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Growth of CuIn(Ga)Se2 Thin Film Solar Cells

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Abstract and Introduction:
Copper indium diselenide (CuInSe2) and copper indium gallium diselenide (CuInGaSe2) thin film solar cells deposited by spray pyrolysis are a low cost way to provide solar energy. Although they are relatively cheap to fabricate, they suffer from low efficiencies because of their small grain sizes. In this work, we investigated the conditions of growth rate and temperature in order to obtain stoichiometric layers of these materials. We also investigated the conditions necessary to grow cadmium sulfide (CdS) by chemical bath deposition, which was used as the n-type window layer for our solar cell structure. Employing cadmium sulfide also increased the photovoltaic solar efficiency of our tandem structure.

CuInSe2 and CuInGaSe2 films were grown on soda lime glass substrates coated with 150 nm of evaporated molybdenum at 350-400°C for 30-60 minutes. Energy dispersive spectroscopy (EDS) data for CuInSe2 indicated the presence of all three elements. Cadmium sulfide (CdS) films were grown in a bath of cadmium chloride (CdCl2), thiourea and aqueous ammonia at 70°C with a pH of 11. EDS on cadmium sulfide indicated the presence of both elements in equal abundance.

Experimental Procedure:
Before deposition on the surface of the soda lime glass substrate, the glass was cleaned thoroughly. The glass was first put in a bath with soap and water followed by a 10 minutes acetone rinse and then a 5 minute methanol rinse. The glass was then cleaned in a 30% hydrochloric acid bath for about 30 minutes, and finally, in aqua regia [1].

The back contact layer, molybdenum (Mo), was deposited on soda lime glass by a technique called electron-beam evaporation. The thickness of the layer was set to 150 nm. The CuInSe2 layer was deposited on the Mo-coated soda lime glass by spray pyrolysis as seen in Figure 1. The thickness of this layer had to be between 1000-2000 nm in order to make the solar cell work efficiently. Initial stock solutions of copper chloride (CuCl2) and indium chloride (InCl3) were prepared.

The rate of deposition for the CdS layer was approximately 3 nm/min which produced a 80 nm thick layer. EDS on CuInGaSe2 indicated the presence of all four elements as seen in Figure 3. When the concentration of Ga and In were split in half, we had a more uniform layer with the growth of CuInSe2 and CuInGaSe2 growth can be seen in Table 1.

The CdS layer was deposited by chemical bath deposition and was the n-type contact for the cell. Initial stock solution of thiourea, CdCl2, and ammonium hydroxide (NH4OH) were made with solution concentrations of 10 mM for CdCl2, 50 mM for thiourea and 1 M for NH4OH. At first NH4OH and CdCl2 were mixed and heated in a water bath until the temperature reached 70°C. Thiourea was added to the bath and the pH was adjusted to 11 with 20% potassium hydroxide (KOH) and the substrate was then quickly immersed. The deposition time was 30 minutes [3].

Results and Conclusion:
The CuInSe2 and CdS layers were deposited more uniformly when the concentrations of the solutions were doubled. EDS data for CdS indicated the presence of both elements as seen in Figure 2. The rate of deposition for the CdS layer was approximately 3 nm/min which produced an 80 nm thick layer. EDS on CuInGaSe2 indicated the presence of all four elements as seen in Figure 3. When the concentration of Ga and In were split in half, we had a more uniform layer with the
The presence of all elements. We also had a better deposition rate when we roughened the surface of our sample. Uniform films of CdS were routinely obtained by chemical bath. Uniform films were more difficult to obtain by spray pyrolysis. Slower spray rates in general produced better films. CIGS films also appeared more uniform than CIS films.

**Future Work:**
Steps need to be taken to increase the growth rate for all layers. Efforts should also be undertaken to determine what parameters affect layer uniformity. Grain sizes need to be determined to see if they can be increase by rapid thermal annealing at high temperatures. Finally, solar cells should be fabricated so efficiency measurements can be performed.

**Acknowledgements:**
I would like to acknowledge the National Science Foundation, the National Nanotechnology Infrastructure Network Research Experience for Undergraduates (NNIN REU) program, and the Howard Nanoscale Science and Engineering Facility (HNF) for this great opportunity. I would also like to thank my principal investigator Dr. Gary L. Harris, my mentor Mr. James Griffin, and other staff and students at HNF including Ms. Bokani Mtemi and Ms. Mpho Musengua for their guidance and support.

**References:**

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<td>1</td>
<td>soda lime glass</td>
<td>2.5x10^{-3} M CuCl2, 0.165M dimethylsulfoxide</td>
<td>275-350°C</td>
<td>5 psi</td>
<td>40-60 psi</td>
<td>High</td>
<td>1 hour</td>
<td>Roughened surface cleaned with H2SO4, HNO3, DI Water</td>
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<td>2</td>
<td>70mm of Moly on soda lime glass</td>
<td>2.5x10^{-3} M CuCl2, 0.165M dimethylsulfoxide</td>
<td>300-350°C</td>
<td>5 psi</td>
<td>40-60 psi</td>
<td>Constant</td>
<td>1 hour</td>
<td>Roughened glass Used a 4 step cleaning bath</td>
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<td>70mm of Moly on soda lime glass</td>
<td>2.5x10^{-3} M CuCl2, 0.165M dimethylsulfoxide</td>
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<td>Low</td>
<td>1 hour</td>
<td>Smooth surface Used a 4 step cleaning bath</td>
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<tr>
<td>4</td>
<td>70mm of Moly on soda lime glass</td>
<td>2.5x10^{-3} M CuCl2, 0.165M dimethylsulfoxide</td>
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<td>50 psi</td>
<td>Constant</td>
<td>35 min</td>
<td>Used a 4 step cleaning bath</td>
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<tr>
<td>5</td>
<td>70mm of Moly on soda lime glass</td>
<td>2.5x10^{-3} M CuCl2, 0.165M dimethylsulfoxide</td>
<td>300-350°C</td>
<td>10 psi</td>
<td>60 psi</td>
<td>High</td>
<td>20 minute</td>
<td>Used a 4 step cleaning bath</td>
</tr>
<tr>
<td>6</td>
<td>Cadmium sulfide on soda lime glass</td>
<td>5x10^{-3} M CuCl2, 12.5x10^{-3} M InCl3, 0.33OM dimethylsulfoxide</td>
<td>350-400°C</td>
<td>5 psi</td>
<td>59 psi</td>
<td>Constant</td>
<td>35 min</td>
<td>Doubled concentration and cadmium sulfide substrate Used a 4 step cleaning bath</td>
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<td>7</td>
<td>85nm of Moly on soda lime glass + a top layer of cadmium sulfide</td>
<td>5x10^{-3} M CuCl2, 12.5x10^{-3} M InCl3, 0.33OM dimethylsulfoxide</td>
<td>300-400°C</td>
<td>5 psi</td>
<td>59 psi</td>
<td>Constant</td>
<td>45 min</td>
<td>85 nm of Molybdenum and doubled concentration Used a 4 step cleaning bath</td>
</tr>
<tr>
<td>8</td>
<td>150nm of Moly on soda lime glass</td>
<td>12.5x10^{-3} M CuCl2, 6.25x10^{-3} M InCl3, 6.25x10^{-3} M GaCl3, 0.33OM dimethylsulfoxide</td>
<td>350-400°C</td>
<td>5 psi</td>
<td>59 psi</td>
<td>Constant</td>
<td>1 hour</td>
<td>Added gallium chloride to make it a CuInGaSe2 cell Used a 4 step cleaning bath</td>
</tr>
</tbody>
</table>

Table 1: Spray pyrolysis growth conditions for CuInSe2 and CuInGaSe2.
Zn Diffusion for High Sensitivity InGaAsN Photodetectors

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Abstract:
The sensitivity of solid-state photodetectors is often limited by surface leakage current along the etched/cleaved side wall under reverse bias voltage, as shown in Figure 1 (a). A significant reduction in leakage current was recently reported for indium gallium arsenide nitride (InGaAsN), using epitaxial growth of an n-i-n structure, followed by spatially selective surface dopant type conversion during metal-organic chemical vapor deposition re-growth using dimethylzinc and diethylzinc [1-3]. The etched/cleaved surface is thus surrounded by the n-type layer and no longer under bias, as shown in Figure 1 (b). In this summer project, we proposed a novel ex situ zinc (Zn) diffusion approach to surface dopant type conversion of n-i-n diodes, using a commercially-available Zn-containing spin-on-glass (SOG). We investigated the influence of annealing time on the diffusion of Zn into gallium arsenide (GaAs). Specifically, we used Hall measurements to investigate the active Zn concentration profiles as a function of annealing time and etch depth. This Zn-SOG surface dopant type conversion approach will be used for the fabrication of low leakage InGaAsN based photodetectors, intended for operation in the 1.3 µm to 1.55 µm wavelength range [4,5].

Procedure:
For GaAs:Zn-SOG diffusion studies, the GaAs wafer surface was first conditioned by heating at 350°C to 400°C for a few minutes in air. Zincsilicafilm 306 was then coated on the wafer surface by spin coating at 3000 rpm for 1 minute. After spinning, the wafer was cured by heating in air for 10-15 minutes at 100°C to 120°C [6]. Annealing was then carried out in a quartz furnace with N\textsubscript{2} overflow, with a GaAs proximity cap to prevent As out-diffusion. Following annealing, the Zincsilicafilm was removed by etching with 10% HF, and the surface was examined in an optical microscope. To identify the optimal annealing conditions for photodetector fabrication, the GaAs:Zn-SOG samples were annealed at 850°C for various durations: 15, 20, 23, 30, and 40 minutes.

To characterize the active Zn concentration depth profile, each ~ 1 x 1 cm\textsuperscript{2} GaAs:Zn-SOG sample was cleaved into fourths, and one corner of each piece was then coated with photoresist as an etch stop. Following baking for 10 minutes at 130°C, wet etching in H\textsubscript{3}PO\textsubscript{4}:H\textsubscript{2}O\textsubscript{2}:H\textsubscript{2}O (1:1:25) was carried out for 0, 38, 75, 113 s, resulting in depths of 0, 135 ± 1, 182 ±14, 325 ± 18 nm, as determined by Dektak profilometry. The etched pieces were then cut into ~ 4 x 4 mm\textsuperscript{2} pieces, and Hall and resistivity measurements were carried out at room temperature.

