Introduction:

Much research has taken place in recent years in the synthesis of ZnO nanowires (NWs) due to their unique electronic and optical properties that make them excellent candidates for the use in nano devices such as nanogenerators, LEDs, gas sensors and biosensors. Additionally, the electronic and optical properties of ZnO NWs can be finely tuned through the use of dopants. Most often, however, research has centered on common synthesis techniques that require either high temperatures, dangerous gases, or the use of an extrinsic catalyst such as Au nanoparticles which makes the synthesis of ZnO NWs impractical or too expensive for many applications. An alternative method for ZnO NW synthesis is to simply heat micron sized Zn particles to around 500°C at 30°C/min in air at ambient pressure. The relatively low temperature and highly pure starting materials make this a promising method for the synthesis of ZnO NWs. This paper reports the results of in-situ HTXRD of the grown ZnO NWs and suggests a possible method for the incorporation of dopants.

Procedure:

Zn powder with particle sizes in the tens of microns were placed flat on a corundum plate and heated in an Aton Paar 1200 HTK furnace open to air attached to a X’Pert Pro MPD diffractometer with a Cu source, parabolic mirror and X’Celerator line detector. After alignments, samples were characterized in-situ from 25 to 135° 2θ with a step size of 0.02° 2θ and time per step of 20 seconds. A baseline scan was performed at RT, and further scans were carried out at 500°C and again at RT. The existence of NWs was confirmed using SEM.

In order to confirm that the ZnO signal was due to the growth of the NWs and not due to the oxide layer on the starting Zn particles, a series of measurements were taken on a X’Pert Pro Alpha-1 diffractometer with a diffracted beam monochromator and similar settings as on the MPD. Size/Strain analysis from peak broadening was performed and instrumental broadening was accounted for using a NIST LaB6 SRM 660a standard which is known to exhibit no peak broadening due to size/strain effects.

For the S doping experiments, S powder was placed next to the ZnO NW in an enclosed MgO container and heated to 575°C in air. After processing, samples were characterized on a X’Pert Pro MRD diffractometer with a Cu source and parallel beam optics. After performing alignments, scans were taken from 30 to 33 degrees 2θ with a step size of 0.02 and a time per step of 20 seconds.

Results/Discussion:

Figure 1 shows a typical HTXRD plot of scans taken at RT and 500°C from the grown ZnO NWs. The appearance of a peak at about 31.7° 2θ shows the formation of the ZnO phase.

Figure 2 shows an overlay of XRD patterns taken from ZnO NW and S doped ZnO NW. The use of parallel beam optics eliminates 2θ shift due to sample height displacement. Therefore, the shift in 20 peak location of about 0.1° is a result of the substitution of S, which has a slightly larger ionic radius than O, into the wurtzite lattice structure. In future studies, photoluminescence could be used to confirm the successful doping of S by showing that the electronic structure of the NWs is changed.

References:


Acknowledgements:

I would like to thank Dr. Robert Snyder and Dr. Z. L. Wang for allowing me to work with their research groups. Additionally, the following people helped me out tremendously with my research: Melanie Kirkham, Phil Graham and Dr. Jung-Il Hong.
Introduction:
Since the discovery of multiwalled carbon nanotubes (MWCNTs) in 1991, there has been an increased interest in their properties and applications. MWCNTs consist of a central tube of nanometric diameter surrounded by graphitic layers separated by ~0.34nm. Some of their outstanding properties include great ductility, high aspect ratio, high tensile strength, and low mass density. They also have a large surface area, versatile electronic behavior, high heat conductivity, and a sufficiently low cost. In order to take advantage of these exceptional qualities, it is necessary to use them in composites.

Carbon-Carbon (C-C) composites are also known for their superior mechanical properties, which are high strength and modulus, high thermal capacity, stable frictional and wear properties, and an excellent ablation resistance at elevated temperature in inert atmosphere. There are many applications for them, such as use as re-entry parts of space vehicles, rocket nozzles and lining parts of missiles, aircraft brake discs, fission reactor, high power accelerator, sports instruments, electronic components, and medical uses.

However, there are drawbacks of the currently produced C-C composites: they oxidize readily at temperatures between 600-700°C, especially in the presence of atomic oxygen. The objective of this study is to improve the qualities of current C-C composites by creating a process that produces new C-C composites through deposition of MWCNTs on graphite structures.

Procedure:
MWCNTs were synthesized by Chemical Vapor Deposition. In this process, metal catalyst Ferrocene was dissolved in liquid hydrocarbon source Xylene to form a feed solution, which was dispersed into a stream of carrier gases Hydrogen and Helium. The feed solution was introduced directly into the reactor, therefore volatilizing the solution. Aligned carbon nanotubes were then grown on the substrate.

Once MWCNTs were produced, C-C composite was made through Chemical Vapor Infiltration. It is a densification technique in which the structure to be densified is placed in a flow of methane and the assembly is raised to 950°C. The pyrolytic carbon obtained by decomposition of methane is deposited in part in voids within the carbon-nanotubes porous structure, thereby filling said voids. To evaluate the samples, pictures from SEM and TEM were taken and carefully analyzed.

Results and Discussion:
SEM pictures of MWCNTs and C-C composite respectfully are shown below.

The figure on the left shows that the produced MWCNTs are aligned well together and have a great directional structure. The figure on the right shows the build-up on the nanotubes. It is clear that the desired densification consisting of carbon graphites onto MWCNTs has occurred. Since we were able to repeat the experiment and duplicate the results, we have a reliable process of making C-C composites.

Conclusion:
While we were able to achieve the desired structure of C-C composite, it is necessary to make thick sheets of the same structure and examine mechanical behavior and properties of the new composition. Much work needs to be accomplished to explore what this material can endure and what limitations it has. When the material has been tested, its applications can be explored.

References:

Introduction

The current world energy crisis has caused great interest in new and improved technologies to produce and store energy. Energy harvesting is one way to store energy by capturing thermal, kinetic, or electric energy that is already present in our environment. This method includes harvesting wind, solar, thermal, and even excess mechanical energy. Mechanical movement can be stored by using piezoelectric materials such as ZnO. Due to their crystalline structure, piezoelectric materials can produce a small electric current when they are mechanically deformed, or inversely, they can deform when a current is passed through them.

An effective piezoelectric generator must have a bristled or textured surface that will deform from small movements. To implement this design, a flexible piezoelectric fabric can be made using two pieces of carbon fiber (CF) that have been coated with carbon nanotubes (CNT) and sandwiched together (Figure 1). The CNT can then be coated with ZnO, creating a bristled piezoelectric surface. In this design, the bottom ZnO coated layer is the piezoelectric and the top gold coated layer deforms the ZnO when moved. The mechanical deformation of the ZnO creates a small voltage on each CNT and the conductive gold coating on the top layer forms a Schottky barrier, thus limiting current to flow to only one direction. CNT are optimal for this design because they have good adhesion to CF and a high aspect ratio which allows for maximum deformation of the ZnO.

Procedure

Woven CF sheets were cut into 4” square pieces and deposited with an iron catalyst about 4 nm thick using a thermal evaporator. Then the CF was placed in a chemical vapor deposition (CVD) furnace where it was heated to 820°C while various hydrocarbon gases flowed over the sample, thus growing the CNTs. The coating of ZnO or gold was applied using RF sputtering and electron beam evaporation. The coatings and CNT growth was characterized using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Electronic testing on the fabric was performed to determine the material’s resistivity.

Results and Discussion

Based on the SEM images in Figure 2, CNT growth and ZnO deposition are homogeneous and complete. The good CNT growth can be attributed to good penetration of the hydrocarbon gases in the CVD through small holes in the fabric. In Figure 3, the TEM image of a single CNT coated with ZnO shows an evenly 1-2nm coating of ZnO. Analysis of a TEM electron diffraction pattern of the deposition layer in Figure 3 confirms that the coating is made of ZnO and that there are preferred orientations in its crystalline structure. Preferred orientations are necessary in the ZnO for there to be a net flow of electrons. Testing resistance in the gold coated layer revealed a very low resistance (<1 Ω) which is necessary for the Schottky barrier. The ZnO coated layer has a significant resistance of 20-80 Ω. This result is expected and confirms complete deposition of the piezoelectric.

