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Nanomaterial Synthesis and Integration for Sensor and Energy Applications

by

Heather Chisako Chiamori

A dissertation submitted in partial satisfaction of the requirements for the degree of Doctor of Philosophy in Engineering - Mechanical Engineering in the Graduate Division of the University of California, Berkeley

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Professor Liwei Lin, Chair
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Nanomaterial Synthesis and Integration for Sensor and Energy Applications

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Heather Chisako Chiamori
Abstract

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University of California, Berkeley

Professor Liwei Lin, Chair

Nanostructures have unique properties that will be leveraged for next generation sensor and energy applications: large surface-to-volume ratios, increased sensitivity at lower input power levels, and higher current densities all contribute to increased functionality of nanostructure devices. The synthesis and integration of carbon-, metal-, and metal oxide-based nanostructures for sensor and energy applications are studied with the goal of nano-to-micro devices utilizing well-established micro- and nano-fabrication tools and techniques: (1) self-assembled, integrated carbon nanotube gas/pressure sensors; (2) titanium dioxide (TiO$_2$) nanostructures for energy applications; and (3) silver nanowires and graphene for biological and optical sensing platforms. Suspended carbon nanotubes are grown by in situ heating of microstructures, self-assembled and integrated directly for electrothermal gas/pressure sensing. Titanium dioxide nanoswords, synthesized by induction heating, exhibit large areas of crystalline faces demonstrating enhanced photocatalytic activity. TiO$_2$ nanosword synthesis is scaled for bulk growth and combined with microfabrication techniques to study solar absorption under visible light irradiation for photoelectrochemical cell applications. Silver nanowires are synthesized using oblique angle deposition (OAD), allowing for control over nanowire porosity and morphology based on substrate deposition angle. Graphene devices are fabricated using nanoinprint lithography (NIL) techniques.

Suspended carbon nanotubes (CNTs) are grown by in situ heating of microstructures, allowing for the placement of CNTs at specific locations without conventional global furnace heating during the synthesis process. These CNT devices are self-assembled and the integration process monitored via electrical feedback. Electrothermal pressure sensing with selective gas and pressure sensing applications has been demonstrated. Furthermore, control and improvement of the self-assembled contact resistances of nano-to-micro interfaces have been investigated by means of local annealing via Joule heating.

Titanium dioxide nanoswords have been synthesized using a rapid induction heating technique. These rutile-phase, single-crystalline nanostructures, typically 40-90 nanometers in thickness, 200-1000 nanometers in width, and up to tens of micrometers in length, exhibit large areas of exposed crystalline faces that show an enhanced photocatalytic reac-
tion. Scaling up the synthesis method for bulk growth and ease of integration with existing microfabrication techniques has been studied for enhanced solar absorption of the titania nanostructures for possible large-scale water splitting applications under direct sunlight.

In the third area of this dissertation, silver nanowires arrays were synthesized using oblique-angle deposition (OAD). Based on the angle of metal deposition, the thin-film porosity and nanowire morphology can be controlled. These nanostructure substrates have been used as biological test platforms for nanotoxicology studies, with trends indicating cell viability decreased as the thin film porosity increased. Finally, experimental results of graphene nanopatterning with nanoimprint lithography (NIL) for electrical and optical devices are discussed. Chemical vapor deposition (CVD) graphene is transferred onto silicon oxide substrates and patterned using different NIL mold configurations.
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– John Burroughs

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Chapter 1

Introduction

1.1 The Potential Impact of Nanomaterials

Nanomaterials are expected to have a profound and lasting impact on society due to their outstanding electrical, optical, mechanical, and thermal properties exhibited relative to their bulk material state. High surface-to-volume ratios make nanostructures especially well-suited for sensor applications, such as chemical and gas sensing, where larger surface areas provide increased active areas for improved sensitivity, fast response, and lower power consumption [1–5]. In addition to supplying critical information about the local environment, sensors can behave as proxy extensions of human senses by collecting data from specific locations that might not be readily or safely accessible and constructing composite pictures of how larger regions are behaving. In the realm of micro- and nano-fabrication, which currently yields transistor nodes of 22 nm and is rapidly heading toward smaller device features [3, 6, 7], the current manufacturing capabilities appear near their limits. As a result, much research effort has been focused on solutions addressing these limitations to bridge the gap between scientific discovery and broad application of these concepts toward large-scale manufacturing capability and deployment. An outgrowth of these efforts is also pioneering and implementation of alternative synthesis and integration techniques to continue this trajectory towards large-scale nanostructure utilization.

With today’s society facing complex energy issues, the search for alternative sources of fuel and power are of tantamount importance. Nanomaterials can provide pathways toward achieving these alternative energy sources through the efficient conversion of solar energy into chemical or electrical energy and decreased dependence on fossil fuel-based materials [8]. Nanostructured surfaces with increased active areas and sensitivity to visible light can continue to improve upon energy conversion efficiencies and decrease fabrication costs as new manufacturing paradigms are implemented.

Nanomaterials also present an opportunity to transform medical and bio-oriented fields. With high sensitivity and the ability to functionalize surfaces for molecular selectivity, materials such as nanowires, nanotubes, and nanorods can produce extremely responsive devices
Additionally, nanostructures have potential use for \textit{in vivo} and \textit{in vitro} diagnosis and treatment of cancer and other disease-fighting therapies [9].

The following sections describe in greater detail the specific areas of focus for this dissertation, beginning with nanomaterial sensors, followed by potential nanostructure-based energy and environmental applications, and closing with the roadmap of the dissertation overview.

\section*{1.2 Sensors}

The need for low-cost, highly sensitive optical and electrical sensors may be fulfilled by the unique properties of nanomaterials: large surface-to-volume ratios that can lead to increased sensitivity, extraordinarily high current densities, and lighter, compact devices running with a smaller power footprint. Nanomaterials are already impacting key areas in detection applications, especially for chemical and biological sensing. The ability to rapidly, and with high sensitivity, recognize minuscule changes in the local environment is important for a multitude of applications including areas such as homeland security, air quality monitoring, fundamental science (searching for dark matter), and industry-based manufacturing and process engineering. Nanomaterials as chemical and biological detection elements are readily integrated into sensor devices since the device and nanostructure size scaling are similar.

Although many sensor designs incorporating nanomaterials are possible, current large-scale manufacturing configurations can include field effect transistors (FET) [1, 4], resistive sensing [10], and resonators [11].

Issues surrounding integration of nanomaterials involve the predetermined placement at specific locations and manipulation of the properties of those structures. The high temperatures often needed for nanostructure synthesis can require post-growth transfer processes that may not be compatible with microelectronics tools, processes, and thermal budget requirements. And yet, these new materials may create new manufacturing paradigms which provide an opportunity to drive down the cost of assembling and manufacturing devices while still taking advantage of the unique properties of nanomaterials.

FET configurations, which were initially based on planar thin film geometry, can be used as sensor devices. The gate voltage controls the nanostructure conductivity and nanostructures in FET configurations can show enhanced sensitivity since the binding of a charged species to a nanowire (NW) or nanotube (NT) causes a measurable change in the depletion or accumulation of charge carriers [1]. Because the bulk portion of the NW or NT can respond to surface charge changes due to binding, additional sensitivity is added such that single molecule detection is possible [1]. The ability to grow dense arrays of nanomaterials using large-scale synthesis methods also allows for integration and potential manufacturability of these types of sensors.

Incorporation of nanomaterials for large-scale deployment in electronic and sensor applications has been limited due to difficulties with synthesis and integration of the materials. In addition to research on different architectures such as spin-based electronics, one approach
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to address shrinking device size limitations is by replacing the conducting channel of a field
effect device with carbon-based nanomaterials such as carbon nanotubes and graphene [5].
According to the International Technology Roadmap, graphene warrants increased atten-
tion to improve progress as an alternate channel material for field effect transistors as the
fundamental limits for silicon-based devices is approached with the goal of technology applica-
tions integration by 2019-2020 [12]. Graphene is an ideal candidate nanomaterial due to its
high current density, high room-temperature mobility, and visible and infrared absorption
properties [5].

First introduced in 1995, nanoimprint lithography (NIL) is a fabrication method for high-
throughput, low-cost, large-area feature arrays by imprinting patterned hard-mold features
onto thermally (and ultraviolet light) responsive resists with patterned features transferred
by etching into the secondary substrate [13, 14]. Depending upon the initial mold design,
which can reach sub-25 nm features, various shapes can be fabricated onto molds and trans-
ferred [13]. NIL-templated nanostructures fabricated directly on substrates can address the
issues of nanomaterial morphology control since the mold features are repeatably patterned
onto subsequent substrates.

Graphene is considered a semimetal due to overlapping conduction and valence bands
and does not have an intrinsic band-gap, which makes its use in FET configurations prob-
lematic [15]. NIL patterning can provide one possible method for creating a band-gap in the
material by imprinting large-area arrays of interconnected nanoribbons since the band-gap
of a nanoribbon scales with its width [5]. NIL masks with feature resolution in the tens of
nanometers, and utilizing established microelectronics fabrication techniques such as reactive
ion etching (RIE), can transfer such patterned features to graphene. Due to almost end-
less possibilities of creating mask morphologies, NIL can produce a suite of nanofabricated
devices and sensing platforms with feature dimensions ranging from milli- to nanometer
morphologies.

Biosensors provide information about a biological or chemical change in the local en-
vironment and are often constructed of biological components integrated with electrical
transducers [16–18]. As a bio-chemical detector, biosensors can detect a multitude of targets
including ethanol, benzene, ions, and biomolecules such as glucose [17]. Plasmonic nanobio-
sensors, which are based on hybrids of biomolecules and plasmon-resonant nanostructures,
are potentially viewed as breakthrough technology for real-time and parallelized analysis [19]
for such applications (Figure 1.1). Key technical challenges for the realization of integrated
plasmonic devices include the controlled synthesis of nanomaterials and resulting morphol-
ogy as well as bioconjugate techniques for surface functionalization of the nanoparticles
[19]. Since localized surface plasmon resonant (LSPR) frequency depends on the nanomate-
rial morphology, e.g. size and shape, control over the synthesis aspect provides frequency
variation from visible to mid-infrared wavelengths of the energy spectrum (Figure 1.1) for
multiple biomedical detection applications [19]. Plasmonic biosensing, especially surface en-
hanced Raman spectroscopy (SERS), is a promising application for graphene-based devices
and sensing platforms [20–23].

For nanoelectromechanical (NEMS) applications, integration of the nanostructure sens-
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Figure 1.1: Nanoparticle morphology-dependent plasmon resonance ranges [24]. (a) gold spheres; (b) silver spheres; (c) SiO$_2$/silver core/shell nanoshells; (d) nanorods; (e) triangles; (f) nanocubes; and (g) nanorices.

...ing element with existing microelectronics at specific locations, and with connections to the macro-world, is necessary to detect changes in the local environment. Key issues preventing widespread nanomaterial integration include difficulties with handling and manipulating nanostructures as well as high growth temperatures that can negatively impact existing microelectronics. Efforts to manipulate nanostructures have involved labor-intensive or complicated processes [1, 4, 25–27], highlighting the challenges of integrating these structures with workable and scalable devices. Although recent research has shown bulk carbon nanotube (CNT) growth processes at lower temperatures [28–30], the ability to control the specific location and placement of CNTs, or other nanowires/nanorods, is important for integration into working devices. A particular advantage provided by the local synthesis method is the selectivity of nanostructure growth at specific locations. Self-assembled devices are synthesized rapidly within minutes and require little post-growth processing. Electrical connections to the macro-world provide both input power for nanostructure growth through Joule heating and bias voltages for sensor detection capability.
1.3 Energy and Environmental Applications

Energy security to sustain societal energy demands is a top priority. Current energy sources can be grouped into three main focus areas: (1) chemical or photophysical energy used to generate heat or electricity, typically oxidation of a hydrocarbon or absorption of solar energy; (2) nuclear processes involving fission or fusion; and (3) thermomechanical energy produced by wind, water, or steam [8]. Alternative energy sources independent of fossil fuels have been pursued to help meet increases in global demand and prepare for depletion of fossil fuels [8]. Of the potential new resources, the sun is viewed as the most reliable and abundant source available with energy obtainable through use of such devices as photovoltaics and photoelectrochemical cells [8]. To improve energy conversion efficiencies for these applications, much research effort has focused on the development of materials that can take advantage of the visible light region.

Metal oxides, such as titanium dioxide (TiO$_2$), form a promising class of materials for energy and environmental applications. They have unique properties that can be enhanced by bulk material doping or surface treatments and are often used for catalysis with other metal elements as well as photocatalysis, photovoltaic, and photoelectrochemical applications [31]. While titanium dioxide has a wide bandgap ($\sim$3 eV) making it stable and corrosion-resistant [31], the material photoresponse is in the ultraviolet light region. Previously, groups have shown visible light response improvement using a variety of methods by doping with metals [32, 33] and non-metals [34–36], dye-sensitization [37], combining with other oxides [31], and more recently through hydrogen-disordered surfaces which demonstrated enhanced sensitivity to visible and infrared light [38].

Since the 1972 landmark publication by Fujishima and Honda [39], where TiO$_2$ was first used as a photoanode to decompose water into its constituent components of hydrogen and oxygen from ultraviolet light excitation, much research effort has been focused on using TiO$_2$ and other metal oxides as photoanode materials for water splitting and other photocatalytic applications.

TiO$_2$ nano- and microparticles, along with zinc oxides, are often used in industrial applications such as pigment for paints and sunscreen materials. TiO$_2$ is also used for gas sensing due to its sensitivity to reducing and oxidizing gases [31] and is an important material for photocatalytic applications such as self-cleaning coatings for windows as well as destroying harmful bacteria from water supplies [40–44]. A well-known energy applications for TiO$_2$, brought to prominence by Grätzel, et al. [37], is as scaffolding for dye-sensitized solar cells (DSSC).

Heterogeneous photocatalysis, one of the most promising applications of TiO$_2$ nanostructures, consists of five stages: (1) transfer of reactants to particle surface; (2) adsorption of reactant at the surface; (3) reaction of adsorbate; (4) desorption of product; and (5) product removal from surface region [45]. Figure 1.2 illustrates the photocatalytic process for a titania nanoparticle (adapted from [45]). When a photon of energy equal to or larger than the bandgap of the material encounters the surface, the photon is absorbed causing generation of electron-hole pairs which migrate to the surface and interact with adsorbed species [45].
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The morphology, shape, and size of nanoparticles can affect overall photocatalytic performance with surfaces of higher energy shown to be more photoactive than equilibrium low index surfaces [46–51]. An emerging field is the design and engineering of nanoparticles with increased areas of specific surface orientations. For example, TiO$_2$ anatase nanoparticles with increased percentage of exposed higher energy surfaces have been demonstrated with the expectation that those surfaces should lead to enhanced photocatalytic activity [52–55]. Although the main impetus of designing nanocrystal surfaces is focused on photocatalysis, other TiO$_2$ applications may also show performance enhancement as well.

Photocatalytic (PEC) cells, which in their simplest form consist of a semiconductor electrode, metallic electrode, and electrolyte [56], occupy a unique position for efficient light energy harvesting compared to photovoltaics and natural photosynthesis [57]. Photovoltaic cells can suffer from high fabrication costs despite higher energy conversion efficiencies while natural photosynthesis, although relatively inexpensive, has inefficient energy conversion processes [57]. PEC cells are a promising option for high conversion efficiencies and associated lower fabrication costs. For TiO$_2$ nanostructures, the ability to sensitize the material to the visible light range while maintaining stability and corrosion-resistance can provide a favorable low-cost material with higher energy conversion efficiencies.

As nanomaterials are increasingly integrated into society, it is worth consideration of how living organisms may be affected by the influx of natural and engineered nanoparticles. Cell and organism response to nanomaterial exposure through waste streams, water, inhalation or absorption through the human body is cause for concern [58]. Evidence suggests that there is a relationship between exposed surface area of a nanoparticle with reactive oxygen species (ROS) generation and resulting inflammation of lung tissue [59], with morphology and phase of nanomaterials influencing risk [58]. Engineered silver nanoparticles were shown to have a dose-dependent affect on zebrafish embryo development [60, 61].

To provide more information about cell response to the morphology, size, and phase of nanomaterials, test platforms of repeatable patterns and shapes could provide invaluable information about these environmental effects on cells. Additionally, fabrication methods with repeatable morphologies can provide additional information of how cells behave when in contact with the increased surface areas of nanostructures.
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1.4 Outline of Dissertation

The promise of nanomaterial applications has been tempered by issues such as placement of nanostructures in specific locations and integration with existing microelectronics platforms. Synthesis techniques that can be scaled up and integrated with existing micro- and nanofabrication processes or by using conventional tools in novel ways, may provide pathways for greater use of nanomaterials in sensor and energy applications. Early nanostructure characterization techniques relied heavily on labor-intensive methods and although important information about the fundamental properties of individual nanostructures was provided, the practicality of employing such methods on a large-scale is not realizable.

New nanomaterials with controlled growth features and well-characterized behavior will be drivers of technological advancements and are still a work in progress. Bridging the gap between the synthesis and integration of these nanostructures with the larger world for useful applications is a main focus of this work. The following chapters give an overview of key areas where nanomaterials can have a profound influence on society through improvement in design and engineering of nanostructures for enhanced performance, large-scale coverage for array-based sensing and testing platforms, by increasing awareness for health and environmental concerns, and pathways for alternative energy options.

As shown in Figure 1.3, this dissertation focuses on the synthesis and integration of nanostructures for sensor, energy, and environmental applications, and is divided into three main sections: (a) electrothermal carbon nanotube gas sensing; (b) titanium dioxide nanostructures for photocatalytic processes; and (c) silver nanowire platforms for biosensing and nanopatterned graphene for electrical and optical sensing.
Figure 1.3: The synthesis and integration of nanostructures for sensor, energy, and environmental applications. (a) Local synthesis of carbon nanotubes with gas sensing demonstration; (b) TiO$_2$ nanosword with large % of exposed, higher energy surfaces with photocatalytic enhancement demonstration. The synthesis process is scaled up with nanostructure doping for visible light enhancement and photoelectrochemical enhancement; (c) Silver nanowires grown with oblique angle deposition for robust, repeatable, large-area platforms for nanophotonic and nanotoxicology experiments; and (d) Nanopatterning of graphene using nanoimprint lithography for large-area fabrication of nanomeshes and metamaterials for electrical and optical sensing applications, including surface enhanced Raman spectroscopy.

Chapter two, the first section, emphasizes the strategic placement and \textit{in situ} characterization and use of as-grown nanostructures as direct sensing elements. The rapid, microelectronics-compatible, local synthesis method is described in detail with a gas sensing demonstration based on an electrothermal effect. The use of a CNT as a Pirani gauge is demonstrated for the first time with a two-terminal connection and resistivity dependent on the number of molecules present in the volume of interest. The ability to conduct \textit{in situ} characterization for improving the contacts is also shown with a local annealing process. Higher temperatures and longer times appear to improve the system resistance with minimal impact on the CNT itself.

Chapter three, representing section two, discusses a unique TiO$_2$ nanostructure (‘nano-
sword’) synthesized using an induction heating process, where eddy currents are generated in the conductive substrate and the resulting resistive heating provides the temperatures required for nanostructure growth. The sword-shaped nanostructures exhibit a large % of exposed higher surface area; photocatalytic experiments of TiO$_2$ nanoswords were conducted using silver reduction to compare results with other low index equilibrium surfaces of rutile titanium dioxide. Here, the idea of engineering specific faces for applications such as photocatalysis is explored. The TiO$_2$ nanosword showed significant photocatalytic enhancement and hydrogen-annealed samples exceeded that performance. Further characterization and a gas sensing device were attempted to extract additional information about the as-grown, oxidized, and hydrogen-annealed nanostructures.

The second half of chapter three focuses on scaling the growth process of titanium dioxide nanostructures for large-area coverage while incorporating the the unique features of the induction heating process. As-grown and hydrogen-annealed samples were tested in a photoelectrochemical experimental setup with the hydrogen-annealed samples exhibiting significant enhancement under one sun illumination. Here, two key issues are related to the large-scale impact and effectiveness of this material: a) can visible light photoresponse be obtained with repeatable results over a long period of time, which could capitalize on using visible solar spectrum to power such devices and translate into viable water-splitting or other clean energy applications; and b) can specific crystalline faces be exploited for improved photocatalytic activity, which could translate into improved sensitivity of the nanostructures for photocatalytic processes.

Chapter four, the third section, is divided into two areas. The first area explores the fabrication of repeatable and large-area coverage of silver nanowires for biosensing and nanotoxicology applications. Using an oblique angle deposition (OAD) process, the porosity of the thin films is controlled by the substrate angle during electron beam metal deposition. The increased surface area of the porous, nanostructured silver surfaces was used to assess the potential toxicity of nanosilver on cells. The cell % viability was shown to decrease, suggesting that substrate morphology may influence cell survivability.

The second area of chapter four focuses on nanopatterning of graphene for electronic, optical, and optoelectronic sensing using nanoimprint lithography (NIL). NIL uses thermal or ultraviolet light sensitive polymers to transfer a previously created mold imprint to another substrate with reactive ion etching (RIE) providing pattern transfer. For a mold containing arrays of pins fabricated by diblock copolymers (tens of nm in diameter), a repeatable and large-area pattern transfer to graphene can occur. With interconnected graphene nanoribbon meshes of specific dimensions, graphene can exhibit a bandgap which enables various sensor configurations for electrical and chemical sensing. Optical features can also be built up onto graphene using NIL patterning capability, providing biosensing opportunities such as surface enhanced Raman spectroscopy (SERS).

Chapter five presents observations and suggestions for future directions of the above investigated nanomaterial synthesis and integration work. Specifically, the contribution of this work to enable synthesis and integration of nanomaterials for large-scale deployment in sensing, energy, and environmental applications is discussed.
Chapter 2

An Electrothermal Carbon Nanotube Gas Sensor

2.1 Introduction

Since their discovery in 1991 [62], carbon nanotubes (CNTs) have since provided a model 1D system for experimental study of their outstanding electronic, optoelectronic, thermal, and optical properties for applications such as electronic switching, logic devices, and photodetectors [5]. Chemical and biosensors consisting of functionalized CNTs have also shown extreme sensitivity and selectivity [5]. CNT gas sensing devices have been shown to operate under fundamentally different mechanisms [63], including sharp tips as gas ionization sensors [64] and electrical conductance or capacitance changes [4, 65, 66]. Factors contributing to limited sensing capabilities for sorption-based CNT sensors include response speed, reversibility, selectivity, diffusion kinetics, and low adsorption energies.

This chapter describes the electrothermal effect of a single multiwalled CNT suspended between two silicon microbridges, device characterization to improve the interfacial CNT-silicon contact, and overview of the local synthesis process. When exposed to different pressures, the electrical resistance of a Joule heated CNT changed proportionally to the conductive heat transfer variance of gas molecules. The local synthesis process was used to fabricate an on-chip single CNT at a specific location within tens of seconds and monitored with a real-time feedback control system. The electrothermal CNT device may have applications for both gas sensing and species differentiation with advantages including compactness, fast and reversible responses, low power consumption, and ease of integration with standard microelectronics fabrication processes. Device characterization and methods to improve the secondary contact resistance were investigated and followed with a pressure sensing demonstration for a self-assembled, integrated nanosensor application.
2.2 Local Synthesis

As shown in Figure 2.1, the local synthesis method provides microelectronics-compatible CNT (or nanowires/nanorods) growth, integration, and placement for self-assembled devices. Resistive heating at specific on-chip locations avoids the required high global temperatures (up to 1000°C) for furnace growth of nanostructures and preserves pre-existing microelectronics [67, 68]. Post-processing and manipulation of nanostructures is minimal since the nanostructures grow in specified regions and are self-assembled into readily integrated microfabricated devices.

Figure 2.1: Conceptual schematic of controlled growth local synthesis method integration with microelectronics for wafer-scale applications [69].
2.2.1 Experimental Details

The local synthesis process uses resistive heating of silicon microbridges to generate the required nanomaterial growth temperatures. The suspended microbridge material consists of a highly doped, single crystalline silicon-on-insulator (SOI) wafer with a device layer of 15 or 20 µm and buried oxide layer of ~2µm thick. The $p^+$-type silicon device layer has a resistivity of $1 \times 10^{-2} \, \Omega \, \text{cm}$ and impurity concentration of $1 \times 10^{19} \, \text{cm}^{-3}$. As shown in Figure 2.2, microbridge lithography and etching are performed using standard micromachining processes [67]. The specimens are diced into 3 or 5 mm$^2$ dies with die size depending on the number and design of the microbridges. To release the microbridges from the sacrificial oxide layer, the samples are placed in a timed hydrofluoric acid (HF, 49%) etch of four minutes, then rinsed in deionized (DI) water. A ten minute piranha (3:1 sulfuric acid:hydrogen peroxide solution) clean followed by a DI water soak is performed prior to the HF etch in order to remove residual organic material from the dicing process. The timed HF etch removes the oxide beneath the bridges, while providing electrical and thermal isolation for the contact pads. Gaps between adjoining microbridges span 5 to 10 µm for U-shaped bridges and 20 to 25 µm for V-shaped bridges. Microbridge dimensions are typically 150 µm in length, 5 µm in width, and 15 to 20 µm thick.