Results and Analysis:
We assume that the active Zn concentration profile follows the so-called “finite source” Gaussian diffusion profile, as shown in Figure 2 (a), where \(x\) is the depth from the unetched surface, \(p_{o}\) is the carrier concentration at the unetched

\[
(a) \quad p(x) = p_{o} \exp\left(-\frac{x^2}{2\sigma^2}\right)
\]

\[
(b) \quad p_{x}(x_{c}) = \int_{x_{c}}^{\infty} p_{o} \exp\left(-\frac{x^2}{2\sigma^2}\right)dx = p_{o} \sqrt{\frac{\pi}{2}} \sigma (1 - erf\left(\frac{x_{c}}{\sqrt{2}\sigma}\right))
\]

Figure 2: (a) “finite source” Gaussian profile assumed for Zn diffusion, (b) integration of the profile in (a) to fit the measured residual sheet carrier density as a function of etch depth.
surface, \( p(x) \) is the carrier concentration at depth \( x \), and \( \sigma \) is the characteristic diffusion length. The experimentally obtained data cannot be directly fit to the Gaussian profile since the measured sheet carrier density is the total residual carrier density in the film. Therefore, the Gaussian profile was integrated to fit the measured residual sheet carrier density, \( p_s(x_s) \), as a function of etch depth, \( x_s \), as shown in Figure 2 (b). For each annealing time, \( p_0 \) and \( \sigma \) were then obtained by fitting the measured data to the integrated Gaussian expression, as summarized in Figure 3. As shown in this table, annealing at 850°C for 15 min yields \( p(200 \text{ nm}) \approx 9 \times 10^{19} \text{ cm}^{-3} \), which is more than double the n-type dopant concentration in the top of the GaAs photodetector structure (5 \( \times \) 10^{18} cm^{-3}), and therefore is sufficient to convert the top layer to p+. Figure 4 shows the best fit Gaussian curve for all of the annealing times, which indicates that as the annealing duration is increased, \( \sigma \) increases and \( p_0 \) decreases.

Since a localized active Zn profile is needed to limit the thickness of the i-layer which is converted to p-type, 850°C for 15 min is identified as the optimal annealing condition for the purpose of photodetector fabrication via surface dopant type conversion of n-i-n diodes.

Conclusions:

We proposed a novel ex situ Zn diffusion approach to surface dopant type conversion of n-i-n diodes, using a commercially available Zn-SOG. We characterized the Zn diffusion profile for GaAs:Zn-SOG samples and concluded that the 15 minute annealing time produces the optimum profile of electrically active Zn. In the future, this approach will be used to reduce leakage currents in InGaAsN-based photodetectors.

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References:


Figure 3: Summarizing Carrier concentrations at the unetched surface, \( p_0 \), and characteristic diffusion lengths, \( \sigma \), for samples with various annealing times.

Figure 4: Carrier concentration, \( n \) vs. etch depth, \( x \).
Graphene Synthesis by CVD on Copper Substrates

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Abstract and Introduction:
Graphene is an extremely interesting and potentially important material with unique and desirable physical characteristics. A few of the practical applications envisioned for graphene include semi-conductor applications, optoelectronics (solar cells, touch screens, liquid crystal displays), graphene based batteries/super-capacitors, and thermal management. To achieve some of these goals though, large, high-quality graphene is needed [1]. Our research focused on synthesis of monolayer graphene on 25 µm thick copper (Cu) substrates, which allowed for lateral growth on the scale of many centimeters; various measurements showed predominantly uniform, monolayer graphene. The graphene was grown using chemical vapor deposition (CVD) with methane and hydrogen gas in a tube furnace vacuum system. The as-grown graphene was characterized using a scanning electron microscope (SEM) to understand growth at different conditions and to find desired growth parameters. The graphene films were then transferred to Si/SiO₂ wafers for further characterization by optical microscopy and micro Raman spectroscopy. To date, we have seen that higher temperature growth results in a faster growth rate with generally higher quality graphene coverage and that the growth mechanism is based on surface adsorption.

Experimental Procedure:
Graphene samples were grown on 25 µm thick copper foil in a quartz tube furnace system using a CVD method involving methane and hydrogen gases [2]. Under vacuum conditions of 10 mtorr, the furnace would be heated with a 2 sccm flow of H₂ present. Temperatures that were tested ranged from 800°C to 1050°C. After 40 minutes of heating to allow the copper foil to anneal, a flow of 35 sccm of methane would be introduced for a growth time ranging from 30 seconds to 15 minutes. A quick cooling method was used (~300°C/min) after growth, and the methane and hydrogen gas flows were continued throughout the cooling process. The graphene films on copper were then characterized using SEM images. After transferring the films to Si/SiO₂ wafers through polymethyl methacrylate (PMMA) coating and iron (III) nitrate etching [2,3], the films would be further analyzed by optical microscopy and Raman spectroscopy.

Figure 1: Growth for 10 minutes - clockwise starting with A, growth temperatures of 900, 950, 1000, and 1050°C, respectively.
Results and Discussion:
The graphene films that were grown on the copper substrates were predominantly uniform monolayer graphene; on the scale of many centimeters, with minimal defects/multilayer flakes. The uniform monolayer growth can be attributed to a surface adsorption growth mechanism due to carbon’s low solubility in copper [4].

The growth mechanism consists of carbon nucleation sites adsorbing to the copper surface and then growing with addition of carbon to the edges of these growth domains. This growth mechanism, as opposed to a precipitation-based mechanism, allows for the monolayer growth, with very little of the multilayer growth that is seen for precipitation-based growth [4]. The growth domains can be seen in Figure 1, with the domains increasing in size from additional carbon atoms being adsorbed to the edges of the nucleation sites until the domains join, forming graphene (Figure 1d). These figures also display the temperature effect on the growth of the graphene sheets. The images show that increasing temperature (in the range we studied) while holding growth time constant results in significantly faster growth at the higher temperatures, with generally larger domains. This shows that the growth rate of the graphene is highly dependent on the temperature of growth and that full high-quality coverage is apparently more easily achieved at these higher temperatures.

Future research on CVD growth of graphene on metals such as Cu can hopefully lead to larger growth domains and improved physical characteristics. Improved electrical properties may also be able to be achieved through some form of doping to create n or p type films. Finally, achieving uniform bi-layer or other n-layer graphene with control of n, vs. only monolayer graphene, is an exciting challenge.

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I would like to thank Professor Rod Ruoff for the opportunity to participate in this program and allowing me to work on this project with his team members. I would also like to thank Dr. Xuesong Li, a postdoctoral fellow in the Ruoff group, for teaching and helping me immensely throughout the research. Additionally, I would like that thank the National Nanotechnology Infrastructure Network Research Experience for Undergraduates (NNIN REU) Program for organizing this program and the National Science Foundation for their contributions to the program and furthering my education.

References:
**Mechanical Properties of Atomic Layer Deposited Tungsten**

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**Abstract:**
Using passive test structures, the residual stress and through-thickness stress gradients for atomic layer deposition (ALD) tungsten on nickel were found to have a mean of 1555 pascals (Pa) and a standard deviation of 144 Pa and a mean of -77 Pa and a standard deviation of 572 Pa, respectively.

**Introduction:**
Because tungsten is a refractory metal, its use as a structural material in micro or nano-electromechanical devices allows the devices to operate at high temperatures. Atomic layer deposition tungsten (WALD) has the additional advantage of low deposition temperatures (120°C) in addition to the perfectly conformal coating of all surfaces—even those that have been undercut. In designing WALD devices, it is important to know the residual stress, which results from the mismatch between the thermal expansion coefficients of the deposited tungsten and the underlying material. Residual stress can cause cantilever structures to curl toward or away from the substrate, changing working distance and function of a device. In addition, residual stress can affect the resonant frequency, which is critical for sensor applications. Characterization of the residual stress should lead to better models and simulations of devices, allowing for the proper design of a functioning WALD device. Using passive test structures, the residual stress and through thickness stress of WALD deposited on nickel was measured.

**Procedure:**
First, a 10 nm thick layer of chromium, followed by 300 nm of nickel were deposited on a silicon substrate via thermal evaporation. Next, 32 nm of WALD was grown on the substrate at 120°C. Bridges and cantilevers were then patterned by optical lithography using spin-coated NR-9 negative resist. A hard-mask was developed by evaporation of a 35 nm thick layer of Ni followed by lift-off. The WALD structures were completed after reactive ion etching (RIE) for 45 seconds. The hard-mask and sacrificial layer were then removed via wet etching, releasing the WALD structures, and a critical point dryer used to avoid stiction caused by surface tension. Finally, a topographical map of the structures was obtained using a light interferometer, which could then be analyzed to find the displacements of the bridges and cantilevers.

**Results and Analysis:**
The bridge structures allowed the compressive residual stress to be extracted, whereas the cantilevers allowed the through thickness stress to be measured. Residual stress can be calculated using Equation 1, where \( \sigma \) is the stress, \( L_{ff} \) is a geometrical constant from Figure 1, \( E \) is Young’s modulus, \( v \) is Poisson’s ratio, \( H \) is the maximum displacement of the beam, and \( h \) is the thickness [1].

\[
\sigma = \frac{E \pi^2}{12(1 - v)L_{ff}^2} (3H^2 + 4h^2)
\]

*Equation 1*

The through thickness stress gradient is found using Equation 2, where \( \Delta \sigma \) is the through thickness stress gradient, \( E \) is Young’s modulus, \( L_{cb} \) and \( h \) are geometrical constants from Figure 2, \( z \) is the deflection at the tip, \( K_0 \) is a constant in \( v \) and \( h \), \( \sigma \) is the stress from Eq. 1, and \( K_1 \) is a constant in \( h \) [1].

\[
\Delta \sigma = \frac{Ehz - K_0 \sigma L_{cb} h}{K_1 L_{cb} h + L_{cb}^2}
\]

*Equation 2*

\[
K_0 = (1.33 + 0.45v)(1.022 - 0.014h)
\]

*Equation 3*

\[
K_1 = 0.0086h^2 - 0.047h + 0.81
\]

*Equation 4*
Young’s modulus was taken to be the same as for bulk tungsten. The mean and standard deviation of the residual stress and stress gradient was found since the unevenness due to the growth process (mainly from the evaporation of nickel) far outweighed the uncertainty in measurement from the light interferometer.

**Conclusion:**
The residual stress of atomic layer deposition tungsten on nickel was found have a mean of 1555 Pa and a standard deviation of 144 Pa. The through thickness stress gradient was found to have a mean of -77 Pa and a standard deviation of 572 Pa. The residual stress is quite small especially when compared to the expected thermal stress for the same thickness of bulk tungsten on nickel, which should be about 331 MPA. The majority of the stress is believed to be thermal stress, but it would seem that the thermal expansion coefficient of WALD is much higher than bulk tungsten. This would not be that surprising as WALD is thought to be a nano-crystalline in structure. It is important to find the thermal expansion of WALD on nickel as the devices utilizing WALD will be operated at high temperatures and therefore could only be properly modeled by taking into account thermal expansion. Since the structure of WALD is different than bulk tungsten, it would be expected to have a different Poisson ratio and Young’s modulus as well.

**Future Work:**
There is much more work to be done to truly understand WALD. Some of these include: finding Young’s modulus, finding the thermal expansion coefficient (that way the stress due to thermal mismatch can be calculated), finding Poisson’s ratio, and seeing how the growth parameters (temperature and time) of WALD affect its properties.