Future Work

Since complete deposition and preferred orientation of ZnO has been confirmed, the research will progress to more characterization and testing of the fabric design. Adhesion of the ZnO and gold coatings from different deposition techniques needs to be analyzed to determine which has the best adhesion. Also, the crystal orientation of the ZnO will be determined for each deposition technique so that the method that produces the fewest preferred orientations can be found. Finally, highly sensitive electrical equipment will need to be purchased in order to test the voltage output of the piezoelectric material and optimize its design.
Monolayer Deposition of Ag and Te on Polycrystalline Gold via Cyclic Voltammetry and Galvanic Replacement
James Guthrie, Georgia Institute of Technology, SURF 2008
Advisor: Faisal Alamgir

Introduction
The ultimate goal of this research is for the analysis of core-shell catalyst systems for the purpose of understanding the causes of their increased catalytic effects and resistance to CO poisoning, a phenomenon found in the literature [1] but not, as yet, fully understood or explored. However, before the final analysis can be conducted, it is necessary to first develop sound methods of creating these core-shell bi-metallic catalyst structures, leading to the current step of the overall research: creating swift and efficient methods for monolayer deposition of one catalytically-relevant metal onto another. A very precise method of monolayer deposition is found in cyclic voltammetry (CV) via underpotential deposition [2], a voltage limited method of deposition for which, through coulomb counting backcalculation, the precise amount of a deposited material can be calculated [3, 4]. The largest issue with CV, however, is that it only applies to certain systems of substrate and depositing material and thus hasn’t the desired versatility for research into the plethora of catalytic bi-metallic systems. The end solution found in this research was a combination of CV and galvanic replacement, a method in which a more noble metal will replace a less noble, by introducing the electrodeposited, low-nobility monolayer into a solution of more noble metal ions. This allows for the precision of CV with the added versatility of galvanic replacement by use of a sacrificial layer of atoms.

Procedure
CV was conducted using a Solartron SI 1287 potentiostat, a custom-designed three-lead cell, a home made Ag/Ag2SO4 reference electrode, a polycrystalline Au substrate polished down to 0.05 micron roughness, and solutions of 1 mM Ag2SO4 in 50 mM H2SO4 and 0.4 mM TeO2 in 50 mM H2SO4. After the deposition of Te onto Au, the resulting bi-metallic system was immersed in a 10 mM Ag2SO4 solution to allow for the galvanic replacement of Te by Ag. Verification of thicknesses and composition of deposited layers will be conducted via ARXPS and AFM, and galvanic replacement verified through EDS and XPS.

Results and Discussion
Preliminary scans were taken simply to characterize polycrystalline Au in 50 mM H2SO4 and bulk deposition of Ag onto polycrystalline Au (Fig 1), primarily to familiarize oneself with CV and get a reference of where the UPD peaks might be and where to scan in order to avoid the oxidation and reduction of Au or the bulk deposition of Ag, both of which could interfere with the UPD deposition or stripping.

After scanning at the bulk deposition level, we attempted to find the location of the UPD peaks for Ag on Au. Two peaks were found, one at ~0.47 V and the other closer to ~0.51 V (fig 2). The coulomb charge density associated with the scan was 509 μC/cm². Using the back calculations, it appears that ~2.3 monolayers had been deposited in this scan. Simply by tweaking the ending voltage up, it was possible to get depositions as low as 1.03 monolayers, well within our range of need of 0.75-1.5 monolayers.

Following the success with Ag deposition, characterization was begun on Te deposition on polycrystalline Au. Bulk deposition was not greatly looked into, as Te has a rate of deposition of about
0.5 monolayers/min, even in bulk deposition, and the bulk deposition peaks greatly coincide with hydrogen evolution. The UPD peaks were found and analysis begun to find the optimal voltage for depositing ~1 monolayer (fig 3). After this deposition, the sample was placed in a Ag2SO4 solution, to allow for galvanic replacement of Te by Ag. The ensuing sample has not yet been characterized, but will be in the following weeks. Crude verification was performed with a 36 hour bulk deposition scan and subsequent immersion, which resulted in a slight color change of the bulk deposit, letting one know that some method of replacement is occurring.

Figure 3: Te UPD on polycrystalline Au at 5 mV/s vs a Ag/Ag2SO4 reference electrode, the charge and current densities shown on the upper graph and the current shown on the lower graph, all vs. voltage.

**Conclusion**

Conclusions can not, as yet, be entirely determined due to the repair status of the SEM and XPS systems we have access to. The CV data, however, points to the deposition of ~1 monolayer of Ag and Te in each case, which leads one to believe this method to be a viable solution to the need for a method of bi-metallic system construction, assuming the theory of galvanic replacement holds up, an assumption which will be verified or negated in the upcoming weeks.

**Acknowledgements**

I would like to give many thanks to Dr. Faisal Alamgir for the plethora of advice given and the free use of his lab. Great thanks also goes to Robert Rettew, for putting up with me for the duration of the program and for always offering a guiding hand in life, research, or necessary cinema.

**References**


Introduction

Isothermal titration calorimetry (ITC) has already proven a powerful tool for use in the investigation of the thermodynamics of molecular interactions. Its direct measurement of the global heat of reaction allows users to determine the enthalpy of reaction ($\Delta H_r$), binding constant ($K_b$), and stoichiometry (N) within a single experiment – and it is the only machine capable of doing so. Because of this versatility, ITC was used to study the binding energies between barium titanate (BT) nanoparticles and ligands of varying binding groups such as phosphonic acids, carboxylic acids, and silanes in order to gain insight into the binding energy hierarchy of these molecular complexes.

Experimental

The ligands under study were octylphosphonic acid (OPA), octadecylphosphonic acid (ODPA), benzene phosphonic acid (phenylPA), trimethoxy(octyl)silane (OTMS), and nonanoic acid. Each ligand was injected at 30mM, except ODPA (at 5mM), into 8.0mg/ml BT (1.4mg/ml for ODPA), with all sets of solutions having 95:5 EtOH/H$_2$O as a buffer. The ITC run was set for 29 injections of 10µl ligand aliquots at 298K using the VP-ITC machinery and package from MicroCal. BET measurements of BT were performed with Krypton in order to obtain the surface area of the used nanoparticles. Finally, thermogravimetric analysis (TGA) was done to arrive at actual grafting densities between the ligands and BT nanoparticles.

Results and Discussion

Table 1 shows the results of the ITC and TGA runs for each ligand-BT combination.

<table>
<thead>
<tr>
<th>Ligand in THF</th>
<th>$\Delta H$ (kcal/mole)</th>
<th>$\Delta H_{sol}$ (kcal/mole)</th>
<th>TGA (% weight loss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPA</td>
<td>-0.24</td>
<td>0.20</td>
<td>82.0</td>
</tr>
<tr>
<td>ODPA</td>
<td>-19.28</td>
<td>16.62</td>
<td></td>
</tr>
<tr>
<td>PhenylPA</td>
<td>-2.74</td>
<td>4.71</td>
<td></td>
</tr>
<tr>
<td>Nonanoic acid</td>
<td>-39.62</td>
<td>158.17</td>
<td></td>
</tr>
<tr>
<td>Silane</td>
<td>-3.4</td>
<td>5.57</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Enthalpy of reaction and TGA % weight loss measurements. OTMS and nonanoic acid showed no binding.

