GROWTH AND APPLICATIONS OF GERMANIUM NANOWIRES

by

LAUREN ASHLEY KLEIN

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ABSTRACT OF THE DISSERTATION

Growth and Applications of Germanium Nanowires

By LAUREN ASHLEY KLEIN

Dissertation Director:
Dr. Eric Garfunkel

Germanium nanowires are grown utilizing a vapor-liquid-solid mechanism in a home-built, hot-wall chemical vapor deposition reactor. These wires are of particular scientific and technological interest due to their relatively low growth temperature, which allows them to be grown on a wide variety of substrates. The wires are fully characterized, utilizing electron microscope techniques, EDX, XPS, RBS, XRD, and electrical measurements. We demonstrate the first growth of germanium nanowires directly on a flexible polymer substrate. An investigation into the growth rate of nanowires reveals that their nucleation cannot be described by a simple diffusion-limited model; a more complicated surface-limited kinetics model must be applied to fully describe growth. We explore the passivation of nanowires, focusing on the deposition of thin-films of robust oxides utilizing atomic layer deposition. Initial electrical measurements are investigated to gain some understanding as to the electrical properties of our wires. We present a novel organic-inorganic heterojunction photovoltaic cell, developed from germanium nanowires and poly (3-hexylthiophene), and demonstrate an increase in external quantum efficiency of the device with the inclusion of the germanium nanowires.
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CHAPTER 1 - Introduction

“But I am not afraid to consider the final question as to whether, ultimately---in the great future---we can arrange the atoms the way we want; the very atoms, all the way down! What would happen if we could arrange the atoms one by one the way we want them (within reason, of course; you can’t put them so that they are chemically unstable, for example).

“Up to now, we have been content to dig in the ground to find minerals. We heat them and we do things on a large scale with them, and we hope to get a pure substance with just so much impurity, and so on. But we must always accept some atomic arrangement that nature gives us. We haven't got anything, say, with a "checkerboard" arrangement, with the impurity atoms exactly arranged 1,000 angstroms apart, or in some other particular pattern.

“What could we do with layered structures with just the right layers? What would the properties of materials be if we could really arrange the atoms the way we want them? They would be very interesting to investigate theoretically. I can't see exactly what would happen, but I can hardly doubt that when we have some control of the arrangement of things on a small scale we will get an enormously greater range of possible properties that substances can have, and of different things that we can do.”

-Richard Feynman, “There’s Plenty of Room at the Bottom”

December 29th, 1959

\[^{1}\]
Dr. Feynman’s prophetic address was given at Caltech during the annual APS meeting, barely a decade after he and many of the other greatest minds that physics has ever known harnessed the power and fury contained within atoms themselves. At the time, it could not even be said that nanotechnology was in its infancy— it was merely at the point of its very conception. Over the next five decades, the field would explode in popularity as we pushed things tinier and tinier, forcing exploration to the very physical limit of matter. “Nanotechnology” was to become a household buzzword, promising to solve all the crises of the world through tiny, omnipotent robots who could repair any artery, hack any computer, and provide us with limitless energy from some as-of-yet to be determined source.

Science-fiction expectations aside, the practical applications of nanotechnology have profoundly changed the way we work, communicate, live, and function as a society. At the time of Feynman’s death in 1988, a top of the line 486 Processor came complete with $10^6$ transistors per die and a whopping 4 M of memory. In the past twenty years, the semiconductor processing industry has not failed to disappoint Dr. Moore with its ever-increasing push towards smaller and faster. Even as engineers never fail to ingeniously design processes to produce devices, still so much remains to be discovered regarding the basic science behind nanosystems. As things decrease in size they do not behave the way we have come to expect from our macro or even micro sized systems, and new riddles appear for us to solve. These riddles are what have opened the door to this dissertation project.
1.1 Justification of Project

There is nothing novel in the study of germanium as a material. Indeed, since the first transistor was produced from this element in 1948 at Bell Labs⁴, germanium has been employed in a large range of electronic devices, now most often finding use in fiber optic and infrared night vision applications.⁴ Germanium has a higher carrier mobility than that of silicon because the effective masses of the electrons and holes are lighter in germanium. This is a property of potential importance in many electronic applications, making germanium attractive as a channel material in field-effect transistors (FET). The electron and hole mobilities of bulk germanium are 3900 cm²/V s and 1900 cm²/V s, respectively, while those of silicon are 1500 cm²/V s and 450 cm²/V s.⁵

Two main issues setting germanium back from the more popularly utilized silicon are availability and the problem of the native germanium oxide. Silicon production is only limited by production capacity, as it is the second most abundant element in the earth’s crust. Germanium is limited by a relative scarcity of sources, and thus is several orders of magnitude more expensive to produce than silicon. Due to this limitation it is extremely unlikely that bulk germanium wafers will ever surpass silicon in large-scale use. However, its use in high performance and niche applications or as ultra thin films, is likely to continue.
Germanium, unlike silicon, does not form a single, stable native oxide. The layer which forms on the germanium surface upon exposure to air, usually a range of sub-oxides has undesired electrical properties and is susceptible to degradation upon exposure to water. Whereas silicon forms a smooth and uniform silicon/silicon dioxide interface when oxidized, the germanium/germanium oxide is quite difficult to create in a pure, defect free germanium/germanium dioxide form, and becomes rough and pitted when in contact with water. This is not an insurmountable issue, however. It is simply important to be able to find an appropriately stable layer (oxide or otherwise) if it is to be useful for device applications. The most investigated methods of germanium passivation involve simple termination of the surface with a layer of hydrogen or chlorine which are utilized to temporarily prepare the germanium surface so it can be studied in more depth or transferred. Other wet chemical methods to passivate the planar germanium surface include the creation of covalent bonds to carbon or sulfur groups through standard organic chemistry synthesis.

While the surface chemistry of silicon has been widely studied, the chemistry of the germanium surface is somewhat less advanced, though analogous in certain instances. Any research into germanium itself necessitates some acknowledgement of this oxide problem.

Increasingly, germanium has enjoyed a popularity as a component of photovoltaic devices. The use of bulk germanium in photovoltaics is an important component of multi-junction concentrator solar cells. Initially, germanium was used to
replace gallium arsenide as the substrate for solar cells on satellites.\textsuperscript{19} Currently, germanium is commonly employed within the base junction or sub-cell as an active layer to harvest low energy photons. With a bandgap of 0.66 eV, germanium is active within the infrared portion of the solar spectrum. In a GaInP/GaAs/Ge triple junction, the germanium is responsible for 10\% or more of the solar cell’s efficiency and is capable of generating more short circuit current, \( J_{sc} \), than the other two sub-cells combined.\textsuperscript{20, 21}

Nano-scale germanium incorporates these material-specific electronic properties with the benefits and opportunities of extremely small size scales and high dimensionalities. The extremely high surface-to-volume ratios of nanostructures can bring about physical and chemical properties which are not evident in their bulk counterparts, for instance increased solubility or catalytic activity. As materials shrink in size to approach their Bohr radius, quantum confinement effects introduce differing electronic and optical properties due to changes in the band gap. Although not relevant to the size scale of nanowires presented in this work, \textit{ab initio} studies on germanium nanowires smaller than one nanometer in diameter have shown changes in the bandgap of the wires due to quantum confinement.\textsuperscript{22} Theoretical studies by Harris and O’Reilly suggest that the bandgap of germanium nanowires could depend on the crystallographic direction along which the wire is oriented if the wire is small enough to be subject to quantum confinement effects. If the wire is oriented along the \(<110>\) direction, the germanium becomes a direct bandgap semiconductor.\textsuperscript{23}
Nanostructures are also interesting from a fundamental scientific standpoint; much remains unknown about interactions specific to nano-sized material. While sometimes analogous, direct comparisons to the properties of bulk material can often not be drawn.

Nanotechnology has moved forward on the idea that, working from basic, nano-scale building blocks, complex devices will be realized through guided self-assembly. This “bottom-up” approach to engineering is a key point in the field; researchers desire the utmost control over the growth and structure of their nanostructures and hope that this will lead to increased performance in their final product. In order for the bottom-up paradigm to be fully achieved, the palette of controllable nanostructures must be varied and complete, consisting of particles, rods, wires, sheets, ribbons, and tubes of varying physical, chemical, and electrical specifications.\textsuperscript{24} Nanowires, in particular, have been created from a large range of materials, including single-element semiconductors like germanium or silicon, composite semiconductors like gallium arsenide or boron nitride, oxides like zinc oxide or titanium oxide, and metals such as gold or silver.\textsuperscript{25-32} The range of different techniques available to construct nanowires affords researchers the luxury of choosing from a variety of starting materials. Methods of growing nanowires will be discussed in more detail in the next section.

Nano-sized semiconductors can be incorporated into matrices of flexible or transparent polymers and retain the benefits of both materials, a property which is extremely desirable for flexible electronic displays or solar cells. There would be a large market for flexible electronic and photonic devices if functionality and performance
could approach that of conventional solid state devices at a reasonable cost.\textsuperscript{33, 34} Polymer films hold great promise as a cost-efficient substrate for potential applications such as those of photovoltaics or display technologies, due in large part to their ease of manufacturing, low cost, and extensive past development. Such integrated systems comprise a large part of our research, to be discussed in this thesis in greater detail.

Aside from the reasons stated above, germanium nanowires have a unique advantage over silicon nanowires: their relatively low growth temperature. Silicon nanowires require temperatures of over 450 °C in order to initiate growth. This not only places constraints on the type of substrate on which the wires may be grown, but also increases the necessary energy and therefore the cost of their processing. As will be seen in the remainder of this dissertation, this relatively low growth temperature of germanium nanowires can be exploited for a significant advantage in the design of composite inorganic/organic systems.

These reasons provide the motivation behind the choice of germanium nanowires as a topic of study for this dissertation: an interesting material in an interesting size regime, rife with unanswered questions regarding growth, surface chemistry, and potential applications.

1.2 Literature Review

Nanostructures, including nanowires, can be synthesized by a variety of techniques, not limited to lithography, electrodeposition, laser and chemical self-
Each technique produces structures with their own unique properties and advantages. For the purposes of this dissertation, the discussion will be limited to nanowires grown through a catalyzed chemical vapor deposition (CVD) process, termed vapor-liquid-solid (VLS) growth.

This method of growth was first described over forty years ago by Wagner and Ellis. They utilized liquid droplets of metal as catalysts to create micro-scale silicon “whiskers,” whose size was dictated by the minimum stable droplet dimensions. While of mild scientific interest, the potential of these structures remained largely untapped until the late 1990s and early 2000s when Charles Lieber and his group out of Harvard brought the size of these whiskers into the nano-regime, and their discussion to the pages of Science. At first, Lieber used laser-ablation to generate energetically stable metal clusters to catalyze nanowire growth. As the science behind nanowire growth progressed, simpler methods to develop nano-catalysts were introduced, as will be explored later in this dissertation.

1.2.1 Vapor-Liquid-Solid Growth Mechanism

The metal-catalyzed growth of semiconductor nanowires at relatively low process temperatures proceeds through the vapor-liquid-solid (VLS) mechanism. During VLS, the germanium source gas, usually germane (GeH₄) or di-germane (Ge₂H₆),
is transported into the reactor which is held at or close to the eutectic temperature of germanium and a metal catalyst. Different metals create liquid eutectics with germanium at different temperatures; gold is most commonly used. As will be discussed in the experimental chapter, gold can be applied as either a thin, sputter coated film or in the form of gold nanoparticles. The presence of the catalyst serves two functions. First, during the introduction of the source gas into the reactor, the metal particles help to crack the precursor into germanium and hydrogen. The second, more vital role of the catalyst is to facilitate nanowire growth.

As the reactor is heated and gas is flowed through the system, the gas comes in contact with the catalyst particles deposited on the desired substrate. After the gas is catalytically cracked, the germanium slowly diffuses into the gold particle until the eutectic composition is reached at 72% gold and 28% germanium. This composition is given in terms of atomic percentages. At this composition, the system becomes a liquid if the temperature is at or higher than the germanium and gold eutectic temperature of 360 °C.

Several groups have investigated the nucleation of nanowires from the gold-germanium eutectic system in detail. At the initial stages of growth the gold catalyst remains a crystalline solid. As the temperature is raised, it begins to combine with the decomposed germane gas and liquefy. This is a surface initiated model of melting; the atoms on the surface begin to disorder at a temperature lower than the bulk melting point and this melt perpetuates into the middle of the crystal. In order to develop a
clearer picture of the nano gold-germanium system (as compared to the bulk phase diagram shown in Figure 1.1) the Chidsey group performed thermodynamic calculations to develop a more relevant phase diagram. They found that if there were no germanium present, due to Gibbs-Thompson pressure effects the gold nanoparticle would begin to melt about ten degrees lower than bulk gold.\textsuperscript{41}

As the atomic percent of germanium is increased to 28% and the temperature is appropriately raised, the gold-germanium eutectic is reached. Supersaturation occurs as the germanium continues to become incorporated into the melt, and precipitation of the nanowire proceeds. It is this critical supersaturation which drives the whole process, as will be discussed in more detail below. Once growth is initiated, the germanium precipitates from the melt, and a nanowire wire grows up from the substrate with the catalyst particle remaining on top. Wires invariably grow in this single direction due to the fact that the area on the top of the wire where it interfaces with the eutectic are more energetically favorable for growth than the vapor/liquid interface surrounding the rest of the liquid catalyst particle.
Bulk phase diagram of the gold-germanium system, showing the eutectic atomic composition of 72% gold and 28% germanium. A system of this mixture will melt at 361°C.

There is some ambiguity regarding just how liquid the gold-germanium system actually becomes in any specific case. It should be noted that germanium nanowire growth is habitually carried out below the eutectic temperature, although growth must first be initiated at 360°C. As will be discussed in the next section, the growth mechanism of nanowires is considered by some to be vapor-solid-solid (VSS) growth instead of VLS. However, regardless of the exact degree of liquidity of the catalyst during any point in the growth, the general method for the formation of nanowires
remains unchallenged. As more germanium diffuses into the alloy the system reaches a supersaturated state. Germanium precipitates out of the catalyst particle, invariably on the side in contact with the substrate surface, resulting in the formation of crystalline nanowires. The sizes of the metal catalyst particles determine the eventual diameter of the nanowires, though, as will be seen, this is not always trivial to control.

Figure 1.2: General schematic of nanowire growth. Nanowires grow away from the surface of the substrate with the gold catalyst particle remaining at the top. Due to the fact that the germanium-eutectic interface is more energetically favorable than the vapor-eutectic interface, nanowires always grow in a single direction.

Semiconducting nanowires synthesized in this manner are generally single-crystal with few defects. The metal catalyst remains at the end of the nanowire during
the growth process, as the solubility of gold in germanium at typical growth temperatures and pressures is extremely low. Studies of nanowires grown in ultra-high vacuum conditions have revealed some remnant gold incorporated into the wire, an effect undesirable in semiconductor applications. Outside of a few anomalous results, transmission electron microscopy has largely confirmed the lack of presence of gold in the wires grown in the work reported here.

1.2.2 VSS Controversy

Much investigation has gone into determining the state of the gold catalyst during nanowire growth. It was suggested that the VLS growth mechanism was not applicable in all cases, and sometimes the gold particle cap is a solid under certain growth conditions and is better described as vapor-solid-solid (VSS) growth. This discrepancy was largely addressed by Kodambaka et al., from IBM’s TJ Watson Research Laboratory, who showed differing nanowire growth conditions through in situ TEM. The researchers discovered that at the same temperature, nanowire growth could proceed via the VLS mechanism or the VSS mechanism depending on pressure and thermal history of the catalyst.

A hysteresis effect was observed regarding temperature; if the system was cooled during growth to the point of catalyst solidification (255°C), it remained solid upon re-heating until a temperature of 435°C was reached. Wires with smaller
diameters were more likely to have solidified catalysts. It was also shown that an increase in digermane pressure during growth led to an increase in the liquidity of the catalyst when all other parameters were held constant.

Figure 1.3: From Kodambaka, et al, *Science, 316*, 729. Reprinted with permission from AAAS.⁴² A) In situ images taken of germanium nanowires grown at $4.8 \times 10^{-6}$ Torr Ge$_2$H$_6$ (left) and at $8.6 \times 10^{-7}$ Torr (middle, initial; right, after 106 minutes) The smaller wire solidifies first as pressure is dropped. B) Histogram of wire count versus diameter recording the observed liquidity of the catalysts.

An important point of consideration is that that this group worked with wires grown under ultra-high-vacuum (UHV) conditions and thus their observations may differ than those of wires grown under low-vacuum or near-atmosphere conditions as is more common. Given their proposal of the importance of pressure dependence on the liquid
state of the catalyst, at common growth conditions found in this dissertation in which germane partial pressure approaches several Torr, a VLS mechanism is the most likely route of nanowire formation.

The Ross group also postulated that nanowire growth below the eutectic temperature of the gold-germanium system (360°C) was not completely due to the Gibbs-Thompson effect as originally thought, but must also be attributed to more complicated kinetic factors brought about by the gold-germanium eutectic system.\(^{43}\) If the nano-size of the catalysts were causing the resistance to solidification at lower temperatures, it would be expected that smaller particles would be less likely to solidify. However, this group observed exactly the opposite, with smaller particles solidifying sooner when pressure is dropped. Instead, the resistance to solidification is attributed to the effects of germanium supersaturation in the gold which inhibits the state change of the catalyst particle.

