_F} = 2\left(\frac{2\pi m_e k_B T}{\hbar}\right)^{1/2} \beta \frac{\partial \mathcal{F}_{-1/2}(\eta)}{\partial \eta}_{|\eta=\eta_{m,l}} \tag{4.16}
\]

The numerically calculated quantities needed for the set of curves \( E_T - E_T^0 = -e\Phi(R,\phi) \) permit evaluation of Equation 4.15, which is plotted for the gate voltages in the experiment on the right Y-axis of Figure 4.8. The peaks at \( V_{GS} - V_T = 0.05 \) V and 0.25 V correspond to the thermally broadened Van-Hove singularities associated with the edges of the two lowest energy sub-bands, \( \{m,l\} = \{1,0\} \) and \( \{m,l\} = \{1,1\} \). The electron density in NWa is only sufficient to fill two sub-bands. Peaks for the density of states at \( V_{GS} - V_T = 0.05 \) V and 0.25 V correspond to quantum capacitances of \( C'_Q = 400 \) and 1000 aF/µm, respectively, still much higher than the gate capacitance of approximately 55 aF/µm.

Experimentally extracted trap energies for NWb with diameter \( d = 28 \pm 2 \) nm are shown in Figure 4.9. A linear fit for the measured variation gives \( \alpha(V_{GS}) = -0.062 \pm 0.007 \) eV/V, and linear fit in the same gate voltage region gives \( \alpha(V_{GS}) = -0.165 \) eV/V and \( \alpha(V_{GS}) = -0.100 \) eV/V for angles \( \phi = -\pi/2 \) and \( \phi = -\pi/2 \), respectively. As expected, the dependence of trap energy on gate voltage is less \( \phi \)-dependent for the smaller diameter nanowire. However, a surface state density of \( D_{ss} = 8 \times 10^{11} \text{cm}^{-2}\text{eV}^{-1} \) is required to obtain a reasonable fit with experiments; otherwise \(|\alpha(V_{GS})|\) is too large. Plotted on the right y-axis in Figure 4.9 shows that the Van-Hove singularity for the first sub-band is significantly thermally broadened, but the the electron density is not sufficient to start filling of the second sub-band at \( V_{GS} - V_T \sim 0.15 \) V in NWb, a consequence of the larger sub-band splitting for the smaller diameter nanowire.
Figure 4.9: Measured variation of trap energy $E_T - E_F$ for NWb at $T = 25$ K (circles) and calculated variation of trap energy using model from main text for angles $\phi = -\pi/2, -3\pi/8, -\pi/4, -\pi/8, 0, \pi/8, \pi/4, 3\pi/8, \pi/2$, with density of states superimposed (Y:left).

### 4.4.2 Two Switching Defects

Another interesting case is that of two traps A and B that are both capturing and emitting electrons in the same nanowire. This process, observed in NWc with diameter $d = 49 \pm 2$ nm at $T = 77$ K, produces a random telegraph signal with four distinct levels of conductance $G_1 < G_2 < G_3 < G_4$ shown as dotted lines in Figure 4.10. Observed transitions in the random telegraph signals are $G_1 \rightleftharpoons G_2$, $G_3 \rightleftharpoons G_4$, $G_2 \rightleftharpoons G_4$, and $G_1 \rightleftharpoons G_3$, but never $G_2 \rightleftharpoons G_3$ nor $G_1 \rightleftharpoons G_4$. A single trap with two active transitions $n - 1 \rightleftharpoons n$ and $n - 1 \rightleftharpoons n$ would produce three levels of conductance and, most likely, three different transitions $G_1 \rightleftharpoons G_2$, $G_1 \rightleftharpoons G_3$ and $G_2 \rightleftharpoons G_3$. Charge transitions on the defects associated with observed conductance transitions are summarized in Table 4.1

Let $t_{ij}$ denote as an interval of time with trap A and B in states $i \in \{0, 1\}$ and $j \in \{0, 1\}$, respectively, where 0 means trap is empty, 1 means it is filled. Using the same principle outlined in Section 4.2.2, defect A’s trapping energy can be evaluated from experimental
Figure 4.10: Random telegraph signal for NWc at $T = 7$ K with four levels of conductance due to capture and emission of electrons from two different defects A and B.

<table>
<thead>
<tr>
<th>Transition</th>
<th>Defect A</th>
<th>Defect B</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_1 \rightleftharpoons G_2$</td>
<td>filled $\rightleftharpoons$ empty</td>
<td>filled</td>
</tr>
<tr>
<td>$G_1 \rightleftharpoons G_3$</td>
<td>filled</td>
<td>filled $\rightleftharpoons$ empty</td>
</tr>
<tr>
<td>$G_2 \rightleftharpoons G_4$</td>
<td>filled $\rightleftharpoons$ empty</td>
<td>empty</td>
</tr>
<tr>
<td>$G_3 \rightleftharpoons G_4$</td>
<td>empty</td>
<td>filled $\rightleftharpoons$ empty</td>
</tr>
</tbody>
</table>

Table 4.1: Mapping of conductance transitions in random telegraph signals to transitions between charge states of two traps A and B
Figure 4.11: Measured trap energy at defect A (red squares) and defect B (blue circles), inferred from times $t_{ij}$, when either trap is either empty (open points) or filled (solid points), and calculated trap energy and density of states $\partial n'/\partial E_F$ for the same gate voltages, from the theoretical model.

Energies are shown in Figure 4.11 for both trap A (squares) and B (circles) when the other trap is filled (solid points) or empty (open points). The symbol size is approximately equal to the measurement uncertainty which stems from the finite number of defect transitions observed per gate voltage. First, the energy level of trap A for the two separate circumstances when trap B is filled ($E_{TA|B1} - E_F$) or empty ($E_{TA|B0} - E_F$) are indistinguishable. That is, the Coulomb repulsion energy at trap A, $\Delta E_A = E_{TA|B1} - E_{TA|B0}$, is similar to the measurement uncertainty for both quantities, which is a few meV. The Coulomb...
repulsion energy at trap B, $\Delta E_B = E_{TB|A1} - E_{TB|A0}$, is negligible and mirrors the same conclusion, as required. Put in a different way, the energy of trap A is not dependent on whether or not trap B is filled with an electron, and vice versa, to within experimental error. For this to be the case, the two defects associated with these trapping levels must be physically located at positions in the nanowire which are several screening lengths apart, or roughly 50 nm under these conditions. Considering that the separation between the source and drain electrodes is 1.2 $\mu$m, it is much more probable that defects in a uniform spatial distribution will be non-interacting.

Second, the rate of change of trap A’s energy with gate voltage $\alpha_A(V_{GS}) = \partial(E_{TA} - E_F)/\partial V_{GS} = -0.149 \pm 0.09$ eV/V is larger in magnitude than the rate of change of trap B’s energy with gate voltage $\alpha_B(V_{GS}) = \partial(E_{TB} - E_F)/\partial V_{GS} = -0.070 \pm 0.05$ eV/V. Theoretical calculations from the model with $D_{ss} = 0$, diameter 49 nm, and $T = 77$ K predict $-0.250 < \alpha(V_{GS}) < -0.169$ eV/V. The calculated trap energy for different angles $-\pi/2 < \phi < \pi/2$ are shown in Figure 4.11 for $D_{ss} = 1.2 \times 10^{12}$ cm$^{-2}$ eV$^{-1}$, one of a small range of surface state densities that is consistent with the data for both traps. Surface potential $\Phi(R, \phi)$ was calculated at several angles $-\pi/2 < \phi < \pi/2$ for fixed values of the surface state density $D_{ss} = 0, 0.4, 0.8, 1.2$ and $1.6 \times 10^{12}$ cm$^{-2}$ eV$^{-1}$. Linear fits were performed to obtain $\alpha$ under each of these conditions, and are plotted in Figure 4.12. Both $\alpha_A(V_{GS})$ and $\alpha_B(V_{GS})$ match the calculated values for only a small range of surface state densities in the model, $D_{ss} = (1.05 \pm 0.25) \times 10^{12}$ cm$^{-2}$ eV$^{-1}$. Results of the surface state density for the three nanowires are summarized in Table 4.2.

### 4.4.3 Discussion

Some general remarks about the measurement method for surface potential are in order. The defect level, whose trapping/detrapping statistics are used to extract surface potential, produces a change in current of 1-10 nA in our 30 – 60 nm diameter InAs NWs at 1 mV bias. This is a consequence of the high sensitivity of conductance of nanowires
Figure 4.12: Plot showing surface state density range $D_{ss} = (1.05 \pm 0.25) \times 10^{12} \text{cm}^{-2} \text{eV}^{-1}$ where $\alpha(V_{GS})$ extracted by a linear fit of the measured data for trap A (red) and trap B (blue) matches the region corresponding to calculations (light blue) bounded by splines passing through values of $\alpha$ calculated for $N_{SS} = 0, 0.4, 0.8, 1.2$ and $1.6 \times 10^{12} \text{cm}^{-2} \text{eV}^{-1}$ (open circles).

<table>
<thead>
<tr>
<th>Nanowire</th>
<th>Diameter (nm)</th>
<th>Temperature (K)</th>
<th>Surface State Density ($\times 10^{12} \text{cm}^{-2} \text{eV}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NWa</td>
<td>59 ± 2</td>
<td>40</td>
<td>0-2</td>
</tr>
<tr>
<td>NWb</td>
<td>28 ± 2</td>
<td>25</td>
<td>0.8-2</td>
</tr>
<tr>
<td>NWc</td>
<td>49 ± 2</td>
<td>77</td>
<td>0.75-1.25</td>
</tr>
</tbody>
</table>

Table 4.2: Summary of surface state densities required for quantitative fit of Trap Energy between experiments and theory.
to localized repulsive charges\cite{154}. In comparison, the gate capacitance $C \sim 100 \text{ aF}$ of a long-channel back-gated nanowire is similar to the error of standard capacitance meters. After all, $C = 100 \text{ aF}$ produces only $dI = 2\pi f C dV \sim 12 \text{ fA}$ of displacement current using a modulation voltage $dV = 10 \text{ mV}$ alternating at $f = 1 \text{ kHz}$, and only $dI = 2\pi f e = 1 \text{ fA}$ displacement current per electron. Moreover, as length of the gate shrinks, $C$ is further reduced making capacitance measurements more difficult, but the changes in conductance due to trapping and emission does not become more difficult to measure.

Additionally, the measured quantity $E_T - E_F$, which can be expressed as $E_T - E_F = e \int dV_{GS} (C/C_G - 1)$ in the coaxial gate case, always increases with increasing surface state density, “stretching out” its dependence on $V_{GS}$ in just the same way that the $C$-$V$ curve is stretched out due to surface/interface states\cite{93}. The surface state density $D_{ss} \approx 10^{12} \text{ cm}^{-2} \text{eV}^{-1}$ estimated in the temperature range 25 – 77 K. This value is higher than those obtained from temperature-dependent C-V measurement of InAs nanowires by Ford et. al.\cite{115}, who also found a freeze out of surface-state modulation at 77 K in their $f = 1$ and 10 kHz capacitance measurements. It is likely that our trap energies include effects of charge redistribution in surface states that are frozen out in their experiments performed at $f = 1 \text{ kHz}$, though differences in sample preparation/measurement cannot be ruled out. Indeed, the method reported herein lends itself naturally to study of slow processes, since arbitrarily long random telegraph signals can be captured, and the capture can take place an arbitrary time after each change of gate voltage.

Most importantly these slow processes can play an important role in $I - V_{GS}$ measurements on nanowires commonly used to estimate field effect mobility, when the sweep time for the gate voltage is comparable to the emission/trapping rate, which could easily be slower than the $C$-$V$ measurement frequency. Therefore, the method described is not only advantageous for measuring gate coupling when there are only a few charges being modulated, but can potentially provide information about slow surface states that
may be even more difficult to obtain by C-V measurements. It is apparent from our self-consistent electrostatic model that for the nanowire field effect transistor’s channel that gate control over the channel, in particular, $\alpha(V_{GS})$ is suppressed from the ideal value for our particular gate geometry by gate-induced modulation of charge in surface states. For NWc with $D_{ss} = (1.05 \pm 0.25) \times 10^{12} \text{cm}^{-2} \text{eV}^{-1}$, a gate voltage modulation $\delta V_{GS} = 100 \text{mV}$ beyond $V_T$ fills $\alpha(V_{GS})\delta V_{GS}2\pi R D_{ss} \approx 15 \text{ electrons/\mu m}$ in surface states and $\int_{V_T}^{V_T+\delta V_{GS}} dV_{GS}\partial n'/\partial E_F \langle \alpha(V_{GS}) \rangle \approx 15 \text{ electrons/\mu m}$ in the conduction band.

The surface potential measurement scheme described herein could easily be used to study electronic structure in nanowires, in particular, Van-Hove singularities or electron-electron interactions, through the connection between surface potential and density of states that is implicit in Equations 4.7 and 4.11. Caution is needed, however, when the gate oxide is very thin (<10 nm), since a contribution to the trap energy from polarization induced on the gate may need to be taken into account[139, 155].

**Comparison with Subthreshold Slope Model**

For gate voltages $V_{GS}$ below the threshold voltage $V_T$ of a field effect transistor, the current flowing from source to drain is proportional to $\exp(e_0(V_{GS} - V_T)/(mk_B T))$, where $m = (C + C_{ss} + C_D)/C$, $C$, $C_{ss}$, and $C_D$ are the gate capacitance, surface-state capacitance, and depletion capacitance, respectively. The change in gate voltage $\Delta V_{GS}$ to obtain a change in current of one decade is called the sub threshold slope, and is given by $S = \ln(10)(mk_B T/e)$. In a nanowire FET, $C_D$ is negligible, and the surface-state capacitance can be estimated by fitting $m$ to the measured current-gate voltage characteristic. The sub threshold characteristic for a typical InAs nanowire is plotted in logarithmic scale in Figure 4.13, with $m \approx 11$ and $S \approx 160 \text{ mV (per decade)}$ at $T = 77 \text{ K}$. The equivalent surface state density $D_{ss}$ in the sub threshold regime can be readily obtained[93, 152] using $D_{ss} \approx e^{-2}C_{ss}/(2\pi R L) \approx 2 \times 10^{12} \text{ cm}^{-2} \text{eV}^{-1}$, similar to the value estimated from the surface potential-gate voltage relationship.
Figure 4.13: Plot of logarithm of conductance vs. gate voltage at $T = 77$ K for typical InAs nanowire field effect transistor, and fit of sub threshold characteristics with $S = 160 \pm 10$ mV/dec.

### 4.5 Electron Capture and Emission Process

The rates for electron capture and emission in random telegraph signals are found to be thermally activated, satisfying $\langle t_H \rangle^{-1} \propto \sigma_{c,\infty} \exp(-\beta E_B)$ and $\langle t_L \rangle^{-1} \propto \sigma_{e,\infty} \exp(-\beta E_X)$ respectively as briefly discussed in Chapter 3, Section 3.4. The multiphonon-emission model developed for capture by deep levels in III-V semiconductors (at first, GaAs and GaP) by Henry and Lang in references [136, 137] predicts just such an activated behaviour. This contrasts the cascade capture[140, 156] and Auger recombination processes[140, 157] which have weak power law temperature dependence.

#### 4.5.1 Multi-phonon Emission

Figure 4.14 is a configuration coordinate diagram of the electronic levels involved in the free-to-bound electronic transition (electron capture) and bound-to-free electronic transition (electron emission). When the electron is in the free state indicated by the blue parabola, and the lattice is in the ground vibrational state at configuration coor-
dinate $Q_1$, the total energy of the electron and the lattice is $E_i$, and the total energy difference between the free and bound electronic states (both evaluated at $Q_1$) is quite significant. Lattice vibrations increase the total energy quadratically in the shift $\Delta Q$ in the configuration coordinate. When there are a sufficient thermal fluctuation away from the equilibrium configuration coordinate such that lattice distortion around the defect is $Q_M - Q_1 \approx \Delta Q$, the two parabolic total energy curves nearly intersect with energy $\approx E_i + E_B$, and the electron-phonon interaction can mediate an electronic transition from the free state to the bound state (electron capture). This thermal-fluctuation increases the total energy by an amount $E_B$, the activation barrier for capture. After the electron capture, the lattice is essentially in the same configuration coordinate $\approx Q_M$ with total energy exceeding the ground vibrational state at configuration coordinate $Q_2$. Consequently, several phonons will be emitted so that the lattice relaxes to the normal coordinate $Q_2$. Theories for multiphonon emission predict capture and emission activation energies $E_B$ and $E_X = E_B + E_0$, respectively[137, 157] and a capture rate

$$\langle t_H \rangle^{-1} = n C_m \exp (-\beta E_B) \quad (4.17)$$

The difference in configuration coordinates of the vibrational ground states of the free and bound electronic states, $Q_1 - Q_2$ implies a total energy difference $S \hbar \omega$, the energy of lattice distortion for a transition. Simple algebraic manipulation of quantities in the configuration coordinate diagram gives $E_B = (E_0 - S \hbar \omega)^2 / 4S \hbar \omega$, where $S$ is the Huang-Rhys factor, the number of phonons of energy $\hbar \omega$ making up the lattice distortion energy $S \hbar \omega$.

### 4.5.2 Temperature Dependence of Capture and Emission Rate

Details are given for two defects observed in NWa. Random telegraph signals were captured for $43 \text{ K} < T < 34 \text{ K}$ and following a temperature cycle up to $300 \text{ K}$ and back to $75 \text{ K}$, for $75 \text{ K} < T < 58 \text{ K}$. Electrons are assumed to be captured from the Fermi
Figure 4.14: Configuration coordinate diagram demonstrating electronic + vibrational energy of free and bound electronic states with thermal equilibrium normal coordinates of $Q_1$ and $Q_2$, respectively. Barrier energy $E_B$ and lattice relaxation energy $S\hbar\omega$ are indicated.

energy $E_F$ of the nanowire, such that $E_0 = E_F - E_T$. Ignoring the possibility that different electronic sub bands may have different capture constants, the mean capture rate is written as

$$\langle t_H \rangle^{-1} = nC_{n0} \exp \left(-\beta \frac{(E_F - E_T - S\hbar\omega)^2}{4S\hbar\omega}\right),$$

(4.18)

where $n = C(V_{GS} - V_T)/(e\pi R^2 L)$ is the electron density in the nanowire, and $C$ is the gate capacitance estimated using Equation 4.2. The capture and emission rates $\langle t_H \rangle^{-1}$ and $\langle t_L \rangle^{-1}$ are both thermally activated, with measured activation energies re-plotted in Figure 4.15a. The measured capture rate is shown in Figure 4.15b for four temperatures $T = 43, 40, 37$ and $34$ K. Using our electrostatic model for $n$ and experimentally measured variation of $E_T - E_F$, we performed least square fits of the capture rate data to the expression, obtaining a capture coefficient $C_{n0} = (1.5 \pm 0.5) \times 10^{-11}$ cm$^{-3}$/s and $S\hbar\omega = 187 \pm 15$ meV corresponding to approximately 8 optical phonons in bulk InAs. The best-fit two-parameter model reproduces very well both the measured gate-voltage dependence of activation energy (Figure 4.15a) and temperature/gate-voltage dependence of capture rate (Figure 4.15b). The temperature dependence of the measured capture rate for the
Figure 4.15: (a) Dependence of activation energies for electron capture (squares, $E_B$) and emission (triangles, $E_X$) by defect in NWa for temperatures $34 < T < 43$ K and least-squares fit of activation energies to multiphonon emission model (lines). (b) Capture rate $\langle t_H \rangle^{-1}$ for NWa at temperatures $T = 43$ (black squares), 40 (red diamonds), 37 (blue triangles), and 34 K (inverted magenta triangles), and least squares fit to expression described in main text.

second defect at 75 K $< T < 58$ K and $V_{GS} = V_T + 1.02$ V, chosen such that the condition $\langle t_H \rangle \approx \langle t_L \rangle$, or equivalently, $E_T \approx E_F$ is obtained, is shown in Figure 4.16. Least squares fit of the capture rate data to $\langle t_H \rangle^{-1} = nC_{n0} \exp(-\beta E_B)$ gives a capture barrier $E_B = 114 \pm 2$ meV. Using $E_B = (E_0 - S\hbar\omega)^2/4S\hbar\omega$ and $E_T - E_F \approx 0$ we obtain $S\hbar\omega \approx 4E_B \approx 460 \pm 50$ meV for this defect.

The capture coefficient is often represented as $C_{n0} = v\sigma_\infty$ where $v$ is the average carrier velocity and $\sigma_\infty$ is the capture cross section. Experimentally we find that carrier concentration is essentially temperature independent in the regime of Figure 4.15, and the calculated Fermi velocity $v_F = \hbar/m_e(3\pi^2n)^{1/3} \approx 5 \times 10^7$ cm/s exceeds the thermal velocity $v_{th} = \sqrt{3k_B T/m} \approx 3 \times 10^7$ cm/s of carriers, so $v = v_F$ is used, giving $\sigma_\infty \approx 3 \times 10^{-19}$ cm$^2$. The second defect in Figure 4.16 has $\sigma_\infty \approx (2.2 \pm 1.1) \times 10^{-17}$ cm$^2$. Cross sections $10^{-19} - 10^{-17}$ cm$^2$ are a bit low for electronic deep levels in semiconductors, but not for bound electronic states at the border of or just inside the 2-3 nm thick disordered native
Figure 4.16: Fit of capture rate data to $(t_H n v_F)^{-1} = \sigma_\infty \exp(-\beta E_B)$ for NWa at $V_{GS} - V_T = 1.02$ V for temperatures $75 \text{ K} < T < 58 \text{ K}$.

oxides[158] InO$_x$ and AsO$_x$ or at their interface InAs nanowire. In this case, the modulus squared of the transition matrix element between the free and bound state, encapsulated by $C_{n0}$ in the theory, can be dramatically suppressed[138, 139].

