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Electrical characterization of semiconducting nanowires

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ELECTRICAL CHARACTERIZATION OF SEMICONDUCTING NANOWIRES

A Thesis

Presented to

The Faculty of the Department of Chemical and Materials Engineering

San Jose State University

In Partial Fulfillment

of the Requirement for the Degree

Master of Science

by

Steven Kuo

December 2007

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ABSTRACT

ELECTRICAL CHARACTERIZATION OF SEMICONDUCTING NANOWIRES

by Steven Kuo

Current semiconductor processing techniques are quickly reaching their physical limitations. One promising solution is nanoelectronics, where semiconducting nanowires can be used as a building block for electronic devices. In particular, TiO_2 nanowires have many potential applications including sensors and solar cell devices. In order to develop and optimize future nanoelectronics devices, characterization of the electronic properties of the nanowire is vital.

Two and four probe measurement devices were created by aligning nanowires across pre-patterned electrodes and by creating additional contacts by FIB deposited platinum. Resistance values for two probe TiO_2 nanowire measurements were $429.6 \text{ k}\Omega$ and $10.2 \text{ M}\Omega$. The discrepancy is attributed to the high contact resistance between the Pt- TiO_2 interface. Four probe measurements on Si nanowire showed reduction in data noise and elimination of contact resistance compared to two probe measurements. The measured resistance for the Si nanowire was $6 \text{ M}\Omega$.

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CHAPTER ONE OVERVIEW OF NANOTECHNOLOGY

Currently one of the most talked about subjects in the science community is nanotechnology. Nanotechnology represents the future of size reduction in all aspects of science. Under the umbrella of nanotechnology falls a variety of applications that can be very beneficial to society such as faster electronics, increased data storage capabilities, tiny sensors, and many others that have yet to be dreamed [1]. The economic impact from nanotechnology is slowly coming to fruition. While more and more employment opportunities have recently emerged, it is hoped that someday nanotechnology will lower operating costs and increase productivity in some industries. In addition, the creation of brand new industries based on nanotechnology will generate even more job opportunities, thereby increasing real wages and improving the standard of living [2].

Although products such as nanoparticles are currently being used in industry, these nanoscale materials simply replace microscopic materials in the same applications. The real promise lies in technologies that are based on whole devices produced on the nanoscale. Of these, nanoelectronics are one of the most heavily researched. Today's current fabrication technologies can only shrink electronic devices to a certain size, and those limits will probably be reached within the next 20 years [3]. In order to continue device shrinkage, a new method must be created to solve this problem. One of these methods involves creating electronic circuits from nanotubes and nanowires which have diameters of only a few hundred nanometers. These structures are magnitudes smaller than the relatively microscopic size of wires in chips today [3]. The so-called "bottom-

up” approach uses nanostructures such as nanotubes and nanowires as the basic building blocks upon which nanoelectronic devices will be built [4].

While carbon nanotubes have been investigated for some time and initially they were considered to be the main building block for nanoelectronics, researchers now believe that nanowires hold much more promise because they are more easily manipulated to achieve the electronic properties that are desired for making devices [3]. The difficulty with carbon nanotubes lies in the fact that they are essentially a single layer of graphitic sheet wrapped up to form a tube. Researchers have shown that the electronic properties are determined by the chirality, an asymmetric mirror image, of the nanotubes [5]. This implies that the properties of carbon nanotubes depend on the diameter and wrapping angles of the graphitic sheet [6]. This causes the nanotubes to exhibit either metallic or semiconducting properties depending on the wrapping angle relative to the zigzag or armchair directions [6]. Modifying and customizing these nanotubes to fit preferred properties in future nanoelectronic devices can be quite difficult, as a reliable method of altering the chirality of nanotubes has yet to be found. Nanowires, on the other hand, can be grown to exact chemical compositions, diameters, lengths, and electronic properties [1]. Therefore the need to increase research on nanowire capabilities is becoming urgent.

Nanowires are, in essence, material in the shape of a wire that is a few hundred nanometers in diameter. Compared to a human hair, nanowires are three orders of magnitude smaller. If one can imagine a standard copper wire a few millimeters thick that has been shrunk down to a thickness of a few hundred nanometers, than one has a

perfect idea of what a nanowire is. Although nanowires might be of the same composition and material as their bulk relatives, they can have different properties due to the fact that their small size classifies them as one-dimensional (1D) structure (see Section 2.1.2) [7]. One-dimensional nanostructures are the smallest structures that can efficiently transport electrons and optical excitations and this property is important in the development of future nanoelectronics applications as they are the smallest structures that can be used [7]. This could provide interesting usages of nanowires that have yet to be discovered. Since nanowires have the ability to serve as both a circuit interconnect and a functional device, they can potentially provide two of the important elements in nanoelectronics [4]. The ability to create numerous nanowires in a small amount of space creates the opportunity to make devices cheaper because of the abundance of the material. Because of economies of scale, this can greatly reduce costs in industries using nanowires [2].

Semiconductors serve as the backbone of the electronic circuit industry. Of the nanowire class of materials, it is no surprise that semiconducting nanowires are considered the building blocks of nanoscale devices. Nanowires made from semiconducting materials such as silicon, gallium nitride, or gallium arsenide will remain semiconductors regardless of diameter because they have inherently semiconducting properties. In addition, studies have shown that their electrical properties can be manipulated through conventional techniques, such as impurity doping and alloying [8]. Semiconducting nanowires are of great interest to the electronic device industry because they can be used to make nanoelectronic devices such as transistors and diodes [9,10]. In

the case of modern planar silicon devices, the silicon wafer acts as the foundation of the device and gates, interconnects and dielectric layers are created on top of the Si wafer. Removing the silicon wafer eliminates the largest structure in an electronic device and thus immediately decreases the size. The ability of a semiconducting nanowire to serve two different roles is a very attractive feature to researchers and engineers.

While certain rudimentary devices have been made [9,10], the development of semiconducting nanowires is still in its beginning stages. The transport properties of the nanowires need to be determined and characterized before useful applications can be produced. Because of the small size of nanowires, it is difficult to characterize their properties on a routine basis. A novel characterization method must be developed in order to have a better understanding of transport phenomena and advance nanoelectronic devices to the next level.

Recently, there have been some promising developments which might solve this problem. One such method is dielectrophoresis, based on the phenomenon that a non-uniform electric field produces a force on any polarizable object [11]. In this case, the polarizable object is the nanowire. By applying an AC or DC electric field between two electrodes, a nonuniform electric field can be created, which will attract the nanowire [12]. The immensely small size of a nanowire makes the ability to manipulate it and move it to a desired place a great advantage. Researchers have already managed to align materials on the nanoscale such as metallic and semiconducting nanowires, nanoparticles and nanotubes [13,14]. Being able to align a nanowire across two electrodes creates the opportunity to measure its properties, much like probing a copper wire with a handheld

multimeter. However, in order to reduce the effects of contact resistance, a four-probe measurement must be made instead. Two extra contacts can be made on the nanowire using focused ion beam platinum deposition to create four contact points, and thus the ability to make four-probe current and voltage readings. From these readings the resistance of the nanowire can be found and with the addition of temperature variation the band gap of a semiconducting nanowire can be determined.

This project focused on characterizing the electrical properties of semiconducting nanowires. Successful growth of titanium dioxide (TiO_2) semiconducting nanowires by the Dholakia Group at the Center for Nanotechnology at NASA Ames Research Center prompted the need to study their electrical properties. Not surprisingly, silicon nanowires have been studied by researchers around the world, but very little information is available for TiO_2 semiconducting nanowires. To continue the research at NASA Ames, temperature dependent electrical characterization was attempted by taking advantage of the phenomenon of dielectrophoresis and creating a four probe measurement system. The goal was to study the properties of semiconducting nanowires, as well as to develop a novel method of electrical characterization of nanowires.

CHAPTER TWO REVIEW OF NANOSCALE MATERIALS

In the bottom-up approach of building nanoelectronic devices there are two distinct classes of materials: nanotubes and nanowires. The former usually refers to carbon nanotubes and the latter to either metallic or semiconducting nanowires. This chapter will provide an overview of the two nanoelectronic materials currently being researched with a more in-depth discussion on nanowires. Section 2.1 first discusses the differences between bulk and nanoscale properties. Section 2.2 briefly discusses nanotube properties and Section 2.3 discusses the synthesis and properties of nanowires. Section 2.4 discusses TiO₂ nanowire applications.

2.1 Bulk vs. Nanoscale Electrical Properties

The characterization of the electrical properties of semiconducting nanowires is crucial to the continuation of nanoelectronic device development. Aside from gathering resistivity and band gap data, there is a need to understand how the properties are affected by nanoscale dimensions. The size effect on resistivity was first explained by Fuchs in 1938 [15]. In bulk form resistivity remains independent of material shape and size. However when the dimensions are decreased in one or two dimensions, for example a thin wire or a thin film, the resistivity starts to increase as the thickness decreases [15]. Fuchs explained that thin films and wires experienced additional scattering at the surfaces of the material due to its increased surface area to volume ratio, in addition to the scattering in bulk materials [15].

Observations by Mayadas and Shatzkes [16] indicate that grain size affects resistivity in polycrystalline material. These results have been reported for thin films and have recently been reported for nanowires. Durkan and Welland [17] reported resistivity increases as the diameter of a gold nanowire is decreased below 50 nm, and when the diameter was decreased to 20 nm the resistivity increased to 1.6 times greater than bulk values. In their study it was concluded that both surface scattering and grain boundary effects influence the increase in resistivity as diameter decreases [17]. Mohanty and Webb [18] also reported increased resistivity with decreased diameter in gold nanowires. In the study, gold nanowires with a cross sectional areas of 785 and 540 nm² had reported resistivity values of 1.83 and 6.35 $\mu\Omega$ cm respectively [18]. Compared to the bulk resistivity value of 2.2 $\mu\Omega$ cm, the smaller nanowire does have increased resistivity.

Steinhögl *et al.* [19] have reported the same phenomenon in rectangular copper wires with dimensions of 100 nm and smaller, as shown in Figure 1. In this plot the line width and height refer to the width and height of the rectangular wire respectively. The smaller height wire of 50 nm had a greater resistivity value when compared to the 230 nm wire. The authors also speculate that the increase in resistivity is due to surface scattering and grain boundary scattering [19].

These studies however, do not include materials without grain boundaries such as single crystalline nanowires. Sugaya *et al.* [20] reported an increase in electron-phonon interactions in InGaAs quantum wires as wire diameter decreased. The authors speculate that this is caused by electron backscattering due to singularities in the 1D density of states (see Section 2.3). This could explain increased resistivity in single crystalline

nanowires, however research is limited and more experiments on electronic properties of nanoscale materials need to be carried out.

Figure 1. Resistivity vs. line width for rectangular Cu wires where height refers to the thickness of the wire [19].

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2.2 Nanotubes

A carbon nanotube is essentially a graphitic sheet with a hexagonal lattice that has been wrapped around to form a tube [6]. Carbon nanotubes were first considered suitable for use in nanoelectronic devices mainly due to the good mechanical and electrical properties they possess, such as very high tensile strength and high electrical conductivity [7]. However, their electrical properties are hard to tune due to their unique structure. In order to alter the properties of nanotubes the chiral angle must be controlled as well as the diameter [6]. The chiral angle refers to the angle at which the graphitic sheet is rolled. In Table 1, data from Wildöer *et al.* [6] demonstrates the effect of the chiral angles and

diameter on the band gap of carbon nanotubes. Unfortunately, a reliable method of controlling the chiral angle is difficult to achieve and not currently available.

Table 1. The effect of chiral angle on the band gap of carbon nanotubes [6].

Tube Number	1	2	3	4
Chiral angle (°)	25	4	7	24
Diameter (nm)	1.4	1.4	2.0	1.2
E _{gap} (eV)	0.55	0.60	0.50	0.65

2.3 Nanowires

Nanowires can be either metallic or semiconducting depending on the composition; this alone makes it a more attractive alternative to carbon nanotubes. Rather than altering the physical structure of the material, the properties of nanowires can be controlled during synthesis. This is possible because nanowires are essentially smaller versions of their bulk counterparts. Because of their narrow diameter they are classified as a one-dimensional structures, which creates some unique properties. For example, in a 1D structure, known as a quantum wire, the density of states function has discrete peaks and exhibits a different behavior compared to 2D and 3D structures. The density of states can be defined as the distribution of allowed electron states as a function of energy [21]. For a 1D structure the density of states is described by Equation 1.

$$Z(E) = CE^{-\frac{1}{2}} \quad \text{Equation 1}$$

where $C = \frac{4\pi L^3 (2m)^{2/3}}{h^3}$, $E = \frac{n^2 h^2}{8mL^2}$ and n is the allowed energy level or quantum

number [21]. For nanowires, this confinement of states might be advantageous to future devices.

While metallic nanowires could be used in components of a nanoelectronic device, such as interconnects, they do not possess the properties needed for other applications. The most promising aspect of nanowires as a building block for nanoelectronics is the ability to be both a circuit interconnect and a functioning device. This phenomenon is seen specifically in semiconducting nanowires. Because nanowires can be grown to a specific composition, a wide variety of bandgaps can be achieved. Additionally, nanowires can be doped to attain desired electrical properties. Li *et al.* [22] have synthesized indium oxide (In_2O_3) nanowires using a laser-ablation chemical vapor deposition technique, which is a variation of the vapor-liquid-solid (VLS) growth method. A resistance of 580 k Ω was reported for In_2O_3 nanowires, however the band gap was not measured [22]. In addition to In_2O_3 , gallium phosphide (GaP) and gallium nitride (GaN) nanowires have been synthesized by Kim *et al.* and Nam *et al.* respectively [23,24]. Resistance ranges of 0.5 to 10 M Ω were reported by Kim *et al.* for GaP [23].