This hypothesis was further supported by Adhikari et al, who calculated nano-scale phase diagrams of the gold-germanium system, showed that a Gibbs-Thompson effect should be responsible for, at most, possible growth at temperature 10 °C below that of the bulk gold-germanium eutectic, as mentioned above. Thus, Gibbs-Thompson pressures alone cannot account for the 70°C- 90°C temperatures below the gold-germanium eutectic temperature at which nanowires have been observed to grow.\(^{41}\)
1.2.3 Epitaxial Growth

Substrate-oriented, epitaxial growth was explored by the Chidsey and McIntyre groups.\textsuperscript{41, 44, 45} Their work introduced a pre-growth oxide removal step to facilitate epitaxial growth on single crystalline silicon substrates and also a two-temperature growth process to minimize unwanted radial growth leading to tapered wires. Wire growth must first be initiated at the gold-germanium eutectic temperature, but can be dropped significantly after a few minutes.\textsuperscript{46} This work also noted that, regardless of the crystal surface of the underlying substrate, the wires will always grow in the $<111>$ crystal direction, with a minority of wires in the $<110>$ direction. This preference for wire growth direction is dictated by the interface between the catalyst particle and the developing wire, not the underlying substrate; wires be single crystalline and predominately $<111>$ even on amorphous substrates. However, if grown epitaxially the nanowires will conform to the crystal plane directions as dictated by the underlying substrate, and thus some order can be achieved.

It was shown that wire orientation to the substrate depends on the exposed crystal face. It is important to note that here we make a distinction between wire orientation on their substrate and the crystallinity of the wire itself. The preference of germanium nanowires for $(111)$ or $(110)$ orientation has been largely confirmed by other groups.\textsuperscript{47, 48}
The fact that growth in the <111> direction is predominate is due to the interface between the budding germanium nanowire and its gold catalyst particle. Lieber and coworkers proposed that this is due to the (111) plane being the lowest energy interface between the liquid gold particle and the solid germanium. The wire will grow in the direction which most suitably minimizes the overall free energy. In this model, nanowire growth is a thermodynamically driven process; the others have purported models in which kinetic factors, relative rates of diffusion and crystallization determine final structure, not simply the thermodynamics.

Epitaxial growth was a step in the right direction toward uniform arrays of vertical nanowires which are desired for some device applications. When grown epitaxially on a (111) substrate, some of the nanowires are indeed vertically oriented, but a large percentage of them jut off at angles. Petkov et al. were able to synthesize dense, vertical arrays of nanowires by utilizing a channeled template of anodic alumina membranes (AAM) into which the gold catalysts were deposited and through which germanium nanowire growth was guided. After growth was completed and the template was removed using chemical methods. These resulting vertical wire arrays are potentially well suited for applications including sensor arrays, solar cells, or vertical transistor arrays.
1.2.4 Removal of Gold

A further advance in preparing germanium nanowires for electronic applications came with the removal of the gold catalyst particle from the wires, as gold is incompatible with CMOS processing. This is due to the fact that gold is a high-lying acceptor and acts as an impurity to poison semiconductor devices.

![Figure 1.4](image)

Figure 1.4: Reproduced with permission from Woodruff et al, *Nano Letters*, 7, 1637. Copyright 2007 American Chemical Society. a) A germanium nanowire with gold cap b) a nanowire etched by exposure to aqueous triiodide solution and c) a nanowire nanowire after an exposure to triiodide and HCl solution. The gold is removed by the triiodide/HCL etch, but the wire remains intact.
The Chidsey group exposed germanium nanowires to standard gold etches common to microelectronics processing. They found that treating nanowires in a triiodide solution with hydrochloric acid removed the gold tip while preserving the integrity of the wire. The HCl was necessary in the solution to help passivate and protect the wires from the chemical treatment. Without its presence, significant etching of the wires was observed.\textsuperscript{51} The results from this study are shown in Figure 1.4, above.

Other researchers avoided the use of gold in the nanowire system altogether, turning to other metals as catalyst particles. The Morral group reported VLS growth of germanium nanowires utilizing bismuth as a catalyst.\textsuperscript{52} This eutectic system produces nanowires in the same relatively low temperature range as the gold-germanium system, with dense growth possible at around 300 °C. The germanium-bismuth eutectic temperature is 271°C, but the extremely low solubility of germanium in bismuth makes growth at the eutectic temperature slow. The downside to this system is that the high partial pressure of germane required to nucleate and grow nanowires, 150 Torr, is fifty times that necessary for the gold-germanium system. Given the extreme toxicity of germane gas, this particular technique is less attractive from the perspective of safety, but may present an attractive alternative to gold catalysts.
1.2.5 Devices

The Lieber group was among the first to test simple field-effect transistors from both p- and n-doped germanium nanowires. Wires can be made p-type through the introduction of diborane ($\text{B}_2\text{H}_6$) gas during growth. For n-type wires, phosphine ($\text{PH}_3$) is utilized. Titanium was used for the source and drain contacts, and they were noted to be ohmic with low contact resistance. Out of seventy-five synthesized devices, the group achieved a yield of 87% functioning devices, with on-currents and transconductances up to 850 mA/mm and 4.9 mA/V, respectively.

Lieber revisited this work in 2006, when his group produced FETs constructed from nanowires consisting of a silicon-germanium core-shell heterostructure. Utilizing an optimized structure with high-$k$ dielectrics in a top-gate geometry, the Harvard group produced a device featuring on-currents and transconductances several times greater than the most advanced MOSFET developed at the time. Lieber also heavily investigated nanowire heterostructures.

The other device thrust heavily investigated by the Harvard group was that of building sensors for chemical detection out of single nanowires. If a simple nanowire FET device is surface functionalized to become sensitive to a specific species, a change in conductance can be observed upon exposing the nanowire to an appropriate gas or liquid. Lieber’s first proof-of-concept device was a rudimentary pH sensor, constructed of a single nanowire which was treated with 3-aminopropyltriethoxysilane. When exposed to environments of varying acidity, the conductivity of the device was linked to
the protonation or deprotonation of the amino groups on the silane molecule.\textsuperscript{56} A schematic of Lieber’s device and a sample of the measurement he was able to take are shown in Figure 1.5.

![Image of Lieber's device and a measurement](image)

Figure 1.5: From Cui et al, Science, 293. Reprinted with permission from AAAS.

A) A diagram of a proof-of-concept pH sensor based on a nanowire functionalized with 3-aminopropyltriethoxysilane. B) Conductance data exhibiting electrical response with changing pH.

Lieber subsequently expanded his nanowire sensor repertoire to include detection of biological species including proteins and DNA.\textsuperscript{57} Detection of single viruses utilizing a nanowire-based sensor has also been achieved.\textsuperscript{58}

The rest of this thesis will build upon the work stated thus far. We investigate the growth of germanium nanowires in more detail, including epitaxial growth, growth on varying substrates including flexible materials and metals. We compare reaction rates and perform some exploration of nanowire kinetics. Various routes of nanowire passivation, including wet chemical methods and atomic layer deposited films are
analyzed utilizing XPS, RBS, and EDX. A rudimentary organic-inorganic heterojunction solar cell utilizing germanium nanowires is presented, as well as simple electrical devices.
CHAPTER 2-Experimental Details

This chapter will detail all experimental design regarding the growth and subsequent modification of germanium nanowires. Substrate processing, catalyst deposition, reactor conditions, post-growth processing and substrate removal will all be presented. In-depth explanation of the home built, hot-wall germanium nanowire growth reactor can be found in Appendix A, and other specific equipment details are located in Appendix B.

2.1 Choice of Substrates

2.1.1 Size Requirements

While the wires themselves are the main focus of investigation, as they can be grown bottom-up on a variety of materials, it is of interest to touch upon some of the considerations in choosing a substrate. Due to practical considerations regarding the dimensions of the tube furnace in the reactor, all substrates in the work reported in this thesis could be no greater than 1” in height or width. A length of no more than four inches is recommended to accommodate the furnace ‘sweet spot’. Most commonly,
however, substrates used are the thickness of a standard silicon wafer, broken into pieces of approximately 1 cm$^2$ in area.

### 2.1.2 Oxides and Metals

For randomly oriented wires, a wide range of substrates have been studied in this work, including metals such as tungsten and molybdenum, and oxides such as glass and indium tin oxide (ITO). The densest growth is achieved on glass substrates. This is due to the excellent adhesion of the colloidal gold catalyst particles to the surface of glass as described in the wet chemical methods section later in this chapter.

### 2.1.3 Single Crystal Substrates for Epitaxial Growth

For the potential vertical applications of nanowires, one desire is eventually to be able to construct devices, grown in ordered arrays directly upon a functional substrate. Germanium nanowires can be grown epitaxially on single crystalline silicon and germanium substrates due to the matched lattices and compatible bonding chemistries, aligning themselves primarily along the $<111>$ crystal plane direction and secondarily to the $<110>$ direction.
2.1.4 Polymers

The demand for highly portable, easily processable, lightweight, flexible substrates for electronic materials has rapidly increased over the past few years, leading to investigations of germanium nanowire growth directly on polymer substrates. Recently, advances in polymer chemistry have produced materials with relatively high melting points as compared to most organic substances. In the near future, it is expected that an increasing amount of these materials will be made commercially available, though not many are on the market today. For the studies contained herein, Kapton (poly(4,4'-oxydiphenylene-pyromellitimide), Dupont) and poly[(4,4'-hexafluoroisopropylidene)diphthalic anhydride-alt-3,6-diaminoacridine hemisulfate] (Sigma-Aldrich) are used. It is the relatively low growth temperature of germanium nanowires which makes growth on any polymer, even those listed above, possible. Both materials possess a glass-transition temperature just above the required growth range for germanium nanowires.

Of course, wires could always be grown on a different substrate and then transferred to the polymers, and this technique is useful in certain instances as will be discussed later. However, for many large-scale applications direct growth would be highly preferable. Growing nanowires on the polymer substrates simplifies the processing of any devices through reduction of the number of necessary steps, and thus
becomes more cost-effective. Direct growth also greatly improves the yield of nanowires present on the substrate.

To prepare the fluorinated polyimide samples, poly[(4,4’-hexafluoroisopropylidene) diphthalic anhydride-alt-3,6-diaminoacridine hemisulfate] is dissolved in dimethyl sulfoxide (DMSO) at a concentration of 10 mg/mL. The solution is subsequently drop cast onto a glass slide while simultaneously heating at 50 °C to expedite solvent removal. It should be noted that by this preparation method, the fluorinated polyimide samples are not flexible, but if bulk material were available, flexible substrates of fluorinated polyimide could easily be treated in the same manner as Kapton.

![Poly[(4,4’-hexafluoroisopropylidene)diphthalic anhydride-alt-3,6-diaminoacridine hemisulfate]](image)

Figure 2.1: Structure of high-melting temperature fluorinated polyimide which was spin-coated on glass slides to produce suitable substrates for nanowire growth.
Kapton samples are cleaned and treated according to the wet chemical procedure described below.

Figure 2.2: Stainless steel holder designed to accommodate Kapton samples. Without this holder, the Kapton would become deformed during nanowire growth due to temperatures approaching its glass transition temperature. This sample holder measures 10 cm x 1.8 cm x 0.4 cm and is secured by small screws around the edges.

The only unique handling required for this material comes during the growth itself. For growth on Kapton a specially designed stainless steel holder was required to keep the thin plastic sheets from deforming during growth. As our growth
temperatures approach the glass transition temperature of Kapton, if the film was not restrained, significant curling of the film would take place, undesirable for subsequent processing and studies. Also, the thin plastic is sufficiently light in weight that without some added anchor, it would be blown out of the hot spot of the furnace as soon as any gas flowed through the reactor.

2.2 Wet Chemical Details

2.2.1 Cleaning

All substrates must be properly and thoroughly cleaned prior to any subsequent processing step. Visible dirt or dust should be gently blown away with a stream of air. Any organic residue is removed from the substrate surface through submersion in a solution of methanol or acetone and treated for ten minutes in an ultrasonic bath.

For single crystal silicon or germanium, an initial treatment with hydrofluoric acid (Sigma Aldrich, 48 wt. % in H₂O, ≥99.99%) is performed to remove the native oxide layer if epitaxial growth is desired. These substrates are placed in a 2% solution of hydrofluoric acid in water for five minutes or until the surface becomes notably hydrophobic, indicating that it has been temporarily passivated and protected from oxide attachment due to hydrogen-termination of any dangling bonds. HF pre-treatment is clearly omitted for any oxide or amorphous substrate, but post-treatment
will be discussed subsequently. Samples must be completely dry before proceeding with gold deposition. It is recommended that they are gently blown with house air or nitrogen until all solvent has been removed.

2.2.2 Gold Deposition

Gold was used in this work to help catalyze nanowire growth. There are a variety of ways to introduce gold into or onto the substrate, with several described below.

2.2.2.1 Sputter Coating

The advantage of sputtering a layer of gold on the surface is that it is independent of surface chemistry; the catalyst can easily be applied to any substrate without deeper consideration of applicable wet chemistry. Gold sputtering is widely available in labs which commonly must prepare electrically conductive samples for analysis. The disadvantage, however, comes from the lack of control of the sizes of the wires grown from sputter coated films versus wet chemical processing of colloidal gold. Films of various thicknesses from 2nm to about 100 nm were applied to the surface of
substrates. A range of preferred thicknesses clearly exist with this kind of processing; if the gold layer is too thick or thin, wire growth is sub-optimal. These effects will be discussed in detail in the next chapter.

During heating in the nanowire reactor, the thin gold films tend to ball up, with gold becoming mobile on the surface. It is, unfortunately, not easy to control or guide this formation. Thus, as wire thickness is related to the size of the catalyst particle from which it forms, on a single substrate a range of wire thicknesses will result if a range of gold catalyst particles are present during growth.

2.2.2.2 Colloids

Wet chemical gold functionalization of substrates affords several advantages over the sputter method, namely, ease of procedure and direct control over nanowire size. Colloidal gold now is readily commercially available in a variety of nanoparticle sizes but can also be synthesized through fairly simple routes if necessary. Citrate or other organic coating prevents aggregation of these nanoparticles in solution and can be subsequently exploited for chemical functionalization. It is this coating which allows for the gold particles to easily be anchored to a surface, as described below. For the nanowire growth performed throughout this work, commercially prepared colloids of 20
were chosen. Other sizes, ranging from 10-150 nm were used in various experiments.

Functionalization consists of a simple, several-step procedure which can be performed in any wet chemical lab without any special equipment. A linker-molecule to anchor the citrate-coated gold nanoparticles must first be adsorbed to the surface of the substrate on which nanowire growth is desired.

3-aminopropyltriethoxysilane (APTES) is used as the linker of preference for oxide and single crystalline substrates. This molecule attaches readily to hydroxyl groups present on a surface through the formation of siloxane bonds. The ability of APTES to form organic monolayers on a substrate has been heavily studied utilizing a wide variety of solvents, concentrations, temperatures, and soak times.67-69 The basic mechanism of attachment of APTES to a surface is two-fold, as illustrated in Figure 2.3. The first step involves the hydrolysis and condensation of the silane molecules in solution, resulting in the release of ethanol. Subsequently, the polymerized silane groups can react at the hydrolyzed substrate surface. Due to the intermolecular attachment of the silane molecules, good films can form even on those substrate surfaces which possess extremely few adsorbed water groups, such as pre-treated single crystalline silicon and germanium substrates. It is rather unexpected that this chemistry should work so well, but it should be noted that the conditions under which the substrates are processed in this thesis are not UHV; indeed the substrates will begin to re-grow a native oxide even after HF treatment.
Figure 2.3: Youngblood et al described the polymerization of APTES when it is in contact with water. The mechanism of APTES connection to a substrate is shown.

Oxide substrates, once cleaned, are placed in a 0.1M solution of APTES (≥98% Sigma-Aldrich) in 2-propanol and allowed to soak for ten to fifteen minutes to give the siloxane linkages enough time to form. For single crystalline silicon or germanium, this soak time must be increased to six hours up to overnight. As the oxide has been removed from these samples as described above, there are very few sites available at which the siloxane bonds can form, and a monolayer of APTES takes a substantially longer time to deposit.
For metal substrates, a diamine linker-molecule is chosen. For the purposes of this work, 1,4-diaminobutane was used to functionalize all metal substrates. The clean substrate is placed in a 0.1M solution of 1,4-diaminobutane (99% Aldrich) for two hours. Such a procedure absolutely must be performed in a functioning chemical hood, as 1,4-diaminobutane (common name: putrescine) emits a strong odor consistent with decaying flesh.

When one of the prepared samples, as described above, is to be removed from its functionalization solution, it is rinsed thoroughly with 2-propanol and completely dried before being transferred to the beaker containing the gold colloidal solution. It is absolutely imperative that the samples, glassware, and tweezers are dry and free of any particulates before coming in contact with in the gold solution, as any contamination will cause rapid aggregation of the nanoparticles.

Colloidal solutions of gold are typically various shades of red, depending on the size of the nanoparticles, but will quickly change to a purple and then a pale blue if impurities are present. In this work, colloidal solutions were most often utilized as received, but on occasions when less dense nanoparticle coverage was desired they were diluted with ultrapure distilled, deionized water. The substrates should be soaked in the gold for ten minutes. Upon removal, a slight sheen on the surface may be visible, particularly on glass or ITO. Once dry, samples may be placed into the CVD reactor.

When heated, gold deposited through this colloidal method still can become mobile on the substrate surface, but as all initial particle sizes are within a known
distribution the resulting wires display a similar size distribution. In effect, it is possible
to much more tightly control the diameter of wires grown from colloidal gold than from
sputtered films.

The initial step in germanium nanowire growth involves a ramping of the furnace
temperature to reach optimal growth conditions. This heating of the substrate also
serves to remove any contamination which may remain from the organic chemicals used
to attach the gold particles themselves. As the boiling points of all reagents used are
below the growth processing temperature by several hundred degrees, they are
completely desorbed when the substrate is heated during the initial stages of the
growth procedure.