4.6 Conclusions

The gate-voltage dependence of surface potential of InAs nanowires was investigated by a novel method, using the statistics of electronic occupation of one or two surface traps, inferred from a random telegraph signal. The method provides direct insight into surface potential modulation in nanowires, of much relevance for nanoelectronic and sensing applications. Measured quantities were reconciled with a theoretical model, requiring surface state density $D_{ss} \approx 10^{12} \text{ cm}^{-2}\text{eV}^{-1}$ for quantitative agreement. The temperature dependence of the electron capture and emission dynamics was used to determine the lattice relaxation energy $S\hbar \omega = 187 \pm 15$ meV and an approximate capture cross section $3 \times 10^{-19} \text{ cm}^2$ for a defect responsible for RTS. Based on the values of the electron capture cross sections measured it is reasonable to assume that the traps are located inside the
disordered native oxides[158] InO$_x$ and AsO$_x$ or at their interface with the InAs nanowire. Controlled electronic passivation of the InAs surface to reduce surface state density and improve electronic mobility is a topic of much current interest[159, 160, 161]. Further improvement of gate control over the channel and electronic mobility are likely as growth and passivation methodology for bare InAs and InAs core/shell nanowires improves. The measured field effect mobility of our bare InAs nanowires is identical to the highest reported values for InAs[115, 159, 161], within errors related to estimation methodology.
Chapter 5

Spectroscopic Measurement of Strong Carrier Reflection by a Single Charge in a Size Quantized Semiconductor Nanowire

5.1 Introduction

Not long after it became possible to study the optical properties of individual semiconductor nanocrystals, it was discovered that charging/discharging of a single trap can completely quench/restore the photo-luminescence of a single CdSe nanocrystal with diameter \( \approx 2 \text{ nm}[128] \). Such processes produce the so-called blinking noise in the luminescence of individual nanocrystals, first observed as intermittence of the photoluminescence signal from a single nanocrystal. Efros et. al. found that the non radiative Auger recombination that occurs when a trap in the nanocrystal is ionized well exceeds the direct radiative rate, quenching the time-averaged radiative recombination, and that such a model could quantitatively reproduce characteristics of bright and dark states observed in blinking
noise experiments[162]. The discreteness of the observed signals of photoluminescence versus time in nanocrystals is not unlike what is expected for individual molecules, as first demonstrated by Basche et. al.[163]. Later, similar experiments showed that semiconductor nanorods[164] and even semiconductor nanowires[165] exhibit similar blinking noise in luminescence.

While disorder originating from ensembles of scatterers emerges in the transport properties of InAs nanowires[166, 167, 168], the relative contributions of scattering by different discrete imperfections has not yet been studied. While step-like features have been observed in the conductance of in Ge/Si core/shell nanowires[124], there is very little evidence for ballistic transport in InAs nanowires. Although Fabry-Pérot resonances have been observed in InAs nanowires[123], no unambiguous sequence of plateaus starting from the first mode have been reported. Rather, properties of nanowires at 4 K seem to be dominated by disorder and there are several studies of weak localization and antilocalization[166, 167, 168], the constructive interference of diffusive time-reversed paths in disordered conductors. In these experiments, the electronic coherence time is often extracted, but the exact nature of the disorder that causes weak localization is not known. Moreover, scattering by a static disorder potential such as that of a trapped electron does not destroy electronic coherence. Other processes including electron-electron interactions and electron scattering by phonons are responsible. Another examples of the signature of ensembles of scatterers is present in the work of Schroer[100], who studied the effect of high densities of stacking faults present in InAs nanowires grown by MOVPE. These planar defects were found to have a tremendous influence on carrier transport at 4.2 K, where tunneling between many Coulomb islands was observed[100].

Meanwhile, it was pointed out in Chapter 3 that random telegraph signals tell us the effect of a single Coulomb scattering centre on the conductance of a nanowire, affording a rare and completely unambiguous connection between transport properties and the smallest amount of localized Coulombic imperfection. Scattering from Coulomb impuri-
ties InAs nanowires is expected to differ from that of typical quantum wires and quantum point contacts in several respects

1. Vacuum dielectric surroundings of nanowire will enhance Coulomb interaction\[169\].

2. Small diameter \( \approx 30 \) nm and effective mass of InAs resulting in large sub-band quantization energies \( \approx 50 \) meV.

3. Nanowire radius is similar to electronic screening length for not so low carrier densities, so that weaker screening is expected.

4. Close proximity of scatterers to the electron gas.

Here we study the gate voltage (and Fermi energy) resolved single-impurity reflection probability. The reflection probability at low electron densities \( n \approx 10 – 30 \) \( \mu \)m, shown in Table 5.1, are very close to unity at \( T = 30 \) K, such that a single impurity can create an electrically insulating state in a nanowire that is essentially still degenerate. In other words, the electrostatic potential produced by one trapped electron can create a weak link of electrical conduction in an otherwise conductive nanowire at 30 K.

We compare the experimental results with microscopic theory of scattering with self-consistent screened Coulomb potentials in nanowires with cylindrical symmetry. The results directly demonstrate that dielectric confinement enhances carrier scattering by

<table>
<thead>
<tr>
<th>Diameter (nm)</th>
<th>Temp (K)</th>
<th>( V_{GS} - V_T ) (mV)</th>
<th>( n / \mu m )</th>
<th>( R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \approx 30 )</td>
<td>30</td>
<td>50</td>
<td>10</td>
<td>0.999</td>
</tr>
<tr>
<td>( \approx 30 )</td>
<td>30</td>
<td>100</td>
<td>20</td>
<td>0.995</td>
</tr>
<tr>
<td>( \approx 30 )</td>
<td>30</td>
<td>150</td>
<td>30</td>
<td>0.980</td>
</tr>
</tbody>
</table>

Table 5.1: Reflection probability upon scattering by a single Coulomb impurity for different gate voltages (carrier concentrations) at \( T = 30 \) K.
an order of magnitude for repulsive impurities. The effect of dielectric confinement is so dramatic that Lindhard screening theory fails completely in the low electron density regime. Under the same circumstances electron back-scattering from ionized acceptor-like states with repulsive potentials is significantly stronger than electron scattering by ionized donor-like states with attractive potentials.

Altogether the experiments in this chapter provide a direct experimental observation of the carrier reflection from single impurities in one dimensional semiconductor nanostructures. The theoretical framework predicts the carrier a scattering strength in very good agreement with experiments provided that dielectric confinement is included, illustrating the considerable importance of this effect. Without dielectric confinement, the signature strong scattering of experiments is underestimated considerably. The combined experiments and theory elucidate a new aspect of scattering by individual dopants in nanostructures, a very important issue in nanoelectronics and nano-sensing applications.

5.1.1 Scattering of Electrons by Individual Coulomb Impurities in Semiconductor Nanowires

In Chapter 1 we discuss Landauer’s connection between transmission probability and conductance for a quasi-one-dimensional (Q1D) electrical conductor. By simple extension, gate spectroscopy of the conductance tells us about the Fermi energy dependence of electronic scattering. This concept is readily specialized to the case of a localized charge fixed at a position $\mathbf{r} = \mathbf{r}_0$ inside a nanowire or on its surface. The fixed charge produces a static scattering potential $U(\mathbf{r} - \mathbf{r}_0)$ that is strong in the vicinity of $\mathbf{r}_0$ and decays with increasing $|\mathbf{r} - \mathbf{r}_0|$ with a characteristic length scale, the Thomas-Fermi screening length. As the radius $R$ shrinks, classical paths for electrons sampling the wings of the potential $U(\mathbf{r} - \mathbf{r}_0)$ become fewer due to the cylindrical confinement, and a greater majority of the possible paths sample the stronger parts of the potential $U(\mathbf{r} - \mathbf{r}_0)$. The scattering
potential encountered by electrons due to a localized charge is not the bare Coulomb potential $U_a(r - r_0)$ of that charge. Rather, the conducting electrons reorganize themselves in space according to their interaction with the trapped electron, balanced by their mutual repulsive interactions with each other. This process produces a total scattering potential $U(r - r_0)$, as seen by an electron in any particular conducting state, which is the superposition of potentials created by the bare impurity and the reorganized charge in the carrier gas. The screening effect in general weakens as dimensionality reduces from 3D to 2D, and from 2D to 1D, for two reasons. First, not all possible field lines of interaction between the fixed charge and mobile charges are screened by electrons in 2D, and even fewer are screened in 1D. Second, screening is modified by changes to electronic density of states. In addition, the Coulomb interaction and exciton binding energy in one-dimensional structures embedded in a material with low dielectric permittivity are much larger than the corresponding values compared with when the surroundings have an identical permittivity [169, 170]. This stronger Coulomb interaction in nanowires surrounded by low dielectric constant environments has been predicted to reduce carrier mobility in nanowires[171]. In this chapter we will show that in the case of semiconductor nanowires where the electron density approaches the screening length, dielectric confinement produces a situation of considerably weaker screening which can result in nearly two orders of magnitude enhancement of reflection probability of electrons at repulsive potentials at moderate temperatures.

5.2 Experimental Results

Several nanowires of diameter $d \approx 25 - 60$ nm and ohmic contacts deposited $L = 1000$ nm apart were measured at temperatures between 30 and 200 K. For InAs nanowires exhibiting random telegraph signals, high and low conductance states were extracted from random telegraph signals with several hundred transitions taken at several fixed
gate voltages within a few hundred mV of the threshold voltage \( V_T \), using the procedure described in Chapter 3. Example random telegraph signals with two well defined conductance levels measured with an AC bias \( V_{DS} < k_B T \) are shown in Figure 5.1a for NW1 \( (d = 28 \pm 2 \text{ nm}) \) at \( T = 25 \text{ K} \) and \( V_{GS} - V_T = 0.115 \text{ V} \) and in Figure 5.1b at \( T = 198 \text{ K} \) and \( V_{GS} - V_T = 0.340 \text{ V} \). The gate voltage dependence of the mean conductances \( G_H \) and \( G_L \) in the high and low conductance state respectively, extracted as described in Chapter 3, are shown in Figure 5.3a for InAs NW3 \( (d = 59 \pm 2 \text{ nm}) \) at \( T = 34 \text{ K} \), Figure 5.3b for InAs NW2 \( (d = 33 \pm 2 \text{ nm}) \) at \( T = 31 \text{ K} \), in Figure 5.3c for InAs NW1 \( (d = 28 \pm 2 \text{ nm}) \) at \( T = 25 \text{ K} \). Large changes in conductance \( \Delta G \equiv G_H - G_L \approx 0.1G_0 \), with \( G_0 = 2e^2/h \), are obtained for both 30 nm diameter nanowires, but trapped charges have a relatively smaller effect \( \Delta G \approx 0.02G_0 \) on NW3 of 60 nm diameter. As explained in Chapter 3, the relative probability of \( \langle t_H \rangle / \langle t_L \rangle \) spent in the state with high conductance \( G_H \) increases with decreasing gate voltage. Since electronic occupation probability of any state in the

Figure 5.1: (a) Gate voltage dependence of high and low conductance states \( G_H = 0.111G_0 \) and \( G_L = 0.008G_0 \) for InAs NW1 \( (d = 28 \pm 2 \text{ nm}) \) at \( T = 25 \text{ K} \) at \( V_{GS} - V_T = 0.115 \text{ V} \) and (b) Gate voltage dependence of high and low conductance states \( G_H = 0.24G_0 \) and \( G_L = 0.15G_0 \) for InAs NW at \( T = 198 \text{ K} \) and \( V_{GS} - V_T = 0.340 \text{ V} \).
Figure 5.2: Gate voltage dependence of high and low conductance states $G_H$ and $G_L$ for (a) InAs NW3 $(d = 59 \pm 2 \text{ nm})$ at $T = 34 \text{ K}$, (b) InAs NW2 $(d = 33 \pm 2 \text{ nm})$ at $T = 31 \text{ K}$, (c) InAs NW1 $(d = 28 \pm 2 \text{ nm})$ at $T = 25 \text{ K}$. 
nanowire decreases with decreasing gate voltage, the low conductance state results from charging the trap state with an additional electron. From the gate capacitance $C \approx 45$ aF/$\mu$m of a 30 nm diameter nanowire back-gated through 100 nm of SiO$_2$, we find that the average carrier number exceeds 20 for $V_{GS} \gtrsim 0.1$ V. Therefore, the conductance change cannot be ascribed to a change in electron density. Rather, a weak link of conductance $G_D \ll G_H$ is formed in the nanowire near the charged defect $r = r_0$ due to the scattering potential $U(r - r_0)$ it produces. Assuming a model where the nanowire's low conductance state can be described by classical (phase-incoherent) conductors in series, we obtain $G_D = (G_L^{-1} - G_H^{-1})^{-1}$, which depends exponentially on $V_{GS}$ as shown in Figure 5.3 for NW1-NW3. Such a model can be justified since electronic coherence length is expected to be less than the nanowire length at 30 K[166, 167, 168]. This is a clear signature of thermally activated electron transport over a barrier many $k_B T$ above the Fermi energy, as illustrated in Figure 5.4. The only carriers with sufficient energy to overcome the barrier are in the tails of the Fermi-Dirac distribution. The lower energy states with higher occupation probability are reflected with a high probability $R = 1 - G_D/G_0$ where
$G_0 = N2e^2/h$, and $N$ is the number of occupied electronic sub-bands. In other words, the scattering potential $U(r)$ prevents formation of a delocalized states connecting the source and drain electrodes at $E_F$. From Figure 5.3 we see that the reflection probability $R = 0.999$ at $V_{GS} - V_T = 0.05$ ($n \approx 10 \text{ e}/\mu\text{m}$) and $R = 0.995$ at $V_{GS} - V_T = 0.1 \text{ V}$ ($n \approx 20 \text{ e}/\mu\text{m}$) in NW1 and NW2 with $d \approx 30 \text{ nm}$. For the same gate voltage $V_{GS} - V_T$, $G_D$ is larger (reflection probability smaller) by more than an order of magnitude for NW3 ($d = 60 \text{ nm}$ diameter) compared with NW1 and NW2, clearly demonstrating a weaker effective barrier experienced by carriers in the larger diameter nanowire. We also conclude that the defect is acceptor-like in nature, since only a repulsive impurity should be able to reflect carriers so efficiently at a temperature $T \approx E_F/k_B$. Moreover, the apparently relatively weak scattering of electrons by the large number of ionized donors responsible for the carrier gas reveals an essential asymmetry in electron scattering by a single attractive and single repulsive Coulomb impurity in a small-diameter nanowire.

This carrier scattering can be further understood by considering other energy and spatial scales relevant for carrier transport. First, the estimated energy quantization between the first (1s) and second (1p) electronic sub-bands $E_{1p} - E_{1s} \approx 50 \text{ meV}$ well exceeds the thermal broadening $k_BT = 2.6 \text{ meV}$ for both NW1 and NW2. Moreover, the linear carrier concentration $n \lesssim 20 /\mu\text{m}$ (gate voltage $V_{GS} - V_T \lesssim 100 - 200 \text{ mV}$) is much less than the carrier density $n_{1p} \approx 130 /\mu\text{m}$ (gate voltage $V_{GS} - V_T \lesssim 600 - 800 \text{ mV}$) at
the onset of starting to fill the second (1p) band. All available evidence therefore points
to operation in the one-dimensional limit of electronic structure. Finally, the mean free
path of carriers $L_{MFP}$ is expected to be less than the nanowire length $L = 1000$ nm in
the high conductance state, since fully quantized steps in conductance are not observed.
As will be discussed in Section 5.4, the effective transmission probability due to multiple
scattering in the 1000 nm long nanowires is estimated to be in the range of $T \approx 0.1 - 0.2$.

Besides their quantization energy greatly exceeding what is typically achieved in tra-
ditional quantum wires and quantum point contacts, a major distinction of $d \approx 30$ nm
back-gated InAs semiconductor nanowire field-effect transistors is their vacuum/SiO$_2$
dielectric environment which has a significantly lower permittivity compared with InAs.
This situation, sometimes called dielectric confinement, is known to enhance Coulomb
interaction[169] and excitonic binding energy[170]. The case of electron scattering by
individual Coulomb impurities in transport experiments on nanowires is also quite in-
teresting, since the Coulomb interaction between conducting electrons and the repul-
sive impurity, and the mutual interaction between conducting electrons should both be
enhanced. A clue that electronic screening effects will be important is the estimated
Thomas-Fermi screening length, evaluated using the long wavelength limit of the linear
Lindhard theory in Section 5.3.2 and plotted in Figure 5.3, is similar to the radius of the
nanowires. Experimental confirmation that size effects are present in spectroscopic tran-
smision through the repulsive barrier are apparent - the larger threshold voltage shifts
observed for the smaller diameter nanowires in Figure 5.2, or equivalently, the higher
reflection probability of the smaller diameter nanowires in Figure 5.3. The problem is
considered theoretically below, and in Section 5.4 we see that dielectric confinement is
essential for the shift in threshold voltage apparent between $G_H$ and $G_L$ at the low carrier
densities in Figure 5.2.
5.3 Coulomb Scattering in Nanowires

The problem of calculating the electronic transmission through an open system with several scatterers can be considered as a problem of scattering through several smaller subsystems, each consisting of one scatterer, cascaded together. A random telegraph signal represents the difference in conductance of the nanowire shown schematically in Figure 5.5b when the applied potential experienced by carriers differs by a single Coulomb impurity. In one dimensional conductors it is particularly convenient to represent the subsystems as matrices $M(E)$ that describe the relationship between right and left fluxes of carriers of energy $E$ incident on the scatterer, $a(z,E)$ and $b(z,E)$ respectively, in Figure 5.5b.

$$\begin{pmatrix} a(z_2,E) \\ b(z_2,E) \end{pmatrix} = \begin{pmatrix} M_{11}(E) & M_{12}(E) \\ M_{21}(E) & M_{22}(E) \end{pmatrix} \begin{pmatrix} a(z_1,E) \\ b(z_1,E) \end{pmatrix}$$ (5.1)

The special cases of coherent and incoherent transport are distinguished by what quantities $a$ and $b$ represent. In the case of incoherent transport the phase of the wavefunction is assumed to be randomized sufficiently by its environment between consecutive scattering events that it can be ignored. In this case, quantities $a$ and $b$ represent transmission probabilities. However, when the phase of the electronic wavefunction is preserved for the duration of cascaded scattering processes, $a$ and $b$ represent transmission probability amplitudes[172]. Phase coherent carrier transport effects such as weak localization, weak anti-localization, and universal conductance fluctuations are negligible in InAs at 30 K[166, 167, 168]. We therefore assume the presence of some phase breaking process between successive scattering events for the calculation of the overall transmission probability of carriers through the nanowire. Due to the small bias $V_{DS} \approx k_BT$, the transmission probabilities $T_R$ and $T_L$ for right-moving and left moving flux are the same and we define $T = T_L = T_R$. By definition, the transmission probabilities satisfy $a(z_2) = Ta(z_1) + (1-T)b(z_2)$ and $b(z_1) = (1-T)a(z_1) + Tb(z_2)$, and therefore

$$M_{11} = (2T - 1)/T,$$ (5.2a)
Figure 5.5: (a) Nanowire with two leads and repulsive scattering potential for its majority carriers. (b) Cascaded transmission matrix method for computing conductance of nanowire with several scatterers along length of nanowire.
\[ M_{21} = -(1 - T)/T, \quad (5.2b) \]
\[ M_{12} = (1 - T)/T, \quad (5.2c) \]
\[ M_{22} = 1/T. \quad (5.2d) \]

Cascading matrix elements with transmission probabilities \( T_1 \) and \( T_2 \) produces an overall transmission probability
\[ T = \frac{T_1 T_2}{T_1 + T_2 + T_1 T_2} \quad (5.3) \]
when there is no energy relaxation between scattering events, and
\[ T = (T_1^{-1} + T_2^{-1})^{-1}. \quad (5.4) \]
when there is an energy relaxation mechanism[95]. Multiplying Equation 5.4 on both sides by \( G_0 = 2e^2/h \) we obtain the formula for two diffusive conductors in series, when the total applied bias is shared between them. The conductance in the low bias case is obtained by integrating the transmission function[95],
\[ G = \frac{2e^2}{h} \int dET(E) \left( -\frac{\partial f(E)}{\partial E} \right). \quad (5.5) \]

The transmission probability \( T(E) \) for electrons in the lowest sub-band of a cylindrical nanowire due to the screened Coulomb potential \( U(z) \) is calculated at the level of the envelope function approximation described in Chapter 1. In experiments, the strongest scattering effects from individual impurities are observed for gate voltages within \( \approx 200 \) mV of the threshold voltage in our gate configuration with \( t_{ox} = 100 \) nm, where only the first electronic sub-band should be occupied (see Chapter 4). Therefore, the higher electronic sub-bands of the nanowire are neglected in scattering calculations. Following references [117] and [173], changes in the transverse part of the envelope wavefunction are neglected in the scattering calculation, which affords tremendous simplifications in the analysis and computational requirements. Within this set of approximations, the envelope wavefunction
\[ \Psi(r) = \phi(z)\varphi_0(r, \theta), \quad (5.6) \]
obeys an effective mass Schrödinger equation along $z$ the direction parallel to the axis of the nanowire,

$$\frac{\hbar^2 \hat{k}_z^2}{2m} \phi(z) \varphi_0(r, \theta) = U(r) \phi(z) \varphi_0(r, \theta) = E \phi(z) \varphi_0(r, \theta).$$

(5.7)

Here, $\phi(z)$ is the envelope wavefunction along the length of the nanowire and $\varphi_0(r, \theta)$ is the transverse envelope wavefunction for the lowest energy sub-band, which satisfies

$$\frac{\hbar^2 (\hat{k}_x^2 + \hat{k}_y^2)}{2m} \varphi_0(r, \theta) = \frac{\hbar^2 \kappa_0^2}{2m} \varphi_0(r, \theta).$$

(5.8)

Forming the inner product by applying the operator $\int \int r \, dr \, d\theta \varphi_0^*(r, \theta)[.]$ we obtain an effective one-dimensional potential Schrödinger equation

$$\frac{\hbar^2 \hat{k}_z^2}{2m} \phi(z) + U(z) \phi(z) = \left( E - \frac{\hbar^2 \kappa_0^2}{2m} \right) \phi(z).$$

(5.9)

Here, $\hat{k}_z = -i d/dz$ is the operator for the $z$ component of the wavevector and

$$U(z) = \int r \, dr \, d\theta |U(r)| \varphi_0(r, \theta)^2$$

(5.10)

is an effective one dimensional potential which, for convenience, is distinguished from the three dimensional potential $U(r)$ by the scalar (rather than vector) position argument. Transmission and reflection probabilities are obtained by direct solution of the envelope functions $\phi(z)$, avoiding problems associated with the Born approximation in one-dimensional conductors[174]. The so-called open boundary conditions[175] are applied for incoming traveling waves with wavevector $k_z$ and energy $E = \hbar^2 k_z^2 / 2m$ relative to the band edge $E = \hbar^2 \kappa_0^2 / 2m$ predicted by the EFA. That is, electrons with $k_z > 0$ incident on the scattering potential from the left hand side, satisfy a traveling wave solution with and envelope function

$$\phi_E(z) = (1/\sqrt{\ell}) \exp(i k_z z) + (r(E)/\sqrt{\ell}) \exp(-i k_z z)$$

(5.11)

for $z$ sufficiently to the left of the impurity, and

$$\phi_E(z) = (t(E)/\sqrt{\ell}) \exp(i k_z z)$$

(5.12)
for \( z \) sufficiently to the right of the impurity. Here, \( t(E) \) and \( r(E) \) are probability amplitudes for transmission and reflection, respectively, of electrons with energy \( E \) incident on the scattering potential. Recall that the total transmission probability for the first sub-band is obtained by integrating the transmission probability \( T(E) = |t(E)|^2 \), see Equation 5.5. The analogous set of boundary conditions is used for waves incident from right hand side contact with \( k < 0 \).