Silicon and germanium nanowires have been grown using the VLS method by Morales *et al.* [25], who have reported that lengths of up to 30 μm have been achieved. Cui *et al.* [46] report resistivity values ranging from 2.3×10^{-2} to 6.9×10^{-3} Ωcm .

2.3.1 Synthesis of Nanowires

Typically nanowires have been synthesized by the vapor-liquid-solid (VLS) growth method. The VLS method has been widely used because the size of the nanocluster catalyst determines the diameter of the nanowire being grown, and thus allows a degree of control of nanowire size [7]. In Figure 2 a diagram of the VLS growth method is shown. A nanocluster catalyst is chosen and then a reactant gas is flowed through at a high enough temperature to cause a reaction with the catalyst. A specific catalyst and nanowire material system is chosen which allows a liquid alloy and solid nanowire material to coexist in equilibrium. At the set temperature, a liquid alloy is formed between the catalyst and the nanowire. This serves as a preferential site to absorb the reactant gas. As the liquid becomes supersaturated with the reactant, it then precipitates out and crystallizes to form a nanowire [7]. Silicon and germanium nanowires have been synthesized using the VLS method described [7].

Figure 2. Basic diagram of the VLS growth mechanism [7].

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Another growth method that has recently been receiving attention is the sol-gel process. The sol-gel process uses an anodized alumina template instead of a catalyst to control the diameter of the nanowire. The template allows for a high density of uniform and controllable pore size. This method also has the added benefits of an easier preparation and lower production cost compared to VLS [26]. The sol-gel process is based on the hydrolysis and condensation of precursors such as metal alkoxides and inorganic salts [26]. The desired nanowire material is first prepared in a precursor solution or sol-gel. The template is then dipped in this solution for a set amount of time. The sol-gel then fills the pores of the anodized alumina template. A schematic of this process is shown in Figure 3. The filled template is then annealed at the desired temperature and time.

Sadeghzadeh *et al.* [26] report successful synthesis of titanium dioxide (TiO_2) nanorods with annealing temperature and time of 400 – 700°C and 2 hours respectively. Metallic nanowires such as boron, bismuth and antimony have also been grown by researchers using the anodized alumina template method [27,28].

2.3.2 Nanowire Devices

Nanoelectronic devices are showing promise as researchers are beginning to build rudimentary devices using nanowires. Cui *et al.* [10] created a transistor using a silicon nanowire. In Figure 4, a field effect transistor is shown using a silicon nanowire and in this case the nanowire is used as both a connection between the source and drain and the backbone of the device. The replacement of the silicon wafer with a silicon nanowire is a space saving feature attractive to circuit designers.

Figure 3. Schematic of empty anodized alumina template before and after dipping in sol-gel solution. The template is then annealed to complete the sol-gel reaction.

Figure 4. A field effect transistor built with a silicon nanowire [10].

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Typically the devices that are being created by researchers today are field effect transistors (FET), because they are the basic building blocks of any electronic circuit and are structurally quite simple to make. To create a field effect transistor, a nanowire is used to bridge two electrodes that act as a source and a drain. Goldberger *et al.* [9] created a zinc oxide (ZnO) FET by laying a ZnO nanowire across two electrodes made from a layer of Ti and Au. Kim *et al.* [8] has created a similar device with a GaP nanowire with the ability to react to UV light, which can be useful in nanoscale optoelectronic devices.

Lieber *et al.* [10] have created a silicon nanowire field effect transistor (SiNW FET) and compared it to a state of the art metal-oxide semiconductor FET (MOSFET). The data in Table 2 shows that the SiNW FET has several advantages to a traditional MOSFET. One of the key items is mobility, as the higher the mobility the faster charge carriers will move. In the SiNW FET, Lieber and coworkers have shown that mobilities fall in a similar range to those in planar Si devices. In some cases, even higher mobilities can be achieved for the SiNW FET [10]. The electron mobility for nanowires is expected to decrease from increased electron-phonon scattering. However, Ramayya *et al.* [29] have shown that higher electron mobilities are possible due to a decrease in density of states for scattering in 1D materials. From this property alone, one can expect the speeds of devices to increase significantly. The band gap for silicon nanowires have been measured by Ma *et al.* [30] and they report that it increases from 1.1 eV to 3.5 eV as the nanowire diameter decreased. These parameters all indicate that nanoelectronic devices will exceed what is capable of conventional devices made today.

Table 2. Comparison of key device parameters between SiNW FET and a traditional MOSFET [4].

	SiNW FET data	Traditional MOSFET
Gate length (nm)	50	50
Gate Oxide Thickness (nm)	1.5	1.5
Mobility (cm^2/Vs)	230-1350	500
I_{on} ($\mu\text{A}/\mu\text{m}$)	2000-5600	650
I_{off} (nA/ μm)	4-45	9
Subthreshold slope (mV/decade)	60	70
Transconductance ($\mu\text{S}/\mu\text{m}$)	2700-7500	650

2.4 TiO_2 Nanowires

Titanium dioxide (TiO_2) is a wide band-gap semiconductor that can be used in applications ranging from photovoltaics to photoluminescence and different types of sensors [31]. The potential applications have created a great demand in research as little is known about the electrical properties of single TiO_2 nanowires. However, bulk material properties of TiO_2 have been well studied in the past, typically in the form of a thin film or bulk crystal. Earle [32] reported a value of 1.7 eV for the band gap in a study on a powder form of TiO_2 that had been pressed and sintered to create a bulk single crystal. Breckenridge *et al.* [33] report resistivities ranging from 0.1 to 100 Ωcm , which was measured over a temperature range of 83 K to 1000 K. For thin-film TiO_2 , Huber *et al.* [34] report the band gap of the material to be in the range of 0.34 - 0.51 eV depending on the diameter of the nanoparticles in the thin-film.

2.5 Summary

Nanotubes and nanowires are being considered as materials to be used in future nanoelectronics devices. Nanowires are considered more promising due to the ability to control their composition during synthesis. Nanoelectronic devices such as transistors have been created using semiconducting nanowires. A better understanding of the properties of semiconducting nanowires is needed to create more complex devices. To achieve this, a novel method of characterizing single nanowires is needed.

CHAPTER THREE REVIEW OF CHARACTERIZATION TECHNIQUES FOR NANOMATERIALS

This chapter will provide an overview of the different methods for characterization of nanomaterials. Section 3.1 discusses the theory of dielectrophoresis. Section 3.1.1 and 3.1.2 discuss the use of dielectrophoresis to align nanotubes and nanowires. Section 3.2 and its subsections discuss four probe measurement theory and the different methods for creating four probe devices. Section 3.3 describes the chamber for temperature dependent measurements. Section 3.4 discusses the use of SEM imaging to verify nanowire alignment.

3.1 Dielectrophoresis

A vital component of this work is aligning nanowires on pre-patterned electrodes. In order to achieve this, the phenomenon of dielectrophoresis is used. The development of the technique was pioneered by H.A. Pohl in his book published in 1978 [35]. Dielectrophoresis is based on existence of a force which acts on any polarizable object in a non-uniform electric field. When a polarizable object is placed in an electric field, a positive charge and negative charge will build on opposite sides of the object and create a pushing and pulling force. In a uniform electric field, this pushing and pulling becomes equal and results in a zero net force. Conversely, placing an object in a nonuniform electric field builds an unequal positive and negative charge, with one side stronger than the other. Since the forces are unequal they will not cancel out and therefore a net force acts on the object [11].

It is with this force created by the nonuniform electric field that very small objects like nanowires can be manipulated. However, because the electric field will also act on the medium that the object is in, it will also influence the way the dielectric force behaves. If the medium has a polarizability that is higher than the object, the object will be pushed to the area with a weaker field; this is termed *negative dielectrophoresis*. When the object has a higher polarizability than the medium it is termed *positive dielectrophoresis*. The object is then pushed toward the higher field region [11]. In general, *positive dielectrophoresis* is used in electric field alignment experiments. Objects such as nanowires are desired to align toward the higher field region, which in this case, are the pre-patterned electrodes.

When a polarizable object is placed in an electric field it acts as a dipole and the force on the dipole can be expressed as Equation 2 [36]. In addition to the force, there will also be a resultant torque that aligns the particle with the field, as expressed in Equation 3.

$$\vec{F} = (\vec{p} \cdot \vec{\nabla}) \vec{E} \quad \text{Equation 2}$$

$$\vec{T} = \vec{p} \times \nabla \vec{E} \quad \text{Equation 3}$$

Where p is the dipole moment, E is the electric field, and $\vec{\nabla}$ is the gradient. This torque effect is what will ultimately cause the nanowires or nanotubes or any other long thin shape to align.

For a spherical particle with a radius r and a dielectric constant of ϵ_p , in a medium with dielectric constant of ϵ_m the new expression can be given by Equation 4, where Z is a geometric factor shown in Equation 5 [37].

$$\vec{F}_{DEP} = Z\epsilon_m K(\omega) \vec{\nabla}(\vec{E}_{rms}^2) \quad \text{Equation 4}$$

$$Z = 2\pi r^3 \quad \text{Equation 5}$$

E_{rms} is the root mean squared value of the electric field, assuming that the field is sinusoidally time dependent. $K(\omega)$ is the Clausius-Mosotti factor where ϵ_p^* and ϵ_m^* are the frequency-dependent complex permittivities of the particle and medium respectively in Equation 6 and ϵ^* is defined by Equation 7 [36].

$$K(\omega) = \text{Re} \left[\frac{\epsilon_p^* - \epsilon_m^*}{\epsilon_p^* + 2\epsilon_m^*} \right] \quad \text{Equation 6}$$

$$\epsilon^* = \epsilon - \frac{i\sigma}{\omega} \quad \text{Equation 7}$$

Where ω is the angular frequency of the applied field, σ is the conductivity and ϵ is the relative permittivity of the particle or medium.

These equations described a spherical particle that is placed in an electric field, however long and thin objects such as nanowires tend to be more polarizable than their spherical counterparts [13]. For a rod, the geometric factor Z in Equation 4 is replaced with Equation 8.

$$Z = \frac{\pi}{2} r^2 l \quad \text{Equation 8}$$

Where r is the radius and l is the length of the rod. The real part of the Clausius-Mossotti factor $K(\omega)$ is different than that for a sphere. The new $K(\omega)$ is given by Equation 9 with

the complex permittivity ϵ^* still equal to Equation 7 [37]. By examining the dielectrophoretic force in Equation 4, we can see that the direction of the dielectrophoretic force is always determined by the sign on $K(\omega)$.

$$K(\omega) = \text{Re} \left[\frac{\epsilon_p^* - \epsilon_m^*}{\epsilon_m^*} \right] \quad \text{Equation 9}$$

Either AC or DC electric fields can be used in dielectrophoretic alignment. The equations that govern the forces are not affected. In general, most researchers have used AC dielectrophoresis because the frequency seems to enhance the alignment effect [38].

To generate the electric fields required to manipulate nanomaterials, an AC voltage must be applied to two metal electrodes. This simple structure can be seen in Figure 5 and it involves a simple gap between two rectangular electrodes. Because the electrodes are planar, fringing effects near the edges will occur and create nonuniform electric fields [11]. The fringing is useful in positive dielectrophoresis, thereby attracting objects to the electrodes. In addition, as the electrodes are created with a smaller gap, higher electric field strengths can be achieved as the field is dictated by the applied voltage divided by the distance between the gaps. Thus it is desirable to create a small gap to maximize field strength [13]. Fortunately, this works in favor of nanowire alignment because the lengths of nanowires are usually on the order of microns.

Figure 5. Electrode setup for dielectrophoretic experiments. b) 3-D model illustrating a nanowire subjected to dielectrophoresis. The nanowire experiences a net dielectric force and aligns with the field lines. This force guides the nanowire toward the electrodes.

3.1.1 Nanotube Alignment by Dielectrophoresis

While the theory of dielectrophoresis was first studied in 1978, the application of the phenomenon to nanoparticles did not occur until 1998. Yamamoto *et al.* successfully aligned carbon nanotubes using AC dielectrophoresis [38]. In their study, nanotubes were dispersed in isopropyl alcohol and then dropped onto aluminum electrodes with a 400 μm gap that was created on a glass substrate. The AC electric field was applied until the suspension evaporated and the frequency was varied from 10Hz to 10MHz. The electric field was measured to be $2.2 \times 10^3 \text{ V}_{\text{rms}}/\text{cm}$ [38]. Successful alignment was verified by a scanning electron microscope (SEM). The study found that frequency plays an important role in successful alignment, as higher frequencies resulted in a higher probability of alignment [38]. Yamamoto *et al.* also demonstrated and reinforced the fact that long thin objects are much more responsive to dielectrophoretic force. The spherical

nanoparticles contained in the suspension were much less responsive than the carbon nanotubes [38].