### 2.2.3 Cleaning Single Crystal Substrates with Hydrofluoric Acid

If epitaxial growth is desired on single crystalline silicon or germanium samples,
an extra wet-chemical process step is required pre-growth. After the gold nanoparticles
have been deposited, the samples should quickly be dipped in dilute 2% hydrofluoric
acid to remove any oxide which may have accumulated during the functionalization
steps. This assures a higher degree of epitaxy compared to samples grown with this
step omitted. The gold nanoparticles remain at the surface undisturbed. This technique
was first described by the Chidsey and McIntyre groups.46
2.3 Low Temperature Chemical Vapor Deposition Reactor

This section focuses on details of experimental interest rather than those of engineering or technical interest. For a full description, schematic diagrams, and the standard operating procedure of the germanium nanowire reactor, please refer to Appendix A.

2.3.1 General Process Conditions

Samples are placed in a quartz boat, specially made to fit the reactor, shown in detail in Appendix A. The samples are oriented face-up with the desired growth surface facing the flowing gas, and they are slowly inserted into the tube furnace with the help of a long glass rod. For flexible substrates, a stainless steel holder is used, as described above. The system is generally purged with nitrogen several times before it is evacuated to a base pressure of about 1 Torr, though this pressure can vary depending on ambient humidity conditions. The temperature is raised to the gold-germanium eutectic temperature of 360°C, at which point germane gas, GeH₄ (5% GeH₄ in He, Voltaix, Inc.) is flowed through the system at 20 sccm. The temperature of the system is commonly dropped to 295°C. Wire growth is found to nucleate best by holding the system at the bulk gold-germanium eutectic temperature 360 °C for several minutes.
After this initial period, the system can be cooled significantly and wire growth will still be observed.

Due to the small flow rate through the mass flow controller, the system pressure rises very slowly. Thus, the initial growth of wires occurs under a constantly increasing partial pressure. Standard growths in the work reported here are performed at a total system pressure of 120 Torr of the germane-helium mixture, which can take about ten minutes to reach. This initial variable pressure has not been shown to have any effect on the growth of the wires, as long as a high enough concentration of gas is built up within a reasonable amount of time. This 120 Torr total pressure corresponds to a partial pressure of 3.6 Torr pure germane gas. Five minutes of growth once the total system pressure reaches 120 Torr are sufficient to produce wires three to five microns in length. Length is dependent on growth time, so for very long wires, a longer time is required. It is, in fact, somewhat difficult to produce wires less than one micron in length using our reactor due to the slow response to pressure and temperature control.

The reactor can best be described as a hot-wall chemical vapor deposition reactor, so the entire system must be heated by the furnace. It is also very slow to cool. This design is in contrast to a cold-wall type chemical vapor deposition reactor, in which only the sample itself is ramped in temperature. The latter affords more control of time at a given temperature, but would have been more difficult for us to implement. Aside from difficulties in growing the shortest of wires, the hot-wall system performs extremely well.
Figure 2.4: General schematic of germanium nanowire growth. Germane (GeH$_4$) gas is flowed through a heated tube furnace at 20 sccm and varying temperatures. The system is vented to a burn box in order to deal with toxic waste gases.

This reactor is equipped with phosphine, PH$_3$, (300 ppm in He, Voltaix, inc.) gas utilized in the system for n-type doping of wires. The use of phosphine to dope germanium nanowires is well documented in the literature.$^{70-73}$ Phosphine exposure must be tightly regulated and not flowed in the system until the nanowire growth is well underway, lest it poison the initiation of the VLS mechanism and block all growth.

### 2.3.2 Tapered Wires

Lack of an appropriate two-regime temperature process will lead to growth of highly tapered wires. The desired growth mechanism of the elongation of the wires is the catalyzed VLS growth, as described in the first chapter. As higher growth
temperatures and pressures are sustained over a long period of time, a competing, purely CVD mechanism appears to initiate and begins to deposit germanium on all surfaces. As the VLS mechanism dominates axial growth throughout the process, pure CVD growth expands wires in a radial direction. As this process is dependent on time, older parts of the wires will accumulate more germanium coating than the newer wire which has formed closer to the catalyst particle. The result is a cone-like nanostructure. Evidence of purely CVD growth is also found on the inner surface of the quartz reactor furnace, which over time has built up a layer of bluish-grey germanium.

If undesired, this structure can usually be avoided by dropping the temperature of the reactor to 295°C within the first five minutes of gas flow. At this point, the VLS process has had sufficient time to initialize and can proceed with a decrease in temperature. Wires exhibiting tapered growth are shown in Figure 2.5, below. In the wire at the foremost of the image, the gold catalyst particle is clearly seen at the tip of the wire. Note that at this end, the diameter of the wire is equivalent to the diameter of the gold particle. As one moves down the wire towards the base, a thickening of nearly three-fold is observed. The extent of the expansion of the base thickness of the wire is a result of the amount of time the un-catalyzed growth is allowed to proceed, and the CVD growth rate at that temperature.
Figure 2.5: Tapering of wires as result of un-catalyzed, radial CVD Growth. Through the VLS mechanism, the initial wire diameter is that of the gold catalyst particle used to nucleate wire growth. The catalyst particle is seen remaining on the top of the wire. Un-catalyzed growth from CVD deposition at temperatures around 360°C serves to widen the wire at the base, which has had the most exposure time.

2.4 Post-Growth Processing

2.4.1 Oxide Removal

Unlike the case of silicon, the native oxide of germanium poses a significant stumbling block to the element’s widespread use in electronics. The native oxide that
forms on germanium in air is a mix of GeO, GeO$_2$, GeOH, and various intermediate oxides, with some species, such as GeO$_2$, being soluble in water. In general, this native oxide can become rough and pitted if heated, exposed to liquid water, or even after exposure to water vapor in ambient air.\textsuperscript{74-76} This leads to defects and a poor interface with the germanium itself. It is thus desirable to prevent this oxide from forming, or to be able to remove it when necessary.\textsuperscript{6}

Samples can be treated with dilute hydrofluoric acid to remove the oxide from the wires, though this is more applicable to chemically inert substrates as to not disturb the attachment of the wires or damage the substrate, as is done in traditional processing methods for oxide removal of planar germanium.\textsuperscript{44} Germanium oxides which have formed on the nanowires are readily removed if the sample is placed in a 2% HF solution for one minute with minimal damage to the nanowires or the polymer substrate.

Of course, upon removal from the acid solution to ambient air, the oxide will immediately begin to re-form. Thus, while removal is useful in some cases, it is far more advantageous to then be able to passivate the surface to resist subsequent oxide growth.
2.4.2 Passivation

Passivation of the germanium surface can be achieved through several methods. Passivation has the added advantage of permitting one to add functionality to the surface.

2.4.2.1 Wet Chemical Passivation

Wet chemical passivation holds the advantage of offering an extremely simple class of methods that can be performed in most chemical laboratories without the need for special equipment. It may not, however, be as robust as other methods. The purpose of this method, however, is generally not to permanently modify the surface but simply temporarily protect it while the sample is transferred through air. It is well documented that the germanium surface can be passivated to prevent oxide growth through exposure to alkanethiols, which form a self-assembled monolayer on the surface.\textsuperscript{6, 7, 77-79} Nanowire samples must be placed in a 0.1M solution of 1-octanethiol (≥97% Aldrich) for twenty-four hours immediately upon removal from the reactor in order to prevent any oxide growth. If it is desired that an older sample be passivated, the oxide should first be removed by the hydrofluoric acid method described above.
2.4.2.2 Atomic Layer Deposition

Atomic layer deposition (ALD) holds an advantage over wet chemical passivation in its ability to form reproducible layers across a series of samples with an extraordinarily high level of morphological control. Materials applied to the germanium nanowire surface through ALD may also impart some desired additional functionality. High-k oxides like aluminum oxide and hafnium dioxide not only prevent the growth of the unwanted germanium oxide, but provide a superior interface for many subsequent electronic applications.

Wires to be coated with $\text{Al}_2\text{O}_3$ were first prepared on glass substrates under standard growth conditions as described above. These substrates were placed in a home-built ALD chamber for deposition. $\text{Al}_2\text{O}_3$ deposition utilizes a trimethylaluminum ($\text{Al}_2(\text{CH}_3)_6$, TMA) precursor which is exposed to the surface alternately with water vapor. The duration of TMA and water pulses are 0.5 seconds, and the deposition temperature is 150 °C. For the specific deposition used for this work, the number of ALD cycles is 100. Thickness and chemical composition of $\text{Al}_2\text{O}_3$ deposition will be confirmed with transmission electron microscopy in the following chapter. Please refer to Appendix B for more specific ALD system details.
2.4.3 Removal of Wires from the Substrate

It is occasionally desirable to remove the nanowires from their substrate in order to perform further studies or incorporate them into a device. There are two methods of nanowire removal which have been used throughout this work: ultrasonication and, for lack of a better term, the smear method. Submerging a prepared nanowire sample in just enough alcohol or chloroform to cover it in the smallest available beaker and placing it into an ultrasonic bath for ten minutes will break off pieces of the wires and shake them into the solvent. The solution will become cloudy and grey once this process occurs.

For best results, ultrasonication should be performed on samples with longer wires, as there is no way to control where or how the wires will fracture. Longer initial wires afford a higher probability that longer wire fragments will wind up in the solution. A drop of the nanowire solution can subsequently be placed on any surface requiring wires or mixed with other chemicals.

While certainly advantageous in terms of ease and sufficient for some applications, the ultrasonication method has two distinct disadvantages. First, wires are broken and damaged during the process. Broken pieces of varying sizes are not always useful, and very often these fragments do not include the gold catalyst which, while advantageous for electronic applications is not desired if the gold-germanium interface is to be studied. Second, it is often difficult to remove wires in high concentrations.
The sample also must be thoroughly dried to drive off any solvent after the deposition, which increases the preparation time significantly.

Figure 2.6: Wires dispersed on a substrate after being removed by ultrasonication. Note the relatively low concentration and large distribution of lengths. Fewer than twenty nanowires are dispersed on an area roughly 600 square microns.

Rutherford backscattering spectroscopy (RBS) performed on a sample both prior to and after thirty minutes of ultrasonication reveals that, in fact, a very small percentage of wires are actually removed from the surface of the substrate through this
method. Analysis of peak areas shows that fewer than 30% of the wires are removed from the surface, as can be seen in Figure 2.7.

![RBS spectra](image)

Figure 2.7: RBS spectra measuring amount of germanium pre- and post- ultrasonication of the sample. Fewer than 30% of the nanowires are removed, as is evident from a comparison of peak areas.

In some cases, a direct transfer of wires is more useful, as it affords a higher concentration of material on the new surface. To perform such a transfer, the nanowire sample is simply pressed in contact with the sample to which the transfer is to occur and the two materials firmly rubbed together in a single direction. The result is a “smear” of nanowires across the surface of the new substrate. This method tends to leave a higher concentration of nanowires on the surface, and these wires are much more uniform in
length then wires deposited through ultrasonication. The majority of the transferred wires still possess their gold catalyst particle at the tip. This is particularly desirable for subsequent analysis, as the gold-germanium interface during growth determines the eventual wire structure. This was the most commonly used method for preparing TEM samples for the work shown in this dissertation. The flexible copper TEM grids when rubbed on the surface of a nanowire substrate, remove a large number of wires. A high concentration of nanowires is particularly important for TEM work so that time is not wasted finding a suitably oriented subject for observation.

Figure 2.8: Transfer of wires to a surface via the “smear method”. Wire lengths still vary. Almost all wires visible contain gold catalyst particle. Concentration is significantly denser when compared to ultrasonicated wires. Here, over 100 nanowires are visible in an area of 800 square microns.
Regardless of the method used to deposit the wires, once attached to their new substrate, they are fairly immobile. Van der Waals forces between the wire and the new substrate are sufficient to hold them in place through inversion, travel, and transfer. Wires observed in a particular location in a microscope on one system can easily be located in the same spot on another campus at a later date.

In summary, we present methods of nanowire growth and post-growth preparation optimized for our specific hot-wall chemical vapor deposition reactor. A specially designed holder was required for dealing with nanowire growth on flexible plastic substrates to prevent deformation of the plastic and also anchor the sample in the furnace. Two methods of nanowire removal from the substrate were investigated, and it is determined that the method of physical removal through pressing the sample in direct contact with another medium removed wires in greater quantities and with their gold colloids remaining on top, a desirable property for interface studies.

The following chapters will discuss the techniques presented in the experimental chapter in more detail, and provide results for various growths as well as the application of the wires from those growths.
Chapter 3- Growth Results and Characterization

This chapter presents results and conclusions of interest from a fundamental scientific standpoint regarding the growth of germanium nanowires and their subsequent characterization utilizing a variety of techniques including microscopy, Rutherford backscattering spectroscopy, X-ray photoelectron spectroscopy, and energy dispersive X-ray analysis. Results from all stages of the growth process, from the initial catalyst deposition to post-growth passivation are presented. Much of the work in this chapter will be published as a chapter in a book on nanowires to be published later this year (2011).  

3.1 Colloidal Gold versus Sputtered Gold Films

The starting gold catalyst is critical to the nanowire formation. As described in the methods section above, both sputter-coated gold films and wet chemical deposition of colloidal gold particles were utilized as sources of gold. For most applications in nanotechnology, it is uniformity in size and spatial distribution which is sought in these wires; variations in length and diameter lead to variations in electrical, physical, and chemical properties. The ideal growth will produce wires as similar in length and diameter as possible.
To obtain the most uniform range of diameters across a single sample during nanowire growth, colloidal catalysts are preferred over sputter-coated films. As the eventual nanowire diameter is determined by the prepared colloid diameter, wires can be grown over large areas with precise control over their size. We used predominantly 10nm and 20nm colloids in these studies. The colloids, as purchased, have a rough concentration of about $10^{11}$ nanoparticles/mL and will generally coat the substrates in a uniform manner when prepared as described above. Less dense areas can be prepared by diluting colloid solutions with distilled, deionized water, as previously described. An undiluted, ten minute soak in a colloidal gold solution leaves about 150 gold particles per square micron uniformly distributed on the sample’s surface. A typical sample with nanowires grown from undiluted gold colloids deposited on a glass surface is shown in Figure 3.1, below.

In Figure 3.1, the wires were grown from 20 nm colloids on a glass substrate under standard growth conditions as described in the experimental section. One will note the general consistency among wire diameters. Prior to heating, the colloids are certified by Ted Pella to be within 18 and 22 nm in diameter. It is observed, however, that wires often differ from this initial diameter range by 10-20 nanometers. There are two reasons for this discrepancy. First, as will be confirmed with transmission electron microscopy results to follow, once exposed to air wires typically grow a 5 nm coating of native oxide, GeOx, making them appear fatter in scanning electron micrographs.
Figure 3.1: Germanium nanowires grown on SiO$_2$ substrate. The nanowires are extremely uniform in diameter and length, with lengths around 2 microns and diameters of about 40 nm.

Secondly, there is the issue of aggregation of gold particles. Once heated, the gold becomes mobile on the substrate surface. Organic linker molecules used to hold the nanoparticles in place vaporize as soon as the temperature reaches 213°C, and the citrate coating used to prevent nanoparticle aggregation evaporates at 175°C. Heating of the substrate must continue, however, until the gold-germanium eutectic temperature of 360°C is reached. During this time, the nanoparticles are free to migrate and combine with other particles. The result is that some wires grown from 20nm colloid particles in general end up being closer to 40 nm in diameter, due to the combination of several original particles. There are, however, no such rules or generalizations which can be made for sputter-coated films.
Figure 3.2: Germanium nanowires grown on Kapton from 6.7 nm gold film. Note the non-uniform distribution of diameters present. Wires vary in diameters by over a factor of ten between the smallest wires and the largest wires. Lengths also vary. Wires were grown under standard conditions.

Figure 3.2, shown above, is a characteristic image consistent with nanowire growth from a sputter-deposited gold film. The wires differ drastically in diameter, with fatter wires reaching several hundred nanometers in diameter and thinner wires with much smaller diameters of 50 nm or less. As can be seen from a comparison of Figures 3.1 and 3.2, the nanowires grown from colloids are more uniform than those that were grown from the sputter-coated films to a significant degree.
The growth on sputter-deposited films results from the diffusion and nucleation of the gold on the substrate surface. A discrete island or particle of gold is required to begin nucleation of the germanium nanowire. It is well known that when heated, thin gold films become mobile resulting in the balling up of the metal on the surface. It is this mechanism which makes it possible to grow wires from an initially contiguous film over the surface of a substrate. There are, however specific limitations as to the deposited thickness of this film. Of the sputter-coated films, reasonable nanowire growth was observed for approximately 5-20 nm thick gold films. Note that these thicknesses were verified using Rutherford backscattering spectroscopy, as shown below, and represent an area-averaged amount of gold.

If insufficient gold is present, very poor growth is observed, resulting in few, if any, actual wires, as can be seen in Figure 3.3. For this thin coating, there is not enough gold to form the necessary nucleating islands. Wire-like masses are observed, but they exist in the plane of the surface and are not free standing, resembling more amorphous germanium masses capped with gold than any useful nanowire structure.

If too much gold is present, an equally significant problem is encountered. Eventually, with the increase of thickness, one approaches a film which acts more closely to a bulk layer of gold. Balling-up and mobility across the surface is hindered, and catalyst islands do not form, making it impossible for nanowire nucleation to begin. As can be seen in Figure 3.4, no growth is observed under these conditions.
Figure 3.3: Poor growth results from 2.8 nm gold film. “Wires” were grown under standard conditions. This gold film was too thin to sustain well-formed nanowire growth.