Transmission and reflection probability amplitudes in these solutions are essentially determined by the scattering potential \( U(z) = \int \int r dr d\theta U(r)|\varphi_0(r, \theta)|^2 \) which includes the effective applied (or bare) potential \( U_a(z) \) due to only point charge \( Q \), and the potential \( U_s(z) \) due to the screening response of the electron gas. In both the Lindhard and the Hartree exact mean-field screening that are considered herein, the scattering potential \( U(r) = -e\Phi(r) \) due to a point charge \( Q \) located at \( r = r_0 \) satisfies Poisson’s equation

\[
\nabla \cdot (-\epsilon(r) \nabla U(r)) = e^2 n(r) - e^2 n_D - eQ \delta(r - r_0) \quad (5.13)
\]

where \( n(r) \) is the electron density and \( n_D \) is the doping density. The exchange and correlation reviewed in Chapter 1, Section 1.4.1 can be taken into account in the electron density \( n(r) \) by introducing a suitable exchange-correlation potential, which modifies the effective 1D Schrödinger equation 5.9 but leaves 5.13 unchanged.

In all cases, the electron density can be written as a sum over densities of the occupied envelope functions, which are described by Equation 5.9 and the open boundary conditions given in Equations 5.11 and 5.12, \( i.e. \)

\[
n(r) = 2 \sum_k f(E(k))|\phi_{E(k)}(z)|^2|\varphi_0(r, \theta)|^2.
\]  

(5.14)

Here, \( f(E) = (1 + \exp(\beta(E - E_F)))^{-1} \) is the Fermi-Dirac distribution describing the probability of occupation of the incident wave.
5.3.1 Bare Coulomb Potential Including Dielectric Mismatch

Calculation of the the Lindhard and the exact mean field screened potentials as described in Sections 5.3.2 and 5.3.3 requires an effective one-dimensional potential energy

\[ U_a(z) = \int \int r \, dr \, d\theta |\varphi_0(r, \theta)|^2 U_a(r) \]  

(5.15)

for the unscreened (or bare) Coulombic interaction with a point charge, \( U_a(r) = -e\Phi(r) \).

Consider a homogeneous dielectric rod of radius \( R \), and dielectric constant \( \epsilon_{in} \) for \( r < R \), surrounded by a medium of dielectric constant \( \epsilon_{out} \) for \( r \geq R \), with a charge \( Q \) located at \( r = r_0 \), as depicted in the inset of Figure 5.6. Inside the cylinder, the potential \( \Phi(r) \) satisfies

\[ -\epsilon_{in} \nabla^2 \Phi(r) = Q\delta(r - r_0), \]  

(5.16)

and at the boundary \( r = R \)

\[ \Phi |_{r \to R^-} = \Phi |_{r \to R^+} \]  

(5.17a)

\[ \epsilon_{in} \frac{\partial \Phi}{\partial r} |_{r \to R^-} = \epsilon_{out} \frac{\partial \Phi}{\partial r} |_{r \to R^+}. \]  

(5.17b)

Motivated by the dielectric structure’s cylindrical symmetry and translational invariance along \( z \), a solution of the form

\[ \Phi(r, r_0) = \sum_q \exp(iq(z - z_0)) \sum_{n=-\infty}^{\infty} \exp(in\theta) \Phi_n(r, r_0, q), \]  

(5.18)

where \( y/x = \tan(\theta) \) and \( r = \sqrt{x^2 + y^2} \), is substituted in the Poisson Equation 5.16. The resulting cylindrical Bessel equation has an inhomogeneous point charge term,

\[ \left( \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} - \left( k^2 + n^2/r^2 \right) \right) \Phi_n(r, r_0, k) = -\frac{Q}{2\pi r\ell\epsilon_{in}}. \]  

(5.19)

The solution provided in reference [170] is outlined below. Each component \( \Phi_n(r, r_0, q) \) is written as the sum of an the inhomogeneous term \( \Phi_{in}^n(r, r_0, q) \) that satisfies Equation 5.16 for all space, and a homogeneous term that satisfies \( -\nabla^2 \Phi_{hom}^n(r) = 0 \). The boundary conditions at \( r = R \) in Equations 5.17a-5.17b are applied to the sum of homogeneous and
inhomogeneous parts and demanding that the total potential decays to zero as $r \to \infty$.

For $r, r_0 \leq R$,

$$
\Phi_n(r, r_0, q) = \Phi_n^{\text{in}}(r, r_0, q) + \Phi_n^{\text{hom}}(r, r_0, q) \quad (5.20)
$$

$$
\Phi_n^{\text{in}}(r, r_0, q) = \frac{Q}{2\pi \epsilon_{\text{in}}} \frac{I_n(k \min(r, r_0))K_n(k \max(r, r_0))}{I_n(k_{\min})(k_{\max})} \quad (5.21)
$$

$$
\Phi_n^{\text{hom}}(r, r_0, q) = \frac{Q}{2\pi \epsilon_{\text{in}}} C_n(r_0, R, k) I_n(kr) \quad (5.22)
$$

$$
C_n(r_0, R, k) = \frac{(\epsilon_{\text{in}} - \epsilon_{\text{out}})(K_n(kR)K_n'(kR)I_n(kr_0))}{\epsilon_{\text{out}} I_n(kR)K_n'(kR) - \epsilon_{\text{in}} I_n'(kR)K_n(kR)} \quad (5.23)
$$

where $I_n(x)$ and $K_n(x)$ are modified Bessel functions of order $n\[176\]$. Only $n = 0$ survives the integral for a nanowire with cylindrical symmetry, since $|\varphi(r, \theta)|^2$ is a function of $r$ only. The effective one-dimensional potential of Equation 5.15 is

$$
U_a(z) = -\frac{eQ}{2\pi \epsilon_{\text{in}}} \left( \int \int rdrd\theta |\varphi_0(r, \theta)|^2 I_n(k \min(r, r_0))K_n(k \max(r, r_0)) + C_0(r_0, R, k) \int \int rdrd\theta |\varphi_0(r, \theta)|^2 I_n(kr) \right) \quad (5.24)
$$

For a nanowire with diameter $d$ exceeding a few nanometers, the bulk permittivity is appropriate$[79]$, which is $\epsilon_{\text{in}} = 15\epsilon_0$ for InAs. The effective one-dimensional bare potential for $\epsilon_{\text{out}} = \epsilon_0$ is compared with the bare potential assuming $\epsilon_{\text{in}} = \epsilon_{\text{out}} = 15\epsilon_0$, in Figure 5.6 for $R = 15$ nm, a near-surface impurity at $r_0 = R - 2$ nm and $z_0 = 0$, and a ground-state envelope wavefunction of $\varphi_0(r, \theta)$ corresponding to a cylindrical hard-wall potential

$$
\varphi_0(r, \theta) = \frac{J_0(\kappa_0 r)}{J_1(\kappa_0 R)\sqrt{\pi R}} \quad (5.25)
$$

with $\kappa_0 = 2.4048/R$. The bare Coulomb interaction is enhanced by a factor of five in the case of vacuum surroundings, compared with homogeneous dielectric $\epsilon_{\text{in}} = \epsilon_{\text{out}} = 15\epsilon_0$ due to Coulomb interaction by field lines penetrating the surrounding vacuum, which are not attenuated by dipoles. Interestingly, the effective bare potential in the case of vacuum dielectric surroundings is larger in the wings compared with the effective bare Coulomb potential for a fictitious quantum wire with $\epsilon_{\text{in}} = \epsilon_{\text{out}} = \epsilon_0$, also shown in Figure 5.6.
Figure 5.6: Effective 1D Coulomb potential $U_a(z)$ for $\epsilon_{\text{in}} = 15\epsilon_0$ and $\epsilon_{\text{out}} = \epsilon_0$ (solid line), $\epsilon_{\text{out}} = \epsilon_{\text{in}} = 15\epsilon_0$ (dotted line) and $\epsilon_{\text{out}} = \epsilon_{\text{in}} = \epsilon_0$ and (dashed line), for near surface impurity for $R = 15$ nm. Inset: Dielectric nanowire with $L \to \infty$ with dielectric constant $\epsilon_{\text{in}}$ inside and $\epsilon_{\text{out}}$ outside.
5.3.2 Linear Mean Field Screening: Lindhard

The first method for determining the self consistent scattering potential $U(z)$ is similar in spirit to that of Lindhard[177], but modified for use with quantum wires[117, 173, 171]. Here, the charge density is corrected to first order in the self-consistent potential. This well known result states that change in charge density is given by

$$\Delta n(r) = \sum_{\alpha,\alpha'} \rho_{\alpha',\alpha}' \Psi_{\alpha'}(r)\Psi^\ast_{\alpha}(r)$$

(5.26)

where $\Psi_{\alpha}(r)$ are the stationary states of the unperturbed system and

$$\rho_{\alpha',\alpha}' = \frac{f(E'_{\alpha}) - f(E_{\alpha})}{E'_{\alpha} - E_{\alpha}} \langle \alpha' | U | \alpha \rangle$$

(5.27)

is the perturbation to the density matrix due to the self consistent potential $U(r)$. We define $U_{s}(r)$ as the potential due to the change in electronic density induced by the bare Coulomb scatterer’s potential $U_{a}(r)$, which satisfies a slightly different Poisson equation given by

$$\nabla \cdot (-\epsilon(r)\nabla U_{s}(r)) = e^2 \Delta n(r).$$

(5.28)

Fourier expanding $U_{s}(r)$ according to

$$U_{s}(r) = \sum_{q} U_{s}(r, \theta, q) \exp(iqz),$$

(5.29)

taking the unperturbed envelope functions $\Psi_{\alpha}(r)$ as described in Equation 5.6 with

$$\phi_{E(k)}(z) = (1/\sqrt{\ell}) \exp(ikz)$$

and assuming $\epsilon(r)$ and $|\phi_0(r, \theta)|^2$ are functions of $r = \sqrt{x^2 + y^2}$ only, we obtain the desired result for the $U_{s}(r, q)$ in terms of the Fourier components of the self-consistent potential $U(q) = \langle k + q, 0 | U(r) | k, 0 \rangle$,

$$U_{s}(r, q) = F(q, E_{F})U^0(r, q)U(q),$$

(5.30)

where

$$F(q, E_{F}) = \sum_{k,\sigma} \frac{f(E(k + q)) - f(E(k))}{E(k + q) - E(k)}$$

(5.31)
is the static Lindhard function and \( U_0(r, q) \) is the mean-field Coulomb interaction potential of electrons with wavevector difference \( q \) in the ground sub band. The latter satisfies the following ordinary differential equation

\[
\frac{1}{r} \frac{d}{dr} \left[ \epsilon(r) r \frac{dU_0(r, q)}{dr} \right] - \epsilon(r)q^2U_0(r, q) = -\frac{e^2|\varphi(r)|^2}{\ell}.
\]  

(5.32)

The self-consistent potential \( U(r) \) is of course the sum of potentials due \( \Delta n(r) \) and \( Q \), such that

\[
U(r, q) = U_a(r, q) + F(q, 0)U_0(r, q)U(q)
\]  

(5.33)

But, consistent with the definition of \( U(q) \) in Equation 5.30, \( U(q) \) can also be obtained from equation 5.33 by integration,

\[
U(q) = \int \text{d}^2r|\varphi_0(r, \theta)|^2U(r, q)
\]  

(5.34a)

\[
U(q) = U_a(q) + F(q, 0)U_0(q)U(q)
\]  

(5.34b)

where \( U^{0,0}(q) \) and \( U_a(q) \) are obtained by from \( U_0(r, q) \) and \( U_a(r, q) \) respectively by an integration analogous to Equation 5.34a. Solving for \( U(q) \) in Equation 5.34b we obtain the desired result for the screened potential[173, 117].

\[
U(q) = \frac{U_a(q)}{1 - F(q, E_F)U^{0,0}(q)}
\]  

(5.35a)

\[
U(z) = \sum_q U(q) \exp(iqz)
\]  

(5.35b)

The first-order correction of electron density in the Lindhard approach reduces calculation \( U(z) \) to a trivial problem

1. Solve a one-dimensional ordinary differential governing \( U_0(r, q) \) including effects of dielectric confinement through \( \epsilon(r) \), and evaluation of a simple integral to obtain \( U^{0,0}(q) \).

2. Convert of the sum in the Lindhard function \( F(q, E_F) \) to a one dimensional integral, which can be evaluated at finite temperatures using the procedure described in reference [178].
3. Determine the Fourier components $U_a(q)$ of the bare potential, including effects of dielectric confinement through $\epsilon(r)$ as discussed in Section 5.3.1.

The Fourier components $U(q)$ (Equation 5.35a) are summed to a real space potential $U(z)$ (Equation 5.35b), and the Quantum Transmitting Boundary Method\[175] is implemented to calculate the $k$-dependent transmission probability amplitude $t(E(k))$ from which the transmission probability $T_0$ for the first sub band at a particular gate voltage (Fermi energy) is obtained by evaluating Equation 5.5. This procedure is both conceptually and computationally straightforward. Unfortunately, the linear expansion of the density matrix in the self-consistent potential in Equations 5.26-5.27, which is the central assumption of Lindhard screening, is found to dramatically overestimate screening of Coulomb potentials in back-gated InAs nanowires. Choosing the carrier concentration as a first-order perturbation in potential results in unphysical (negative!) carrier concentrations in the nanowire due to the large potential $U_a(z)$ in the case of dielectric mismatch, whose effect on the electron density can not be reasonably expected to be treated perturbatively.

5.3.3 Exact Mean Field Screening

The Lindhard approach, where first order perturbation theory in the potential is used to obtain the density, linearizes the problem of finding the screened potential $U(z)$, but apparently suffers from serious problems in the case of strong scattering encountered when nanowires have dielectric confinement. This can be remedied by solving the electrostatic potential self-consistently with electron density according to Equations 5.36a-5.36d, without the use of perturbation theory, and employing the same open boundary conditions for the envelope wavefunctions described in Equations 5.11-5.12.

\[
\nabla \cdot (-\epsilon(r)\nabla U_s(r)) = e^2(n(r) - N_D) \quad (5.36a)
\]

\[
n(r) = 2\sum_k f(E(k))|\phi_{E(k)}(z)|^2|\varphi_0(r, \theta)|^2 \quad (5.36b)
\]
\[
\frac{\hbar^2 k^2}{2m} \phi_{E(k)}(z) + V(z) \phi_{E(k)}(z) = \left( E - \frac{\hbar^2 k^2}{2m} \right) \phi_{E(k)}(z) \quad (5.36c)
\]

\[
V(z) = \int \int r dr d\theta |\varphi_0(r, \theta)|^2 (U_a(r) + U_s(r) + U_{xc}(r)) \quad (5.36d)
\]

Here, \( U_a(r) \) is the bare potential due to the localized charge \( Q \) and \( U_{xc}(r) \) is an exchange-correlation potential. For the moment we neglect \( U_{xc}(r) \).

Evaluation of the probability amplitudes \( t(E) \) needed to calculate the overall transmission probability of carriers by Equation 5.5 essentially requires simultaneous solution of the scattering potential \( V(z) \) and envelope wavefunctions \( \phi_{E(k)}(z) \) in Poisson and Schrödinger Equations 5.36a and 5.36c, respectively. Upon substitution of Equations 5.36b-5.36d into Equation 5.36a, the resulting Poisson equation governing \( U_s(r) \) is nonlinear and is not amenable to solution by exact methods. Therefore, we seek an iterative solution to the problem.

As in Section 5.3.2 on Lindhard screening, it is assumed that that \( \epsilon(r) \) and \( |\varphi_0(r, \theta)|^2 \) are functions of \( r = \sqrt{x^2 + y^2} \) only. Writing

\[
n(z) = \sum_q n(q) \exp(iqz) = 2 \sum_k f(E(k)) |\phi_{E(k)}(z)|^2 \quad (5.37)
\]

such that

\[
n(r) = |\varphi_0(r, \theta)|^2 \sum_q n(q) \exp(iqz) \quad (5.38)
\]

we can formulate a problem for the iterative solution of the effective one dimensional potential,

\[
U_s(z) = \int dx dy \left[ U_s(r)|\varphi_0(r, \theta)|^2 \right] \quad (5.39)
\]

in terms of a charge density residual, as follows.

Exploiting the relationship of Equation 5.37 we can solve for \( n(z) \) implied by the Poisson equation 5.36a by substituting Equation 5.38 and 5.29, giving

\[
U_s(r, q) = U^0(r, q) \ell n(q) \quad (5.40)
\]

and

\[
n(q) = \frac{U_s(q)}{\ell U^0,0(q)} \quad (5.41)
\]
where $U_0^0(r,q)$ and $U_0^0(q)$ are the same quantities used in the earlier Lindhard analysis, given by Equation 5.32. Then, $n(z)$ can be obtained from $U_s(q)$ by the appropriate Fourier expansion in 5.37, or equivalently, by a convolution integral with the real space potential $U_s(z)$,

$$n(z) = \int_{-\ell/2}^{\ell/2} dz' [K(z-z')U_s(z')] , (5.42)$$

where the kernel $K(z)$ is given by

$$K(z) = \sum_q \frac{\exp(iqz)}{U_0^0(q)\ell} . (5.43)$$

The residual $F(z)$ is defined as the difference in charge density implied by the Poisson and Schrödinger equations

$$F[U_s(z)] = \int_{-\ell/2}^{\ell/2} dz' [K(z-z')U_s(z')] - 2 \sum_k f(E(k))|\phi_{E(k)}(z)|^2 . (5.44)$$

Solving $F[U_s(z)] = 0$ to within a relative error $\epsilon = \int dz F([U_s])^2/\int dz (n(z))^2$ of some specified tolerance is carried out by a predictor-corrector scheme employing, for the inner “corrector” loop, a Newton-Raphson scheme using the approximate Jacobian recently described by Vasileska et al.[179].

### 5.3.4 Screened Coulomb Impurity Potentials and Reflection Probabilities

The bare Coulomb potential of the fixed repulsive charge at the surface of a 30 nm diameter InAs nanowire, with $\approx 50$ meV height, is compared to the exact-mean-field screened potential for the case of dielectric confinement and homogeneous dielectric in Figure 5.7a for $n = 10$ e/$\mu$m and in Figure 5.7b for $n = 20$ e/$\mu$m. The dielectric confinement triples the peak value of the screened potential from $\approx 7$ to $\approx 19$ meV in the first case, and approximately doubles it from $\approx 5$ meV to $\approx 11$ meV in the second case. The predicted screened potential for the case of dielectric confinement ($\epsilon_{in} = 15\epsilon_0$ decays to zero faster at its tails, but is stronger at the defect location $z = 0$,
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Figure 5.7: Bare Coulomb potential (dashed) and screened Coulomb potential for $\epsilon_{\text{in}} = 15\epsilon_0$, $\epsilon_{\text{out}} = \epsilon_0$ (solid) and $\epsilon_{\text{in}} = \epsilon_{\text{out}} = 15\epsilon_0$ (dotted) or (a) $n = 10$ e/µm and (b) $n = 20$ e/µm, at 30 K.
compared with the bare potential for the case $\epsilon_{\text{out}} = \epsilon_0$) for cases considered in Figure 5.7a and 5.7b. Screened Coulomb potentials for the case of Lindhard screening are not shown. The carrier-energy resolved reflection probabilities $|r(E - E_0)|^2$ are shown for both repulsively (solid lines) and attractively (dashed lines) charged Coulomb impurities in Figure 5.8a and 5.8b, for the same conditions as 5.7a and 5.7b, respectively. Here, $E_0$ refers to the edge (smallest allowed energy) in the lowest electronic sub-band. Case (a) of $n = 10 / \mu m$ reflects higher energy carriers more efficiently compared with case (b) $n = 20 / \mu m$ due to the higher barrier height in the former. The lower carrier density electron gas does not screen as effectively the strong bare Coulomb potential. Also apparent is the disparity in reflection probability between acceptors and donors. Considering the indicated Fermi Energy position $E_F$ and small thermal broadening $k_B T$, we expect very little total transmission $T = \int dE T(E)(-\partial f/\partial E)$ in case (b) and even less in the lower carrier density case (a).