In research done by Chen *et al.* [39], carbon nanotubes were again successfully aligned by AC dielectrophoresis. Similar to work done by Yamamoto *et al.*, carbon nanotubes were suspended in ethanol and placed on gold electrodes. However, the electrodes were altered to form interdigitated fingers and the gap between fingers was much smaller at 25 μ m [39]. Work done by Chen *et al.* [39] again reinforced the influence of frequency in aligning nanostructures. Figure 6 shows a comparison of carbon nanotubes aligned at 5 MHz with a voltage of 10 V_{p-p} compared to 500Hz with the same voltage. The nanotubes are clearly heavily influenced by the higher frequency. Chen and coworkers also demonstrated that the strength of the electric field is an important factor. Nanotubes were greater in concentration near the edges and corners of the electrodes where the electric field is stronger [39]. It should also be noted that Chen *et al.* were only able to align dense ropes of carbon nanotubes. However, in order to measure electrical properties a single nanostructure needs to be isolated.

Z. Chen and coworkers were able to build on work done by Chen *et al.* and Yamamoto *et al.* and successfully align a single carbon nanotube. They theorized that if alignment is based on electric field strength and frequency and if field strength is dependent on gap spacing, applying a high frequency coupled with a small gap spacing would be the best way to attract a single nanotube [40]. Since the electric field is determined by the gap size, a small gap of 1.5 μ m was chosen to maximize field strength. Based on past research, Z. Chen *et al.* chose a high frequency of 2 MHz and applied 20

V_{p-p} to successfully align the nanotubes. They also determined that as long as the frequency is greater than 100 kHz and the electric field is greater than 5 V/ μm the nanotube will successfully align [40].

Figure 6. AFM images of aligned carbon nanotubes. (a) Nanotubes aligned with a frequency of 5 MHz and 10 V_{pp} . (b) Aligned with a frequency of 500 Hz and 10 V_{pp} [39].

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3.1.2 Nanowire Alignment by Dielectrophoresis

Metallic nanowires were aligned by Smith *et al.* [12] using field strengths of 1.0×10^4 to 1.4×10^4 V/cm and 5 to 70 V_{rms} . They used gold nanowires that were 8 μm long and 350 nm in diameter. The nanowires were suspended in a solution of isopropyl alcohol and deposited on an interdigitated finger pattern. The electrodes were fabricated using a 50 nm layer of titanium on a 150nm layer of gold, patterned on a silicon substrate

with an insulating layer of silicon dioxide [12]. The interdigitated finger pattern can be seen in Figure 7, in which gold nanowires are aligned across the fingers.

Work done by Smith *et al.* again proved that a higher frequency and electric field enhance the alignment of nanowires. They also discovered that alignment times were reduced by almost half by increasing the applied AC voltage [12]. One theory suggested by the authors is that the influence of frequency is due to the polarization of the dielectric medium that the nanowires are in. At low frequency the medium acts to shield the charge separation on the nanowire. As the frequency is increased the polar molecules are unable to reorient fast enough which allows the nanowire to build charge separation [12].

Very little work has been done in aligning semiconducting nanowires, however, Duan *et al.* [41] successfully aligned indium phosphide semiconducting nanowires with a diameter of 30 nm to produce a field effect transistor. The electric field strength was measured at 10^7 V/m with electrode spacing of 25 μm [41]. Kim *et al.* [42] was able to align gallium nitride nanowires using dielectrophoresis. It was also found that using a 10 Vpp coupled with a frequency between 10 kHz and 20 MHz provided the most success in alignment [42].

Figure 7. Gold nanowires aligned on Ti/Au interdigitated electrodes [12].

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3.2 Four Probe Electrical Measurements

Section 3.2.1 discusses the theory of four probe electrical measurements. Section 3.2.2 discusses the use of the focused ion beam tool to create four probe devices. In Section 3.2.3, four probe measurements by other researchers are discussed. Section 3.2.4 discusses the use of temperature dependent four probe measurements as a means to determine the band gap of materials.

3.2.1 Four Probe Theory

One of the most widely used techniques for semiconductor electrical characterization is the four point probe method [43]. To determine a material's resistance, Ohm's Law, shown in Equation 10, is used. A known current is sourced and passed through a specimen with an unknown resistance. The voltage is then measured

and the resistance is determined by dividing the measured voltage by the sourced current. This is known as a two point probe measurement.

$$R = \frac{V}{I} \quad \text{Equation 10}$$

Electrical measurements based on this have been made on nanowires by researchers. The drawback to using a two point probe is the inclusion of all other resistance values that are in series with the device being tested. In this case the contact resistance between the nanowire and electrode, the resistance of the electrodes and the metal transmission lines are all included with the nanowire being tested. Thus the measured resistance is then $R_{\text{meas}} = R_{\text{NW}} + R_{\text{c1}} + R_{\text{c2}} + R_{\text{metal lines}}$ as shown in Figure 8 [44].

Figure 8. Two probe I-V measurements include all resistances measured in series with the nanowire.

In the case of semiconductors, contact resistances are typically very high and will greatly affect the measured resistance values. These high contact resistances are usually due to the metal-semiconductor interface. The potential for a large mismatch between the

work functions of the metal and semiconductor can result in high-resistance Schottky contacts. Low resistance ohmic contacts occur when the work functions are more closely matched. While four probe measurements cannot determine whether a Schottky or ohmic contact is present, it can reduce the measured contact resistance.

To determine the resistance of just the specimen being tested, a four point probe measurement is employed. In four point probe measurements, the four contacts are typically placed on the corners of a square sample. However, due to the geometry of a nanowire, the four probes can be aligned in a row along the length of a sample as shown in Figure 9. In Figure 9, the contact resistances are shown at each of the four probe contacts.

Figure 9. Schematic for a four probe measurement on a nanowire.

The current is sourced and passed through the two outer contacts and the voltage is measured across the inner electrodes [44]. The voltage measurement is typically made

through an electrometer because of its high input impedance. This high impedance minimizes the current that will run through the electrometer electrodes compared to the current running through the specimen. Thus only a small contact voltage will be included since $V_{\text{small}} = I_{\text{small}} * R_C$. The measured resistance still follows Equation 10; however it does not contain any significant input from the contact resistances.

Once resistance is determined experimentally, resistivity can be extracted if the sample geometry is known. The resistivity is defined by Equation 11[45].

$$\rho = \frac{RA}{L} = \frac{1}{\sigma} \quad \text{Equation 11}$$

Where R , A , and L are the resistance, the cross-sectional area and the length of the material respectively. The conductivity, σ , is the reciprocal of resistivity, ρ .

3.2.2 Four Probe Contact Fabrication on Nanowires by Focused Ion Beam

To make four point probe measurements on nanowires, contacts need to be created on wires that are only nanometers in diameter. Goldberger *et al.* [9] were able to make a four point probe device by dispersing a suspension of zinc oxide nanowires onto a silicon wafer with pre-patterned chromium/gold probe pads. Electron beam lithography was then used to create titanium contacts between the probe pads and nanowire as seen in Figure 10 [9]. Cui *et al.* [46] also used e-beam lithography to define contacts on silicon nanowires for transport measurements.

There is, however, a disadvantage to these methods. The only way to determine where the nanowire is after dispersion on the wafer is by finding it through a scanning electron microscope. Alignment markers on the wafer are then used as guides for e-beam

lithography. In other words, this method is very much a “guess and check” process and can be very tedious and time consuming. Additionally, e-beam lithography involves many process steps that include spin coating the device with a polymer, exposing the pattern and developing it.

Figure 10. SEM micrograph of four point probe device with ZnO nanowire [9].

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The use of nanowire alignment by dielectrophoresis helps solve half of this problem. Because electrodes are fabricated to align the nanowires, two of the four contacts needed are already made. When the nanowire is aligned across the two electrodes, the two outer contacts for sourcing current can be used. However, the use of dielectrophoretic alignment still leaves another problem of creating two more contacts for four probe measurements without the use of e-beam lithography.

An alternative solution to this issue has recently surfaced. An ion-assisted deposition process through the use of a focused ion beam (FIB) makes it possible to

contact individual nanomaterials without the use of a mask or lithographic process. Vilà *et al.* [47] deposited metallic contacts on tin oxide nanowires using the FIB technique to measure electrical properties. Motayed *et al.* [50] have also used platinum (Pt) contacts to create an electrical characterization device by ion assisted deposition on a gallium nitride nanowire. An SEM image of these contacts are shown in Figure 11. In both cases, the metallic contacts were platinum deposited by decomposition of an organometallic precursor gas that was injected into the path of a 30 keV Ga⁺ ion beam [47,50].

The use of FIB Pt deposition creates some challenging issues. Although the ion beam can be finely focused, the organometallic gas used in Pt deposition cannot be focused like the ion beam. The result is that in addition to the defined Pt deposition, the process will also produce a surrounding thin “halo” around it [48]. If the deposition areas are close enough to each other, the “halos” of Pt overlap which can lead to shorting of the electrodes. In the case that there is overlapping, ion beam milling can be utilized in removing it. While the potential “halo” effect can be corrected, another concern in FIB Pt deposition is the possibility of creating defects and ion implantation from the Ga⁺ ions [48,49]. Nam *et al.* [49] have shown that the use of FIB assisted Pt deposition on a GaN nanowire can lead to unwanted Ga⁺ ion implantation, with ion implant depths of up to 40 nm. Because of the nature of the FIB tool, irradiation from accelerated electrons during imaging and accelerated ions during deposition and milling are inevitable and should be considered when making electrical measurements.

Figure 11. SEM micrograph of Pt deposited by focused ion beam assisted deposition [50].

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In Figure 12, a schematic of a possible electrode pattern is shown. The contact pads on the left and right are created to align the nanowire. After alignment, the focused ion beam deposition is used to create two new contacts directly on the nanowire to measure the voltage. Alignment by dielectrophoresis will cut down on time spent hoping for a nanowire to make contact and ensure that a single nanowire is ready for characterization. This process eliminates the need to search for nanowires that have “fallen” onto pre-patterned electrodes.

Figure 12. Basic schematic of a 4 point probe system on a nanowire. The nanowire is first aligned on the two electrodes on the sides. Focused ion beam deposition is used to write the contacts in the center.

3.2.3 Fundamentals of Focused Ion Beam

The use of focused ion beam systems is an attractive approach in creating electrical contacts to nanowires [50]. While the nanowire can be aligned to pre-patterned electrodes via dielectrophoresis it is still a technical challenge to individually create contacts on the nanowire. The use of a direct writing technique such as the focused ion beam (FIB) system allows the user to perform quick localized milling of materials and also deposition of conducting metals with precision down to the nanowire [50,51].

The focused ion beam is generated in an ion column that is very similar to the column used in scanning electron microscopes (SEM). The main difference is that a gallium ion (Ga^+) beam is produced instead of an electron beam. The ions are generated from a liquid-metal-ion source by application of a strong electric field which causes the

emission of the positively charged gallium ions. The ions are then accelerated and focused through a series of electrostatic lenses and apertures as shown in Figure 13. Typically the accelerating voltage is in the range of 10-50 keV [52]. In most cases, FIB systems are part of a so-called dual beam tool where both an electron column and ion column are present. In this case, the ion column is typically tilted at an angle of 52° and the electron column is normal to the specimen as shown in Figure 14. Images of the specimen can be viewed either by electron emission from electron or ion excitation.

Figure 13. Simplified schematic diagram of a FIB ion column.

Figure 14. Dual beam FIB/SEM schematic.

One of the effects of the energetic ions bombarding the specimen surface is the ability to mill away material. Typically in a SEM, the electrons being accelerated toward the specimen cause secondary electron emission which can be detected by sensors located inside the SEM chamber. Gallium ions on the other hand are much bigger and when the ions hit the surface they displace surface atoms, effectively sputtering away material. In Figure 15, the ion beam is scanned over a user-defined shape and the Ga^+ ions sputter away material. The rate at which material is removed is dependent on the ion current set by the user.

Figure 15. The ion beam is rastered over a user-defined shape and the substrate material is sputtered away.

In addition to the milling capabilities, the FIB tool is capable of depositing metal and insulator materials. The ability to quickly deposit metal in a localized area is a big advantage over other traditional metal deposition methods. Platinum metal can be deposited by introducing an organometallic precursor gas to the system by a gas injection needle. For platinum deposition, the organometallic precursor is (trimethyl)methylcyclopentadienyl-platinum. The precursor gas is sprayed onto the surface where it is adsorbed. The ion beam subsequently decomposes the precursor gas, the reaction by-products are removed by the vacuum system and the desired platinum remains on the surface of the specimen [52]. This process is shown in Figure 16. It

should be noted that the metal deposited is not pure; organic contamination such as carbon and Ga⁺ ions that have been implanted are typically present.

Figure 16. Basic schematic of platinum deposition via FIB.

3.2.4 Measurements by Four Probe Test Structures

Four point probe measurements have been made on metallic and semiconducting nanowires [20,23]. Typically current vs. voltage plots are recorded to calculate resistance values as discussed in Section 3.4.1. Goldberger *et al.* [9] compared I-V plots from four probe and two probe test methods which are shown in Figure 17. In this plot, the resistance is the reciprocal of the slope. Therefore, the measured two probe resistance is higher than the four probe. The influence of contact resistance on the measurements made by the two probe method was reported to have 2 to 10 times the resistance of the

zinc oxide nanowire that was tested. The resistivity of the zinc oxide nanowire was found to be $4.37 \Omega \text{ cm}$ [9]. De Marzi *et al.* [53] reported successful electrical measurements by using four probe contacts created by the focused ion beam tool. They reported a resistivity value of $33 \mu\Omega \text{ cm}$ for a platinum nanowire. They were also able to extract an estimated contact resistance of 405Ω [53].