Figure 2.2: Fabrication process for silicon microbridges [67]. (a) SOI wafer with device layer thickness of 15 or 20 µm; (b) Device layer patterning and etching of microbridges; (c) Sacrificial layer etching to release the micro bridges from the substrate; (d) Catalyst evaporation; (e) Electrical connections via wirebonding for Joule heating of substrate; and (f) Nanostructure growth on heated microbridge substrate. Growth conditions are listed in Table 2.1.
Once the microbridges are released from the oxide layer, a catalyst layer (iron or nickel-iron) of one to five nm thickness is deposited using thermal or electron beam deposition. Following the metal deposition, the dies are individually attached to a 24-pin ceramic package and wirebonded for electrical connections. Figure 2.3 shows the experimental chamber setup for local synthesis and a scanning electron microscopy (SEM) image of the resulting CNT suspended between two silicon microbridges. The package is mounted inside the vacuum chamber and the circuit connected as shown in Figure 2.5(a). Electrical feedthroughs allow the data acquisition system and other monitoring equipment to be connected to the individual device.

Figure 2.3: Experimental setup for local synthesis. The die containing microstructures is bonded to a 24-pin ceramic package, electrically connected, and placed inside the vacuum chamber. Electrical feedthroughs allow direct connection to the structures for heating of the substrate and monitoring nanostructure growth. An SEM image of as-grown CNT resulting from local synthesis is shown in the enlarged image. Growth conditions are listed in Table 2.1.

Once the package is connected properly, the chamber is sealed and the system pumped down to ~250 Torr. Pressure gauges on either side of the inlet/outlet of the chamber monitor the pressure while the flowmeters control the gas flow rates. Typical growth conditions are shown in Table 2.1. Prior to CNT growth, the chamber is purged and argon gas flowed (~100 sccm) for several minutes to remove oxygen from the system. The system is then pumped down with the flowrate remaining at 100 sccm and power applied to the microbridges until heated sufficiently for CNT growth. Figure 2.4(a) shows a top view SEM image of the wirebonded pads and microbridges. The wirebonds do not touch each other. Figure 2.4(b) is a post-growth SEM image of CNTs located farther away from the "hot spot". The CNTs grow from wherever the catalyst layer has nucleated into small nanoparticles.

As shown in Figure 2.5(a), a bias voltage $V_1$ is applied to the microline heaters which is incrementally increased over time. Once the microstructure temperature reaches the appropriate growth temperature, acetylene ($C_2H_2$) is flowed through the chamber at 50 to 60 sccm with the balance of argon gas maintaining the same flowrate through the chamber during
both the heating and growth processes. The CNT growth occurs by means of a chemical vapor deposition (CVD) process, activated when the carbon-based gas flows over the heated microbridge and interacts with the catalyst layer.

Figure 2.5: Schematics of CNT growth via localized synthesis method [69].
A second bias voltage, $V_2$, provides an electric field and growth direction for the CNTs (Figure 2.5(b)). Using a voltage-divider configuration, a resistor ($R \sim 18 \text{ M}\Omega$) is applied to the secondary silicon microbridge to prevent excess current flow through the device once the CNT contacts the second microstructure. An electrical feedback system is used to monitor voltage jumps that occur when CNTs make contact with the secondary microbridge [69]. The typical growth conditions are shown in Table 2.1.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>850-900°C</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_2$/Ar gas</td>
<td>60 / 55 sccm</td>
</tr>
<tr>
<td>Chamber Pressure</td>
<td>250 Torr</td>
</tr>
<tr>
<td>Microbridge Gap Distance</td>
<td>5-20 $\mu$m</td>
</tr>
<tr>
<td>Voltage Bias, $V_2$</td>
<td>2-5 V</td>
</tr>
<tr>
<td>Electric Field ($V_2$/gap)</td>
<td>0.2 - 1 V $\mu$m$^{-1}$</td>
</tr>
<tr>
<td>Catalyst Thickness (Ni/Fe)</td>
<td>1-5 nm</td>
</tr>
</tbody>
</table>

2.2.2 Results

As shown in the SEM image of Figure 2.3, multiple CNTs grow outward from the heated microstructure, but only one or several CNTs typically will grow across the gap between the two microbridges. Since the successful CNT growth location is often off-center and is correlated to the micro bridge "hotspot", the Thompson effect should be considered when designing microstructures for local synthesis processes [67]. Typical CNT growth results include diameters and lengths ranging from 10 to 50 nm and 5 to 25 $\mu$m, respectively. Growth rates vary from 0.25 $\mu$m min$^{-1}$ [67] to upwards of tens of $\mu$m min$^{-1}$ [70].

Immediately following growth, a current-voltage (I-V) scan is performed to evaluate the condition of the CNT and contact with the secondary substrate. The sweep is performed three times to establish the stability of the CNT device. Figure 2.6 shows typical I-V curves taken immediately following growth. In Figure 2.6(a), the linear behavior indicates ohmic contacts between the CNT and each microbridge. Although the I-V curve in Figure 2.6(b) appeared to represent a rectifying behavior, this particular response may be the result of several factors including a native oxide barrier layer present between the CNT and the silicon substrate, and/or an end or tip CNT contact with the secondary microstructure.
Figure 2.6: Typical post-growth I-V curves of suspended CNTs. (a) Ohmic; and (b) Schottky-type responses. Three I-V curves are taken to verify the contact stability.

2.3 Characterization

2.3.1 Overview

The local synthesis method is a platform suitable for direct integration with pre-existing microelectronics since only specific regions, rather than the global environment, are heated during the synthesis process. The direct growth of nanostructures does not require post-processing transfer to different substrates, which simplifies the integration process and allows the microbridge system to serve as the sensing platform. One issue of consideration is the contact resistance of the secondary substrate during the process which can be high or low depending on how the nanostructure and microbridge connect. Previous efforts to improve the contact resistance between nanostructures and substrates have included electrical breakdown [71], carbide or silicide formation [72–74], electron beam irradiation [75], ultrasonic bonding [76], rapid thermal annealing [77], or Joule heating of large platinum or palladium contacts deposited via ebeam lithography [78–80].

Here, single CNTs are used to investigate the contact resistance resulting from the local synthesis growth process and effects of local annealing methods to improve the resulting electrical contact. Equation 2.1 describes the total resistance of the silicon-CNT-silicon system as a function of individual resistances [81]:

\[
R_{Total} = R_{Si, growth} + R_{Contact1} + R_{CNT} + R_{Contact2} + R_{Si, secondary}
\]  

(2.1)

where \( R_{Total} \) is the total resistance of the system, \( R_{Si, growth} \) and \( R_{Si, secondary} \) are the resistance of the growth and secondary substrates (\( \sim \)several hundred \( \Omega \)), \( R_{CNT} \) is the resistance of the
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CNT (ranging from Ω to kΩ [82]), $R_{Contact1}$ is the contact resistance of the growth structure (assumed small), and $R_{Contact2}$ is the contact resistance between the as-grown CNT and the secondary substrate (the highest expected resistance value). $R_{Total}$ can be measured post-growth while the sample remains under inert conditions inside the chamber.

2.3.2 Improving Contact Resistance

As shown in Figure 2.7, multiwalled CNTs are grown across microbridge gaps of 5 to 20 µm. Once a successful connection is detected by the voltmeter and indicated by a voltage increase, a current-voltage (I-V) scan is run from -1 to 1 V using a semiconductor parameter analyzer (HP-4145B) to establish the stability of the CNT and contact.

Without opening the chamber to atmosphere after the growth process and maintaining a pressure of $3.3 \times 10^4$ Pa with an argon gas flow rate of 100 sccm, the chamber is initially purged with argon gas to remove residual carbon-based gases. The annealing process begins once the contact is determined to be stable by the I-V curves. Figure 2.8 shows schematics of the two low- and one high-power annealing techniques evaluated. As shown in Figure 2.8(a), the first low-power annealing process involves incrementally increasing the voltage on the growth side (0.5 V every 5 seconds), generating an electric current from the growth side through the CNT with voltage monitoring on the secondary side. Thus, power flows through the entire silicon-CNT-silicon system. To check the stability of the contact, three I-V curves are recorded each minute. During the power ramp-up process, the voltage is increased until the power output reaches 25 to 28 µW. The power range is intentionally kept low to avoid damaging the CNT connection [79] and is also based on previous experimental evidence.

Figure 2.7: SEM image (top view) of CNT spanning V-shaped microbridge gap of ~8µm [81].
showing high power input through the entire system can destroy the CNT. The voltage is held constant once the desired power range is achieved and then decreased incrementally (0.5 V every 5 seconds) until zero voltage. Initial and post-anneal I-V curves can then be compared for changes due to the annealing process. As shown by Equation 2.1, the resistance between the CNT and secondary microbridge ($R_{\text{Contact2}}$) is expected to dominate all other resistances such that the contact area should become locally heated.

As shown in Figure 2.8(b), the low-power (option 2) and high-power techniques are similar in that the only the secondary microbridge is heated. For the low-power technique, power is monitored through the secondary microbridge side and increased to 30 mW (0.5 V every 5-10 seconds) with both microbridges monitored for current output. Any drastic decreases in current indicate that the CNT is either broken or no longer connected to the microbridge. Since $R_{\text{Contact2}}$ again dominates the system, the local area where the CNT contacts the secondary microbridge is expected to heat up with little current flowing through the CNT to the growth side and avoiding damage due to high power flux through the CNT.

![Figure 2.8: Schematics of annealing techniques. (a) Low-power (option 1) annealing. Voltage is incrementally increased through the entire silicon-CNT-silicon system and output current is monitored; (b) Low-power (option 2) and high-power annealing processes occur as the secondary microbridge is Joule heated. [81].](image)

The high-power annealing technique is similar to the low-power (option 2) process. Only the secondary microbridge is heated by incrementally increasing the voltage by 0.5 V every 5 to 10 seconds until the desired temperature is achieved, typically $>600^\circ\text{C}$, and visually noted by a dull red emission from the secondary bridge. The currents through both bridges (growth and secondary) are monitored during the process while the temperature is held constant for the desired time. Post-annealing I-V curves are taken to confirm that the CNT-silicon microbridge connection remains intact and robust.

As shown in Figure 2.9, power and temperature estimates for the three techniques are based on the results of an ANSYS® (v. 11.0) simulation. The low-power (option 2) process of heating the secondary bridge has approximately 30 mW of power input into the system with an estimated bridge temperature of less than 100$^\circ\text{C}$. The first low-power pro-
cess (Figure 2.8(a)), with current flowing through the entire system, is not evaluated by the simulation. In this case, low temperatures are assumed since the power input is in the $\mu$W range. The high-power technique has power input ranges of 100 to 150 mW and estimated bridge temperatures greater than 600°C.

### 2.3.3 Results

As shown in Figure 2.10, stable I-V measurements of pre- and post-anneal results can be used to compare the resistance values which are calculated by assuming a linear I-V relationship. Equation 2.2 is used to calculate the percentage change of the resistance ratio

$$\text{Resistance Ratio Change (\%)} = \frac{R_{\text{Final}} - R_{\text{Initial}}}{R_{\text{Initial}}}$$

which is defined as the difference in pre- and post-annealing resistances divided by the as-growth resistance.

Table 2.2 gives additional details of the fifteen samples tested thus far, including information about the annealing technique and catalyst-only or catalyst-metal stack (molybdenum-aluminum) beneath as developed in our lab [83]. Nine samples exhibited a decrease in calculated resistance ratio with two of those samples showing a decrease >50%. The pre- and post-annealing resistances are tabulated in histogram format (Figure 2.11) for direct comparison.

As shown in Figure 2.12, resistance ratio percentage changes are plotted versus time and as a function of annealing temperature. All times for low-power annealing samples are three minutes or less except for one sample annealed for approximately five minutes. As noted
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Figure 2.10: Simulation of microbridge temperatures at different power inputs [81].

Figure 2.11: Histogram of resistance values estimated from pre- and post-anneal I-V measurements [81].
<table>
<thead>
<tr>
<th>CNT Sample No.</th>
<th>Pre-Anneal Resistance (kΩ)</th>
<th>Post-Anneal Resistance (kΩ)</th>
<th>Metal Stack&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Annealing Method&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6,800</td>
<td>3,400</td>
<td>A</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>250</td>
<td>100</td>
<td>A</td>
<td>3</td>
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<tr>
<td>3</td>
<td>540</td>
<td>910</td>
<td>A</td>
<td>3</td>
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<tr>
<td>4</td>
<td>120</td>
<td>890</td>
<td>A</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>110</td>
<td>90</td>
<td>B</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>2,100</td>
<td>1,600</td>
<td>B</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>540</td>
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<td>B</td>
<td>2</td>
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<td>8</td>
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<td>B</td>
<td>1</td>
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<td>13</td>
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<td>1</td>
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<td>14</td>
<td>160</td>
<td>160</td>
<td>A</td>
<td>2</td>
</tr>
<tr>
<td>15</td>
<td>420</td>
<td>570</td>
<td>B</td>
<td>1</td>
</tr>
</tbody>
</table>

<sup>a</sup> Metal thin film evaporated onto the microbridges: (A) iron only; (B) molybdenum-aluminum-iron stack; <sup>b</sup> Annealing methods are as follows: (1) low-power (option 1) entire system; (2) low-power (option 2) secondary side only; (3) high-power, secondary side only.

In Table 2.2, both low-power techniques use either thin films of iron catalyst alone or on top of the molybdenum-aluminum stack. Although the metal stack has shown significant reduction in resistance for CNT forests and substrates [83], the metal stack beneath the catalyst layer does not appear to notably affect the CNT-silicon resistance of locally grown CNTs at low-power annealing temperatures.

For higher power and longer time annealing, the secondary microbridge temperatures are estimated at 500 to 900°C based on input power values of 100 to 150 mW. All four samples annealed with this technique demonstrated decreased resistances after annealing with one resistance ratio decreasing more than 80%. Due to the promising results shown, higher-power or longer-time annealing processes should be investigated for potential impact on resistance values.
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2.4 Pressure Sensing Demonstration

In addition to taking advantage of the unique properties that nanostructures exhibit, several driving forces for nanomaterial research and device integration include the desire to shrink device features and lower power consumption. Miniaturization provides the capability for low-cost and widely-distributed sensor networks. Lower power consumption enables large arrays so that sensors can perform environmental information-gathering with minimal maintenance. As sensors become less invasive in terms of space and require less power, another issue to consider is a biomimicry aspect. A gas sensor can potentially act as an "electronic nose" by providing differentiation among multiple gas species at particular locations and transmitting such information as a snapshot of real-time local conditions. An example of an "electronic nose" can include arrays of chemical-based field effect transistor (chemFET) sensors with each individual FET capable of evaluating a specific gas species [84]. The local synthesis of CNTs may provide another mechanism for array sensing on a large scale.

In this section, a self-assembled CNT pressure sensing device based on an electrothermal mechanism is demonstrated (Figure 2.13). The CNT device is synthesized using the local synthesis platform, self-assembled within seconds, and can begin functioning immediately after growth. Evidence suggests that this system can be used for gas sensing based on the electrothermal behavior and since carbon nanotubes are extremely sensitive to their surrounding environment, electronic "tuning" of devices may also be possible [65]. The device shown in Figure 2.13 was used for the pressure sensing demonstration.

Figure 2.12: Resistance Ratio Change (%) versus annealing time with respect to estimated temperatures of secondary microbridge [81].
As shown in Figure 2.14, the electrothermal response of the CNT-silicon device is based on energy conservation of the system and consists of energy conducted at the contacts ($W_C$), through the gas ($W_G$; shown as $W_{gas1}$ and $W_{gas2}$), and by radiation ($W_R$). The total energy of the system ($W_{Total}$) can then be described as

$$W_{Total} = W_R + W_G + 2W_C$$

(2.3)

where $2W_C$ represents the two CNT-silicon microbridge contacts and the heat conduction from the CNT to the microstructures through the contacts, $W_G$ is the heat transfer between gas molecules and the system with associated thermal conductivity values, and $W_R$ represents the radiative heat transfer from the system to the surrounding environment. The low power applied to the single, suspended CNT also heats it as energy is dissipated through one of
the previously described mechanisms. Both gas species and pressure can affect how much the overall system resistance will change.

The relationship between pressure and energy loss through the gas can be described by three distinct regions dependent upon the Knudsen number, $K_n$ (see Appendix). $K_n$ is a dimensionless number based on the ratio of the mean free path ($\lambda$) between gas molecules and the length scale involved, $D$ (here, the CNT diameter).

In the molecular regime, intermolecular collisions among gas molecules will occur more frequently than collisions between the CNT and chamber walls [85]. As discussed in theories of thermal conductivity gauges [85, 86], gas molecules will impinge on the surface of the CNT carrying an energy distribution corresponding to $T_O$. After a short dwell time on the CNT surface, energy transfer has occurred such that the gas molecule leaving the CNT will now have an energy distribution corresponding to $T_{CNT}$. The heat transfer between a single CNT and an arbitrary coaxial cylinder surrounding the CNT system can be described by the following equation [87]:

$$W_G = \frac{1}{4(\gamma - 1)} \alpha \sqrt{\frac{2R}{\pi MT_O}} (T_{CNT} - T_O)p$$  \hspace{1cm} (2.4)

where $\gamma$ is the ratio of specific heats of the gas, $\alpha$ is the thermal accommodation coefficient accounting for the heat transfer between the CNT-molecule interaction and depends on the particular gas molecule, $R$ is the universal gas constant, $M$ is the molecular mass of the gas, and $p$ is the pressure. $T_{CNT}$ and $T_O$ represent the Maxwellian energy distribution of the CNT and surrounding environment, respectively. Considering Equation 2.4, $W_G$ is proportional to $p$ if all other parameters are held constant. As the total energy in the device is increased as a function of input power, the CNT system runs "hotter" causing an increase in $T_{CNT}$. $W_G$ would then be expected to increase and provide improved device pressure sensitivity.

The pressure sensing configuration is built upon the local synthesis device architecture described in previous sections. Here, the electrical configuration is changed to incorporate a resistor, $R$, in a voltage divider configuration. As shown in Figure 2.15, $R$ is approximately 100 kΩ, chosen to match the estimated CNT resistance and maintain steady current flux through the system.

### 2.4.1 Results

The device exhibited an electrothermal behavior with the CNT acting as a variable resistor and output depending on the number of gas molecule collisions with the CNT [70]. At higher pressures, more gas molecules are expected to collide with and dwell on the surface of the CNT (Figure 2.16). The resulting energy transfer from the hot CNT to the gas molecule is expected to lower the temperature of the CNT. At lower pressures, where fewer collisions between the CNT and gas molecules occur, the CNT will maintain its temperature due to the low power input and a different resistance output is expected and denoted by a change in the I-V measurements. As shown in Figure 2.17(a), the initial I-V curve taken at atmospheric
pressure is linear (blue curve) and suggests that both CNT-silicon contacts are ohmic at low power input. As the pressure decreased, the I-V curve became non-linear (Figure 2.17(a), red curve). The I-V curves were taken immediately following growth of the CNT in an argon environment with no additional exposure to air or oxygen prior to these measurements. Such exposure could potentially alter the CNT response since CNTs have been shown to be extremely sensitive to oxygen [65]. The nonlinear behavior is similar to a Pirani (thermal conductivity) gauge response to changes in pressure [88]. As expected, the device pressure sensitivity is greatly improved as the input power to the system increased (Figure 2.17(b)).

![Figure 2.15: Pressure sensing configuration. R is \(\sim 100 \text{ k}\Omega\).](image)

The CNT resistance behavior was measured over a temperature range of 200 to 400 K. The temperature coefficient of resistance (TCR) is estimated at -0.137% K (see Appendix for TCR curve). At pressures of \(10^5\) and \(6.5 \times 10^3\) Pa, the expected CNT temperature increase

![Figure 2.16: Schematic of electrothermal pressure sensing mechanism at atmospheric and low pressures [70].](image)
over ambient is 40 and 140 K, respectively [70]. Electron scattering due to hot nonequilibrium optical phonons is not expected for this device due to the low power input [70].

The sensing capabilities of the device were determined in a high-vacuum chamber of the SEM (LEO 1550) and results compared to the in situ Pirani and ion gauge readings as a function of pumping time. Initially the Pirani gauge of the SEM will respond to pressure range $10^{-4}$ to $10^{-1}$ Pa followed by the ion gauge for pressures less than $10^{-1}$ Pa. The device was exposed to five cycles of alternating nitrogen and air environments with the CNT exhibiting a steady and repeatable response (Figure 2.18, red curve) to a pressure range of $10^{2}$ to $10^{5}$ Pa. Once the high-vacuum regime was reached, the CNT output remained constant. The SEM Pirani and ion gauge curve responses are blue and green, respectively.

Figure 2.19 shows the CNT device output voltage data as a function of pressure. The output voltage changes from 1 V and converges to approximately 0.97 V as pressure drops below $10^{3}$ Pa. Based on this information, the baseline energy loss for the CNT can be established for an ideal case where the total energy loss is dependent on losses through the contacts and radiation only ($W_{Total} = W_C + W_R$) or considered pressure independent energy losses [88]. $W_{Total}$ is experimentally determined from the power input to the system ($W_{Total} = V^2 R^{-1}$).

Using Equation 2.5, $W_R$ can be estimated with

$$W_R = \epsilon \sigma (T_{CNT}^4 - T_O^4) A$$  \hspace{1cm} (2.5)$$

where $\epsilon$ is the emissivity, $\sigma$ is the Stefan-Boltzmann constant, and $A$ is the cross-sectional
Figure 2.18: Output voltage and pressure as a function of SEM chamber pumping time [70].

Figure 2.19: The pressure sensing baseline values are determined from $W_C$ and $W_R$. As pressure increases, the influence of energy losses via molecular collisions affects the device output [70].
area of the CNT. For a CNT with a φ20 nm and 25 µm length, the estimated loss due to radiation is less than 20 nW.

An approximation for the energy loss through the contacts can be found using Equation 2.6

\[ \frac{1}{2} W_C = k_{CNT} A \frac{dT_{CNT}}{dl} |_{l=0} \]  

(2.6)

where \( k_{CNT} \) is the thermal conductivity of the CNT, \( A \) is the interfacial contact area between the CNT and silicon microstructure, and \( \frac{dT_{CNT}}{dl} \) at \( l = 0 \) is the slope of the CNT temperature profile at the CNT-silicon microbridge growth interface. Radiation losses are three orders of magnitude less than the losses due to conduction at the contacts and considered negligible. \( W_C \) can then be approximated as \( W_{Total} \), i.e. \( W_C = W_{Total} - W_R \) which is \( \sim 7.5 \) µW. Thus, the baseline pressure sensing limit is dominated by the energy losses at the contact. Interestingly, the thermal conductivity of the CNT can be determined from Equation 2.6 and requires an estimate for \( \frac{dT_{CNT}}{dl} \) at \( l = 0 \). A simplified model describing a symmetric, first-order approximation of the CNT temperature profile is constructed (Figure 2.20) with \( \frac{dT_{CNT}}{dl} \) taken from the initial slope of the curve and estimated at \( 2 \times 10^7 \) K m\(^{-1}\). An estimated value for \( k_{CNT} \) is \(< 300 \) W m\(^{-1}\) K\(^{-1}\) which falls within the lower end range of previously reported experimental and theoretical values [89–92]. In this case, though, the lower value for \( k_{CNT} \) is beneficial for the thermal-resistive sensing effects. A combination of lower \( k_{CNT} \), smaller CNT/substrate interfacial contact area (i.e. smaller diameter), and/or less steep slope of \( \frac{dT_{CNT}}{dl} \) by having an increased CNT length would contribute to decreasing the value of \( W_C \) and thus increasing the baseline pressure sensing limit.
As the pressure increases and more gas molecules are involved in the heat transfer process, the resulting output voltage curve follows a linear relationship with pressure. At lower pressures, this proportional relationship of the energy loss through molecular collisions is dependent on the density of gas molecules [88]. As shown in Figure 2.21, the CNT device is able to closely track changes in nitrogen pressure ranges repeatably and with fast response for 800 seconds. Here, the small scale of the CNT as sensing element provides improved response and sensitivity [4].
2.5 Conclusions

A significant advantage of the local synthesis method is that nanostructure growth can occur at pre-determined locations and is compatible with existing CMOS fabrication techniques. Post-processing of nanostructures is minimal and experimental testing can be conducted immediately following growth in the vacuum chamber. Additionally, annealing for improved electrical contacts can be performed immediately following growth, avoiding effects from exposure to air. An electrothermal CNT pressure sensing device was demonstrated with baseline pressure sensing limits determined experimentally, providing a method to determine the thermal conductivity of the CNT without invasive characterization techniques. Since the typical Pirani gauge pressure range is $10^{-1}$ to $10^3$ [88], the CNT pressure sensing device can also expand practical Pirani gauge sensing to include the pressures of $10^3$ to atmosphere.
Chapter 3

Titanium Dioxide Nanostructures

3.1 Introduction

Titanium dioxide (TiO$_2$) is one of the most well-studied metal oxide surfaces and considered an ideal surface science test platform since it is easily reducible, has a stable rutile phase (100) surface, and is a wide bandgap semiconductor ($\sim$3 eV) [31]. TiO$_2$ materials are used in applications such as pigments in paints and cosmetics, photocatalysis, solar cells, gas sensing, implantable biocoatings, and corrosion-resistant coatings [31].