Figure 3.4: Poor growth results from 77 nm gold film. No nanowires are evident as the gold layer becomes thicker and approaches a bulk surface. This suppresses the ability of discrete islands of gold to form and catalyze nanowire growth.
Thicknesses of sputter-coated gold films were confirmed through Rutherford backscattering spectroscopy (RBS) as shown in the spectra in Figure 3.5, below.

Figure 3.5: RBS spectra confirming area-averaged gold thickness on Kapton.

A) 77 nm B) 2.8 nm
3.2 Length and Time

The length of nanowires on a given sample is dependant mainly on the length of time for which those wires were allowed to grow. Across a series of samples, longer wires will result from longer processing times. For a given sample, it is important to keep in mind that the time of growth for each individual wire among all of those contained on a particular sample can be slightly different from the others. Some variation in length among a particular sample is always evident, likely due to gas diffusion. As the samples often lay flat in the reactor or are partially obstructed by other samples or the contours of the quartz boat in which they are mounted, certain areas of a particular sample may see more gas over a course of a growth than others. Thus their effective growth time is actually slightly longer than other wires within the same sample.

Please note that it is somewhat difficult to analyze lengths of wires specifically through scanning electron microscopy, as it is not always evident the exact orientation of any particular wire and thus some apparent foreshortening or lengthening due to a wire pointing off at an angle may not be taken into account. In addition, even on a well-calibrated instrument, scale bars may vary by 5%. Best estimates are given throughout this work.

It is generally observed that the length uniformity is also much better in the case of colloidal growth compared to that of sputter-coated films. It is reasonable to
conclude that as these wires are nucleating from gold particles which are not uniform in size that they will begin growth at different moments in time and thus have different effective growth times. It takes longer for a larger particle of gold to supersaturate with germanium and begin to precipitate the nanowire than it does for a smaller particle. It is also extremely difficult to assign initiation times to any particular wire as, given the high mobility of gold on the surface, we cannot be certain at what point during the heating any particular gold particle is formed. Figure 3.6, below, shows wires grown from a sputter-coated gold film. The wires presented vary greatly in diameter, from about 40 nm to 400 nm. Wire lengths also vary significantly.

Figure 3.6: Nanowires grown under standard conditions from 10 nm sputter coated gold film. The uniformity of the wires varies greatly, with the thickest measured wire to be 407 nm in diameter. Thinner wires are on the order of 40 nm in diameter. Lengths also vary significantly.
Growths are generally not performed for longer than a total of fifteen minutes, during which the initial ten minutes pressure of germane gas is continually increasing to reach the desired partial pressure. This is followed by an additional five minutes of growth. Longer growths are certainly possible, but as the wires begin to become very long and tangled, it becomes difficult to distinguish them. From rough estimates of the length of the wires, it is inferred that at this pressure, the wire growth rate is about 250 nanometers per minute. This agrees with growth rates reported by Jagannathan et al.\textsuperscript{46} Wires longer than ten microns begin to curve and fall under their own weight, as shown in Figure 3.7.

Figure 3.7: Wires grown for a half hour are too long and tangled to distinguish from one another. Wires in this growth reach over ten microns in length. These wires bend under their own weight, obscuring any underlying patterning.
If one is particularly interested in observing wires in an ordered or epitaxial arrangement, wires with lengths no more than 1-2 microns are preferred. Also, it is easier to observe epitaxial arrangement if the gold nanoparticle catalyst solution is diluted before application to the substrate, resulting in sparser wire growth. Directed wire growth due to epitaxy is completely obscured if the wires grow too long in the manner shown above.

3.3 Pressure and Temperature

To investigate the effect of pressure, samples were prepared with identical growth conditions as described in the methods chapter, and are grown with only germane partial pressure allowed to vary. For the nanowires pictured in Figure 3.8, a two-temperature procedure was used, initiating at 380°C and dropping to 300 °C. These wires were grown on a silicon (100) substrate. The partial pressure of germane gas used was varied among the growths, ranging from 1.6 Torr to 6 Torr.

Two changes are evident through comparison of these growths: a wire growth rate increase and an increase in wire yield. Although the times of the growths were the same, at 6 Torr GeH₄, wires appear to average 4-5 microns in length, while at 1.6 Torr, they do not reach over two microns. The generally-accepted VLS mechanism assumes that liquid eutectic droplets are required for a high nanowire yield as described above.
Thus, this pressure dependence of length indicates that supersaturation of the gold catalyst and thus crystallization of the wire can happen more rapidly with increased germane partial pressure. This may be due to one of two factors: either the increased pressure allows for the reaction at the catalyst to proceed more rapidly, or the increased pressure facilitates gas diffusion to the catalyst site. A simple application of Henry’s law describes that at a given temperature, the concentration of a substance in a liquid is proportional to its partial pressure above that liquid. To a first level approximation, we can assume that there is more germanium present in the gold catalyst particle at higher partial pressures, and thus supersaturation and growth should proceed more rapidly.

Picraux’s research group from Arizona State University demonstrated that the growth rate of germanium nanowires scales linearly with the flux \( J_{\text{gas}} \) of precursor gas on the substrate surface, assuming that the temperature of the system is high enough so as to not be affected by surface reaction rate limitations. This group worked with digermane gas at pressures several orders of magnitude lower than those presented herein. It is straightforward to utilize the Hertz-Knudsen equation to calculate the molecular flux incident on the substrate surface:

\[
J_{\text{germane}} = \frac{P}{\sqrt{2\pi nkT}}
\]

*Equation 1: The Hertz Knudsen Equation*
where $J_{\text{germane}}$ is the flux in molecules/cm$^2$s, $P$ is pressure in Pascal, $m$ is the mass of the germane molecule in kilograms, $k$ is Boltzmann’s constant and $T$ is temperature in Kelvin. It should be noted that this approximation will not be perfect, as temperature and pressure often vary during growth, especially during the initial ramp-up period.

Extrapolating Picraux’s linear relationship to our higher pressure system, one would uncover the result that even at 1.6 Torr germane, the nanowires should grow at nearly 2 microns/minute. In reality, the observed rate of growth of our wires is nearly an order of magnitude lower than this. The conclusion is that while at lower pressures the limiting factor for nanowire growth rate is gas diffusion to the substrate surface, while at higher pressures the kinetics at the gold catalyst become more important. There exists some saturation point in the effectiveness of flux increase on growth rate. The wire can still only form as quickly as the precursor gas can be cracked and incorporated into the nanoparticle. Picraux expounds his explanation by attributing the observed growth rate to the Gibbs-Thompson effect, the importance of which was subsequently disproven by the Ross group of IBM as discussed in Chapter 1.42
Figure 3.8: Comparative images illustrating pressure dependence of germanium nanowires. Growths at A) 1.6 Torr GeH₄, B) 3.2 Torr GeH₄, and C) 6 Torr GeH₄.

In addition to the observed growth rate dependence on the germane pressure, we noted that the growth yield is dependent on the germane pressure as well. Referring to Figure 3.8A, one will note large sections of substrate devoid of nanowire growth. The fact that the substrate is so highly visible can be taken as a marker for poor, low yield growth. As all substrates were treated under the same conditions with colloidal gold as described previously, it can be assumed that each substrate started out with the same distribution of catalyst particles on its surface. Some of this perceived
increase in the 6 Torr sample (Figure 3.8C) in yield may stem from the fact that the wires are simply longer and more interwoven making it harder to see blank sections of the substrate. However, this cannot account for the great difference between the two growth conditions. For the growth at 1.6 Torr, a large fraction of the colloids did not nucleate or grow nanowires at all. This result is again likely due to the fact that large numbers of the catalyst particles did not reach a supersaturated condition before the end of the growth procedure due to the fact that there was not a high enough pressure to drive the surface controlled kinetics mechanism as described above. We thus seemingly observe a threshold effect for nanowire nucleation which requires further kinetics studies to be more clearly elucidated. As noted, a controversy over the specific mechanism occurring at the gold-germanium interface is present in the literature and requires further investigation.

At higher pressures, added presence of germane may also lead to increased non-catalyzed gas decomposition on the surface and thus lead to an increased conformal coating on the nanowire surfaces by conventional CVD growth. This would contribute to nanowire base broadening and tapering of the wires, which is generally undesirable as it detracts from their uniformity along the growth axis which could lead to varying properties as one moves along a wire. As a result, the germane pressure should be optimized within a certain window to control tapering while producing a good yield. Through systematic study, we found that a germane partial pressure in the range of 3 – 6 Torr (corresponding to a total system pressure between 120 and 200 Torr, respectively) produces the most consistent nanowires in terms of growth and yield.
3.4 Branched Wires

We were not able to achieve consistent, reproducible growth of branched-wire structures. Although a few images of branched structures have been reported by Lieber, they have not been obtained on a large, reproducible scale. Trials were attempted in which grown wires were subjected to a second wet-chemical processing step in attempts to attach gold colloids along the length of a wire. Post-growth microscopy of these samples simply revealed a lengthening of the original wire and no branches.

The micrograph in Figure 3.9 documents an atypical result achieved quite unexpectedly from a growth on Kapton beginning with a 5 nm sputter-coated film. Note the prominent wire in the center of the micrograph which has developed branches. These side growths are at consistent, perpendicular angles to the original wire, suggesting epitaxial growth dictated by the parent wire’s own crystalline structure. The secondary wires are smaller in diameter than their parent wire by approximately a factor of ten. These structures were a purely serendipitous find, however, and are likely present in a statistically small amount in all growths. As is evident from TEM results to follow, gold droplets are occasionally left behind on the body of the wire as it grows. It is these errant spots from which such unintentional wires must spring.
Figure 3.9: Micrograph revealing atypical growth of branched structure. Such structures were not reliably reproduced.

3.5 Growth on Metals

As described in the experimental chapter, metal substrates are easily functionalized with gold catalyst particles. In an effort to produce nanowires on a variety of interesting materials, wires were grown on both molybdenum and tungsten substrates.
Figure 3.10: Germanium nanowires grown on molybdenum under standard conditions. Wires are highly tapered, to an extent that CVD sidewall deposition is proceeding more rapidly than it usually does on non-molybdenum substrates. This suggests that perhaps the molybdenum substrate plays a part in altering the structure of the wire.

Germanium nanowires grown on molybdenum can be seen in Figure 3.10. These wires were revealed to be shorter and more conical than those typically found on other substrates. This sample was analyzed in the TEM with energy dispersive x-ray analysis, and no evidence of molybdenum incorporation into the wire was found. The difference in shape of these wires may result from some interaction with the gold catalyst on the
molybdenum surface, but more studies are needed before a concrete conclusion can be
given.

Figure 3.11: Germanium nanowires grown on tungsten under standard
conditions. Wires appear typical, with no evident growth affects from their
tungsten substrate.

Figure 3.11, above, shows germanium nanowires grown on a piece of tungsten
foil. These wires exhibit no unusual growth characteristics.
3.6 Epitaxial and Heteroepitaxial Growth

Figure 3.13 shows epitaxial growth of germanium nanowires on a germanium (111) substrate. They were grown in a dual temperature growth with an initial temperature of 400°C, followed by a lowering of the temperature to 295°C after two minutes. Wires were grown under a partial pressure of 0.8 Torr germane, and prepared from 20 nm gold colloids as described above. For epitaxial growth, an initial temperature higher than the gold-germanium eutectic temperature is utilized. This higher temperature helps to drive off any remaining water or surface impurities that may remain on the substrate and disrupt epitaxy. As wires grow predominately along the <111> crystal direction (with secondary growth along the <110> crystal direction), when grown on a (111) substrate a large proportion of wires grow normal to the surface.

Figure 3.12: Schematic of epitaxial nanowire growth on a (111) substrate.
Figure 3.13: Typical SEM images of epitaxially grown germanium nanowires on a germanium (111) substrate. A) Top view, B) side view. As the (111) axis is oriented perpendicular to the surface, many of the nanowires grow vertically.
Samples grown on a (100) substrate will not contain any wires normal to the surface, as can be seen from the schematic shown in Figure 3.14, above. Although it appears from the side view that one of the <111> oriented wires is normal to the surface, the reader is reminded that this is just perspective, and this wire is actually angled towards the reader, coming out of the page. Figure 3.15, below, shows top and side views of nanowires grown on a germanium (100) substrate. Again, regardless of the substrate crystallinity, the wires preferentially grow along the <111> axis, as outlined in Figure 3.14.
Figure 3.15: Typical SEM images of epitaxially grown germanium nanowires on germanium (100) substrate. a) Top view b) Side view. As the wires are still orienting along the (111) axis, none of them grow normal to the substrate.
Figure 3.16: Typical SEM images of germanium nanowires epitaxially grown on silicon (111) (A and B) and silicon (100) (C and D) substrates, showing top views (A and C) and side views (B and D).

We achieved hetero-epitaxial growth on single crystal silicon substrates prepared as stated in the methods chapter. This is possible due to the relatively low lattice mismatch between silicon and germanium (4.2%) and similar bonding properties between the two elements. These growths are illustrated in Figure 3.16, above. The nanowires shown in these images were grown in a two-temperature method beginning at 400°C and dropping to 295°C, and 0.8 Torr germane partial pressure.
Figure 3.17: X-ray crystallography data from germanium nanowires grown on silicon (100) substrate. XRD pattern from germanium nanowires epitaxially grown on a silicon (100) substrate, showing peaks from a large diffraction angle sweep (A), and peaks near silicon (220) Bragg peak (B), silicon (111) Bragg peak (C), and silicon (311) Bragg peak (D). Low background noise indicates good crystallinity.

In order to help confirm wire crystallinity, growth orientation and lattice constants, X-ray diffraction (XRD) was performed on epitaxially-grown germanium nanowires on silicon substrates. The XRD pattern from the nanowires grown on a silicon
(100) substrate is shown in Figure 3.17. Sharp germanium (111), (220), and (311) peaks are observed, in addition to a gold (111) peak and silicon substrate peaks. A high degree of crystallinity of the germanium nanowires is indicated by the low background of the spectra shown. The germanium peaks closely match those of cubic germanium, and they are best observed close to analogous silicon Bragg peaks. This latter observation indicates a similar or identical orientation of the germanium nanowires with respect to silicon, as expected from the visual confirmation of the epitaxial nature of the nanowires. A high degree of order for the germanium (111) planes is observed, which further confirms the <111> growth axis of most nanowires in addition to the epitaxial geometry of the nanowires. The germanium lattice constant is determined to be $5.66 \pm 0.01$ Å, within experimental error of the bulk germanium value (5.657 Å).

The germanium areal density and depth profile are measured by Rutherford Backscattering Spectrometry (RBS) using 2 MeV helium ions. An RBS spectrum is shown in Figure 3.18, along with the simulation performed with the SIMNRA modeling code. The nanowires tested by this method were grown following a 360°C and 300 °C two-temperature procedure under a germane partial pressure of 3.2 Torr. The area-averaged density of germanium and gold are determined to be $6.96 \times 10^{16}$ atoms/cm$^2$ and $5.6 \times 10^{13}$ atoms/cm$^2$, respectively. From these values, an average length of 21 μm for nanowires can be very roughly estimated if we assume every catalyst particle grows one nanowire and the nanowires are the same as the catalyst in diameter with no tapering. However, based on SEM characterization for these particular samples, the average length of nanowires is estimated to be approximately 13 μm, indicating a length
discrepancy. Also, as mentioned previously, when grown from 20 nm catalysts wires are more typically around 40 nm in diameter, as a result of gold agglomeration. Thus, the assumption for the very simple length calculation may not be particularly accurate.

Figure 3.18: RBS spectrum of germanium nanowires epitaxially grown on a silicon (100) substrate. The area-averaged density of germanium and gold are determined to be $6.96 \times 10^{16}$ atoms/cm$^2$ and $5.6 \times 10^{13}$ atoms/cm$^2$, respectively.
3.7 Growth on Flexible Substrates

There would be a large market for flexible electronic and photonic devices if functionality and performance could approach that of conventional solid state devices at a reasonable cost. Polymer films hold great promise as a cost-efficient substrate for potential applications, like those of photovoltaics or display technologies. This is in large part due to their ease of manufacturing, low cost, and extensive past development.

Other complex materials combinations are being explored, including integrating inorganic nanoparticles or small molecule organics with polymers. Two classes of methods for integrating semiconductor nanowires with flexible materials are: (i) transferring wires from a sacrificial growth substrate to a new material via contact printing or solution deposition, and (ii) direct integration via solution growth or very low temperature VSS growth. In the former method, nanowires must first be grown on some other substrate and then harvested. Direct growth saves time, reduces the risk of damage to the nanowires during harvesting, and also securely fastens the wires to the substrate. The wires grown in this study were anchored to the polymer with sufficient integrity to withstand extensive flexing of the substrate and were manufactured at standard VLS growth temperatures.

The relatively low decomposition temperatures of most polymers cannot survive the growth temperature used in most VLS processing. However, the growth
temperatures of germanium nanowires does allow for direct growth on thermally stable polymers. Polyimides, such as Kapton, are one class of polymers that offer promise. Specific polymer processing is described in detail above. The work described here presents the first germanium nanowires successfully grown directly on flexible substrates utilizing the standard processing temperatures needed to support VLS growth for the gold-germanium system.

Germanium nanowires grown on Kapton and fluorinated polyimide samples produce a high yield of nanowires with good mechanical and chemical robustness. Wires produced the specific growths shown in the following images are slightly tapered, due to un-catalyzed CVD deposition on the sides of the wire as growth proceeds.