Figure 17. Comparison of I-V curves based on 4 probe and 2 probe measurements [9].

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3.2.5 Temperature Dependent Four Probe Measurement

The interest in resistivity is two-fold. The basic values need to be known to create a device and more importantly, for a semiconducting material, the effect of temperature on resistivity is important. While the resistivity for both metals and semiconductors are affected by temperature, they behave quite differently. In a metal, as temperature is

increased, resistivity increases. In a semiconductor, as temperature is increased the resistivity decreases, except at very low temperature.

As electrons are moving around they can collide with the lattice atoms of the metal or semiconductor. Resistivity can be thought of as the result of collisions of these electrons with the lattice atoms. As more collisions per second occur, the resistivity become higher. Another way of describing this phenomenon is by looking at the mobility of the electron. In Equation 12 the relationship between conductivity, resistivity and mobility is shown [45].

$$\sigma = \frac{1}{\rho} = \mu Ne \quad \text{Equation 12}$$

Where σ is the conductivity, ρ is the resistivity, μ is the mobility of the electron, N is the carrier concentration, and e is the charge of an electron. As temperature increases, the thermal energy causes the lattice atoms of the metal or semiconductor to oscillate with larger amplitude. This increases the probability of an electron colliding with a lattice atom and thereby decreases the electron mobility μ . A decrease in mobility will result in a decrease in conductivity, and consequently an increase in resistivity [45].

While this is true for a metal as well as a semiconductor, there is an additional temperature dependent behavior in a semiconductor. In semiconductors there exists a band gap between the conduction and valence bands and the Fermi level lies in the gap. The band gap in semiconductors is small enough (1-3 eV), that thermal energy can excite electrons from the valence band to jump into the conduction band and leave an electron hole that can also carry current [45]. As temperature increases more electrons are

promoted into the conduction band and an equal number of holes are created. This increase in carrier concentration, N , dominates the decreased electron mobility μ , in Equation 12 and thus the conductivity of a semiconductor increases with temperature, and resistivity decreases [45].

The size of the band gap can be determined by the relationship between conductivity and temperature in semiconductors. The dependence of conductivity on temperature is similar to other thermally activated process. The process can be expressed by the Arrhenius Equation in Equation 13.

$$k = A * e^{\frac{-E_a}{R*T}} \quad \text{Equation 13}$$

Where k is the rate coefficient, A is a constant, E_a is the activation energy, R is the universal gas constant, and T is the temperature in Kelvin. Equation 13 can be rewritten as Equation 14 for the relationship between conductivity and temperature.

$$\sigma = \sigma_o * e^{\frac{-E_g}{2k*T}} \quad \text{Equation 14}$$

In this case conductivity, σ , is the measured value, σ_o is a constant, E_g is the band gap, k is Boltzmann's constant and T is the temperature in Kelvin. By taking the natural log of both sides, Equation 14 can be expressed as Equation 15.

$$\ln \sigma = \ln \left[\sigma_o * \frac{-E_g}{2k * T} \right] = \ln \sigma_o - \frac{E_g}{2kT} \quad \text{Equation 15}$$

By measuring conductivity as a function of temperature and by plotting $\ln \sigma$ versus $1/T$, the band gap, E_g , of the semiconductor can be found from the resulting slope.

Temperature dependent I-V measurements on zinc oxide nanowires have been made by Goldberger *et al.* by placing the test specimen in a cryostat [9]. They reported that as temperature decreased, nanowire conductivity decreased as well; however, band gap information was not reported by this investigation [9]. De Marzi *et al.* [53] reported using a cryostat to make variable temperature measurements on platinum nanowires. They reported that as temperature decreased, the resistance decreased as well [53]. They did not report resistivity values as a function of temperature, however, if the platinum wires were of similar dimension it would be safe to assume that the resistivity decreases with temperature.

3.3 Micro-miniature Refrigerator

Cryostats can be used in temperature dependent measurements; however, they require using liquid nitrogen or liquid helium to cool the samples. Instead, a micro-miniature refrigerator can be used. The samples can be cooled through the use of the Joule-Thomson effect. Joule-Thomson cooling is a process in which a non-ideal gas expands from high pressure to low pressure at constant enthalpy. Samples can be cooled from room temperature down to 80 K. The advantage of using this apparatus over a cryostat is more precise temperature control and the ability to use nitrogen gas instead of liquid nitrogen. The micro-miniature refrigerator is enclosed in a chamber to operate at low pressure. Figure 18a shows the MMR Technologies chamber that was used to provide the cooling in temperature dependent measurements. Figure 18b shows a closer view of the spring loaded probe tips in the chamber; the white pad is the cooling stage.

Figure 18. a) MMR Technologies chamber for temperature dependent measurements. b) Cooling stage with four spring loaded probe tips.

3.4 Scanning Electron Microscope

A scanning electron microscope (SEM) is typically used for surface characterization. An SEM is able to produce high resolution images of the surfaces being examined. Most SEM's employ a technique where electrons are thermionically emitted from a tungsten or lanthanum hexaboride cathode and are accelerated toward an anode [54]. Electrons can also be generated by field emission. The electron beam that is generated has an energy range of a few hundred eV up to 50 keV depending on the system being used. The electron beam is focused using condenser lenses and creates a very small spot size on the order of nanometers. The beam is passed through a series of scanning coils that raster it in a rectangular area.

The accelerated electrons hit the surface of the specimen and are scattered by the atoms on the surface. Some electrons are knocked off and called secondary electrons; these typically are low energy and originate from the surface. The most common use of an SEM is surface characterization and involves the detection of these electrons. The

secondary electrons are detected by a scintillator-photomultiplier device that creates the signals used to create the images that are displayed by the SEM [54]. The resolution of a typical field emission SEM is in the range of nanometers. The resolution is satisfactory for the type of work that is needed for this project.

3.5 Summary

Manipulation of nanomaterials by dielectrophoresis is a powerful technique that can be used to align nanowires and nanotubes onto pre-patterned electrodes. It eliminates “guess and check” methods of contacting nanowires for electrical characterization. The alignment can be used in creating four probe measurement devices. Four probe measurements generally give a more accurate reading of the material, as it excludes the contact resistance that is in two probe measurements. The four probe devices can be created by using FIB deposited Pt contacts. The SEM tool can be used for all imaging purposes.

CHAPTER FOUR EXPERIMENTAL METHODS

The objective of this research was to develop a method to characterize the electrical properties of nanowires. This was achieved by aligning a single nanowire across two electrodes by E-field alignment to create a four probe measurement device using the focused ion beam technique.

In this chapter, the methods of research will be presented. In Section 4.1 and 4.2 a method of removing nanowires synthesized using the anodized alumina template and VLS processes are discussed. In Section 4.3 the method for finding successful alignment of the nanomaterials and possible candidates for I-V measurements are discussed. Section 4.4.1 to Section 4.4.3 reviews the three different E-field alignment experiments. Section 4.5 discusses the contacts created by the focused ion beam. Section 4.6 discusses the methods of making electrical measurements and temperature dependent measurements.

4.1 TiO₂ Nanowire Isolation from Template

A method was developed to remove the titanium dioxide (TiO₂) nanowires synthesized by the sol-gel anodized alumina template process described in Section 2.3.1. The TiO₂ nanowires were synthesized by Rebka Endale from the Dholakia Group at NASA Ames Research Center. The alumina template was partially dissolved for 9 minutes using a 6 molar aqueous sodium hydroxide solution. The partially dissolved template and the exposed TiO₂ nanowires are shown in an SEM image in Figure 19. It was then rinsed with de-ionized (DI) water and moved to a microtube (Axygen) filled

with 1 mL of DI water. A brief 3 second sonication in a VWR 150D ultrasonic cleaner was used to agitate the nanowires off of the template. The microtube was placed in a Fischer Scientific Micro 16 centrifuge for 1 min and 30 seconds at 2000 g allowing for separation of the template and nanowires. A schematic of this process can be seen in Figure 20.

Figure 19. Partially dissolved anodized alumina template exposing TiO_2 nanowires. a) Top-down view b) Angled view.

4.2 Silicon Nanowire Isolation from Substrate

Silicon (Si) nanowires are easier to remove from the substrate. The Si nanowires were synthesized on silicon wafer substrates by the vapor-liquid-solid (VLS) method at NASA Ames Research Center by Aaron Mao from San Jose State University. The substrates containing the Si nanowires were placed in a microtube (Axygen) filled with 1 mL of DI water. A brief 5s sonication in a VWR 150D ultrasonic cleaner was used to agitate the nanowires off the substrate. The microtube was placed in a Fischer Scientific

Micro 16 centrifuge for 1 min and 30 seconds at 2000g allowing for separation of the substrate and nanowires.

Figure 20. Schematic of nanowire removal process from anodized alumina template.

4.3 Nanomaterial Alignment Verification

Primary SEM imaging was done at the Center for Nanotechnology at NASA Ames Research Center. The electron microscope used was a Hitachi S-4000 field emission SEM with an accelerating voltage range of 0.5 to 30 kV. Additional SEM imaging was performed at the SJSU Materials Characterization Center and the Stanford Nanocharacterization Laboratory. The electron microscopes were an FEI Quanta 200 and an FEI XL30 Sirion respectively. The SEM was used both to image the effects of E-field on nanoparticles in the first stage experiments, as well as to verify nanowire alignment in the second and third stage experiments. Nanowire alignment was considered to be successful if the wires were aligned across the electrode gap.

4.4 E-Field Alignment Experiments

The alignment of nanowires on a four probe measurement device required three preliminary E-field alignment experiments. Proof-of-concept experiments on E-field alignment were carried out using latex and gold nanoparticles and TiO₂ nanowires. An interdigitated electrode structure was designed and fabricated to maximize alignment sites. For single nanowire temperature dependent measurements a new device was designed and fabricated. Section 4.4.1 discusses the first stage E-field alignment experiments in which different nanomaterials were used to determine if the alignment worked and to find optimal alignment parameters. Sections 4.4.2. and 4.4.3 discusses how the E-field alignment experiments are expanded to using an interdigitated electrode structure and a four probe device structure respectively.

The nanowire alignment and resistivity studies were performed at NASA Ames Research Center. The design of the masks was done at NASA Ames Research Center and the masks were plotted at San Jose State University (SJSU) and manufactured by Compugraphics. The nanowires were characterized at NASA Ames Research Center and at SJSU. Focused ion beam platinum deposition and ion beam milling were performed at the Stanford Nanocharacterization Lab.

4.4.1 First Stage E-Field Alignment Experiments

Following the method described by Yamamoto *et al.* [38], samples of 50 nm layer nickel (Ni) were deposited on glass slides cleaned with methanol and de-ionized water. The thin film of Ni was deposited using a VCR Group Inc. TM 200S Ion Beam Sputterer system. A glass substrate was chosen because of its insulating properties, and the ability to create a good insulating gap between the Ni electrodes. To create the separation between the Ni electrodes, a wire shadow mask with 0.2 mm diameter was used. Figure 21a shows the layout of the wires and Figure 21b shows the Ni electrodes as shaded regions. The substrate is separated into six sections to maximize amount of experiments per substrate.

Following the substrate preparation, enamel coated copper wiring was connected to the Ni electrodes via silver paste from Ted Pella, Inc. The copper wires were then connected to a Stanford Research Systems DS345 Function Generator by a MIL-C-17 spec coaxial cable. For the first stage experiments, 0.26 μm diameter uniform latex

spheres from Ted Pella, Inc., 2 nm diameter gold nanoparticles and TiO₂ nanowires suspended in DI water were used.

An AC potential was applied before the droplet was placed on the substrate. A Stanford Research Systems DS345 function generator was used to source the AC potential. The nanoparticles were subjected to an AC potential of 10 V_{pp} with frequencies 25 Hz and 30MHz, for either 2 or 5 min. A 0.50 μ L droplet of either the latex or gold nanoparticles and TiO₂ nanowires were dispersed down the middle of the prepared substrate as shown in Figure 22. After the allotted time, the applied field was removed and the droplet was allowed to air dry.

Figure 21. a) Glass substrate with 0.2 mm wire shadow mask. b) Shaded regions indicate Ni layers.

Figure 22. Position of gold and latex nanoparticles and TiO₂ nanowire droplets on Ni coated glass.

The specimens were then examined under a Hitachi 4100 scanning electron microscope (SEM). Results from these experiments showed that both the gold and latex nanoparticles are influenced by the E-field. Pearl chaining of the latex nanoparticles and dendrite growth of the gold nanoparticles were observed. TiO₂ nanowires were observed to align along the edges of the Ni electrodes. These results are described in detail in Section 5.1. The first stage experiment was considered successful.

4.4.2 Second Stage E-Field Alignment Experiments

A new electrode pattern was designed to conduct initial nanowire E-field alignment experiments. This design, shown in Figure 23, is based on an interdigitated structure and was chosen to maximize the probability of multiple nanowire alignment. The gap spacing between fingers varies from 3 μm to 6 μm in 1 μm steps. This decrease in gap spacing compared to the first stage E-field allowed for the possibility of a single nanowire to bridge the gap. Each device was designed to be 1 cm^2 and contain four of

the interdigitated structures shown in Figure 23, with each structure having a different gap spacing. The design was made into a chrome on glass mask and was used to pattern metal on a silicon wafer.

Figure 23. First mask design for e-field alignment experiments.