![Figure 2: Schematic of cantilever structure.](image)

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**References:**
Photon-Enhanced Crystallization Kinetics and In Situ High Temperature Conductivity Studies in Ultra-Thin La\textsubscript{0.6}Sr\textsubscript{0.4}Co\textsubscript{0.8}Fe\textsubscript{0.2}O\textsubscript{3-δ} Films

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Abstract and Introduction:
Solid oxide fuel cells (SOFCs) have drawn attention for electrical power generation because of their low emissions, high efficiency, and flexibility in fuel sources [1]. SOFCs typically operate at temperatures at or above 700°C, creating issues with thermal stress, material selection, and device packaging [2,3]. Efforts are being made to reduce SOFC operating temperatures to between 200°C and 600°C utilizing thin film device structures, reducing many of the impacts of the aforementioned factors [4]. However, reduced operating temperature may also decrease the ionic/electronic conductivity and decrease oxygen reduction reaction rate at the cathodes [5]. Thus, it is critical to advance synthesis routes for high performance cathodes with superior electrical conductivity [6,7].

La\textsubscript{1-x}Sr\textsubscript{x}Co\textsubscript{y}Fe\textsubscript{1-y}O\textsubscript{3-δ} has been explored as a possible cathode material for use in SOFCs [8]. LSCF exhibits mixed ionic and electronic conductivity and high electrocatalytic activity [9]. Synthesis of La\textsubscript{0.6}Sr\textsubscript{0.4}Co\textsubscript{0.8}Fe\textsubscript{0.2}O\textsubscript{3-δ} by RF-sputtering has been shown to produce functional films with crystallization temperatures in the vicinity of 450°C without producing interfacial reaction products with yttria-stabilized zirconia (YSZ) [9,10].

The interaction of energetic UV photons with oxygen can produce oxygen radicals or ozone, dramatically increasing oxygen reactivity on surfaces and enhancing oxygen incorporation into thin films [11]. In this paper, we demonstrate that photo-excitation during crystallization leads to enhanced oxygen incorporation into a prototypical perovskite oxide that in turn results in a significant improvement in the high temperature conductivity. Further, utilizing in situ conductivity measurements, we show an enhancement in crystallization kinetics arising from photo-excitation.

Experimental Procedure:
La\textsubscript{0.6}Sr\textsubscript{0.4}Co\textsubscript{0.8}Fe\textsubscript{0.2}O\textsubscript{3-δ} thin films were RF-sputtered from a stoichiometric target (AJA International) onto single crystalline YSZ substrates. Sputtering was carried out in 5 × 10\textsuperscript{-3} Torr of argon plasma starting from a base pressure of 3 × 10\textsuperscript{-8} Torr with a gun power of 60 W. In situ high temperature conductivity studies were also performed on 60 nm thin LSCF films on similar substrates with platinum electrodes in air. Photon sources in-built into the probe station enable in situ exposure while heating experiments as well as electrical conductivity. The temperature was continuously monitored using thermocouples. LSCF films were characterized by x-ray diffraction (XRD).

Figure 1: XRD profile of LSCF films annealed at 450°C.
two-theta peak is 0.1° higher for the film crystallized under UV irradiation compared to the film annealed without UV, indicating a slight decrease in the average lattice parameter of the LSCF thin film. Enhanced oxygen incorporation during annealing could possibly decrease the overall oxygen deficiency in the film, reducing the number of oxygen vacancies [11].

In situ conductivity studies were performed on LSCF thin films during and prior to the onset of crystallization. Sample temperature was held at 450°C for 40 minutes to observe LSCF conductivity changes with time. Film resistance was calculated via linear regression to tabulate in-plane LSCF conductivity. Upon crystallization, a conductivity increase of approximately 100x can be observed, serving as a suitable in situ probe of the structural evolution. The onset temperature for this change in conductivity is ~ 440°C in films crystallized both with and without UV assist as observed in Figure 2. The conductivity of the LSCF films measured 248 S-cm⁻¹ and 588 S-cm⁻¹ at 450°C after 50 minutes for samples annealed with and without UV irradiation respectively. Upon increasing temperature to 557°C, conductivities measured 320 S-cm⁻¹ and 618 S-cm⁻¹ in films annealed without UV irradiation and with UV irradiation respectively.

Figure 3 shows the evolution of in-plane conductivities for LSCF films annealed both with and without UV at 450°C. With time, the film conductivities annealed with and without UV approach a maximum asymptotically. The rate at which the films approach their maximum conductivity is differs. The LSCF film crystallized under UV approaches its maximum conductivity at 450°C faster than the film crystallized without. This suggests that the crystallization rate of LSCF thin films is influenced by oxygen incorporation.

Conclusion:
We have demonstrated that UV assisted crystallization of RF-sputtered La₀.⁶Sr₀.₄Co₀.₈Fe₀.₂O₃₋δ thin films leads to higher in-plane electronic conductivity and more rapid crystallization. A decrease in lattice parameter was observed in films annealed under UV irradiation, indicating increased oxygen concentration or decreased in oxygen vacancy concentration in the LSCF film due to the greater presence of oxygen radicals and ozone during crystallization. More rapid crystallization was also observed in films annealed under UV irradiation. The results indicate that UV enhanced crystallization of LSCF ultra-thin films could provide an increase in cathode performance.

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References:
Annealing Thin-Film Block Copolymers to Achieve Ordered Morphologies

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Abstract:
A proton exchange membrane fuel cell requires a membrane that selectively allows for the passage of protons. One way to accomplish proton conductivity is to use sulfonated self-assembling block copolymers. The negative charge of the sulfonic acid groups in one of the block copolymer phases imparts the desired cation or proton conductivity. It is likely that the morphology of the film affects the conductivity; however, before the conductivity-morphology connection can be quantified, there must first be an understanding of the morphologies of sulfonated films as well as a reliable way of inducing them. To accomplish morphological control of sulfonated block copolymers, annealing was conducted on unsulfonated and sulfonated systems. The process of annealing uses solvents or heat to allow the polymer to become mobile and the phases to separate and align in reference to each other. This work tests annealing on unsulfonated copolymers, as well as whether sulfonated copolymers can be successfully annealed, and what phases result.

Introduction:
Block copolymers form morphologies with domains on the order of 10-100 nm due to separation of the different chemical phases of the polymer chain. When the polymers are allowed to move, the different blocks will naturally self-assemble into distinct phases based on the composition and volume fractions of the polymer constituents. By heating a polymer past its glass transition temperature ($T_g$) or using solvent to depress the $T_g$, the polymer chains become mobile and rearrange towards an equilibrium structure.

This work is directed at testing various ways of arranging an unsulfonated block copolymer, and to determine if the behavior of sulfonated copolymer analog is at all similar. Experiments were conducted on poly(hexyl methacrylate)-b-polystyrene-b-poly(hexyl methacrylate) (PHMA-b-PS-b-PHMA). This triblock copolymer was chosen due to the low glass transition temperature of poly(hexyl methacrylate). The low $T_g$ allows annealing to be conducted at lower temperatures, decreasing the chances of the copolymer decomposing.

Methods:
Unsulfonated PHMA-b-PS-b-PHMA in dioxane and 100% sulfonated PHMA-b-PS-b-PHMA in dimethylformamide were used. The films were spun cast onto silicon wafers coated with a poly(styrene) brush. After the wafers were rinsed with ethyl alcohol, the brush was made by casting 1% w/v polystyrene in THF, baking under vacuum at 195°C for 2.5 h, and then rinsing away the excess poly(styrene) with toluene. 15 µL of 0.1 wt % polymer solution were spin cast at 1000, 2000, and 3000 rpm to achieve varying film thicknesses on the order of 100 to 200 nm. The thickness of the spun cast films was measured using profilometry. Samples were subjected to thermal annealing or vapor annealing. Thermal annealing was conducted under vacuum at 180°C for 8 hours with cooling to room temperature under vacuum. Non-selective solvent vapor annealing was conducted under a saturated dioxane atmosphere for the unsulfonated samples and dimethylformamide for the sulfonated samples at 24°C for 24 hours. The samples were examined using atomic force microscopy and field emission scanning electron microscopy.

Results:
Figure 1 displays the disorganized mixed lamellar and cylindrical morphologies of unsulfonated PHMA-b-PS-b-PHMA. The morphological domains are 30 to 70 nm in width. Both thermal and vapor annealing increased the order of the unsulfonated PHMA-b-PS-b-PHMA domains. After annealing, the lamellar structures were aligned parallel to one another with less cylindrical domains.

While the morphologies of Figure 1 are disorganized, Figure 2, a 3000 rpm spin cast sample after vapor annealing, shows aligned morphologies.
Figure 3 shows an unannealed sulfonated PHMA-b-PS-b-PHMA spun cast at 1000 rpm. The sulfonated poly(styrene) midblock has aggregated, causing the film to be different than the unsulfonated sample. This morphology does not change with thermal or vapor annealing, which is displayed by Figure 4, a vapor annealed sulfonated PHMA-b-PS-b-PHMA.

Conclusions:
The unsulfonated PHMA-b-PS-b-PHMA triblock copolymer showed disordered morphologies in the as-cast state, but upon either thermal or vapor annealing showed a mixture of aligned lamellar and cylindrical morphology. These results indicate that temperatures of 180°C or the use of a non-selective solvent were sufficient to allow re-arrangement of the phases. Sulfonated PHMA-b-PS-b-PHMA did not show domain arrangement in the as-cast state and instead showed an aggregated structure that may be a result of the sulfonated polymer’s solution behavior. The sulfonated copolymer does not seem to form the same morphologies as the unsulfonated copolymer. Neither thermal nor vapor annealing caused a significant difference in the phase behavior of the sulfonated PHMA-b-PS-b-PHMA. The aggregated sulfonated PS domains prevented annealing.

Future Work:
One reason that annealing could not be achieved in the sulfonated sample is that sulfonation has raised the glass transition temperature (T_g) of polystyrene such that 180°C is no longer sufficient for annealing. To test this increase in the T_g, annealing will be attempted at higher temperatures. Also, as this project only examined 0% and 100% sulfonated copolymer, research will be done on partially sulfonated copolymers to determine if their behavior is intermediate to the unsulfonated or fully sulfonated samples.

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References:

Figure 1: Unannealed unsulfonated PHMA spin cast.
Figure 2: Vapor annealed sulfonated PHMA spin cast.
Figure 3: Unannealed sulfonated PHMA spin cast.
Figure 4: Vapor annealed sulfonated PHMA spin cast.
Pattern Deposition of Nanoparticles of Different Shapes by an Aerosol Route

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Introduction:
The electrospray system disperses highly-charged, mono-disperse droplets which can be showered over a plate of large area. By varying the liquid feed flowrate and voltage of the system, nano-sized particles can be distributed over the area. Using the soft lithography technique of micro-contact molding, a certain pattern can be imprinted on a polymer coated plate. This molding reveals a silver substrate in the pattern outlined by the nonconductive polymer. The electrospray apparatus can be used to spray highly positively-charged nanoparticles that are then deposited on the surface in the respective pattern. An electric field is established between spray head and substrate, assisting the containment of the sprayed particles in the desired area. Before spraying particles the polymer-coated surface is charged by electrospraying a highly conductive solution. The gold nanoparticles used range in size from 10 to 20 nm and are generally conglomerated inside the desired pattern after spraying. Being able to control the positioning and patterning of nanoparticles by use of the electrospray system will allow a much larger area to be covered in a much shorter time compared to existed deposition experiments.