As can be seen, ODPA had the highest heat release during the binding reaction followed by OPA and then phenylPA. However, to compute the binding energy (D), one uses equation (1) that was derived by Ferreira et al.

$$\Delta H_f = -D - (\Delta H_{sol} + \Delta H_{gib}) = (E_2 - E_{2NN})$$ (1)

With some simplifications (see Ferreira et al.) equation (1) becomes

$$\Delta H_f = -D - \Delta H_{sol} - 11.56$$ (2)

which is measured in kJ/mole. Here, $\Delta H_f$ is the total heat measured from the ITC and $\Delta H_{sol}$ is the heat of solvation for the ligand. Again, $\Delta H_{sol}$ values from Ferreira et al. were used for OPA and ODPA to estimate D in this study while phenylIPA’s $\Delta H_{sol}$ was estimated via extrapolation of the trend between carbon number and enthalpy as found in Ferreira et al. The resulting D values are found in Table 2.

<table>
<thead>
<tr>
<th>Ligand in THF</th>
<th>$\Delta H_{sol}$ (kJ/mole)</th>
<th>D (kJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPA</td>
<td>-48.17</td>
<td>184.0</td>
</tr>
<tr>
<td>ODPA</td>
<td>-25.29</td>
<td>148.17</td>
</tr>
<tr>
<td>PhenylPA</td>
<td>-43.11</td>
<td>55.57</td>
</tr>
</tbody>
</table>

Table 2. $\Delta H_{sol}$ and resulting D values as computed from equation (2).

From these D values it is apparent that ODPA had the highest binding energy, then OPA, and finally phenylPA. This is expected as all phosphonic acids bind readily to metal oxide surfaces, but an increasing alkyl chain length helps make binding more favorable as a result of the stabilizing van der Waals forces. Finally, the BET surface area that was obtained was 19.02 m$^2$/g.

Conclusion

ITC results and computations from equation (2) showed that ODPA had the strongest binding interaction with the BT nanoparticles, followed by OPA and then phenylPA. As discussed above, this trend is not surprising as more stabilizing forces can interact with longer alkyl chains. Carboxylic acids and silanes did not bind at all under the conditions used in this work, which further supports FTIR evidence found by Kim et al.

Acknowledgements

I would like to thank Seth Marder and Peter Hotchkiss for taking time out of their busy schedules to teach me so much with this research. Also, Phil Kim provided invaluable advice and support throughout my stay. Finally, I am indebted to Nick Hud and his lab for the use of their VP-ITC and knowledge thereof.

References


Kim, P; Jones, S; Hotchkiss, P; Haddock, J; Kippelen, B; Marder, S; Perry, J. Advanced Materials. 19. 2007. 1001-1005.
Shock Compaction of Textured Permanent Magnets
Janessa Rowland, Georgia Tech, SURF 2008 Fellow
Faculty Advisor: Dr. Naresh Thadani    Graduate Mentor; Chris Wernhberg

Introduction

Naval ships today are run on fuel and chemicals, which take up space to store and can be potentially dangerous. Electromagnetic powered ships will cut down the cost, maintenance and storage space needed compared to the use of chemicals and fuel. While magnets are used everyday to generate electricity, the energy these magnets supply is not strong enough for massive power generation. Textured Nanostructured Permanent Magnets have the potential for providing high energy product that is needed for naval applications. The objective of this present study is to investigate texture generation during shock compaction of Pr2 Fe14 B nanostructured powder.

Procedure

Approximately five grams of Pr2 Fe14B nanostructured powder was placed into a three layer sieve, the smallest particles being less than 20 um and the largest greater than 40um. The sieve was then placed in an ultra sonic cleaner that separated the powder into three different sizes, small (<20um), medium (20- 44 um) and large (>44 um) particles. From the smallest and largest particle powders, pellets were formed using a hydraulic pressing machine. The pellets were then mounted onto copper rods and impacted onto a rigid steel anvil at speeds of 50 – 500 m/s using 7.62 mm diameter helium gas gun. The impacted samples were then characterized for degree of compaction and texture.

Results and Discussion

Two pellets composed of particles 40 um and larger were shot in the helium gas gun, one at 135 m/s and the other at 180 m/s. Two pellets composed of particles 20 um and smaller were shot at 90 m/s and 135 m/s. The pellet shot at 90 m/s did not compact at all. The pellets shot at 135 m/s compacted and in some areas began to plastically deform. There was more bond breakage and deformation. Figure one shows the pellet shot at 180 m/s compacted. The sample was plastically deformed in more areas than the previous shots. While it was believed that when the samples plastically deformed the particles would align themselves in the magnetic plane of 0, 0, C, in all the samples we tested none of them showed strong indication of alignment in the magnetic plane. Future test would have to be performed.

Conclusion

Through shock compaction, the minimum speed range to successfully compact the nanostructured powder was discovered to be between 90m/s and 135m/s. The samples also showed through SEM bond breakage and plastic deformation. There was however not a strong indication of particles realigning in the magnetic plane of 0,0,C. More tests would need to be performed.
Shock Compaction of Textured Nanostructured Permanent Magnets

Janessa Rowland, Georgia Tech, SURF 2008 Fellow

Faculty Advisor: Dr. Naresh Thadhani    Graduate Mentor; Chris Wernhberg

Introduction

Naval ships today are run on fuel and chemicals, which take up space to store and can be potentially dangerous. Electromagnetic powered ships will cut down the cost, maintenance and storage space needed compared to the use of chemicals and fuel. While magnets are used everyday to generate electricity, the energy these magnets supply is not strong enough for massive power generation. Textured Nanostructured Permanent Magnets have the potential for providing high energy product that is needed for naval applications. The objective of this present study is to investigate texture generation during shock compaction of Pr2 Fe14 B nanostructured powder.

Procedure

Approximately five grams of Pr2 Fe14B nanostructured powder was placed into a three layer sieve, the smallest particles being less than 20 μm and the largest greater than 44μm. The sieve was then placed in an ultra sonic shaker that separated the powder into three different sizes, small (<20μm), medium (20- 44 μm) and large (>44 μm) particles. From the smallest and largest particle powders, pellets were formed using a hydraulic pressing machine. The pellets were then mounted onto copper rods and impacted onto a rigid steel anvil at speeds of 50 – 500 m/s using 7.62 mm diameter helium gas gun. The impacted samples were then characterized for degree of compaction and texture via x-ray diffraction

Results and Discussion

<table>
<thead>
<tr>
<th>Sample</th>
<th>Powder Size</th>
<th>Impact Speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>Fine Powder</td>
<td>90 m/s</td>
</tr>
<tr>
<td>Sample 2</td>
<td>Fine Powder</td>
<td>135 m/s</td>
</tr>
<tr>
<td>Sample 3</td>
<td>Corse Powder</td>
<td>135 m/s</td>
</tr>
<tr>
<td>Sample 4</td>
<td>Corse Powder</td>
<td>180 m/s</td>
</tr>
</tbody>
</table>

Table 1.

The samples that were shot are listed in Table 1. according to the powder size and impact speed. The pellet shot at 90 m/s did not compact at all.

Figure 1. 2.53KX magnification of sample (40μm> particles) shot at 180 m/s

The pellets shot at 135 m/s compacted and in some areas began to plastically deform. There was more fracture and limited deformation. Figure 1. shows the pellet shot at 180 m/s compacted. The sample was plastically deformed in more areas than in the previous shots. While it was expected that when the sample plastically deformed the particles would align themselves in the 0,0,C magnetic plane direction, the results from x-ray diffraction were inconclusive. Further evidence will require texture measurements. Additional tests would have to be performed under high impact conditions.

Conclusion

The minimum impact speed range to successfully compact the nanostructed powder was found to be between 90m/s and 135m/s. The samples also showed evidence of inter-particle bonding, plastic deformation, and intra-particle fracture increasing with impact velocity. There was only limited particle alignment observed in the shock compacted magnet. Further characterization of 0,0,C texture needs to be performed.