4.4.2a Wafer Processing

The mask was used with traditional wafer processing techniques to create the designed electrode pattern. For these devices, an etch-back process is used. In this process a positive photoresist is spun onto a silicon wafer coated with an aluminum film. For a positive photoresist, the ultraviolet exposed areas become soluble in the developer and the areas that are not exposed remain insoluble. The main processing steps are discussed below; the detailed processing traveler is included in Appendix A.

The first step was to pre-clean the silicon (Si) wafers. A series of etches including a buffered oxide (BOE), hydrogen peroxide (RCA), and Piranha were used to clean the wafer of any residual oxides, organics, and metals. After cleaning, the wafers were placed in the furnace for oxidation.

The silicon dioxide (SiO_2) layer was grown for the purpose of insulating the aluminum (Al) from the Si wafer. To rapidly grow a thick SiO_2 layer, a wet oxidation process was used. A 700 nm thick layer of SiO_2 was grown on the bare Si wafer at the San Jose State University Microelectronics Process Engineering Laboratory (MPEL). Oxide thickness was measured using a NanoSpec 210. After the oxide was grown, Al was deposited on the wafers. The deposition was completed using a filament evaporator. Wafers were placed in a bell jar where the pressure was pumped down to 10^{-6} Torr. Aluminum clips were hung on a tungsten filament located inside the bell jar. The filament heats up by passing a current which melts the Al. The evaporated Al condenses on the wafers due to the lower surface temperature. A 200 nm film of Al was deposited by the filament evaporator.

The electrodes were defined by first spin coating the wafer with a layer of hexamethyldisilazane (HMDS) to promote adhesion of the photoresist to the Al layer. A positive photoresist (JSR IX560) was then spin coated and baked at 110°C to ensure adhesion. The spin coating and baking were all performed using a MTI Multifab Coater. The glass mask was loaded into a Quintel Q4000 Aligner to expose the photoresist to UV radiation for approximately 6 seconds, creating the pattern. The wafer was then developed in a 3% tetramethylammonium (TMAH) solution for 30 sec. The unwanted Al

was wet etched away using a combination of phosphoric and nitric acid. Finally the remaining photoresist was removed by a resist stripper. The wafer was rinsed in DI water to clean for use. The schematic of the process steps are shown in

Figure 24.

Figure 24. Cross sections of process steps for Al electrodes on Si/SiO₂ wafer. a) Cleaned bare Si wafer. b) Oxide layer is grown. c) Al layer is deposited on. d) Photoresist is spun on the wafer. e) A mask is used in photolithography and the exposed photoresist

The finished mask and devices on the silicon wafer are shown in Figure 25a and Figure 25b respectively. Thirty-two devices are contained on each finished wafer. The wafer was then diced into individual devices by American Precision Dicing. The different gap sizes are labeled as “3x3” for a 3 μm gap and follows the same format for the other gap sizes. A finished device is shown in Figure 26.

Figure 25. a) Chrome on glass mask. b) Si wafer with devices patterned with aluminum.

Figure 26. Optical image of 1 cm^2 device. Each H-structure is denoted by a number corresponding to the gap size which ranges from 3 to 6 μm .

4.4.2b Alignment Experiments on Processed Devices

After the devices were made, alignment experiments on latex nanoparticles using an AC potential with frequencies of 25 Hz, 2 kHz or 30 MHz and voltage of 10 V_{pp} were conducted. For each 1 cm² device, a set frequency was used for all gap sizes. In TiO₂ nanowires experiments, an AC potential with a frequency of 2 kHz and voltage of 10 V_{pp} were conducted for each device. Because of the small size of the contact pads on the test devices, a Lakeshore probe station connected with a Stanford Research Systems DS345 function generator was used to pass the AC potential. The probes used for alignment are shown in Figure 27.

The probes were then connected to the contact pads on the 3 μm gap structure. For each run, the AC field was applied before droplets of either latex nanoparticles or TiO₂ nanowires were dispersed. The droplets of the latex or TiO₂ solution were then placed on the 3 μm gap sizes shown in Figure 28. After the field application for 2 min, the droplet was allowed to air dry. The procedure was repeated for the remaining gap sizes and the process was repeated again for each frequency tested. Pearl chaining of the latex nanoparticles were observed at all frequencies tested. Alignment of TiO₂ nanowires was most successful at frequencies of 2 kHz and 10 V_{pp}. These results are described in detail in Section 5.2.

Figure 27. Lakeshore probe station chamber. The probes were used to make contact with the device during alignment experiments.

Figure 28. Location of where droplets of latex or TiO_2 were dispersed on each device.

4.4.3 Third Stage E-Field Alignment Experiments

The mask in the second stage E-field experiments was redesigned for the purpose of adding two more contact pads for four probe measurements and making it easier to create contacts with the focused ion beam (FIB). In the second stage device design, the interdigitated electrodes fingers were 2 mm in length and 1 mm in total height. These

large dimensions made it very difficult and tedious to isolate a single nanowire. Thus, creating a four probe device using the FIB was not feasible with the previous design.

Three new designs were created for the four probe measurements. Device “X” and Device “L” shown in Figure 29 and Figure 30, respectively, were designed to allow more freedom of movement and smaller deposition dimensions when using the FIB. An interdigitated structure called Device “H” shown in Figure 31 was designed with shortened finger lengths. These redesigns also included much larger contact pads at the four corners of the devices. This was added to accommodate the size and placement of the spring loaded probes in the chamber described in Section 3.3.

The larger feature sizes of the new devices did not require the use of a chrome on glass mask. Instead, a mylar transparency mask was created by using a high resolution plotter capable of 10 μm features. The plotting and layout was prepared by CAD/ART Services. In Device “X”, Device “L” and Device “H”, the pre-patterned electrodes are 10 μm in width and the gap sizes are 10 μm .

The new devices were fabricated at the SJSU MPEL using the same process steps outlined in Section 4.4.2a. Figure 32 shows SEM images of the finished devices. Device “X” and “L” are shown in Figure 32a and b and Figure 32c and d respectively. The modified interdigitated electrode Device “H” is shown in Figure 32e and f.

Figure 29. Four probe measurement Device "X".

Figure 30. Four probe measurement Device "L".

Figure 31. Four probe measurement Device “H”.

To align the nanowires, the Lakeshore probe station connected to a Stanford Research Systems DS345 function generator was used to pass the AC potential across the electrodes. Procedures optimized from the previous E-field experiments were used. An AC potential with a frequency of 2 kHz and a 10 V_{pp} bias was applied to the device before the nanowires were dispersed. A suspension of either the Si or TiO₂ nanowires was then dispersed on the center of the device as shown in Figure 33. After the field application the droplet was allowed to air dry. This procedure was repeated for each of the three different devices. Alignment was successful for both the Si and TiO₂ nanowires and is discussed in detail in Section 5.4.

Figure 32. SEM images of third stage four probe devices. a-b) Device "X" c-d) Device "L" e-f) Device "H".

After the alignment was completed, an SEM was used to find candidates to create the additional contacts needed on the nanowire for four probe measurements. Good candidates were nanowires that were aligned across a gap. The contacts were created by using a focused ion beam as described in detail in Section 4.5.

Figure 33. Droplet of nanowire suspension dispersed on Device "X".

4.5 Two and Four Probe Devices by FIB

Electrical measurements were made on two and four probe devices. These devices were fabricated using the focused ion beam technique. The two probe devices were made using nanowire alignment selected from experiments in Section 4.4.2. Four probe devices were made using nanowire alignment selected from experiments in Section 4.4.3.

A total of two devices were made for two probe I-V measurements. In the second stage E-field alignment, some of the pre-patterned electrodes needed to be cut in order to ensure only one direct path during I-V measurements. This was done by using the milling feature in the FIB. Milling was performed using the FEI 235 Strata FIB/SEM with a 30 keV ion beam using a 30 pA current aperture. The dwell time and overlap for the Ga⁺ ion beam was set at 1.0 μ s and 50%, respectively. For larger aluminum structures a 300 pA current aperture was used with all other variables held the same.

The platinum (Pt) lines deposited were 1 μm in width and 0.5 μm in depth. The platinum was deposited with a 30 keV Ga⁺ ion beam in conjunction with a 10 pA - 100 pA current aperture. The dwell time and overlap was set at 0.2 μs and -50% respectively. Figure 34 shows Device 1 where the deposition of the Pt and milling of the pre-patterned Al electrodes have been made. Another two probe device, Device 2, was created using the same process and is shown in Figure 35. Following the procedures in Section 4.6.1, two probe I-V measurements were made on the devices created. These results are described in detail in Section 5.3.

Figure 34. Device 1: 300 nm thick Pt contacts and lines deposited by FIB deposition. The trenches were ion milled to a depth of 300 nm.

Figure 35. Device 2: 300 nm Pt lines and trenches created by FIB.

High resolution SEM images of Device 1 are shown in Figure 36. From Figure 36a, the diameter of the TiO_2 was determined to be approximately 200 nm. The length of the nanowire was determined to be approximately 5 μm from analysis of Figure 36c. A complete SEM image of Device 1 is shown in Figure 36d. For the four probe devices, Pt lines with a width of 0.4 μm and a depth 0.25 μm were deposited using the same parameters as described for the two probe devices. Ion beam milling was not needed because of the redesigned mask described in Section 4.4.3.

A total of 4, four probe devices were created using aligned Si and TiO_2 nanowires. Figure 37 shows a completed four probe device with a 200 nm TiO_2 nanowire with FIB deposited Pt contacts. Figure 38a shows the 125 nm Si nanowire that was aligned on the four probe device. Figure 38b shows the aligned nanowire with Pt contact pads deposited at the ends of the nanowire to ensure contact to the pre-patterned

electrodes. Figure 38c shows the Pt deposition starting from the other two electrodes. In Figure 38d, the finished four probe device is shown.

Figure 36. Detailed SEM images of Device 1 at different magnification. a) 200 nm dia. b) TiO_2 nanowire with Pt contact pads c) 5 μm length d) Complete two probe device.

Figure 39a and b shows two other four probe devices made with Si nanowires. Electrical measurements were then made on these devices using procedures described in Section 4.6.1 and 4.6.2.

Figure 37. Aligned TiO₂ nanowire in contacted by FIB deposited Pt.

Figure 38. Aligned Si nanowire contacted with FIB deposited Pt contacts. a) Si NW Dia. = 180 nm. b-d) Steps toward completing the four probe device.

Figure 39. a-b) Additional four probe devices created with aligned Si nanowires and FIB deposited Pt.

4.6 Electrical Characterization of Nanowires

The goal of this project was to characterize the electronic properties of semiconducting nanowires. The process of creating an electrode pattern for E-field alignment, aligning the nanowire, and creating two additional electrodes by focused ion beam platinum deposition was discussed in the previous sections. The next two sections discuss resistance measurement methods and temperature dependent measurements.

4.6.1 Resistance Measurements

The electrical resistance of the semiconducting nanowires was measured by electrical characterization experiments using room temperature two probe and four probe devices. As discussed in Section 3.2.1, two probe measurements of resistance include any contact resistances, while four probe measurements in principle determine only the resistance of the nanowire.

For two probe measurements, the Lakeshore probe station was used as described in Section 4.4.2 and is shown in Figure 40. The probe station was connected to an HP 4156A analyzer. A voltage was passed through the device and the subsequent current was measured. A voltage sweep of -1.5 to 1.5 V was used. As a guide, voltage sweep values were kept similar to those used by Hernández-Ramírez *et al.* in a study of tin oxide nanowires [55]. I-V plots were analyzed to determine the resistance of the nanowire. The dimensions of each wire were determined from SEM images, and the resistivity was calculated as discussed in Section 3.2.1.

Figure 40. Lakeshore probe station used for two probe I-V measurement.

The four probe I-V measurements were conducted at the San Jose State University MPEL. The four probe devices were contacted using a Signatone probe

station and probe card. An HP 4156A analyzer was connected to a probe card and the measurements were controlled using the Metrics ICS software program. A current sweep of $-0.1\ \mu\text{A}$ to $0.1\ \mu\text{A}$ was sourced through the outer electrodes and the subsequent voltage was measured. A two probe versus four probe measurement study was also conducted. For the two probe study the outer electrodes in Figure 38d were used. A voltage sweep of -2 to $2\ \text{V}$ was used and the subsequent current response was measured. The results of the two probe and four probe studies are discussed in detail in Section 5.3 and 5.5 respectively.

4.6.2 Temperature Dependent Electrical Characterization

Third stage E-field devices were developed to fit into the micro-miniature refrigerator described in this section and Section 3.3 for electrical measurements. The instrument setup was completed and tested with a known resistance sample.

A MMR Technologies, Inc. micro-miniature refrigerator was setup to vary the temperature of the sample. The temperature was swept from 80 to $300\ \text{K}$, and was controlled using a MMR Technologies, Inc. K-20 Temperature Controller. The K-20 has the ability to control the rate of cooling or heating and acquire and plot time vs. temperature. A Keithley 6220 Current Source and a Keithley 6514 Electrometer were setup to source current and measure voltage respectively. The complete setup can be seen in Figure 41.

The Keithley instruments was setup to generate the current vs. voltage plot to determine resistance. Additionally, communication with the MMR Technologies cooler was needed to determine the temperature of the specimen as a function of time.

Communication with the instruments was achieved using a program called National Instruments LabVIEW. National Instruments LabVIEW is a graphical development tool that can be used to interface with instruments and handle data acquisition. LabVIEW consists of two sections, the front panel and the block diagram. The front panel of the program contains the graphical interface that allows the user to control the instruments. The block panel contains the coding that was completed to run the program.