There has been much research done in the field of controlling the size, shape and phases of nanoparticles, but controlling the placement of these particles has presented itself as a challenge [1]. A precise patterning of nanoparticles would be greatly beneficial in some areas of interest, and even a loose patterning of a large amount of these particles would prove to be practical in some applications.

This experiment attempted to find an efficient way to quickly and accurately deposit nanoparticles in a given pattern. An electrospray device developed in our lab was used to shower highly charged nanoparticles onto an opposite charged patterned substrate outlined with nonconductive polymer, consequently depositing them in the desired pattern.

Experimental Procedure:
An elastomer stamp was created from a master with our micron-sized pattern on it (in this case, 10 µm holes). This stamp was used for micro-contact molding to imprint the pattern on our photoresist, which was a silicon wafer coated with silver. This left a pattern on the highly conductive silver that was outlined by a nonconductive polymer (see Figure 1). This process was set up so we could mass produce our patterned plates in a quick and efficient manner. In one hour, as many as 15 plates could be patterned and ready for spraying.

After the plates had been patterned, they were ready to be sprayed by the electrospray device. This device is a particle generation/dispersion system used to shower monodisperse droplets over a large area. In this experiment, we were able to use it to shower individual nanoparticles over the prepared patterns. The particles being used were 10-20 nm gold colloid nanoparticles. The liquid in which the nanoparticles were suspended was fed into the system by a syringe pump so the flow rate could easily be controlled. As the suspension flowed through a capillary towards a very sharp tip, the particles were subjected to an divergent electrical field established by applying a high voltage between the capillary and plate. The established electric field was also used to help contain the particles and keep them focused in the desired area [2].
Before the gold particles were sprayed, we introduced a highly conductive pre-spray solution of nitric acid and ethanol to charge the surface of our plates. The plate charging helped to target the spray particles towards the highly conductive silver patterns and away from the non-conductive polymer. After 30 minutes of the pre-spray and 30 minutes of electrospray by the nanoparticles, the process was complete.

Results were then obtained by use of the scanning electron microscope (SEM) to inspect deposited particles on the plates, and to obtain data of the distribution of deposited nanoparticles.

Future Work:
This experiment demonstrated that a large percentage of the particles could be conglomerated inside the target holes compared to being outside on the non-conductive surface. We weren’t able to achieve full accuracy, but future experiments will be geared toward reaching that goal. Also, new patterns and different types of particles will be used to conduct the experiment.

Acknowledgements:
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References:

Results and Discussion:
After many trials, our experiment eventually led to a 75% successful rate of nanoparticles in the holes, compared to being outside of the holes. Figure 2 shows a close up of the holes with the particles enhanced in size for better viewing. This success was mainly attributed to the correct combination of our lithography method for producing the patterns, the use of the unipolar charger, and the introduction of the pre-spray solution to help charge our surface before the shower of nanoparticles. Micro-contact molding replaced micro-contact printing which had produced silver holes with a silicon outline, which didn’t work because the silicon provided a semi-conductive surface that attracted particles. The unipolar charger resulted in a successful but random distribution of particles on our molded plates, compared to using no charger and a bipolar charger, which had yielded no particles on the surface. After the success of the unipolar charger, the pre-spray solution allowed a much more accurate focusing of particles into the patterned holes. Increasing the conductivity of this solution produced even better results.
**Growth of Silicon, Germanium, Si\(_x\)Ge\(_{1-x}\) and Various Polytypes of Silicon Carbide Nanowires**

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**Abstract:**  
The silicon-germanium (SiGe) alloy has played an important role in the semiconductor industry because of its inexpensive production and high power capabilities [1]. Silicon carbide (SiC) has also played an important role due to its high thermal conductivity and wide energy band gap [2]. In this study, silicon, germanium, Si\(_x\)Ge\(_{1-x}\), and various polytypes of SiC nanowires were grown via a chemical vapor deposition (CVD) reactor. Nanowires are 1-dimensional nanostructures with very interesting properties such as a high electron mobilities, several times higher than conventional structures. Polytypes of SiC were grown on silicon substrates using silane and propane with nickel (Ni) as a catalyst. The polytypes were achieved by varying the temperature of the CVD reactor during growth. In doing this, we changed the phase of the nanowires from cubic SiC (3C) to hexagonal SiC (6H). The silicon, germanium, and Si\(_x\)Ge\(_{1-x}\) structures were grown using silane and germane. X-ray and other characterization techniques were used to examine the structure and nature of the 1-dimensional system.

**Introduction:**  
With its low energy band gap, high mobility, and ability to synthesize nanowires at low temperatures, germanium has become one of the key players in the semiconductor industry [3]. Silicon-germanium’s high power capabilities make it ideal for wireless communications devices [1]. Silicon carbide is another key player in the semiconductor industry because of its high thermal conductivity. Polytypes of silicon carbide refer to the stacking structure of the silicon and carbon atoms, with the basic crystalline structures being cubic (3C), hexagonal (6H), and rhombohedral (15R), with each structure having its own unique optical and electronic properties.

**Experimental Procedure:**  
Silicon (100) substrates were cut into 1 cm × 1 cm sized pieces and cleaned using detergent, trichloroethylene, acetone, and methanol. Electron-beam evaporation was used for the deposition of a 10 nm film of nickel for silicon nanowire catalysis, and a 10 nm film of aluminum was deposited for SiC nanowire catalysis. A thin gold film of approximately 10 nm was required for germanium and silicon-germanium nanowires catalysis, and was deposited by thermal evaporation. Nanowire growth took place in a cold wall, temperature controlled, horizontal CVD reactor. Germanium nanowires were grown with germane (GeH\(_4\)) as the precursor gas, while silicon-germanium nanowires required germane and silane (SiH\(_4\)). Silane and propane (C\(_3\)H\(_8\)) were the precursor gases used for silicon carbide nanowires. In each reaction, hydrogen was used as the carrier gas. Hydrogen created a laminar flow within the growth chamber and was also used as a carrier gas for the precursors.

**Results and Conclusions:**  
Gold proved to be an effective catalyst for both the germanium [4] and silicon-germanium nanowires. Germanium nanowire growth was achieved at 800°C and a growth time of 30 minutes. Growth was sparse across the sample, but denser along the edge (Figure 1). The silicon-germanium wires, while technically not “nano” in size, were successfully grown at 900°C (Figure 2). Energy dispersive spectroscopy (EDS) was performed on the wires and it was determined that there was in fact the presence of both silicon and germanium along the wire. Silicon nanowire growth was attempted, but efforts were unsuccessful, even though silicon nanowires had been successfully grown previously in this reactor.
Nickel proved to be an effective catalyst for various polytypes of silicon carbide nanowires. To grow different polytypes required changing the growth temperature at different times during the growth cycle. This was done to examine the temperature dependence on polytype formation. During the first growth cycle, the temperature was ramped to 1050°C and held for 15 minutes, then ramped to 1336°C and held for another 15 minutes, and then ramped down to 1050°C and held for a final 15 minutes. SEM imaging showed that there were a plethora of wires of different lengths and diameters (Figure 3). The tips of these wires appeared to be hexagonal, which may indicate different polytypes were successfully formed. The second growth was done with only one temperature change, 1050°C to 1330°C. The wires appeared to have a hexagonal shape and may be evidence of a phase shift dependence on temperature, which would further proved that different polytypes of silicon carbide were obtained.

**Future Work:**

In the future, the nanowires should be probed to determine their electrical properties. Photoluminescence data should also be collected to determine the purity of the nanowires, along with transmission electron microscopy (TEM) to determine their exact crystalline structure along the length of the nanowires.

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**References:**


Materials for CZTS Photovoltaic Devices

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Abstract and Introduction:
Thin film solar cells made of copper indium gallium selenide (CuIn\(_{1-x}\)Ga\(_x\)Se\(_2\) or CIGS) combined with cadmium sulfide (CdS) to form a \(p^n\) heterojunction are nearing the commercial production stage. However, indium and selenium are rare, and cadmium is toxic, so CIGS solar cells are not a good option for large scale energy production. Copper zinc tin sulfide (Cu\(_2\)ZnSnS\(_4\) or CZTS) is modeled after CIGS, but uses abundant, environmentally friendly materials. CdS, which forms the heterojunction with CZTS, must be replaced with zinc sulfide (ZnS). Zinc is also useful in the compound CdZnS in CIGS solar cells to tune the band gap. In the first half of this project, deposition of ZnS and CdZnS was explored. ZnS deposition on glass slides looks promising and merits further investigation. CdZnS deposition on molybdenum coated glass slides was unsuccessful as x-ray diffraction (XRD) and energy-dispersive x-ray spectroscopy (EDX) revealed no Zn was present in the film. In the second part of this project, a method for depositing CZTS was developed. Zinc, copper and tin were deposited using thermal evaporation on molybdenum coated quartz slides. The CZT stack was annealed with sulfur powder in a Petri® dish. The CZTS films were analyzed using XRD and scanning electron microscopy (SEM).

Methods and Results:
Cadmium and zinc sulfide films were deposited using chemical bath deposition. CdS films are easily deposited in a chemical bath consisting of deionized water (DI water), CdSO\(_4\), thiourea, and NH\(_4\)OH at temperatures between 50°C and 90°C in under an hour. Replacing some or all of the CdSO\(_4\) in the CdS bath with ZnSO\(_4\) did not lead to ZnS or CdZnS deposition. O’Brien and McAleese [1] suggest adding hydrazine, triethanolamine, or ethanolamine to promote ZnS deposition. ZnS films were deposited on scratched glass slides using the bath described above, with the addition of triethanolamine at 70°C for 1.5 to 4.5 hours. The transmission measurements are shown in Figure 1. It was found that a deposition time of at least 2.5 hours was needed for an appreciable film thickness.

Next, the deposition of CdZnS was attempted using the bath composition described above for ZnS. The ratio of 3:7 for Cd:Zn was chosen because Dona and Herrero [2] determined that ratio yields the highest stability CdZnS compound. Deposition was first done on scratched glass slides, then on molybdenum coated glass slides. The transmission measurements on the glass slides suggested some Zn may have deposited, but XRD and EDX on the molybdenum coated slides showed the film contained only CdS.

CZTS films were deposited on quartz slides coated with molybdenum, using e-beam evaporation or sputtering. Sputtered films were found to be better quality than e-beam evaporated films. Layers of zinc, copper, and tin were deposited using thermal evaporation. The order Zn/Cu/Sn was used because Araki et al. [3] showed it produced the most efficient solar cell. Ratios of Cu/(Zn+Sn) between 0.85 and 0.96 and Zn/Sn between 1.05 and 1.3 were used.