The wires shown in Figure 3.19 were grown at 360°C for fifteen minutes from 10 nm gold colloid particles. Remaining catalysts can be observed at the tips of the wires. When observed with the naked eye, after growth the normally orange Kapton substrate is visibly covered with a continuous layer of a brownish substance, affording instant confirmation of the success of nanowire growth, as this is a typical observation of successful nanowire growth.
Figure 3.19: Side view scanning electron micrograph images of germanium nanowires on Kapton. Wires are about 4 microns in length, and are randomly oriented on the substrate. Good density is achieved.
Figure 3.20: Germanium nanowires grown on Kapton. Inset image shows wires from the height of the Kapton fold. Nanowires can remain well-attached to the substrate even after bending and flexing of the polymer.

Growth of nanowires on Kapton or other polymers did not noticeably differ from growth on any other amorphous substrate. To confirm mechanical robustness after growth, the nanowires on a polymer substrate was extensively bent and flexed. No detachment or damage to the wires was evident. Figure 3.20 is an SEM image of germanium nanowires on Kapton imaged while the Kapton substrate was held in a bent position.
Figure 3.21: Top view scanning electron micrograph image of germanium nanowires grown on poly[(4,4’-hexafluoroisopropylidene) diphthalic anhydride-alt-3,6-diaminoacridine hemisulfate]. Wire growth is dense and nicely uniform.

The wires shown in Figure 3.20, above, were grown on a fluorinated polyimide sample at 360°C for fifteen minutes from 10 nm gold colloid particles. Good density and uniformity in length and diameter is observed.
3.7.1 Atomic Force Microscopy Studies on Kapton

For germanium nanowire growth at 360°C as used in part of this work, the temperature is close to the glass transition temperature of Kapton. It was necessary to determine if this would have any effect on the gold catalyst particles deposited on the surface during the pre-treatment, particularly if the gold could become embedded within the polymer during the initial heating. In order to examine the location and morphology of the gold nanoparticle catalysts under growth conditions, atomic force microscopy (AFM) was employed. AFM images were obtained using a Digital Instruments MultiMode AFM with a Nanoscope IV controller operating in TappingMode. VISTAprobes non-contact mode silicon cantilevers with a spring constant of 0.40 N/m, resonant frequency of 300 kHz, and nominal tip radii of 10 nm were used.

Scans were performed on Kapton films treated with APTES and colloidal gold particles of 50 nm in diameter, as described in the methods section, and an untreated Kapton film as a control. Both samples were imaged before and after heating in N\textsubscript{2} at 360 °C for fifteen minutes to mimic the conditions present during nanowire growth. Figure 3.22, below, reveals that gold remains in colloidal form on the surface of the polymer and does not appear to migrate into the bulk of the polymer.
Upon heating, the colloids do appear to aggregate and form particles roughly twice their initial diameter. As can be seen from Figure 3.22A, the colloids appear to be roughly 100 nm in diameter post-heating. Aggregation of the colloids is expected due to the increasing mobility of gold on surfaces at higher temperatures. This, in turn, is
consistent with the typical observation of nanowires possessing diameters larger than the initial catalyst size.

3.8 Nanowire Oxide Treatment

3.8.1 Oxide Removal

As discussed in Chapters 1 and 2, the native oxide of germanium poses a significant problem which must be addressed in order to utilize germanium nanowires to their full potential in most electronic and photonic applications. The native oxide must be prevented from growing, or removed after it has developed. Under ambient conditions, germanium surfaces undergo rapid oxidation to GeO followed by conversion to the thermodynamically more stable GeO$_2$. Both oxides can be removed through traditional processing methods such as treatment with a dilute aqueous HF solution.

Our studies show that the germanium oxides are readily removed in a 2% HF solution for one minute with minimal damage to the nanowires (or a polymer substrate, if present). The chemical robustness of the polymer substrate is key if the eventual goal for such a system is printable electronics on a polymer. Flexible polymer sheets and any deposited components must be able to withstand wet chemical processing to be of use. As can be seen in Figure 3.23 below, nanowires exposed to the HF treatment described above retain their structure and attachment to the Kapton surface.
Figure 3.23: Nanowires grown on a Kapton substrate dip retain their integrity after an HF dip.

3.8.2 Passivation

There are several kinds of passivation methods for germanium surfaces that can be envisioned to help block native oxide formation. One method to passivate germanium involves capping the surface with organic thiols. A general schematic of the self-assembled monolayer adsorbed on the germanium surface using this method is shown in Figure 3.24.
Figure 3.24: Simple schematic outlining a self-assembled monolayer of alkanethiols adsorbed on the germanium surface.

Germanium nanowire samples grown on polymers were placed in a 0.1M solution of 1-octanethiol for twenty-four hours immediately upon removal from the reactor. To confirm the level of oxide on the surface, X-ray photoelectron spectroscopy (XPS) was used. For the following spectra, data were collected using Al Kα anode source with a cylindrical mirror analyzer. The full-width half-max (FWHM) of the carbon 1s peak (2.4 eV) was used as the FWHM for the deconvolution of the germanium 2p peaks. The carbon 1s is a single Gaussian and represents the energy resolution of the instrument at the pass energy utilized. When the germanium 2p ½ peak is deconvoluted into three individual peaks, the peak with the lowest binding energy was assigned to that of bulk germanium. All spectra were shifted to ensure that this peak was centered at 1217.0 eV.
Figure 3.25: XPS spectra of Ge 2p3/2 and 2p1/2 for non-passivated (a) and passivated (b) germanium nanowires. The oxide shoulder is not apparent for the thiol-passivated sample.
A comparison of the passivated sample with the non-passivated sample reveals a substantial decrease in the surface oxidation for samples that had been passivated with thiols. Non-passivated samples possess a substantial oxide layer consisting primarily of GeO$_2$, with a smaller contribution from GeO, as can be seen in Figure 3.25A. The passivated species also exhibits a small higher binding energy shoulder consisting of a single peak attributed primarily to GeO, as can be seen in figure 3.25B. However, the contribution relative to the bulk germanium peak is greatly reduced from that of the non-passivated sample. The presence of GeO suggests that even the brief exposure of the sample to atmosphere while transferring from the growth chamber to the thiol solution is enough to partially oxidize the germanium. However, as previously mentioned the stability of the polymer substrate is sufficient for a dilute HF wash to remove this oxide coating prior to passivation, thus greatly reducing the presence of oxide.

Passivation between processing steps and passivation/packaging at the end of processing are key in realizing device applications. The growth, processing and passivation methods detailed in this work are all found to lead to a flexible and well-integrated nanowire-polymer hybrid film, of potential importance for a range of flexible applications such as batteries, solar cells, sensors and transistors.
3.8.2.1 Stability of Organic Layers over Time

It is necessary for the passivating layer to be stable over time if it is to be of any real use. XPS was used to monitor the oxide growth of wires which are treated with 1-octanethiol immediately after being removed from the reactor. The same sample is then revisited 24 hours later. The spectra are shown in Figure 3.26A, below. As compared with a non-passivated sample, the passivated sample exhibits nominal oxide growth. After 24 hours, an oxide shoulder is evident, but does not reach the level of the non-passivated sample.

Oxide growth can also be monitored by observing the photoluminescence of the sample over time. In Figure 3.26B, below, the photoluminescence signal at a wavelength of 500 nm is monitored over time for both non-passivated and octanethiol passivated samples. Under ambient conditions, the signal due to the oxide sharply increases until about 200 minutes of exposure, indicating that the oxide grows in spite of the passivating layer. However, the signal eventually levels off to a value less than that of a non-passivated sample, indicating that the passivating layer manages to permanently prevent at least a portion of the oxide growth.
Figure 3.26 A) XPS data showing a comparison of thiol-passivated germanium nanowires and nonpassivated germanium nanowires B) Photoluminescence (PL) spectra of passivated wires as compared to non-passivated wires. Both spectra indicate that thiol passivation is only stable in air for a period of a few hours before it begins to degrade and oxide re-forms.

The octanethiols form a self-assembled monolayer on the surface of the wire to which they attach. While these layers, in theory, are adsorbed in a defect-free coating, in reality they are not always perfectly attached. In time, oxide can still form on the areas of the wire which are exposed due to pinholes in the octanethiol coating or displacement reactions. Thus, this wet chemical passivation technique offers a short-term technically simple solution to germanium native oxide. For a more robust, long-term solution to the oxide issue, another method is needed.
3.8.2.2 Atomic Layer Deposition

A more stable passivating layer must be deposited through some method other than a wet chemical procedure. For conformal coatings on nanostructures, atomic layer deposition presents us with an attractive solution. ALD offers an extremely reproducible method of depositing material with high level of control on the order of a single monolayer up to 10-20nm in thickness. Using ALD, we are able to not only introduce a layer to retard the unwanted growth of germanium oxides, but actually deposit a material with some appropriate functionality. To this end, high-k oxides are deposited on germanium nanowires mainly because of their use in highly scaled CMOS.

Hafnium dioxide (HfO$_2$) and Al$_2$O$_3$ were deposited on germanium nanowires and found to not significantly alter their structure. The deposition of HfO$_2$ was monitored with RBS, as outlined in Figure 3.27, below.

In one set of experiments, nanowires were exposed to ten cycles of HfO$_2$ deposition, which was measured to be approximately 12.6 Å in thickness. Through RBS, the germanium areal density on the silicon substrate was found to be 21.6x10$^{15}$ atoms/cm$^2$, which relates to a coverage of approximately 3.6% of the substrate surface. The RBS spectrum is shown in Figure 3.26. As can be seen from the micrographs in
Figure 3.27, this particular growth was very sparse, and the images are very similar both before and after the deposition owing to the excellent conformality of ALD growth.

Figure 3.27: RBS spectra of germanium nanowires grown on silicon coated with HfO₂. The germanium areal density on the silicon substrate was found to be $2.16 \times 10^{15}$ atoms/cm², which relates to a coverage of approximately 3.6% of the substrate surface.
Figure 3.27: a): before and b): after 10 cycles of atomic layer deposition of HfO$_2$ on germanium nanowires grown on silicon (100) substrate. No significant difference in morphology is observed.
ALD of aluminum oxide (Al$_2$O$_3$) on germanium nanowires was also achieved, and will be discussed more fully in the next section involving transmission electron microscopy and energy dispersive X-ray analysis results.

### 3.9 Transmission Electron Microscopy

Transmission electron microscopy is perhaps one of the most elegant tools at the disposal of the researchers in the world of nanoscience, and is indispensable in elucidating the true atomic scale structure of these wires. Bright-field images are taken using a JEOL 2010F field-emission TEM/STEM system at 200kV accelerating voltage.

#### 3.9.1 Uncoated Germanium Nanowires

In the bright-field image shown in Figure 3.29, the lattice planes of the single-crystalline nanowire are clearly visible, as is the approximately 5 nm coating of oxide which has developed on the germanium surface while being transferred through air from the reactor to the instrument. Figure 3.30 shows a close-up image detailing the high level of crystallinity of the wire.
Figure 3.29: Bright field image of germanium nanowire. Lattice fringes indicate excellent crystallinity. Approximately 5nm of amorphous oxide can be seen on the sides of the wire.

Bright-field TEM confirms the excellent crystallinity within each wire through imaging of the lattice fringes. The light gray, amorphous oxide surrounding the wire is not uniform, but appears to be between 5-8 nm in thickness. Note that the oxide on the top edge of the wire, where it was broken, is substantially thinner than the oxide on the sides of the wire. It had less time to grow in this region.
Figure 3.30: Bright field TEM image of a portion of a germanium nanowire, detailing its high level of wire crystallinity.

It is important to note that prior to insertion into the TEM, wires should be baked in a low temperature oven at about 150 °C for two hours to drive off any contaminants which may react with the electron beam. The oven used for this research was at ambient atmosphere.

As can be seen in the TEM image in Figure 3.31, the gold catalyst which remains at the top of the wire is often no longer spherical in shape, but becomes faceted when the gold cools and phase segregates from the germanium. Such faceting can also be observed in an analogous SEM image, shown in Figure 3.32. Also, there is evidence that tiny gold droplets, less than 2nm in diameter, have separated themselves from the main catalyst and remain on the side of the wire. It is this dislodged gold which may be
responsible for rare branched growth noted previously, or for the radial CVD growth observed under some processing conditions. Lattice fringes in the large gold particle are evident, and it is interesting to notice that the interface between the gold and the germanium wire is not sharp.

![TEM of germanium nanowire](image)

**Figure 3.31**: TEM of germanium nanowire, highlighting the gold catalyst and the gold-germanium interface. Lattice fringes are evident in the gold, and smaller gold particles can be seen beneath the catalyst on the right of the image.

The Chidsey group reported that one of the reasons it is possible to sustain germanium nanowire growth below the gold-germanium eutectic temperature is that there exists a kinetic barrier to the final recrystallization of a liquid gold particle to a solid.\(^{41}\) Also, the germanium nanowire is precipitating at step sites on the liquid-solid
interface. It is evidence of these steps which is observed by the varied interface in Figure 3.32. As gold-germanium phase segregation occurs when the wire is cooled at the end of the growth process, it is reasonable to interpret this rough interface as a result of such segregation.

Figure 3.32: SEM image of a relatively large catalyst particle (approximately 250 nm) atop a germanium nanowire. This image is complementary to Figure 3.30.

The wire in the micrograph shown in Figure 3.33, below, is coated with contamination, likely due to oil from a diffusion pump, as no bake was performed on this sample prior to investigation. The highlighted square represents the area from which EDX spectra was acquired.
Figure 3.33: Bright field image showing gold catalyst particle, highlighting region (square) from which the EDX spectrum in Figure 3.33 was taken.

To confirm the presence of the elements believed to be contained within the nanowire structure, energy dispersive x-ray analysis (EDX) was performed on this wire as a representative sample. The results presented below confirm that the dark tetrahedron is indeed the gold catalyst, and that it is not completely phase-segregated but still contains a significant portion of germanium. A prevalent copper peak is expected in all results due to the TEM grid. Silicon and oxygen are typical contaminants.
Figure 3.34: EDX analysis of gold catalyst at the top of a germanium nanowire, as highlighted in Figure 3.33. Relative areas between the germanium and gold peaks indicate that a significant amount of germanium is still present in the solidified catalyst particle.

In the spectrum shown above in Figure 3.34, the electron beam was focused over the gold catalyst particle, as outlined by the dashed square in Figure 3.33. Gold and germanium are predominant peaks in the spectrum. It is expected that there is residual germanium remaining in the gold particle due to its solubility over the course of
the growth. The after a nanowire growth has been completed, the system is cooled fairly rapidly. It is likely that the gold recrystallizes before all of its composite germanium has precipitated out. This model also helps to account for the variations in the interface between the gold and the germanium, as seen in Figure 3.31.

In Figure 3.35, below, the electron beam has been moved from the catalyst and focused over only the bulk of the wire. This confirms that very little, if any, gold is present in the wire body within the sensitivity of the EDX detector, a limit of about a 1% concentration. Previous research has determined the solubility of gold in germanium to be about $10^{15}$ atoms/cm$^2$. For more detailed analysis, a technique such as secondary ion mass spectrometry (SIMS) or pulsed-laser atom probe tomography (PLEAT). This latter technique has recently been successfully utilized to determine the solubility of magnesium in germanium nanowires. As noted above, gold droplets may be present on the wire in localized areas, but in general, the bulk of the nanowire is largely free from gold contaminants. As discussed elsewhere in this dissertation, this is of primary importance if the nanowires are to be used in any application compatible with CMOS processing.
Figure 3.35: EDX analysis of the same germanium wire, with the electron beam moved away from the catalyst particle. Gold is not prevalent in the bulk of the wire in concentrations within the detection limits of the EDX detector.

3.9.2 ALD Coated Wires

As mentioned previously, several schemes for the passivation and functionalization of nanowires are investigated in this work. Atomic layer deposition is a
new, yet reliable method to deposit highly controllable, conformal growth of ultra-thin films on surfaces, and is applied in this case to germanium nanowires.

Figure 3.36: Germanium nanowire coated with approximately 9 nm of aluminum oxide which was grown utilizing atomic layer deposition. Note the excellent uniformity along the length of the wire. TEM confirms the expected layer thickness of 9nm.
Wires were coated with approximately 9 nm of Al\textsubscript{2}O\textsubscript{3}, as determined by the number of cycles to which the sample was exposed during the ALD growth process. The thickness of ALD deposition was confirmed with transmission electron microscopy, shown in Figure 3.36. The germanium nanowire pictured is approximately 40 nm in diameter, as evidenced by the dark grey cylinder. The light grey coating measuring approximately 9 nm is the aluminum oxide. Note the exceptional uniformity of the coating along the length of the wire. The TEM-measured thickness corresponds precisely with the expected thickness based on the number of ALD cycles performed.

TEM images were also taken of wires coated with 100 cycles of hafnium dioxide, revealing a semicrystalline structure on the germanium nanowire surface.

Figure 3.37: TEM image highlighting the HfO\textsubscript{2}-germanium interface. Crystalline domains of the oxide layer are clearly evident by the presence of the lattice fringes.
3.9.3 Energy Dispersive X-ray Analysis Results of ALD Coated Wires

The Al$_2$O$_3$ coating on the wires is clearly confirmed through EDX. The spectrum shown in Figure 3.38 was taken from a spot (towards the center of the wire) containing both the wire itself and the coating.

![EDX spectrum](image)

Figure 3.38: EDX results from a germanium nanowire coated with aluminum oxide, confirming the composition of the layers evident in the TEM image shown in 3.39.

Germanium and aluminum peaks are clearly visible, as well as a substantial oxygen peak. This oxygen is likely primarily due to the deposited oxide layer, but as the nanowires used to create this sample were exposed to air before the atomic
layer deposition, there is probably also some remaining germanium oxide on the wire surface, at the interface between the germanium and the aluminum oxide. However, utilizing EDX it is not possible to differentiate the oxygen signal from the germanium oxides and the oxygen signal from the deposited oxide. Again, the substantial copper peak stems from the TEM grid on which the sample is prepared. This is a representative spectrum, and no corresponding micrograph was taken for this wire.