Acknowledgements

I would like to thank Dr. Thadhμani for allowing me to work in his lab and all the graduate students in the lab who helped me this summer especially Chris Wernhberg.
Electroless Copper and Gold Depositions on Porous Silicon
Jenna Campbell, Georgia Institute of Technology, SURF 2008 Fellow
Advisor: Dr. James Gole

Introduction
A unique property of porous silicon is its ability to photoluminesce. When placed under ultraviolet light, porous silicon that has been electrochemically etched in a varying number of electrolytic solutions will photoluminesce giving off a red-orange glow when excited by UV light as the photoluminescence is strong. The photoluminescent qualities of porous silicon can be utilized to create electroluminescence. Plating the wafer and a portion of the porous silicon with a conductive metal, such as gold, platinum or copper, and then running a current through the wafer will encourage the silicon to electroluminesce. Previous research resulted in a 10⁻⁵ percent quantum yield.¹ If the resistivity of the porous silicon surface itself is too high the electroless coating techniques being introduced can provide a considerable improvement to the system.

By successfully converting the photoluminescence to electroluminescence an innovative photocatalyst can be developed which can greatly influence the field of chemistry.

Procedure
Silicon wafers are cleaned using 49% HF to remove the oxides from the surface and trichloroethylene to strip the organics off of the substrate. Boron doped, p-type polished silicon wafers with a resistivity range from 1-20 Ω-cm are the substrates used to create the porous structures. Hybrid and aqueous electrolytic solutions generate photoluminescent porous silicon. Silicon etches for 30-60 minutes with a low current density (2.75 mA/cm²), is rinsed with methanol after the etch and is left to dry.

Electroless gold or copper metallizing baths are deposited on the substrate as shown below in Figure 1.² With low resistance contacts attached to the Si, the coated wafer is then attached to a power supply through which a current is sent, and electroluminescence is ideal.

Results and Discussion
For the most successful electroluminescence time was spent configuring ideal etching conditions to get a highly photoluminescent etch. Judging by the naked eye, silicon etched in an aqueous electrolytic solution consisting of 49% HF and methanol at a volumetric ratio of 1:3 respectively luminances red-orange visible light when exposed to UV rays. After etching, the Si is cleaned with MeOH to remove HF residue. The MeOH does not affect the luminescence of the silicon once it dries.

The next step was to find a metallizing bath to coat the edges of the porous silicon to lower the resistance of the system. The first coating was an HF-based copper metallizing bath that produces thin Cu deposits in minutes. After directly removing the porous structure from the Cu solution and attaching it to the power supply, the Cu oxidizes, and the sample becomes unusable.³ To avoid rapid oxidation, a bright electroless gold metallizing bath from Transene Company, Inc. was used to plate the silicon substrates. The Transene Au solution takes hours to plate, and it was difficult to coat the proper areas of the silicon wafer (as seen in Figure 1) without interfering with the porous structure. The most successful plating techniques came from an unpublished method created by Dr. M. Schlesinger. By sending the Si substrate through a series of baths and rinses, a Cu coating was successfully deposited. This series of baths, now proven successful, is the basis for an electroless gold coating that should be ideal for the system.

Conclusion
Ultimately, the system will consist of an aqueous etch with gold plating since the thin copper coatings are not very effective due to their rapid oxidation rates. If the resistivity of the system remains too high after the coatings are worked into the system, then work will need to be done in developing low resistance contacts for the system. Lying gold nanowires across the silicon to lower the resistivity of the porous silicon surface and facilitate photoluminescent site excitation is another way the resistance of the system can be lowered if the gold plating is not effective enough.

Acknowledgements
I would like to thank Dr. James Gole for giving me the opportunity to work in his lab and for his guidance throughout this project, Serdar Ozdemir for the advice he provided, and Dr. Mordechay Schlesinger for sharing his plating techniques and being ever ready to help us when we ran into problems. I would also like to thank the coordinators of the SURF 2008 program for making the program such a fun experience and allowing me to participate and NSF.

References
MECHANISMS OF HIGH PERFORMANCE ELECTRICALLY CONDUCTIVE ADHESIVES FOR LEAD-FREE INTERCONNECTS

Jeremy Moskowitz, Georgia Tech, SURF 2008 Fellow
Faculty Advisor: Dr. C. P. Wong   Graduate Mentor: Rongwei Zhang

Introduction: In recent years, the use of tin/lead (Sn/Pb) solder in semiconductor materials has become a major concern. Due to the toxicity of lead and government regulations in other countries, research has been focused on formulating a substitute with comparable properties. Lead is not only harmful, but difficult to recycle in semiconductors and has a short life span of 2-3 years. Remarkable advancements have been made towards removing lead from the electronics industry.

Electrically conductive adhesives (ECAs) are one promising alternative to tin/lead solder. They are advantageous because they are environmentally friendly, have mild processing conditions, require few processing steps which reduces cost, and they can also achieve very fine pitch. However, in contrast to tin/lead solder, ECAs have lesser electrical conductivity as well as conductivity fatigue. Before going into industry, their adhesion strength and current-carrying-capability also need to be improved. The objective of this research is to study the mechanisms of using both sintering and surfactants in order to investigate their uses in ECAs.

Experimental: Samples of nano-ECAs were prepared using an epoxy resin consisting of bisphenol-A, hardener, and a catalyst. Silver flakes and silver nano-particles were used as conductive fillers. The total percentage of silver in the mixture was 80% weight.

The samples were cured at 150°C for one hour and then annealed to 180°C for 10-min, 30-min, 60-min respectively, or even further annealed at 200°C for 60-min. Bulk resistivity and contact resistance were measured according to previous methods.1, 2

Results and Discussion: The bulk resistivity of nano-ECAs is shown in Fig. 1. The bulk resistivity decreases dramatically after annealing at 180°C for 10 minutes. The cross-sections of nano-ECAs were shown in Fig. 2. Annealing at 180°C for longer time (30 minutes and 60 minutes) can further reduce the resistivity.

This proves that sintering can occur in short periods of time, thus annealing silver nano-particles and reducing surface contact points. Further annealing at 200°C does not increase the conductivity much.

Figure 1. Bulk resistivity for different curing processes

Figure 2. SEM images of cross-section of nano-ECAs (a) cured at 150°C for 60-min (b) annealed at 180°C for 10-min.

The contact resistance of nano-ECA with acid is lower than that without acid and both show stable contact resistance on gold during 85°C and 85% relative humidity (RH) aging for about 600 hours (Fig. 3).

Conclusions: With introduction of sintering of silver nanoparticles, the electrical properties of ECA can be significantly improved. Moreover, the formulated nano-ECA showed stable contact resistance on Au. The superior electrical conductivity of nano-ECAs will enable the application of nano-ECAs in fine pitch and high performance interconnects in microelectronics.

Acknowledgements: I would like to thank Dr. C. P. Wong for allowing me to use space in his lab and for providing me this experience; Rongwei Zhang for spending time teaching me and being a superb mentor; my program coordinators Drs. Thadini, Gokhale, Summers, and Milam; Ms. White for her assistance; and my program sponsors: the National Science Foundation and Georgia Institute of Technology.

References
Nanomaterials for Carbon Monofluoride (Li/CFx) Primary Batteries
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Faculty Advisor: Gleb Yushin                     Mentor: Alexandre Magasinski

Introduction:
Primary batteries cannot be recharged after use. Their high energy to mass ratio makes them favorable for applications in aerospace, military, and aviation. Batteries are constructed of two main parts: an anode and a cathode. During discharge, electrons flow from the anode, through the device being powered, and to the cathode. Lithium, having a high energy to mass ratio, has been the anode material of choice, but problems have been encountered finding a cathode material that has a high energy to mass ratio.

Carbon monofluoride, CFx, has the highest theoretical specific capacity of any cathode material, 864 mAh/g. The difficulty with using CFx is that the material is an electronic insulator, and thus is unable to discharge fully at high discharge rates. Recent advances in production technique allow for CFx powders to be produced on the nano-scale with increased surface activity. This study aims to use chemical vapor deposition (CVD) techniques to coat CFx particles with a conductive, carbon layer (Figure 1) that will increase electronic properties on the surface of the particles. The effects of the carbon coatings and reduction in particle size will be compared to increases in performance.