One of the promising energy applications for TiO$_2$ nanostructures is in heterogeneous photocatalysis for removal of organic pollutants from air and water or reduction of metals such as silver [93, 94]. The orientation of the TiO$_2$ crystalline surface plays a key role in the amount of silver reduced on rutile surfaces with $\{101\}$ facets generating increased silver deposition over the $\{110\}$ orientation [48, 49].

Recently, highly reactive TiO$_2$ anatase nanoparticle surfaces were engineered by design, exposing a high percentage of fluorine-terminated $\{001\}$ facets compared to the thermodynamically stable $\{101\}$ facet [53, 54]. Based on first principles calculations, anatase $\{001\}$ facets were shown more reactive for water-dissociation reactions and nanoparticles with large areas of higher reactivity facets could be used for more efficient photocatalytic processes [55].

The broad, exposed surfaces of the rutile TiO$_2$ nanosword have been identified as $\{101\}$ and $\{001\}$ faces [95] and considered higher energy surfaces for the rutile phase (based on the Wulff construction) than the thermodynamically stable $\{110\}$ surfaces [47, 96]. Enhanced photoreactivity has been demonstrated on these particular rutile surfaces through ethane evolution [97], oxidation of lead ions [51], and reduction of silver [48, 49].

The presence of hydrogen is thought to increase the number of oxygen vacancies in the TiO$_2$ nanomaterial since hydrogen enters the rutile structure and can form hydroxyl ions on the surface [98]. These states, called Ti$^{3+}$ centers, are considered responsible for the electronic conductivity while the exact nature of these properties is still under debate [99]. Additionally, oxygen vacancies are considered sites for water dissociation since two hydroxyl groups can form at each vacancy when a proton is transferred to an oxygen atom at the
CHAPTER 3. TITANIUM DIOXIDE NANOSTRUCTURES

In the first section of this chapter, experiments and further characterization of individual TiO$_2$ nanoswords are investigated for heterogeneous photocatalysis and gas sensing applications. Due to the increased proportion of exposed higher energy surfaces, TiO$_2$ nanoswords are expected to improve performance of the material with increased silver reduction and improved oxygen sensing compared to bulk thermodynamically-favored (110) surfaces. The silver reduction experiments were performed on rutile TiO$_2$ nanoswords and bulk rutile surfaces (110) and (101) to compare the photocatalytic activity of each and determine whether TiO$_2$ nanoswords would exhibit enhanced photocatalytic performance. Hydrogen-annealing was also performed on TiO$_2$ samples resulting in improved photocatalytic results. Auger electron spectroscopy (AES) and photoluminescence (PL) measurements were taken of as-grown, oxidized, and hydrogen-annealed samples to obtain additional information about the atomic concentration of elements in TiO$_2$ nanoswords.

The second half of the chapter addresses the need for scaling up the TiO$_2$ nanosword growth process using a furnace-based approach and expanding on the potential photocatalytic improvement observed for hydrogen-annealed samples. Since many applications require bulk synthesis of nanomaterials covering large areas, a furnace based approach is used to implement the basic principles of the induction heating process which is further expanded to titania nanoparticles and nanostructures growth on conductive, insulating, and transparent substrates. Transmission measurements of transparent samples were taken to evaluate any improvement in visible light absorption occurring as a result of the hydrogen-annealing process and photoelectrochemical (PEC) tests were performed on as-grown and hydrogen-annealed samples. By creating additional oxygen vacancies in the material, the hydrogen-annealing process may improve the photocatalytic response into the visible light region since oxygen vacancies have been shown to dissociate water by forming two hydroxyl groups for every vacancy [100]. Hydrogen-annealed samples may present an opportunity to improve visible light absorption without having to incorporate metal [31, 101–104] or non-metal [34–36, 105, 106] dopants. Recently, nanoscale particles of anatase TiO$_2$ were shown to have significantly increased solar absorption after a long hydrogenation process introduced mid-gap electronic states and reduced the band gap [38]. Rapid hydrogen-annealing of TiO$_2$ nanostructures may provide similar material response with a disorder process that takes minutes and is microelectronics-compatible.

3.2 Synthesis I: Individual Nanoswords

3.2.1 Induction Heating

Induction heating is used in applications such as heating electrically conductive materials prior to metalworking or heat treatment, welding, or melting as well as packaging and curing [107]. Electrical currents are internally induced in the electrically conductive material, typically metals-based, and the induced eddy currents result in Joule heating of the material
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[107]. Basic induction heating setups include an alternating current source (AC), water-cooled coil, and the workpiece. Power supplied to the coil, frequency and magnitude of AC current can be adjusted to generate heat within the microstructures and carrier substrate [107]. Microelectromechanical systems (MEMS) have benefitted from incorporation of induction heating, providing new methods for rapid bonding to dissimilar materials for packaging applications [108, 109].

For synthesis of nanostructures, the basic process of using induction heating involves exposing a conductive material to electromagnetic fields and creating eddy currents within the substrate. When combined with desired gas flow through the chamber, the resulting resistive heating within the bulk of the material due to Joule heating provides the necessary substrate temperatures to activate nanostructure growth.

The induction heater setup (Nova Star 1M, Ameritherm Inc., power range of 27 to 1500 W, operation frequency of 11.7 MHz.) provides a method to synthesize a unique titanium dioxide nanostructure. Based on a technique developed by Sosnowchik et al., and reported elsewhere [110, 111], titanium sheets (99% pure, 500 µm thickness, 3 mm x 3 mm) and copper transmission electron microscopy (TEM) grids (300 and 500 mesh TEM grids, Pacific Grid Tech) were coated with a 50 to 300 nm thick thermally evaporated thin-film of titanium (99.95% pure, 5 to 7 Å s⁻¹, 1 to 3 × 10⁻⁶ Torr). Prior to thin-film deposition, the titanium substrates were cleaned in acetone and isopropyl alcohol. The copper grids were used as delivered.

As shown in Figure 3.1, titanium-coated samples were affixed to a ceramic holder using carbon paint then placed inside a quartz chamber at approximately 6.5 mm below center (and within the coils) of an eight-turn, 12.7 mm inner diameter, 3.25 mm pitch copper inductor [110]. Once sealed, the chamber was evacuated and purged with acetylene (6 slpm) at a pressure of 50 Torr. Power (600 to 900 W) was initiated at a frequency of 11.7 MHz and monitored using a real-time optical pyrometry setup so that the heating profile could be adjusted as necessary. After several minutes, the power was turned off, the system vented, and samples removed from the synthesis chamber. Examples of the resulting nanoswords are shown in the accompanying SEM image of Figure 3.1.

As shown in Figure 3.2(a), the as-grown, self-sourced nanostructures are synthesized in minutes, consisting of a broad, flat plane terminating at a triangular tip. The general characteristics of TiO₂ nanoswords are given in Table 3.1. Much work was done previously to shed light on the crystallinity and other properties of the nanostructure [111] so that the TiO₂ nanoswords were determined to be rutile phase and single crystalline. The exposed, broad face of the TiO₂ nanosword was shown to be a higher energy plane than expected under equilibrium conditions and thus should provide increased photocatalytic activity [111]. Several groups have attempted to intentionally synthesize nanoparticles with larger, higher energy faces for improved catalytic activity [51, 54, 55].

Thermal gradients throughout the substrate are evident from the optical pyrometry scans used during the growth process and it appears that larger substrates may exhibit larger gradients [112]. Thermal gradients exist across the surface of a heavily doped silicon chip with the center as much as 10°C cooler than the edges, potentially influencing where ideal growth
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Figure 3.1: Schematic of induction heating coil and relative position of sample within the vertical quartz chamber and SEM images of as-synthesized TiO$_2$ nanoswords [110].

![Schematic and SEM images of nanoswords](image)

(a) SEM images with geometry labels.  
(b) Synthesis statistics

Figure 3.2: SEM images of nanoswords and growth statistics [110, 111].

![SEM images and synthesis statistics](image)

Table 3.1: TiO$_2$ nanoswords characteristics [110].

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>40 - 89 nm</td>
</tr>
<tr>
<td>Width</td>
<td>200 - 1100 nm</td>
</tr>
<tr>
<td>Length</td>
<td>3.75 - 10.5 $\mu$m</td>
</tr>
<tr>
<td>Tip Curvature</td>
<td>2 - 3 nm</td>
</tr>
<tr>
<td>Taper Angle</td>
<td>$80^\circ$</td>
</tr>
<tr>
<td>Tip Angle</td>
<td>$114^\circ$</td>
</tr>
</tbody>
</table>
locations exist since the majority of nanoswords congregate at the edges of substrates and TEM grids [112]. Additionally, gradual heating of the chip holder can influence the substrate temperatures such that a one minute test can show a temperature increase of 100° C [112].

TiO₂ nanosword growth tends to occur at the edges of the substrates, and in particular, at the inner edges of copper TEM grids. Attempts at bulk growth on titanium sheet met with mixed success. Nanostructures synthesized on copper TEM grids, with tips protruding into the open regions, lend themselves to a simple, non-solvent based transfer method.

Using a pick-and-place method [113], individual nanoswords were identified using probe station optics and individually moved from copper TEM grids (or titanium substrates) to alternative substrates via tungsten probe tips of micromanipulators. Individual nanostructures are attracted to the probe tip by van der Waals forces and gently broken away from the original substrate at the root, then placed on a different substrate for further testing. Although the process is time-consuming and labor-intensive, the benefit of placing nanostructures at specific locations for further experimental testing at the individual nanostructure level is useful. This method was employed for the photocatalysis and gas sensor experimental devices.

3.3 TiO₂ Nanoswords Photocatalysis

Heterogenous photocatalysis involves the formation of electrons and holes due to light illumination of a metal oxide semiconductor with an energy greater than that of the bandgap, producing highly oxidizing surface species that can bind with and remove contaminants from water or solution [44]. The initial photocatalytic splitting of water into hydrogen and oxygen on a TiO₂ electrode demonstrated the ability to produce hydrogen for alternative fuel applications [39]. Since the bandgap of TiO₂ (3 eV for rutile [31]) is large, the energy required for photocatalytic response is typically in the UV range. As discussed earlier, the ability to enhance photocatalytic response of TiO₂ nanoparticles and nanostructures is of interest since anisotropic photoreactivity has been demonstrated [48, 49, 114] and engineering of higher energy surfaces is possible [53–55, 115].

The uniquely shaped, rutile TiO₂ nanosword exhibited a large exposed area of higher energy {101} surfaces compared to the equilibrium {110} surfaces [111]. The (110) surface has the least number of dangling bonds relative to other low-index TiO₂ surfaces and has the lowest calculated surface energy [46]. The next higher surface energy is the (101) surface which contains a relatively higher number of dangling bonds [46]. These additional dangling bonds are expected to provide additional sites for surface reactions to occur, potentially leading to enhanced photocatalytic response of the TiO₂ nanoswords.

A series of experiments was designed to investigate the photocatalytic activity of the exposed face of the TiO₂ nanosword compared to bulk rutile TiO₂ substrates by the reduction of silver from solution. As shown in Figure 3.3, the experimental setup consisted of a UV light source (UVP mercury pen ray, 365 nm) and petri dish for the silver nitrate solution and samples. Initially in a dark environment, (110) and (101) substrates and TiO₂ nanosword
samples were placed in $\sim 8$ mL of silver nitrate solution (0.1 N, Acros Organics) and exposed to UV light for specified durations of time. The light was then switched off and samples cleaned in DI water and dried in a nitrogen stream. The amount of silver reduced on the TiO$_2$ samples was quantified by SEM imaging and atomic force microscopy (AFM) (Veeco Dimension 3100).

![Figure 3.3: Experimental setup to compare photocatalytic response of TiO$_2$ nanoswords and bulk rutile TiO$_2$ substrates {110} and {101} by silver reduction [111].](image)

The UV lamp used for the experiments was calibrated as a function of distance using a power meter (Coherent Fieldmate), as shown in Figure 3.4, so that the height of the lamp above the sample (17 mm) yielded light intensity of 7 mW cm$^{-2}$. The sensor aperture diameter of the power meter was 19 mm.
3.3.1 Sample Preparation

TiO$_2$ nanoswords were positioned onto cleaved (5 mm x 5 mm) 120 nm, MOS-quality, dry thermal oxide on silicon substrates using the pick-and-place method previously described [113]. The oxide layer provided electrical isolation of the nanosword from the silicon substrate. As shown in Figure 3.5, a substrate feature was chosen to designate the general location of the nanosword for the desired number of samples and then optical images were taken with a digital camera for quick evaluation. Once placed on the sample substrate, the as-grown TiO$_2$ nanoswords were given a one minute oxygen plasma treatment (Plasma-Therm PK-12 RIE) at 50 W, 100 sccm, to provide a minimal descum for any residual organics potentially on the substrate or nanosword. Samples were then cleaned in a piranha bath (3:1 ratio sulfuric acid to hydrogen peroxide) for 10 minutes, rinsed in DI water and dried in a nitrogen stream. A final oxygen plasma clean (one minute, 50 W, 100 sccm) was performed on the samples prior to photocatalytic testing. Hydrogen-annealed samples were initially cleaned in a five minute oxygen plasma treatment (50 W, 100 sccm), then underwent a rapid thermal anneal (A.G. Associates Rapid Thermal Annealing System) for 15 seconds at 800$^\circ$C in a nitrogen/10% hydrogen environment. When samples cooled to room temperature, a final oxygen plasma clean (1 minute, 50 W, 100 sccm) was performed to remove any residual organics before photocatalytic testing.

The polished rutile TiO$_2$ substrates were (110) and (101) surfaces (Surfacenet GmbH and MTI corporation) with orientations confirmed as (110) and (101) by x-ray diffraction (XRD) (Siemens D5000 diffractometer, Cu K$_\alpha$ radiation, $\lambda = 1.5418\,\text{Å}$). Figure 3.6(a) and 3.6(b) show the XRD scans for (110) and (101) surfaces, respectively.

The rutile TiO$_2$ substrates (1 cm x 1 cm) were diced into 1.5 mm x 1.5 mm substrates. First, a thin layer of photoresist was spin-coated onto the substrate to prevent chips from
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Figure 3.5: TiO$_2$ nanosword locations on cleaved substrates.

Figure 3.6: XRD scans confirming orientation of (110) (a) and (101) (b) surfaces [111].
damaging the surface during the dicing procedure. After dicing, the photoresist was removed with PRS-3000 (J.T. Baker) heated to \(80^\circ\text{C}\) for 10 minutes followed by a rinse in IPA and DI water. Samples were then placed in piranha solution (3:1 sulfuric acid:hydrogen peroxide) for 10 minutes to remove any residual organic material. Substrates were rinsed in DI water and dried in a nitrogen stream. In an attempt to obtain atomically smooth surfaces \[116\], substrates were thermally annealed in air for one hour \(\left(800^\circ\text{C}, 20^\circ\text{C} \text{ min}^{-1} \text{ ramp rate}\right)\). A final oxygen plasma treatment was performed on the substrates \(\left(1 \text{ min}, 50 \text{ W}, 100 \text{ sccm}\right)\) prior to photocatalytic testing.

### 3.3.2 Experimental Results

As shown in Figures 3.7 - 3.9, SEM images qualitatively show the silver deposition comparison of (110) and TiO\(_2\) nanoswords after one, 17, and 60 minute tests. After one minute of UV light exposure, the silver particles appearing on both surfaces are small and scattered, increasing in size and coverage as the duration of UV light exposure increased.

![SEM images comparing one minute exposure to UV light of (110) surface and TiO\(_2\) nanosword.](image)

Figure 3.7: SEM images comparing one minute exposure to UV light of (110) surface and TiO\(_2\) nanosword.
A direct comparison of a TiO$_2$ nanosword on (110) control substrate is shown in Figure 3.10. The ten minute UV light exposure generated silver particles of larger magnitude and increased frequency on the TiO$_2$ nanosword surface compared to the (110) surface.

AFM measurements were used to quantify amounts of silver deposited on (110) and (101) substrates as well as as-grown and hydrogen-annealed TiO$_2$ nanoswords (Figure 3.11). For 1:1 aspect ratios, scan sizes were 1 $\mu$m and between 1-2 $\mu$m for (110) and (101) substrates, and between 1-2 $\mu$m for the TiO$_2$ nanoswords (scan rate 1 Hz), subsequently parsed into 200 nm x 200 nm sections with silver amounts averaged [111]. Additional information on the AFM scans and standard error plot are located in the Appendix.
Based on the above data, the quantum efficiencies and reaction rates were calculated for hydrogen-annealed and as-grown nanoswords, and (101) and (110) substrates as 1.49, 0.42, 0.27, and 0.01 % and 19.7, 5.6, 3.5, and 0.15 Å min⁻¹, respectively [111]. The intensity of light was calculated as 1.3 x 10¹⁶ photons cm⁻² sec⁻¹ based on the calibrated 7 mW cm⁻² power per area value [111].

The results of the silver reduction experiments demonstrated the possibility of engineering TiO₂ nanostructure morphologies that can improve the photocatalytic response. The (101) surface of the TiO₂ nanoswords showed an order of magnitude increase in the measured silver deposited compared to the thermodynamically favored (110) surface. Another significant increase in silver deposition was observed for the hydrogen-annealed TiO₂ nanoswords when compared with the as-grown TiO₂ nanoswords. Hydrogen-annealing of TiO₂ is believed to increase the number of oxygen vacancies on the surface [98, 117] which in turn increases the number of surface hydroxyl ions present that can react with silver ions in solution [94]. Hydrogen is attracted to dangling bonds [38], so with a TiO₂ nanosword (101) face dominating the exposed surfaces, the concentration should be largest near the surface and may explain the increase in photocatalytic activity for silver reduction. Further characterization of the hydrogen-annealed TiO₂ nanoswords would be required to better understand the increased photocatalytic response.
Figure 3.11: Quantitative comparison of TiO$_2$ nanoswords (as-grown and hydrogen-annealed) with polished TiO$_2$ (110) and (101) surfaces over time (1, 5, 10, 17, 40, and 60 minutes). The (110) surface produces the least amount of silver, and the (101) surface and as-grown TiO$_2$ nanosword have similar amounts of silver deposited, although the nanosword appears more photocatalytically active. Over an order of magnitude increase in silver deposited was demonstrated from (110) to (101) and TiO$_2$ nanoswords photocatalytic response. An increase in silver deposited was also noted for hydrogen-annealed TiO$_2$ nanoswords compared to as-grown [111].
3.4 TiO$_2$ Nanoswords Gas Sensing

When gas molecules adsorb on the surface of a metal oxide, the conductivity of the material may change as a result. Thin-film solid state metal oxides can enable next generation sensing devices since low cost, low power, and microelectronics-compatible techniques can fabricate such devices [118]. Incorporating nanostructures can improve sensitivity due to increases in surface-to-volume ratio.

TiO$_2$ is a material of interest for gas sensing due to conductivity changes upon exposure to oxidizing or reducing gases and typically used for oxygen sensing. Over a range of partial pressures and at high temperatures, TiO$_2$ behaves as a bulk defect oxygen sensor [31]. With temperatures between 500 and 700° C, a semiconducting oxide typically has bulk oxygen vacancies at thermal equilibrium with oxygen partial pressure in the environment and measured with bulk resistances [119]. At low temperatures (below 500°C), adsorbed molecules may form ionic bonds and when combined with platinum can be used as a Schottky-diode device [31, 119]. Recently, room temperature gas sensing was demonstrated for zinc oxide with ultraviolet light enhancement [120]. Given the higher energy exposed planes of the TiO$_2$ nanoswords, the (101) surfaces may provide additional sites for oxygen molecules to adsorb and change the conductivity of the device. Combined with ultraviolet light or heating of the nanostructure to enable desorption of molecules, room temperature TiO$_2$ oxygen sensing may be enabled with benefits of increased surface sites for interaction with oxygen (titanium interstitials) [31], surface-to-volume ratio, as well as low-power operation, low-cost fabrication and integration, and microelectronics-compatibility.

3.4.1 Experimental Details and Results

To perform gas-sensing experiments, the existing vacuum chamber at Sandia National Laboratories was used. Advantages of this particular vacuum chamber included pressures down to $10^{-6}$ Torr, a heated substrate holder to 475 K, micromanipulators for in situ measurements, and configurable for a variety of gases.

Several modifications were required to allow input of different gases into the system since house nitrogen was the only gas used prior to these experiments. Care had to be taken to avoid contaminating the chamber since it was a multi-use platform for testing other sensitive nanostructure devices. The contamination issue immediately ruled out testing with carbon monoxide which could have deleterious effects on other users samples. Additionally, hydrogen testing was problematic due to safety issues inherent to the setup. The simplest approach would be to test the titanium dioxide gas sensor devices in oxygen environments.

The gas chamber is a vacuum probe station (TTP4 Probe Station Desert Cryogenics, now Lakeshore) capable of reaching $10^{-6}$ Torr using a turbo pump. As shown in Figure 3.12, a gas manifold was constructed of vacuum-rated fittings and valves and attached to the vacuum chamber. A pressure regulator specific for the cylinder size was placed on the inlet side and to a valve controlling the gas flow into the vacuum chamber at the opposite end. Valves were also placed to allow inlet control of the house nitrogen flow into the chamber.
A separate roughing pump was used for purging the manifold separately from the vacuum chamber and a convectron gauge placed in the system to monitor the manifold pressure. The vacuum chamber had a four probe arm configuration (ZN50 probes) attached to a specimen stage that could be heated up to $\sim 475$ K, limited by the heat tolerance of the cables located inside the chamber.

Portable two-component mixtures (MiniMAT gas cylinders, 103 L) with oxygen concentrations of 100 ppm, 1%, and 10% with a balance of nitrogen gas were ordered (Matheson). Since individual nanostructure lengths ranged from 6 to 12 $\mu$m, conventional lithographic techniques were used to fabricate the titania gas sensor devices. Samples were fabricated on 1 $\mu$m-thick oxide layers on silicon wafers with subsequent samples fabricated on 100 nm oxide-on-silicon wafers. Two terminal contacts were used for each titanium dioxide device sample to fabricate resistive devices. The process flow is shown in Figure 3.13.
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Figure 3.13: Process flow for fabricating gas sensing device. (1) Coat wafer with photoresist; (2) Photoresist exposure and development; (3) Metal alignment marks deposition and liftoff; (4) Individually place TiO$_2$ nanosword on substrate; (5) Photoresist spin-coating, exposure, and development of nanosword; (6) Metal contacts deposition and liftoff. In later fabrication efforts, it was found the nanosword was easily identifiable under the aligner microscope and was aligned manually between contacts.

The choice of contact materials was based on the work function (WF) values obtained for titanium dioxide and electron affinity of contact metals. Values for the work function of titanium dioxide varied from 4.2 to 4.16 eV for rutile TiO$_2$ (110) [121]. Several contact materials were used including gold, silver, and aluminum with adhesion layers of titanium (since ebeam deposition was used as the primary method of depositing the metals) and chromium.

The process flow was later modified to include a bi-layer photoresist process to facilitate a clean liftoff. The first layer was a non-photoreactive UV light resistant resist (LOR1A, Microchem) spin-coated on the nanosword at 4000 rpm for 30 seconds and soft-baked at 150°C for 90 seconds on a hotplate. The same process and conditions were followed for the top layer using a photoactive resist (Rohm Haas S1805 positive PR). After patterning, ebeam metal evaporation was used to deposit metal for the electrodes and remover PG was used for liftoff.