The CZT stack was placed in a fused silica Petri® dish with sulfur powder and annealed at 560°C, so the film was exposed to a sulfur vapor environment. Previously, the annealing step had been done in an atmosphere of hydrogen.
sulfide and nitrogen gases, but this project elected to use the sulfur powder method because of the toxicity of H$_2$S. Sulfur amounts between 4 mg and 20 mg were tested. XRD of the resulting films showed remaining copper and zinc suggesting that sulfur was not being incorporated into the film. SEM images showed that the crystalline CZTS structure was not obtained.

A weight, of approximately 470g, was obtained to hold down the lid of the Petri dish so that the increasing pressure from the evaporating sulfur would not lift the lid, allowing the sulfur vapor to escape. The amount of sulfur added was increased to 30 mg, resulting in higher CZTS peaks. XRD of this film is shown in Figure 2. Part of the CZTS film was scratched off after deposition to obtain a molybdenum contact.

Complete solar cells are formed by depositing CdS in a chemical bath followed by sputtering zinc oxide and aluminum doped zinc oxide.

**Conclusions and Future Work:**

Zinc sulfide deposition on glass slides looks promising and merits further investigation. Deposition on molybdenum coated slides will allow verification that it is ZnS, and then deposition on CZTS films can be attempted. The addition of a weight during the sulfur anneal step led to CZTS formation. This process will be used to characterize CZTS films and relate deposition parameters to solar cell efficiencies.

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**References:**

Metallization for High Temperature Electronics

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Abstract:
With its wide band gap and large thermal conductivity, silicon carbide can replace silicon as the semiconductor for high temperature and high power electronics. This study investigated metallic capping materials that could withstand elevated temperatures, while maintaining a low sheet resistance. Sputtered gold and ruthenium films were monitored for agglomeration through microscopy and for sheet resistance through the van der Pauw technique. Low resistance, pure gold films demonstrated significant agglomeration upon annealing at 600°C. Pure ruthenium, however, withstood agglomeration through 50 hours of annealing while sustaining an acceptably low sheet resistance. Despite the popularity of gold, a capping layer of 150 nm of ruthenium provides high-quality adhesion and low resistance through continued annealing at 600°C.

Introduction:
Wide band gap semiconductors such as silicon carbide can be utilized for high temperature devices. In comparing silicon carbide to silicon electronics, the power to size ratio increases, in addition to an efficiency improvement and a reduction in physical size [1]. With the wide band gap, thermal electrons remain unlikely to surmount the energy barrier and contribute leakage current. In order to realize the full potential of these wide band gap semiconductors, robust metal contact layers must be implemented that can also withstand the high temperatures resulting from significant power operation. As a capping material for electronics, gold has been a popular metal choice due to its low resistivity and limited oxidation. However, gold-based films agglomerated into mounds as shown in Figure 1 during annealing at 600°C. This research aimed to discern a capping metal or gold alloy with strong adhesion to titanium nitride and low resistance after prolonged annealing in air.

Experimental Procedure:
For economical reasons, silicon pieces were used with a diffusion barrier of grown oxide. A 100 nm titanium layer was sputtered onto the substrate before annealing in nitrogen to produce a titanium nitride thin film. The capping metal film was sputtered onto the titanium nitride contact layer. Various thicknesses of gold, ruthenium, and different co-sputtered gold-ruthenium films were investigated as capping metals. Samples were cycled through annealing in air at 600°C and measuring the sheet resistance. The sheet resistance, or resistance over film thickness, was measured with a four point probe van der Pauw technique. This technique obtained voltages and currents along each pair of the sample’s sides to calculate sheet resistance, correcting for shape irregularities [2]. Adhesion was tested with tape. Both an optical microscope and a field emission scanning electron microscope (FESEM) were employed for detecting agglomerations.

Results:
Although possessing a lower sheet resistance upon deposition, the gold films agglomerated rapidly during the annealing process. When the film pulls itself into mounds, the gold minimizes its surface energy. However, the agglomeration increases the sheet resistance and permits oxygen diffusion.
Possibly caused by stress in the films, the agglomeration in gold films had a fractal appearance similar to that reported by Gadkari et al. [3]. Pure ruthenium demonstrated an initial drop in sheet resistance before rising slowly with prolonged annealing, as shown in Figure 2. The sheet resistance remained very low at 2.6 Ω/square, even after 50h of annealing. The ruthenium film was agglomeration-free at 44h, as shown in Figure 3. Co-sputtered alloys of ruthenium and gold showed an early onset of agglomeration and increased sheet resistance.

High-quality adhesion in a sample was valued for material compatibility in the device. Whereas the gold-based films had weak adhesion, ruthenium films showed strong adhesion to the titanium nitride layer. When layered, gold and ruthenium adhered considerably to each other as well.

With annealing time, the gold-based films darkened towards a brass color. Ruthenium experienced various color changes through the annealing process. Initially a shiny silver color, ruthenium passed from orange to red to purple by three hours of annealing. The purple hue continued deepening. After 20h of annealing, however, a dark blue color was prevalent. The color change may be constructive light interference of a surface oxide. The oxide composition likely would be ruthenium oxide or ruthenium-titanium oxide. Auger electron spectroscopy revealed only ruthenium and oxygen present at the surface. Notably, Rard and others mentioned that ruthenium (IV) oxide, RuO₂, was a dark blue color [4]. Further, RuO₂ has been noted as a conductive oxide, which would help retain the low sheet resistance [4].

**Conclusions and Future Work:**

Although gold initially had a lower sheet resistance, ruthenium maintained a lower sheet resistance throughout annealing compared to the gold-based films. Ruthenium also possessed better adhesion than gold to titanium nitride. A metal capping layer of 150 nm ruthenium has been recommended from this study for further inquiry. Ruthenium being less expensive than gold, the thin 150 nm requirement creates a financially viable solution. Future work will investigate the specific composition of the oxide and further evaluate ruthenium as a possible metallization layer for silicon carbide devices.

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**References:**


Characterization of Thermally Induced Bilayer Distortions

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Abstract:
Supported lipid bilayer (SLB) is a promising biologically inspired surface coating and model system for reconstructing membrane processes. We apply thermal stress to SLB and report on the resulting structural distortions. Thermal stress induces long, thin, flexible protrusions (worms) in the SLB that are unstable and eventually collapse into giant vesicles. We examine the length distribution, and collapse of SLB worms as a means toward better understanding the material properties of SLB.

Introduction:
Lipids are molecules composed of a hydrophilic head and hydrophobic tail. In the presence of water these molecules self assemble into a bilayer structure. Supported lipid bilayer (SLB) is a lipid bilayer that has been deposited on a substrate such as glass [1,2]. SLB holds great promise as a biocompatible surface coating and a model for studying membrane processes such as membrane embedded proteins [3]. Understanding SLB mechanics could potentially lead to a more efficient membrane permeable drug delivery system. We studied the response of the SLB to thermal stress and the resulting structural distortions.

Experimental Procedure:
We prepared a vesicle solution of 97% 1, 2-dimyristoyl-sn-glycero-3-phosphocholine (DMPC) and 3% of the fluorescent phospholipid N-(7-nitrobenzoxa-2, 3-diazol-4-yl)-dimyristoyl-phosphatidyle ethanolamine (NBD – DMPE). Our vesicle preparation followed a standard protocol [4]. Briefly, a lipid film was dried on the surface of a clean glass vial and placed under vacuum for 24 hrs. Then, the film was hydrated with 150 mM PBS (buffer), freeze/thawed, and extruded through a series of membranes with decreasing pore sizes (200 nm, 100 nm, 20 nm). A clean piece of borosilicate glass was exposed to buffer for ~ 30 minutes in a temperature-controlled flowcell. After the temperature stabilized to 30ºC, the buffer was replaced by vesicle solution. The glass was exposed to 0.1 mg/mL vesicle solution for 15 min before rinsing with buffer to remove vesicles from the bulk solution. The glass surface was then imaged in epifluorescence using an inverted microscope and a CCD camera. A spot was bleached by reducing an aperture and increasing the current of the LED light source. An image was taken directly after the bleach and 30 minutes later to check for fluorescence recovery. The surface was imaged at 30 seconds intervals as the temperature was increased to 37ºC.

Figure 1: A. Bilayer at 30ºC.
B. Bilayer at 39ºC worms grow.
C. Worms at 41ºC bilayer collapse.
**Results and Conclusion:**

We checked the bleached spot for recovery. Recovery indicated that the surface was covered in SLB. At 37°C, we observed the appearance of bright round spots—as the temperature increased these spots elongated into varied-sized, floppy worm-like structures or simply “worms” (Figure 1). While the temperature continued its increase, some of the worms continued to grow; others remained constant, while others collapsed into bright round spots.

We hypothesized that the worms were a result of thermal expansion. Since the SLB was confined to a fixed area (i.e. borosilicate glass) and it expanded faster than the area it was confined to, it tended to protrude from that surface. However, these protrusions were unfavorable and thus collapsed to a more stable geometry, i.e. giant vesicles.

We analyzed the growth and collapse (Figure 2) of the worms and obtained a rate of growth and collapse. We analyzed the length distribution of the worms (Figure 3).

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**References:**


Characterization of the Diffusivity of Conductive Polymers in Nanochannel Confinement

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Abstract:
The fabrication of nanochannels for analyzing molecular behavior at the single-molecule level is a rising phenomenon in material science. This methodology has been applied in research areas including the controlled transport of biological species, nanoelectromechanical systems (NEMS) studies, and the stabilization of the release rates of small molecules in drug delivery. Interest in the distinctive mechanical, electrical, and optical properties of the conductive polymer poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), widely used in organic electronics (sensors, solar cells, LED), induces further research concerning this molecule under a nano-confining environment. In this work, we fabricate nanochannels on a quartz substrate using electron beam lithography, and furthermore, use these nano-devices to characterize the diffusivity of PEDOT:PSS. Observation under an optical microscope allows for characterization of the molecule's diffusivity, while images obtained from the SEM will confirm existence of these molecules confined in the nanochannels. The ability to characterize PEDOT:PSS in such nano-confinement will impose a strong foundation on further research on this conductive polymer.

Introduction:
The study of diffusion in nanochannel confinement is a rising phenomena in nanotechnology research. Nanochannels provide an environment in which biological species can be controlled at the single-molecule level. Furthermore, they are easily integrated with other detection device units such as nanowires, transistors, and optical waveguides [1]. The diffusion of molecules into nanochannels is commonly used in research areas including deoxyribonucleic acid (DNA) stretching studies.