Results and Discussion:
When batteries made with standard micron grade CFx were discharged at rates varying between, a direct correlation between discharge rate and specific capacity was observed. The use of CVD carbon on the samples was found to increase the capacity at higher discharge rates. It is believed that deposited carbon adhered to the surfaces of the CFx particles and effectively increased the conductivity of the particles. Because the rate of reaction, and ultimately the capacity of the battery, is dependant on the ability of the particles to react with the surroundings, the carbon acted to enhance the kinetics around the particle. Similarly, when 2065 CFx with a carbon coating was tested, the specific capacity was higher than that of CFx.

![Specific Capacity vs Discharge Rate](image)

The size of the powder also played a role in the overall specific capacity of the batteries, especially at elevated discharge rates. When discharged at an elevated rate, batteries made from 2065 grade CFx performed 39% longer than the 1000 grade equivalent. When coated with carbon, both of the samples increased in specific capacity, but the 2065 grade discharged with a 29% higher specific capacity than the 1000 grade equivalent (Figure 2). It is understood that the higher surface area of the 2065 grade powder may have allowed for better interactions with the surrounding electrolyte. Because the electronically insulating CFx may have hindered interactions of atoms at some parts of the particles, slower discharge rates would be required to obtain similar results for 1000 and 2065 grade powders, as was the result.

Conclusions:
The decomposition of acetonitrile was used to deposit carbon coatings on the surface of CFx particles. Increased specific capacity was measured for carbon coated samples of both 1000 and 2065 grade powders, especially at higher discharge rates. Particle size was also measured to have an inverse affect on the specific capacity.

Experimental Procedure:
Carbon was deposited on CFx powder through a decomposition of acetonitrile. Argon gas was bubbled through a tube containing acetonitrile, carrying the vapors to a decomposition chamber. The decomposition product continued to a deposition chamber, where it was deposited on CFx powders. Temperatures of the decomposition and deposition chambers were varied, as well as the length of time that acetonitrile was deposited. Cathodes were tape cast on 17 micrometer, conductively coated copper foil, and used 5 wt% KF Polymer binder. Standard 2016 button-cell batteries were pressed, and the samples were tested at a variety of discharge rates. Micron-scale 1000 grade and nano-scale 2065 grade CFx powders were used.
Introduction

Ferroelectric crystals are able to exhibit a spontaneous dielectric polarization switchable among multiple directions through the application of an electric field. This, in turn, results in the formation of a hysteresis loop comparing dielectric polarization versus electric field. This hysteretic effect can be utilized for memory functions, such as ferroelectric RAM, by switching between different polarized states. In addition, all ferroelectrics exhibit piezoelectric and pyroelectric properties. The former of these is the ability of the crystal to generate an electric potential in response to a mechanical stress, or change shape due to the presence of an electric field. Pyroelectricity is the ability of the crystal to modify its spontaneous dielectric dipole in response to a changing temperature. Both of these properties make ferroelectrics essential for ultrasounds, infrared cameras, and a multitude of other microelectronic applications.

Many of these applications require accurate, reliable ferroelectric properties. This can be difficult to achieve during production as the ferroelectric effect depends on the orientation of the unit cells within the crystalline lattice (anisotropy). Defects can also affect movement of the domain walls within the crystal. These, in turn, affect the polarization magnitude under an applied electric field. Lead Zirconium Titanate (PZT) exhibits a very large dielectric constant near its morphotropic phase boundary giving it excellent ferroelectric properties. For this reason, it is the ferroelectric ceramic of choice for many applications, hence its selection for this work. The objective of the research is to develop and analyze ceramic thin films of PZT 52/48. A spin coater was used to spin the PZT sol-gel precursor on the substrate. After each deposition, the sample was heat treated on a hot plate at 350 °C for one minute. Upon completion of each set of two layers, the sample was inserted into a Rapid Thermal Processing Unit (RTPU) which used halogen lights to crystallize the deposited PZT at 700 °C. Rapidly approaching this temperature sought to minimize the presence of the undesired non-ferroelectric pyrochlore phase while enhancing the presence of the ferroelectrically-active perovskite phase. Crystals with 2, 4, 6, 8 and 10 layers were created and then analyzed using an X'Pert Pro Alpha-1 x-ray diffraction machine. This unit tilted the crystals while bombarding them with alpha particles in a Θ-2Θ scan mode, measuring the diffraction pattern for range of 2θ between 20° and 60°, allowing identification of the crystallographic phase and prevalent crystallographic orientation.

Results and Discussion

Based on data from the x-ray diffraction, it can be seen that crystals deposited with 2, 4, 6, 8 and 10 layers of PZT exhibited intensity peaks at the same 2θ angles despite having differences in thickness. From this, it can be deduced that the average response of the films will not be affected by the anisotropy of the PZT crystal itself, as the average orientation of the films is invariant for the range of thicknesses studied.

Unfortunately, during the course of the research the equipment necessary for analyzing the electrical characteristics of the ferroelectrics became damaged and unusable. Because of this, the P-E hysteresis loop is available only for the 10-layer thick films.

Conclusion

The data from the x-ray diffraction is promising but remains inconclusive. It appears that the crystalline structures were consistent samples of increasing thickness. This research will be continued over the course of the next year. Future research plans include measurement of dielectric polarization versus electric field hysteresis loops, capacitance-electric field, and capacitance versus AC field frequency in order to determine how thickness can affect these properties. Another thrust will be made for deposition of these ferroelectric films on magnetically active substrate (modified GaN and GaAs) in order to create artificial/composite multiferroic materials.
Nanof-Sized Light Emitters for Gamma Ray Detectors

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Advisors: Dr. Chris Summers, Dr. Brent Wagner, and Dr. Zhitaok Kang

Introduction

Scintillators, materials that absorb and reemit photons, are used in radiation detectors to transform high energy radiation into low energy rays.

Current materials for this application are expensive and inefficient. Germanium has good properties at extremely low temperatures. Sodium iodide works at ambient temperatures, but large defect-free crystals must be made, and it is susceptible to water.

Composites, particularly quantum dots (QD) in transparent matrices, offer a potential alternative. Particles smaller than 10 to 20 nanometers undergo a quantum effect that permits scintillation. Their emission and absorption frequencies can be tuned by controlling their size, making them versatile.

Several criteria must be met by the components of such a composite. The QD's should not absorb the light that they produce, and they should contain heavy atoms to stop gamma rays. A high concentration is also desired. The matrix is ideally transparent to the incoming radiation and the scintillation light.

The objective of the present study is to synthesize and purify CdTe QD's, and then introduce them into a methyl methacrylate (MMA) matrix. The effects of synthesis parameters will be studied, and the preparation method will be improved to make it practical to use in future studies. The synthesis will be verified using optical studies. The reliability of computer simulations of a sodium iodide detector will be tested.

Experimental Procedure

CdTe QD's are synthesized by combining two precursors [1]. The tellurium precursor is made by reacting sodium borohydride, tellurium powder, and water in a nitrogen atmosphere. The cadmium precursor is made by mixing cadmium perchlorate with mercaptopropionic acid and then raising its pH. The precursors are mixed in an inert atmosphere and then heated. The amount of heating controls the growth of the nanoparticles.

To purify QD's, propanol is added to the solution, and then it is centrifuged, decanted, and dried with nitrogen.

To polymerize QD's, a surfactant is diluted in MMA or styrene. This is mixed with a water solution of QD's. Upon separation, the monomer retains the QD's. An initiator is used to cure using heat.

Optical testing consists of absorption and photoluminescence measurements performed on different spectrometers.