As shown in Figure 3.14(a), the conductivity of the material decreased as the concentration of oxygen increased (red line). The sample was initially placed in the vacuum chamber and pumped down overnight (~16 hours) with steady state conditions at 2.5 x 10$^{-6}$ Torr (blue line). I-V curves were taken from 1 to -1 V (not shown here) and 3 to -3 V although the curve is shown only from 0 to 3 V. Figure 3.14(b) shows stability measurements of the device at vacuum 2.5 x 10$^{-6}$ (blue line), 1% O$_2$/N$_2$ (red line), and 10% O$_2$/N$_2$ (green line) at...
3 V input for the same sample in the chamber during one test session. Again, as expected, the conductivity decreased as more oxygen was introduced into the chamber. Results for all samples were not necessarily consistent and although fast switching would be expected for a nanostructure, the inability to desorb molecules quickly from the surface would affect response time, requiring that the sample be heated, exposed to UV light, or returned to vacuum.

![Graph](image)

**Figure 3.14:** Oxygen gas sensing experimental results. (a) I-V curve showing decrease of conductivity (red line) as more oxygen is introduced into the chamber (375 Torr, 10% O₂/N₂) compared to the initial measurement (blue line) taken under vacuum (2.5 x 10⁻⁶ Torr); (b) Stability measurement over time for TiO₂ nanosword vacuum 2.5 x 10⁻⁶ (blue line), 1% O₂/N₂ (red line), and 10% O₂/N₂ (green line) at 3 V. As more oxygen is introduced into the chamber, the conductivity of the material decreases.

As shown in Figure 3.15, experiments showed an increase in conductivity when the sample was exposed to ultraviolet (UV) light (8 W, 365 nm, 33 mm from source). The sample (batch 279) was ~2 µm in length with chromium-gold contacts. Lithography was performed for these samples as previously described. Although the nanosword response showed a limited UV enhancement and return to the original I-V curve, other samples did not exhibit similar responses. Further testing would be required to definitively show the room temperature UV enhancement for these nanostructures in gas sensing applications.
3.5 Further Materials Characterization

3.5.1 Auger Electron Spectroscopy

To further understand the effects of oxidation and hydrogen-annealing on individual TiO$_2$ nanoswords, both Auger electron spectroscopy (AES) and photoluminescence measurements (PL) were taken. AES is a material surface characterization technique that uses electrons to bombard a material with particular electron energies (typically between 3 to 30 keV) and based on the secondary emitted electron spectra, the surface chemical composition can be determined for typically the first 2 to 10 atomic layers [122]. The several monolayers where the probability of an electron to escape matter are considered the electron escape depth [122].

The surface and depth profile scans were used to determine the concentration of elements in individual nanostructures based on oxidized, as-grown, and hydrogen-annealed samples. Individual nanoswords were placed on a conductive silicon substrate ($<$1 cm x 1 cm) and treated: sample 1 was heated in air at 800$^\circ$C for 1 hour; sample 2 consisted of several as-grown structures with no additional surface modification; and sample 3 was treated in an argon/10% hydrogen-anneal at 800$^\circ$C for 15 sec. The locations of nanostructures on substrates were mapped out to minimize time searching for samples on the substrate. AES scans were conducted at pressures of $\sim$10$^{-9}$ Torr. The results of surface scans are shown in Figures 3.16, 3.17, and 3.18 for as-grown, oxidized, and hydrogen-annealed TiO$_2$ nanoswords, respectively.
Figure 3.16: Auger spectroscopy surface scans of an as-grown TiO$_2$ nanosword.

Figure 3.17: Auger spectroscopy surface scans of an oxidized TiO$_2$ nanosword.
The surface scans of the three samples confirm atomic % of titanium and oxygen. In Figure 3.19, both titanium and oxygen are present in the sample although the ratio is not exactly 1 to 2. Carbon and silicon are likely from the electron beam and silicon substrate. In the oxidized sample of Figure 3.20, other elements in addition to titanium and oxygen are carbon, silicon, potassium, and tin. Potassium contamination may be from the silicon substrate and tin may be a consequence of using a shared furnace tube at high temperatures which allowed tin atoms to potentially contaminate the sample. In Figure 3.18, the hydrogen-annealed sample exhibits a much larger carbon concentration and significantly less titanium than the as-grown sample. The hydrogen-annealed sample scan also suggested fewer oxygen atoms remain in the hydrogen-annealed samples which is expected since hydrogen can diffuse into TiO\(_2\) and combine with oxygen to produce hydroxyl ions and increase the number of oxygen vacancies [98]. Further studies are required, though, to understand the true nature of the TiO\(_2\) nanoswords and surface processes including factors such as sample preparation, cleanliness of equipment, and comparison with bulk samples which could remove the silicon surface influence on measurements.

AES depth or profile scans were also taken. Here, the material is sputtered beyond the few nanometer depth limit and the scans are considered a destructive process. Although the sputtered area should be larger than the area of interest by 3 to 10 times [122], the spot size of the beam is much larger (hundreds of nanometers) than the TiO\(_2\) nanosword so the scans included much more silicon substrate material and interpretation of data may be problematic. The resulting depth profiles are shown in Figures 3.19, 3.20, and 3.21 for as-grown, oxidized, and hydrogen-annealed TiO\(_2\) nanosword samples, respectively.
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Figure 3.19: Auger spectroscopy depth profiles of an as-grown TiO$_2$ nanosword on silicon substrate.

Figure 3.20: Auger spectroscopy depth profiles of an oxidized TiO$_2$ nanosword on silicon substrate.
In Figure 3.19, the as-grown TiO$_2$ nanosword appears to have a steady % of atomic oxygen through a depth of 6 nm and the titanium atomic % was low at the surface and higher as the scan depth increased.

The oxidized nanosword of Figure 3.20 showed a much higher atomic % of oxygen at the surface even though the scan was stopped at approximately 2.5 nm due to charging of the substrate and sample. The hydrogen-annealed sample (Figure 3.21) had a much lower atomic % of oxygen at the surface which increased slightly with depth and dropped off significantly at $\sim 10$ nm. The reducing environment created by hydrogen-annealing created oxygen vacancies as well as hydroxyl ions [98]. The silicon signal is perhaps from the substrate effects and the carbon may be from the use of an electron beam [123]. Although not clear where the carbide signal originates from, nor why it is only present with the as-grown and hydrogen-annealed samples, it may be possible that the oxidized sample measurements were taken incorrectly or show errors due to charging. The carbide signal could be from a residual amount of acetylene used in the synthesis process although not confirmed with these scans. The titanium atomic % is low at the surface for all samples and the rate of increase varies as the scan depth increases. The main aspect separating the three samples appears to be the concentration of oxygen at the surface and through the depth, perhaps indicating the number of oxygen vacancies present at the surface and is dependent on the type of processing used.

Due to the uncertainty surrounding the nature of the carbide signal, additional tests would need to be performed with a larger sample population. Carbon contamination has been shown to affect the several monolayers of the surface [124] and although the carbide signal does decrease after several nanometers, it still contributes 5 to 10 % of the scan at 6 nm.
depth. While surveying the substrates, the nanostructures were noted to charge up under the electron beam even though lower primary electron energies were used. The difficulty in determining the chemical composition of the nanoswords may be due to the sample size smaller than the beam diameter (the diameter of backscattered electrons is similar to the beam diameter [122]) which results in material outside of the nanosword edges included in the data. Further studies and other techniques with larger sample populations would be required to determine the exact composition and stoichiometry of the as-grown and modified titania nanomaterial.

### 3.5.2 Photoluminesence Microscopy

Photoluminesence microscopy (PL) is a non-destructive technique to evaluate charge carrier recombination dynamics with quantum effects causing blue shifts evident as nanostructure size decreases [125]. A specific wavelength (UV or visible light) is used to excite an electron from the valence band to the conduction band. The photons are absorbed by the material then emitted typically at a wavelength shifted from the original wavelength. The emission spectra of peak positions can give information about defect levels in the material [126].

Although PL scans of as-grown TiO$_2$ nanoswords (copper TEM grid substrates) exhibited an emission peak at 436 nm [112], measurements of oxidized or hydrogen-annealed samples had yet been taken. Other demonstrations of photoluminescence properties on bulk rutile TiO$_2$ nanowires showed emission peaks at 380 nm [127]. PL scans of as-grown, oxidized, and hydrogen-annealed nanoswords were attempted using 400 nm wavelength. The individual nanoswords were placed on silicon oxide on silicon substrates and did not exhibit photoemission. An attempt to use several nanoswords clustered on a copper TEM grid did not produce a photoresponse either. One reason for the lack of a photoemission is that the density of nanostructures is low and the detector was not able to record such a photoresponse. As a comparison, similar tests using a bulk batch of ZnO nanowires with much higher nanostructure density produced a PL response. Another reason may be that this particular batch of rutile titania structures may have a bandgap larger than 3 eV (413 nm) [31] and thus not able to generate a PL photoresponse unless a higher energy wavelength was used.

### 3.6 Synthesis II: Bulk Nanostructures

#### 3.6.1 Furnace-based Synthesis

Scaling up the induction heater growth process is attractive since the exposed faces of the TiO$_2$ nanoswords demonstrated enhanced photocatalytic activity. Bulk growth of TiO$_2$ nanoswords would enable larger scale applications since the surface-to-volume advantage could be augmented by increased activity at the surface. The sample sizes would readily lend themselves to larger scale testing which is important for energy and environmental applications such as water splitting.
Initially, the prevailing consensus was that the oxygen content due to leakage into the induction heater system was the main contributor to the unique morphology of the TiO$_2$ nanoswords. A secondary factor considered was the rapid heating and cooling aspect of the induction heating process. Although discussed briefly, little consideration was given to the role of hydrogen in the growth process. In fact, it seemed desirable to remove the hydrogen from the system where high growth temperatures and mixing of oxygen and hydrogen could be problematic on a large scale. Since the general notion of oxygen leakage into the system contributed to the overall synthesis of TiO$_2$ nanoswords, it was thought that the process could be transferred to a furnace-based method which could provide larger substrates for bulk testing. The rough estimate of 4.1 sccm oxygen flowrate into the system provided a baseline value for the synthesis of TiO$_2$ nanoswords on the bulk scale [112] and additional oxygen leakage tests were conducted (see Appendix). Transferring induction heater growth parameters to a furnace-based process would remove the substrate-and-synthesis coupling since the eddy currents generated by the induction heating process would no longer influence nanostructure growth. Transparent substrates could then be used for a variety of applications involving photo-processes.

As shown in Figure 3.22, furnace growth was performed in a Thermo Scientific Lindberg/Blue M tube furnace capable of reaching temperatures of 1100°C. A two-inch quartz process tube was used as the growth chamber. As a multi-use tool, there are multiple cylinders of different gases (methane, argon, argon/2% hydrogen, nitrogen, ethylene, hydrogen, oxygen) hooked up to the system and controlled by both digital and rotameter flowmeters. For the furnace growth of titanium dioxide nanostructures, argon and argon/2% hydrogen gases are the balance of the oxygen intentionally introduced during the growth process.

Figure 3.22: Image of tube furnace used for the growth process.

Titanium and quartz substrates were prepared for the growth process by deposition of a titanium thin-film using thermal or electron beam (ebeam) evaporation. Thin-film
thicknesses ranged from 134 to 500 nm. Prior to metal deposition, the quartz substrates were cleaned using piranha (3:1 sulfuric acid and hydrogen peroxide solution) to remove organic and metal contaminants. Titanium sheet substrates were cleaned in acetone, briefly sonicated, then rinsed in isopropyl alcohol (IPA) and deionized (DI) water and dried in a nitrogen stream.

Quartz samples were cleaved, set on top of an alumina holder, and placed inside the quartz tube. The ends of the tube were sealed with a pressure sensor on one end to monitor the chamber pressure and the tube evacuated to the base pressure of the pump. The sample was placed outside of the furnace while the zones heated up and later inserted into the heated region by moving the tube (Figure 3.22). Argon (or argon/2% hydrogen) flowed at 140 sccm until the tube filled to atmospheric pressure. When the furnace was heated to the appropriate temperature, oxygen was then flowed into the tube and the sample moved into the center region of the furnace. After approximately 10 minutes, the temperature control and oxygen flow were shut down to begin cooling while the balance (inert) gas continued to flow during the cool down. The sample was removed from the hot heating zone by sliding the furnace tube so that the samples were outside of the furnace body, promoting rapid substrate cooling. Although the surrounding gases remain at higher temperatures during cool down, the continuous inert gas flow should assist with cooling down the sample compared with leaving the sample inside the heating zones. The furnace environment should be cooled to <500°C before evacuating the chamber of gases with the pump, since heated oxygen (and potentially hydrogen) are both inside the furnace tube. Cooling continues until the chamber can be safely opened and exposed to air.

3.6.2 Results

Initial efforts to grow titanium dioxide nanostructures used ranges of oxygen flowrates from 1.6 to 6.3 sccm and furnace temperatures of 860 to 970°C. Successful runs centered on 880 to 890°C and 3 to 6 sccm oxygen with the balance 140 sccm argon (or argon/2% hydrogen). The furnace growth temperature range is supported by previous temperature synthesis tests in the induction heater [112]. Figure 3.23 shows optical images of pre- and post-furnace runs with quartz and titanium substrates, and the post-growth insulating quartz substrate can be used as a check on whether the titanium material has changed to titania since it becomes transparent when oxidized (Figure 3.24). As shown in Figure 3.25, initial successful runs were demonstrated on 5 mm x 5 mm titanium substrates (214 nm titanium thin-film).
Figure 3.23: Comparison of TiO$_2$ nanostructure growth (10 min, 880$^\circ$C). (a) Pre-growth; and (b) Post-growth. Note how the TiO$_2$ is transparent on the quartz substrate.

Figure 3.24: Post-growth titania nanostructures on quartz substrates. Note that after the furnace process, quartz substrates are nearly transparent.

Figure 3.25: Initial nanosword growth in furnace. During synthesis, argon/2% hydrogen is used as the balance gas with (a) 3.14, (b) 6.29, and (c) 9.39 sccm of oxygen.

Subsequent growth runs were performed on titanium sheet, copper TEM grids, copper sheet, and quartz wafer substrates. The flowrates used were 140 sccm argon and 3 to 5 sccm for oxygen, typically for 10 to 12 minutes. The titanium thin-films of 400, 103, 500, and 500
nm thicknesses were deposited on quartz, copper TEM grids, copper sheet, and titanium sheet substrates, respectively.

To verify that the nanostructures were rutile TiO$_2$, XRD measurements were performed. As shown in Figure 3.26, the XRD results confirm rutile phase TiO$_2$ (JCPDS 21 - 1276).

![Figure 3.26: XRD measurements confirm TiO$_2$ rutile phase nanomaterial.](image)

The titanium thin-film had poor adhesion to the copper sheet substrate, with most of the thin-film flaking off during the run, and no growth was evident (SEM images not shown here). The titania structures formed on the copper TEM grids were much larger, particle-shaped structures, lacking individually separate structures. Figure 3.27(a) shows as-grown titania nanostructures on quartz substrates with roughly estimated lengths of tens to several hundred nanometers, widths ranging from 20 to 50 nm, and thickness variations of 10 to 20 nm. A thin oxidized layer of titania grains located below the nanostructures is also evident.

The induction heater synthesized TiO$_2$ nanosword tip has a typical taper angle of 90° for the {001} type I nanosword and a 114° taper angle on the {101} type II nanosword [111]. Using image processing software [128], the taper angle of several nanostructures was measured at an angle of ~90°, which was a similar geometrical angle as the type I nanosword (type II was used in the following photocatalytic experiments with large % of exposed (101) surface), indicating partial success with synthesis of nanosword-like structures on an insulating substrate. As shown in Figure 3.27(b), titanium thin-film on titanium sheet substrates yielded titania nanostructures. Using image processing software[128], typical geometrical characteristics of titania nanostructures on titanium sheet measured included lengths of 150 to 350 nm, widths of 25 to 50 nm, and thicknesses of 10 to 20 nm. The growth rate was 15 to 35 nm min$^{-1}$. The furnace-based process can produce TiO$_2$ nanostructures using argon only growth as well as argon/2% hydrogen growth. Other samples on quartz substrates (400 and 700 nm thicknesses) were also grown using the furnace process. The same furnace runs with various substrates generates different morphologies, suggesting that the roughness and structure of the substrate plays in the growth process. The role of an oxidized seed layer on
the titanium sheet [129] may help the growth of titania nanostructures compared with other substrates.

![SEM images of furnace growth nanostructures. (a) Quartz substrates; (b) Titanium substrates.](image)

Figure 3.27: SEM images of furnace growth nanostructures. (a) Quartz substrates; (b) Titanium substrates. In (a), a sword-like nanostructure is evident from the close-up image. Here argon is used as the balance gas.

With initial success of the furnace growth process, in situ and post-process non-metal doping of nanostructures was attempted. As TiO$_2$ has a large band gap (3 eV for rutile [31]), doping of TiO$_2$ can allow greater use of the solar spectrum by improving visible light absorption and photoreactivity. As described by Asahi et al., three parameters should be met when doping TiO$_2$ for visible light absorption: (1) Create impurity states within the bandgap that absorb visible light; (2) Conduction band minimums and impurity states need to be as high as TiO$_2$ or higher than H$_2$/H$_2$O level; and (3) Allow photoexcited charge carriers move to surface reaction sites by having impurity states within the bandgap overlapping with TiO$_2$ band states [34]. Based on their predictive models, nitrogen and sulfur were found to be the most suitable elements for substitutional doping while carbon and phosphorus impurity states were too deep within the bandgap to fulfill all three criteria [34]. Nitrogen-doping of TiO$_2$ can occur by controlled hydrolysis during TiO$_2$ particle formation [36, 130], ball-milling in ammonia-water solutions [131], ion implantation [132], sputtering titanium or TiO$_2$ in a nitrogen environment or calcining with ammonia at higher temperatures [34, 130, 133–135]. While transition-metal doping of TiO$_2$ has been demonstrated and Fe$^{3+}$ and Cu$^{2+}$ shown to inhibit electron-hole recombination, large concentrations of cationic impurities can produce localized d-levels that provide recombination centers and no longer enhance visible light photocatalytic response [34, 93, 132].

For nitrogen-doping of TiO$_2$ furnace-based nanostructures, alternative doping methods were considered since gases such as ammonia are not currently plumbed into the gas system. During the synthesis process, nitrogen was used as the balance gas instead of argon and the samples, which were yellowish when pulled out of the furnace, exhibited a nanopar-
Carbon-doping was attempted by modifying a carbon nanotube growth recipe utilized in our lab [83], where after purging and evacuating the tube an argon:ethylene mixture (611:90 sccm) was flowed over the nanostructures at 700°C for 10 minutes at atmospheric pressure. The hydrogen conditioning step typically used prior to CNT growth was omitted in this case, although it could potentially serve to provide hydrogen-annealing and some carbon-doping for the nanostructures. As shown in Figure 3.28, the post-processed samples of nitrogen (N) and carbon (C) are compared with the as-grown (STD) furnace nanostructures. The nitrogen-annealed sample appears similar to the as-grown sample (argon and oxygen flow) although formation of titanium nitrides or titanium oxynitrides cannot be ruled out. The post-growth carbon-doped sample appears darker, potentially due to successful carbon-doping or more likely the breakdown of ethylene at high temperatures such that some limited hydrogen-annealing may have occurred on the titania surface. Another possibility is the coating of the surface with carbonaceous material rather than carbon atoms having diffused into the material.

Figure 3.28: Comparison of as-grown (STD), nitrogen-doped (N), and carbon-doped (C) titania nanostructures on quartz. The carbon-doped sample is slightly darker, possibly indicating successful doping with carbon and/or annealing with hydrogen from the breakdown of methane at high temperatures.

### 3.6.3 Hydrogen Annealing and Characterization

In semiconductor fabrication methods involving ion implantation, rapid thermal annealing is a process typically used to electrically activate and repair damage from implanted impurities by diffusion of silicon and impurity atoms to lattice and substitutional sites, respectively [136]. The steep slope of the temperature profile minimizes diffusion of dopants and maintains a low, effective $Dt$ product, which is the diffusion coefficient times the time. As shown in
Equation 3.1, the diffusion coefficient \( D \) represents an exponential temperature dependence of substitutional and interstitial atoms in silicon [136]:

\[
D = D_0 e^{\frac{-E_A}{kT}}
\]  

(3.1)

where \( D_0 \) is the maximum diffusion coefficient at infinite temperature, \( E_A \) is the activation energy, \( k \) is Boltzmann’s constant, and \( T \) is the temperature. The relationship between the diffusion coefficient and temperature is an Arrhenius behavior and not restricted to silicon only. The overarching concept behind the product \( Dt \) is the thermal budget required to minimize dopant diffusion and interface degradation [137]. Another value used to roughly quantify the thermal budget is the product \( Tt \) which is the temperature \( (T) \) times the time \( (t) \). Both methods used on their own can be problematic for determining actual thermal budgets [137], but here are considered for use as a possible qualitative framework for dopant diffusion and interface issues of hydrogen-annealing of TiO\(_2\) nanostructures.

As noted previously, hydrogen is attracted to dangling bonds and hydrogenation of TiO\(_2\) nanoparticles has shown formation of a disordered surface region [38]. TiO\(_2\) nanoswords with large percentage of exposed (101) surface may also experience increased hydrogen concentration near the surface that contributes to enhanced photocatalytic activity for silver reduction. A demonstration of hydrogenated TiO\(_2\) nanowires showed an improvement in the photoelectrochemical (PEC) response after a long time, low temperature process [138], but did not consider any surface disorder that may be present due to the hydrogenation process. The increase in visible light absorption came mainly in the UV region for nanowires of 100 to 200 nm diameters and lengths of 2 to 3 \( \mu \)m [138], while hydrogenated nanoparticles (\( \sim \)8 nm diameter) showed optical absorption well into the IR range [38]. Improved understanding of the hydrogen-doping process, especially for nanowires, can yield improvements for device-oriented PEC and hydrogen generation applications. Nanowires, especially those grown directly on the device substrate, should exhibit better adhesion to the substrate surface through direct contact as well as providing pathways for rapid and continuous carrier transport [139, 140].

The hydrogen-annealing process used previously for individual TiO\(_2\) nanoswords was performed on the bulk, furnace-grown samples. The exposure of TiO\(_2\) to reducing environments increases the number of oxygen vacancies on the surface [98, 117] which leads to increased surface concentrations of hydroxyl ion formation – sites that are active for water dissociation [100]. The thermal budget of the hydrogen-annealed titania nanostructures is on par or low relative to other hydrogenation processes [38], leaving room for optimizing the process with different temperature-and-time combinations.

Hydrogen-annealed samples underwent a rapid thermal anneal (A.G. Associates Rapid Thermal Annealing System) for 15 to 60 seconds at 800\(^\circ\)C in a nitrogen/10% hydrogen environment.
3.6.4 Transmittance Measurements

Spectral transmittance measurements (Perkin Elmer Lambda Spectrophotometer, integrating sphere wavelength interval 2 nm) were taken of the as-grown, hydrogen-annealed, and non-metal doped samples. The sample was irradiated at the nanostructured front face of quartz samples. The opening of the window for sample placement is \( \sim1 \) inch diameter and since the quartz samples were often smaller than the original opening, a separate mask with smaller diameter holes was also used. Calibration of the system occurred with the smaller mask in place. As shown in Figure 3.29, a preliminary measurement of a quartz substrate showed the minimal influence of the substrate on the transmittance measurement. The quartz substrate % transmittance is greater than 90% for the wavelength range of 200 to 2000 nm. No correction was made for the substrate. Due to significant charging of the substrates and poor imaging conditions, no SEM images are shown here of the substrates.

![Figure 3.29: Quartz % transmittance measurement from 200 to 2000 nm wavelength range. The substrate has greater than 90% transmittance.](image)

Figures 3.30 - 3.32 show comparison transmittance measurements of as-grown, non-metal doped, and hydrogen-annealed doped titania nanostructures on quartz substrates. The fringe patterns exhibited by the samples indicate the thin-film effects of the nanostructured surface on transparent substrates. The thin-film complex refractive index \( \eta = n - ik \) and thicknesses could be extracted from transmission data using successive approximations and interpolation or continuous functions [141, 142]. Figure 3.30 shows a direct comparison of as-grown nanostructures (STD) with samples annealed in a nitrogen/10% hydrogen environment at 800°C for 15 seconds (STD+A). The hydrogen-annealed samples exhibited decreased transmittance in the visible light region compared to the as-grown sample, indicating that more energy has been absorbed by the material and suggesting that hydrogen is providing the enhancement mechanism.
Figure 3.30: Comparison of % transmittance measurement from 200 to 1000 nm wavelength range of as-grown (STD, black) and hydrogen-annealed (STD+A, blue) samples. The hydrogen-annealed samples show decreased % transmittance in the visible wavelength range indicating increased absorption by the material.