5.4 Comparison and Discussion

Spectrally resolved reflection probabilities $R(E) = |r(E)|^2$ were calculated for single-acceptor scattering potentials corresponding to several different values of $E_F - E_0$, and therefore, carrier density. The carrier-energy integrated conductance through each of these scattering potentials,

$$G_D = \frac{2e^2}{\hbar} \int dE (1 - R(E)) \left(-\frac{\partial f}{\partial E}\right),$$

(5.45)
is also associated with a Fermi energy $E_F - E_0$. To compare with experimental data, the Fermi energy is converted to a gate voltage, using the electrostatic model that successfully described the carrier trapping statistics in Chapter 4. This model maps a Fermi energy to a gate voltage $V_{GS} - V_T$ considering a realistic gate geometry, density-of-states of a quantum wire, a surface state density $D_{ss} = 2 \times 10^{12} \text{cm}^{-2} \text{eV}^{-1}$ that reproduces the measured subthreshold characteristics of the nanowire when the defect is unoccupied. When this
Chapter 5. Scattering by a Single Coulomb Impurity

Figure 5.8: Energy dependence of reflection probability $|r(E - E_0)|^2$ for repulsive (solid) and attractive impurities (dashed) for (a) $n = 10 \, \text{e}/\mu\text{m}$ and (b) $n = 20 \, \text{e}/\mu\text{m}$, at 30 K. Fermi energy is marked on top scale, and thermal broadening scale $k_B T = 2.6 \, \text{meV}$ is indicated.
mapping is performed, the gate-voltage dependence of the calculated defect conductance $G_D$ in the realistic case of dielectric mismatch (solid red line) and no dielectric mismatch (dotted line) between the nanowire and its surroundings, is plotted in Figure 5.9a for the 30 nm diameter NW at $T = 30$ K. The experimentally extracted defect conductance $G_D = (G_L^{-1} - G_H^{-1})^{-1}$ for NW1 and NW2 (triangles and circles, respectively) is shown alongside calculations in the same Figure. Calculated scattering from the exact mean-field screened potential including dielectric mismatch much more closely reproduces the experimental data compared to the case of no dielectric mismatch. However, calculated scattering with dielectric mismatch is apparently still slightly weaker compared to the experimental data for gate voltages $V_{GS} - V_T \gtrsim 0.1$ V. The carrier energy integrated transmission for $T(E) = 1$ is also shown in Figure 5.9a (dashed line). For $k_B T \ll E_F$ a perfect step-like structure would be expected, but is not obtained in this case since the thermal broadening is not negligible.

It is also possible to compare the measured dependence of $G_H$ and $G_L$ with what is expected from the defect conductance calculation (calculated $G_D$). The calculated gate-voltage dependence of $G_H$ (dashed line) and $G_L^{-1} = (G_H^{-1} + G_D^{-1})^{-1}$ (solid line) are shown in Figure 5.9b. In this Figure, $G_H$ was obtained by assuming an energy independent scattering rate $T(E) = 0.16$ (dashed line) that matches well the experimentally measured $G_H$, shown as square data points in Figure 5.9b. The calculated curves $G_H$ and $G_L$ are related by an approximate threshold voltage shift of $\Delta V_T = 93 \pm 5$ mV, in close agreement with the measured threshold voltage shift $\Delta V_T = 100 \pm 5$ mV and $\Delta V_T = 120 \pm 10$ mV for NW2 at $T = 31$ K and NW1 at $T = 25$ K, respectively. Calculated conductance corresponding to scattering by a repulsive impurity with no dielectric mismatch, plotted as a dotted line in Figure 5.9b, shows only a small $\approx 20$ mV shift in threshold voltage from $G_H$, emphasizing the importance of dielectric confinement in the electron scattering.

The results for single-donor scattering are not shown in Figure 5.9a since they are so close to the nominal $T(E) = 1$ case, with typical integrated transmission probability
Figure 5.9: (a) Integrated transmission through $T(k) = 1$ (dashed line), repulsive screened impurity with $\epsilon_{\text{out}} = \epsilon_{\text{in}} = 15\epsilon_0$ (dotted line), and repulsive screened impurity with $\epsilon_{\text{out}} = \epsilon_0$ and $\epsilon_{\text{in}} = 15\epsilon_0$ (solid line). Data points for $G_D$ extracted from $G_D = (G_H^{-1} - G_L^{-1})^{-1}$ are also shown for NW1 and NW2 (filled circles, triangles). (b) Integrated transmission through $T(k) = 0.16$ (dashed line), and same scatterer cascaded in series with repulsive screened impurity with $\epsilon_{\text{out}} = \epsilon_{\text{in}} = 15\epsilon_0$ (dotted line), and repulsive screened impurity with $\epsilon_{\text{out}} = \epsilon_0$ and $\epsilon_{\text{in}} = 15\epsilon_0$ (solid line), at 30 K. Measured $G_H$ and $G_L$ are shown for NW2.
is $0.9 - 0.95$ and no significant dependence on Fermi energy (gate voltage), quite unlike the dramatic scattering by acceptors. Approximately 10-20 ionized donors would be necessary to produce the scattering rate of $T = 0.13$ in the high conductance state. Other contributions from surface roughness scattering could also play an important role.

### 5.5 Conclusions

The gate voltage dependence of the two conductance states of random telegraph signals in $\approx 30$ nm diameter InAs nanowires were studied. These signals afford a rare connection between electrical measurements and microscopic disorder not usually possible in transport experiments, but of crucial importance in nanostructures. Strong, spectrally resolved reflection probability of $R \approx 0.999, 0.995, 0.980$ for $n \approx 10, 20, 30$ /µm was observed. Measurements were compared with a microscopic model for exact carrier scattering by a single Coulomb impurity. Both linear mean field (Lindhard) and exact mean-field screening were used to calculate the screened Coulomb potential, with the former failing due to the large Coulomb interaction arising due to dielectric confinement in the InAs nanowires. Reflection from attractive and repulsive defects was found to be highly asymmetric, with calculations of scattering by repulsive impurities producing reflection probabilities in good agreement with experiment only possible if dielectric confinement is taken into account. Scattering is considerably underestimated if dielectric confinement is neglected.
Chapter 6

Charge Sensitivity of Nanowire Field Effect Transistors

6.1 Introduction

Future solid-state technologies such as ultra-sensitive chemical sensors with the capability to resolve the presence of individual molecules, and memory devices with ultra-low power consumption must be able to detect ever smaller amounts of charge at the fastest possible speed. Moreover, proposals for storage and processing of quantum information, encoded in the spin of electrons or holes confined in engineered semiconductor structures, call for sensitive charge detectors for quantum bit readout by spin-to-charge conversion techniques[20, 21]. Meanwhile, spin-to-charge conversion and readout by a charge detector is useful for fundamental studies of spin in semiconductor quantum dots[180, 21] and impurities in silicon[181, 77].

In this chapter, the two conductance levels and background noise spectrum of random telegraph signals are measured to determine the responsivity and sensitivity of InAs nanowire field-effect transistors (NWFETs) to charge at temperatures in the range $\approx 30$ and $\approx 200$ K. Electron capture and emission by the defect can also be viewed as
an effective gating process and it is physically equivalent to applying an appropriately modulated voltage to, for example, a sufficiently narrow (10 − 20 nm) gate. Results on an InAs NWFET with NW diameter \( d = 28 \pm 2 \) nm demonstrate a charge sensitivity of \( \delta Q = 40 \ \mu \text{eHz}^{-1/2} \) at \( T = 25 \) K and \( \delta Q = 60 \ \mu \text{eHz}^{-1/2} \) at \( T = 200 \) K. A different InAs NWFET with \( d = 34 \pm 2 \) nm has a charge sensitivity of \( \delta Q = 25 \ \mu \text{eHz}^{-1/2} \) at \( T = 90 \) K.

The measured charge sensitivity \( \delta Q \) of our NWFETs in the temperature range 30-200 K is orders of magnitude better than Silicon MOSFET based electrometers at 1 K, \( \delta Q \approx 10^{-2} \ \text{eHz}^{-1/2} \) [63], owing to the quasi-one-dimensional electron gas of the NWFET. The charge sensitivity of the NWFET also exceeds that of state-of-the-art nano-electromechanical-systems (NEMs) based electrometers by several orders of magnitude. The best reported charge sensitivity of NEMs based electrometers are \( \delta Q \approx 10^{-2} \ \text{eHz}^{-1/2} \) at \( T = 4 \) K [182] and \( \delta Q \approx 10 \ \text{eHz}^{-1/2} \) at \( T = 300 \) K [183]. Finally, the measured NWFET charge sensitivity is only an order of magnitude away from state-of-the-art single electron transistors [184, 64] (SETs), the most sensitive electrometers in existence, which typically operate at or below 4.2 K. The best SET electrometers have a charge sensitivity of \( \delta Q = 2 \ \mu \text{eHz}^{-1/2} \) at 4.2 K and \( \delta Q = 0.9 \ \mu \text{eHz}^{-1/2} \) at 40 mK [64]. Demonstrated InAs NWFET charge sensitivity at 90 K is on par with reported performance of carbon-nanotube-based SETs at 10 K [185]. The origin of the high charge sensitivity at high temperatures is the quasi-one-dimensional geometry of the InAs nanowire, in particular the miniaturization of its diameter \( c.f. \) length scales discussed in Chapter 5, and the excellent carrier transport properties of InAs nanowires grown by MBE.

Background noise in the random telegraph signals is found to be limited by external instrumentation rather than the intrinsic high-frequency electrical noise in nanowires. Theoretical charge sensitivity of the NWFET is discussed in terms of the theory of scattering and noise in nanoscale conductors and transistors. The predicted high frequency, intrinsic noise limited charge sensitivity \( \delta Q^i \) of measured nanowires is obtained by multiplying the measured responsivity \( \mathcal{R} \) by the worst-case intrinsic current noise estimated
by theoretical considerations[66]. We find \( \delta Q^i = 4 \mu \text{eHz}^{-1/2} (d = 28 \pm 2 \text{ nm}, T = 25K) \), 15 \( \mu \text{eHz}^{-1/2} (d = 28 \pm \text{ nm}, T = 198K) \), and 30 \( \mu \text{eHz}^{-1/2} (d = 34 \pm 2 \text{ nm}, T = 90K) \).

Further improvements to charge sensitivity should be possible through reduction of InAs NWFET diameter and by engineering the NWFET structure and/or material closer to the fully ballistic limit where mean free path is similar to or longer than the distance between source and drain electrodes. A scheme for capacitive coupling of charge to the NWFET is discussed, introducing the idea of a locally gated NWFET electrometer. The latter is limited by instrumentation and parasitics of the test structure in the measurements performed. Applications benefiting from ultrahigh charge sensitivity near room temperature include low-power memories storing just a few electrons per bit, high-speed molecular detection down to a single molecule, and readout of the spin state of electrons in quantum dots and electronic impurities intentionally introduced into semiconductors.

### 6.2 Principles of Electrometry

In sensing devices, two quantitative figures of merit are of particular interest, namely, the responsivity and the sensitivity. The former is defined as the ratio of the output of the sensor to its input. For a linear sensor, the output is proportional to the input, and the input and output are generally different quantities with different physical units. The term electrometer is used in this chapter to describe a charge sensor, and should not be confused with an alternative definition which has also been adopted: that of a voltage amplifier with extremely high input resistance. For electrometers of the type we are referring, the responsivity which we denote as \( R \) is most conveniently given in units Ae\(^{-1}\) (or Se\(^{-1}\)), the change in the current (or conductance) of an electrically biased sensor, per unit electronic charge \( e = 1.6 \times 10^{-19} \text{ C} \) coupled to its input. The sensitivity is defined as the inverse of the signal to noise ratio, which can be obtained by multiplying the the root-mean-square (RMS) noise and the responsivity as defined above. It is common for
the mean square noise current to be proportional to the total measurement bandwidth, and in this case the sensitivity of an electrometer is given in units eHz$^{-1/2}$. This quantity can be understood as the input charge producing a response which is equal to the RMS noise for a particular measurement bandwidth. Practically this is the smallest charge that can be detected for a given bandwidth. The sensor’s response is also normally a function of the frequency of the input signal, so the frequency response of responsivity and sensitivity are both of interest.

Physical realizations of electrometers can be classified in terms of the structure which is used, the measured quantity $M$ that responds to the external charge, and the coupling mechanism of the charge to the property being measured. In this section the responsivity and sensitivity are clarified in terms of mathematical expressions for the noise-corrupted, measurement $M(t)$ of bandwidth $\delta f$, which holds irrespective of the physical realization of the electrometer. The charge responsivity $R_M$ is given by

$$R_M = \frac{\partial \langle M(t) \rangle}{\partial Q},$$  \hspace{1cm} (6.1)

where $\langle M(t) \rangle$ describes the time-averaged (mean-value) of $M(t)$. From the total RMS noise power for a measurement

$$\langle \delta M(t)^2 \rangle^{1/2} = \left( \langle M(t) - \langle M(t) \rangle \rangle^2 \right)^{1/2},$$  \hspace{1cm} (6.2)

we obtain the charge sensitivity for a particular bandwidth $\delta f$,

$$\delta Q = \frac{1}{R_M} \frac{\langle \delta M(t)^2 \rangle^{1/2}}{\delta f}.$$  \hspace{1cm} (6.3)

In the limit of long observation times, the measured mean square noise power $\langle \delta M(t)^2 \rangle$ should converge to

$$r_{MM}(\tau)_{\tau=0} = E[M(t)M(t-\tau)]_{\tau=0}$$  \hspace{1cm} (6.4)

where $r_{MM}(\tau)$ is the autocorrelation function and $E[\cdot] = \int_{-\infty}^{\infty} dt [\cdot]$ is the expectation value of the process. The Wiener-Khinchin theorem\cite{186} states that the power spectral
density $S_{MM}(f)$ of a wide-sense-stationary random process is the Fourier transform of the corresponding autocorrelation function,

$$S_{MM}(f) = \int_{-\infty}^{\infty} d\tau r_{MM}(\tau) \exp(-2\pi i f \tau). \quad (6.5)$$

Over a frequency range $f_1 < f < f_2$ where the autospectral density $S_{MM}(f)$ is white, the noise power for a measurement $M(t)$ with bandwidth $\delta f = f_2 - f_1$ in this range can therefore be written as

$$\langle \delta M(t)^2 \rangle^{1/2} = S_{MM}^{1/2} \delta f. \quad (6.6)$$

In this situation, the charge sensitivity becomes

$$\delta Q = \frac{1}{R_M} S_{MM}^{1/2}. \quad (6.7)$$

Take as an example a fictitious electrometer with both exceptional charge sensitivity $\delta Q = 10^{-6} \text{ eHz}^{-1/2}$, and bandwidth $10^9 \text{ Hz}$, defined as stated in Section 6.1. Practically, this means that in a measurement of duration $10^{-8}$ seconds (measurement bandwidth $\delta f = 100 \text{ MHz}$), the input referred root-mean-square noise at the output of the electrometer is $\delta q = \delta Q \times \delta f^{1/2} = 10^{-6} \text{ eHz}^{-1/2} \times 10^4 \text{Hz}^{1/2} = 10^{-2}e$. Then, there is enough signal output from the electrometer to resolve the presence of any quantity of charge exceeding roughly $0.01e$ in 10 ns.

### 6.3 Responsivity, Electrical Noise and Charge Sensitivity in InAs NWFETs

The charge responsivity, electrical noise, and charge sensitivity of InAs NWFETs is described below. Stochastic capture and emission of electrons from individual defects producing random telegraph signals are measured and analyzed, as a function of gate voltage, to obtain the responsivity of both conductance and current to single charges. The scheme for measuring random telegraph noise waveforms is the same as presented
in Chapters 3-5, except that the alternating bias $V_{DS}$ was applied at a higher frequency $f = 12.5$ kHz. The current through the nanowire was measured at the drain terminal using high precision, variable gain current preamplifier, and its magnitude determined by a lock-in amplifier (Stanford Research Systems SR830) operating with a time constant of 100 $\mu$s. Current waveforms were obtained by a sampling digital oscilloscope (Agilent 54845a) whose 1 MΩ input was connected to the 50 Ω impedance, full-bandwidth $X$-channel output of the lock-in amplifier after the proper phase was determined. Low-pass filters discussed in Section 1.3.3 were removed to increase measurement bandwidth, which nevertheless remains modest (approximately 50 kHz), primarily limited by the cabling capacitance and room temperature current preamplifier. The Fast Fourier Transform (FFT) algorithm was exploited to convert time domain waveforms containing random telegraph signals into the frequency domain, from which the autospectral current noise density was obtained. Results for NWFET autospectral current noise density and sensitivity are discussed in terms of electronic noise theory of nanoscale transistors.

A random telegraph signal for NWi, a 28 nm diameter InAs NW, is shown in Figure 6.1(a) for a temperature of 25 K, gate voltage $V_{GS} - V_T = 0.115$ V, and source-drain bias $V_{DS} = 3$ mV RMS. Changes in conductance between $G_H = 0.111G_0$ and $G_L = 0.008G_0$, associated with empty and filled trap states are observed. As usual, $G_0 = 2e^2/h$, corresponding to the maximum conductance of two spin degenerate sub-bands of a quantum wire, and the threshold voltage $V_T$ is defined by the dependence of $G_H$ on $V_{GS}$. NWii, a second 34 nm diameter InAs NWFET exhibited the random telegraph signals shown in Figure 6.1(b), where $G_H = 0.169G_0$ and $G_L = 0.122G_0$, at $T = 90$ K. The gate and source-drain bias are $V_{GS} - V_T = 0.200$ V and $V_{DS} = 4$ mV RMS, respectively. The third random telegraph signal of Figure 6.1(c) was recorded measuring NWi at $T = 198$ K, using a higher gate voltage overdrive $V_{GS} - V_T = 0.340$ V and an bias $V_{DS} = 4$ mV RMS. High and low conductance states are $G_H = 0.24G_0$ and $G_L = 0.15G_0$, respectively. The conductance and current responsivity are obtained by applying the definitions given
in Section 6.1 to the random telegraph signals, giving

\[ \mathcal{R}_G = \frac{(G_H - G_L)}{e} \]  \hspace{1cm} (6.8a)

\[ \mathcal{R}_I = \mathcal{R}_G V_{DS} \]  \hspace{1cm} (6.8b)

Results for the conductance and current responsivity are summarized in columns 7 and 8 of Table 6.1, for both NWi and NWii.

High and low conductance states were extracted from random telegraph signals at number of gate voltages near the threshold voltage. In the case of NWi at 198 K the trap energy was more than a few \( k_B T \) above the Fermi energy for \( V_{GS} - V_T \approx 0.2 \) V, making transitions for smaller gate voltages increasingly unlikely. Results for high and
<table>
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<th>Diam. (nm)</th>
<th>Temp. (K)</th>
<th>$G_H$ ($G_0$)</th>
<th>$G_L$ ($G_0$)</th>
<th>$V_{DS}$ (mV)</th>
<th>$V_{GS} - V_T$ (V)</th>
<th>$\mathcal{R}_G$ ($\mu S/e$)</th>
<th>$\mathcal{R}_I$ (nA/e)</th>
<th>$S_{1/2}^{1/2}$ meas</th>
<th>$S_{1/2}^{1/2}$ limit (pAHz$^{-1/2}$)</th>
<th>$\delta Q$ meas (µeHz$^{-1/2}$)</th>
<th>$\delta Q$ limit (µeHz$^{-1/2}$)</th>
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<td>4.0</td>
<td>0.340</td>
<td>5.8</td>
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<td>0.34</td>
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<td>90</td>
<td>0.169</td>
<td>0.122</td>
<td>4.0</td>
<td>0.200</td>
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<td>15</td>
<td>0.36</td>
<td>0.27</td>
<td>25</td>
<td>18</td>
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</tbody>
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Table 6.1: Conditions and values for conductance responsivity, current responsivity, measured high frequency noise limit, theoretical high frequency noise limit, measured sensitivity, and intrinsic high frequency noise limited sensitivity for measured InAs NWFETs NWi. *Values given were averaged over $f = 3.8 - 4$ kHz, after correcting for the spectral response of the lockin by multiplying by 1.4 at $f = 4$ kHz.
low conductance states are shown in Figure 6.2a for NWi at $T = 25$ K, Figure 6.3a for NWii at $T = 90$ K, and Figure 6.4a for NWi, $T = 198$ K.