Simulation Procedure

The simulation is done in Monte Carlo N-Particle Transport Code (MCNP). A cylindrical model of a sodium iodide detector is specified. To analyze the accuracy of the simulation, the counts under the simulated deposition peaks are compared to experimental data. The experimental counts are measured using a mixed source of americium 241, cesium 137, and cobalt 60. Each of these sources is simulated independently.

Results

Lead and mercury were substituted for tellurium in this procedure without alteration, but synthesis failed. The amount of surfactant needed was tested. This amount varied with the ratio of quantum dot solution to polymer amount, but did not vary with the concentration of QD's. It was also found

References

that the optimal temperature to polymerize MMA is lower than for styrene.

The absorption and emission spectrum shifted to larger wavelengths in solutions that were heated for longer times. However, the trend is difficult to observe in small time differences. Figure 1 shows this shift for three samples that were heated for different times.

![Figure 1: Absorption and emission of 2, 6, and 23 hour samples of CdTe quantum dot water solutions before purifying.](image)

The results of the computer simulation are summarized in Table 1. Note that there are two peaks for cobalt 60.

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<th>Material</th>
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<th>Simulation Count</th>
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Discussion

As Figure 1 shows, the frequency shifts are not obvious for short heating time differences because the heating temperature and rate were not well controlled. In other samples, not shown, higher times did not necessarily imply longer wavelengths. However, the trend is evident between longer time intervals, showing that QDs were effectively synthesized, and that the frequencies shift with heating time.

The size of QDs can be calculated from their absorption peaks [2]. The samples shown in Figure 1 correspond to 18, 26, and 35 nanometers, in order of increasing time.

The procedure used to prepare CdTe QDs was improved by reducing the number of steps required and by finding alternative methods to reduce the time needed to prepare a batch. This allows for a higher reproducibility of experiments as well as more productivity.

The ratios between simulation and experimental values are within one order of magnitude, which is an acceptable starting point. The code overestimates counts because it does not take into account all the mechanisms occurring during scintillation. Adjustments to the code will have to be made in the future to keep this discrepancy low.

Conclusion

QDs offer a versatile and viable alternative for radiation detectors. Their preparation is well controlled and understood. Work is needed in order to implement computer simulations.

The prepared samples need to be tested under gamma radiation instead of low energy light. Other quantum dot materials, matrices, and glass ceramics remain to be studied.

References

Optical Properties of Thiophene Membranes in Differing pH Values
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Mentor: Veronika Kozlovskaya

Introduction
The sodium poly[2-(3-thienyl)ethyloxy-4-butylsulfonate] polymer (PTH) is a unique polymer with pH-dependent optical properties. When in an aqueous solution, in basic conditions such as at pH > 7, it is reddish and has a pronounced absorption peak at ~ 430 nm. While in acidic conditions of pH 2, it becomes dark green with the additional absorption maximum at 780 nm. Layer-by-layer (LbL) deposition of polymers at surfaces is a versatile way to create ultrathin polymer membranes with controlled properties. Layers of a polyanion and a polycation can be stepwise deposited onto a surface through a spin-assisted (SA) self-assembly producing robust LbL films. SA-LbL deposition enables the experimenter to easily vary thickness and thus some properties of the membrane by varying the number of the deposited layers.

The optical properties of PTH (color, photoluminescence) are clearly pH-dependent when in aqueous solution, but it has not been shown that PTH-containing membranes react similarly. This experiment aims to create robust PTH membranes with tunable optical properties by self-assembly of PTH with 20%-quaternized poly(4-vinylpyridine) (Q20), poly(dimethyldiallylamino hydrochloride) (PDDA), branched poly(ethyleneimine) (PEI), or poly(allylamine hydrochloride)(PAH) polycations.

Procedure
PTH and the four polycations were dissolved in 0.01 M TRIS buffer and then adjusted to necessary pH with HCl and NaOH. Clean silica wafers or clean quartz slides were then put into a spin-coater and alternating layers of thiophene and polycation were deposited by spinning at 4,000 RPM up to a total of 20 bilayers. Two washes of 0.01 M TRIS buffer at the same pH were done in between each layer to remove excess of polymers. If systems would not adhere well at a certain pH, 3 bilayers of 0.2% PAH and 0.2% PSS were deposited first. During later experiments, spacer layers of PAH/PSS were deposited in between thiophene and polycation layers to ensure the polymer was not self-quenching.

The optical thickness of the films on silica wafers was determined with a spectroscopic ellipsometer. Optical properties were studied using a UV-Vis spectrophotometer or a spectrofluorophotometer.

Results and Discussion
Due to its sulfonate groups, PTH can electrostatically self-assemble with the polycations. This allows for creating thin PTH membranes. First, growth of PTH films at different pHs was examined to determine the effect of the deposition pH on the thickness and robustness of the films. Q20 and PDDA membranes grew at pH 7.5, 4, and 2.5, while PEI only adhered at 7.5 and 4. PAH was the least robust by only adhering at 7.5. Q20 membranes were typically the thickest, followed by PEI and PDDA membranes (Figure 1). Lower pH at the time of deposition generally caused slightly lower membrane thickness (approximately 10%). Using pre-layers of PAH/PSS encouraged greater membrane thickness.

Conclusion
We have shown that robust PTH/polycation LbL membranes can be grown. Absorbance maxima of the produced films depend mostly on the polycation nature. The right combination of polycation, deposition pH, and pre-bilayers or spacer layers needs to be found to ensure strong and steady optical changes with full reversibility.
INTRODUCTION
Cancer is a complicated and prevalent disease. New drug delivery systems have been researched to target and treat cancer effectively. Current research aims at creating a multifunctional therapeutic unit with an intrinsic release mechanism for drug delivery. This study focuses on a model drug delivery vehicle using DNA as a biomaterials assembly tool. Therapeutic colloidosome assembly and disassembly is DNA-mediated. The challenge with using DNA as a biomaterials assembly tool is protecting DNA assemblies from biological nucleases aimed at clipping foreign DNA. DNA may be protected by steric hindrance if immobilized to a surface. The objective of this study is to investigate protecting surface-bound single-stranded DNA (ssDNA) from enzymatic degradation. Changing the DNA density allows us to observe the effects of DNA density on the ability of enzyme DNAsI to cleave surface immobilized strands. Greater DNA surface density causes an increase in steric hindrance, which creates little free volume for enzyme activity.

PROCEDURE
Fluorescently labeled ssDNA were attached to 1μm polystyrene microspheres using EDAC coupling. Polystyrene beads were incubated at room temperature with FITC labeled A20-NH₃ DNA and coupling agent, EDAC for two hours. Coupled beads were washed after two hours 3 times in 0.02% PBS/Tween. DNAsI was used to digest coupled beads. Coupled beads were washed in 60μL NE DNAsI Buffer and incubated with 0.2μL DNAsI at 37°C for up to 24 hours. Flow cytometry was used to detect fluorescently labeled DNA strands on particle surfaces before and after enzymatic processing. Fluorescence intensity was calibrated using a MESF standard curve.

RESULTS AND DISCUSSION
Enzymatic processing using DNAsI on ssDNA (Fig. 1) revealed 71.17%, 66.24%, and 63.26% immobilized ssDNA remains after enzymatic exposure of 10 minutes, 1 hour, and 24 hours.

**Figure 1. DNAsI Digest on FITC Probes at varied EDAC.** Fluorescently labeled ssDNA at varied surface densities were exposed to enzyme DNAsI for 10 minutes, 1 hour, and 24 hours. Values were averaged from four trials.

Optimal DNA density was also researched. Polystyrene microspheres were coupled with 5μL, 10μL, 25μL 50μL 100μL EDAC to vary DNA density. Surface densities were measured in oligonucleotides/μm². Results show maximum surface densities at 25μL EDAC, after which surface densities plateaued between 25-50μL EDAC. Compared to results at 25μL and 50μL EDAC, surface densities were slightly lower at 100μL EDAC. This observation may be attributed to fluorescence quenching and requires ongoing investigation.