Transmittance measurements of titania samples grown in a nitrogen environment (N) and hydrogen-annealed (N+A) are compared with as-grown (STD) samples in Figure 3.31. Since the samples grown in a nitrogen environment do not exhibit improved transmittance and appear similar to the results of the as-grown samples, the formation of titanium oxynitrides with improved visible light absorption is not successful with this growth method. The transmittance is shown to decrease slightly for the hydrogen-annealed sample, indicating energy absorption had increased.

Figure 3.32 shows a comparison of carbon-doped samples (post-processing method) with as-grown and hydrogen-annealed samples transmittance results. The carbon-doped sample (C) shows improved transmittance in the visible light region, which suggests that either the post-process carbon-doping was successful, or that the hydrogen from the ethylene gas flow performed an annealing step, or more likely a combination of both. Further characterization of the material would be required to determine the structure of the material. The hydrogen-annealed, carbon-doped sample showed a decrease in transmittance when compared with the carbon-doped and as-grown samples, suggesting that the material absorbed more energy in the visible light region.
Figure 3.31: Transmittance measurements comparing titania samples. (a) Samples grown in nitrogen (N, black), grown in nitrogen and hydrogen-annealed (N+A, blue), and as-grown (STD, yellow) with no post-processing; and (b) Samples grown in nitrogen and hydrogen-annealed (N+A, blue) samples compared with as-grown (STD, yellow) samples only.

Subsequent transmittance measurements showed similar results, although some samples also showed little or no change. For Figure 3.33, spectral absorbance was calculated for as-
grown and hydrogen-annealed (one minute) samples as $\text{Absorbance}_\lambda = 100 - \text{Reflectance}_\lambda - \text{Transmittance}_\lambda$. The hydrogen-annealing process appears to have improved the absorbance of the sample compared to the as-grown sample.

Figure 3.33: Comparison of % absorbance measurement from 200 to 2000 nm wavelength range of as-grown (STD, black) and hydrogen-annealed (1 min, blue) samples. The hydrogen-annealed sample showed improved % absorbance in the visible wavelength range.

The promising results of rapid hydrogen-annealing are expected to improve with denser and higher quality nanostructures on transparent substrates since the increased surface area should provide more disordered surface area for enhanced photoactivity in the visible light region. Optimization of the thermal budget for the samples would also provide guidance on what the TiO$_2$ samples can handle for temperatures and times exposed to the hydrogen-annealing process.

3.6.5 Photoelectrochemical Testing

Photoelectrochemical (PEC) cells provide a unique opportunity to convert light into electrical energy or chemical fuels with efficiency and cost considerations between photovoltaics (high cost, high efficiency) and photosynthesis (low cost, low efficiency) [57]. While photovoltaic cells have efficient energy conversion, they suffer from high fabrication costs and additional constraints requiring storage devices for the generated electrical energy [57]. Photosynthesis is an inexpensive and inefficient process for producing stored chemical energy, converting only 3 to 4% of total incident solar energy [57].

When designing PEC cells, the following issues should be considered for the semiconductor and electrolyte [143]: (1) Bandgap energy; (2) Band edge locations; (3) Stability; (4) Doping level; (5) Crystallinity; (6) Surface treatment; and (7) Redox couple. Although the
material bandgap energy should be small to allow electron-hole pair generation at visible and infrared light ranges, semiconductors often suffer from degradation after prolonged periods of irradiation [143]. Rutile TiO$_2$ is an ideal PEC material candidate since it is stable and corrosion-resistant although the rather large bandgap (3 to 3.2 eV) has spurred much of the research for reducing the bandgap and sensitizing the material to visible light irradiation [31, 144]. Band edge locations for TiO$_2$ relative to standard potentials of the H$_2$/H$_2$O redox couple are suitable for the splitting of water at the material surface although the pH of the electrolyte solution will affect the band edge positions [39, 93, 144]. PEC cells performance is affected by surface states and pretreatment or modifications have often been employed to reduce potential electron-hole recombination centers [143]. It may be that rapid hydrogen-annealing and long-time hydrogenation processes [38, 111, 138] minimize the influence of surface defects by creating a disordered surface region that sensitizes the material to visible and IR irradiation and provides charge trapping sites on the surface while leaving the crystalline core intact [38].

Sample preparation for PEC testing required that the backside of the titanium substrates be mechanically polished (fine grit sandpaper) and the surface blown off with compressed air to remove dust and contaminants. Substrate resistance was checked using a multimeter. Copper wire (24 AWG) was then attached to the substrate backside using conductive paste (DuPont 4929N) through a 5.75-inch pipet (VWR) and allowed to cure. The resistance was checked a second time to verify appropriate conductivity and the backside was then sealed with non-sagging extra-fast set two-part epoxy (Hardman, Cole Parmer). Epoxy should also be applied to the top of the pipet to seal the copper wire into place although was not done for this set of tests. Eight samples (Figure 3.34) were initially tested with different growth conditions and control substrates. Table 3.2 shows a breakdown of the samples used for PEC testing.

The as-grown and hydrogen-annealed titania nanostructures were tested in a PEC setup. As shown in Figure 3.35, a pyrex cell (quartz window) containing 0.5 M sodium chloride solution (pH $\sim$7) was irradiated with a 300 W solar simulator (Xe lamp) through an AM
Table 3.2: TiO$_2$ furnace growth and hydrogen-annealing samples for PEC testing.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Synthesis Gases</th>
<th>Temperature /°C</th>
<th>Growth Time /min</th>
<th>H$_2$ Annealing /sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ar + O$_2$</td>
<td>880</td>
<td>10</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>Ar + O$_2$</td>
<td>880</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>Ar only</td>
<td>880</td>
<td>12</td>
<td>–</td>
</tr>
<tr>
<td>4</td>
<td>Ar only</td>
<td>880</td>
<td>12</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>Ar only</td>
<td>890</td>
<td>12</td>
<td>–</td>
</tr>
<tr>
<td>6</td>
<td>Ar only</td>
<td>890</td>
<td>12</td>
<td>15</td>
</tr>
</tbody>
</table>

a) the pre-synthesis mechanically-roughened surfaces of samples 1, 3, and 8 were not found to influence growth; b) samples 6 and 7 were fabricated as reference samples with (6) titanium thin-film deposited on titanium sheet and (7) titanium sheet substrate only; c) initial titanium thin-film thickness for all samples was 500 nm.

1.5 G filter (Oriel 81092) with light intensity of 100 mW cm$^{-2}$. A three-electrode PEC setup was used for the tests with a coiled platinum wire counter electrode and Ag/AgCl reference electrode. Nitrogen gas was bubbled in solution continuously during the tests to removed dissolved oxygen and prevent reduction at the platinum counter electrode. Current-potential measurements were taken using a potentiostat (Pine Instruments Bipotentiostat) with an anodic (positive) potential scan at 5 mV s$^{-1}$. Light was mechanically chopped at approximately 0.2 Hz.
Figure 3.35: The PEC cell setup which includes solar simulator (100 mW cm\(^{-2}\)) with pyrex cell (quartz window) containing platinum counterelectrode, TiO\(_2\) photoanode, Ag/AgCl reference electrode, nitrogen gas bubbler to prevent oxidation at the counterelectrode submerged in 0.5 M sodium chloride solution.

As shown in Figure 3.36, the PEC results comparing photocurrent for as-grown and hydrogen-annealed samples (800\(^\circ\)C, 15 seconds) with the titanium sheet are shown. All results were normalized with respect to the exposed surface area (2 cm\(^2\) or 1 cm\(^2\)). The samples grown in argon only and 890\(^\circ\)C (plot not shown) exhibited odd behavior perhaps due to poor contacts and require another round of testing to rule out issues with the PEC sample construction.
Figure 3.36: PEC test results comparing as-grown TiO\textsubscript{2} (black), hydrogen-annealed (red), and reference sample titanium sheet (green). The hydrogen-annealed sample exhibited significantly higher photocurrent than the reference and as-grown samples.

The trends shown for the hydrogen-annealed sample suggests that the photocurrent can be markedly improved over TiO\textsubscript{2} samples only and warrants further investigation as to the level of disorder introduced into the sample and whether that can be optimized for enhanced photocurrent generation.

3.6.6 Conclusions

TiO\textsubscript{2} nanostructures with exposed, broad higher energy surfaces could potentially open a new class of nanomaterial synthesis with improved control over the majority of nanostructure surfaces exposed and additional advantages of dry and microelectronics-compatible processes.

The first synthesis method, induction heating, is a rapid and potentially cost-effective method for nanostructure growth. The fast process can synthesize nanostructures within minutes compared with other processes that can take hours. As a dry synthesis process, it avoids the wet chemistry methods often required for nanoparticle synthesis as well as potential contamination from solvents and other chemicals. Beyond the cleaning of the substrates and subsequent deposition of the titanium thin-film, the self-sourced growth process requires minimal preparation to grow unique nanostructures.

The induction heater setup can theoretically be scaled up to accommodate larger substrates based on increasing the coil dimensions, but it remains to be seen whether the process
can be implemented in this manner. Although evidence for scaling up the process exists, significant modification to current setups would be required. Nanomaterial synthesis and integration for large-scale deployment will require substrates larger than the mm x mm sizes currently used which led to transferring induction heater growth parameters to a furnace-based processes. The furnace-based growth process has the distinct advantages of scaling up for large area coverage and synthesis on both conductive and insulating substrates.

Of note, though, is that not all furnace runs were successful in generating nanostructures and would sometimes exhibit a nanoparticle morphologies. Although optimization of the process will be required, several issues may contribute the growth disparities. The furnace process lacks the rapid cooling mechanism of the induction heating process since safety concerns exist with evacuating hot gases from the furnace tube immediately following growth. Based on the experimental furnace results thus far, an overabundance of oxygen may be another potential factor contributing to complete oxidation of the titanium thin-film and preventing TiO$_2$ nanosword growth. This perspective lends support to the idea that hydrogen may be a necessary component for TiO$_2$ nanosword synthesis in that it prevents the oxidation of the titanium surface and allows continued self-sourcing of the vapor for growth. Hydrogen in the growth environment also contributes to synthesis of n-type TiO$_2$ which is a reduced form of the material [31]. The acetylene environment initially used in the induction heating process has an abundance of hydrogen available which potentially prevents oxidation of the titanium layer.

An unknown factor is the influence of furnace users prior to TiO$_2$ nanostructure growth. Typical flowrates for other users are much higher and the sensitivity of their runs to the oxygen leakage are far less than for the titanium dioxide nanostructures. Additionally, runs performed in a reducing (hydrogen) environment may have contributed to the successful TiO$_2$ nanostructure runs, but the amount of residual hydrogen in the system remains unknown and the purging process used before each run may not remove all previously used gases from the system. Given the evidence of varied oxygen effects and the possibilities of growing structures in flowrates up to 50 sccm in the induction heating setup [145], it appears that the hydrogen concentration in the flow has a significant effect on the final morphology of the nanostructures.

The PEC results indicate that hydrogen-annealing can enhance the photocatalytic response of furnace-grown nanostructures. With the use of higher quality nanostructures, improved results for the hydrogen-annealing process are expected. Due to the short times and high temperatures used in the process, the thermal budget is acceptable for rutile nanostructures and is significantly less than other demonstrated hydrogenation processes [38]. Additional times and temperatures should be considered for optimizing the process. Potentially increasing the thermal budget for furnace-grown nanostructures could yield an increased thickness of a disordered surface layer.

With improved connections of nanostructures to the substrate due to direct growth and the ability to optimize the synthesis process for higher aspect ratio structures, rapid hydrogen-annealing can provide a fast and efficient method to create disordered surfaces for robust, device-oriented photoelectrochemical energy applications.
Chapter 4

Silver Nanowires and Graphene for Biological and Optical Sensing

4.1 Introduction

Methods for creating large areas of dense nanostructure arrays with regular and repeatable locations for growth and control over morphology are necessary for furthering nanomaterial integration into sensor and energy applications. Two potential synthesis and patterning techniques for nanometer-scale device features with controlled and repeatable patterning are glancing angle deposition (GLAD) and nanoimprint lithography (NIL). Both fabrication techniques are currently outside of conventional lithography methods, but possess potential integration pathways for sensor applications.

This first part of this chapter examines the potential applications of silver nanowires synthesized by oblique angle deposition (OAD), which is a subset method of the GLAD process, for fabricating bio- and nanotoxicology sensing platforms. Interest in nanostructure effects on cells and organisms has increased as nanomaterials are integrated in novel ways for societal use, including how these nanomaterials impact cells during and after device use. Here, initial studies on how nanowires impact cell viability are examined with results indicating increased surface area and nanowire morphologies are more toxic to cells. This study is one of the first to integrate cell viability testing directly with nanomaterial substrates for nanotoxicology studies.

The second half of the chapter focuses on nanopatterning of graphene using nanoimprint lithography (NIL). Due to the outstanding electrical and optical properties of graphene, the capability of graphene-based devices can be extended using NIL patterning to address issues such as repeatability. NIL patterning can transfer features to graphene substrates with etching or by building-up metamaterials for incorporating a bandgap into the material for electronics or building a repeatable test platform for surface enhanced Raman spectroscopy (SERS).
4.2 Silver Nanowire Nanotoxicology Platform

4.2.1 Nanosilver

Nanosilver (less than 100 nm length scale) exhibits strong antibacterial activity, effectively able to kill many types of Gram-negative and Gram-positive bacteria including *Salmonella*, *Acinetobacter*, *Escherichia*, *Listeria*, *Staphylococcus*, and *Streptococcus* as well as increasing the effectiveness of antibacterial activity for antibiotics [146]. Nanosilver will bind with protein molecules and inhibit cellular metabolism making it an attractive material treatment for polymers and fibers [147]. Nanosilver displays antifungal and antiviral properties even having shown effectiveness at preventing HIV-1 virus replication [148]. Although silver is considered non-toxic to humans, silver ions are toxic and the effects of nanosilver are still to be determined [149]. Exposure to nanomaterials, such as nanosilver, can occur through multiple routes including gastrointestinal tract via ingestion, inhalation into the lungs, dermal contact uptake into the lymphatic channels, and injection into the bloodstream [59, 150]. Studies have shown that there is relation between exposed surface area of a nanoparticle, reactive oxygen species (ROS) generation, and inflammation of lung tissue [59].

As shown in Figure 4.1, multiple interaction mechanisms between biological tissues and nanomaterials exist with much work needed to determine effects of material composition, surface functionalization or residuals, electronic structure, and solubility on cell health [59]. Cytotoxicity can also depend on the type of cell exposed to a particular nanomaterial. For example, TiO$_2$ particles were shown to be highly inflammatory and induce fibrosis in the trachea whereas TiO$_2$ at 1000 µg mL$^{-1}$ on bronchiolar epithelial cells showed only moderate toxicity [151].

Critical factors influencing nanosilver surface activity are the size and morphology of the nanoparticles. The antibacterial activity of nanosilver is size dependent with smaller particles (averaging $\varnothing$ 10 nm) exhibiting greater activity due to the larger surface-to-volume ratio [146, 148]. Strong antibacterial activity is also a function of particle shape and crystallographic surface structure. Triangular nanoplates have high atomic density $\{111\}$ facets dominating the percentage of exposed surface area with associated increased antibacterial activity compared to spherical or rod-shaped particles [146].

The bioactivity of nanosilver is due to the chemisorbed Ag$^+$ ions that form on the particle
surface, influencing the level of antibacterial activity which in turn is directly dependent on oxygen sensitivity [152]. The role of silver oxidation as dependent on Ag\(^{+}\) generation is still under determination, but evidence from previous studies suggests oxygen and water play a large role in the antibacterial activity of nanosilver. For metallic silver melted and cooled in hydrogen, silver bactericidal properties were not evident nor recovered after three months whereas silver metal heated and cooled in air (or heated in hydrogen and cooled in air) showed significant inhibition with exposure to water providing an additional increase in inhibition activity [153].

Nanosilver can enter the environment through smelting, manufacture and disposal processes, and leaks from municipal and/or industrial water treatment plants [146]. Conventional thought is that silver is not considered harmful to human health and the environment, although the physicochemical properties of nano-sized silver interacting with biological tissue may be cause for concern and understanding these potential outcomes is critical for future diagnostic and therapeutic applications [59, 154]. Recently, nanosilver has been shown to affect zebrafish embryo development as well as potentially causing DNA damage and chromosomal aberrations [60, 61]. The surface reactivity of nanosilver is suggested to be one of the major causes of cytotoxicity since increased surface area provides additional atoms available to react with the surrounding environment [155]. Yet, the relationship between particle size, morphology, and reactivity towards cellular toxic response is still not clearly defined.

One of the difficulties associated with determining toxicity of nanomaterials lies in the variable synthesis processes. Often, chemical routes are used to create nanoparticles and wide distributions of diameter sizes are possible. Additional issues with surfactants and residual chemicals from fabricating these particles may affect cytotoxicity outcomes. One study showed silver colloid particles of \(\varnothing 2\) to \(3\) nm were less toxic to skin than larger particles (\(\varnothing \approx 30\) nm). Other studies emphasize the smaller sizes are more toxic and others state that not enough data currently exists to determine nanomaterial toxicity [59, 146, 148, 151]. Clearly, additional information is needed to help determine whether nanosilver is toxic to biological tissue as well as ways to develop nanomaterials and platforms to be used for therapeutic applications such as drug delivery or antibacterial activity enhancement. Most studies have focused on nanoparticles with less emphasis on nanowire and nanorod morphologies. A potential non-chemical, non-solvent based method to generate repeatable substrates of uniform nanowires and nanorods for nanotoxicology platforms is glancing angle deposition (GLAD). The GLAD technique and application as a nanotoxicology test platform is discussed in the rest of this section.

### 4.2.2 Glancing Angle Deposition (GLAD)

Glancing angle deposition (GLAD) techniques provide a way to add functionality to thin-films by controlling the resulting porosity. Initially developed by Jensen and Brett [156–159], the process is based on material physical vapor deposition with a rotating growth substrate typically held at high oblique angles relative to the vapor flux direction [157, 158]. A significant advantage of GLAD involves the lack of global temperature changes
compared to furnace synthesis processes and the ability to build-up nanostructures based on existing thin-film deposition techniques without chemical synthesis and potential resulting contamination. Metals and oxides are well-suited for this deposition technique limited only by choices of source materials available.

GLAD nanostructure growth is based on ballistic shadowing as incident vapor hits the cool substrate and randomly distributes into nucleation sites that create uneven regions on the surface by casting shadows on regions behind them [160]. As nuclei increase in size, they prevent additional flux from reaching shadowed regions of the substrate and quickly dominate the film growth process [160]. At high oblique substrate angles, a low-density film will develop column-shaped structures [157]. As shown in Figure 4.2, the resulting nanostructures are tilted in the direction of the incident vapor and the porosity is dependent on the angle of deposition normal to the vapor flux. The angle $\alpha$ is between the incident vapor flux direction and normal to the substrate while $\beta$ is the resulting tilt angle of the nanowires relative to the substrate normal.

Figure 4.2: Schematic illustrating the influence of material deposition angle, $\alpha$, on the resulting nanostructure growth angle, $\beta$. The shadows cast by the growing nanostructures prevent further growth in those regions. With a rotating substrate, the shadowed region can encircle nanostructures by 360°.

An empirically-derived curve relating the vapor angle of incidence with the resulting nanowire tilt angle is described with the following equation [160]:

$$\tan \alpha = 2 \tan \beta$$

(4.1)

where $\alpha$ and $\beta$ are the angles between the incident vapor direction and the nanowire growth direction both with the substrate normal, respectively. While this equation provides a basic relationship between $\alpha$ and $\beta$, it tends to breakdown as $\alpha$ becomes more oblique. Several
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models have emerged to estimate the growth morphology dependent on the tilt angles, but all tend to vary significantly at the high oblique angles [160].

![Figure 4.3: Schematic of vapor deposition tooling describing OAD and GLAD processes. Angle $\alpha$ is the angle measured from the substrate normal to the vapor flux and angle $\phi$ represents the substrate axis of rotation during GLAD. For the OAD process, angle $\phi$ is stationary.](image)

As shown in Figure 4.3, the GLAD setup consists of a substrate holder held at a preset angle $\alpha$ relative to the vapor flux direction. The substrate holder is also rotated along angle $\phi$ and the substrate should be in direct line-of-sight of the vapor flux. The GLAD process can be modified to a simpler process by using oblique angle deposition (OAD) growth instead. The OAD process entails nanostructure growth based on the angle of incident vapor flux relative to the growth substrate, but the angle of substrate rotation ($\phi$) is fixed. The GLAD method is particularly well-suited for growing nanowires, helical wires, and even angular box-like shapes due to the circular shadowing effect around each nanostructure and the ability to control the rotation speed and direction for in situ changing of the deposition line of sight. The angled nanostructures can provide fast turnaround time for fabrication of test platforms for applications such as nanotoxicology and surface enhanced raman spectroscopy (SERS), a bio- and chemical sensing platform capable of detecting single molecules [161, 162].

Prior to material deposition, a seed layer can be created by lithographically-patterning the substrates from which specific locations of organized arrays of nanowires are synthesized. Several examples of non-patterned and patterned GLAD substrates are shown in Figure 4.4 [19].
Figure 4.4: Examples of GLAD morphologies [24]. (A) Non-patterned substrates: silver spheres (a) and tilt nanowires (b) [this work]; silicon chevrons (c) and helical posts (d) [163], and nanotubes (e) [164]. (B) GLAD patterned substrates used in combination with ebeam lithography (a, b) [163, 165], nanosphere lithography (c) [166], and photolithography (d) [167], and (e) [this work].
4.2.3 GLAD Synthesis of Silver Nanowires

The following synthesis experiments were performed using a subset technique of the GLAD process called oblique angle deposition (OAD). In this case, the angle $\phi$ is held constant, so that the substrate is not rotating during the deposition. Synthesis was performed on both flat and lithographically patterned substrates in an ebeam evaporator (ULTEK) as shown in Figure 4.5. In general, a high vacuum deposition is considered line-of-sight so that deposition occurs at surfaces the vapor flux initially contacts. The cryo-pumped system can reach base pressures of $2 \times 10^{-7}$ Torr and film thicknesses are monitored with a thin-film crystal monitor (Inficon). A unique feature of this tool is the water-cooled substrate holder. For later tests, the substrate holder cooling water is replaced with antifreeze (50-50 ethylene glycol and water) to promote increased substrate cooling using a chiller (NESLAB RTE-111).

![Figure 4.5: Ultek electron beam evaporator used for the OAD growth process. The water cooled stage angle is adjusted using the goniometer, allowing angle $\alpha$ to vary from 0° to 90°.](image)

Substrates were placed on the water-cooled stage using metal clips and the angle $\alpha$ (Figure 4.3) chosen between 0 to 90° for each run. For all samples, an adhesion layer of titanium was first deposited followed by silver for nanowire growth. Prior to deposition, glass or silicon substrates were cleaned in a piranha bath (3:1 sulfuric acid:hydrogen peroxide, 10 min), rinsed in DI water for approximately 10 minutes and dried in a nitrogen stream. Since substrate cooling temperatures can influence the morphology of the resulting nanostructures [168], cooling fluid tests from -12.4°C to ambient were also performed.

For the nanotoxicology tests, samples were fabricated to provide a broad range of substrate morphologies, including fine particles to thin-films of varying porosity to nanowires and finally large area grains of micron-sized diameters. Fine particles (~50 nm diameter) were synthesized on both glass and silicon substrates with silver deposited at $\alpha =0^\circ$. Both glass and silicon were chosen since the fine particle morphology would not have complete coverage over the entire sample area and the underlying substrate may influence cell viability. For larger, micron-sized silver grains, OAD substrate samples fabricated at $\alpha =0^\circ$ were
The samples were annealed at 400°C for 30 minutes.