A spectrum was also taken from a spot focused to be only on the Al$_2$O$_3$ deposition layer itself, a position shown by the spot labeled “e” in Figure 3.39, below. In performing this task, it was critical to work as quickly as possible. When the electron beam is focused and held over the oxide coating, it degrades very rapidly and the sample becomes contaminated from an unknown silicon source, possibly pump oil. Within thirty seconds of exposure to the electron beam during EDX acquisition, a hole is burned completely through the oxide layer, and a large curve of deposited contaminant becomes visible. The EDX spectrum is shown in Figure 3.40. Figure 3.41 shows the aftermath of the electron beam exposure.
Figure 3.39: Aluminum oxide coated nanowire prior to EDX acquisition. Spot ‘e’ signifies site of electron beam for analysis. The nanowire is the darker area in the center, measuring about 20 nm in diameter. The ALD coating is, again, uniform with a depth of 9 nm.
Figure 3.40: EDX spectrum of Al$_2$O$_3$ coating. The point on the wire from which this spectrum was taken is shown as point “e” in Figure 3.39. The large silicon peak is due to contamination from diffusion pump oil. There is no germanium present in the aluminum oxide layer (within the detection limit of the EDX).

No germanium peak is observed in the spectrum above, suggesting a sharp interface between the aluminum oxide coating and the germanium nanowire.
In summary, results were presented for germanium nanowires grown on a variety of materials. If a single crystalline substrate lattice matched to germanium is properly cleaned prior to growth, nanowires will grow epitaxially, aligning themselves to the <111> crystal direction. Our epitaxial work is in agreement with prior results published by other groups.

We found that at the partial pressures of germane utilized throughout this study, a simple diffusion-limited kinetics model is insufficient to describe the complexities of nanowire growth kinetics. Building on the work of the Picraux group, we extended their
model dependent only on gas flux to our own observed growths. Such a model predicts an abnormally high growth rate of almost 8 microns/minute, while the actual observed nanowire growth rate is 250nm/minute. Thus it is concluded that the nucleation of the nanowires at higher partial pressures is dependent on surface-limited kinetics.

Two methods of gold catalyst preparation are prepared. Substrates prepared from commercially available colloidal gold through a simple wet-chemical procedure offer better control over the uniformity of the size and length of wires as compared to sputter coated films.

This work presents the first growth of germanium nanowires on a flexible, organic substrate. The high glass transition temperature of polyimide plastics such as Kapton make it possible for such materials to withstand the relatively low processing temperatures needed to produce germanium nanowires. AFM studies confirm that gold catalyst particles do not migrate into the surface of the polymer during the heating phase of growth.

Passivation methods were explored, both wet chemical and robust atomic layer deposited films. Oxide growth was monitored utilizing XPS, and it was found that thiol passivation on germanium nanowires only prevents oxide growth temporarily, in accordance with earlier studies. We present analysis of highly uniform, conformal ALD growth of aluminum and hafnium oxides on germanium nanowires.

This concludes the growth and analysis portion of this dissertation. Applications of the wires shown thus far will be explored in the remaining pages.
Chapter 4- Devices

This chapter focuses largely on the more practical applications of germanium nanowires and their incorporations into relevant technologies. A germanium nanowire-based hybrid organic-inorganic solar cell will be discussed in depth. Some of this work was published, and is reprinted with permission from Du Pasquier, et al. “Photoinduced charge transfer between poly(3-hexylthiophene) and germanium nanowires” Applied Physics Letters, 91, Copyright 2007, American Institute of Physics. Later in this chapter, electrical measurements taken from simple electrical devices are explored to provide more insight into the electrical properties of germanium nanowires and to help pinpoint to which technologies these nanowires may be applied in the future.

4.1 Solar Cell

The magnitude of the issue of energy in today’s world cannot be understated. Renewable energy sources such as photovoltaics are heralded as the energy sources of the future, yet still face large hurdles which must be overcome before research devices will be practical for large scale implementation. The trade-off in solar cell design is one of efficiency versus cost; solid-state multi-junction solar cells now reach almost 45% efficiency, but are prohibitively expensive for mass production due to complex
processing and incorporation of rare materials. If such devices are used in concentrated solar structures, the cost does drop, but not to a level competitive with current rates of mass-produced electricity. On the other hand, relatively low efficiency organic photovoltaics offer the promise of delivering easy to produce, large scale and increasingly inexpensive devices. It is not necessary, however, for such devices will to match their multi-junction counterparts in efficiency. If the efficiency of organic based solar cells could be improved a relatively small amount, up to about 15%, and their materials and manufacturing costs kept low, their ease of processing would swing the balance in their favor.

Within the category of organic solar cells fall several sub-categories, including that of semiconducting polymer-based solar cells. Of known semiconductor polymers, the most investigated is poly (3-hexylthiophene) (P3HT). The combination of P3HT and 1-(3-methoxycarbonyl) propyl-1phenyl-(6,6)-C61 (PCBM), a functionalized fullerene in a bulk heterojunction configuration affords a power conversion efficiency of approximately 8%.\textsuperscript{93} The organic bulk heterojunction of P3HT:PCBM facilitates the separation and diffusion of charge carriers to their respective electrodes. A photon is absorbed by the P3HT creating an exciton that diffuses to the interface between the two bulk components and dissociates. PCBM with a higher electron affinity is the electron acceptor while the hole remains within the P3HT.

An alternative to PCBM and other fullerene derivatives in an all-organic structure is to use inorganic semiconducting nanowires. Zinc oxide, cadmium selenide, silicon, and titanium dioxide nanowires have been utilized with an active polymer layer of hybrid
organic-inorganic photovoltaic devices. Other more complex nanowire structures have also been proposed based on first principles calculations.\textsuperscript{94-99} When incorporated into the active layer in such a way, one of the key benefits of nanowires over fullerenes is their one-dimensional nature which could provide a rapid transport path for charge carriers.

In one study we used germanium nanowires in combination with the P3HT to produce a hybrid organic/inorganic solar cell. PCBM was not used in this design. A simple schematic diagram of our solar cell structure and a possible energy level diagram are shown in Figure 4.1.

Figure 4.1: (a) Simplified device structure and (b) possible energy band diagram for P3HT-GeNW bulk heterojunction solar cell.
To prepare the cell, germanium nanowires were synthesized under standard growth conditions as described previously, and then detached from their substrate via an ultrasonication method into a solution of chloroform. The resulting mixture was combined with 0.5 mL of a P3HT solution (10 mg/mL in chloroform) by 50 μL increments. The solutions were spin coated (50 μl at 1500 rpm) on prepared indium tin oxide (ITO) on glass (Delta Technologies, 15 Ω sq−1) pre-coated with about 50 nm of poly (3,4-ethylenedioxythiophene) poly-(styrenesulfonate) (PEDOT-PSS). Two samples were prepared with varying nanowire concentrations. Samples P3HT-GeNW 1 and 2 contain 50 and 200 μL of germanium nanowire solution, respectively.

Absorption spectra were taken but are not presented here. These spectra in the 250–950 nm range had a maximum at 520 nm, which can be attributed to P3HT. In our P3HT-GeNW composites, no absorption related to the nanowires was observed, due to the low bandgap of germanium and its low relative concentration in the composite. The only visible change in the spectra was a slight red shift of the P3HT absorption shoulder. This is usually attributed to π–π stacking in closely-packed, crystalline P3HT domains. Thus, one interpretation of the change in absorption is that mixing with germanium nanowires induces enhanced crystallinity in the P3HT. Photoluminescence of the samples was measured at room temperature with monochromatic 500 nm excitation and an Ocean Optics S2000 diode array detector.

Although germanium displays photoluminescence at low temperature, it is strongly attenuated at room temperature. Thus, the photoluminescence observed in our room temperature studies is most likely due to P3HT, in agreement with other
A significant quenching of the photoluminescent yield is observed in samples containing nanowires, as can be seen in Figure 4.2A. It is observed that the quenching increased when the P3HT-GeNW solution was ultrasonicated prior to spin coating. Ultrasonication of the solution has the effect of dispersing the nanowires more within the P3HT. The dispersion may, in part, be improved by breaking of the nanowires due to a prolonged period in the ultrasonic bath, resulting in more, shorter wires.

Figure 4.2: Room temperature (a) photoluminescence from 500 nm excitation and (b) external quantum efficiency of photon-to-electron conversion of pure P3HT and P3HT-GeNW films spin coated on ITO. Presence of the germanium nanowires increases the EQE with respect to neat P3HT. Photoluminescence is also attenuated, implying a decrease in undesired exciton recombination.
The photoluminescence quenching indicates that excitons generated in the P3HT upon illumination at 500 nm do not recombine radiatively in the presence of the nanowires. Instead, a fraction of the excitons dissociate at the P3HT-GeNW interface, enhancing the fraction of free electrons and holes capable of generating a photocurrent.

Figure 4.3: Photoluminescence spectra detailing emission from P3HT with mixed with varying levels of germanium nanowire solution. Peak shoulders attributed to interchain emission from the P3HT vary with nanowire concentration, indicating that the germanium nanowires affect how the P3HT solidifies.

The preceding photoluminescence spectra, shown in Figure 4.3, provide a more detailed picture than those shown in Figure 4.2. Here, several varying concentrations of germanium nanowire solution, ranging from 50 microliters to 200 microliters, were
incorporated into the P3HT in an attempt to gain a more quantitative understanding of the role of the nanowires in the device. Variations in the peak shoulders due to interchain emission from the P3HT are clearly evident, more strongly indicating that the nanowires serve to affect the arrangement of the polymer as it solidifies.

Figure 4.4: Photoluminescence is monitored with respect to germanium nanowire concentration. As compared to pristine P3HT, even a small concentration of germanium (400 ppb) greatly attenuates the photoluminescence signal as unwanted exciton recombination is prevented.

In a further attempt to quantify the amount attenuation of exciton recombination promoted by the inclusion of germanium nanowires in the P3HT, photoluminescence was monitored with respect to the concentration of nanowires utilized in various
devices. The concentration of germanium in the P3HT is exceedingly small ranging from 200-400 ppb. A significant drop in photoluminescence signal is seen with the incorporation of even this tiny amount of nanowires, as compared to pristine P3HT. These results are shown in Figure 4.4.

Next, the external quantum efficiency (EQE) of photocurrent generation was measured in the 300–800 nm range with a monochromator and chopper, and detected via a lock-in amplifier. These results are presented in Figure 4.2B, above. Electrical contacts were made to the top of the P3HT-nanowire films with a gallium-indium eutectic. This eutectic is liquid at room temperature and has a work function of 4.2 eV. Assuming the band diagram shown in Figure 4.1 is reasonable, the gallium-indium system is well suited for extracting electrons from germanium nanowires, although the charge may also drop directly from the germanium conduction band into the electrode. The device area was constant, and imposed by the size of the illumination spot, which was 1 mm.

An EQE of 1.4% was measured in pristine P3HT, while 2.2% and 4% were measured at 550 nm in samples P3HT-GeNW 1 and 2, respectively. This is consistent with the light quenching data, indicating that percolation pathways for holes and electrons to the electrodes are created within the bulk heterojunction.

These efficiencies, when placed in context of current organic solar cell technologies are not particularly impressive. However, it is important to recall that the devices reported upon above are extremely simple and non-optimized. Future studies improving upon the design of the nanowire photovoltaic device could lead to vastly
improved results. Although these numbers are not good from an absolute perspective, they do show that there are some promises for improvement in device properties when germanium nanowires are incorporated into the P3HT active layer. These data are consistent with a model in which the electron transport is enhanced by the presence of the nanowires, without significant trapping of the holes in the germanium or interface.

Finally, $I-V$ curves were recorded under illumination of by halogen light source of intensity equivalent to 100 mW/cm$^2$ of AM 1.5G simulated sunlight. In the devices which included nanowires, the forward current was significantly increased, but the devices still had a good diode characteristic in the dark, with little reverse current down to $-1$ V. This is consistent with the observation that as-prepared the germanium nanowires are intrinsically $p$-type semiconductors and enhance the overall conductivity of the system. A reduction in open-circuit voltage and an increase in short-circuit photocurrent are observed when the nanowires are mixed with P3HT, as can be seen in Figure 4.5, below.
Figure 4.5: $I$-$V$ curves in the dark (dashed line) and under 100 mW/cm$^2$ (solid line) halogen light for pure P3HT and P3HT+GeNW 1 device. In the inset is shown a semilog $I$-$V$ plot under illumination for P3HT, P3HT-GeNW 1, and P3HT-GeNW 2. The reduced VOC observed in the hybrid device is believed to result from the presence of native oxides, also evidenced by the hysteresis in the $I$-$V$ curve.

For this set of experiments, the germanium nanowires were not passivated or exposed to any type of pre-treatment to remove the native oxide. Therefore, the wires used were coated with GeO$_x$ as has been described elsewhere in this dissertation. Wang et al. have shown by x-ray photoemission spectroscopy that such an oxide layer results in band bending of the germanium. This results in an increased work function in $p$-type germanium nanowires, which would logically lead to a reduction of open-circuit
voltage when the wires are included in a photovoltaic device. The open-circuit voltage in bulk heterojunction solar cells can be approximated as highest occupied molecular orbital (HOMO)$_o$-lowest unoccupied molecular orbital (LUMO)$_o$−2(0.2) V to account for losses at electrodes. If we take the HOMO level of P3HT as 5.1 eV and the $E_c$ of the germanium nanowires as 3.8 eV, then the theoretical open circuit voltage should be 5.1−3.8−0.4=0.9 V.

Another sign of the presence of GeO$_2$ is the hysteresis. This indicates charging and discharging of defects in the dielectric. Similar hysteresis has been observed in field effect transistors built with germanium nanowires and was attributed to water adsorption at the surface of oxidized germanium. The hysteresis could be suppressed with passivation of the nanowires by reaction with various species, including thiols. Future work on optimized devices should include further investigations on the effects of utilizing passivated wires within a bulk heterojunction photovoltaic device.

4.2 Electrical Testing

Better understanding and control the electrical properties of the nanowires grown for the purpose of this research will lead to improvements in the devices in which they are eventually incorporated. As noted in section 4.1, the photovoltaic cell designed from the nanowires was an extremely simple, proof-of-concept device. Tunable
electronic properties would give us greater control in optimizing the performance of solar cells produced in the future.

We tried several methods to measure the electrical properties of doped and undoped nanowires through the preparation of extremely simple devices. No top contacts were utilized for these initial measurements; solutions of ultrasonicated wires were simply placed dropwise onto prepared titanium pads.

Figure 4.6: SEM image of a simple, single nanowire electrical device. The nanowire is resting on two titanium contact pads. This device corresponds with the electrical measurements shown in Figures 4.7-4.9.

These pads were investigated via scanning electron microscopy to find where, by chance, a wire happened to span two pads and was suitable for testing. Due to significant oxidation of the wire and the fact that this method does not produce a good ohmic electrical contact between the wire and the prepared pad substrate, the system was annealed. An initial anneal of 350°C was performed, and when this was found to be
insufficient, a second anneal to 400 °C was performed. The structure of the simple device is seen in Figure 4.6.

The measurements pictured in Figures 4.7-4.9 below were taken from such simply prepared samples. The first measurement, Figure 4.7 was taken before the sample was annealed to the higher temperature. A poor contact is evident, likely due to the oxide present on the surface of the nanowire, and the fact that the wires were simply drop cast onto the pre-prepared pads. A second, higher heating was necessary to improve the performance. After a 400 °C anneal, the contacts are greatly improved as evidenced in Figure 4.8. Ohmic behavior is implied by the straightening of the curve.

![After 350C anneal, without gate bias](image)

Figure 4.7: Electrical measurement of a single nanowire, without gate bias, taken after a 350 °C anneal. Poor contacts are observed, indicating that the wire is not yet in good electrical contact with the prepared test pads.
Figure 4.8- Electrical measurement of a simple, single nanowire device, without gate bias after a 400°C anneal. The ohmic contacts with the substrate are now formed, as evidenced by the straightening of the curve.
Figure 4.9- IV Measurement of two-contact germanium nanowire device. The large hysteresis may result from that water vapor attacking the germanium oxide layer which coats the nanowire, leaving it pitted and electrically defective.

In Figure 4.9, the IV measurement of a germanium nanowire is shown. The large hysteresis may result from that water vapor attacking the germanium oxide layer which coats the nanowire, leaving it pitted and electrically defective. This effect has been observed by other groups monitoring the transistor behavior of a single nanowire.106
4.3 Preparation of Samples with a Focused Ion Beam

Preparing nanowires for electrical testing consisted of several labor-intensive steps. Custom-prepared pads were metalized through e-beam deposition. Germanium nanowires grown under standard conditions and dispersed in solvent through the ultrasonication method referred to in the experimental chapter. A drop or two of this solution was placed on the prepared pads, and the solvent was evaporated off completely. Top contacts were then drawn to viable wires utilizing a focused-ion-beam (FIB) system. Although the wires were deposited randomly on the surface, a suitably dense solution would yield two or three candidate nanowires possessing the requisite length and positioning for connection to the prepared pads. Top contacts were deposited using platinum metal, though this was confirmed to be heavily contaminated with gallium due to the ion source of the FIB. Representative images of nanowires before and after FIB deposition are shown in Figures 4.10 and 4.11, respectively. A four-contact device is shown in Figure 4.12.
Figure 4.10: Germanium nanowire (center) before FIB deposition

Figure 4.11: Germanium nanowire after being connected to two test pads with platinum lines deposited via FIB
Testing of the samples prepared with the focused ion beam is ongoing at the time of the publication of this dissertation, and will fall largely on the shoulders of the researcher who inherits this project. Thus far, highly reproducible measurements possessing good consistency among many wires with the same dopant level have not been achieved. Future work should include more analysis of four-contact nanowire devices, made from both doped and un-doped samples. The overall goal of this future work will be to more fully probe the electrical structure of the nanowires so that they can be tuned sufficiently to be incorporated into more efficient solar and other devices, as discussed in the first part of this chapter.