CONCLUSION
DNAsI digests on ssDNA show 63.26% immobilized strands remain after 24 hour exposure, with majority of cleavage occurring in the first 10 minutes of exposure. Further cleavage is not significant over prolonged periods of time. Surface-immobilized ssDNA may be protected from enzymatic degradation. This shows great promise for using DNA as a biomaterials assembly tool. Future research may investigate using ssDNA tails to protect primary probe sequences from being cleaved by enzymes.
**Introduction:** The focus of the research was to determine the potential benefits in material properties that a poly (para-phenylene) polymer nanocomposite could offer. Single-walled (SWCNT) and multi-walled (MWCNT) carbon nanotubes as well as carbon nanofibers (CNF) have been widely employed as reinforcing agents in polymer matrices with the goal of improving mechanical and thermal properties. It was hypothesized that such modifications to poly (para-phenylene) could yield a nanocomposite with similar enhancements.

SWCNT, MWCNT (Swan Chemicals), and CNF (Pyrograf Products) were used to create the fiber network within the polymer matrix. For the polymer matrix, a thermoplastic resin known commercially as PrimoSpire-250 was chosen based on its strength due to the poly (para-phenylene) molecular structure.

**Experimental:** Polymer batches consisting of 0 (neat), 0.5, 1, and 3 wt% of each nanofiller were melt mixed in a Brabender Intellig-Torque Plasti-Corder batch mixer equipped with roller blades. It was estimated that the shear force obtained from using a melt mixer would be sufficient to disperse the fillers. Processing parameters for a 45 gram batch sample was 260°C, 40 rpm, and a run time of 8 minutes. Each batch was mixed in a nitrogen environment to prevent degradation.

A loading technique was developed to reduce torque loads experienced by the machine. 25 grams of PrimoSpire were loaded initially followed by 10 grams of resin and an appropriate amount of nanotubes at the 70 second mark. The rest of the resin was added to the mixer at the 120 second mark. Samples were then dried at 180°C for two hours before compression molded into sheets at 290°C and 7 tons. Tensile test samples were die cut at 182°C and tested according to ASTM D368 standards on an Instron (model 5566). Tensile modulus was calculated based on the initial slope of a stress-strain diagram, and the strength was calculated at the fracture load. Scanning electron microscopy (SEM) was used to view fracture surfaces. Thermal gravimetric analysis (TGA) was performed on a TA Instruments TGA Q 5000 at 10°C/min from 40°C to 700°C in nitrogen (25mL/min) to determine thermal stability.

**Results:** Table 1 shows that at 1 wt% concentration, PrimoSpire/CNF demonstrates an increase in toughness and yield strain while the nanotube composites experienced either a slight decrease or statistically insignificant change in mechanical properties. MWCNT nanocomposite properties at other concentrations (data not shown) also displayed negligible changes.

**Conclusions:** The brief mechanical behavior characterization, accompanied by thermal analysis and SEM imaging, provided insight to some of PrimoSpire nanocomposite’s tendencies. The method of melt mixing poly (para-phenylene) to create nanocomposites proved to be ineffective at the given parameters. Batch mixing proved unsuccessful as a means to disperse the SWCNT and MWCNT throughout the matrix at all levels of concentration as evident from the SEM images. Agglomerates of fillers could potentially act as defects in the material and thus weaken the matrix integrity by the decreasing material properties as shown in Table 1.

Although melt mixing was suitable for dispersing CNFs, a CNF pullout was present. Pullout could be minimized with better adhesion of the CNF to the polymer matrix. Since both CNF and poly (para-phenylene) possess a high degree of nonpolarity and a molecularly rigid structure, interfacial interactions is potentially minimal. Adding functional groups to both the polymer matrix and the CNF to increase the intermolecular forces could possibly increase matrix adhesion.

Increasing concentration of well-dispersed CNF yielded slight improvements in derivative thermogravimetric mass loss. This phenomenon could be explained by the presence of the CNF network acting as a barrier to lower mass flux of polymer out of the sample.

**References**
Synthesis of Alumina from Micellar Templates of Surfactants
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University of Campinas Research Advisors: Dr. W. Loh and Dr. C.A. Bertran
IREP 2008: Georgia Institute of Technology and University of Campinas, Brazil

INTRODUCTION
Surfactants, also known as surface-active agents, adsorb at surfaces and interfaces in order to lower the free energy of a phase boundary. Because of their properties, surfactants are commonly used in soaps and detergents. This property of surfactants can be explained by its amphiphilic nature. Surfactant molecules consist of a lyophilic (soluble) and lyophobic (insoluble) end. When the concentration of surfactants in a medium reaches a critical concentration, aggregates known as micelles are formed. A variety of micellar structures can be formed depending on the type of surfactant, solvent, and relative concentrations of the components in the system.

The goal of this project was to use micellar structures as a template for the synthesis of alumina. Two types of surfactant systems with different micellar structures were synthesized and tested for its compatibility as a template for alumina growth.

METHODS
The first micellar template was created using a complex salt (cetyltrimethylammonium polyacrylate) that consisted of a cationic surfactant and a polymeric counterion. The complex salt \((C_{16}TAP_{\text{A}})_{\text{knot}}\) was synthesized by first converting \(C_{16}\text{TABr}\) into \(C_{16}\text{TAOH}\) by using an ion exchange resin. The \(C_{16}\text{TAOH}\) was then titrated with a high molecular weight polycrylic acid (M.W. 450,000 g/mol) until the equivalence point was reached. Once the equivalence point was determined, an additional titration was performed and stopped at the pH that corresponded to the equivalence point. Once the system was prepared it was placed in a refrigerator to equilibrate overnight. Upon reaching equilibrium, the solution was freeze-dried.

The complex salt was then mixed in a solution with a specified concentration of butanol and water, which was known to produce a reverse worm-like micellar structure. It was proposed that an aluminum nitrate/urea solution could be introduced to the system, and due to its polar nature, it would gather inside of the worm-like channels and react to form alumina instead of mixing with the butanol. From this reaction, it was desired to retrieve long cylindrical structures of alumina after dissolving the polymer surfactant complex. Six samples were prepared with varying concentrations of an aluminum nitrate solution in order to evaluate its interactions with the system.

The second micellar template was created using a non-ionic surfactant, Renex-100. A liquid crystalline micellar template had been formed previously by mixing a solution of Renex-100, cyclohexane, and a calcium phosphate solution. In this case, the calcium phosphate solution was replaced with an aluminum nitrate solution. By mass percentage, the composition was 45.5% Renex-100, 45.5% aluminum nitrate solution and 9% cyclohexane.

RESULTS & DISCUSSION
In order to determine how the aluminum nitrate reacted with the different surfactant systems, the systems were evaluated using birefringence evaluations, small angle x-ray scattering (SAXS), x-ray diffraction (XRD) and scanning electron microscopy (SEM). Due to time constraints, the second system has only been evaluated for birefringence at this time.

Results from all techniques mentioned above confirmed that the addition of the aluminum nitrate solution destroyed the existing micellar template and produced a disorganized, amorphous structure. The samples evaluated did not exhibit birefringence (characteristic of organized structures), and presented broad, single peaks when evaluated with x-rays. SEM images also showed structures with no apparent order. These results can be explained by the strength of the interaction between the aluminum ion and the counterion of the complex salt.

An optical microscope was used to observe the second system (with Renex-100) between two crossed polarizers to determine if it maintained its liquid crystalline structure after the addition of the aluminum nitrate solution. Birefringence was observed, indicating that the order was maintained. Further analysis will be conducted using SEM and XRD to characterize the structure present.