### 6.3.1 Autospectral Current Noise Density for RTS Waveforms

The autospectral current noise density was obtained from RTS waveforms by Fourier analysis exploiting the Fast Fourier Transform (FFT), according to the procedure outlined in reference [187] which is summarized below. Suppose we have waveforms $i_k(t)$, $k = 1, 2, ..., n_d$ each with duration $T$. The autospectral density $S_{ii}(f)$ of waveforms $i_k(t)$ is
Figure 6.3: For NWii with $d = 34$ nm at $T = 90$ K (a) Gate voltage dependence of high and low conductance states $G_H$ (filled squares) and $G_L$ (filled circles) respectively, corresponding to empty and filled states of defect, charge sensitivity $\delta Q$ obtained using measured autospectral density (open squares), white noise limit at $V_{DS} = 4$ mV (open circles), and white noise limit at $V_{DS} = 1.5k_B T$ (open triangles). (b) Square root of current autospectral density, $S_{1/2}(f)$, for $V_{GS} - V_T = 0.050, 0.100, 0.150$ V. Arrow indicates direction of increasing gate voltage.
Figure 6.4: For NWi with $d = 28$ nm at $T = 198$ K (a) Gate voltage dependence high and low conductance states $G_H$ (filled squares) and $G_L$ (filled circles) respectively, corresponding to empty and filled states of defect, charge sensitivity $\delta Q$ obtained using measured autospectral density (open squares), white noise limit at $V_{DS} = 4$ mV (open circles), and white noise limit at $V_{DS} = 1.5k_B T$ (open triangles). (b) Square root of current autospectral density, $S_{II}^{1/2}(f)$, for $V_{GS} - V_T = 0.260, 0.300, 0.380$ V. Arrow indicates direction of increasing gate voltage.
obtained by
\[
S_{ii}(f) = \frac{1}{n_d T} \sum_{k=1}^{n_d} |I_k(f, T)|^2 \tag{6.9}
\]
where \( I_k(f, T) \) is the Fourier transform of the waveform \( i_k(t) \), i.e.
\[
I_k(f, T) = \int_0^T i_k(t) \exp(-i2\pi ft)dt. \tag{6.10}
\]
The sampling process for the signal \( i_k(t) \) yields \( i_k(n\Delta t) \), with \( n = 0, 1, ..., N - 1 \), where \( \Delta t = T/N \) is the sampling period and \( f_s = N/T \) is the sampling rate. The Fourier components of each waveform \( k = 1, 2, ..., n_d \) are
\[
I_k(f) = \Delta t \left[ \sum_{n=0}^{N-1} i_k(n\Delta t) \exp(-i2\pi fn\Delta t) \right]. \tag{6.11}
\]
Notice that the quantity in the square brackets evaluated at \( f = j/(N\Delta t) \) is exactly the discrete Fourier transform \( I_{kj} \) of the samples \( i_k(n\Delta t) \), that is
\[
I_{kj} = \sum_{n=0}^{N-1} i_k(n\Delta t) \exp(-i2\pi jn/N). \tag{6.12}
\]
A sampled version \( S_{ii}(f_j) \) of the autospectral current density can therefore be obtained from a sampled version of the waveform \( i_k(t) \),
\[
S_{ii}(f_j) = \frac{\Delta t}{n_d N} \sum_{k=1}^{n_d} |I_{kj}|^2 \tag{6.13}
\]
where \( X_{kj} \) are obtained by fast Fourier transform (FFT) of \( x_k(n\delta t) \). For NWi at \( T = 25 \) K and \( T = 198 \) K, a collection of \( n_d = 50 \) waveforms with bandwidth 10 kHz sampled \( N = 2^{16} \) times at a rate \( f_s = 25 \text{ kHz} \) \( (T = 2.6214 \text{ s}) \) were converted into the autospectral current density using this formulation. Results for NWi at \( T = 25 \) K are shown for several gate voltages in Figure 6.2b, which converge to a nearly constant value of \( S_{ii}^{1/2} \approx 0.8 \) pAHZ\(^{-1/2} \) in the frequency window \( f = 3 - 4 \) kHz for \( V_{GS} - V_T = 0.115 \) and 0.140 V, and \( \approx 0.5 \) pAHZ\(^{-1/2} \) for \( V_{GS} - V_T = 0.015, 0.040, 0.065 \) and 0.090 V. The low frequency noise spectrum of a random telegraph signal\[127\] has an autospectral density
\[
S_{II}(f) \propto \pi^{-1} \left( \frac{\langle t_H \rangle \langle t_L \rangle}{\langle t_H \rangle^2 + \langle t_L \rangle^2} \right) \left( \frac{\tau^{-1}}{(2\pi f)^2 + \tau^{-2}} \right) \tag{6.14}
\]
where $\tau^{-1} = \langle t_L \rangle^{-1} + \langle t_H \rangle^{-1}$ is the sum of electron capture and emission rates. This Lorentzian spectrum combines with other weakly coupled fluctuators to produce the observed low frequency noise which dominates for $f \lesssim 2$ kHz.

The noise floor in $S_{II}^{1/2}(f)$ in Figures 6.2b, 6.3b and 6.4b arises from the digitizing oscilloscope’s input noise, when it is referred to the input of the current preamplifier in the employed configuration. The oscilloscope’s gain must be chosen such that lock-in output corresponding to both the high and low current states of the random telegraph signals are both within scale, and the noise at this step in the data acquisition is the dominant spectrally white noise source in the measurement, much larger than the measured noise floor of $S_{II}^{1/2}(f) \approx 0.06$ pAHZ$^{-1/2}$ of the current preamplifier. The two sets of gate voltages $V_{GS} - V_T = \{0.115, 0.140\}$ V and $V_{GS} - V_T = \{0.015, 0.040, 0.065, 0.090\}$ V have different noise floors for $S_{II}(f)$ at $f = 4$ kHz since different oscilloscope input ranges were employed.

For NWii at $T = 90$ K, only a single waveform ($n_d = 1$) with $N = 2^{16}$ samples was measured, at the same sampling rate. Autospectral current density $S_{II}^{1/2}(f)$ is shown in Figure 6.3b for three gate voltages $V_{GS} - V_T = 0.050, 0.100$ and $0.150$ V. Due to the marginally lower conductance change $G_H - G_L \lesssim 0.05G_0$ it was possible to use a smaller input range for the oscilloscope, making better use of its input gain, and resulting in a slightly smaller current noise $S_{II}^{1/2}(f) = 0.3$ pAHZ$^{-1/2}$ at $f \approx 4$ kHz. Similar contributions from the random telegraph signals and other low frequency noise sources are observed for frequencies $f \lesssim 2$ kHz, as expected. Results for NWi at $T = 198$ K are shown in Figure 6.4b for three gate voltages $V_{GS} - V_T = 0.240, 0.300$ and $0.380$ V, with $S_{II}^{1/2}(f) = 0.9$ pAHZ$^{-1/2}$ at $f \approx 4$ kHz.

Measured autospectral current density at $f = 4$ kHz is summarized in Table 6.1, column 7, for the measurements performed at $T = 25, 90, \text{and} 198$ K. The gate-voltage dependence of the equivalent charge sensitivity for $T = 25, 90 \text{and} 198$ K is given in Figure 6.2a, Figure 6.3a, and Figure 6.4a respectively, as open squares. Peak values are
40 $\mu$Hz$^{-1/2}$, 25 $\mu$Hz$^{-1/2}$, and 60 $\mu$Hz$^{-1/2}$ for these three temperatures, respectively.

6.3.2 Intrinsic Noise Sources

The transition from 1/f-like low frequency noise of the measured InAs NWFETs to a flat, frequency independent input referred voltage noise of the oscilloscope’s input occurs for $f \gtrsim 2$ kHz. Improvements to instrumentation will overcome these limitations, but intrinsic high frequency noise sources are expected to take over at some frequency $f > 2$ kHz. One unavoidable source of electrical noise in conductors is thermal fluctuations which arise when the occupation number of the electrically conducting states fluctuate around their mean value\cite{66} due to energy transfer from e.g., lattice vibrations. Another unavoidable source of electrical noise is shot noise, which arises from the discrete, indivisible nature of electron charge $e = 1.602 \times 10^{-19}$ C.

The autospectral density of thermal noise is essentially white up to a frequency $f = k_B T/h$ well above the measurement bandwidth. The result

$$S_{ii}(f) = 4k_B T \left( g_d + \frac{g_m}{2\gamma} \right)$$

was recently derived for one-dimensional nano-transistors by Chaste coworkers\cite{188} using the scattering theory of thermal noise\cite{66}. Here, $g_d = \partial I/\partial V_{DS}|_{\langle V_{GS} \rangle}$ is the differential conductance, $g_m = \partial I/\partial V_{GS}|_{\langle V_{DS} \rangle}$ is the transconductance, $T$ is the electronic temperature, and $\gamma = \partial \Phi/\partial V_{GS}$ is the ratio of channel potential $\Phi$ to gate potential $V_{GS}$. The quantity $\gamma$ can be re-expressed as $\gamma = C_q/C$, where $C_q$ is the quantum capacitance, and the total gate capacitance $C$ satisfies $C^{-1} = C_q^{-1} + C_g^{-1}$, where $C_g$ is the geometrical gate capacitance. While the differential conductance $g_d$ is purely an electron transport property of the system, the transconductance $g_m$ is both a transport property, a geometrical property, and a function of the bias from source to drain. In the linear regime of transistor operation with $V_{DS} < V_{GS} - V_T$\cite{120}, the transconductance is given by

$$g_m = \mu_{FE} C \langle V_{DS} \rangle / L^2$$

(6.16)
where $\mu_{FE}$ is the field effect mobility, $C$ is the total gate capacitance, $L$ is the distance between source and drain electrodes, and $\langle V_{DS} \rangle$ is the average value of the drain bias.

The shot noise current autospectral density is also predicted to be white in the frequency range of interest\[66\], with

$$S_{II}^{s}(f) = 2eF \langle I \rangle \tag{6.17}$$

where $F$ describes the character of the noise as super-Poissonian ($F > 1$), sub-Poissonian ($F < 1$) or Poissonian ($F = 1$), and $I$ is either the mean current $I = GV_{DS}$ in the case of a constant DC bias $V_{DS}$ or the root-mean-square current $I = gV_{DS}$ in the case of an AC root-mean-square bias $V_{DS}$. The Poissonian limit ($F = 1$) is most often associated with either high temperatures (classical carrier distributions), and/or strong scattering\[66\], and reproduces Schottky’s famous result $S_{II}(f) = 2eI[120]$. Summing the power of individual noise sources we obtain for the total white autospectral density of intrinsic current noise,

$$S_{II}^{i} = 4k_{B}T \left( g_{d} + \frac{g_{m}}{2\gamma} \right) + 2eIF. \tag{6.18}$$

### 6.3.3 Comparison between Measured and White-Noise-Limited Sensitivity

The intrinsic current noise discussed in Section 6.3.2 places a lower bound on the current noise of the NWFET and an upper bound

$$\delta Q \geq \frac{\delta q}{\delta I} \sqrt{S_{II}^{i}(f)} \tag{6.19}$$

on their charge sensitivity, where $S_{II}^{i}$ is given by Equation 6.18. Measurements in this chapter were performed with a purely alternating RMS AC bias $V_{DS}$ with zero mean value. Consequently, $g_{m} = 0$ in Equations 6.15 and 6.18, and the average current flowing through the NWFET is $G = (G_{H} + G_{L})V_{DS}/2$. Substituting into Equations 6.18 and
6.19, the lower bound on sensitivity is obtained,
\[ \delta Q \geq e \left( \frac{G_H + G_L}{G_H - G_L} \right)^{1/2} \left( \frac{e}{(G_H - G_L)V_{DS}} \right)^{1/2} \left( \frac{2k_BT}{eV_{DS}} + F \right)^{1/2}. \]  

Assuming the Poisson value \((F = 1)\) for the intrinsic autospectral density of shot noise, and bias \(V_{DS}\) and conductances \(G_H\) and \(G_L\) in Table 6.1 we obtain total autospectral noise density \(\sqrt{S_{II}}(f) = 0.1, 0.27,\) and \(0.34\) pAHz\(^{-1/2}\) for NWi at 25 K, NWii at 90 K, and NWi at 198 K, respectively. As expected, these are below the measured values \(1.1,\) \(0.25,\) and \(0.36,\) and \(1.3\) pAHz\(^{-1/2}\) for the same conditions, which, as explained in Section 6.3.1, contain instrumentation-related contributions. The corresponding sensitivity evaluated using Equation 6.20 and the same parameters from Table 6.1 give white-noise-limited charge sensitivity of \(\delta Q = 4, 18,\) and \(14\) eHz\(^{-1/2}\) at 25 K, 90 K, and 198 K, respectively. Therefore, even at the bias \(V_{DS} = 3(4)\) mV at 25 K (90 and 198 K) there is considerable room for improvement of charge sensitivity by improvement of instrumentation for data acquisition. The predicted, white-noise-limited charge sensitivity are plotted as a function of gate voltage, as open circles, in Figures 6.2a, 6.3a and 6.4a for temperatures 25, 90, and 198 K respectively, and are summarized in Table 6.1.

### 6.3.4 Bias and Diameter Dependence of Charge Sensitivity

Further improvements to charge sensitivity \(\delta Q\) can be achieved by increasing the source-drain bias \(V_{DS}\) to at least \(1.5k_BT/e\) from \(0.5k_BT/e\) and \(0.25k_BT/e\) at temperatures 90, and 198 K, respectively. The basic reasoning is as follows:

1. Responsivity \(R = \delta I/\delta q\) increases linearly with increasing bias in this regime

2. In this regime, RMS thermal noise \(\sqrt{4k_BTG\delta f}\) does not depend on \(V_{DS}\) and dominates shot noise \(\sqrt{2eGV_{DS}}\), which increases in proportion to \(\sqrt{V_{DS}}\), as the most important contribution to total RMS current noise \(\sqrt{4k_BTG\delta f + 2eGV_{DS}\delta f}\).

3. Therefore, signal to noise ratio increases linearly with \(V_{DS}\) in this regime.
The predicted, white-noise-limited charge sensitivity at $V_{DS} = 1.5k_B T/e$ is plotted as function of gate voltage, as open triangles, in Figures 6.2a, 6.3a and 6.4a for temperatures 25, 90, and 198 K respectively. Remarkably, the predicted charge sensitivity is $\approx 2 \mu \text{eHz}^{-1/2}$ at 198 K, which is identical to the record charge sensitivity for SETs at 4.2 K[64, 189, 190]. Further increase in bias $V_{DS}$ beyond $1.5k_B T/e$ is expected to heat the electron gas. Under these circumstances the quantities $G_H$ and $G_L$, which determine the intrinsic charge sensitivity in Equation 6.20 and correspond to the absence and presence of a single charge, may start to decrease with increasing $V_{DS}$. Recently, a charge sensitivity of $13 \times 10^{-6} \text{eHz}^{-1/2}$ was observed single walled semiconducting carbon nanotube FETs cooled to 4.2 K and biased with $V_{DS} = 300 \text{mV}=837k_B T/e$, well into the hot-electron regime[188].

The diameter dependence of the maximum change in conductance $G_H - G_L$ and the white-noise-limited charge sensitivity $\delta Q$ are plotted in Figure 6.5a and 6.5b, respectively, for several NWFETs measured at temperatures clustered around $T = 30 \text{K}$ and a bias of $V_{DS} = 3 \text{mV}$. From the discussion of Chapter 5 it is clear that the carrier reflection probability for a single charge in a InAs NWFET increases with decreasing diameter. This supports through use of the Landauer formula[96] the experimentally observed trend of larger changes in conductance due to single charges in smaller diameter nanowires, shown Figure 6.5a, and directly translates into their higher sensitivity to charge (lower $\delta Q$) in smaller diameter nanowires, shown in Figure 6.5b. One additional advantage for InAs NWFET based electrometers is the high electron mobility of InAs which increases the signal to noise ratio, and therefore, sensitivity.

6.4 NWFET Electrometer with a Local Gate

When the charge to be measured is not physically located close to the nanowire, it is still possible to obtain a considerable response by coupling the charge to the nanowire by a
local gate between two source and drain electrodes, separated from the nanowire by a thin (< 10 nm) gate dielectric, as shown schematically in Figure 6.6a. To maintain the localized nature of the potential, a gate of length \( L_G \ll 2\lambda \) can be employed, where \( \lambda \gg 15 \text{ nm} \) is the electronic screening length in the first sub-band of an InAs nanowire. The gate oxide should also be no thicker than the screening length. Obviously, this situation is physically not too different from coupling a point charge, and is definitely technologically achievable by modern lithographic processes. A charge \( Q_E \), added to a node that is capacitively coupled to the gate of a nanowire FET, can be readily understood in terms of the equivalent circuit in Figure 6.6b. Here, the influence of the gate charge \( Q_G \) on the conductance of the nanowire channel is represented as a voltage controlled current source (diamond symbol). Consider a thin metallic trace that couples to the charge \( Q_E \) by a coupling capacitor \( C_C \) and to the nanowire by a gate coupling capacitor \( C_G \). The capacitances \( C_{s1} \) and \( C_{s2} \) are unwanted (parasitic) capacitances to ground. Two
Figure 6.6: (a) Schematic of nanowire FET with gate oxide and wrap-around local gate (b) Simplified equivalent circuit diagram for charge $Q$ coupled to nanowire by $C_G$ through source capacitances $C_{S2}$, $C_{S1}$, and output capacitance $C_e$. 
additional constraints

\[ Q_E = Q_{s2} + Q_C \]  
\[ 0 = Q_C + Q_{s1} + Q_G \]

reflect the charge \( Q_E \) added to the large circled node in Figure 6.6b, and the resulting charge rearrangement on the gate node of the nanowire, respectively. Assuming the channel potential is close to ground, we obtain

\[ Q_G = \frac{C_G}{C_G + C_{s1} + C_{s2} + (C_{s1} + C_G)C_{s2}/C_C} Q_E. \]  
\[ (6.23) \]

It is clear that parasitic source capacitances \( C_{s1} \) and \( C_{s2} \) prevent full coupling of \( Q_E \) to \( Q_G \). In other words, for efficient transfer of charge to the gate, the source capacitances should be as small as possible compared with the nanowire’s local gate capacitance. An important special case is when \( C_{s2} \ll C_C \), which gives

\[ Q_G \approx \frac{C_G}{C_G + C_{s1} + C_{s2}} Q_E. \]  
\[ (6.24) \]

The dominant parasitic source capacitance on the gate is most likely to the substrate, so suitable substrate design procedures are necessary. The simplified circuit model in Figure 6.6b can be easily mapped to the situation of coupling of charge to the nanowire FET from a floating gate or single electron transistor.

6.5 Comparison with Existing Electrometer Technology

Below we very briefly survey four modern solid-state electrometer technologies in the context of the results presented in this chapter. The first three are electronic devices where a charge is capacitively coupled to the device, influencing its conductance and therefore, the electrical current that flows through it at a constant voltage bias. Among them the first is
the conventional FET, a structure which traces its roots to Lilienfield’s patents[191, 192] but at its current level of miniaturization can be used as an electrometer, and is commercially sold as such. The second is the SET where a net current flows by electron tunneling from one lead onto a nanometer scale island, and to the other lead. Capacitive coupling of an electron on the gate of a single electron transistor changes the energy of electrons on the island, suppressing the current. The final nanoelectronic device is a quantum point contact, a electrostatic constriction the squeezes carriers in a two-dimensional electron gas into a channel where electrons or holes in a well defined number of transverse conducting modes flow ballistically, i.e., without scattering. Here, conditions for channel formation are modified in the presence of an capacitively coupled external charge. The final electrometry system discussed is that of a nano-electro-mechanical oscillator, in which electric force modifies the mechanical properties of the system, which can be measured by e.g., deflection of an optical beam incident on the structure.

6.5.1 Conventional FETs

All field effect transistors are essentially charge sensors, but the charge sensitivity of conventional planar Silicon FETs is essentially limited by geometrical arguments since the channel width $W$ is likely larger than several Thomas Fermi screening lengths. The potential induced by a localized charge in such a system is easily bypassed by electrons freedom to flow around it, laterally. Moreover, the sensitivity of conductance to electrons distributed as a polarization charge across a gate electrode of area $W \times L$ is also limited, for essentially any channel length $L$, because the potential induced in the channel from a single electron delocalized on a metallic gate is too homogeneous and weak to appreciably deplete or scatter carriers. This limits the responsivity $R_I$ of FETs to moderate values. The mean square current noise due to purely thermal fluctuations[120] is given by $S_{II}^T = 4k_B T G$, where $G = \partial I / \partial V_{DS}|_{V_{GS}}$ is the conductance of the FET. The mean square shot noise associated with the discreteness of charge remains at $S_{II}^S = 2eGV_{DS}$ until the lowest
temperatures. Mainly as a consequence of the small responsivity, the charge sensitivity remains relatively low even at 2 K, approximately $dQ = 10^{-2} \text{ eHz}^{-1/2}$ [63].

### 6.5.2 SETs

The charge sensitivity of the SET can be quite high relative to other electrometers, both because the responsivity $R_I$ of current to charge $Q$ on the gate of an SET is relatively high, and since the autospectral shot noise current density can be suppressed below the classical value $S_{II}(f) = 2eI$. The high responsivity can be understood on the basis of the elastic electron transport mechanism of the SET in the context of the constant interaction model discussed in Section 1.4.5. Despite the simplicity of the this model, it captures the essential behaviour for the present discussion. Under the conditions that each tunneling barrier has a resistance of the order of $R_L \approx R_R \gtrsim \hbar/e^2 \approx 26 \text{ k}\Omega$, and $e^2/C_\Sigma \gtrsim k_BT$, the number of electrons on the island, and the amount of energy needed to add an electron to the island, are well defined. Changing the gate voltage by $\delta V_{GS}$ changes the $n$-electron chemical potential on the dot by

$$\delta \mu(n) = -e(C_G/C_\Sigma)\delta V_{GS},$$

such that a charge $-q$ on the gate gives $\delta \mu(N) = qe/C_\Sigma$. For large enough $q$ that the chemical potential $\mu_{dot}$ is no longer aligned within $\approx k_BT$ of the leads, the sequential tunneling process becomes much less likely, simply because a smaller fraction of electrons in the upstream lead have sufficient energy to charge the island. A single charge on the gate $C_\Sigma = 100 \text{ aF}$ produces a chemical potential change of $\delta \mu(N) \approx 1.6 \text{ meV}$, enough to significantly change the conductance of a SET at a temperature $T = 4.2$ K ($k_BT = 0.36 \text{ mV}$).