4.2.3.1 Etching Seed Layers

To provide better control over the specific location of nanostructures, a seed layer can be patterned prior to the OAD or GLAD process. The seed layer creates an uneven surface that promotes shadowing so that the initial nucleation phase immediately progresses to formation of nanostructures. With conventional lithography, a post pattern defines seed layer locations for silver nanowire growth. The overall etching scheme is two-fold. First, an anisotropic dry etch is performed on lithographically patterned silicon oxide on silicon substrates, then wet etching using hydrofluoric acid to reduce the diameter size of the posts. The goal would be to use conventional methods to obtain different diameter sizes of post arrays using two-part etching rather than the more expensive and time-consuming ebeam lithography. Ideally, the diameters for seed layers could be reduced such that a single nanowire could grow on a post tip. As shown in Figure 4.6, the process flow involves spinning a layer of photoresist onto a silicon/silicon oxide wafer, exposing and developing the photoresist to define features and use as an etch mask, performing an anisotropic plasma etch to create posts, then wet etching in hydrofluoric acid (49% or buffered) to reduce the diameter of the posts. After removing the photoresist, the seed layers can then be coated, functionalized, or processed by other methods.

As a proof of concept demonstration, a gradient post mask design [169] was used to pattern post arrays of uniform radius (diameters from 2, 2.5, 3, 3.5, 4, 4.5 to 5 µm) on clean silicon/silicon oxide substrates (GCA 6200 Wafer Stepper) with a silicon oxide layer of approximately 2.5 µm thickness. An array mode exposure test was performed at 0.01 second intervals to determine the ideal exposure time (post exposure bake 120°C, developed for 60 sec). For 1.3 µm g-line photoresist, an exposure time of 0.36 sec was chosen. Two methods were considered for anisotropic etching. A multi-use parallel plate etcher (Plasma-Therm PK-12 RIE) with a water-cooled substrate provided an anisotropic oxide plasma etch to create post arrays using a standard oxide etch recipe (O2 4 sccm, CHF3 80 sccm, 150W) with an expected etch rate of 300 to 400 Å min\(^{-1}\). Although the chuck is water-cooled, the etching process was alternated 3 minutes active and 1 minute cooling to avoid overheating of the substrate for a total of 25 minutes of etching. The etch rate was verified at \(\sim40\) nm min\(^{-1}\) with a resulting measured oxide thickness of 1µm. The patterned photoresist, which serves as a mask to prevent etching of the substrate beneath it, was hard baked at 120°C for 1 hour prior to etching. Figure 4.7 shows the etching results for the parallel plate (a-b) reactive ion etches.

The second anisotropic etch process was performed with a magnetically enhanced reactive ion etch (RIE) for oxide etching (Applied Materials, Centura MxP+). This tool uses an applied rotating magnetic field, increasing residence time of free electrons in the plasma.
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Figure 4.6: The process flow for creating seed layers using conventional photolithography includes a silicon oxide etch to generate posts with a photoresist mask followed by wet etching (hydrofluoric acid 45% or buffered) to reduce the overall diameter of the posts. The photoresist is removed using acetone or other suitable solvent then post-processing of the seed layer can proceed, including coating or functionalization.

Using a standard oxide etch recipe, power of 700 W and pressure of 200 mT generated a plasma consisting of 150 sccm Argon, 15 sccm CF₄, and 45 sccm CHF₃. The estimated etch rate was 4500 Å min⁻¹ with an oxide to silicon selectivity of 9:1. The patterned photoresist was again used as an etch mask, although a hard bake was not performed for these etches. Figure 4.7 (c-d) are examples of the anisotropic etch. Most notable is the smoother sidewall and the less angular post wall (c-d) compared with (a-b) etches.

The second component of the seed layer etching consisted of wet etching to reduce the overall diameters of the posts. Several types of buffered (BHF) and unbuffered hydrofluoric (HF) acids were available for oxide etching. The estimated thermal oxide etch rates of hydrofluoric acid (HF) and buffered hydrofluoric acid (BHF) are as follows (nm min⁻¹): concentrated HF (49%) = 2300; 10:1 HF = 23; 25:1 HF = 9.7; 100:1 HF = 2.3; 5:1 BHF = 100; and 10:1 BHF = 50 [170]. Wet etching tests were performed using a 10:1 BHF, which consists of 10 parts 40% ammonium fluoride (NH₄F) to 1 part 49% concentrated HF and a consistent etch rate. Once buffered solutions reach equilibrium several hours after mixing, the etch rates are considered stable at 50 nm min⁻¹ for 10:1 BHF [170]. The wet
Figure 4.7: SiO$_2$ etch results with reactive ion etching using a parallel plate (a-b) or magnetic-field enhanced (c-d) plasma etching techniques. For (a) and (b), the photoresist mask was hard baked for 1 hour ($120^\circ$C) prior to etching in an O$_2$ and CHF$_3$ plasma. The edge surface of closeup (b) appears uneven due to the alternating 3 minute plasma etch and 1 minute cool-down. For (c) and (d), the sidewall of the etched posts is much smoother due to the magnetic field which increases the amount of time free electrons exist in the plasma.
etch time must be controlled such that the oxide layer is not completely removed from the silicon substrate to avoid removing all of the seed layer. Wet etches are typically isotropic so material is removed from all exposed faces of the oxide. The photoresist mask should reduce exposure of the top portion of the post to the etch solution, although the photoresist mask will not longer maintain direct contact as the sides shrink in size. As smaller diameters are reached, the photoresist mask will eventually be unsupported and the post entirely exposed. Oxide wet etches in 10:1 BHF at \( \sim 50 \text{ nm min}^{-1} \) rate were performed for 20 and 26 minutes to remove \( \sim 1 \mu\text{m} \) and \( \sim 1.3 \mu\text{m} \), respectively. The smallest diameter post of 2 \( \mu\text{m} \) determined the minimum allowable etching. Figures 4.8 and 4.9 show the wet etch results. The posts in Figures 4.8 (a-b) were originally \( \phi 2.5 \mu\text{m} \). After wet etching for 20 minutes, the lower post diameter was \( \sim 900 \text{ nm} \) and the upper post diameter was \( \sim 385 \text{ nm} \). The post height changed little, from \( 1 \mu\text{m} \) to 965 nm. The 26 minute wet etch yielded more dramatic results with Figures 4.8(c-d) yielding a sharp tip and much reduced dimensions from the original \( \phi 2 \mu\text{m} \). The post height was reduced to 470 nm from 1 \( \mu\text{m} \) and the base diameter approximately 200 to 250 nm. In Figures 4.8 (e-f), the original post diameter was 4.5 \( \mu\text{m} \) reduced to approximately 3 \( \mu\text{m} \) base diameter, which is near the expected etch rate of 50 \( \text{nm min}^{-1} \).

For the magnetically enhanced anisotropic plasma etching, a 20 minute etch changed the post diameter from 3 \( \mu\text{m} \) to \( \sim 1.6 \mu\text{m} \). The height of the post remains \( \sim 1 \mu\text{m} \), although a much sharper tip angle is seen in Figures 4.9(b) compared to the parallel plate etched photoresist masks. The sharper tips suggest that the photoresist did not adhere as well to the oxide layer and that a hard mask may help improve that contact. The photoresist mask for all images in Figure 4.9 are \( \phi 3 \mu\text{m} \). Despite the eventual loss of the photoresist mask, the individual posts appear to reduce in size following the original etching lines. With a deep reactive ion etch (DRIE) that allows deep etches with straight sidewalls, the wet etching portion for diameter reduction would be improved. Following etching, the substrates were then ready for photoresist removal in acetone or other solvent and metal seed layer coating or deposition.

### 4.2.4 Synthesis Results

As shown in Table 4.1, a series of silver nanowire OAD runs were performed. The runs were also repeated six months later (substrate cooling temperature, \(-12^\circ\text{C}\)) to allow for changes in the surface conditions of the silver nanowires (oxidation concerns) when tested. As shown in Figure 4.10, the morphology of the thin-film changes as the substrate angle \( \alpha \) becomes steeper. Based on cross-sectional profile images of the nanowires on substrates, the geometrical characteristics of an 85° run can be determined [128]. Overall nanowire lengths are dependent on the total material deposited (here, \( \sim 1 \mu\text{m} \)) and range from 250 to 350 nm with nanowire diameters at 25 to 50 nm. The angle, \( \beta \), between the nanowire direction and normal to the substrate is estimated at 51 to 53°, which is in agreement with an empirically derived curve of Equation 4.1 even at such high oblique angles of synthesis.

As shown in Figure 4.11, the shadowed area behind the post in the OAD process depends on the initial diameter and height of the post. For the GLAD process, the substrate would
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Figure 4.8: SiO$_2$ wet etch results using 10:1 BHF for 20 (a-b) and 26 (c-f) minutes from parallel plate etcher.
Figure 4.9: SiO$_2$ wet etch results using 10:1 BHF for 20 (a-b) and 26 (c-f) minutes from magnetically enhanced etch tool.
Table 4.1: Silver nanowire synthesis conditions used to fabricate the nanotoxicology test platforms. A six-inch silicon wafer was used for the substrates in each case except for the 50 nm thickness deposition which was performed on both glass and silicon.

<table>
<thead>
<tr>
<th>α</th>
<th>Ti Rate nm s⁻¹</th>
<th>Ti Thickness nm</th>
<th>Ag Rate nm s⁻¹</th>
<th>Ag Thickness deposited nm</th>
<th>Ag Thickness measured (avg) nm</th>
<th>Cooling Temp °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>90</td>
<td>0.2</td>
<td>40.2</td>
<td>0.3</td>
<td>2000</td>
<td>300</td>
<td>4</td>
</tr>
<tr>
<td>85</td>
<td>0.2</td>
<td>40.8</td>
<td>0.1 til 677.3</td>
<td>2000</td>
<td>300</td>
<td>4</td>
</tr>
<tr>
<td>75</td>
<td>0.2</td>
<td>42</td>
<td>0.3</td>
<td>673</td>
<td>300</td>
<td>4</td>
</tr>
<tr>
<td>0</td>
<td>0.2</td>
<td>11.8</td>
<td>0.2</td>
<td>300.5</td>
<td>300</td>
<td>4</td>
</tr>
<tr>
<td>90</td>
<td>0.02</td>
<td>4</td>
<td>0.3</td>
<td>1007</td>
<td>200</td>
<td>-12</td>
</tr>
<tr>
<td>85</td>
<td>0.02</td>
<td>4</td>
<td>0.3</td>
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<td>75</td>
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<td>0</td>
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<tr>
<td>85</td>
<td>0.02</td>
<td>4</td>
<td>0.2</td>
<td>50*</td>
<td>–</td>
<td>-12</td>
</tr>
</tbody>
</table>

*Fine nanoparticle morphology. Silver was deposited on both glass and silicon substrates.

rotate about φ (Figure 4.3), resulting in a shadowed region encompassing 360° about each post and nanowire growth occurring only at the exposed post region.

Figures 4.12 show additional SEM images of fabricated silver seed layers.

4.2.5 Nanotoxicity of Silver Nanowires

Cell viability dependent on OAD-fabricated nanowire morphologies was investigated. Key elements of the study focused specifically on how increased porosity and subsequent increased surface area would affect cell life. The cell lines used in the experiments included A549 and RLe-6TN. The A549 cell line consists of human alveolar adenocarcinoma cells, essentially cancerous lung tissue [171]. RLe-6TN cells are derived from rat lung cells (rat lung epithelial-T-antigen negative) and used for in vitro studies for pulmonary toxicity and carcinogenesis [172, 173]. A Luciferase assay was also performed, but the initial results indicate further analysis is required (See Appendix).

MTS (3-(4,5-dimethylthiazol-2-yl)-5-(3-carboxymethoxyphenyl)-2-(4-sulfophenyl)-2H-tetrazolium) assays are a colorimetric method used to assess cytotoxicity of cells by measuring mitochondrial metabolic rate to indirectly determine cell viability [174, 175]. As cells bio-reduce MTS, a water-soluble formazan product is produced in the presence of phenazinemethosulfate (PMS) with the amount proportional to number and viability of cells [176, 177]. Absorbance of the formazan product (490 nm wavelength) is measured directly from the
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Figure 4.10: SEM images of OAD silver nanowire growth comparison of substrate angle ($\alpha$) relative to vapor flux direction. (a) $90^\circ$; (b) $85^\circ$; (c) $75^\circ$; and (d) $0^\circ$ angles are used for these samples. Substrate temperature was approximately -12°C. The morphology change dependency on substrate angle normal to the vapor flux is evident with steeper angles yielding greater separation between nanowires.

multiplates without additional processing and cell viability can be directly determined [175, 176].

Table C.1 in the Appendix provides detailed nanowire and substrate information used in the cell viability tests. The typical preparation involved cleaving nanowire substrates into 1 cm x 1 cm dies followed by cleaning with ethanol and placement into the wells of 24-well multiplates. Cells were then cultured on these substrates and cell viability evaluated using MTS assays. Tests were performed using CellTiter 96 AQueous One Solution Cell Proliferation Assay (MTS) from Promega [178]. See Appendix for additional sample and test information.

For Figures 4.13 and 4.14, the primary and secondary Y-axes indicate the absorbance of the formazan product at 490 nm and % cell viability, respectively.

For the MTS assay shown in Figure 4.14, RLe-6TN cells were used. The Group I samples
Figure 4.11: SEM images of OAD silver nanowire growth on lithographically patterned substrates. The posts were both anisotropically and wet etched prior to the OAD deposition. The shadowed region is evident in (a-b) and a single nanowire appears to be on the tip of the post (c). Another close view shows nanowire bundles on the post tip, dependent on the size of the post (d).

(0° through 90°) were allowed to naturally oxidize in air over a six month period. Group II samples (0° through 90°) were fabricated immediately prior to the toxicity tests (For additional information about specific samples, see Appendix). As shown in Figure 4.14, the blue bars indicate the formazan absorbance measured at 490 nm and the red line data indicates % cell viability normalized to the glass slide (100%). The plain silicon wafer and glass slide both exhibit the highest cell viability at 80% and 100%, respectively. The lowest survival % occurred on substrates synthesized at 85° and 90°. Samples from both Group I and Group II were annealed in argon and air (30 min, 300°C). Samples were also synthesized with fine particle morphology (50 nm thickness of silver deposited at 85°) on both silicon and glass substrates.
Figure 4.12: SEM images of OAD silver nanowire growth on lithographically patterned substrates.
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4.2.5.1 Trends Based on Morphology

As expected, the results indicate that nanowire morphologies fabricated at 90° and 85° are more toxic than thin-films (0°) potentially due to increased exposed surface area in contact with the cells.

4.2.5.2 Trends Based on Oxidation

Oxygen species may play a role in cytotoxicity since Group I samples (fabricated six months prior to testing) showed overall lower cell viability than Group II samples. Comparing annealed in argon samples to their original state (M1 vs M8 and M10 vs M9), toxicity was reduced relative to the original sample. The samples annealed in air (M20 and M21) are more toxic than samples annealed in argon (M8 and M9). The most toxic sample (Group I, 90°) was oxidized in air for approximately six months with cell viability of 17%.

Figure 4.13: Cell viability using MTS assay. Absorbance of formazan product at 490 nm is proportional to the cell viability. The yellow bar indicates absorbance measured at 490 nm and the green line corresponds to cell viability. Assays were performed on three separate samples of each substrate type. The increased porosity samples fabricated at 85° and 90° (M2, M3, M5) showed the most toxicity to A549 cells. Here, ”Wafer” is the same as M0. See Appendix Table C.1 for details of substrate types.
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4.2.6 Conclusion

The GLAD process is a wafer-scale method for nanowire growth and can be readily incorporated into existing microfabrication techniques. The morphology of the film depends on the initial substrate angles ($\alpha$ and $\phi$) relative to the vapor flux. OAD is a modified version of GLAD where $\phi$ is held fixed during the deposition. A seed layer created from lithographically-patterned substrates can provide greater control over the location of nanowires and nanowire bundles.

Using the OAD-fabricated substrates, the cytotoxicity of silver nanowires was evaluated. The results indicate that increased porosity and oxidation of silver nanowires substrates is more toxic to cells.
4.3 Nanopatterning Graphene for Sensor Applications

4.3.1 Graphene

First isolated in 2004, graphene is a monolayer of carbon atoms arranged in a honeycomb lattice with outstanding mechanical, electrical, and optical properties [179]. Graphene exhibits an ambipolar electric field effect with charge carrier mobilities up to 15,000 cm$^2$ V$^{-1}$ s$^{-1}$, ballistic transport, and high current densities greater than $10^8$ A cm$^{-2}$ [179]. Graphene demonstrates strong interband transitions and absorbs photons across the visible and infrared light spectrum, making it a potential candidate material for optoelectronic applications [180, 181]. Graphene is also considered a semimetal with overlapping conduction and valence bands and also exhibits a lower on-off resistance ratio of $\sim$30 at 300 K [179].

For graphene to be considered a viable material for technology applications, large-scale deposition techniques as well as the generation and control of a bandgap are required [12]. For research considerations, mechanical exfoliation methods are typically employed [179], but scaling up such a process is difficult since the graphene flakes must be individually located prior to further processing techniques. At this time, chemical vapor deposition (CVD) graphene for large-area synthesis on metal (copper and nickel) substrates is a promising synthesis method [182, 183]. Although CVD graphene is not synthesized in a direct microelectronics-compatible method, large areas of graphene have been transferred from copper foils to silicon dioxide/silicon (SiO$_2$/Si) substrates then processed for device or experimental applications [5, 184].

The lack of a bandgap is a major technical issue for future graphene nanoelectronics since large current on-off ratios are required for switching of transistors [185]. Techniques yielding electrical switching capability in graphene include hydrogenation [186], doping [187], and bilayer graphene [185]. Inducing bandgaps in graphene also occurs through fabrication of nanoribbons synthesized by sonication or electron-beam lithography, but to date, processing is difficult to control with repeatable results [188–190]. Although graphene bandgap engineering by spatial confinement (nanoribbons) or lateral-superlattice potential (nanomesh) is promising, confinement widths of $\sim$10 nm are needed for room temperature operation [191]. Current semiconductor fabrication technologies are fast approaching these nanoscale feature sizes, but methods such as serial electron beam lithography are time-consuming for large area coverage as well as expensive for manufacturing applications. NIL techniques using diblock copolymer (DBCP) hybrid masks are potential pattern transfer techniques that can achieve sub-25 nm feature sizes with low cost and large-area coverage.

Recently, graphene nanomeshes (large area interconnected nanoribbons) were demonstrated with much higher on-off currents ($\sim$100 at room temperature for widths >10 nm) and bandgaps that increased as the width of the nanoribbon decreased [192–194]. The fabrication process involved a combination of self-assembly techniques such as DBCP features assembled directly on SiO$_2$-coated graphene that was mechanically exfoliated from highly oriented pyrolytic graphite [194, 195]. With this method, repeatability of features is difficult to establish. Another demonstration included NIL masks made from DBCP features im-
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printed on a thin-film of polystyrene, but thus far shown for graphene flakes printed by an electrostatic method [196, 197], which requires a labor-intensive search for suitable samples since each print may produce several or few layers of graphene [192].

Figure 4.15: Graphene devices and sensing platforms. (A) Etching nano-sized holes in graphene to generate nanoribbon meshes where the bandgap of the materials scales with the nanoribbon width; and (B) Building repeatable nanostructures on graphene for electrical and optical biosensing.

For optical and optoelectronic applications, graphene is emerging as a viable candidate material since control over optical transitions by gate modulation [181], broadband optical modulation [198], and recently, gate-tuning of graphene plasmons [199, 200] have been demonstrated. Photodetectors typically operate by absorption of photons that create electron-hole pairs separated by an electric field where the bandwidth is limited by the absorption of the material [201]. In the case of graphene, since light is absorbed from ultraviolet to terahertz range, the possibility of using the material for photodetection is possible [201]. With high mobilities thus far demonstrated, the response should be ultrafast as well [202].

An efficient quenching of photoluminescence (PL) was demonstrated from gold films deposited on single and multiple layer graphene substrates on silicon dioxide/silicon substrates [203, 204] with gold/single layer graphene (SLG) yielding the best results. Chemical enhancement (CE) of the graphene SERS signal has been presented [20, 203, 205], although those findings are still an active area of research [204]. Control over particle morphology and spacing combined with the effects of graphene PL quenching and improved bonding with molecular material is an area that NIL-templated graphene-based substrates can potentially improve detection sensitivity.

Graphene was initially obtained by mechanical exfoliation of highly oriented pyrolytic graphite, which involved the repeated peeling of samples using an adhesive tape to remove several and few layers of graphene and transfer to another substrate [179]. Since then, a mul-
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titude of fabrication methods have emerged, including epitaxial growth from silicon carbide [206, 207], single crystal transition metals Ni(111) [208], Ru(0001) [209, 210], and Ir(0001) [211], solution processed graphite oxide films [212, 213], and even solid carbon sources [214]. Perhaps the most promising graphene synthesis method is chemical vapor deposition (CVD) graphene grown on nickel or copper foils and thin-films [182–184, 215–218]. CVD graphene layer control on thick nickel substrates has proven difficult due to saturation effects and cooling rates in large furnace configurations [184], although growth on nickel thin-films has been demonstrated [183] and recent progress has been made with a localized synthesis process [219]. CVD graphene on copper substrates provide large area coverage and high quality films are obtainable with low temperature mobilities of 7,350 cm² V⁻¹ s⁻¹ [218]. For these experiments, CVD graphene on copper foil is transferred to 90 and 300 nm SiO₂ on silicon substrates.

4.3.2 Nanoimprint Lithography (NIL)

A powerful method for patterning sub-micron features is based on nanoimprint lithography. First reported in 1995 by Chou et al., nanoimprint lithography (NIL) is a high-throughput, low-cost manufacturing method to fabricate nanostructures in the tens of nanometer feature range [13]. Typically a hard mask consisting of micro- or nanoscale features is fabricated from metal, dielectric, or semiconductor material and placed on top of a polymer thin-film at high temperature and pressure [14]. As the mask and substrate are pressed together, the viscous polymer follows the imprint mold topography resulting in variations of thickness in the polymer film [14]. Once the process is completed and the mold separated from the substrate, the patterned polymer on the substrate is then transferred using a reactive ion etch (RIE). Nanoscale features as diverse as rectangular, cylindrical, and diamond-shaped nanoblocks [220], nanodisks [221], and flat, pillared, or grated nanostructures [222] have been fabricated with this process. The mold is typically fabricated by nanopattern exposure using electron beam lithography or diblock copolymer self assembly [192, 193] followed by metal deposition on the template and selective RIE etching [223]. NIL has become a fabrication method for localized surface plasmon resonance platforms as well [24].

Diblock copolymer (DBCP) nanolithography is a hybrid technique of molecular self-assembly of micro- and nanoscale domains phase separated into different morphologies by volume fraction and length of polymer chains [224]. When combined with lithographic patterning, macroscale area coverage of nano-sized features is possible. The size, shape, and spacing of features can be controlled with this "bottom up" self-assembly process and orientations can vary from spheres and cylinders to bicontinuous gyroids and lamellae [225]. For the fabrication of NIL masks, the DBCP features are assembled directly on the substrate that will become the NIL mask. The two polymers are typically a poly(styrene- b-methyl methacrylate) (PS-b-PMMA) BCP [225] and feature geometries dependent on the desired application. For nanoelectronic patterning of graphene, a post diameter is desirable since the resulting low spots in the imprinted topology can be etched with an oxygen plasma creating
an array of holes in the material. The same mold can be used for building up nanomaterials on graphene, requiring the addition of a protective layer over the graphene.

### 4.3.2.1 Process Flows

The process flow the graphene imprint is shown in Figure 4.16. Initially, once the graphene is transferred to the substrate of choice, a thin layer of PMMA (MR-1 thermal resist, Microresist Technology, Germany) is spin-coated onto the surface. After a short bake on the hotplate (200°C, 2 minutes), the wafer and mold are loaded for imprinting (Nanonex 2000). The wafer and mold are heated above the glass transition temperature of the resist, allowing the resist flow to match and fill the mold topography. After several minutes, the mold and substrate are released. An RIE oxygen plasma etch is used to transfer the mold design into the substrate by removing the exposed graphene and low regions of the resist, leaving an array of holes. The hole diameters can be adjusted by the etch time, thus controlling the nanoribbon mesh width. Prior to spin coating with PMMA, the substrate is baked for several minutes at 180 to 200°C for dehydration purposes.