Figure 41. MMR Technologies cooler with K-20 temperature controller, Keithley current source and electrometer.

The Keithley and MMR instruments communicate with the computer via a GPIB cable that is connected to a National Instruments PCI-GPIB IEEE 488.2 card located in a computer. The final interface program was created with the ability to display and record the voltage, resistance, and temperature in real-time. Figure 42 shows the completed

program with graphs displaying the voltage, resistance and temperature. Four probe temperature dependent measurements were attempted with this setup. However, due to a possible error from the electrometer the study was not successful and the results are discussed in Section 5.

Figure 42. Screenshot of completed LabVIEW program.

CHAPTER FIVE RESULTS AND DISCUSSION

5.1 First Stage E-Field Alignment

The purpose of these experiments was to determine whether the E-field alignment was a viable method to manipulate nanomaterials. Latex and gold nanoparticles and TiO₂ nanowires were used in these experiments. AC potential with frequencies of 25 Hz and 30 MHz and voltage of 10 V_{pp} were used in this study. The results are shown and discussed below.

Latex nanoparticles

Latex nanoparticles 260 nm in diameter were subjected to an applied AC potential of 25 Hz and 30 MHz at 10 V_{pp} for 2 min. Figure 43 shows pearl chain formation of the latex nanoparticles bridging the gap of the electrodes using a frequency of 25 Hz.

Figure 43. a) SEM micrograph of latex pearl chain formation across a 200 μm gap at 10 V_{pp} 25Hz for 2 min. b) Close up view of the pearl chain formation.

To study the effect of frequency on the pearl chain formation, the latex nanoparticles were subjected to the same experiment with a 30 MHz field. The latex beads subjected to 25 Hz had significantly more prominent pearl chain formation than the 30 MHz specimen, as shown in a side by side comparison is shown in Figure 44. This could be due to the fact that at the MHz frequency, the polarity changes too rapidly for the latex to respond. A high resolution SEM image of latex bead pearl chain formation is shown in Figure 45.

Figure 44. The pearl chain formation is noticeably different with different frequency. a) Latex beads under applied field at 25 Hz 10 V_{pp} for 2 min. b) Latex beads under applied field at 30 MHz 10 V_{pp} for 2 min.

Figure 45. SEM image of latex beads forming a pearl chain.

It has been established by Pohl and Jones [35,36] that the pearl chaining is due to dipole-dipole interactions. When two latex beads come close to each other this polarization will cause them to react to each other. The latex bead will “see” the other latex bead in which case a mutual attraction occurs due to the opposite charges and continues on to form long chains. The interactions between the particles are independent of whether the particles are experiencing positive or negative dielectrophoresis, which is due to the fact that the field will change the orientation of the dipole in both cases [56]. The pearl chain formation will follow the electric field lines, otherwise particles aligning perpendicular to the field will repel. Typically the pearl chaining will start at the edge of the electrode where the electric field is greatest. When the latex nanoparticles are placed in an electric field they will polarize as depicted in Figure 46.

Figure 46. Schematic of latex beads in an electric field.

Au nanoparticles

Gold nanoparticles were also studied in this experiment to compare with the latex beads. In a metal nanoparticle, the dielectric constant is essentially infinite. This reduces the real part of the complex Clausius-Mosotti factor seen in Equation 6 to $K(\omega) \approx 1$.

Since $K(\omega)$ is always positive, the force F_{DEP} will always be positive and the nanoparticles will be attracted to regions where high fields exist.

A dispersion of 2 nm diameter gold nanoparticles was subjected to an applied AC potential of 25 Hz and 30 MHz and voltage of 10 V_{pp} for 1 and 2 min. In the low frequency range of 25 Hz, chaining and dendritic growth was observed along the edges of the electrode and is shown in Figure 47a. In the high frequency range of 30 MHz, no dendrites or chaining were observed and is shown in Figure 47b.

Figure 47. 2 nm Au nanoparticles under an applied AC field. a) 25 Hz 10 V_{pp} b) 30 MHz 10 V_{pp}.

Figure 48 shows a comparison of 100 nm gold nanoparticles subjected to the applied AC potential for 1 min and 2 min. The chaining and dendrite growth is much more pronounced in the 2 min case. The larger 100 nm nanoparticles were used to enhance the dendrite and chaining. The only changes between the 2 nm and 100 nm nanoparticles are the geometric factor in Equation 4. The larger particles increase the

geometric factor and in turn increase the dielectrophoretic force. The formation of the chains and dendrites can be attributed to the dielectrophoretic forces that result from AC field induced dipole motion in the nanoparticles along the electric field [35]. As the period of field application is increased, the dendrite branches and chaining will have more time to grow.

Figure 48. Dendrite growth of 100 nm Au nanoparticles with AC field of 25 Hz at 10V_{pp}. a) 1 min b) 2 min.

TiO₂ Nanowire

Titanium dioxide (TiO₂) nanowires were subjected to an applied AC potential of 25 Hz and 10 V_{pp} for 2 min. Figure 49 shows TiO₂ nanowires aligned and attracted toward the edges of the Ni electrodes. A nanowire is highly anisotropic compared to the isotropic nature of spheres such as the latex and gold nanoparticles. Thus the polarizability of nanowires is dependent on their orientation with respect to the electric field. Here the nanowire follows a different Clausius-Mossotti factor as described in Equation 9.

Figure 49. TiO_2 nanowires aligned along the length of one side of the Ni electrode using 10 V_{pp} and 25 Hz.

As long as the dielectric constant of the nanowire is greater than that of the medium, it should undergo a positive dielectric force, thus moving in the direction of the non-uniform field. The nanowires will also attempt to align in the direction of the field due to the torque which results from the dielectrophoretic force [57]. Since the non-uniform fields are closest to the edges of the electrodes, it is expected to see the nanowires in that region.

The TiO_2 nanowires were not long enough to span the $200 \mu\text{m}$ gap of the Ni electrodes. In order to have the nanowires bridge a gap, the second stage devices were designed with a much smaller gap size.

5.2 Second Stage E-Field Alignment

Latex nanoparticles

To enhance the pearl chaining found in the experiments using the $200 \mu\text{m}$ gap, the latex nanoparticles were deposited onto the interdigitated Al electrodes. By decreasing the gap size to $4 \mu\text{m}$ from $200 \mu\text{m}$, the effective field strength was increased. The latex

nanoparticles were subjected to an applied AC potential of 25 Hz and voltage of 10 V_{pp} for 2 min. Figure 50 shows pearl chain formation across a 4 μm gap and Figure 51 shows that the pearl chain formation was repeated over the span of many fingers.

Figure 50. Latex pearl chain formation across a 4 μm gap at 25 Hz and 10 V_{pp}.

Figure 51. Long range latex pearl chain formation across 4 μm at 25 Hz and 10 V_{pp}.

Keeping a voltage of 10 V_{pp} and a time of 2 min, the frequency was varied to 2 kHz and 30 MHz. Figure 52a and b shows pearl chain formation across a 4 μm gap using an applied AC potential of 2 kHz and 30 MHz respectively. It should be noted that in the 30 MHz case, the latex beads did not completely span the electrode gap as in experiments with lower frequencies. This could be due to the fact that the polarity switches much too rapidly for the pearl chain to form completely. Given a longer field application time, it is possible that pearl chain formation across the gap can occur at frequencies of 30 MHz. These results suggest that the frequency does not affect the latex beads ability to form pearl chains, but rather how fast the pearl chains can form.

Figure 52. Latex bead pearl chain formation across a 4 μm gap. a) 2 kHz b) 30 MHz.

TiO₂ Nanowires

The interdigitated electrodes were also used in aligning TiO₂ nanowires. Figure 53 shows the TiO₂ nanowires without being subjected to the E-field. Using a frequency

Figure 54 and Figure 55 shows TiO_2 nanowire bridging a $4\ \mu\text{m}$ $5\ \mu\text{m}$ gap, respectively.

Acc.V. Scit.Micro. Top 950
5.00kV 2.0k 14mm X10.5k

Figure 54. TiO₂ nanowire aligned across 4 μm gap of interdigitated electrode.

Figure 55. TiO₂ nanowire aligned across 5 μm gap.

The alignment procedure can be seen to be effective over a large range in area as shown in Figure 56. In some cases the nanowires did not completely align across the gap between the electrodes, because the nanowires were not long enough. Figure 57 shows examples of alignment across a 4 μm gap size. In this study, nanowires that aligned across the gap like the nanowires in Figure 57 were deemed successful. The large area of the interdigitated electrodes made it difficult to conduct a quantitative study. Thus, the number of nanowires aligned per experiment was not recorded. Therefore, statistical information on the frequency of alignment was not included in this thesis.

The successful alignment of the TiO₂ nanowires proves that dielectrophoresis is a viable technique for nanomaterial self-assembly. While the alignment was successful, the frequency used did not match with those reported by other researchers [38,39,42].

Figure 56. a) Large area alignment of TiO_2 nanowires on Al interdigitated electrodes.

Figure 57. Various examples of aligned TiO_2 nanowires across interdigitated electrodes of $4\ \mu\text{m}$ gap size. Alignment was achieved using a frequency of 2 kHz and $10\ \text{V}_{\text{pp}}$.

To investigate this frequency discrepancy, the dielectrophoretic force (DEP) on the TiO₂ nanowire was calculated using Equation 4 and Equation 9 in Section 3.1 where the real part of the Clausius-Mossotti factor was solved using 3.98×10^{-10} for $\epsilon_{p,\text{TiO}_2}$ and 7.08×10^{-10} for $\epsilon_{m,\text{H}_2\text{O}}$. The conductivity, σ , of water and TiO₂ were taken as 5.5×10^{-6} S/m and 1×10^{-14} S/m respectively. It should be noted that the calculation of the DEP force was under the assumption that the E-field along the wire is constant. The plot of dielectrophoretic force versus frequency is shown in Figure 58. A detailed derivation of the real part of the Clausius-Mossotti factor can be found in Appendix B.

Examination of the plot reveals that at frequencies higher than 10 kHz the DEP force reaches a plateau, which indicates that higher frequencies are not necessary. The 2 kHz used in the experiments are well within range of the higher end of the DEP force. Upon further examination, frequencies as low as 100 Hz should produce a positive DEP force which will attract the nanowire toward the electrodes. Thus, it is reasonable that the use of a frequency of 2 kHz is viable for the alignment of TiO₂. It has been suggested by Dimaki *et al.* [58] that the magnitude and the direction of the DEP force is highly dependent on the properties of the material under the applied field. Since TiO₂ was not the material of study in other work, it would explain why researchers used different frequencies.

Figure 58. Dielectrophoretic Force vs. Frequency for a TiO_2 nanowire with a diameter of 200 nm and length of 5 μm .

5.3 Two Probe Electrical Measurements

The I-V characteristic for both Device 1 and Device 2 are shown in Figure 59 and Figure 60. It can be seen in both cases that the I-V plot is not linear and instead exhibits possible Schottky contact behavior. It has been suggested by Hernández-Ramírez *et al.* [55] that such nonlinear behavior can be explained by a back to back Schottky barrier that occurs at the Pt to TiO_2 nanowire contacts. Nam *et al.* [49] and Hernández-Ramírez *et al.* [55] both have reported back to back Schottky barrier for FIB deposited Pt contacts on nanowires, for gallium nitride and tin oxide respectively.

Figure 59. Two probe Device 1 I-V characteristic of single TiO_2 nanowire contacted by Pt deposition via FIB.

Figure 60. Two probe Device 2 I-V characteristic of single TiO_2 nanowire contacted by Pt deposition via FIB.

The nonlinear behavior can possibly originate from the Pt-TiO₂ Schottky barrier of height $\Phi_B = 1.7$ eV which is derived from the difference between the Pt work function, $\Phi_{Pt} = 5.6$ eV [59], and the electron affinity of TiO₂, $\chi_{TiO_2} = 3.9$ eV [60]. As the voltage is swept from negative to positive the current is limited by the barrier height that the electrons encounter, and little current flows until there is a breakdown at the junction.

To determine the resistance and resistivity values for the nanowires the I-V plots were re-plotted from -0.2 to 0.2 V to show the linear region of the data collected. In Figure 61 and Figure 62, the linear plots for Device 1 and 2 respectively are shown. The resistance of the nanowire can be found using Ohm's Law stated in Equation 10 and is the reciprocal of the slope of the plots in Figure 61 and Figure 62. Device 1 resistance was found to be ~430 k Ω and Device 2 was 10 M Ω .

The physical dimensions for the TiO₂ nanowires in Device 1 and 2 were determined through analysis of SEM images and were found to be approximately 200 nm in diameter and 6 μ m in length and 200 nm and 5 μ m respectively. The resistance and resistivity values are shown below in Table 3 and the calculations can be found in Appendix C.

The resistivity values obtained in the two probe measurements fall within range of previously reported values for TiO₂. As previously stated in Section 2.3.2, Breckenridge *et al.* [33] reported resistivity values of 0.1 – 100 Ω cm for rutile bulk single crystal TiO₂. It was also reported by Miyata *et al.* [61] that for an anatase TiO₂ thin film the resistivity was 0.26 Ω cm, also cited in Table 3 for comparison. It is a reasonable assumption that

the resistivity of nanowires should be within a few magnitudes of the resistivity of a thin film.

Figure 61. Device 1: I-V curve re-plotted for linear region.

Figure 62. Device 2: I-V curve re-plotted for linear region.

Table 3. Resistance, Resistivity and Conductivity values for Device 1 and 2.