In practice, the highest charge sensitivity is obtained not by operating the SET in the regime of sequential tunneling, but rather, in a higher bias regime where higher order processes contribute to transport, but Coulomb oscillations are still present[184]. Besides
the high responsivity, the mean square shot noise in such systems was first predicted\[193\] and later verified\[194\] to be suppressed below the classical value $2eGV_{DS}$ in the single electron tunneling regime described above, due to correlations, \textit{i.e.}, the same electron-electron interactions which produce Coulomb blockade.

Use of external cabling and room temperature amplifiers normally imposes a stray capacitance $C \approx 0.1 - 1 \text{ nF}$, which, due to the minimum resistance $R \approx e^2/h$ of the SET, imposes a bandwidth limitation $f = 1/(2\pi RC)$ of a few kHz\[184\]. The available charge measurement bandwidth has been improved to nearly 100 MHz\[184\] by insertion of the SET into a resonant LC circuit, and measurement of its scattering parameters by microwave techniques. This is particularly important, since sensitivity below a few kHz is typically limited by 1/f noise\[195\]. State of the art SET electrometers are summarized in Table 6.2. The intrinsic speed limit of the SET is given approximately by the time constant of the tunnel junctions, $f = 1/(2\pi RC_{\Sigma}) \approx 10 \text{ GHz}\[184\]$. While high temperature operation is possible in principle, fabrication of metallic SETs with total capacitance $C_{\Sigma}$ small enough requires both tiny feature sizes ($\sim 10 \text{ nm}$) and small tunneling capacitance. The latter is generally associated with higher resistance devices, which are in turn associated with lower charge sensitivity\[189\].

6.5.3 QPCs

Quantum Point Contacts have been extensively used as charge detectors at Liquid Helium temperatures\[196\]. The mechanism of responsivity can be understood in terms of the Landauer-Büttiker formula\[98\] for the zero temperature conductance of $2N$ spin-polarized one dimensional sub bands each with a transmission coefficient $T_{i,\sigma}$,

$$G = \frac{e^2}{h} \sum_{N,\sigma = \pm 1/2} T_{i,\sigma}. \quad (6.26)$$

Depending on how strongly the charge can couple to the transmission coefficient of the channel, large charge responsivity can be realized. However, weak lateral confinement and
resulting small sub-band splitting $E_N - E_{N-1}$ of the split-gate, etched, and anodically oxidized QPCs restrict their operation temperature to below 4.2 K[94]. The analysis in Chapter 5 suggests that QPCs with smaller lateral dimensions should retain high charge sensitivity at high temperatures, but so far there is no literature available on this. Similar to SETs, cabling capacitance to room temperature amplifiers limits their bandwidth. Therefore, high frequency measurement schemes similar to those employed in SETs have recently been employed demonstrating both high charge sensitivity of $10^{-4}$ - $10^{-5}$ eHz$^{-1/2}$ close to the intrinsic, shot-noise limit, and bandwidth of tens of kHz to a few MHz.[197, 190]

### 6.5.4 MEMs and NEMs

Recent advances in micromachining make MEMs and NEMs based sensors of much current interest[198]. Common to MEMs and NEMs-based electrometers is electrostatic coupling between conductors with at least one of the conductors integrated on a flexible mechanical structure whose displacement or resonance frequency is influenced by the coupled charge, and subsequently measured. The earliest example is a a micron-scale torsion bar resonator placed in vacuum and cooled to 4.2 Kelvin[182]. A Coulomb force

$$F_E = \frac{q_0^2}{Cd}$$  \hspace{1cm} (6.27)

is experienced by the torsional oscillator due to its capacitive coupling $C$ to an external charge $q_0$ on a metallic gate a distance $d$ away from the rotator. This force influences the torsional oscillator’s motion (resonant frequency, or phase, when driven at a constant frequency), which in turns couples by electromotive force to room-temperature electronics. A peak charge sensitivity $10^{-1}$ eHz$^{-1/2}$ was obtained, at 4.2 K. When limited by thermal noise of the voltmeter, Cleland et. al. predict that the device can be operated with a bandwidth of 10 kHz and sensitivity of $10^{-4}$ eHz$^{-1/2}$ at 4.2 K.[182]. A more recent MEMs modulated capacitor design boasts simplified readout and a charge sensitivity of
4 eHz\(^{-1/2}\) at room temperature[183].

### 6.6 Conclusions

The single charge capture and emission in a random random signal was compared with the spectral background of white noise. Very high equivalent charge sensitivities of \(dQ \approx 40 \mu\text{eHz}^{-1/2}\) at 25 K, \(dQ \approx 25 \mu\text{eHz}^{-1/2}\) at 90 K, and \(dQ \approx 60 \mu\text{eHz}^{-1/2}\) at 200 K were obtained for \(d \approx 30\) nm NWFETs. Experimentally obtained charge sensitivities, plotted in Figure 6.7 (filled squares) were found to be limited by instrumentation, and conservative estimates of white-noise limited charge sensitivities (filled triangles) for measured nanowires are even better (\(dQ \approx 4 \mu\text{eHz}^{-1/2}\) at 25 K, \(dQ \approx 20 \mu\text{eHz}^{-1/2}\) at 90 K, and \(dQ \approx 15 \mu\text{eHz}^{-1/2}\) at 200 K). Comparison of the temperature and equivalent sensitivity of NWFETs with other systems demonstrates that NWFETs can provide a combination of high charge sensitivity and high temperature operation that has not been demonstrated by other devices including planar FETs (open diamonds), SETs (open squares), and NEMS-based systems (open triangles). The highest charge sensitivities reported for SETs cluster towards high sensitivity but low temperatures, whereas literature on NEMS-based electrometers demonstrate sensitivity on the order of \(1 - 0.01\) eHz\(^{-1/2}\). NWFET device optimization (channel length, nanowire diameter) and material optimization (electronic properties) are realistic and promising avenues for obtaining higher changes in conductance due to single charges, and ultimately, higher intrinsic-noise-limited charge sensitivities even at higher operating temperatures.
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<th>Temp (Kelvin)</th>
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<th>$f_{BW}$ (Hz)</th>
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Table 6.2: Characteristics of commercial and laboratory electrometers.
Figure 6.7: Comparison with field-effect transistor, single-electron-transistor, and nano-electro-mechanical-systems electrometer technologies.
Chapter 7

Photocurrent Spectral Response of ZnSe Nanowires

7.1 Introduction

With its room temperature bandgap of 2.7 eV, Zinc Selenide (ZnSe) is an interesting material for visible light emitters and detectors due to its near-bandgap optical absorption and emission at 470 nm, small lattice mismatch $\Delta a/a = (a_{\text{ZnSe}} - a_{\text{GaAs}})/a_{\text{GaAs}} \approx 0.3\%$ [49] with technologically important Gallium Arsenide substrates, and recently, successful P-doping and subsequent demonstration of bulk PN junction diodes[200, 201]. There are a number of reports on synthesis[202, 203, 204] and optical properties[202, 203, 205] of ZnSe nanowires. Well oriented arrays of ZnSe nanowires were grown on GaAs substrates[202] and optical properties have been shown to depend significantly on growth conditions[203].

Meanwhile, ZnSe nanowire-based electronic and opto-electronic devices have not received comparable attention in the literature. In this chapter, we electrically characterize individual, unintentionally doped ZnSe nanowires with diameter $\approx 80 - 100$ nm, metal-semiconductor junctions between ZnSe nanowires and bilayer Ti/Au ohmic contacts, and the photocurrent spectral responsivity of a ZnSe nanowire with two such contacts. The
contacts were patterned lithographically using a lift-off process, with metals deposited by physical vapour deposition, subsequently annealed by rapid thermal annealing.

Specific contact resistivity[206] and ZnSe nanowire’s intrinsic resistivity were found to be $\rho_c = 0.024 \ \Omega \text{cm}^2$ and $\rho_s \approx 1 \ \Omega \text{cm}$ at room temperature, respectively. The spectral photocurrent response of a single, $100 \pm 10$ nm diameter ZnSe nanowire was experimentally measured at room temperature, exhibiting a strong turn on in photoresponse for wavelengths shorter than 470 nm at room temperature. This is consistent with the diameter of ZnSe nanowires which well exceeds the diameter $\sim 2 - 4$ nm below which they can be expected to exhibit size quantization[202].

The responsivity of ZnSe nanowires biased at 2.0 V was found to be $22 \pm 2$ A/W for photoexcitation at 400 nm, the shortest wavelength studied. The spectral response of the photocurrent in the range $400 - 470$ nm is analyzed in the context of a simple model of spectral absorption in bulk ZnSe crystals to obtain an estimate of the photoconductive gain $g \sim 500$ which is appreciable despite the low bias voltage of 2.0 V. Moreover, the low bias excludes the possibility of an avalanche-type process in producing the observed gain. Instead, the gain is equal to the ratio of excess carrier lifetime $\tau$ to the transit time $\tau_{tr}$ of carriers through the nanowire, and the latter is estimated to be at least $\tau \approx 50 - 500$ ns. This comfortably exceeds the room temperature bimolecular recombination lifetime in ZnSe[207]. Combined with the slow transient response of the photocurrent, this suggests a rapid selective trapping of one species of carriers, enhancing the lifetime of the opposite species as previously discussed for nanowire photodetectors by Soci et. al.[208]. A thematic connection emerges with previous chapters on carrier trapping, and in particular Chapter 6, where the carrier localization is important for producing the high charge sensitivity.
7.2 Nanowire Growth and Device Fabrication

ZnSe nanowires with $80 \sim 100$ nm nominal diameter and length of approximately $10 \sim 30$ $\mu$m were grown by CVD methods using ZnSe powder and the detailed procedure outlined in reference [203] and subsequently transferred from the growth substrate to a host silicon substrate covered with 100 nm of SiO$_2$, and their coordinates were recorded with respect to a predefined metallic marker grid using an electron beam lithography (EBL) system. After the transfer of nanowires to the host substrate, a copolymer/PMMA bilayer resist film was deposited on the nanowire substrate, and EBL was used to define two and four-terminal contact configurations along the length of selected ZnSe nanowires. Typical spacing between contacts was $2 \sim 6$ $\mu$m. Electron beam evaporation was used to deposit Ti (30 nm) / Au (220 nm) contacts through the resist mask, at a base pressure of $\approx 2 \times 10^{-7}$ mbar. After liftoff, samples were annealed in a home built rapid thermal annealing system at 325 $^\circ$C for 2 minutes that was purged with flowing nitrogen gas. SEM images of two and four contact structures fabricated on ZnSe nanowires are shown in Figure 7.1a and b respectively, and wafers containing such patterns were diced and subsequently mounted for electrical measurements.

Figure 7.1: SEM images of (a) two and (b) four Ti/Au electrodes (bright regions) deposited on individual ZnSe nanowires. (scale: 2 $\mu$m).
Chapter 7. Photocurrent Spectral Response of ZnSe Nanowires

7.3 Electrical Characteristics of ZnSe Nanowires and Ti/Au Ohmic Contacts

The current-voltage (I-V) characteristics of nanowires with two Ti/Au electrodes were measured using a Hewlett-Packard (HP) 4140B picoammeter, by biasing one electrode and measuring current flowing at the opposite electrode. Measured I-V characteristics for NW #1 and NW #2 are shown in Figure 7.2. Least-squares fit of the data to a linear relationship between current and voltage gives a resistance of $126 \pm 1 \, \text{M}\Omega$ and $51 \pm 1 \, \text{M}\Omega$ for NW #1 and NW #2 with distance $L_w = 5.5 \, \mu\text{m}$ and $L_w = 5.0 \, \mu\text{m}$ between contacts, respectively. Current-voltage characteristics for these two nanowires are typical of the half dozen ZnSe nanowires measured, which are linear and symmetric up to the maximum voltage measured ($\pm 8 \, \text{V}$). The extent to which the I-V characteristics are influenced by the series resistance of the contacts can not be determined from simple two-terminal measurements.

![Figure 7.2: Measured current voltage characteristics for NW #1 and NW #2 and least-squares fit to linear current-voltage characteristics (lines).](image)

A ZnSe nanowire with four annealed Ti/Au electrodes (with width $L_c = 1.0 \, \mu\text{m}$, separated by a distance $L_w = 4.0 \, \mu\text{m}$) was measured to independently study the electrical resistances of the metal-semiconductor junction and the semiconductor nanowire. Again
the I-V characteristics of the series combination of the nanowire and two contacts were obtained by applying a potential $V$ across electrodes 2 and 3 and measuring the current $I$ at terminal 3, with terminals 1 and 4 floating. Within the model of Figure 7.3a, the measured I-V characteristic reflect the series combination of the resistance $R_w$ of the ZnSe nanowire and the resistance $2R_c$ of two oppositely biased metal-semiconductor junctions, such that $R_w + 2R_c = V/I$. A four-terminal measurement was carried out to remove, as much as possible, the effects of contact resistance. A potential $V_{14}$ was applied across end terminals 1 and 4, and both the current $I$ flowing from terminals 1 to 4, and the potential difference $V_{23}$ between terminals 2 and 3 were measured using an ammeter and two voltmeters with high internal input resistance. The use of a high input resistance voltmeter ensures that a negligibly small current flows in terminals 2 and 3, in order that there is no potential difference across the contact resistance of electrodes 2 and 3.

The gap between electrodes $L_w \sim 5 \mu m$ exceeds considerably the expected electron mean free path $L_e \sim 10 - 100 \text{ nm}$ of lightly doped, single crystal ZnSe at room temperature[49]. Therefore, we consider charge transport within the semi-classical drift-diffusion approximation[118]. Within the simplified model of Figure 7.3b, which holds when $L_c$ is small compared to $L_w$, the current-voltage characteristic satisfies $R_w = V_{23}/I$, from which $R_w = 8.9 \pm 0.5 \text{ M} \Omega$ is obtained. The current-voltage characteristic $I - 2V_c$ of the metal-semiconductor junction is obtained using the relation $2V_c(I) + V_m(I) = V(I)$, valid for a constant current $I$, where $2V_c$ is the sum of the voltages across the two metal-semiconductor junctions. The current-voltage characteristics of the nanowire $I - V_{23}$, contacts $I - 2V_c$, and the series combination of the two, $I - V_{14}$, are shown in Figure 7.4.

The extracted current-voltage characteristic $I - 2V_c$ is that of two oppositely biased metal-semiconductor junctions in series combination. If carrier transport through the junction was dominated by thermionic emission, the total current through the series combination of junctions would be limited by the current through the reverse biased junction, and would not increase with increasing voltage in the manner observed. We
conclude that the metal-semiconductor junction barrier is either of negligible height at the temperature considered, or is penetrable by quantum mechanical tunneling, \( i.e. \), field emission, even for relatively small applied bias.

\[ x_{N+Lc/2} \]

\[ x_{N-Lc/2} \]

\[ \rho_{c} \]

\[ \frac{2\pi r F dx}{\pi r^2} \]

\[ \frac{\rho_{s} dx}{\pi r^2} \]

\[ R_{c} \]

\[ R_{w} \]

\[ l_{2} \]

\[ l_{3} \]

\[ R_{1} \]

\[ R_{2} \]

\[ R_{3} \]

\[ R_{4} \]

\[ V_{c} \]

\[ x_{N+Lc/2} \]

\[ x_{N-Lc/2} \]

\[ I_{1} \]

\[ I_{2} \]

\[ I_{3} \]

Figure 7.3: (a) Equivalent model in two-terminal measurement showing path of current flow (dark resistors) and (b) Equivalent model in four-terminal measurement showing path of current flow (dark resistors). (c) Transmission length model for metal-nanowire junction. Nanowire has resistivity \( \rho_{s} \) and metal-semiconductor junction specific contact resistivity \( \rho_{c} \).

### 7.3.1 Resistivity of ZnSe Nanowires

The resistivity of the ZnSe segment of length \( L_{w} = 4.0 \mu m \), radius \( R = 40 \text{ nm} \), and resistance \( R_{w} = 8.9 \text{ M\Omega} \) nanowire is \( \rho_{s} = \pi r^{2} R_{w}/L_{w} \approx 1 \text{ \Omega cm} \). The resistivity of our unintentionally doped ZnSe nanowires is comparable to that of epitaxial films of unintentionally doped n-type ZnSe prepared under near-stoichiometric conditions[209].
7.3.2 Transmission-Length Model for Nanowire Ohmic Contacts

The specific contact resistivity $\rho_c$ is defined as the ratio of the voltage drop $V_c$ across a metal-semiconductor interface to the current density $J$ flowing through it. For junctions where the metal-semiconductor interface is not parallel to the direction of current flow in the semiconductor, the transmission length model\[206, 210\] can be used to establish a relationship between the contact resistance $R_C$ which manifests itself in experiments, and the specific contact resistivity $\rho_c$, which describes the metal-semiconductor junction properties. Within this model, shown in Figure 7.3c, the metal semiconductor junction of length $L_c$ is broken up into arbitrarily small segments of length $dx$ whose properties are described by resistances

$$ R_1(x) = \frac{\rho_s}{\pi R^2} dx $$  \hspace{1cm} (7.1) \\

associated with current flow along the axis of the nanowire, and resistances

$$ R_2(x) = \frac{\rho_c}{2\pi RF} dx $$  \hspace{1cm} (7.2)
associated with current flow perpendicular to the nanowire’s surface, where $0 < F < 1$ is the fraction of the nanowire’s circumference covered by the ohmic contact. While the current $I_1$ ($I_2$) flowing through resistances $R_1(x)dx$ in region $x < x_N - L_c/2$ ($x > x_N + L_c/2$) does not depend on $x$, the current flowing through resistances $R_1(x)dx$ depends on $x$ in the region $x_N - L/2 < x < x_N + L/2$, regardless of the value of $I_2$, due to the network of interface resistances described by $R_2(x)$.

The potential at any node associated with a coordinate $x$ is obtained by summing currents at that node,

$$
\frac{V(x) - V(x + dx)}{dx} \frac{\pi R^2}{\rho_s} + \frac{V(x) - V(x - dx)}{dx} \frac{\pi R^2}{\rho_s} + \frac{(V(x) - V_C)2\pi RFdx}{\rho_c} = 0. \tag{7.3}
$$

Taking the limit $dx \to 0$ we obtain a second order differential equation governing the potential $V(x)$ for $x_N - L/2 < x < x_N + L/2$,

$$
\frac{d^2(V(x) - V_C)}{dx^2} = \frac{V(x) - V_C}{L_T^2} \tag{7.4}
$$

where $L_C = \sqrt{(\rho_c R)/(\rho_s 2F)}$ is the transfer length, which effectively describes the length $L_T$ of the region of the contact of total length $L_c$ where appreciable current flows parallel the normal vector of the interface[206]. This model provides the spatial distribution of potential and current flowing through the contact interface, given appropriate boundary conditions that are readily derived by summing currents at $x = x_N - L_c/2$ and $x = x_N + L_c/2$,

$$
\frac{dV}{dx}(x_N - L_c/2) = -I_1 \tag{7.5}
$$

$$
\frac{dV}{dx}(x_N + L_c/2) = +I_3 = -I_1 - I_2. \tag{7.6}
$$
7.3.3 Specific Contact Resistivity

Applying the boundary conditions in Equations 7.6 for a two-terminal measurement circuit in Figure 7.3a into Equation 7.4,

\[
R_c = \frac{V_c}{I} \tag{7.7}
\]

\[
= \frac{(V_C - V(x_N + L/2))}{I_1|_{I_1=0, I_2=I_3=I}} \tag{7.8}
\]

\[
= \frac{\rho_s L_T}{\pi r^2} \coth(L_c/L_T). \tag{7.9}
\]

Linearizing the measured (superlinear) \( I - 2V_c \) characteristic (Figure 7.4) around \( V = 0 \) we obtain the linearized low bias contact resistance, where it reaches its highest value \( R_c = \frac{1}{2} \frac{\partial V_c}{\partial I}|_{V_c=0} = 9.0 \pm 0.5 \, \text{MΩ} \). Solving Equation 7.9 using \( L_c = 1.0 \, \mu\text{m} \), the nanowire radius \( R = 40 \, \text{nm} \), and resistivity \( \rho_s = 1 \, \Omega\text{cm} \) gives \( \rho_c = 2.4 \times 10^{-2} \, \Omega\text{cm}^2 \) for the specific contact resistivity. Most notably, this value is comparable to the best reported values for ohmic contacts to bulk crystals and thin films of n-type ZnSe. In one report, annealed multilayer Ti/Pt/Au contacts to thin films of n-type ZnSe were found to have a specific contact resistivity of \( 8.8 \times 10^{-2} \, \Omega\text{cm}^2 \), \( 6.2 \times 10^{-2} \, \Omega\text{cm}^2 \), and \( 3.4 \times 10^{-4} \, \Omega\text{cm}^2 \) for Ga and Cl doped samples with electron concentration of \( 5 \times 10^{16} \, \text{cm}^{-3} \), \( 4 \times 10^{18} \, \text{cm}^{-3} \), and \( 2 \times 10^{19} \, \text{cm}^{-3} \), respectively[211]. Annealed Indium contacts to n-type ZnSe thin films also had similar specific contact resistivities[212]. In comparison, state-of-the-art technology for ohmic contact formation to \( \text{e.g., } n\text{-type GaAs is quite advanced}[213], \) with specific contact resistivities only considered satisfactory if below \( 10^{-5} \, \Omega\text{cm}^2[213] \). While ohmic contact formation to n-type ZnSe is relatively straightforward, it is thought to be limited at high annealing temperatures by interfacial barriers created by reactions at the interface between the semiconductor and metal[214].
7.4 Spectral Photocurrent Response of ZnSe Nanowire Photodetectors

The steady-state photocurrent spectral response of a single ZnSe nanowire with diameter $100 \pm 10$ nm was measured. A tungsten lamp - regulated by an Oriel 68931 radiometric power supply and spectrally filtered by a monochromator - provided the optical excitation focused to a spot size of 0.5 mm diameter on the substrate by a reflective object lens, at normal incidence to the substrate, as shown in Figure 7.5a. A bias of 2.0 V was applied across the two Ti/Au contacts (see Figure 7.5b), and current measurements were performed using a high-precision programmable electrometer ammeter, Keithley Instruments Model 617. A programmable shutter was inserted into the optical path so that current flowing through the nanowire could be measured with and without optical excitation for each wavelength.