In conclusion, we have shown that photoinduced charge transfer in P3HT-GeNW bulk heterojunctions can be observed. The inclusion of germanium nanowires in a hybrid photovoltaic device was novel at the time of its publication. The photoinduced charge transfer is evidenced by the inverse correlation between the photoluminescence
quenching and the external photocurrent quantum efficiency. We have quantified the amount of germanium in our solar cells down to the part per billion range, and showed an increase attenuation in photoluminescence signal with an increase in nanowire concentration. This resulted in a significant increase of the EQE of devices fabricated using a mixed P3HT-GeNW active layer. However, the p-type conductivity and native oxide layer of the germanium nanowires resulted in a low open-circuit voltage and photocurrent. The reduction of the open-circuit voltage is consistent with band bending of the nanowires caused by the GeO$_2$ surface oxide. Germanium nanowires included in the device likely improve quantum efficiency by improving the crystallinity of the P3HT. Contact optimization, $n$ doping, and surface treatments of the germanium nanowires, as well as other material and structural optimization, are expected to improve these results, and can be implemented in future studies.

Methods for preparing simple nanowire FET devices were explored. A 400 °C anneal was necessary to achieve good ohmic contacts between a nanowire which was simply placed on top of two titanium test pads. For more robust devices, a focused ion beam system was utilized to create two- and four-terminal devices. Consistent results among many wires of the same dopant level were not achieved, and this requires further optimization and study.
Chapter 5- Summary and Conclusions

We present a comprehensive study of germanium nanowires grown utilizing the vapor-liquid-solid growth mechanism. Germanium nanowires were first investigated in the late 1990s, drawing attention because of their interesting physical, electrical, and chemical properties. Other groups worked to describe and optimize nanowire growth and apply these grown wires to both simple electrical devices and more complicated ones such as sensors. Our nanowires are single crystalline, as confirmed with XRD and TEM, and grow oriented along the <111> crystal direction. Previous work by other groups has emphasized the importance of the thermodynamics and kinetics of the gold-germanium system from which nanowire growth nucleates. We extend a simple, diffusion-limited surface model to our nanowire growth, and find that it is insufficient to describe the intricacies of the growth at higher partial pressures of germane. Nanowire growth is a surface-limited process in partial pressure ranges on the order of 1 Torr, resulting in a growth rate of 250 nm/minute at 295 °C.

We present the first direct growth of germanium nanowires on a flexible organic substrate, and confirm that there is no migration of the catalyst or the wire into the polymer utilizing AFM. This work is an important first step towards the development of low cost, easily processable flexible electronics. A comparison of methods to deposit gold catalysts on the surface is performed, and it is found that commercially available gold colloids dispersed on a substrate’s surface through simple wet chemical processing affords the best control over wire length and diameter.
We investigated the stability of wet chemical passivation on germanium nanowires through the application of self-assembled monolayers of alkanethiols, whose attachment to germanium has been previously well characterized. Using XPS and photoluminescence spectra, we show that these layers are only suitable to prevent oxide for about six hours before they begin to degrade and the native oxide layer re-forms on the germanium surface.

We also utilized the newer, but highly valuable technique of atomic layer deposition to apply thin films of aluminum and hafnium oxides to the surface of our wires. This technique has the advantage of producing highly controllable, uniform, and robust thin-films on topographically complicated substrates. We confirmed the thickness and composition of our films utilizing TEM and EDX, and showed that there is very little, if any, intermixing between the germanium and the deposited oxide layer as confirmed within the detection limit of the EDX. The combination of VLS nanowire growth with ALD holds promise for the creation of more complicated, highly controllable electronic nanostructures in the future.

There exists a growing interest in photovoltaic devices based on organic technologies. Such devices are traditionally limited by low efficiencies, which have not yet reached over 8%, but hold promise to potentially be very low in cost. Using germanium nanowires and poly (3-hexylthiophene), we developed a simple, proof of concept organic-inorganic heterostructure photovoltaic device and demonstrated that this device has increased external quantum efficiency as compared to a device lacking germanium nanowires. We have shown that photoinduced charge transfer in P3HT-
GeNW bulk heterojunctions can be observed. The inclusion of germanium nanowires in a hybrid photovoltaic device was novel at the time of its publication. The increase in external quantum efficiency in the device is accompanied by a decrease in photoluminescence signal, indicating that the presence of germanium nanowires in the solar cell lead to a decrease in unwanted exciton recombination. We have quantified the amount of germanium in our solar cells down to the part per billion range, and showed an increase attenuation in photoluminescence signal with an increase in nanowire concentration.

The $p$-type conductivity and native oxide layer of the germanium nanowires resulted in a low open-circuit voltage and photocurrent. The reduction of the open-circuit voltage is consistent with band bending of the nanowires caused by the GeO$_2$ surface oxide. Germanium nanowires included in the device likely improve quantum efficiency by improving the crystallinity of the P3HT. Contact optimization, $n$ doping, and surface treatments of the germanium nanowires, as well as other material and structural optimization, are expected to improve these results, and can be implemented in future studies.

Finally, we investigated several methods for the preparation of simple electrical devices made from single germanium nanowires in order to better probe the electrical properties of the nanowires grown utilizing our growth methods. We show ohmic contact from a device utilizing a single nanowire dispersed across two titanium test pads. Future work to extend this dissertation project might include deeper
investigations into the electronic properties of doped and un-doped germanium nanowires.
APPENDIX A- Standard Operating Procedure for Germanium Nanowire Growth

A1 Basic Overview

This appendix will explain in complete detail all the parts and functions of the home-built, hot-wall germanium nanowire reactor used for the production of nanowires as outlined in this work. This equipment is located in the Micro-Electronics Research Laboratory (MERL) clean room in the Engineering building on Busch Campus. Clean room training and authorization is required before operation of the reactor may commence.

The entire system consists of a gas cabinet, which houses the germane and phosphine gas cylinders, and the CVD system, consisting of upstream gas lines, a quartz reactor tube and tube furnace, downstream pumping lines, and a mechanical pump (rotary vane) charged with Fomblin. The reactor exhaust is fed to an in-house abatement box, which is located outside of the operating area. The electronic control chassis located beneath the furnace is built to control the furnace temperature, reactor pressure and all the pneumatic valves. The hydride detector is placed in the top Plexiglas enclosure, and can detect nearby germane or phosphine by diffusion.
A1.1 Technical Details of Featured Components

1. **Germane and Phosphine gas panels**: These panels are for flushing out hazardous gases from the line, eliminating the possibility of their release into work atmosphere when disconnecting the line from gas cylinder for cylinder change; for flushing out air with N2 purge after germane cylinder change. They are strongly recommended for use with toxic, corrosive or flammable gases.

   The gas panels include the following safety features:
   - An excess flow valve will automatically shut off if the gas flow exceeds the preset limit.
   - It protects against line or instrument rupture, fire, or malfunctioning valves, and prevents uncontrolled flow of gases. This feature is critical with toxic, or flammable gases such as germane. The emergency shut-down valve is normally open. Push the shut-down button on the Emergency shut-off box (on top of one of the gas cabinets) to shut off germane in case of emergency. See Clean room personnel for more information on Emergency shut-off valves outside of the gas cabinets.

2. **Germane Control Pneumatic Valve, PV2**: This normally closed pneumatic valve is interlocked to the germane detector (both the alarm relay and fault relay) and the Baratron pressure module. If process pressure exceeds the set point due to pump failure, the control valve will automatically close. This valve is also tripped when the red Emergency Shut Down button (labeled “push to shut down
germane”) on the control panel is pressed. In the event of a power outage, it will shut off automatically.

3. **Check valves**: Check valves crack open at a small positive differential pressure (cracking pressure) to allow unrestricted forward flow, and reseal at a small negative (reverse) differential pressure (reseal pressure) to prevent reverse flow. For the model 401-V or 401-K that we used, the cracking pressure is ~1 psig. The max reseal back pressure is ~ 4 psig. For the SS-4C-KZ-1/3-SC11, the cracking pressure is 1/3 psi, and the reseal pressure is up to 6 psi.

4. **Particulate filters**: These prevent germanium dust from entering and clogging pumping line and valves. An elbow fitted with an SS sieve is attached to the top port of the cross to further reduce the particulates that could be swept into the pumping line. Another SS sieve trap is installed before the pneumatic angle valve on the pump to reduce any back streaming of oil going into the pumping line and reactor, and prevent particles and condensables from entering pump.

5. **Pressure relief valve**: This works similarly to check valve, but has a higher cracking pressure. It will reseal when forward pressure drops below the cracking pressure. It is used here for releasing gas when reactor pressure gets too high. For model S530-S1, the cracking pressure is field adjustable with a wrench, from 3-50 psig. We adjusted it to ~21 psi for our application.

6. **Solenoid valve**: The solenoid valve is used to adjust the pumping conductance based on Baratron readings in order to control reactor pressure during nanowire growth. Because of the relatively low flow rate of germane, we need a valve with
a very small controllable conductance. Most commonly used throttle valves (butterfly, pendulum etc.) are not suitable, hence a proportional solenoid valve is used for this purpose. It is similar or identical to valves used inside a MFC.

7. **Nitrogen**: Nitrogen is used to dilute germane and reaction gases to below the pyrophoric concentration before letting the gas into the pump inlet. This prevents germane gas accumulation in the oil reservoir of the vacuum pump, and also helps to protect the pump Viton seals and the pump itself from corrosion. For 10-20 sccm of 5% germane, we need 50-100 sccm of N\textsubscript{2} introduced. Nitrogen is also introduced at pump outlet to sweep gases to the burnbox.

8. **Pump inlet Pneumatic Valve**: This valve shuts off in the event of a power failure so that oil and air cannot go upstream into the line.

9. **Mechanical pump**: The pump used in this system is charged with Fomblin, and is suitable for pumping germane and corrosive gases. The pump outlet is constructed of air-tight metal tubing. Oil mist eliminators that contain filter cartridges should not be used since they cause a pressure drop favoring condensation, and these filters are usually combustible and should never used in conjunction with the pyrophoric gasses present in the system.

10. **Control scheme**: The control circuit is illustrated in Figure A1. When the fault relay or low relay of the hydride detector triggers, the Baratron measured pressure exceeds its “alarm1” set point, the red emergency push button is pushed, or a power outage occurs, PV2 will automatically shuts off. When the
hydride detector mid relay is triggered, a siren will go off. Both the siren and the hydride detector are on a UPS. When PV2 and AV3 are set to auto, the temperature PID controller will automate the opening, closing of these valves according to the ramp and soak setting of the temperature controller, i.e., closes PV2 and opens AV2 when ramp starts, and opens PV2 and closes AV2 when temperature soak starts, and closes PV2 and opens AV2 at the end of the soak. Please note that while automatic runs are possible with this system, they are not recommended and have never been utilized during the growths outlined in this dissertation. When the proportional solenoid valve is set to PID, the pressure PID controller will automatically control the opening and closing of the valve to achieve pressure control.
Figure A1: Circuit Control Scheme
A1.2 Safety

This reactor utilizes both germane and phosphine gases, which pose extreme health dangers. Both are pyrophoric and toxic in minute levels if inhaled. Toxic levels occur before the gasses are able to be detected by scent, so extreme care must be taken if there is even the slightest suspicion of a leak or disturbance within the reactor. The reactor is outfitted with a general hydride gas detector which will emit an alarm if any such gas is detected. Before attempting to operate this reactor, the operator must be intimately familiar with all emergency procedures of the MERL facility, including emergency all-stop locations, exits, headcount staging areas, etc. A visual inspection of the equipment should always be performed before starting any run to ensure the absence of cracks or dents in any tubing or component. As this equipment is home built, it does not have some of the foolproof lock-ins of a commercial system. Thus, one cannot stress enough exactly how imperative it is for the operator to be completely aware of the proper reactor procedure. The final line of exposure defense is the Plexiglas box outfitted around the reactor. During operation, the doors to this box should remain closed at all possible times.

1. Gas cylinder storage area temperatures should not exceed 125ºF (52ºC), and should be free from combustible materials and free from ignition sources. Never apply flame or local heat to any part of a cylinder. Avoid sparks. Direct flame
exposure on the cylinder wall can cause a catastrophic failure of the cylinder releasing the contents into a massive fireball and explosion.

2. Reverse flow back into germane cylinder may cause rupture. Check Valves are in place to prevent this from happening.

3. Germane can ignite and generate hydrogen gas on contact with water.

4. Always use two people for cylinder change. Return empty cylinders to Voltaix, inc.

5. The recommended regulator for systems involving germane are diaphragm regulators with an SS diaphragm. All regulators should be equipped with a bonnet vent that is capable of withstanding a diaphragm rupture and should be piped to route the escaping gas to a suitable and safe place.

6. Take great precaution during the initiation of flow. Do not become impatient and open by-pass valves. Allow the system to reach operating pressure via the MFC.

7. Dedicated inert gas cylinders located in the same gas cabinet or exhausted enclosure are ideal for this application. Ideally, each purge cylinder and the cylinder it supports should share an enclosure. However, if adequate backflow protection is provided for the purge gas source, the cylinders may be located external to the germane gas enclosure.

8. Redundant backflow check valves are in place to prevent contamination of the purge gas cylinder with germane. Do not return potentially contaminated purge
gas cylinder without explicit instructions from the cylinder gas supplier. If backflow of germane is suspected, the system should be treated as if germane is present.

9. Gas line needs careful grounding to protect from accidental contact of the metal with loose or frayed power wires. Grounding of all metal parts in contact with flammable gases also suppresses static electricity generation. Isolate electrical wiring from gas lines to minimize damage during fire.

10. Do not use rotameters for hazardous gases. The needle valves of rotameters frequently leak.

11. Do not modify system to include liquid nitrogen traps in vacuum line and system lines, as oxygen entering the system may be condensed and create a highly explosive mixture. Do not modify system to include cryogenic pumps (including gas refrigerator, molecular sieve sorption pumps and cold traps).

12. Do not use oil or grease on germane gas handling fittings or equipment.

13. Hydride detector should be able to initiate local visual and audible alarms. The high level alarm for germane is factory set at 600 ppb (TLV=200 ppb), and this high level alarm is interlocked to the emergency shutoff valve of the gas cylinder. It is not necessary to automatically shut down when the low level is activated (factory set at 200 ppb), however the system should be checked and manually shut down as soon as possible. The hydride detector should be equipped with a backup power.
14. Gas-line and reactor pressure should be monitored for toxic, flammable or corrosive gases. The pressure monitor should be interlocked to the emergency shutoff valve.

15. It is well known that germane gas, in the absence of an ignition source, can decompose to germanium and hydrogen via an exothermic reaction at 280 °C. The energy released during this decomposition in a closed system results in a significant temperature increase along with a considerable pressure rise. This pressure surge is due not only to heating, but also to the formation of two molecules of free hydrogen for each molecule of germane decomposed.

16. Plastic pneumatic tubing should be used to actuate the germane emergency shutoff valve. The intent is for the plastic to melt during a fire condition and cause the germane or phosphine valve to automatically fail closed.

17. The system should be visually inspected before each use with attention paid to all fittings, valve bonnets, pressure gauge inlets, etc. Occasionally, germanium built up within the reactor through the CVD process will shatter and flake in the furnace tube. This can lead to germanium shards present on the quickflange O-ring fitting at the reactor inlet, compromising the seal. Always be sure that the O-ring is free from particulates before proceeding.

18. Leaks may cause fire or form explosive mixtures with air. If a leak occurs, immediately evacuate all personnel. Use proper personal protective equipment to shut off the germane supply if there is a fire and if it can be done without risk. If the flow of gas cannot be shut off, allow the fire to burn out. Do not attempt
to extinguish the fire before the gas flow is completely stopped. Contact supplier for information on disposition of cylinders involved in fire. Combustion products can be controlled with a water spray or fog. Ventilate the area of the leak prior to the return of personnel.

19. Excessive pressure may develop in gas cylinders, reactor, or gas lines if exposed to fire, which may result in explosion regardless of the cylinder's content.

20. Germane gas is heavier than air and may collect in low areas or travel long distances along the ground to a distant source of ignition and flash back to leak. Combustion by-products may be toxic.

21. Consult a clean room technician or processing gas expert before making ANY modifications to this system. Proper purging MUST be performed before removing or replacing any valve, cylinder, pump, or other component. Gases can accumulate within the system.
A1.3 Glassware

Figure A2: Glass boat utilized to hold and insert samples into reactor. Discoloration results from chemical vapor deposition of germanium which builds up over several growths. The boat is inserted and removed from the reactor with a glass rod.

Always remember that **HOT GLASS LOOKS JUST LIKE COLD GLASS.** Before handling any glassware which has been recently removed from the furnace, ensure that
it is at a safe temperature to avoid severe burns. Alternatively, use a heat-protective glove.

**A2- Procedure**

**A2.1 Initialization**

1) Go to the back room, and turn on the burn box. The burn box must reach at least 700 degrees Celsius before germane or phosphine can be introduced safely. The heating ramp-up can take nearly twenty minutes. Occasionally, the box will fault, indicated by an alarm. It must be reset as soon as possible. Monitor the temperature of the burn box throughout growth. For operational details regarding the burn box, please see the clean room staff. DO NOT attempt to use this equipment without proper training.