The process flow for building metamaterials using NIL is shown in Figure 4.17. In this case, the graphene is coated with a metal layer prior to spin-coating PMMA onto the surface, which protects the graphene from the oxygen etching process. The process flow is as follows: (1) PMMA is spin-coated onto the graphene and metal layer; (2) The NIL process is performed at high temperature (200°C) and high pressure, allowing the resist to soften and flow into the mold topography; (3) Once mold and substrate are separated, an oxygen etch process is used to breakthrough the PMMA low spots, exposing the metal layer beneath; (4) The metal layer is wet-etched to expose the graphene; (5) Noble metals are deposited onto the graphene; (6) The PMMA is removed using an appropriate solvent; (7) The metal is etched away leaving only the noble metal features; (8) Metal electrodes can be fabricated or surface functionalization performed prior to testing. Although additional steps are required, the metal protective layer provides the ability to imprint on graphene without affecting the quality of the graphene. Thermally evaporated aluminum has been shown as a sacrificial metal successfully protecting graphene during the oxygen etching process [213], although thin-films on the order of 1 to 2 nm oxidize immediately in contact with air. Thermally evaporated aluminum molecules are less energetic than other deposition processes such as sputtering [226] and can be deposited with minimal defect creation in graphene [226]. Thermal annealing can also improve the quality of graphene post-processing, although the graphene and SiO₂ coupling needs to be considered since heavy hole doping and impaired mobility are potential outcomes [227–229].

### 4.3.2.2 NIL molds and process details

For these experiments, the Nanonex NX-2000 tool at Sandia National Laboratories was used for nanoimprinting (Figure 4.18).
Figure 4.16: Process flow for bandgap etching. (1) A layer of PMMA is spin coated onto the substrate; (2) Mold topology transfer occurs as PMMA is heated above the glass transition temperature under high pressure; (3) After the process, the mold and substrate are separated and the pattern is transferred into the substrate using oxygen plasma etching; (4) The etching process is followed by PMMA removal; and (5) Metal contacts are deposited by thermal or ebeam evaporation.
Figure 4.17: Process flow for SERS metamaterials. (1) A layer of PMMA is spin-coated onto the graphene substrate which was previously coated by a protective metal layer; (2) The PMMA is heated above its glass transition temperature under high pressure for mold topology transfer; (3) Once mold and substrate are separated, the pattern is transferred into the substrate using oxygen plasma etching; (4) The metal protective layer is etched to expose the graphene; (5) Metal dots are deposited; (6) The PMMA is removed with an appropriate solvent; (7) The metal layer is etched away leaving only gold dots; and (8) Metal electrodes are deposited and/or surface functionalization is performed prior to testing.
Several sets of molds were used for the NIL process with feature sizes ranging from the low hundreds to tens of nanometers. For larger features, imprints were made with post masks of varying diameters as shown in Figures 4.19 and 4.20 with 3000 Å and 1350 Å pin depth, respectively. Figure 4.19 shows the long range order and post closeup of the 3000 Å pin length silicon masks. The post diameter is 200 nm and the pitch is \( \sim 700 \text{ nm} \). The NIL process included pre- and post- process controls. The system is initially ramped to the appropriate temperature (here, 200°C). Once the temperature set point is reached, the process is enabled at 200°C and 400 psi for 5 minutes. After five minutes, the temperature is ramped down to 60°C, then the system vents to ambient pressure and allowed to degas for 15 minutes. The samples are then removed and the mold/substrate mechanically separated.

Prior to the NIL process, the substrate was first cleaned in acetone and isopropyl alcohol (IPA) rinses for several minutes. After a short dehydration bake at 180 to 200°C for several and up to 30 minutes in a vacuum oven, a PMMA (MR-1, Microchem) layer diluted 75% with anisole (99%, Sigma-Aldrich) was spin-coated onto the sample at 2500 rpm for 60 seconds followed with a soft bake at 200°C for two minutes. The PMMA layer thickness was measured three times at different locations on the substrate using a NanoSpec film thickness measuring tool.

The typical DBCP mask used for the experiments is shown in Figure 4.21 and fabricated by a collaborator (University of Wisconsin). This mask was fabricated on a four-inch silicon wafer with 75% feature coverage. Multiple mold sizes of DBCP masks (with feature coverage ranging from inches to full wafers) are available. Several of the DBCP molds suffered from PMMA-loading after NIL runs. To mitigate the PMMA build-up, molds were cleaned in a piranha bath (3:1 sulfuric acid:hydrogen peroxide at 120°C) then coated in an integrated UV/ozone cleaner and molecular vapor coater (Nanonex Ultra-100) using a proprietary surfactant for mold release (Nanonex NXT-130). Nanoimprinting with sub-100 nm features
Figure 4.19: SEM images of NIL mold with post diameter 200 nm, \(~700\ \text{nm}\) pitch, and 3000 \(\text{Å}\) post depth showing long-range order (a) and closeup post image (b).

Figure 4.20: SEM images of NIL mold used for imprinting: (a) top view; (b) oblique view. The mold feature dimensions are \(\varnothing115-120\ \text{nm},\ 200\ \text{nm}\) pitch, and 275 nm pillar height. This particular mold was purchased from an outside vendor (Eulitha).
requires additional care and vigilance with the process since the success of the process can depend on a multitude of factors including the mold-release agent, cleanliness of substrates, and tool bladder integrity during the imprint process. Additional available masks fabricated from diblock copolymers are shown in the Appendix.

![Figure 4.21: DBCP NIL mold with feature size 20 to 30 nm.](image)

### 4.3.2.3 Transferring Graphene

The technique to transfer graphene is based on using a polymer thin-film backbone on the graphene as a protective layer while the metal substrate (copper or nickel) is etched away [182–184]. The basic process used for transferring graphene-on-metal foil involves drop- or spin-casting a layer of poly(methyl methacrylate) (PMMA) onto the graphene-on-foil. The metal substrate is etched away, leaving the graphene and PMMA layers. After rinsing, the PMMA/graphene layer is then transferred to the desired substrate and the PMMA dissolved using a solvent. The substrate is then ready for further processing. Although efficient, the transfer technique suffers from a host of difficulties during the transfer to another substrate, including the tearing/folding of graphene, residual PMMA, and incomplete etching of metal substrates. Cleanliness is critical for the successful transfer of CVD graphene. Significant research effort has been focused on improving the transfer method with potential solutions ranging from thermal anneals to remove residual PMMA [227–229] to different etching techniques [230, 231]. Several methods also involve transfer processes with poly(dimethylsiloxane) (PDMS) supports or stamps [183, 216, 230, 232–234]. PDMS can provide an overall cleaner transfer process with less polymer residue remaining, but was not suitable for these NIL experiments due to potential contamination of the current NIL setup.

For these experiments, CVD graphene-on-copper foil (Graphene Supermarket) was used. The resists used for transferring graphene included both MR-1 (thermal resist) and 950 PMMA C 4% (ebeam resist) (MicroChem), which were spin-coated onto the graphene prior to
transfer. Initially graphene was transferred onto 300 nm SiO$_2$ and later 90 nm SiO$_2$, allowing for optical observation of the number of graphene layers under a microscope. Figure 4.22 shows initial transfers of graphene onto 300 nm SiO$_2$ on silicon taken with a digital camera to evaluate the transferred graphene condition. In Figure 4.22(a), the original 4 mm x 4 mm graphene sample has regions of torn or overlapping material with incomplete coverage over the wafer. The bright spots of Figure 4.22(b) are examples of the PMMA residue remaining after the transfer process. The typical sizes of graphene samples were 5 mm x 5 mm and 10 mm x 10 mm coupons on cleaved and full wafer substrates. The etchant used for graphene transfer was an aqueous iron (III) chloride (FeCl$_3$) solution (1 M) as described in [183].

![Figure 4.22](image1.png)

Figure 4.22: Microscope images of transferred graphene on 300 nm SiO$_2$ on silicon. A digital camera was held to the eyepiece for quick evaluation of the transfer process. (a) The graphene is torn and folded over in multiple locations; and (b) Bright spots of residual PMMA still remain on the graphene surface.

Multiple efforts were attempted to clean the transferred graphene of the residual polymers, including use of 1-methyl-2-Pyrrolidinone (NMP) (99%, Acros Organics), remover PG (MicroChem) an NMP-based solvent stripper, and thermal annealing (both 1- and 2-inch vacuum tube furnaces). Both NMP and especially remover PG were found to leave fine PMMA residues. Test imprints following the process flow (sans graphene) and incorporating NMP or remover PG did not yield successful imprints and use of those particular solvents was limited as a method to remove PMMA from the graphene surface. As will be discussed in the next section, the initial evidence from graphene imprints indicated that the residual polymer left an ”island” preventing the polymer flow from evenly filling the mold topography. It was later discovered that PMMA loading on the molds could also contribute to such results, leaving questions as to whether the residual PMMA affected the imprint results or that the older, hardened PMMA on the mold caused incomplete pattern transfer.
Many research groups have attempted to improve the transfer capability of graphene and while that is not the goal of this research, a significant amount of time was expended attempting to clean graphene surfaces and obtain transfers with less tearing and folding of the graphene. Cleaning processes such as piranha- and RCA- (Radio Corporation of America) cleans were attempted since both processes are widely used in microelectronics fabrication for cleaning wafers [235]. Piranha cleans typically consist of a 3:1 ratio of sulfuric acid to hydrogen peroxide by creating an exothermic reaction that removes organic surface contaminants and some metals [170]. Wafers are placed in a heated bath \((120^\circ \text{C})\) for \(\sim 10\) minutes then rinsed in DI water until a resistivity of 10 M\(\Omega\) cm is reached. The RCA-clean process typically involves two steps: RCA-1 and RCA-2 [235, 236]. RCA-1 removes organic surface residues using a 5:1:1 ratio of DI water, ammonium hydroxide, and hydrogen peroxide, respectively. Samples are submerged for five minutes at a temperature of 70\(^\circ\)C then rinsed in DI water for 5 minutes. To remove remaining metallic residues, samples are submerged in RCA-2 solution of 6 parts DI water to 1 part hydrochloric acid to 1 part hydrogen peroxide for five minutes at 70\(^\circ\)C. Samples are then rinsed in DI water until the resistivity of 10 M\(\Omega\) cm is obtained. Test samples of graphene transferred to SiO\(_2\)/silicon substrates in both piranha- and RCA-cleans resulted in tearing and removal of graphene mainly due to bubble generation on the graphene surface at these high temperatures. The remaining graphene is no longer a sheet, rather many flakes. The standard surface cleaning technologies at higher temperatures are not conducive to successful removal of PMMA residue and metallic contaminants without destroying portions of the graphene.

Incorporating a modified RCA clean improved the transfer process dramatically [231]. Based on techniques demonstrated by Liang et al. [231], the graphene transfer process followed conventional steps of spin coating PMMA onto graphene-on-copper-foil then etching in ferric chloride (or other appropriate copper etchant) and rinsing in DI water. The additional steps for the modified RCA-clean are similar to the standard RCA-cleans except for the following [231]: (1) Samples are submerged for 15 minutes rather than five minutes; (2) The temperature is ambient and not raised to 70\(^\circ\)C; and (3) The order of cleans is RCA-2 to remove metallic contaminants first followed by RCA-1 to remove any remaining organic contaminants. Additionally, it was found that the process only works with the protective PMMA layer on top of the graphene. Without that PMMA layer, the graphene becomes shredded in all cases and whatever graphene remains on the surface is a flake-like condition. The modified RCA-clean works in this case because the resulting chemical reaction causes bubble generation of which the frequency and size are a function of temperature and is mitigated by maintaining the solution at ambient temperature. The process still provides enough cleaning capability to yield extremely clean graphene surfaces.

As shown in Figure 4.23, the microscope images (2x) were taken with a digital camera for quick optical evaluation of the transfer process. The transferred graphene show relatively flat and continuous material with little tearing or folding onto itself. Many of the metallic contaminants between the graphene and SiO\(_2\) surface are removed. One other issue is that for these particular samples, the PMMA spin-coated onto the graphene is 495 PMMA A (2%), not 950 PMMA C (4 %).
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4.3.3 Nanoimprinting Results

The imprinting capability of the Nanonex 2000 was expanded to include imprinting on SiO$_2$ substrates. Previously, silicon substrates were used for the majority of imprints. The adhesion of silicon oxide to PMMA was questionable since the properties of each are dissimilar [237].

As shown in Figure 4.24, the diblock copolymer mold can imprint onto SiO$_2$ surfaces without apparent adhesion issues. The larger holes indicate defects from the initial mold and are not a result of the imprinting process. The next steps involve combining the transfer of graphene with the imprinting process.

A successful imprint on graphene is shown in Figure 4.26. This mask was made through a University of New Mexico/Sandia National Laboratories collaboration. The imprint is from the mask shown in Figure 4.19(b).
The NIL mask was fabricated at Sandia National Laboratories (NM), and consists of four rows by nine column sectors of pins. Rows A-D have pin pitches of 500, 1000, 500, and 250 nm, respectively. Pin thicknesses are uniform length of 1350 Å. The pin diameters are initially at 50 nm, although during mask fabrication the dosage was increased for each successive sector and resulted in a change of pin diameter from the original dimensions. Figure 4.26 shows a post imprint on PMMA with the pin diameter \( \sim 75 \) nm and pitch of approximately 250 nm.

Figure 4.25: SEM images of NIL features successfully transferred onto PMMA and graphene. The pin shape is squarish with a "diameter" of \( \sim 270 \) nm and height of 3000 Å(a) and closeup view (b).

Figure 4.27(a) shows a microscope image of a successful imprint and etching of graphene. The NIL mold (Eulitha) used for the imprint is shown in Figure 4.20. The mold geometry features have pillar diameters of 115 to 120 nm, pitch of 200 nm, and height of 275 nm. Prior to the NIL process, the graphene and substrate were cleaned, dehydration-baked, then
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Figure 4.26: SEM image successful NIL imprint on graphene. The mask has 50 nm dot size of increasing dosage and pin depth of 1350 Å. Increasing the dosage affects the overall diameter of the pin size. Here, the pin diameter is \( \sim 75 \) nm with a pitch of approximately 250 nm.

coated with 340 nm of PMMA and soft baked for 2 minutes at 200°C. The oxygen plasma breakthrough etch (Oxford) was 19 seconds. The oxygen plasma etch is typically performed with the following conditions: forward power 13 W, ICP 150, and oxygen flow rate of 50 sccm. Although the wafer holder can be heated up to 400°C, the temperature was maintained at 25°C for these etches. Depending on the thickness of the PMMA, the etch times can vary for several to tens of seconds.

Figure 4.27: Successful nanoimprint and etch of graphene: (a) Microscope image with etched graphene features evident, taken at 1000x magnification. Bright yellow-orange regions indicate residual copper remains from the etch process; and (b) SEM image of NIL mold used for imprint, with feature dimensions of \( \varnothing \)115 to 120 nm, 200 nm pitch, and 275 nm pillar height.

Multiple attempts to imprint using the DBCP NIL mold were met with mixed results.
The imprints appeared to suffer from resist tearup or PMMA buildup. As shown in Figure 4.28, the formation of PMMA free-form shapes and islands of (a) and (b) perhaps indicate the influence of outgassing residual solvents on the surface of the graphene/substrate where the solvent vapor prevents tight contact of the mold with the substrate and prevents the PMMA from flowing into the mold regions. Another potential reason are “high” spots of interference that prevent the mold from direct contact with the PMMA/graphene substrate such as residual PMMA (perhaps hardened by multiple previous processing steps) or incomplete metal removal. The DBCP pin depth is $\sim 30 \text{ nm}$ so any metal particles or other contamination not removed can potentially block the mold from contacting the substrate. The PMMA tearup of the top layer from a thick layer of PMMA (Figure 4.28(c)) suggests that the mold is contacting the top of these thicker island formations and when the mold/substrate are separated following the NIL process, the top layer of PMMA tears away and remains on the mold surface. Figure 4.28(d) shows a successful DBCP NIL imprint, although the formation of PMMA islands and non-uniform features distributed over the substrate complicates the timed oxygen plasma etch.

It was later discovered that several of the molds experienced severe PMMA-buildup on the surface of the DBCP features, which may have affected the initial DBCP imprint results. PMMA buildup is not typical of the larger feature molds and only seems to be an issue with the sub-25 nm features involved with the DBCP molds, perhaps due to the close-packed nature of the feature distribution on the mold.

As shown in Figure 4.29, the buildup can occur quite rapidly and appears to be dependent upon constant vigilance of confirming the surfactant (Nanonex, NXT-130) is in working order. If the mold-release agent is working, the PMMA should release from the mold and remain on the surface. One factor to consider is the adhesion of PMMA to graphene. It may be that PMMA prefers the silicon mold rather than adhering to the graphene, based on the surface energies available at each surface. Or another factor is the potential buildup of solvent on the graphene surface that once the higher temperatures and pressures of the NIL process are activated, outgassing of the solvent can prevent the expected imprint from occurring. In cases where the mold-release agent is non-active, the PMMA will adhere to the DBCP surface and tear off from the PMMA on the imprint surface.
Figure 4.28: SEM images of post-NIL imprint PMMA tearup and buildup of islands: (a) Free form PMMA shapes perhaps indicate the influence of outgassing residual solvents on the surface of the graphene/substrate, which prevent the PMMA from flowing into all mold regions; (b) Formation of PMMA islands which are significantly thicker than the original spin-cast layer of PMMA, suggesting that there is interference between the mold and graphene/substrate (residual PMMA, metal particles, other contamination); (c) Tearup of thick PMMA island top layer, perhaps contributing to loading of the mold surface with PMMA; and (d) Successful DBCP NIL imprint, but the formation of PMMA islands complicates the timed oxygen plasma etch and causes pattern transfer to the substrate to be problematic. Any low spots on the PMMA imprint will transfer by etching to the surface. For this sample, the large, low area regions will be etched away before DBCP pattern can be successfully transferred to the graphene substrate.
4.4 Conclusions

The promising NIL imprint results of 75 nm post diameters and successful imprint and etching of ~115 to 120 nm diameter features into graphene suggests the DBCP NIL graphene-based imprints are close to reality. With extra care to maintain ultra-clean DBCP mold surfaces, use of proper surfactants, and improved transfer techniques of cleaned graphene (using the modified RCA-clean or similar process), many issues preventing successful DBCP imprints can be addressed. New DBCP molds are available and additional testing can perhaps achieve the desired large-area nanoscale features on graphene substrates for electrical, optical, and optoelectronic sensor applications.
Chapter 5

Conclusions and Future Directions

This dissertation has focused on synthesis and integration of nanostructures for sensor, energy, and environmental applications. The previous chapters have described the synthesis techniques used, each with advantages and disadvantages addressing either microelectronics-compatibility, direct integration, scaling up for large-area coverage, or providing repeatable and regular nanopatterning capability. Platforms for bio-, electronic, and optical sensing as well as bulk nanopatterning techniques such as nanoimprint lithography (NIL) to fabricate graphene devices for electronic and optoelectronic sensing have been demonstrated.

The local synthesis and induction heating nanostructure synthesis processes were both based on Joule heating of the substrate. With local synthesis, a highly doped microbridge was resistively heated to growth temperatures resulting in suspended multiwalled CNTs spanning gaps of 5 to 20 µm. The fast, microelectronics-compatible process included a feedback control system which showed when CNT contact on the secondary bridge was detected. The process allowed direct placement of nanostructures at specific locations based on substrate design and provided means for in situ sensing immediately after synthesis. The electrical contacts were shown to improve by annealing of the secondary substrate and avoiding overheating of the CNT.

The induction heating growth technique was based on internally induced eddy currents resulting in Joule heating of the conductive substrate for nanostructure synthesis. The rapid heating and cooling of the process yielded unique TiO$_2$ nanoswords with large % of exposed higher energy surfaces. Based on the evidence of anisotropic photochemical reactivity of bulk TiO$_2$ shown for silver reduction [48, 49], the enhanced photocatalytic response of TiO$_2$ nanoswords was demonstrated. Additionally, hydrogen-annealed TiO$_2$ nanoswords showed greater enhancement than as-grown nanoswords for silver reduction.

To scale up the induction heating process for large area coverage, furnace-based approaches were then employed for titania nanostructure synthesis. By transferring the induction heater growth parameters to the furnace, the restriction of conductive substrates was removed and growth could occur on insulating and transparent substrates as well. Rapid hydrogen-annealing of TiO$_2$ samples was performed with additional characterization showing an increase in visible light sensitivity based on transmission measurements. Further,
photoelectrochemical (PEC) cell experiments taken at one sun illumination and in a sodium chloride solution suggest that the hydrogen-annealed samples can significantly improve the resulting photocurrent.

Nanostructures will impact biosensing applications and one of the urgent issues with large-scale nanomaterial incorporation are residual effects on living organisms. Since morphology, size, and phase affect the reactivity of nanostructures, the effects may translate to cells as well. Cell viability was investigated for increasingly porous silver thin-films based on bulk synthesis processes oblique angle deposition (OAD) and glancing angle deposition (GLAD). Both OAD and GLAD do not involve the high temperatures of the furnace environment and thin film porosity is controlled by the substrate deposition angle. The repeatable fabrication of large area substrates could further increase knowledge of how cells respond when in contact with nanostructures.

Finally, nanopatterning using nanoimprint lithography (NIL) was applied to chemical vapor deposited graphene for etching of nanomeshes and building up metamaterials for electronic and optoelectronic sensing devices. NIL is well-suited for creating repeatable, large-area substrates with features sizes limited only by the mask dimensions. The low-cost and high-throughput process, combined with large area graphene samples, could fabricate regular arrays of nanofeatures on graphene, potentially creating a new class of graphene-based sensors.

The next section discusses observations and offers suggestion for future directions of synthesis and integration of nanostructures for sensor, energy, and environmental applications.

5.1 Integration and Placement of Nanostructures

5.1.1 Local Synthesis of CNT Sensors

Integration and specific placement of nanostructures continue to impede development of nanostructure-based devices, especially for direct connection to the macroworld. Key issues of preventing widespread nanomaterial integration with microelectronics include difficulties with handling and manipulating nanostructures as well as high growth temperatures that can negatively impact existing microelectronics. Efforts to manipulate nanostructures have involved labor-intensive or complicated processes [1, 4, 25–27], all of which highlight the challenges of integrating these structures into workable and scalable devices. Although recent research has shown bulk CNT growth processes at lower temperatures [28–30], the ability to control the specific location and placement of CNTs, or other nanowires/nanorods, is important for integration into working devices and an advantage provided by the local synthesis method. The local synthesis method provides a simple and fast technique to grow nanostructures in specific locations. The self-assembled device can be readily used in applications such as gas sensing, where multiple sensor arrays could be designed for specific locations as required. The electrical contact can also be improved using in situ annealing techniques that are performed immediately post-growth.
Since the local synthesis process is inherently microelectronics-compatible, one direction to improve the growth process is modification of the MEMS-based bridge designs and techniques for controlling the growth process. Initial work incorporating a feedback loop for controlled synthesis has been demonstrated by a collaborating group, where the power input is constant and monitored continually [238].

Design of microstructure elements can improve control over substrate heating and related thermal gradients. To move in this direction, masks for next generation microbridges have been designed based on simulated heating profiles (ANSYS®, v. 11.0), as shown in Figures 5.1 and 5.2.

Figure 5.1: Heating profiles of existing (a) and new (b) U-shaped microbridges.

Figure 5.2: Heating profiles of existing (a) and new (b) V-shaped microbridges.
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Figure 5.3: Section of new mask design based on modified silicon microbridge geometries.

New bridge designs focus on tapering and/or enlarging portions of the microline heaters to accommodate temperature gradients that exist within the structures during heating. By creating larger regions of localized growth, the local synthesis method can be expanded for single or bulk growth of nanostructures. Figure 5.3 is a schematic of the completed designs which are now ready for silicon fabrication.

For device applications, the gas sensing capability of the suspended CNT can be expanded in several directions. As pointed out in chapter 2, the sensing range can be improved by using longer and smaller diameter CNTs. CNT diameters are typically determined by the catalyst size, thus decreasing the thin-film thickness or changing the method of catalyst deposition should yield smaller diameter CNTs. The applied electric field appears to direct the growth of CNTs from the growth to the secondary substrate so optimization of the electric field for local synthesis could potentially assist growth over longer gaps between microbridges.

The gas species sensing capability is an area that could be further explored. CNTs have shown extreme sensitivity to a variety of gas species, including oxygen [65], nitric oxide and ammonia [4]. Since the CNT electrothermal response is independent of molecular adsorption/desorption kinetics for changes in conductivity, the response can be fast. Figure 5.4 also suggests the response for different gases is possible [70]. Additional experiments with gases such as oxygen or ammonia should be investigated for the CNT system.
5.1.2 TiO$_2$ Nanostructures for Enhanced Photocatalytic Activity

Induction heating is a rapid, and potentially cost-effective, method for nanostructure growth. The fast process can synthesize nanostructures in mere minutes compared with other growth processes that can take hours. The process is dry, avoiding the wet chemistry methods often required for nanoparticle synthesis as well as possible contamination from solvents and other chemicals. Beyond the cleaning of the substrates and subsequent deposition of the titanium thin film, the self-sourced growth process requires little additional preparation for TiO$_2$ nanostructure growth.