REFERENCES

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Thank you to the MSE Department at the Georgia Institute of Technology along with support from NSF for providing me with this valuable research opportunity. I would also like to thank Dr. Loh, Dr. Bertran and the students (Ana Maria, Juliana, Stella, Dani, Tiago) in their research groups for their support.
Thermomechanical Fatigue of a Directionally Solidified Ni-Base Superalloy

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Introduction
In an effort to increase efficiency and energy output of gas turbines, there has been a push over the past several years to increase the firing temperatures. The problem is, however, that increasing the temperature also reduces the fatigue life for the turbine materials, especially for materials in the blade section where conditions are the harshest. Developing and optimizing materials which can withstand the extreme conditions has been a continuous challenge to many material engineers.

Because of its high yield strength and resistance to creep and oxidation, turbine manufacturers have been using directionally solidified nickel-base superalloys in the blade section. The objective of this research is to characterize the thermomechanical fatigue behavior of one such material, CM247LC-DS, in the presence of varying stress concentrations. This involves performing tests which mimic the thermal and mechanical stresses endured by the turbine blades. Upon conclusion of the research, fatigue life models for the material will be predicted, and manufacturers will use the data for current and future design work.

Procedure
The orientation of the specimens was either longitudinal or transverse, and the gauge section was either smooth (kt=1) or notched (kt=2). Specimens were loaded into a servo-hydraulic test frame and continuously cycled between compression and tension and between 500°C and 950°C. For in-phase (IP) tests, maximum tension corresponded to maximum temperature, and for out-of-phase (OP) tests, maximum compression corresponded to maximum temperature. The heat was provided by an induction heater whose coils were centered around the gauge section. Force was measured by the test frame and displacement by an extensometer. Specimens were cycled until failure.

Results and Discussion
Crack initiation was defined as a 5% load drop for axial displacement-controlled (DC) tests and a 10% stiffness drop for force-controlled (FC) tests, which corresponded to a crack length between 0.5 mm and 1.0 mm. The results of the tests are shown in Figure 1.

All of the smooth specimen tests were DC and OP, with failure resulting primarily from fatigue and cracking of the surface oxide layers which form at high temperatures. Stress-strain hysteresis for one of these specimens can be seen in Figure 2.

Conclusions

Notched specimens, however, were conducted in both FC and DC. For the IP FC test, creep ratcheting lead to failure by creep rupture rather than cyclic fatigue. For the notched DC IP test, notch strengthening and stress relaxation at the peak temperature caused a shift in the stress-strain curve toward the compressive direction, which also reduced the maximum tensile load and extended fatigue life. The notched OP DC data point lies very close to the OP FC curve, indicating that control mode in this case did not significantly affect the damage mechanism.

We have begun constructing stress-life curves for our material while varying load, phase, orientation, stress concentration, and control method. Further testing is needed to generate a comprehensive fatigue life prediction model.
Characterization of GaN based Semiconductors
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Faculty Advisor: Dr. Ian Ferguson     Graduate Advisor: Nola Li

Introduction
The growth and characterization of GaN based semiconductors is important to many different fields and applications. GaN is the leading semiconductor in the LED industry and plays a vital role in solid-state lighting. GaN is also widely used in solar cells which can reach upwards of 45% in efficiency. We are also looking at GaN for its possible viability as a multiferroic material suitable for use in spintronics.

New recipes and growths of GaN are being made around the clock in our lab and it is vital that these new semiconductors are characterized for all the possible properties they might have. The objective of this study was to characterize GaN based semiconductors for properties that would make them suitable for solid-state lighting, solar cells, and spintronics applications.

Procedure
Materials were analyzed using two different tests: VSM and photo luminescence. A 7400 LakeShore vibrating sample magnetometer was used to find the hysteresis of induced magnetic fields. Photo luminescent (PL) measurements were conducted using a 248nm laser, a monochromator, and a photo multiplier tube (PMT). Results for both procedures were then graphed with Origin. Tests measuring Magnetic Circular Dichroism (MCD), the Anomalous Hall Effect (AHE), and various ferroelectric properties were also planned, but unfortunately did not come together in time.

Results and Discussion
About ten samples were measured using VSM and about thirty samples were characterized using photoluminescence. Fig. 1 shows what the results of a typical photo luminescence measurement looks like. The materials characterized by the VSM didn’t show any unique properties, but there were some suitable LEDs characterized by PL. A ferroelectric tester was setup, but no tests were run with it. Parts of the MCD system were repaired, but it’s still not running. Studies were done on how to set up an AHE system, but it didn’t get put together.

Conclusion
A lot of good data on various GaN semiconductors was gained this summer in addition to setting up the PL, VSM, and ferroelectric systems that are ready to take measurements. The MCD system only needs a few more repairs. The AHE system needs to be built but there is a rough outline as to how it should be built. When all these tests are in place interesting materials can be characterized easily and efficiently.
**Introduction**

Duplex Stainless Steel is formed from two phases of iron, austenite (FCC) and ferrite (BCC), which have been treated with elements such as chromium to reduce corrosion susceptibility. Austenitic stainless steels are characteristically tough while Ferritic stainless steels are characteristically corrosion resistant. [1] In mixing the two phases, the resultant duplex stainless steel exhibits generally greater strength and corrosion resistance than single phase stainless steels.

In typical samples of the most common duplex grade, 2205, austenite and ferrite phases are distributed homogeneously at roughly equal volume fraction in the microstructure. Since the two phases will tend not to fail at equal rates, it is important to understand the corrosion susceptibility of the individual phases within the microstructure. With this knowledge, the material can then be subjected to heat treatment to influence homogeneity and volume fraction of the two phases to provide for the best possible mix of strength and corrosion resistance.

**Materials Selection and Procedure**

Samples of DSS 2205 were prepared from 1cm² squares with a thickness of approximately 2 mm. Several samples were heat-treated at 1100°C for one hour in an Argon Purged environment. All samples were polished to 0.05 micron and etched using a 40% NaOH solution. Optical microscopy at 200x showed the as-received samples to have a ferrite-austenite volume fraction of 50-50 while the heat-treated samples displayed a ferrite-austenite volume fraction of 60-40.

Samples were then subjected to a battery of potentiodynamic and cyclic polarization corrosion tests. Electrochemistry was performed using a custom made glass microcell with a 300 micron capillary tip and a Gamry potentiostat. A Ag/AgCl reference electrode with a KCl salt bridge, a Pt counter electrode, and a 3.5 wt.% NaCl aqueous test solution were used for electrochemical tests. This setup is depicted in Figure 1. Samples were mounted in bakelite with a contact wire spot welded on the surface. Random spots were chosen for comparison testing between the heat-treated and as-received samples. Three areas of high concentration of each of the two phases within the heat-treated sample were identified at 50x and marked macroscopically. These six spots were used for comparison testing between the two phases.

**Results and Discussion**

Polarization curves show heat-treated samples having generally lower corrosion potentials than as-received samples. Similarly, ferrite spots in the heat treated sample have generally lower corrosion potentials than austenite spots in the same sample. Ferrite spot locations achieved passivation at earlier voltages than austenite spot locations. The ferrite spots held to this state of passivation for longer periods of time and thus had a controlled rate of corrosion. Austenite spots tended to have a fluctuating corrosion rate, and did not show long periods of passivation. Finally, ferrite spots broke the passivation state into the transpassive state at higher voltages than the austenite spots. Figure 2 details aggregate polarization curves of the ferrite and austenite phase while Figure 3 details a micrograph of two selected spots after corrosion at 50x.

**Conclusions**

We can reasonably conclude that the ferrite phase is generally more resistant to corrosion than the austenite phase. The ferrite phase reaches equilibrium between anodic and cathodic corrosion more rapidly and maintains a controlled passivation state for a longer period of time before reaching accelerated transpassive corrosion. Similar results from comparison between the as-received sample and the heat-treated sample are obtained since the heat-treated sample displays a greater volume fraction of ferrite. Future work can be done to make comparisons of other properties, such as toughness, with respect to ferrite percentage. In addition it may be possible to anneal samples in such a way so as to isolate austenite phases so that failure of the austenite phase due to corrosion does not result in failure of the whole microstructure. [2]

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**References**