We have applied this idea for characterizing the polymer, PEDOT:PSS. PEDOT:PSS is a conductive, transparent polymer with unique electrical and optical properties, making it ideal for organic electronics research [2]. However, there is no research on the diffusivity properties of PEDOT:PSS. Therefore, in this work, we have designed and fabricated a nanochannel device for characterizing the diffusivity properties of PEDOT:PSS under nanoscopic confinement.

Experimental Procedure:
A 100 mm wafer was first spin-coated with ZEP-520A photoresist (~ 300 nm thickness). Next, a 20 nm layer of the conductive polymer,
The wafer consisted of a set of ten of the nanochannel devices. Each consisted of various channel widths ranging from 20 nm to 200 nm in increments of 20 nm. There were two sets of these patterns to show consistency. They were then written onto the ZEP-coated quartz substrate using the RAITH electron beam (e-beam). Following the e-beam exposure, the spacer was removed using a spin-rinse dryer, and the wafer was developed in xylene. When submerged in xylene, the areas of the ZEP resist that were exposed to the electron beam during exposure, were removed. Finally, the substrate was etched using the AMT etcher (oxide etcher) creating a 500-600 nm depth for the nanochannels. The ZEP resist was stripped by submerging the wafer in sulfuric acid for 20 minutes and the fabrication process was complete.

To characterize the diffusivity properties of PEDOT:PSS using these nanochannel devices, we deposited the PEDOT:PSS solution into the trapezoidal area of the nanochannel device. As the solution diffused into the nanochannels, its diffusion and mobility could be characterized in various ways.

**Results and Discussion:**

After the first e-beam write, there were three major issues that we encountered. First, there was poor adhesion of the ZEP resist. Weak bonding between the resist and the quartz substrate caused areas of deformation in the pattern. Our solution to this problem was to prime the wafer with hexamethyldisilazane (HMDS) to create better adhesion of the ZEP resist. Secondly, we noticed stitch breaks in the pattern. The e-beam writes in 40 µm write fields. At every shift in write field, due to the properties of the quartz substrate, the wafer would begin charging and slightly deflect the electron beam, causing a shift in the pattern write. To compensate for this charging, we coated a second layer of spacer. Finally, we noticed that after the e-beam write, the strips of ZEP resist between the nanochannels were so thin (< 300 nm) that during development, they would be easily shifted off of the pattern leaving hairy-like structures of ZEP resist on the wafer surface. The solution to this issue was to increase the spacing between the nanochannels to one micron.

After making these adjustments, the patterns were written again under the e-beam. Results can be observed at different magnifications in Figure 1. The write was successful and we had completed nanochannel devices to be used for diffusion characterization.

Following the etching of the pattern and stripping of the photoresist, the nanochannel devices were used for the diffusion tests. Preliminary diffusion results show the PEDOT:PSS solution diffused into the channels of the nanochannels devices with channel widths of 180 nm and 200 nm. The results of the diffusion using the nanochannel devices with channel widths of 180 nm can be seen in the optical image in Figure 2.

**Conclusions and Future Work:**

We successfully fabricated a nanochannel device on a quartz substrate to be used for diffusion purposes. Moreover, we were able to begin preliminary diffusion work with PEDOT:PSS using these nanochannel devices. In the future, we would like to attempt to fabricate these nanochannel devices on other substrates. We would also like to characterize the diffusion properties of other polymers and DNA, using these nanochannel devices.

**Acknowledgements:**

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**References:**

Atomic Layer Deposition of High Constant Gate Dielectrics for Thin Film Transistors

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Abstract:
Transparent insulating oxides with high dielectric constant ($\kappa$) are desired for thin film transistors that form the basis of current flat panel displays and future flexible and transparent electronics. This project uses atomic layer deposition (ALD) in order to grow these oxide films. ALD deposits precisely one monolayer of film with every cycle so that thicknesses can be controlled at the atomic level. An Oxford OpAL ALD tool was used in this work to deposit thin films of aluminum oxide ($\text{Al}_2\text{O}_3$) and hafnium oxide ($\text{HfO}_2$) under varying parameters of temperature, plasma power, and pressure. In addition, the effects of thermal annealing the films after deposition were examined. Optimal growth parameters were found in order to maximize the dielectric constant and minimize leakage current density through the films, as these parameters are critical in determining the ultimate performance of thin film transistors. By maximizing the dielectric constant and maintaining low leakage in a thin dielectric layer, a higher capacitance from the oxide is achieved which allows for better gate control of the drain current in a thin film transistor. The results of the study will be applied to current research on zinc oxide and zinc telluride thin film transistors.

Experimental Procedure:
In the ALD process, the films are grown with repeated cycles of precursor doses and purging stages shown in Figure 1. The film growth is self limiting and based on surface reactions, which allows for the atomic scale control of the deposition. For the oxides grown in this project, two precursors are used: one for the oxide and one for the other element (Al or Hf). In order to improve the oxidation of the thin film, some of the depositions were aided by oxygen plasma. An alternative oxygen-providing precursor used was water. The other precursors for $\text{Al}_2\text{O}_3$ and $\text{HfO}_2$ were tri-methyl aluminum and tetrakis(ethylmethylamino) hafnium respectively.

Oxide thin films were deposited on silicon wafers, including $\text{HfO}_2$ with plasma, $\text{Al}_2\text{O}_3$ with plasma, and $\text{Al}_2\text{O}_3$ with water. The films were grown with varying parameters of temperature, plasma power, and pressure. The temperatures ranged from 100°C to 300°C in increments of 50°C and were controlled through a table heater within the growth chamber. The plasma power was directly controlled through the tool software and ranged from 100W to 300W in increments of 50W. The last parameter of pressure was controlled by the precursor and purging gas flows of the chamber. The pressure ranged from 100 mTorr to 500 mTorr in increments of 100 mTorr. Each film was grown for 300 cycles and nominally 300 Å thick.

Capacitors were fabricated to test the electrical properties of the oxide thin films. Capacitors were fabricated by depositing metal contacts with radii of 340 µm, consisting of a layer titanium and platinum 200 Å and 1000 Å in thickness respectively. The dielectric constants of the thin films were determined by measuring the capacitance, using known
values for the film thickness and contact area. In addition, the leakage current was measured for a voltage sweep ranging from -20 V to 20 V.

The optimal growth parameters for HfO$_2$ were found to be 300°C at 250 W using the default pressure, but both the plasma power and pressures were found to have little effect on the electrical properties of the films. For Al$_2$O$_3$ with plasma, the optimal parameters were 250°C at 300 mTorr.

With Al$_2$O$_3$, the pressure had little effect as well. However, higher plasma powers had significantly higher leakage current in the films. This was likely due to a larger amount of reflected power as the plasma power increased. Finally, for Al$_2$O$_3$ with water, the optimal parameters were 300°C at default pressure. Again, pressure did not have a significant effect on film growth. Results of the experiment are summarized in Figures 2 to 7.

**Summary Results and Future Work:**
Initial work on the effects of annealing was begun with anneals at 400°C and 500°C for 30 minutes with oxygen gas. In addition, literature was found indicating that an anneal can decrease leakage current by orders of magnitude, but experiments have only been run for HfO$_2$ grown with water and anneals using forming (N$_2$/H$_2$) gas. No conclusive results have been found currently for HfO$_2$ with plasma or thermally grown Al$_2$O$_3$. In addition, initial zinc oxide thin film transistors will be created using the optimal parameters for the films.

Future work will apply results of the study to improved zinc oxide and zinc telluride thin film transistors. Applications of these may be used for low power electronic displays and potentially in flexible electronics.

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**References:**

Characterization and Acid Diffusion Studies of Cyclodextrin and its Carborane Inclusion Complex

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Abstract:
In order to move forward, the semiconductor industry is dependent on improvements in the lithographic process, most importantly the development of new resist materials. As pattern dimensions continue to decrease, issues of line edge roughness arise. Molecular glasses are an attractive alternative to polymeric resists, as they are able to incorporate an amorphous structure and high transition temperature (T_g) with a small size that can show improved line edge roughness. Cyclodextrin has shown promise as a 193 nm resist, though it exhibits poor etch resistance. By introducing carborane into the cyclodextrin core, we have shown that the etch resistance of cyclodextrin is around that of PHOST, an industry standard photoresist. However, we also see an increase in line edge roughness. We intend to observe the differences in acid diffusion between the non-carborane and carborane resist by creating bilayers and measuring film thicknesses before and after development. Using this data, we can now modify cyclodextrin core with carborane to inhibit acid diffusion and show improved patterning capability with high etch resistance.

Introduction:
tert-butyl ester protected methyl β cyclodextrin has been used as a 193 nm molecular glass resist and has good patterning abilities. Unfortunately, this resist exhibits poor etch resistance, so carborane was added. The addition of carborane increased the etch resistance to the equivalence of polyhydroxystyrene but increased the line edge roughness. We believe that the photoacid generator sits in the pocket of the cyclodextrin molecule, which inhibits the acid from diffusing beyond exposed regions. We hypothesize that the carborane sits in the cyclodextrin pocket, which blocks the photoacid generator’s ability to do so, increasing the acid diffusion.

Experimental Procedure:
Our studies were carried out using tert-butyl ester protected methyl β cyclodextrin, shown in Figure 1. Carborane was added to the cyclodextrin core, creating a host-guest complex. The complex was dissolved in Ethyl-l-Lactate to make a 5% weight solution. The photoacid generator used was triphenylsulfonium triflate (5% weight with respect to resist). We then spun this solution on HMDS primed silicon wafers. In order to find optimal post application bake (PAB) and post exposure bake (PEB) temperatures, we used a combinatorial tool. The setup consists of an aluminum plate with an ice bath and a hot plate on either end. The combinatorial tool allows us to have a temperature gradient across the wafer, so we can find the optimal PAB and PEB temperatures on one patterned wafer. The optimal exposure dose used for patterning was 30.45 mJ/cm². An ABM contact aligner with a 254 nm mirror was used to expose the resist and create patterns. Supercritical carbon dioxide (scCO₂) was used to develop the exposed resist, at 5000 psi for 5 minutes.

The acid diffusion studies were done using bilayers of resist, with and with out photoacid generator (PAG). Bilayers of resist were made by spinning the cyclodextrin resist with PAG on a silicon wafer. Next we spun cyclodextrin without PAG on a polydimethylsiloxane stamp that had been cleaned using oxygen plasma. The wafer and stamp were pressed together and let sit until fully wetted. Pressure and heat were applied for twenty seconds, and then the set was cooled. Finally the stamp was peeled off, leaving two layers of resist on the wafer, with the resist with PAG on the bottom. These were then exposed at varying doses and post exposure baked which started the diffusion of the acid. The wafer was then

Figure 1: tert-butyl ester protected methyl β cyclodextrin without carborane (left) and tert-butyl ester protected methyl β cyclodextrin with carborane (right).
developed using scCO₂ at 5000 psi for 5 minutes. With this type of development, the polar, or exposed portion of the resist remains, so the areas where the acid had traveled would also remain allowing us to see how far the acid diffused (Figure 2). Measurements were taken on the wafer with only the bottom layer containing resist with PAG, the wafer with both layers of resist, and after development on each exposure section. The vertical diffusion will replicate the horizontal diffusion, and we should be able to see a difference in diffusion between cyclodextrin with and without carborane.