The uniquely shaped TiO$_2$ nanosword with large % of higher energy surfaces has been shown to exhibit enhanced photocatalytic activity compared with other low index surfaces. The engineering of specific nanostructure surfaces becomes increasingly important for synthesis processes, since controlling nanostructure morphology will play a significant role in the effectiveness of the materials for future applications and enhancement of device performance. If higher energy surfaces can be intentionally created and stabilized, the surface-to-volume benefits of nanostructures can be augmented by increased activity at the nanomaterial surface, which can lead to improved device and energy generation efficiencies.

Although the induction heating process is a fast and simple method for synthesis of nanostructures, it has been limited by the small sample sizes thus far produced. Since the current temperature characterization of the growth process requires that the sample be placed inside the coil diameter, the coil itself restricts the overall sample size. Additionally, the small substrate sizes (3 mm x 3 mm and 5 mm x 5 mm) necessitated techniques to move nanostructures individually for placement on desired substrates, a time-consuming
and unscalable process. Another minor limitation is the required conductive substrate for eddy current generation, which prevented growth of nanostructures directly on transparent substrates such as quartz or fluorine-doped tin oxide for light harvesting applications. Simple modifications to the induction heating setup could include a larger diameter coil and/or placement and characterization of the growth process with the sample at a location outside of the coil. The substrate size would then be limited only by the chamber size. Larger substrates also allow growth temperature characterization using other instruments such as infrared (IR) camera calibration for direct measurements and allow other methods of inferring temperatures to be confirmation of the substrate temperatures at specific applied power levels.

The small sample sizes and conductive substrate requirements provided the impetus to pursue transferring the induction heater growth parameters to a furnace-based process. Furnace growth of nanostructures is a viable option if the appropriate conditions are available. While most parameters were successfully transferred, the large volume of the two inch diameter furnace tube (6 foot length) has several issues to be addressed: (1) At high growth temperatures, and with the large volume, it becomes difficult to safely flow both oxygen and hydrogen (or acetylene) simultaneously; (2) The shared user furnace setup, while important for all lab projects, can provide potential contamination of gases by cross-flow, leaky valves, or residual gases remaining in the system prior to runs; (3) The shared user furnace setup was subject to constant modification, which meant that newly installed equipment could provide new leakage points within the system. These issues may explain why some of the furnace runs were not as successful at producing nanostructures and instead produced dense nanoparticle coverage.

The significance of hydrogen in the growth process should be investigated further. Fluorine-terminated surfaces of anatase crystals led to increased higher energy surfaces of anatase particles [54] and a similar effect may occur during the induction heating process with use of acetylene gas flow. Testing hydrogen effects may be best served in the induction heating setup since the chamber has a smaller volume and the rapid heating and cooling of the system mitigates any effects of having hydrogen and oxygen mixing at high temperatures. Initial growth of TiO$_2$ nanoswords was performed in an acetylene and argon environment with oxygen leakage providing the balance of the oxygen contribution. In the large furnace chamber volume, it is difficult to replicate these conditions safely and was motivation for argon-only and mixed argon+oxygen flows. Unfortunately, the multi-user furnace setup was also subject to constant modification which appeared to cause additional and unmeasurable oxygen leakage into the furnace system. It is possible that significant amounts of oxygen in the flow would cause oxidation of the TiO$_2$ surface and prevent further nanostructure growth. The presence of hydrogen in the induction heater process flow may have prevented oxidation as well.

Based on these observations and experimental results, the furnace growth process could be transferred to a smaller furnace environment which should allow greater control over the system and gases as well as stabilizing the infrastructure such that constant changes (and potential leakage points) are mitigated. The smaller furnace would also provide the
opportunity to include a rapid-cooling component that is missing from the large furnace setup. Although the large furnace samples can be moved out of the heating zones after the appropriate synthesis time, the two inch diameter furnace tube is still subject to ambient heating as the furnace heating zones cool down over time. The smaller furnaces have the capability of rapid cooling by simply opening the lid and exposing the heating zone to ambient air. The temperature of the system should drop rapidly as a result, and the gases can be pumped out safely and quickly. In this case, it may be possible to introduce some amount of hydrogen into the system under controlled conditions.

Another consideration for the furnace growth setup is the ratio of inert gas to oxygen in the flow. Due to the large volume furnace conditions, the flow of argon was restricted to a maximum of 140 sccm initially. After further modifications were made to the system, the maximum flow of inert gas allowable was ~80 sccm due to the rise in ambient pressure as the gases heated up in the tube. In this case, the inert gas to oxygen ratio was 140:6 or 80:5, ranging from 16 to 23. Other experiments in the induction heater setup could run argon flow rates up to 6,000 sccm and 50 sccm oxygen [145]. The ratio in this case is 6000:50, or ~120, which is significantly higher. Depending on how the system is configured, it may be possible to increase the gas flow rate and inert:oxygen gas ratio with the smaller furnace.

Hydrogen-annealing of TiO\textsubscript{2} nanostructures has shown significant photocatalytic enhancement results as well as photocurrent increases compared with control samples for PEC cell experiments. There appears to be an opportunity to further understanding of the enhancement mechanism since the level and depth of surface disorder has not yet been investigated for nanowire morphologies. Modeling and controlling the hydrogen drive-in process may be possible and looking at existing semiconductor fabrication processes may provide a good start point. More specifically, understanding whether the $Dt$ product can be used as a first-order parameter for hydrogen disorder by initially considering the optically black samples then quantitatively evaluating TEM measurements to understand more about the disorder layer thickness. As noted by Chen et al., the hydrogenation process was performed in 20.0 bar $H_2$ atmosphere at 200$^\circ$C for five days, which produced a one nm thick disordered layer of an eight nm diameter nanoparticle [38]. What thickness of a disordered layer is produced using a rapid thermal annealing process is unknown and whether that can be optimized for enhanced photocatalytic activity should be investigated further. With improved quality and increased density of nanostructures, hydrogen-annealing of large-area samples may show improved PEC cell results similar to how the single crystalline TiO\textsubscript{2} nanoswords showed significant enhancement for photocatalytic processes.

### 5.1.3 Nanopatterning for Graphene-based Sensors

Nanoimprint lithography is a low-cost, high-throughput pattern transfer method that can fabricate sub-25 nm features dependent on the initial mask feature design. Dense arrays of diblock copolymer posts were imprinted in PMMA on silicon substrates and later demonstrated on silicon dioxide surfaces. The addition of graphene to the substrate surface causes difficulty with the imprint process. Several issues may be involved as described in chapter
four, where the adhesion of the graphene to the PMMA is nonideal when separating the
mask from the substrate, initial cleanliness problems of imprint masks or graphene surface,
or chemical or mechanical difficulties associated with the mask passivation or tool bladders.
The PMMA used in the pattern transfer process is based on an established protocol that
works well for silicon substrates and was later shown to work on silicon dioxide surfaces. The
main issue with densely packed features is the ability to maintain a clean mask surface after
imprinting, in preparation for the next imprint. The PMMA layer is expected to perform
multiple duties including acting as a protective buffer between the two hard surfaces as well
as transferring the nanopattern at high temperature and high pressure. If the PMMA layer is
too thin, direct contact of the mask with the substrate is possible and can damage the mask.
For layers of PMMA that are too thick, the pattern may transfer, but the etching times
are increased and feature degradation may occur such that the pattern will not completely
transfer. Additionally, the PMMA can have preferential adhesion to the mask rather than
the substrate and when the two are separated, PMMA tear off from the graphene substrate
can occur. Other polymers or blends should be considered for imprinting on silicon dioxide
and graphene, such as polystyrene, which has low adhesion to graphene in its native state
but can be treated with plasma to tune adhesion [239].

Typically masks with larger features (\(\sim 100\) nm and larger) do not require regular cleaning
after imprinting, most likely due to the larger features and pitch. For densely packed diblock
copolymer masks, a cleaning process was implemented as a necessary step although several
masks were still shown to have significant residual PMMA remaining post-cleaning. Since the
PMMA is heated and allowed to flow into all open spaces of the mask, the dense features may
prevent a clean post-process separation. Another factor to consider is the slight sidewall etch
that occurs during reactive ion etching processes that are used during the mask fabrication
process. Typically a chrome mask is used to protect mask features during etching, and this
minimal sidewall etch can create a small overhang at the post tips. When the hard mask is
removed, a slightly-bowed pillar shape may result, although difficult to confirm with SEM
or AFM given the densely packed features. A possible solution to this overhang is to etch
the silicon slightly (and at low power) so that only approximately one to two nanometers
is removed. The etch should remove the overhang as well as create a sloping sidewall that
should result in post-NIL separation without polymer tearoff.

5.1.4 Biosensing with OAD and GLAD substrates

Oblique angle deposition (OAD) and glancing angle deposition (GLAD) are wafer-scale,
physical vapor deposition processes that can create large areas of dense nanostructure arrays.
Fabricating regular and repeatable nanostructured arrays depends on the deposition angle,
which controls the thin film porosity. The clean and dry method can be readily incorporated
into existing microfabrication techniques, providing integration capability of lithographically
defined seed layers and patterned substrates for improved control over nanowire placement.
Glancing angle deposition (GLAD) combines the steep substrate deposition angles with
control over the substrate rotation capability. Different morphologies were demonstrated
and the substrates were used to investigate cell % viability in contact with increasingly porous substrates. Trends indicated that the nanowire morphologies had the lowest cell % viability. Further tests should be performed with these test platforms to establish the mechanism of cell death. Silicon nanowires were shown to penetrate cell membranes with minimal impact of cell viability [240] and the effects of silver nanowire uptake should also be considered since morphology may influence cell survivability [146, 149, 241]. The use of GLAD to create test substrates will provide greater control over nanowire morphology with shape control such as chevrons or zigzags possible [156, 158, 160]. The shape control can also open areas for optical testing such as SERS, given the large area and uniform coverage with nanostructures. Further investigation with nanopatterned seed layers should provide additional control over morphology.

The next step beyond OAD synthesis of nanowires is incorporation of a rotating stage in the ebeam deposition tool for the GLAD process. The parts for GLAD fabrication have been designed and machined with only final retrofitting of the ebeam tool needed to begin synthesis of nanowires using the GLAD technique.
Appendix A

Pressure Sensing Overview

A.1 CNT Contact with Secondary Microstructure

The complex nature of the silicon/CNT heterojunctions was explored by previous researchers [242]. Briefly, both tip and line contacts can play a role in the resulting I-V curves post-growth of CNTs. As shown in Figure A.1, CNT root-growth implies that the catalyst particle remains attached to the growth substrate and the CNT can continue growing as long as the CNT is able to precipitate from the catalyst particle [27]. In this case, the CNT contact with the secondary structure may be a line contact, where the sidewall of the CNT contacts the secondary substrate with multiple contact locations. Figure A.4 provides further evidence of the tip-growth terminated upon contact with the colder secondary structure. Based upon a heterojunction energy band diagram (Figure A.3) [242], the Ohmic behavior is expected for contacts with highly doped silicon, since the narrowed barrier width allows electron tunneling. The contact resistivity for this particular contact based on the simplified model is $10^{-5}$ to $10^{-4} \, \Omega \, \text{cm}^2$ [242].
Figure A.1: This schematic illustrates the potential type of contact that a locally synthesized CNT can make with the secondary microstructure. The top part shows the CNT root growth, where the tip is free of the catalyst and can form a line contact with the secondary structure. The bottom image shows the tip-growth of a CNT. Here, the catalyst leads the CNT growth, possibly influenced by the electric field. The heated tip may be quenched by the colder secondary microstructure, immediately stopping the growth process [70, 242].

Figure A.2: The SEM image showing CNT line contact with multiple locations of CNT/Si contact [242].
Figure A.3: The SEM image showing CNT line contact with multiple locations of CNT/Si contact [242].
Figure A.4: Additional examples of local synthesis CNT growth contact types. (a) CNT growth termination immediately after contact with the secondary microstructure (tip-growth); (b) and (c) CNT line contact with secondary structure (root growth).
A.2 Heat Transfer Due to Molecular Collisions

The molecular regimes as determined by the Knudsen number. From [86].

Figure A.5: Molecular regimes as determined by the Knudsen number, $K_n$ [86].

A.3 Temperature Coefficient of Resistance (TCR)

Figure A.6: Change in CNT resistance v. temperature [70].
Appendix B

Titanium Dioxide Nanostructures

B.1 Induction Heating

B.1.1 Oxygen Leakage

An unknown factor is where the oxygen enters into the system since it is not intentional given the initial acetylene purge and flow through the chamber. Oxygen leakage into the induction heating setup was initially investigated with a rough pressure change estimate of 0.17 Torr/sec from estimated volume of 342 cm$^3$ [112]. Based on equation B.1,

$$\frac{dn(t)}{dt} = \frac{V}{RT} \frac{dP(t)}{dt}$$ (B.1)

where $n$ is the number of moles of gas, $V$ is the chamber volume, $R$ is the universal gas constant, $T$ is temperature, and $P$ is pressure, the flow rate of gas into the chamber is approximately 4.1 sccm [112].

The system was reconfigured to accommodate different gases by the addition of four flowmeters to facilitate studies on the role of gases on nanostructure synthesis and expand the potential nanostructure growth capabilities. Since scaling up the process using acetylene could prove problematic, the new flowmeters would allow argon and argon/2% hydrogen to be used as synthesis gases along with controlled introduction of oxygen into the process. Figure B.1 shows a schematic of the modified test setup [145].

Another test for oxygen leakage was conducted for the modified induction heater setup using three pressure gauges (P1, P2, and P4) throughout the system and including the new flowmeters. The system was pumped down and stabilized at the pump base pressure. A section of the system was then closed off, the pump turned off, and pressure changes across the different gauges recorded in 10 second intervals. As shown in Figure B.2, multiple runs of pressure vs. time values are plotted for the old and new flowmeters.

Table B.1 gives the test parameters and resulting flow rates based on the data taken at each particular flowmeter. Briefly, the time at the synthesis pressure was determined then each pressure/time curve was fit with a polynomial (n=2) and evaluated at the synthesis
Figure B.1: Schematic of induction heating modified test setup. Four additional high- and low-range flowmeters were added to the system. Not shown are the old flowmeters that remain connected to the system. Schematic from [145].

Pressure for the derivative to obtain $\frac{dP(t)}{dt}$. The mean of the different values is considered the average rate. A multiplier of 0.2 is used since oxygen is approximately 20% of air. Using Equation B.1, the flow rate of gas into the system is determined in standard cubic centimeters per minute (sccm).

Table B.1: Induction heating system oxygen leakage test parameters. Leakage calculated at ~50 Torr, the synthesis pressure.

<table>
<thead>
<tr>
<th>Gauge</th>
<th>Flowmeters</th>
<th>$\frac{dP(t)}{dt}$ (Torr/s)</th>
<th>Flow rate (sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>new</td>
<td>0.81</td>
<td>21.9</td>
</tr>
<tr>
<td>2</td>
<td>new</td>
<td>0.81</td>
<td>21.7</td>
</tr>
<tr>
<td>1</td>
<td>old</td>
<td>0.50</td>
<td>13.3</td>
</tr>
<tr>
<td>2</td>
<td>old</td>
<td>0.50</td>
<td>13.4</td>
</tr>
<tr>
<td>4</td>
<td>old</td>
<td>0.50</td>
<td>13.6</td>
</tr>
</tbody>
</table>

It appears that the increased number of flowmeters introduced additional locations for oxygen leakage. The increase of oxygen flow into the system may change the TiO$_2$ nanostructure growth dynamics.
Figure B.2: Pressure vs. time data for oxygen leakage tests.
Figure B.3: Partial schematic of modified induction heating system showing location of new flowmeters.
B.2 AFM Scans for Photocatalytic Reduction of Silver

AFM scans were used to determine the amount of silver reduced onto the TiO$_2$ nanosword and bulk rutile (110) and (101) surfaces [111]. Based on each scan (256 lines data gathered, 512 data points per line), image pixel resolution was calculated at 1.95 x 3.91 nm$^2$ and 3.91 x 7.81 nm$^2$ for 1:1 aspect ratio of 1 µm and 2 µm scan sizes, respectively. The first order flattening function was used to normalize the data (Nanoscope software, version 5.31) with the bare sections (uncoated with silver) of rutile substrate or thermal oxide on silicon as the references for rutile substrates and nanoswords, respectively. AFM tip height confirmed with NIST traceable calibrated references (VLSI Standards, Inc., Model SHS 180QC, 13.8±0.9 nm and Model SHS-440QC, 44.5±0.9 nm). Lateral dimension confirmed with 145 nm pitch AFM calibration grating (Ted Pella, Inc., #642-1AFM, accuracy ±1 nm) with a new tip (TESPAW) used for each sample. Each parsed 200 nm x 200 nm section of data represents a single data point for the corresponding substrate or nanosword, UV exposure time, conditioning step, with at least 50 data points used. These expanded data include statistical information (mean, standard deviation, standard error of the mean, and sample population).

Figures B.4 and B.5 show the results of measurements for as-grown and hydrogen annealed TiO$_2$ nanoswords, respectively. Figures B.6 and B.7 show the results of AFM scans for (101) and (110) polished bulk rutile TiO$_2$ surfaces.

Figure B.8 shows the AFM plot of reduced silver comparison including standard error of the mean error bars [111].
Figure B.4: AFM scans of silver reduced on as-grown TiO$_2$ nanoswords for 60, 17, 10, 5, and 1 minutes [111].
Figure B.5: AFM scans of silver reduced on hydrogen-annealed TiO\textsubscript{2} nanoswords for 60, 17, 10, 5, and 1 minutes [111].
Figure B.6: AFM scans of silver reduced on bulk rutile TiO$_2$ (101) surfaces for 60, 17, 10, 5, and 1 minutes [111].
Figure B.7: AFM scans of silver reduced on bulk rutile TiO$_2$ (110) surfaces for 60, 40, and 17 minutes [111].
Figure B.8: Quantitative comparison of TiO$_2$ nanoswords (as-grown and hydrogen annealed) with polished TiO$_2$ (110) and (101) surfaces over time (1, 5, 10, 17, 40, and 60 minutes), including standard error of the mean error bars [111].
Appendix C

Silver Nanowire Nanotoxicology Tests

C.1 Experimental Protocols

C.1.1 MTS Assays

The protocols used for the nanotoxicology experiments were provided by our collaborators. As shown in Figure C.1, the MTS assay process flow is as follows: (1) 1 cm x 1 cm substrates of silver nanowires placed into wells of 24-well multiplate, (2) A549 (human, adenocarcinomic) cells seeded at density of 50000 cells/well containing 500µL medium/well, incubated at 37°C with 5% CO₂ for 24 hours; (3) each wafer sample transferred to new well; (4) 250µL of DMEM medium, high glucose, 10% FBS and 50µL of MTS solution; (5) incubated at same conditions of (2) for 1 hour, then 100µL each sample transferred to 96-well multiplate for absorbance measurements (490 nm wavelength). Additives such as DMEM and FBS help provided consistent cell growth and morphology over time and with passages [243]. Here, both A549 and RLe-6TN cell lines were used for separate experiments. Tests were performed using CellTiter 96 AQueous One Solution Cell Proliferation Assay (MTS) from Promega [178].

C.1.2 Luciferase Assays

Luciferase assay protocols used HeLa based cells containing HIV-LTR luciferase reporter gene. The protocol is as follows: (1) grow stable HeLa cells containing the HIV-LTF luciferase reporter gene; (2) Trypsin is used (24 hours later) to detach cells, with cells then seeded into the 24-well multiplate containing the silver nanowire substrates; (3) at different time points, samples are washed in phosphate-buffered saline (PBS) followed with trypsin treatment to detach cells from the substrates; (4) cells are collected in PBS, then spun down; (5) cells are then aspirated from the supernatant, washed in PBS again, and spun down; (6) cell lysis buffer for luciferase assay used to break cells and spin down (remove) cell debris; (7) substrates are added into the supernatant using the luciferase assay kit, with signals detected using a luminometer.
Luciferase reporter systems are considered a sensitive and quantitative method providing the ability to measure gene expression in living cells via bioluminescence without external illumination with low background emission [244]. In vivo monitoring of gene expression is possible due to the interaction of luciferase with substrate luciferin in the presence of magnesium and adenosine triphosphate (ATP), and monitored using high sensitivity charged coupled devices (CCD) cameras [245]. For cytotoxicity applications, the measured luminescence indicates the number of cell deaths based on protease activity released from cells that have ceased membrane activity [246]. The highest number of cell deaths, as indicated by the measured luminescence, occurred on samples M3-M5 (85° and 90° deposition angles).

Based on the results, more questions than answers are apparent. These tests should be re-run to evaluate what other factors may be influencing the results since they do not agree well with the multiple runs of the MTS assays. Thus, these results are not reported without further investigation.

C.2 Silver Nanowire Experimental Designations
# Silver Nanowire Nanotoxicology Tests

## Table C.1: Silver nanowire morphology-dependent nanotoxicology testing sample designations.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Material</th>
<th>Angle or Condition</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>M0</td>
<td>Si</td>
<td>Cleaned Wafer</td>
<td>Piranha-clean (3:1)</td>
</tr>
<tr>
<td>M1</td>
<td>Ag</td>
<td>0°</td>
<td>42 nm Ti adhesion layer; 300.5 nm silver, control sample</td>
</tr>
<tr>
<td>M2</td>
<td>Ag</td>
<td>90°</td>
<td>Up*</td>
</tr>
<tr>
<td>M3</td>
<td>Ag</td>
<td>90°</td>
<td>Down**</td>
</tr>
<tr>
<td>M4</td>
<td>Ag</td>
<td>85°</td>
<td>Up</td>
</tr>
<tr>
<td>M5</td>
<td>Ag</td>
<td>85°</td>
<td>Down</td>
</tr>
<tr>
<td>M6</td>
<td>Ag</td>
<td>75°</td>
<td>Up</td>
</tr>
<tr>
<td>M7</td>
<td>Ag</td>
<td>75°</td>
<td>Down</td>
</tr>
<tr>
<td>M8</td>
<td>Ag</td>
<td>0°</td>
<td>Annealed samples; Argon environment; Samples from M1</td>
</tr>
<tr>
<td>M9</td>
<td>Ag</td>
<td>0°</td>
<td>3 nm Ti adhesion layer; 200.3 nm silver; Annealed samples; Argon environment; Samples from M10</td>
</tr>
<tr>
<td>M10</td>
<td>Ag</td>
<td>0°</td>
<td>3 nm Ti adhesion layer; 200.3 nm silver, control sample</td>
</tr>
<tr>
<td>M11</td>
<td>Ag</td>
<td>85°</td>
<td>4 nm Ti adhesion layer; 50 nm silver; Si substrate; Fine particle morphology</td>
</tr>
<tr>
<td>M12</td>
<td>Ag</td>
<td>90°</td>
<td>Up</td>
</tr>
<tr>
<td>M13</td>
<td>Ag</td>
<td>90°</td>
<td>Down</td>
</tr>
<tr>
<td>M14</td>
<td>Ag</td>
<td>85°</td>
<td>Up</td>
</tr>
<tr>
<td>M15</td>
<td>Ag</td>
<td>85°</td>
<td>Down</td>
</tr>
<tr>
<td>M16</td>
<td>Ag</td>
<td>75°</td>
<td>Up</td>
</tr>
<tr>
<td>M17</td>
<td>Ag</td>
<td>75°</td>
<td>Down</td>
</tr>
<tr>
<td>M18</td>
<td>Glass</td>
<td>Cleaned cover slide</td>
<td>slide 1 cm</td>
</tr>
<tr>
<td>M19</td>
<td>Ag</td>
<td>85°</td>
<td>4 nm Ti as the adhesive layer; 50 nm silver; Glass cover slide, Ø1 cm; fine particle morphology</td>
</tr>
<tr>
<td>M20</td>
<td>Ag</td>
<td>0°</td>
<td>Annealed samples; Air environment; Samples from M1</td>
</tr>
<tr>
<td>M21</td>
<td>Ag</td>
<td>0°</td>
<td>3 nm Ti adhesion layer; 200.3 nm silver; Annealed samples; Air environment; Samples from M10</td>
</tr>
</tbody>
</table>

*Up represents the upper portion of the wafer relative to source material. **Down represents the lower portion of the wafer relative to the source material (closer to the source material). Samples are taken from the respective sections of the wafer.
Appendix D

Graphene for Optical Sensing

D.1 Additional diblock copolymer masks

As shown in Figure D.1, diblock copolymer masks were available with other morphologies, including grooves and holes.
Figure D.1: SEM images of NIL masks with additional morphologies fabricated from diblock copolymers, including grooves (a-c), and holes (d-e).
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