TiO ₂	Resistance	Resistivity	Conductivity
Device 1	429.6 k Ω	0.22 Ω cm	4.54 (Ω cm) ⁻¹
Device 2	10.2 M Ω	6.42 Ω cm	0.15 (Ω cm) ⁻¹
Miyata <i>et al.</i> (thin film)	-	0.26 Ω cm	-

The resistivity for Device 2 is an order of magnitude larger than Device 1 and the previously reported value for the thin film. The difference in resistivity values for Device 1 and 2 could be most easily explained by poor contacts (i.e. high contact resistance) between the nanowire and electrodes. As explained in Section 3.2.1, two probe I-V measurements include all resistance values that are in series with the nanowire. The resistance of the deposited Pt lines and Al electrodes were calculated to see if they add any significant value to the overall measured resistance. The resistivity for FIB deposited Pt is 5.0×10^{-4} Ω cm and the resistivity for Al is 265 $\mu\Omega$ cm [50]. Using these values and the dimensions of the electrodes the resistance contribution was calculated to be approximately 3250 Ω . This is negligible compared to the overall measured resistance. If this assumption is correct and if $R_{\text{meas}} = R_{\text{NW}} + R_{\text{c1}} + R_{\text{c2}} + R_{\text{metal lines}}$, then the remaining contribution comes from the contact resistances and the nanowire. Assuming that the resistance of TiO₂ nanowires does not vary significantly, the contact resistances are the only other factor that would remain. Thus, the discrepancy between Device 1 and 2 could be explained by poor contacts. However, more two probe I-V measurements would be needed to confirm if the measured values are accurate or just isolated incidences.

Another particular concern is the possibility of unintentional implantation from the energetic Ga⁺ ions that bombard the surface of the material as ions are being scanned for an image or during the Pt deposition process. Nam *et al.* [49] reported that for gallium nitride nanowires, the Ga⁺ ion irradiation is known to create nitrogen (N) vacancies and amorphization in the nanowire. These N vacancies have been shown to lower the barrier height [49]. It is possible that the implantation of Ga⁺ ions into the TiO₂ nanowire lead to a modification in their electrical behavior.

Comparing Device 1 and Device 2 in Figure 63, it is evident that there was more Pt deposited in Device 1 in Figure 63a when compared to Device 2 in Figure 63b. This becomes important due to the fact that if more Pt is being deposited, more ions are being unintentionally implanted into the surface of the device. In addition, precise deposition of the Pt requires imaging through the ion beam as in dual beam systems like the one used here the electron beam is tilted at 52° as described earlier in Section 3.2.3. With each ion beam image that is taken, more and more ions are being implanted. However, a more in-depth study on the crystal structure and the effect of Ga⁺ ions on the nanowire and the FIB-Pt/nanowire interface would be needed to fully understand this phenomenon. As discussed below, four probe measurements provide a more accurate measurement of nanowire resistance.

Figure 63. Comparison between measured TiO_2 devices. a) Device 1 b) Device 2.

5.4 Third Stage E-Field Alignment

For the third stage E-field alignment experiments, a new set of devices described in Section 4.4.3 were fabricated in order to create four probe contacts to the nanowire. Less Pt deposition was needed due to closer proximity to the pre-patterned electrodes. Four probe devices were created using E-field alignment and FIB Pt deposition for TiO_2 and Si nanowires. In Figure 64, various SEM images show alignment of either TiO_2 or Si nanowires. Figure 64a,c and e show TiO_2 and Si nanowires aligned on Device “X”. Figure 64b and f show Si nanowires aligned on Device “H”, and Figure 64d show Si nanowires aligned on Device “H”. All the nanowires were aligned using an applied AC potential with a frequency of 2 kHz and voltage of 10 V_{pp} . The debris in Figure 64a can be attributed to very small pieces of broken template which was created during sonication of the template.

Figure 64. Alignment of TiO₂ and Si nanowires on third stage designs. a)TiO₂ b-f) Si.

5.5 Four Probe Electrical Measurements

A four probe I-V experiment was conducted on a silicon (Si) nanowire to see if resistance could be measured. The four probe device used in this experiment is shown in Figure 38 in Section 4.5. The current was swept from $-0.1 \mu\text{A}$ to $0.1 \mu\text{A}$ and the subsequent voltage was measured. Figure 65 shows the I-V plot for the four probe device. The I-V plot is linear compared to the plots for Device 1 and 2 shown in Figure 59 and Figure 60 in Section 5.3 respectively.

Figure 65. Four probe I-V plot for a 125 nm diameter silicon nanowire.

Using the same four probe device, a two probe I-V measurement using the two outer contacts was made for comparison. The voltage was swept from -2 V to 2 V and the current was measured. Figure 66 shows the I-V plot for the two probe measurement. The I-V plot is noisy compared to the four probe measurement in Figure 65.

Figure 66. Two probe I-V plot on a 125 nm diameter silicon nanowire.

The resistivity was calculated using a diameter of 125 nm and a length of 3 μm measured from the SEM image shown in Figure 38. The 3 μm length is the measured length between the two inner electrodes in Figure 38. Table 4 shows the resistivity of the two devices. The resistance value for the two probe measurement was approximately 33 times higher than the four probe measurement. The resistivity of 2.45 Ωcm from the four probe measurement falls within an order of magnitude of bulk intrinsic Si. The calculations can be found in Appendix C. Assuming the relation $R_{\text{meas}} = R_{\text{NW}} + R_{\text{c1}} + R_{\text{c2}} + R_{\text{metal lines}}$ holds true for the two probe measurements, the total resistance contribution from the two contacts can be estimated. The resistance from the pre-patterned aluminum electrodes, $R_{\text{metal lines}}$ is negligible, which leaves the resistance of the nanowire and the contacts. If $R_{\text{NW}} = 6 \text{ M}\Omega$ and $R_{\text{meas}} = 200 \text{ M}\Omega$ then the total contact resistance, $R_{\text{c1}} + R_{\text{c2}}$ is 194 $\text{M}\Omega$ or 97 $\text{M}\Omega$ at each contact.

Table 4. Two probe vs. four probe resistance values and the contact resistance for a silicon nanowire.

	Resistance	Resistivity	Conductivity
Four probe measurement	6 M Ω	2.45 Ωcm	40.74 (Ωcm) ⁻¹
Two probe measurement	200 M Ω	-	-
Total contact resistance	194 M Ω	-	-

This experiment indicates a clear difference between two and four probe I-V measurements. Similar to the findings by Goldberger *et al.* [9] in Section 3.2.4, the measured four probe resistance was much lower than the measured two probe resistance. Assuming that the Pt and Al electrodes add a negligible amount of resistance, the calculated total contact resistance of 194 M Ω is the biggest contributing factor in the discrepancy between the two measurements. In addition to the lower resistance measurement, the measured data was also noticeable less noisy. The linear four probe I-V plot in Figure 65 also suggest that the contacts between the Si nanowire and the deposited Pt are ohmic, unlike the Pt-TiO₂ nanowire contact discussed in Section 5.3. Pt-Si ohmic contacts have been used before in traditional semiconducting devices, however such contacts were annealed at high temperature.

5.6 Temperature Dependent I-V Measurements

Four probe temperature dependent electrical measurements in the MMR Technologies micro-miniature refrigerator setup described in Section 4.6.2 proved to be unsuccessful. An error occurred during attempts to measure the TiO₂ nanowire shown in Figure 37 and the Si nanowire shown in Figure 39b in Section 4.5. A current of 1 nA was supplied through the two outer contacts and the subsequent voltage behavior could

not be measured. Measurements using the same current on the Si nanowire shown in Figure 39b also resulted in the same error.

It was suspected that there were contact issues with the deposited Pt and that they needed repair with the FIB. Failure of the devices was discovered during inspection with the FIB. Figure 67a shows the TiO₂ nanowire device before temperature experiments were conducted. The SEM image in Figure 67b shows failure of the pre-patterned Al electrodes in addition to the Pt contact lines. Figure 68a and b show before and after SEM images of the four probe Si nanowire device.

Figure 67. TiO₂ nanowire a) Before attempt at four probe I-V measurement. b) After 1 nA was supplied.

Figure 68. Si nanowire a) Before attempt at four probe I-V measurement. b) After 1 nA was supplied.

To determine the cause of this problem, Pt lines were deposited directly onto Device “X” as shown in Figure 69a. The supplied current was lowered from 1 nA to 0.1 nA in case the current used in the first two runs was too high. However, the same issue occurred and the device also failed, as shown in Figure 69b.

Figure 69. FIB deposited Pt electrodes created to test cryocooler setup. a) Before test b) After 0.1 nA was supplied.

A platinum sample shown in Figure 69 was created to see if the device failure was caused by the nanowires. From analysis of the SEM images in Figure 70a and b, it is interesting to see that the pre-patterned Al electrodes in Figure 70a have failed in a manner that is similar to melting. Further examination reveals that the deposited Pt has either been destroyed or de-laminated from the surface. The de-lamination can be clearly seen in Figure 70b.

It is possible that the cause of the device failure is most likely the contacts between the pre-patterned Al electrodes, the FIB deposited Pt, and the Pt-nanowire interface. It has been reported that the resistivity value of FIB deposited Pt is typically one or two orders of magnitude higher than that of bulk Pt [50]. A contact resistance of 194 M Ω was calculated earlier in this section. This highly resistive interface might cause unwanted Joule heating and caused the devices to fail. However, one caveat is that the current of 1 nA was used in the study. This would lead to the conclusion that not enough current was involved to cause the type of failure seen. However it is possible the electrometer was misused as an ohmmeter during the experiment. In the ohmmeter function, the electrometer sources its own current of approximately 1 mA, this value is six orders of magnitude larger than the 1 nA sourced. The large increase of current and the high contact resistance suggest that Joule heating at the contacts is a plausible explanation of the device failure. This suggestion needs more study before a conclusion can be made and are thus not provided in this thesis.

Figure 70. Pt electrode failure after attempts at four probe measurements. a) 6500x magnification b) 20,000x magnification.

CHAPTER SIX SUMMARY AND CONCLUSIONS

In this thesis, a technique was developed to measure the electrical properties of a single semiconducting nanowire. Dielectrophoretic alignment and focused ion beam (FIB) platinum (Pt) deposition were used to create a four probe device structure to measure the resistance of nanowire.

6.1 Summary of Work

To investigate dielectrophoretic alignment, gold (Au) and latex nanoparticle behavior was studied using a simple nickel (Ni) electrode with a 200 μm gap. Gold and latex nanoparticles exhibited dendrite growth and pearl chain formation respectively. TiO_2 nanowires were also aligned along the edges of the Ni electrodes. An applied AC potential of 25 Hz and voltage of 10 V_{pp} were used in these experiments.

An interdigitated device structure was designed with varying gap sizes between the digits. The interdigitated devices were designed at NASA Ames Research Center and fabricated at the SJSU Microelectronics Processing Lab (MPEL) using traditional semiconductor processing techniques. Latex nanoparticles showed pearl chaining across 4 μm sized gaps using an applied AC potential of 25 Hz, 2 kHz, and 30 MHz all at a voltage of 10 V_{pp} . TiO_2 nanowires were successfully aligned across the interdigitated electrodes using an applied AC potential of 2 kHz and voltage of 10 V_{pp} . Numerical modeling showed at any of the frequencies used, a positive dielectrophoretic (DEP) force would exist, leading to nanowire alignment. Moreover, the force and direction of the DEP force is highly dependent on material property.

Focused ion beam nanoprocessing was used to deposit Pt contact pads onto the aligned nanowire and to mill away material to isolate the nanowire for electrical measurements. Two probe I-V measurements were made using the interdigitated device structure. Two TiO₂ nanowires were measured resulting in measured resistivity of 0.22 Ωcm and 6.42 Ωcm. The discrepancy between the two measurements can be explained by high contact resistance between the Pt and TiO₂ nanowire interface. Electrical properties of single TiO₂ nanowires have not been reported before, but thin film TiO₂ resistivity has been reported as 0.22 Ωcm. The I-V characteristics of the two measurements exhibited Schottky behavior and are most likely due to a back to back Schottky barrier.

Four probe I-V measurements were completed for Si nanowire. For Si nanowire a resistance of 6 MΩ and resistivity of 2.45 Ωcm was determined. Two probe I-V measurements on the same device were made as a comparison, giving a resistance of 200 MΩ. This study confirms that four probe measurements are able to remove contact resistance and provide an accurate measurement of nanowire resistivity.

A micro-miniature refrigerator from MMR Technologies was built for temperature dependent measurements. An instrument control interface between the current source and electrometer was developed and programmed using LabVIEW. New devices tailored toward four probe temperature dependent measurements were designed and fabricated at the SJSU MPEL. Alignment of TiO₂ and Si nanowires were successful using an applied AC potential of 2 kHz and voltage of 10 V_{pp}. Attempts at temperature dependent electrical measurements could not be made due to device failure. It is

suggested that the failure could be attributed to high contact resistance causing excessive Joule heating.

6.2 Suggestions for Future Work

Only three complete measurements were made in this study. Thus, statistical results cannot be provided. It is suggested that in a future study, multiple measurements on the same type of nanowire should be conducted.

The pre-patterned electrodes in this study were fabricated using aluminum. Due to the native oxide that exists on aluminum, it is suggested that gold electrodes be used instead. Gold has been widely used for electrical measurements because of it is a good conductor that does not react to air and most reagents. A gold lift-off process could be developed at SJSU, using contact pads fabricated from gold with a titanium adhesion layer.