**Results:**

Based on results obtained using the combinatorial technique, the optimal patterns for cyclodextrin without carborane (Figure 3, top) were observed at PAB of 109°C and PEB 99°C. The optimal patterns for cyclodextrin with carborane (Figure 3, bottom) were observed at a PAB of 107°C and a PEB of 99°C.

In order to obtain the data for the acid diffusion tests, we subtracted the resist thickness with PAG (no bilayer) from the resist thickness after development. We ran the experiment with the first batch of cyclodextrin, but the results were inconclusive. The second batch of cyclodextrin was more consistent and we can definitively say that the diffusion of acid is greater in the carborane complex than without carborane (Figure 4). Even when the swelling from development was taken into account, the data still showed that the acid diffusion was greater in the carborane complex.

**Future Work:**

Now that we have proven that acid diffusion is the cause of the patterns having greater line edge roughness, we can modify our cyclodextrin molecule to include PAG groups incorporated in the structure. This should decrease the acid diffusion so we can have a resist that is both etch resistant and produces high resolution patterns.

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**References:**

Elemental Analysis of Ge-SiₙGe₁₋ₙ Core-Shell Nanowire Heterostructures

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Abstract:
We investigate Ge-SiₙGe₁₋ₙ core-shell nanowire heterostructures, where the silicon germanium (SiₙGe₁₋ₙ) shell is grown in situ on the Ge nanowire core using ultra-high-vacuum chemical vapor deposition. Transmission electron microscopy shows that the SiₙGe₁₋ₙ shell is single crystal and grows epitaxially on the Ge cores. To determine the shell thickness and elemental composition of these nanowire heterostructures, we employ energy dispersive x-ray spectroscopy and electron energy-loss spectroscopy. We show that by tuning the growth conditions, the shell thickness and the relative content of the SiₙGe₁₋ₙ shell can be controlled, enabling radial band engineering in these nanowire heterostructures.

Introduction:
Semiconductor nanowires are of interest for electronic, photonic, and sensing applications. Nanowire heterostructures are attractive building blocks for low-power, high-speed electronics, due to their reduced dimensionality and the ability to engineer their electronic properties. Here we study Ge-SiₙGe₁₋ₙ core-shell nanowire heterostructures, and characterized their dimensions and content in order to enable radial strain and band engineering in this system. The valence band of the SiₙGe₁₋ₙ shell lies below the valence band of the Ge core, which allows for the engineering of one-dimensional hole gases confined to the Ge core [1,2]. We employ high-resolution transmission electron microscopy (TEM) to analyze the crystal structure of the Ge-SiₙGe₁₋ₙ core-shell heterostructure, and energy dispersive x-ray spectroscopy (EDX) and electron energy-loss spectroscopy (EELS) to determine the elemental content [3,4].

Experimental Procedure:
The Ge-SiₙGe₁₋ₙ core-shell nanowires are grown using a combination of low pressure and ultra-high-vacuum (UHV) chemical vapor deposition (CVD). The Ge cores are grown via the vapor-liquid-solid (VLS) mechanism and using Au catalysts [5,6]. The SiₙGe₁₋ₙ shell is then grown epitaxially on the Ge core using UHVCVD techniques and with various molar ratios of SiH₄ and GeH₄ (Figure 1) [5].

After growth the nanowires are harvested in an ethanol solution and deposited on a TEM copper grid. For analysis we use an FEI Tecnai TF20 microscope, equipped with high-angle annular dark field (HAADF) detectors and EDX and EELS spectrometers. The EDX and EELS data were collected using scanning TEM (STEM) linescans (Figure 2).

Figure 1: (a) Ge-SiₙGe₁₋ₙ nanowire core-shell growth. (b) Transmission electron micrograph of a Ge-SiₙGe₁₋ₙ core-shell heterostructure.

Figure 2: EDX/EELS point spectra (a) EDX spectrum showing the Si and Ge K-lines; (b) EELS spectrum showing the zero-loss and plasmon peaks and the Si L₂,₃/Ge M₄,₅ edges; (c) The EELS spectrum after background subtraction, showing the edges more clearly.
Results:

In order to analyze the EDX data, the Si and Ge concentrations are modeled as following:

\[
\psi_{\text{Si}}(x) = 2X_{\text{Si}} \cdot h_{\text{shell}}(x)
\]

and

\[
\psi_{\text{Ge}}(x) = 2X_{\text{Ge}} \cdot h_{\text{shell}}(x) + 2h_{\text{core}}(x).
\]

Here \(X_{\text{Si}}\) represents the percentage of Si in the shell, and \(h_{\text{shell}}(x)\) the nanowire thickness spanned by the electron beam at position \(x\). The concentrations are then convoluted with a Gaussian beam profile in order to compare with the measured EDX data [5].

The data of Figure 3 reveals the formation of a ~ 5 nm thick SiO\(_2\) layer on the nanowire surface, which we associated with the O\(_2\) plasma clean of the TEM sample. Interestingly, this causes the Ge atoms in the shell to move towards the core, a phenomenon known as Ge condensation [7]. This accumulation of Si atoms at the shell surface leads to larger and wider Si peaks than expected.

The EELS data shown in Figure 4 agrees qualitatively with the EDX data of Figure 3. However, we note the EELS analysis is sensitive to background subtraction, and the Ge M\(_{2,3}\) edge is not suitable for core thickness measurements because of its weakness and proximity to the stronger Si L\(_{2,3}\) edge [3].

Conclusions:

Transmission electron microscopy reveals single crystal Si\(_{x}\)Ge\(_{1-x}\) shells epitaxially grown on the Ge cores. The EDX data allows a quantitative determination of the Si\(_{x}\)Ge\(_{1-x}\) shell content and shell thickness. The EELS elemental analysis data is qualitatively consistent with EDX, and reveals the core-shell boundary more clearly.

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References:


Visible Optical Properties of Pulse-Laser-Melted Silicon with S, Se, Te, B, P and As

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Introduction:
Recent research has demonstrated that laser-structured chalcogen-laden silicon (Si) exhibits enhanced electro-optical properties when compared with ordinary Si [1-3]. On the other hand, unstructured Si is more desirable for a wide variety of device architectures. Ion implantation followed by pulsed-laser-melting-induced rapid solidification provides a method to fabricate chalcogen-laden Si with a smooth surface and crystalline interior structure [4,5]. Sulfur-laden Si, fabricated through ion implantation and pulsed-laser-melting, has been shown to absorb light strongly in the near infrared region [5]. Until this work, the properties of laser-melted, chalcogen-laden Si in the visible spectrum have not been characterized. Furthermore, little has been done to compare these materials with Si supersaturated with common dopants such as boron. Here we present the preliminary results on the visible optical properties of pulse-laser-melted Si implanted with sulfur, selenium, tellurium, boron, arsenic and phosphorus (S, Se, Te, B, As and P, respectively).

Experimental Techniques:
Si on insulator (SOI) with dimensions shown in Figure 1 was used in this experiment. The 260 nm layer of p-Si(100) was ion implanted at room temperature with either $^{32}$S$^+$ at 80 keV, $^{80}$Se$^+$ at 125 keV, $^{130}$Te$^+$ at 120 keV, $^{11}$B$^+$ at 35 keV, $^{75}$As$^+$ at 110 keV or $^{31}$P$^+$ at 65 keV. Samples to be implanted at $1 \times 10^{14}$ and $1 \times 10^{15}$ S$^+$/cm$^2$ were first implanted with $3 \times 10^{15}$ atom/cm$^2$ Si at 70 keV to produce a uniform amorphous layer. The implantation dose ranged from $1 \times 10^{14}$ to $3 \times 10^{16}$ ions/cm$^2$. The ion-implanted samples were melted via irradiation with a pulsed XeCl$^+_2$ excimer laser (308 nm, 25 ns FWHM and 50 ns total duration) with a spatially homogenized beam. The laser fluence was controlled to be around 0.6-0.7 J/cm$^2$, which was chosen to melt to a depth between 210 and 250 nm. Time-resolved reflectivity of a low-power Ar$^+$ ion laser (488 nm) was used to monitor the melt duration [6].

The implantation dose ranged from $1 \times 10^{14}$ to $3 \times 10^{16}$ ions/cm$^2$. The ion-implanted samples were melted via irradiation with a pulsed XeCl$^+_2$ excimer laser (308 nm, 25 ns FWHM and 50 ns total duration) with a spatially homogenized beam. The laser fluence was controlled to be around 0.6-0.7 J/cm$^2$, which was chosen to melt to a depth between 210 and 250 nm. Time-resolved reflectivity of a low-power Ar$^+$ ion laser (488 nm) was used to monitor the melt duration [6].

After melting, the molten layer re-solidifies as a single crystal within a few nanoseconds so that a large amount of impurity atoms remain trapped within the alloy. The concentrations of implanted impurities were typically 2–4 orders of magnitude higher than equilibrium solubility [7]. Electron backscattering diffraction on a scanning electron microscope was conducted to confirm the single-crystal nature of the laser-melted layer of each sample.

In order to measure the visible optical properties of the ion-implanted layer, the bottom layer of plain Si (500 µm thick) must be removed. We polished this layer down to roughly 200 µm. The polished sample was then mounted onto a fused quartz substrate with SU-8 photoresist. The rest of the plain Si layer was removed by inductively-coupled plasma reactive ion etching. The schematic of a fully processed sample is shown in Figure 2.

We measured the transmittance of each sample with a Hitachi U-4001 spectrophotometer. A reflectance free method from Swanepoel was adopted to calculate the optical constants from transmittance only [8]. This method exploits the dependency of thin film interference fringes on the real (n) and imaginary (k) refractive indices. Such dependency allows the determination of n, k and the absorption coefficient $\alpha$ ($\alpha = 4\pi k/\lambda$), by simply interpolating smooth curves along the maxima and the minima of the fringes [8].

Results and Discussion:
Table 1 shows the real refractive indices n and the absorption coefficients $\alpha$ at 700 nm of samples implanted with different elements to different doses. All implanted samples have
refractive indices smaller than ordinary Si. The $\alpha$ of a low dose ($1 \times 10^{15}$ ions/cm$^2$) sulfur-implanted sample exhibits little difference from ordinary Si. However, the $\alpha$ of a high dose ($1 \times 10^{16}$ ions/cm$^2$) sulfur-implanted sample is increased by approximately 400% compared to ordinary Si at 700 nm. Figure 3 illustrates the $\alpha(\lambda)$ curves of both pure Si [9] and S-implanted Si at $1 \times 10^{16}$ ions/cm$^2$ from 500 nm to 1.2 $\mu$m, which again shows the significant in-crease in absorption coefficient of the S-implanted sample.