![Figure 7.5: (a) Schematic diagram of optical setup providing monochromatic excitation to nanowire (b) closeup schematic of normal incidence of monochromatic source.](image)

The photocurrent $I_{pc}$, defined as the difference in current flowing with the shutter open and closed, was measured for excitation wavelengths between 400 and 700 nm. The spectrum of measured photocurrent, shown in Figure 7.6a exhibited a turn-on at 470 nm.
near the fundamental absorption edge of bulk ZnSe (460–465 nm)[215]. This is consistent with the relatively large diameter $d = 80 \pm 10$ nm of the ZnSe nanowire, which is not expected to exhibit size quantization[202]. We do not observe any photoresponse for wavelengths between this fundamental absorption edge and 700 nm. The photocurrent turnoff has a slow relaxation component that persists seconds after the optical excitation is turned off, but the current always returns to the dark level after approximately thirty seconds. We found that increasing the bias to 4.0 V for one second, then returning it to 2.0 V always rapidly returned the current to the dark level. The slow decay observed is probably related to trapping by surface or bulk traps in the nanowire’s interior, producing the so-called persistent photoconductivity, which can apparently be quenched by applying a voltage large enough to empty the trap levels by field emission.

![Figure 7.6](image_url)

Figure 7.6: (a) Spectrum of measured photocurrent of ZnSe nanowire and (b) Spectrum of excitation intensity measured using a calibrated Si diode.

The incident optical intensity of the excitation spot of $d = 0.5$ mm, plotted in Figure 7.6b, was measured using a calibrated Newport 818-SL silicon diode photodetector and Newport 835 optical power meter (Newport Corporation, Irvine, CA). The incident intensity changes by only a factor of two between the largest wavelength where photocurrent is observed ($\lambda = 470$ nm, $I = 1.14$ mWcm$^{-2}$), and the short wavelength operating limit of the silicon diode photodetector ($\lambda = 400$ nm, $I = 0.52$ mWcm$^{-2}$). The measured
photocurrent $I_{pc}$ and excitation intensity $I$ were used to extract the spectral responsivity at 2.0 V bias, $\mathcal{R}(\lambda) = I_{pc}/P_{opt}$ where $P_{opt}$ is optical power incident on the nanowire. The latter is the product of the measured optical intensity $I$ and the effective cross sectional area $A$ of the nanowire, which is defined as $A = 2L_wR$, for simplicity. The spectral photocurrent responsivity shown in Figure 7.7, which is as high as $\mathcal{R} = 22 \pm 2 \text{ A/W}$ at 400 nm, comparable to that of high performance ZnSe photodetectors under similar electrical bias conditions[216].

The photoresponse of our ZnSe nanowires which have a linear current-voltage characteristic can be understood from the point of view of the change in conductance induced by the steady state excess carrier population, itself produced by the balance between generation and recombination of excess carriers, the former induced by the incident radiation, and the latter characterized by a carrier lifetime $\tau$. Associated with the excess carrier lifetime $\tau$ is a photoconductive gain $g$ given by the ratio of the carrier lifetime to the transit time $\tau_{tr}$ of carriers through the system.

![Figure 7.7: Spectral responsivity of ZnSe nanowire at 2.0 V bias.](image)
7.4.1 Photoconductive Gain

The photoconductive gain reveals how many excess carriers travel from electrode 1 to electrode 2 in Figure 7.5b on the average timescale $\tau$ of excess carrier recombination. Because the responsivity $R$ is directly proportional to the photoconductive gain, as will be shown below, it is a quantity of particular interest in nanoscale photoconductors. We obtain an estimate of this gain by considering the responsivity in terms of the photoconductance $\Delta G$ of the ZnSe nanowire. Simple geometrical arguments give

$$\Delta G = \int_{|r|<R} d^2r \Delta \sigma / L_w, \quad (7.10)$$

where $\Delta \sigma = e_0 \mu \Delta n$ is the photoconductivity, $e_0$ is the electronic charge, $\mu$ is the carrier mobility, and $L_w$ is the length of the nanowire, and the integral is performed over the cross-sectional area of the nanowire of radius $R$. Assuming for simplicity that the ZnSe nanowire has a rectangular cross section of side length $d = 2R$, the cross-sectional integral of the carrier density due to incident intensity $I$ can be approximated as

$$\int_{-R}^{R} dx \int_{-R}^{R} dy \Delta n = 2RI\lambda \tau \eta / h c \eta_e, \quad (7.11)$$

where $R$ is the nanowire radius, $hc/\lambda$ is the photon energy, $\eta_e = (1 - \exp(-2\alpha(\lambda)R)) (1 - r)$ is the external quantum efficiency, $r$ is the reflectance at the air/ZnSe interface, and $\alpha(\lambda)$ is the absorption coefficient for radiation at wavelength $\lambda$[217]. Substituting $I_{pc} = V \Delta G$ and $P_{opt} = I_2 RL$ we obtain

$$R = g \left( \frac{e}{hc/\lambda} \right) \eta_e \quad (7.12)$$

where $g = \tau / \tau_{tr}$ is the photoconductive gain and $\tau_{tr} = L_w^2 / V \mu$ is the transit time. The peak responsivity at $\lambda = 400$ nm implies a photoconductive gain of $g \sim 500$, using $r \sim 0.1$, obtained assuming the ZnSe nanowire has bulk-like optical characteristics[215], which is justified due to its large diameter. Assuming an upper bound for the carrier mobility in the range $10 - 100$ cm$^2$V$^{-1}$s$^{-1}$[49], the lifetime of excess carriers producing photocurrent is at least $\tau = 50 - 500$ ns. This seems excessively high[207] and suggests
that a large number of trap sites rapidly capture one carrier, prolonging the other carrier’s lifetime. Nevertheless, the carrier lifetime $\tau \sim 50 - 500$ ns obtained from this analysis is still considerably shorter than the slow decay of several seconds discussed in Section 7.4. This presents no contradiction however since the traps involved could have an ensemble of lifetimes and the estimate for mobility is an upper bound. The direct proportionality of responsivity $R$ to gain $g \sim 500$, and therefore, carrier lifetime $\tau \sim 50 - 500$ ns implies that larger responsivity can be obtained by increasing carrier lifetime, at the expense of the photoconductor’s turn-off time. The extent to which this approach can be useful depends on the desired measurement bandwidth, which varies from one technological application to another. One application for which an array of high-gain photodetectors may be useful is in imaging technology, where photo sensing bandwidth need not exceed 100 Hz in typical situations.

For bulk ZnSe, the absorption coefficient for 400 nm radiation is approximately $1.5 \times 10^5$ cm$^{-1}$[215], so that at this wavelength, $\alpha d = 1.5$, and the full absorption regime $\alpha d \gg 1$ is only reached for $\lambda < 350$ nm. This explains why the observed spectral responsivity $R(\lambda)$ does not have the characteristic sawtooth shape[218] typical of bulk photoconductors, in the wavelength region of the experiment. Given the similarity between the exciton binding energy of ZnSe ($17$ meV) [215] and the thermal energy at room temperature ($k_B T = 25.6$ meV), the broadened peak that appears in the photocurrent (at $\sim 2.75$ eV) could be evidence of excitonic absorption. This has also been observed in ZnSe thin film photodetectors. [219]

7.5 Conclusions

Metallic Ti/Au electrodes were deposited and annealed at 350 °C on unintentionally doped ZnSe nanowires grown by chemical vapour deposition. Four terminal measurements demonstrate that the metal-semiconductor junctions is non-rectifying, has a spe-
specific contact resistivity of $\rho_c \approx 0.024 \ \Omega \text{cm}^2$, and that ZnSe nanowires have an electrical resistivity $\rho_s \approx 1 \ \Omega \text{cm}$. The spectral photocurrent responsivity of the nanowire reaches $\mathcal{R} = 22 \ \text{A/W}$ at 2.0 V bias and 400 nm. A photoconductive gain $g \sim 500$ was extracted, establishing that excess carriers travel from one electrode to the other several hundred times before recombining. The corresponding excess carrier lifetime is estimated to be $\tau \sim 50 - 500 \ \text{ns}$, which places an intrinsic turn-off transient, and therefore, speed limit on the nanowire based photoconductor. Since $\alpha d \lesssim 1$, the shape of the spectral response is essentially determined by the absorption coefficient of ZnSe.
Chapter 8

Summary and Outlook

This thesis presents a set of experiments that advances the understanding of critical issues such as electronic structure, strain relaxation, magnetic doping and scattering from single impurities, in the carrier transport properties of semiconductor nanowires, structures whose diameter imparts quasi-one-dimensional behaviour to the carriers. A novel method for characterization of the (gate voltage dependent) surface potential of single nanowire field-effect transistors (FETs) is described that is based on analysis of random telegraph signals and complements well established capacitance-voltage (CV) characterization of FETs, the latter which is difficult to apply to nanostructures due to their tiny gate capacitance that decreases with decreasing size. The same random telegraph signals were used as a novel method to spectroscopically study the strong carrier reflection at a single Coulomb impurity in a nanowire. Extending this, we show that InAs nanowires can operate is extremely sensitive charge sensors (electrometers) at high temperatures (200 K), a combination of characteristics that is not achieved by existing technology. Finally, ZnSe nanowire photodetectors are studied, and it is found that they can have very high responsivity and a large internal gain multiplication effect realized by rapid selective trapping of excited carriers.

Chapter 2 studies the carrier transport properties of InAs and InAs/GaAs core/shell...
nanowires grown by MBE, with emphasis on the relationship between field effect mobility and strain relaxation and electronic structure. Carrier transport properties of the InAs nanowires exhibited effects of electronic sub-band quantization even up to 77 K. However, InAs nanowires that had GaAs shells grown by radial heteroepitaxy were studied by transmission electron microscopy exhibited incoherent strain relaxation - linked directly to imaged edge dislocations - for even the smallest InAs diameter and shell thickness studied, \( d = 20 \) nm, and \( t = 2 \) nm, respectively. Correlated with the strain relaxation in the GaAs-shell InAs nanowires was a nearly ten-fold decrease in field effect mobility. Meanwhile, the field-effect mobility of the uncapped InAs semiconductor nanowires, \( \mu_{\text{FE}} = 2000 - 4000 \ \text{cm}^2\text{V}^{-1}\text{s}^{-1} \) at 300 K and \( \mu_{\text{FE}} = 10000 - 20000 \ \text{cm}^2\text{V}^{-1}\text{s}^{-1} \) at 30 K was among the highest reported in the literature[115]. Furthermore, \( \mu_{\text{FE}} = 20000 \ \text{cm}^2\text{V}^{-1}\text{s}^{-1} \) is similar to what has been observed for InAs/InP core/shell nanowires at 4 K[159, 161] where signatures of ballistic effects have not yet been observed. In comparison, single wall carbon nanotubes with length \( \approx 300 \ \mu\text{m} \) can have extremely large room temperature field effect mobility \( \mu_{\text{FE}} \approx 100,000 \ \text{cm}^2\text{V}^{-1}\text{s}^{-1} \)[121]. Nevertheless, the highest field effect mobility in single nanotube devices with channel lengths \( L \approx 3 \ \mu\text{m} \) is \( \mu_{\text{FE}} \approx 4000 \ \text{cm}^2\text{V}^{-1}\text{s}^{-1} \)[102]. The discrepancy between long and short nanotubes arise due to enhanced role of carrier scattering at the contact interface and mode mismatch related contact resistances in the latter. Goals for future work include growth and fabrication of InAs nanowire field effect transistors that more closely approach the ballistic limit, exploration of further miniaturization of InAs nanowires’ diameter, and its influence on carrier transport properties. The latter would likely also permit exploration of the possibility of coherently strained, dislocation free InAs/GaAs core/shell nanowires. Presented together as the unified discussion in Chapter 2, these results are presented in our papers already in press[220, 221] and another paper in preparation. The last set of results relevant to the discussion in Chapter 2 are in Appendix A on ferromagnetic Mn-doped ZnO nanowires[69, 222]. For a single Mn-doped ZnO nanowire with diameter
Chapter 8. Summary and Outlook

\[ d = 350 \text{ nm}, \text{ carrier density and mobility were found to be } n_0 = 3.6 \times 10^{17} \text{ cm}^{-3} \text{ and } \mu_{FE} = 35 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \text{ respectively at } T = 225 \text{ K}, \text{ and both were found to monotonically decrease as a function of temperature down to 12 K where they reach } 3.2 \times 10^{17} \text{ cm}^{-3} \text{ and } 6.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}, \text{ respectively, consistent with a degenerate semiclassical electron gas whose conduction is limited by ionized impurity scattering. The large diameter of the ZnO:Mn nanowires compared with the diameter } 2 - 3 \text{ nm where electronic sub-band quantization can be expected to occur ensures their electrical properties behave according to the semiclassical, bulk limit. Future work on this material system should address the very challenging problem of determining the relationship between electrical properties and magnetism, where there has been some recent progress for Mn-doped ZnO thin films [223, 224, 225]. These studies are motivated by the prediction of room temperature ferromagnetism in heavily p-doped and Mn-doped ZnO[61], experimental observation of the same in bulk n-type samples[226, 62] and n-type nanowires[69], and the potential applications of such materials in future spin-based electronics. Field-effect transistors fabricated using one dimensional structures such as those studied in this thesis offer the tantalizing technological and scientific possibility to control the magnetism externally, by tuning the carrier concentration from p-type to n-type by an external gate electrode.

The random telegraph signals (RTS) in conductance of InAs nanowires were studied in Chapter 3, and assigned to fluctuation of the charge state on a single defect. Chapter 4 based on our paper (reference [227]), demonstrates a novel method providing the first direct measurements of the gate-voltage dependent channel potential of a single nanowire field effect transistor, using the statistics of the time-sequence of stochastic capture and emission of single electron from a single electronic defect. This relationship is of considerable technological relevance for emerging nanoelectronics and sensing applications, and we show how in the circumstances corresponding to our experiment, it closely approximates the integrated density of electronic states. Crucially, the method succeeds for small nanostructures where standard capacitance-voltage spectroscopy, which provides related
information, is quite difficult to employ due to the tiny gate capacitance \([115, 71, 72, 73]\). These results were obtained in a regime where quantum mechanics necessarily blurs the distinction between surface and bulk properties. This is taken into account in the detailed analysis presented, which also shows that the evolution of channel potential with gate voltage is suppressed even in the accumulation regime due to the screening effects of surface states with \(D_{ss} = 1 - 2 \times 10^{12} \text{ cm}^{-2}\text{eV}^{-1}\). Dynamics of electron capture and emission by these defects was interpreted in terms of a model for multiphonon emission, with parameters consistent with spatial location of the trap on the surface of the nanowire. Within a wider perspective, the work is a new example reinforcing the notion that intrinsic fluctuations in nanoscale systems are not just “noise”. Rather, RTS fluctuations of conductance (in the “1/f” category of noise) can tell us something about the physical system being studied, that the mean value of the conductance can not. This is a very important idea in nanoscale systems where fluctuations such can be nearly as large the mean value. Future work should include a comparison and/or correlations between quasi-equilibrium properties obtained by capacitance-voltage spectroscopy and analysis of RTS. Extending ideas about noise beyond RTS, shot noise could be used as a probe for electronic structure and scattering\[66\] in small diameter InAs nanowires.

The same random telegraph signals whose temporal statistics and dynamics were considered, also afford a direct connection between conductances \(G_H\) and \(G_L\) in a random telegraph signal and transmission \(T_{\text{imp}} = (G_L^{-1} - G_H^{-1})^{-1}/G_0\), \((G_0 = 2e^2/h)\), of nanowire’s quasi-one-dimensional carriers through the scattering potential of a single Coulomb impurity. In Chapter 5 we studied the reflection probability \(R_{\text{imp}} = 1 - T_{\text{imp}}\) spectroscopically (as a function of gate voltage/Fermi energy) and found reflection probabilities approaching unity \((R \approx 0.98 - 0.999)\) even for an electron gas of intermediate degeneracy in 30 nm diameter InAs nanowires at 30 K. Results were compared with microscopic theory of electron scattering by Coulomb impurities in nanowires with electronic sub-band quantization and dielectric confinement, using exact mean-field screening
in the envelope function approximation. Dielectric confinement, which is known to enhance the bare Coulomb interaction and excitonic binding energy\[169, 170\], was found to be essential to reproduce the observed strong scattering of carriers for moderate to small electron densities $n$ between 10 and 30 /µm, for repulsive Coulomb impurities. In comparison, attractive Coulomb impurities had a relatively small effect on scattering, with reflection probability only $0.1 - 0.05$, demonstrating their relatively small influence on carrier transport, and a strong asymmetry in the relative contributions to scattering by Coulomb impurities of same/opposite sign as the charge carrier. A publication on this topic is also in preparation.

Chapter 6 considers the application of charge sensing by small diameter semiconductor nanowires, relevant for technological goals such as realization of quantum computers, chemical sensors that can detect single molecules, and memory chips with ultra-low power consumption; applications that require detection of ever smaller amounts of charge at the fastest possible speed. State of the art metallic single-electron-transistor (SET) electrometers offer charge sensitivity of $\approx 2 \times 10^{-6} \text{eHz}^{-1/2}$ at 4 K, but traditional metallic SETs have difficulty operating at temperatures above approximately 10-20 K, restricting their technological applications. We show that a single InAs nanowire FET (NWFET) with measured and noise limited charge sensitivity summarized in Figures 6.2, 6.3 and 6.4, can provide performance approaching that of SETs at temperatures as high as 200 K. The key, as first described in our paper (reference [154]) and later described in this thesis, is to enhance the interaction between the target electron and the conducting electrons by squeezing the diameter of the nanowire as small as possible to enhance coupling of the Coulomb potential to the electron gas, reducing carrier concentration so the electronic screening length exceeds the diameter, and using a low dielectric permittivity environment for the nanowire to further weaken screening. The results of this chapter opens several avenues for additional investigation and applications. First, fabrication and characterization of locally gated nanowire electrometers is suggested as a method to couple a
programmable charge to the nanowire. Preferably, a gate length $L \approx 2\lambda$ (where $\lambda$ is the Thomas-Fermi screening length) should be employed to maintain highest possible charge sensitivity. Incremental improvements in sensitivity are possible by bringing operation of the NWFET as close as possible to the ballistic, and extension of results presented Chapter 2. Total bandwidth of the NWFET electrometer could also then be studied, with e.g., the NWFET placed in a suitable impedance transformation network.

In Chapter 7, the first process for ohmic contact fabrication on individual ZnSe nanowires was reported and properties of the metal-semiconductor junctions quantified. Our paper (reference [228]) associated with Chapter 7 was the first to measure the spectral photocurrent responsivity of a single nanowire, a key performance metric describing the amount of electrical current generated per Watt of incident optical power. The very high spectral responsivity of 20 A/W, similar to that of expensive epitaxial ZnSe thin-film based photodetectors, implying a gain of $g \approx 500$, the number of electrons collected at the biased terminals of the nanowire photodetector per optically generated electron-hole pairs, to fast selective trapping of one of the two carriers. This conclusion made from the steady-state photocurrent response was corroborated by observation of a slow component in the transient photocurrent decay upon removal of the illumination. The high gain at a relatively low bias of 2.0 V could be useful in applications where high sensitivity is required at low operating voltages. The relationship $g = \tau/\tau_{tr}$ between photoconductive gain $g$, carrier lifetime $\tau$, and transit time $\tau_{tr}$ implies that higher responsivity can be obtained by increasing carrier lifetime. However, ZnSe nanowire photodetectors measured in this thesis exhibited a noticeable turn-off transient ($< 1$ s) that is likely to be linked to the large gain, setting up a tradeoff between gain and bandwidth for nanowire’s with selective trapping as a gain mechanism. Future work on photoconductive ZnSe nanowires should focus on determining the signal-to-noise ratio for photodetection, engineering of the properties of trapping centres to trade off gain and lifetime, and fabrication of nanowire-Schottky barrier diodes to minimize dark current.
For charge and photon sensing applications considered in Chapters 6 and 7 respectively, it is noteworthy in hindsight that carrier trapping plays an important but different role in enhancing responsivity and sensitivity. Localization of the charge enhances the scattering rate (Chapter 5) of low density, high mobility carriers, and therefore also the charge sensitivity, as discussed in Chapter 6. When one species of photo-generated excess carriers is rapidly and selectively trapped, the lifetime of the other species can be dramatically boosted[208] providing a large number of excess carriers collected at the device terminals per incident photon, i.e., photoconductive gain.
Appendix A

Electron transport in degenerate Mn-doped ZnO nanowires

A.1 Introduction

Spurred by the discovery of magnetic order in the first “dilute magnetic semiconductors”, Manganese-doped InAs (with Curie Temperature 7.5 K for 0.5 atomic % Mn)[229] and shortly thereafter, Manganese-doped GaAs (with Curie Temperature 110 K)[230], significant research efforts have been directed at finding a dilute transition metal-doped semiconductor exhibiting ferromagnetism at room temperature. Such a material would be very valuable for proposed semiconductor-based spintronic devices, where information is encoded and manipulated in the spin of degree of freedom of carriers[231, 232]. Interest in magnetic doping of ZnO exploded in the year 2000 after the theoretical prediction that dilute (\(\sim 5\) at \%) transition metal doping could produce hole-mediated ferromagnetism in ZnO at room temperature, for hole densities exceeding \(\approx 3 \times 10^{20}\) cm\(^{-3}\)[61]. Only three years later, room temperature ferromagnetism was experimentally observed in ZnO thin films doped with \(< 4\) at \% Manganese[62]. However, p-type doping was not employed, and transition metal incorporation in the Zn sublattice is not expected to produce shal-
low acceptors, since the valence shells of Zn and Mn are isoelectronic. Rather, n-type conduction was found, prompting speculation about the origin of the observed magnetism and whether or not it is mediated by carriers, since the latter is a necessity for spintronic devices. More recent studies have demonstrated room temperature ferromagnetism in n-type Mn-doped ZnO films with carrier densities in the range $1 \times 10^{17} \text{ cm}^{-3} - 4 \times 10^{19} \text{ cm}^{-3}$, albeit with weaker than expected magnetization[233, 226, 234]. The origin of the observed magnetism and the relationship between magnetic and electronic properties is a subject of much recent debate[223, 224, 225]. One recent study[223] found that strong magnetism accompanied by spin splitting of the conduction band is possible in strongly n-type dilute Mn-doped ZnO. The authors found that ferromagnetism was quenched for intermediate electron densities and returns in the electrically insulating regime. Another clue for the correlation between electrical and magnetic properties is that the presence of native point defects, particularly, oxygen vacancies, reportedly has an influence on magnetism[226]. Indeed, the origin of room temperature ferromagnetism in transition metal doped ZnO is acknowledged as among the most controversial topics in condensed matter physics and magnetism[224].