2) This nanowire system shares an exhaust line to the burn box with the furnace on the opposite wall. If that furnace has recently been run, the exhaust line will be open to air and MUST be sealed with a quickflange before proceeding.
Figure A3: Furnace adjacent to nanowire reactor. Quickflange must be in place as in the top photograph before operation may commence.
3) Open the valves for house nitrogen and compressed air, located on the lower right of the reactor. Nitrogen is used to purge the reactor and prevent backflow. Compressed air is necessary for the proper function of pneumatic valves.

Figure A4: Nitrogen (blue) and Compressed Air (orange) Valves on lower right of reactor

4) Open the exhaust valve around the back of the system, marked CVT. (A, Figure A5)
Figure A5: Left side of the reactor. A) exhaust valve B) germane and phosphine lines leading to gas cylinders in back room, C) opening to furnace, sealed with quickflange D)hydride gas detector
5) Switch on the main power. This turns on the mechanical pump. (A, Figure A6)

6) Switch on the pressure control, Baratron, temperature control (A, B, C, Figure A7) and MFC controllers (B, Figure A6)
Figure A7: Reactor Control panel showing A) Pressure Control B) Baratron C) Temperature Control and D) Germane Emergency-Off Button
A2.2 Back Room Gas Panels and Burn Box

Figure A8: Diagram of Phosphine Purge Panel
Figure A9: Diagram of germane purge panel
Figure A10: Germane in gas cabinet. Valves marked are those which are opened or closed during growth
Process gases are located near the burn box in a separate room from the reactor itself.

Figure A11: Phosphine gas cabinet. Valves marked are those which are opened or closed during growth.
The phosphine system has an additional safety control located on top of the phosphine gas cabinet. In order for phosphine to be introduced into the system, the valve must be open on this additional control.

![Control box located on top of the phosphine gas cabinet](image)

Figure A12: Control box located on top of the phosphine gas cabinet

### A2.3 Reactor Control Panel

Once the burn box and process gasses have been initialized as described above, and the mechanical pump has been turned on, the reactor control panel may be used for the rest of the initialization sequence. Some manual valves must also be activated. Please refer to Figure A13 for the reactor control panel, and Figure A14 for the manual valves. Manuals for the mass flow, temperature, and pressure controllers can be
obtained from their respective manufactures, and, outside of basic operation, they will not be discussed in detail.

1) Open AV3. This opens the system to the pump up until the Proportional Solenoid Valve. The pressure controller should indicate a decrease.

2) Open the Proportional Solenoid Valve, which is marked PSV in Figure A13.

3) Open AV2. The system back end of the system has now completed its pump and the pressure controller should read approximately 1 Torr.

![Diagram of reactor control panel]

Figure A13: Close up of reactor control panel

4) Open the large black manual valve located on the upper left of the system. This will vent the remainder of the system. The airflow is very rapid, so if
samples are already loaded in the chamber, open this valve slowly, as it the rush of air has the tendency to knock them off their glass boat. Allow the system to once again reach pressure equilibrium.

5) Once the system has reached a pressure of about 1 Torr, PV3 and PV4 can be opened. This prevents oil backstreaming into the system. Adjust the nitrogen flow to be 200 sccm on the flow meter on the front of the reactor.
Figure A14: Reactor Manual Valves
A2.4 Initial Nitrogen Purge

Regardless of the conditions under which the system was left before the initialization procedure was followed, (The reactor may be left pumped down or under nitrogen, at atmosphere) it is highly recommended that an initial nitrogen purge is performed before the quickflange port is opened to load a sample. It is possible that if the system was not shut down correctly, some germane may remain in the reactor. This initial purge removes the risk of accidental exposure.

1) Close AV3. The system is now closed off from the pump.

2) Open the Manual Nitrogen Valve a small amount. Keep your hand on the valve and your eyes on the pressure gauge to avoid over-filling the system. This backfills the system with nitrogen. MAKE SURE THE SYSTEM PRESSURE DOES NOT RISE ABOVE ATMOSPHERIC PRESSURE (760 Torr).

3) When the system pressure reaches 760 Torr, close the manual nitrogen valve.

4) Open AV3, and allow the system to pump out.

5) Repeat steps 1-4 several times to fully purge the system. It should now be safe and free of toxins.

6) After the final backfill, do not open AV3. Allow the system to fill to about 760 Torr. This prepares the system for sample loading.


**A2.5 Opening the Reactor to Air- Loading the Sample**

1) **Confirm that all process gas valves, both pneumatic and manual, are closed.**
   This includes the manual valves immediately after the germane and phosphine mass flow controllers. The red emergency off button should be pressed in to ensure that accidental turn-on of germane is not possible.

2) Follow the instructions for the nitrogen purge, as outlined above. Bring the system up to atmospheric pressure.

3) Close PV3 and PV4. These valves must be closed **before** the pump is turned off.
   AV2 and PSV may be left open during the loading of the sample.

4) Flip the main power switch to the “off” position to turn off the pump.

5) Quickly flip AV3 open and closed. This relieves any excess pressure in the system. It is better to have the system slightly under atmospheric pressure when the quickflange port is going to be opened.

6) Close the black manual valve on the top left of the system. This valve isolates the exhaust from the reactor and must **never** be left open when the reactor is open to air.

7) Open the furnace. If the furnace is closed, no light can enter the quartz tube and it will be very difficult to see what you are doing.

8) Open the quickflange port by unscrewing the clamp. Check the o-ring for any germanium particles. If it is dirty, use compressed air to remove the
contaminants. It is vitally important that the o-ring is free of particulates so that a tight seal is formed.

9) Load the sample boat into the reactor. Appropriate sample dimensions and glassware are discussed elsewhere in this dissertation.

10) Using the long, hooked glass rod, slowly push the sample boat into the tube furnace. Take care not to drop any samples, as they can be difficult to fish out once they’ve left the boat.

11) Insert the boat into the sweet spot of the reactor. The heating potential of the furnace rapidly drops off to either side of this spot, and nanowire growth will not be observed if the samples are placed far from the heat. The glass rod is marked with a black line to indicate the best position for growth. If for some reason this rod is lost or damaged, the best site of heating coincides with the area of heaviest CVD growth on the walls of the tube furnace.

12) Remove the glass rod and close the quickflange port by placing the o-ring and steel stop over the reactor opening. Attach the clamp and make sure you have a good seal before proceeding.

13) Follow steps 1-5 under Reactor Control Panel in section A2.3 to prepare the system for growth.
A2.6 Germanium Nanowire Growth

1) Before beginning the procedure to introduce any process gas confirm that:
   
a. **Burn box** has reached at least 700 degrees Celsius and is functioning properly.

b. **System pressure** has reached equilibrium, around 1 Torr.

c. **Quickflange port** is sealed and free of leaks.

d. **All Plexiglas doors** are closed.

e. **Germane and Phosphine Pneumatic Valves** are closed. Confirm that all MFC manual bypass valves on these gas lines are also closed.

2) Secure the lid of the furnace, and turn it on by turning the dial to “8”.

3) Set the desired initial temperature using the temperature control panel. For most growth needs, a temperature of 360 degrees Celsius is sufficient. If the furnace is cold, it may take several minutes to reach this temperature. Do not introduce germane until this temperature is reached.

4) Set the desired pressure using the pressure control panel. 120 Torr is common for growths.

5) Enter the back room and ensure that the germane gas panel is configured as described in section A2.2. Open cylinder valve A and manual valve D (Figure A8). Germane is now introduced in the line leading to the reactor, up until the germane pneumatic valve, PV2.
6) Return to the reactor in the main room. Unlock the emergency-off red button with the key. This key should be kept in a safe place accessible only to the main reactor operator at all times to prevent unauthorized, unsafe use of the system. **DO NOT** leave the key with the reactor where it might be misused.

7) Open the germane manual valve which connects the germane line to the main reactor line, seen in Figure A12. A system pressure increase may be observed. This is only residual nitrogen left from the previous shut-down purge. Close the Plexiglas door.

8) On the reactor control panel, close AV2, and switch PSV to PID. Leave AV3, PV3, and PV4 open. Confirm that the furnace temperature has reached its desired limit. The system is now prepared for the introduction of germane.

9) Open PV2, the germane pneumatic valve. Germane from the line can now flow through the MFC and into the system.

10) Monitor the flow rate of germane on the MFC controller and the pressure of the system with the pressure controller. The flow rate should read approximately 20.00 sccm for the duration of the growth. If there is an unexpected drop in flow rate, return to the back room and confirm that all is well with the purge panel and tank.

11) **Do not under any circumstances open the MFC bypass valves while germane is flowing through the system.** These valves exist solely to purge around the MFCs if they should ever malfunction and need to be replaced. Opening these valves removes all controlled flow of germane, and the system could reach dangerous
pressures. Due to the relatively slow flow rate of germane, it will take several minutes for the system to reach its desired growth pressure. This will not affect the quality of the wires.

12) As the pressure set point is reached, the proportional solenoid valve will automatically open or close to maintain it. The indicator light for this valve will glow proportionally with the amount that the valve has been opened.

13) After about 5 minutes, if a two-temperature growth is desired, (as recommended to avoid tapered wires) adjust the temperature controller to a lower temperature. You do not need to make any adjustments on the furnace itself.

14) Allow growth to continue as long as necessary. **DO NOT LEAVE THE REACTOR UNATTENDED WHILE GROWTH IS IN PROGRESS.**

15) When growth is complete, close PV2, the germane pneumatic valve.

16) Press the red emergency-off button.

17) Open AV2.

18) Switch PSV to “open.” Watch the MFC rate drop to 0.00 sccm. The system is now evacuated.

19) Turn the furnace off, and open the cover to expedite cool-down.

20) Perform at least ten nitrogen purges, as described in A2.4, steps 1-4. At this point, we are evacuating the entire line all the way back to the germane pneumatic valve, PV2.
21) Close the germane manual valve which connects the germane line to the main system line.

22) Purge the system a few more times. After the final purge, fill the system with nitrogen to atmospheric pressure as described in A2.4

23) Follow the instructions in A2.5 to remove the sample. Again, **hot glass looks just like cold glass.** Take great care to avoid burns when removing the boat. It is not recommended to attempt removal if the system temperature is still greater than 100 degrees Celsius.

**A2.7 Reactor Shut Down**

1) It is recommended that after the sample boat is removed, a final nitrogen purge is performed so that the system is left under nitrogen and not ambient air.

2) After the system has been filled with nitrogen, close PV3 and PV4.

3) Turn off the pump. Quickly flip AV3 open and closed to alleviate any pressure.

4) Close the **large black manual valve** on top of the system.

5) Close AV2 and PSV.

6) Double-check that the red emergency-off button is in its locked position. Double check that the furnace is off and all valves are closed.

7) Close the manual valves on the lower right of the reactor for the nitrogen and compressed air.

8) Turn off the pressure, mass flow, and temperature controllers.
9) Close the exhaust valve on the wall marked CVT.

10) In the back room, close any process gas valves which were opened during the course of growth.

11) Turn off the burn box.

**A2.8 Doped Growth**

For growth of phosphorous doped germanium nanowires, the procedure is essentially the same as outlined in section A2.6. Note that the germane and phosphine MFCs share a single read-out device and only one flow rate can be read at a time. Germane gas corresponds to channel 1 on the controller, and phosphine gas corresponds to channel 3 on the controller. Channel 2 on the controller does not work correctly, so no MFCs should be added here.

1) Follow steps 1-5 as indicated in A2.6.

2) In the back room, ensure that the phosphine purge panel is configured as in section A2.2. Open valve A as marked in Figure A9, and also open the valve on the Gas Safety Monitor control panel as shown in Figure A10. Phosphine is now in the line to the system up until the phosphine pneumatic valve.

3) Follow steps 6-13 as outlined in section A2.6. After returning to the reactor, make sure to open the phosphine manual valve after the phosphine MFC.

4) Open the phosphine pneumatic valve and monitor the phosphine flow with channel 3 on the MFC readout. The phosphine pneumatic valve is open when
the switch is in the downward position. Do not introduce phosphine gas until the wires have had time to begin their growth, as this will poison the VLS mechanism.

5) When the desired doping period has ended, close the phosphine pneumatic valve.

6) Follow the remaining instructions in section A2.6 to conclude the growth. Refer to section A2.7 for reactor shutdown.

**A2.9 Full System Purge**

In several instances, purging beyond the germane phosphine mass flow controllers may be necessary. In the event of a mass flow controller failure, each controller is fully bypassed using manual valves. This enables the user to safely backfill with nitrogen and then pump out the space around the MFC. The affected unit can then be removed for repair. To perform this purge, the main nitrogen line manual valve must be open, as well as the nitrogen inlet manual valve and MFC bypass manual valve as outlined in the figure below. Purging can continue as outlined in section A2.4, steps 1-4.
Figure A15: Schematic detailing the setup around the mass flow controllers, outlining the manual bypass valves.

In the event of a process gas tank change or major modification to the system, the gas lines affected must be evacuated all the way to the cylinder. **Consult a cleanroom technician before attempting a cylinder change.** As shown in section A1.5, both gas panels are fitted with the venturi option to ensure safer, speedier pump downs. It is recommended to purge the system out in segments for safety.
Appendix B- Equipment Details

This appendix outlines all instrumentation utilized in this work which has not already been covered in detail elsewhere.

B1 Microscopes

B1.1 Scanning Electron Microscopes

B1.1.1 Tungsten Filament

Some of the presented images were collected on a JEOL tungsten filament scanning electron microscope located in the chemistry department of Rutgers University. While not state-of-the art, its capabilities were sufficient for much of the work presented herein.

B1.1.2 Princeton Field Emission System

Some of the presented images were collected on a FEI XL30 FEG scanning electron microscope at the Imaging Analysis Center at Princeton University. This high-resolution field-emission SEM has an optimum image resolution of 2nm.
B1.1.3 Rutgers Field Emission System

Some of the presented images were collected on a Zeiss Sigma Field Emission scanning electron microscope located in the Ceramics department of Rutgers University. It has a resolution up to 1.7nm at 15 kV and 3.0nm at 1 kV.

B1.2 Transmission Electron Microscope

Bright-field images are taken using a JEOL 2010F field-emission TEM/STEM system at 200kV accelerating voltage.

B1.3 Focused Ion Beam

All focused ion beam work was performed with a Strata DB-235 dual-beam focused ion beam and scanning electron microscope (FIB/SEM) system. This work was performed at both the Imaging and Analysis Center at Princeton University and the Naval Research Laboratory. The Liquid Metal Ion Source (LMIS) used consists of gallium ions in contact with a heated tungsten wire. Gallium ions are accelerated to between 5-
50 keV depending on the substrate, and the beam current is held on the order of 10 nA during deposition.

**B2 Energy-Dispersive X-Ray Detectors**

**B2.1 FESEM Detector**

The detector used for SEM EDX analysis is an Oxford INCAPentaFET-x3. This detector is a SiLi detector with a crystal area three times larger than a normal SiLi detector. The manufacturer quotes the resolution at 129eV at MnKα, 65eV at FKα, 56eV at CKα.

**B2.2 TEM Detector**

For TEM samples, a Bruker XFLASH Silicon Drift Detector is used. This detector has the advantage of operating without liquid nitrogen, as the boiling liquid causes vibration. The manufacturer claims the detector is insusceptible to incomplete charge collection, with a superior energy resolution of 123 eV Mn Kα, 46 eV C Kα, 54 eV F Kα.
B3 Atomic Layer Deposition

Our home-built ALD chamber was designed by Chien-Lan Hsueh. The following is a rough description of the system and operating procedures.

Preceding deposition, the whole system is pumped down to $10^6$-$10^7$ Torr for an hour. Several pneumatic valves are installed to control the flow of gases and produce the alternative pulses of precursors in ALD, as can be seen in Figure B3.1. The flow rate of purging N$_2$ is set to 300 cc per minute by a mass flow controller. The whole ALD system is monitored and controlled with a LabView program with a USB 12-bit DAQ board. Custom designed ALD growth parameters including temperature set points, gas pulse sequence, duration of cycles, and number of cycles are controlled through LabView.

A Baratron pressure gauge and thermocouples are used to monitor the pressures and temperatures of the reactor, gas lines, and precursor bottles at all times. Al$_2$O$_3$ films are deposited using this system using trimethylaluminum (TMA) as an aluminum precursor. TMA is introduced into the system alternatively with water. The duration of TMA and water pulses are 0.5 seconds each, and the deposition temperature is 150 °C.
Figure B3.1 Schematic of ALD system
References

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Curriculum Vitae

Lauren Klein
lauklein@rci.rutgers.edu

Degrees
Rutgers University, Ph.D in chemistry May 2011
Vassar College, AB, with honors in Chemistry May 2005

Fellowships and Awards
NSF IGERT Fellowship “Nanotechnology and Clean Energy” August 2009-August 2010
GAANN Fellowship August 2006-August 2008
University Excellence Fellowship August 2005-August 2006
Jeffrey M Chance Memorial Prize for Excellence in Chemistry May 2005

Research
Growth and Applications of Germanium Nanowires, with Dr. Eric Garfunkel, Adviser

Classes Taught
Energy and Climate Change- Interdisciplinary science course open to freshmen of all majors covering major topics in energy usage and climate change.

Chemistry 161- General chemistry
Chemistry 171- General chemistry lab

Publications and Conference Proceedings

Germanium Nanowires/poly (3-hexylthiophene) composites for Photovoltaic Applications. 236th ACS National Meeting, 2008

“Photoinduced charge transfer between poly(3-hexylthiophene) and germanium nanowires” Appl. Phys. Lett. 91, 183501 (2007)