Similarly, low dose selenium-implanted samples ($1 \times 10^{14}$ and $1 \times 10^{15}$ ions/cm$^2$) exhibit only a small increase in the $\alpha$ compared to ordinary Si, while the difference in the $\alpha$ becomes more significant for high implantation doses. In particular, the absorption coefficient increases with the implantation dose. For the $3 \times 10^{16}$ ion/cm$^2$ Se-implanted sample, $\alpha$ is an order of magnitude higher than that of ordinary Si. Only high dose ($1 \times 10^{16}$ ion/cm$^2$) samples were processed and measured for Si supersaturated with Te, P, As and B. As shown in Table 1, high dose Te-implanted Si also possesses a much higher $\alpha$ than ordinary Si. Samples implanted with P, As and B also exhibit some increase in the $\alpha$. However, such increase is relatively small compared to the three chalcogen elements investigated.

Comparing only the samples with an implantation dose of $1 \times 10^{16}$ ion/cm$^2$, Se-implanted Si exhibits highest absorption among all elements, which is followed by S-implanted Si and Te-implanted Si. These preliminary results demonstrate chalcogen-laden Si absorbs visible light much more strongly than ordinary Si. The absorption mechanism is unknown, but hypotheses exist about the formation of an impurity band and about the formation of dopant nano-clusters. Potential applications of these strong-light-absorbing materials include the fabrication of low-cost photodetectors and photovoltaics since a thinner (and thus cheaper) layer could absorb all of the relevant light. Opto-electronic conversion for photodetectors has been demonstrated for laser-structured chalcogen-laden Si, but not yet in other settings.

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**References:**
Synthesis and Properties of Manganese Oxide Nanoparticles for Environmental Applications

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Abstract and Introduction:
Manganese oxide nanoparticles (MnO₂ NPs) can be utilized for advanced materials in batteries, as well as other applications, such as water treatment and imaging contrast agents [1]. To have more efficient performance, these materials need particles of defined size, while remaining benign to the environment. In this work, we synthesized NPs with a biomineralization approach and investigated antimicrobial effects. MnO₂ NPs were synthesized using the iron storage protein ferritin that provides an 8 nm cavity in which these particles form.

We compared the sizes and morphologies of biomimetically synthesized NPs to those from inorganic synthesis using dynamic light scattering (DLS), transmission electron microscopy (TEM), high resolution TEM (HR-TEM), and atomic force microscopy (AFM). DLS showed sizes of particle aggregates as a function of reaction time. Electron diffraction patterns were collected by HR-TEM to identify the phase of NPs and determine particle size. AFM was used to investigate morphologies and sizes of the particles. To study antimicrobial effects of both synthetic methods, Shewanella was studied while in solution with MnO₂ NPs. Our findings from this work will provide fundamental information of the potential toxicities of NPs generated by different pathways.

Materials and Methods:
To synthesize MnO₂ NPs biomimetically, apoferritin and manganese (II) tetrahydrate were added to doubly filtered deionized water. The pH of the reaction volume was brought to 9 with sodium hydroxide, and the reaction was rotated in a test tube for six hours. The inorganic synthesis was prepared in the same manner but without the protein. To investigate particle morphologies, TEM imaging was performed using a FEI Tecnai G² Spirit microscope. Samples were prepared by drying the reaction mixture on carbon-coated Formvar-covered copper TEM grids. HR-TEM imaging was performed on JEOL JEM-2100F with imaging using Gatan Orius SD1000B camera to determine particle size and phase by calculating d-spacing. To determine hydrodynamic particle size, DLS data was taken over time during the synthesis incubation using Malvern 1011155 Zetasizer Nanoseries. The particle morphology, before and after trypsin treatment, was examined by AFM with a Veeco Nanoscope microscope.

The protein layer was digested by adding trypsin 1:20 (w:w) to the reaction volume and was incubated for fifteen minutes. To study antimicrobial effects of NPs from different syntheses, manganese oxides at concentrations of 100 µg/mL, 20 µg/mL and 2 µg/mL were incubated in MR-1 media.

Figure 1, left: DLS data of inorganic synthesis as labeled “Mn” and biomimetic synthesis as labeled “Mn+apoferritin” with the corresponding incubation times. Figure 2, above: TEM image of inorganic synthesis displaying crystalline nanorods of various sizes.
with *Shewanella oneidensis* MR-1 at 32°C. Bacteria was added until the media had an optical density of 0.2 A at 600 nm. Optical density measurements were taken over 24 hours on ThermoScientific Genesys UV spectrophotometer.

**Results and Discussion:**

DLS data indicated particles measured were of aggregate size, not individual particle size. The gradual increase of size during the reaction showed aggregation as a function of time. At final incubation time, the biomimetic synthesis yielded smaller particle aggregates than the inorganic synthesis. This trend can be explained by the amount of available aqueous manganese ions in solution for nanoparticle formation.

Crystalline nanorods of various sizes in the inorganic synthesis were observed by TEM while few nanorods and spherical nanoparticles were found in the biomimetic synthesis. Particle size of 7-8 nm was verified by HR-TEM and was consistent with the limits of the protein cavity. The particles showed lattice fringes indicating crystalline material while previous work reported amorphous particles [2]. The d-spacing was calculated to be 3.407 Å corresponding to manganite. Unlike our synthesis, previous work used buffer at pH 9 as the reaction volume. The contribution of the buffer to the crystallinity of MnO₂ needs to be investigated further. Using AFM, we concluded trypsin removed the protein layer. The data of the biomimetic synthesis demonstrated peaks with particle height of 12 nm corresponding to protein and larger heights indicating protein aggregates. Digestion of biomimetic synthesis displayed height peaks at 8 nm indicating manganese oxide nanoparticles without the protein shell.

Antimicrobial studies on *Shewanella* were performed using particles of the biomimetic synthesis with and without the protein layer. The inorganic synthesis was also studied using incubation times of one and six hours. The bacteria exposed to particles of both synthetic methods showed minor inhibition in the lag and log phases of the growth curve, but recovered from the stress in the stable phase. In the log phase at eight hours, the inorganic synthesis showed greater inhibition than the biomimetic synthesis.

**Conclusion:**

Biomimetic manganese oxides were successfully synthesized from the adopted synthetic method [2]. TEM images indicated the nanoparticles formed within protein shells. We determined the sizes of hydrodynamic and individual nanoparticles by DLS and HR-TEM respectively. The particle morphologies were probed with AFM before and after protein digestion confirming the protein layer was removed from the nanoparticles. Antimicrobial studies of both the biomimetic and inorganic synthesis with respect to *Shewanella* indicated only minor inhibition in the lag and log phases of the growth curve.

Our findings report MnO₂ NPs synthesized from a controlled biomimetic method show promise for use in advanced materials that are friendly to the environment.

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**References:**


Large-Area Chemical Vapor Deposition of Graphene over Thin Films of Cobalt

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Abstract:
The synthesis of graphene over thin films of cobalt was demonstrated by chemical vapor deposition, using methane as a precursor. At sufficiently high temperatures, decomposition of methane led to dissolution of carbon in the cobalt film. Upon subsequent cooling of the metal film to room temperature, the solubility of carbon in cobalt is reduced, leading to segregation of some carbon atoms to the surface in the form of graphene. Subsequently, etching away the underlying cobalt made it possible to transfer the graphene film to arbitrary substrates, including insulator substrates such as silicon dioxide. Further analysis of the graphene films revealed that they generally consisted of a large continuous region of thin few-layer graphene, with many patches of thicker multi-layer graphene present throughout the film. Raman spectroscopy confirmed the presence of single-layer regions, as well as the presence of defects pervasive throughout the films.

Introduction:
Graphene, first identified in 2004, is a one-atom thick sheet of carbon atoms, wherein the carbon atoms are arranged in a 2-dimensional hexagonal lattice. The common material graphite can be viewed as a large number of graphene sheets stacked together.

Single-layer graphene has many favorable electronic properties, such as a high electron mobility, that may lead to transistors that operate much faster than conventional silicon devices. However, these properties are substantially degraded when graphene is present in multiple layers.

Unfortunately, it is very difficult to produce large, continuous layers of single-layer or even few-layer graphene. Most graphene used in research is obtained by “mechanical exfoliation,” a process that is inefficient, labor-intensive, and non-scalable. For this project, we sought to develop a practical method to synthesize large graphene films using chemical vapor deposition.

Experimental Procedure:
For this project, we began by depositing a 100 nm film of polycrystalline cobalt on a silicon dioxide substrate using electron-beam evaporation. We then exposed this cobalt to methane and hydrogen at approximately 850°C for a few seconds. Methane molecules (CH₄) were adsorbed at the cobalt surface and hydrogen was then desorbed from the surface, leaving the remaining carbon atoms to dissolve in the cobalt film. The methane had thus decomposed into carbon and hydrogen according to the reaction:

\[ \text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \]

Any amorphous carbon on the surface was etched away by the high-temperature hydrogen gas. Afterwards, as the cobalt cools to room temperature, the solubility of carbon in the cobalt decreases. This causes some of the dissolved carbon to segregate out to the surface, forming a continuous film of graphene, as shown in Figure 1.

The cobalt was subsequently etched away, and the graphene was transferred to a new silicon dioxide substrate. Further analysis was then performed using optical microscopy, scanning electron microscopy, atomic force microscopy, and Raman spectroscopy.
Results and Conclusions:
Researchers have already successfully grown graphene over thin films of nickel [1]. We therefore began by growing graphene both over nickel and over cobalt, and compared the results as shown in Figure 2. From this comparison, we found that using cobalt instead of nickel virtually eliminated the thickest, most undesirable regions.

Ultimately, we found that drastically shorter growth processes, on the order of minutes instead of hours, yielded significantly better results, as shown in Figure 3. Unfortunately, thicker patches were still present throughout, which we believed to be due to the polycrystalline nature of the original cobalt surface. Scanning electron microscopy revealed microscopic cracks in the graphene, while atomic force microscopy revealed small growths over the graphene.

We also analyzed our films using Raman spectroscopy over a region that we thought might be single-layer graphene, with the Raman spectrum shown in Figure 4. The relative strength of the 2D peak (~ 2700 cm\(^{-1}\)) to the G peak (~ 1581 cm\(^{-1}\)) suggests the presence of single-layer or bilayer graphene. Further analysis of the 2D peak revealed that it could be fit to a single Lorentzian curve, which strongly supports the presence of single-layer graphene. However, the strength of the D peak (~ 1350 cm\(^{-1}\)) indicates a substantial presence of microscopic defects throughout our film. This is in addition to the thicker multilayer patches previously mentioned.

Future Work:
Most crucially, the electronic properties of these films must be measured by fabricating devices. As well, continued Raman studies may allow us to estimate what percentage of the total graphene films is single-layer, bilayer, multilayer, etc. Furthermore, since Raman spectroscopy indicates a strong presence of defects, the source of these defects must be determined so as to minimize them. It is likely that these defects arise during the transfer process, however this is not yet confirmed.

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