Herein we report fabrication and electrical measurements of single nanowire field effect transistors with 1 atomic % Mn-doped ZnO nanowires synthesized by Philipose et. al.[69], that are n-type. Philipose et. al. recently reported growth and magnetic measurements of single-crystal (1 – 4 atomic %) Mn-doped ZnO nanowires with diameter 40 – 100 nm prepared by Au-catalyzed VLS growth. Ferromagnetism with a Curie Temperature above 400 K [69] was obtained. The authors performed transmission electron microscopy (TEM) studies showing no secondary phases, and the Mn incorporation fraction was established independently by energy-dispersive X-ray spectroscopy (EDXS) and inductively coupled plasma mass spectroscopy (ICPMS). In this chapter we present variable temperature electrical measurements of back-gated, Mn-doped field-effect transistor structures to elucidate their electronic properties. We establish that nanowires
from the same sample that exhibit ferromagnetism are n-type conductors. The relatively large effective mass of electrons in ZnO dictates that their carriers do not experience any appreciable quantum mechanical confinement[235] for nanowire diameters in the range studied, and indeed the electron gas in these Mn-doped ZnO nanowires behaves semi-classically. At a temperature of 225 K, the field-effect mobility and free electron density of a typical Mn-doped ZnO nanowire, estimated using the charge control model, were 35 cm$^2$V$^{-1}$s$^{-1}$ and $3.6 \times 10^{17}$ cm$^{-3}$ respectively. The latter varies weakly with temperature down to 12 K, signifying that the material is degenerate. Field-effect mobility decreases with decreasing temperature but saturates at 12 K, in a manner consistent with ionized impurity scattering in a degenerate semiconductor.

A.2 Nanowire Growth and Structural Characterization

Manganese-doped ZnO nanowires were grown by Au-catalyzed chemical vapour deposition on Silicon (001) oriented substrates, in a quartz tube furnace. Argon carrier gas was used to carry source materials evaporating from two sources, (1) an alumina crucible with a 1:1 mixture of ZnO and graphite source powders held at 900 °C, and (2) an alumina crucible with MnO$_2$ source powder held at 700 °C. Silicon (001) substrates coated with 5-10 nm thin film of Au were placed downstream of source materials at 700 °C. The growth time was 1 hour. Scanning electron microscopy was used to examine the morphology of the nanowires grown on the substrates, revealing a nominal length of 5-10 µm and diameter that depends on the thickness of the deposited film, anywhere from $\approx 50 - 500$ nm. A lattice-fringe high resolution transmission electron microscopy (HRTEM) image of the nanowire is shown in the inset of Figure A.1. Manganese content revealed independently by Energy-Dispersive X-Ray Spectroscopy (EDXS) and Inductively Coupled Mass Spectroscopy (ICPMS) was found to be 1-4 atomic %, with EDXS images revealing
uniform distribution throughout the wires. Transmission Electron Microscopy shown in Figure A.1 was used to determine the crystal structure of nanowires which is hexagonal (Wurtzite) with an interplanar spacing of 5.2 Å and no inclusions or Mn-rich secondary phases. Further details on preparation and structural characterization of nanowires are provided in references [236] and [69].

A.3 Magnetic Properties

Magnetization measurements using a SQUID magnetometer showed the background diamagnetic contribution of the Silicon substrate with a distinct hysteretic magnetization loop overlayed on top. Figure A.2a shows the variation of magnetization $M$ with applied field $H$ for a Mn-doped ZnO sample with 1 atomic % Mn, taken at 300 K. The coercive field required to change the sign of the magnetization, is $H_c = 40$ Oe, and the remnant magnetization is $M_r = 2.5 \times 10^{-6}$ emu[237]. The temperature dependence of both the coercive field and remnant magnetization are shown for the same sample is it was warmed.
Figure A.2: (a) Magnetization Loop for at 300 K for 1 at % Mn-doped ZnO Nanowires and (b) Temperature dependence of coercive field, remnant magnetization, and field cooled magnetization between 4 and 400 K.

from 1.8 K to 400 K in Figure A.2b, after cooling it to 1.8 K in a field of 100 Oe. From the observed saturation magnetization, the magnetic moment per Mn atom is estimated to be in the range of 0.3\(\mu_B\) to 1.2\(\mu_B\), which is less than the maximum moment 5\(\mu_B\), but in good agreement with values even in the most recently published literature[225].

On the origin of the magnetism in Mn-doped ZnO, several important comments are in order. First, and most obviously, control ZnO nanowires with no Mn doping did not exhibit ferromagnetism. Second, the observed hysteresis cannot be attributed to ferromagnetic impurity phases, since there is no known phase of manganese oxide or zinc-manganese with a Curie temperature exceeding 300 K. All known manganese oxide phases are antiferromagnetic with the exception of Mn3O4, which has a Curie temperature below 45 K. Moreover, metallic manganese itself is paramagnetic, while direct exchange between Mn ions is antiferromagnetic. Further details on magnetic characteristics of Mn-doped ZnO nanowires prepared using the method described in Section A.2 are given in references [236] and [69].
Figure A.3: (a) Scanning electron micrograph of two Ti/Au electrodes fabricated on Mn-doped ZnO nanowire and (b) Electrical measurement setup with programmable voltage sources on electrodes (drain and gate), and ammeter connected to source electrode.

A.4 Device Fabrication

Mn-doped ZnO nanowires grown by VLS with 1 atomic % Manganese content were transferred from a donor Silicon substrate to a p+ Silicon host substrate \( (p_0 \approx 10^{19} \text{ cm}^{-3}) \) covered with a 100 nm thick layer of SiO\(_2\). The location of selected nanowires on the host substrate were recorded with respect to predefined markers using an electron beam lithography (EBL) system. After spin coating a copolymer-PMMA resist mask and subsequent patterning by electron beam lithography, metallic Ti/Au electrodes were deposited by electron beam evaporation at a base pressure of \( \approx 2 \times 10^{-7} \text{ mbar} \). After liftoff and cleaning, the host substrate was transferred to a rapid thermal annealing system and annealed at 325 °C for 2 minutes under flowing nitrogen gas, to reduce contact resistance of the interface between Ti and ZnO[238, 239]. After annealing, host substrates were diced and mounted for cryogenic electrical measurements in a copper chip carrier. Electrical contact to the back-gate was established by indium bonding to the substrate. Scanning electron microscopy (SEM), shown in Fig. A.3a, shows the structure of the deposited electrodes after fabrication.
A.5 Field-Effect Transistor Measurements

Current-voltage characteristics were measured at room temperature in rough vacuum, using a Hewlett-Packard 4140B picoammeter to measure the current $I_{DS}$ at the source terminal and two programmable DC voltage sources connected to the drain and gate electrodes providing biases $V_{DS}$ and $V_{GS}$ respectively, as shown in Figure A.3b. The measured current-voltage $I_{DS} - V_{DS}$ characteristics of a $R = 175$ nm radius Mn-doped ZnO nanowire are shown in Figure A.4a, with the gate and source terminals held at ground potential, for temperatures $T$ between 12 and 230 K, with the sample held in vacuum in a closed-cycle He cryostat. These characteristics exhibited no noticeable nonlinearity, verifying that annealed Ti/Au contacts are Ohmic. Moreover, conductance remained appreciable throughout the entire temperature range, illustrating that the carrier gas is not thermally activated for temperatures above 12 K. Current through the nanowire was measured for several gate voltages with the source grounded and the drain terminal held at a fixed bias $V_{DS} = 2.0$ V (Figure A.4b). Like all other ZnO:Mn nanowires studied, increasing the gate voltage $V_{GS}$ increases the conductance of the wires indicating that nanowires have have a free-carrier gas at zero gate bias comprised of free electrons. Owing to the lack of rectifying PN of Schottky junctions at the source and drain contacts, the nanowire field effect transistor is of the depletion mode variety[120]. However, the large radius of the nanowire ensures that the nanowire is impossible to fully deplete within the range of gate voltages $|V_{GS}| < 30$ V that will not damage the SiO$_2$ gate dielectric.

The charge control model for field effect transistors[120] was used to extract the equilibrium carrier density $n_0$ and field effect mobility $\mu_{FE}$ from the measured $I_{DS}$-$V_{GS}$ characteristics according to

$$n_0 = \frac{V_T C}{eAL}, \quad (A.1a)$$

$$\mu_{FE} = \frac{\partial I_{DS}}{\partial V_{GS}} \frac{L^2}{CV_{DS}}, \quad (A.1b)$$

where $C$ is the gate capacitance to the nanowire, $V_T$ is the threshold gate voltage to fully
deplete the nanowire, $L = 6.0 \, \mu m$ is the distance between adjacent Ti/Au electrodes, $R = 175 \, nm$ is the nanowire radius, and $A = \pi R^2$ is the nanowire’s cross-sectional area.

The back-gate capacitance was estimated in the vicinity of $V_{GS} = 0$ using the finite element method for two cases, an electron gas at the surface of the nanowire, or throughout its the bulk. The electron density was treated in the semiclassical, Thomas-Fermi approximation\[81\],

$$n(r) = N_C \mathcal{F}_1( \frac{E_F - E_C - e\Phi(r)}{k_B T} ),$$  \hspace{1cm} (A.2)

where $\mathcal{F}_j(\eta) = 1/\Gamma(j+1) \int_0^\infty du u^j (1 + \exp(u - \eta))^{-1}$ is the complete Fermi-Dirac integral of order $j$, $N_C = 2 (2\pi m_e k_B T / h^2)^{3/2}$ is the effective density of states of ZnO, $m_e = 0.24 m_0$ is the effective mass for electrons in ZnO\[49\], $T$ is the electron temperature, and $\Phi(r)$ is the electrostatic potential which satisfies the self-consistent Poisson equation, given by

$$\nabla \cdot (-\epsilon(r) \nabla \Phi(r)) = e_0 (N_D H(R - r) - n(r) + N_{SD} \delta(r - R)).$$  \hspace{1cm} (A.3)

Here, $\epsilon(r)$ is the position dependent dielectric permittivity ($3.9 \epsilon_0$ and $7.8 \epsilon_0$ for SiO$_2$ and ZnO, respectively\[49\]), and $N_D$ and $N_{SD}$ are ionized bulk donor density and surface donor densities, respectively, $\delta(x)$ is a Dirac delta function, $H(x)$ is a Heaviside step function, $z$ is directed along the length axis of the nanowire, and $r = \sqrt{x^2 + y^2}$ is the
Figure A.5: Solution domain for electrostatic potential $\Phi(r)$ bounded by Neumann conditions on top and sides and Dirichlet condition $\Phi(x, y = -t_{ox}) = V_{GS}$ on the back-gate, for $V_{GS} = -5.0$ V.

radial coordinate. The solution space for the FEM calculation is shown in Figure A.5. The capacitance per unit length,

$$C/L = L^{-1} \partial Q/\partial V_{GS}$$  \hspace{1cm} (A.4)

$$= e \int \int \frac{dxdyn(x, y)}{\partial V_{GS}}$$  \hspace{1cm} (A.5)

extracted from the self-consistent FEM solution to $\Phi(r)$ and $n(r)$ works out to $C/L \approx 110$ aF/$\mu$m at $V_{GS} = 0$, for both the surface and bulk electron gas.

The threshold voltage $V_T$ was obtained by extrapolating (to zero conductance) the linear $I_{DS} - V_{GS}$ characteristic for $V_{GS} < -10$ V. The carrier density, inferred from $C$ and $V_T$ obtained as described above, is plotted in Figure A.6a, decreases from $3.6 \times 10^{17}$ cm$^{-3}$ to $3.2 \times 10^{17}$ cm$^{-3}$, and can not be reconciled with the temperature dependence of electron density $n_0 \propto \exp(-\Delta E_d/2kT)$ in a non-degenerate n-type semiconductor with a donor ionization energy $\Delta E_d$[240]. From the high residual conductivity at 12 K it can be concluded that Mn-doped ZnO nanowires are in fact degenerate at low temperatures[241, 242].
Appendix A. Electron transport in degenerate Mn-doped ZnO nanowires

We have estimated the effective degree of degeneracy, \( \eta_0 = \frac{(E_F - E_C)}{kT} \), of the mobile carriers by solving \( n_0 = N_C F_{1/2}(\eta) \). We find that \( \eta_0 \) increases monotonically from \(-2\) to \(6\) for temperatures from \(225\) K to \(12\) K, and that the Fermi energy saturates to about \(6.5\) meV above the conduction band edge for \(T < 30\) K. Within this picture, a non-degenerate semiconductor has \( \eta \ll 0 \).

Studies have shown that undoped ZnO thin films [243, 244, 245] and nanowires [246, 247, 248] are often naturally n-type with free electron density commonly falling between \(10^{16}\) and \(10^{18}\) cm\(^{-3}\). This is normally attributed to donor-like intrinsic point defects such as Oxygen vacancies and Zinc interstitials. The latter, which has an ionization energy of around \(30\) meV, is thought to be a dominant shallow donor in undoped ZnO [249]. In contrast, substitution of Mn into the Zn sublattice of ZnO (Mn\(_{\text{Zn}}\)) should not contribute shallow donor or acceptor levels, since the outer shell of Mn is isoelectronic with Zn [62]. Indeed, strong n-type conductivity has been observed in otherwise undoped ferromagnetic Mn-doped ZnO \((n_0 \approx 1 \times 10^{17} \text{ cm}^{-3} - 4 \times 10^{19} \text{ cm}^{-3})\) [233, 226, 234]. In one report, [226] annealing the sample in an Oxygen ambient quenched the observed ferromagnetism along with electrical conductivity, illustrating the interplay between intrinsic defects, electrical

Figure A.6: Temperature dependence of carrier density (diamonds) and \( \eta \) (circles), and (b) Measured temperature dependence of field effect mobility (circles) plotted with asymptotically degenerate (dash-dot) and nondegenerate (dashed) temperature dependences.
properties, and magnetic properties of Mn-doped ZnO. The observed carrier density is probably due to a large density of intrinsic defects - whose presence is confirmed by strong green luminescence accompanying well defined near-band edge emission in our photoluminescence spectroscopy measurements [69] - as opposed to Mn\textsubscript{Zn}. We cannot rule out the possibility of surface related conductivity, which have been observed in ZnO[250], however the conclusions about degeneracy and carrier type are not affected even if surface conductivity is assumed. The demonstrated gate control of free carrier density suggests that it may be possible to electrically control the magnetization of Mn-doped ZnO nanowires, and use them as a tunable source of spin-polarized electrons.

The field effect mobility defined in Equation A.1b is the change in conductivity per unit of free charge density induced by the backgate. In homogeneous unipolar samples the field effect mobility is smaller than the drift mobility if gating changes the occupation of bulk or surface related bound states (in which conduction is limited to hopping) or if carrier density is modulated mostly at the semiconductor/oxide interface region, where scattering is usually enhanced[217]. Because of the relatively high carrier density and large diameter of our nanowires, the effect of the former is probably minimal. We numerically evaluate \( \frac{\partial I_{DS}}{\partial V_{GS}} \) at \( V_{GS} = 0 \) V and find that the field effect mobility (see Fig. A.6b) decreases monotonically from 35 cm\(^2\)V\(^{-1}\)s\(^{-1}\) to 6.5 cm\(^2\)V\(^{-1}\)s\(^{-1}\), for temperatures between 225 K and 12 K.

In high quality non-degenerate ZnO thin films and bulk crystals, mobility is dominated by polar optical phonon, piezoelectric acoustic phonon, and ionized impurity scattering at high, moderate, and low temperatures, respectively[244]. Electron mobility initially increases with decreasing temperature, and the transition to ionized impurity dominated scattering is accompanied by a peak in the mobility curve. For lower temperatures the mobility has a \( T^{3/2} \) temperature dependence[245]. We do not observe a regime where mobility increases with decreasing temperature, and the field effect mobility is well below the expected value for polar optical phonon-limited mobility. Therefore, it is likely that
ionized impurity scattering is the dominant process in the temperature range studied. Brooks-Herring ionized impurity scattering theory predicts $T^{3/2}$ and $T^0$ dependences assuming asymptotically non-degenerate or degenerate distributions respectively[251], and the measured field effect mobility fits these dependences well in the high temperature and low temperature limits, respectively (see Fig. A.6b). Using the measured carrier density to infer the temperature dependent equilibrium carrier distribution function $f_0(E, E_F, T)$, we have computed the low-field mobility

$$\mu_{II} = \frac{e}{m_e} \int_0^\infty \tau_{II}(E) E^{3/2} \frac{\partial f_0}{\partial E} dE$$

(A.6)

in a spherical parabolic band with $k^2 = 2m_eE/h^2$ using the Brooks-Herring ionized impurity momentum relaxation time $\tau_{II}(E)$

$$1/\tau_{II}(E) = \frac{C}{k^3} \left[ \ln(1 + 4k^2\lambda^2) - \frac{4k^2\lambda^2}{1 + 4k^2\lambda^2} \right].$$

(A.7)

The prefactor $C = N_I e^4 m_e/8\pi\epsilon_s^2 h^3$ depends on the the relative dielectric constant $\epsilon_s = 7.8\epsilon_0$ for ZnO, and the total ionized impurity density $N_I$. Numerically evaluating the screening length

$$\lambda = \sqrt{\frac{\epsilon_s k_B T F_{1/2}(\eta)}{e^2 n F_{-1/2}(\eta)}}$$

(A.8)

and mobility $\mu_{II}$ using full carrier statistics predicts that the mobility should make a smooth transition from a high temperature $T^{3/2}$ regime to a low temperature $T^0$ regime. This lends further support to our interpretation of increasing degeneracy at low temperatures. Quantitative comparison between the measured high temperature mobility and the Brooks-Herring theory indicates the ionized impurity density should be an order of magnitude larger than the carrier density. One possible explanation is a high degree of compensation. Indeed, as-grown n-type ZnO can be self-compensated[243], though similar studies on Mn-doped ZnO are not yet available. The field effect mobility varies with temperature more weakly for large $|V_{gs}|$, in comparison to $V_{gs} = 0$ V. It is not clear what role surface scattering and charging plays in the channel under these circumstances.
A.6 Conclusions

Manganese-doped ZnO nanowires were electrically characterized by field effect transistor measurements and found to be n-type, consistent with other reports of ferromagnetic dilute Mn-doped ZnO[62, 226], and exhibited non-activated electron transport from room temperature down to 12 K and semiclassical, bulk-like behaviour. For a single wire with diameter $d = 350$ nm, carrier density and mobility were found to be $n_0 = 3.6 \times 10^{17}$ cm$^{-3}$ and $\mu_{FE} = 35$ cm$^2$V$^{-1}$s$^{-1}$ respectively at $T = 225$ K. Carrier density and field effect mobility were found to monotonically decrease as a function of temperature down to 12 K where they reach $3.2 \times 10^{17}$ cm$^{-3}$ and $6.5$ cm$^2$V$^{-1}$s$^{-1}$, which are both consistent with a degenerate electron gas whose conduction is limited by ionized impurity scattering. We attribute the presence of the electron gas to intrinsic defects, rather than Mn$_{Zn}$, but further magnetotransport or magnetooptical measurements are required to determine if the conduction band in our Mn-doped ZnO nanowires is spin polarized, as recently reported for n-type Mn-doped ZnO[223]. If so, gate voltage modulation of the electron density in Mn-doped ZnO nanowires could potentially be used to electrically control their magnetic properties, paving the way for possible applications in room temperature spintronics.
Appendix B

Contributions

B.1 Peer Reviewed Publications


**B.2 Articles In Preparation**

• J. Salfi, S. V. Nair, I. G. Savelyev, H. E. Ruda, *Breakdown of linear screening and enhancement of backscattering by a single Coulomb impurity for dielectrically confined electrons in nanowires*. Based on Chapter 5

• J. Salfi, S. V. Nair, I. G. Savelyev, H. E. Ruda, *Ballistic transport in the first two subbands of InAs nanowires up to 77 K*. Based on results in Chapter 2

B.3 Contributed Posters and Oral Presentations


Bibliography


[38] International technology roadmap for semiconductors. www.itrs.net.