Temperature dependent I-V measurements on single semiconducting nanowires can be the topic of future study using the technique developed in this thesis. Using this technique, the band gap and resistivity of single semiconducting nanowires can be determined. Changing the pre-patterned electrodes to gold could improve the contact resistance that might have caused device failure during initial attempts. The electronic equipment in the temperature dependent system could be tested to ensure that no excess current is being supplied during measurement.

One possible study is the size effects on the band gap of semiconducting nanowires. This can be studied by controlling the diameter of the nanowire during synthesis. Various diameter nanowires can then be aligned and tested using the

developed technique and the correlation between band gap and diameter size can be found.

Another study that can be done is an extensive study on the effects of focused ion beam platinum deposition on nanowire crystal structure and the effects of unintentional doping in electrical characterization. Through the use of a high resolution transmission electron microscopy (HRTEM), images of the structure before and after FIB Pt deposition can be determined. However, there are inherent difficulties as the HRTEM require samples that are thin enough for electrons to pass through and often an FIB is used for HRTEM sample preparation which can lead to even more alteration. Studies of the effect of damage and doping done by the energetic ions can then be studied using the technique in this thesis.

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APPENDIX A WAFER PROCESSING TRAVELLER

Step	Step Name	Process Detail 1	Process Detail 2	Time	Process Detail 3	Process Detail 4
Clean	Estimated Time =	61 min				
1	Piranha	Bath Temp 110 C	H2SO4 (75%) + H2O2 (25%)	5	Use Diffusion Clean Bench	Use Proper PPE
2	Dump Rinse			5		
3	BOE Dip	Bath Temp 20 C	20:1 BOE	2	Use Diffusion Clean Bench	Use Proper PPE
4	Dump Rinse			5		
5	Piranha	Bath Temp 110 C	H2SO4 (75%) + H2O2 (25%)	5	Use Diffusion Clean Bench	Use Proper PPE
6	Dump Rinse			5		
7	BOE Dip	Bath Temp 20 C	20:1 BOE	2	Use Diffusion Clean Bench	Use Proper PPE
8	Dump Rinse			5		
9	RCA	Bath Temp 70 C	HCl:H2O2:H2O 1:1:6	10	Use Diffusion Clean Bench	Use Proper PPE
10	Dump Rinse			5		
11	BOE Dip	Bath Temp 20 C	20:1 BOE	2	Use Diffusion Clean Bench	Use Proper PPE
12	Dump Rinse			5		
13	Spin Rinse Dry	Turn on N2		5	Use correct SRD	
14	Take wafers out	Turn off N2	Dot in, H out	0		

Step	Step Name	Process Detail 1	Process Detail 2	Time	Process Detail 3	Process Detail 4
Step	Step Name	Process Detail 1	Process Detail 2	Time	Process Detail 3	Process Detail 4
Screen Oxide	Estimated Time =	115 min				
1	Load	900 C	N2:4SLM	10	Shiny side of wafer facing into furnace, every other slot use 2 dummies in front and back	Push quartz boat until last wafer is part cermaic ring
2	Push	900 C	N2:4SLM	15	Use quartz rod	
3	Ramp	900 C to 1100 C	N2:4SLM	15	Cap on, restrictor on door open	
4	Stabilize	1100 C	N2:4SLM	5	Cap on, restrictor on door open	
5	Soak	1100 C	O2:10SLM	30	Cap on, restrictor on door open	
6	Purge	1100 C	N2:10SLM	10	Cap on, restrictor on door open	
7	Pull	1100 C	N2:4SLM	20	Use quartz rod	
8	Cool	Room Temp	Transfer wafer to cool quartz boats	10	Turn off gas flows	Ramp furnace back down
Step	Step Name	Process Detail 1	Process Detail 2	Time	Process Detail 3	Process Detail 4
Pre Oxide Clean	Estimated time =	10 min				
1	Piranha	Bath Temp 110 C	H2SO4 (75%) + H2O2 (25%)	5	Use Diffusion Clean Bench	Use Proper PPE
2	Dump Rinse			5		

Step	Step Name	Process Detail 1	Process Detail 2	Time	Process Detail 3	Process Detail 4
Field Oxide	Estimated time =	115 min				
1	Load	900 C	N2:4SLM	10	Shiny side of wafer facing into furnace, every other slot use 2 dummies in front and back	Push quartz boat until last wafer is past ceramic ring
2	Push	900 C	N2:4SLM	15	Use quartz rod	
3	Ramp	900 C to 1100 C	N2:4SLM	15	Cap on, restrictor on door open	
4	Stabilize	1100 C	N2:4SLM	5	Cap on, restrictor on door open	
5	Soak	1100 C	4SLM Wet	60	Cap on, restrictor on door open	7mL HCl at T = 95 C Ensure N2 is flowing if light is on and H2O is boiling
7	Pull	1100 C	N2:4SLM	20	Use quartz rod	
8	Cool	Room Temp	Transfer wafer to cool quartz boats	10	Turn off gas flows	Ramp furnace back down
9	Inspect	Measure Oxide Thickness	Should be over 4000Å	10	Nanospec	5 points per wafer
Step	Step Name	Process Detail 1	Process Detail 2	Time	Process Detail 3	Process Detail 4
Metallize	Estimated time =	60 min				
1	Load	Load wafers into evaporation chamber		5		Be sure to fill all slots
2	Al Clips	Place 20-21 Al clips on W filament		5		Be sure to clamp ends of Al clips
3	Pump down	Down to 10-6 Torr		20		Make sure bell jar is leaking
4	Evaporate			5		Make sure all liquid Al beads are gone
5	Pump up			5		
6	Remove	Take wafers out		2		

Step	Step Name	Process Detail 1	Process Detail 2	Time	Process Detail 3	Process Detail 4
Mask Lithography	Estimated time =	16 min				
1	Singe	125 C	Air	1	Hotplate	Vacuum on
2	Prime	3000 rpm	HMDS Prime	0.5	Use manual dispenser	
3	Spin PR	3000 rpm	Shipley	1	Use manual dispenser	
4	Pre-Bake	110 C	Air	1		
5	Expose			1		
6	Post Expose Bake	110 C	Air	1		
7	Develop	Room temp	Developer	0.5	1.75% TMHA in DI	
8	Hard Bake	120 C	Air	1	Hotplate	
9	Inspect			10	Inspect wafers for alignment and quality	
Step	Step Name	Process Detail 1	Process Detail 2	Time	Process Detail 3	Process Detail 4
Al Etch	Estimated time =	15 min				
1	Al Etch	Bath Temp 60 C	Al Etch Make sure its fresh	5	Use Etch Clean Bench	Use Proper PPE
2	Dump Rinse			5		
3	Spin Rinse Dry	Turn on N2		5	Use correct SRD	
4	Take out wafers	Turn off N2	Dot in H out	0		
PR Strip	Estimated time =	20 min				
1	Stripper	Bath Temp 60 C	Microstrip 2001 Stripper	10	Stripper Bench	Use Proper PPE
2	Dump Rinse			5		
3	Spin Rinse Dry	Turn on N2		5	Use correct SRD	
4	Take out wafers	Turn off N2	Dot in, H out	0		

APPENDIX B DIELECTROPHORETIC FORCE CALCULATION

$$\vec{F}_{DEP} = Z\epsilon_m K(\omega) \vec{\nabla}(\vec{E}_{rms}^2); \text{ Dielectrophoretic force}$$

where

$$Z = \frac{\pi}{2} r^2 l; \text{ Geometric factor for a rod}$$

and

$$K(\omega) = \text{Re} \left[\frac{\epsilon_p^* - \epsilon_m^*}{\epsilon_m^*} \right]; \text{ is the real part of the Claussius-Mossotti factor for a rod}$$

where

$$\epsilon^* = \epsilon - \frac{i\sigma}{\omega}; \text{ is the complex permittivity, where } \sigma \text{ is the conductivity, } \epsilon \text{ is the permittivity and } \omega = 2\pi f \text{ the angular frequency of the applied field}$$

ϵ_m = the dielectric constant of the medium

In the calculation, it is assumed that the field is constant throughout the sample. Therefore, the estimation of $\vec{F}_{DEP}$ is then just:

$$\vec{F}_{DEP} = Z\epsilon_m K(\omega)$$

For the TiO₂ nanowire the geometric factor is:

$$Z = \frac{\pi}{2} \bullet (100 \times 10^{-9} \text{ m})^2 \bullet 5 \times 10^{-6} \text{ m} = \underline{1.57 \times 10^{-19} \text{ m}^3}$$

$$\epsilon_m = 7.08 \times 10^{-10}$$

$$K(\omega) = \frac{\epsilon_p^* - \epsilon_m^*}{\epsilon_m^*} = \frac{\left(\epsilon_p - \frac{i\sigma_p}{\omega} \right) - \left(\epsilon_m - \frac{i\sigma_m}{\omega} \right)}{\left(\epsilon_m - \frac{i\sigma_m}{\omega} \right)} = \frac{\left(\epsilon_p - \frac{i\sigma_p}{\omega} \right)}{\left(\epsilon_m - \frac{i\sigma_m}{\omega} \right)} - \frac{\left(\epsilon_m - \frac{i\sigma_m}{\omega} \right)}{\left(\epsilon_m - \frac{i\sigma_m}{\omega} \right)} =$$

$$= \frac{\left(\varepsilon_p - \frac{i\sigma_p}{\omega}\right)}{\left(\varepsilon_m - \frac{i\sigma_m}{\omega}\right)} \bullet \frac{\left(\varepsilon_m + \frac{i\sigma_m}{\omega}\right)}{\left(\varepsilon_m + \frac{i\sigma_m}{\omega}\right)} = \frac{\varepsilon_p \varepsilon_m + i\varepsilon_p \frac{\sigma_m}{\omega} - i\varepsilon_m \frac{\sigma_p}{\omega} + \frac{\sigma_p \sigma_m}{\omega^2}}{\varepsilon_m^2 + i\varepsilon_m \frac{\sigma_m}{\omega} - i\varepsilon_m \frac{\sigma_m}{\omega} + \frac{\sigma_m^2}{\omega^2}}$$

$$= \frac{\left(\varepsilon_p \varepsilon_m + \frac{\sigma_p \sigma_m}{\omega^2}\right) - i\left(\varepsilon_p \frac{\sigma_m}{\omega} - \varepsilon_m \frac{\sigma_p}{\omega}\right)}{\varepsilon_m^2 + \frac{\sigma_m^2}{\omega^2}} = \frac{\varepsilon_p \varepsilon_m + \frac{\sigma_p \sigma_m}{\omega^2}}{\varepsilon_m^2 + \frac{\sigma_m^2}{\omega^2}}$$

APPENDIX C RESISTIVITY CALCULATION

Device 1:

$$\text{Slope} = \frac{2.3274 \mu A}{V}; R = \frac{V}{2.3274 \times 10^{-6} A} = \underline{429.66 k\Omega}$$

Resistivity $\rho = \frac{RA}{L}$; where R = resistance, A = cross-sectional area, L = length

$$\rho = \frac{429.66 \times 10^3 \Omega \cdot (100 \times 10^{-9} m)^2 \pi}{6 \times 10^{-6} m} = 0.22 \times 10^{-2} \Omega m = \underline{0.22 \Omega cm}$$

$$\sigma = \frac{1}{\rho} = \frac{1}{0.22 \Omega cm} = \underline{4.54 (\Omega cm)^{-1}}$$

Device 2:

$$\text{Slope} = \frac{0.0978 \mu A}{V}; R = \frac{V}{0.0978 \times 10^{-6} A} = \underline{10.2 M\Omega}$$

Resistivity $\rho = \frac{RA}{L}$; where R = resistance, A = cross-sectional area, L = length

$$\rho = \frac{10.2 \times 10^6 \Omega \cdot (100 \times 10^{-9} m)^2 \pi}{5 \times 10^{-6} m} = 6.42 \times 10^{-2} \Omega m = \underline{6.42 \Omega cm}$$

$$\sigma = \frac{1}{\rho} = \frac{1}{6.42 \Omega cm} = \underline{0.15 (\Omega cm)^{-1}}$$

Silicon nanowire device

Four probe:

$$\text{Slope} = R = \underline{6M\Omega}$$

Resistivity $\rho = \frac{RA}{L}$; where R = resistance, A = cross-sectional area, L = length

$$\rho = \frac{6 \times 10^6 \Omega \cdot (62.5 \times 10^{-9} m)^2 \pi}{3 \times 10^{-6} m} = 2.45 \times 10^{-2} \Omega m = \underline{2.45 \Omega cm}$$

$$\sigma = \frac{1}{\rho} = \frac{1}{2.45 \Omega cm} = \underline{40.74 (\Omega cm)^{-1}}$$

Two Probe:

$$\text{Slope} = \frac{5nA}{V}; R = \frac{V}{5 \times 10^{-9} A} = \underline{200 M\Omega}$$

Resistivity $\rho = \frac{RA}{L}$; where R = resistance, A = cross-sectional area, L = length

$$\rho = \frac{200 \times 10^6 \Omega \cdot (62.5 \times 10^{-9} m)^2 \pi}{15 \times 10^{-6} m} = 0.164 \Omega m = \underline{16.4 \Omega cm}$$

$$\sigma = \frac{1}{\rho} = \frac{1}{16.4 \Omega cm} = \underline{0.06 (\Omega cm)^{-1}}$$