### 2010 NUE Summer Research Participants:

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<thead>
<tr>
<th>Student</th>
<th>Yr.</th>
<th>Professor</th>
</tr>
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<tbody>
<tr>
<td>Matt Oleksiak (Chemical Engineering)</td>
<td>Sr.</td>
<td>I Shah (Materials Sci. &amp; Engineering)</td>
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<tr>
<td>Evan Sinicin (Physics)</td>
<td>So.</td>
<td>M Doty (Physics)</td>
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<tr>
<td>Thomas Christini (Chemical Engineering)</td>
<td>So</td>
<td>J Zide (Materials Sci. &amp; Engineering)</td>
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<tr>
<td>Phil Guerieri (Mechanical engineering)</td>
<td>So</td>
<td>V Roy (Mechanical Engineering)</td>
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<tr>
<td>Peter Fenimore (Mechanical engineering)</td>
<td>So</td>
<td>A Prasad (Mechanical Engineering)</td>
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<tr>
<td>Lisa Thomanek (Chemical Engineering)</td>
<td>So</td>
<td>J Chen (Chemical Engineering)</td>
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<tr>
<td>Ivor Fazlic (Electrical Engineering)</td>
<td>So</td>
<td>J Kolodzey (Electrical Engineering)</td>
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<tr>
<td>Teodor Stanev (Physics)</td>
<td>Jr</td>
<td>B Walker (Physics)</td>
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</table>

T Powers (Philosophy)
M Mackay (Materials Sci. & Engineering)
L1₀ Phase FePt Nanoparticles Synthesis and Characterization:

Matt Oleksiak is working on synthesizing iron platinum (FePt) nanoparticles as part of a multilayer structure with boron nitride (BN) through sputtering. The goal of this synthesis is to create FePt particles in the L1₀ phase to obtain a high magnetic anisotropy. This allows for hard magnetic particles that can have a magnetic moment that will not be affected by ambient thermal energy. In order to obtain this structure a series of layers are deposited separately to form this structure, as seen in Figure 1.

Figure 1. SEM of FePt/BN multilayers

With this multilayer structure confirmed, samples have been annealed and vibrating sample magnetometry (VSM) has been performed to measure the saturation magnetization and the
coercivity of the sample. The L1$_0$ ordered phase should exhibit a broad hysteresis loop, therefore high coercivity, however this is not observed in the VSM data shown in Figure 2.

![Graph showing hysteresis loop](image)

**Figure 2.** VSM data for FePt/BN multilayer annealed at 1000 °C for 1 hour

As seen above the coercivity is not high enough to suggest that the L1$_0$ phase has been obtained, especially after annealing at 1000 °C for 1 hour. Work is being done to correct the composition issues and then continue characterization studies.
NUE Project 2:

Student: Evan Sinicin Physics
Faculty: M Doty Physics

**Time Dependent Photoluminescence Study of Quantum Dot Interactions:**

Funding through the Nanoscale Undergraduate Engineering at the University of Delaware has provided me with the opportunity to engage in exciting, new, and important research on the nanoscale level. Under the supervision of Dr. Shah, and Dr. Doty of the Materials Science Department my project consists of exploring the fundamental interactions of Quantum Dots, an area of research pursued passionately by researchers world-wide. During the summer months, I was taught the current paradigm of quantum dot interactions and was guided towards exploring the current hypothesis on the distance dependence of these interactions. I have constructed a device that can accurately stretch a substrate upon which quantum dots are deposited. This stretching combined with timed Photoluminescence measurements can help us derive a coherent model of distance dependent interactions, and lead us in the direction of optimizing quantum dot performance in various applications.

![Figure 1: Time dependent photoluminescence data](image)

\( R^2 \text{ (red)} = 0.965 \)
Growth and characterization of novel thin-film semiconductor and thermodynamic properties of nanostructures:

My research has consisted of the growth and characterization of novel thin-film semiconductors, including InGaAs and InGaBiAs. Unfortunately, due to malfunctions in our Molecular Beam Epitaxy (MBE) growth chamber, we have not grown any samples other than calibration samples. The machine is currently being repaired. I have gone through cleanroom training and have been helping to repair the MBE. It should be operational again within the coming weeks. However, despite the MBE setbacks, I have been constructing a Photoluminescence Table that will be used to measure the optical properties of the samples that we will grow. I have learned a great deal about optics during the building and aligning process. We also use the Hall Effect to measure the carrier concentration and mobility of the samples.

The most recent development in the research is a new paper we are writing to be titled A Basic Thermodynamic Model for the Doping and Alloying of Nanoparticles. The paper deals with the thermodynamic limits that arise when trying to dope smaller and smaller nanoparticles (on the order of a cube with 5-100 atoms per side). We have found through mathematical models involving Gibbs free energy that for large values of \( \frac{\Delta U}{k_B T} \), where \( \Delta U \) is the difference in bond energy between the host and dopant atoms, that the maximum attainable doping concentration decreases with decreasing particle size. However, when we consider small values of \( \frac{\Delta U}{k_B T} \), which describe systems that involve allying, rather than doping, the maximum attainable concentration increases as particle size decreases. We also found, using simple thermodynamic principles, that doping tends to occur at the face of the particle for small particles, and in the bulk for larger particles. We hope to publish our paper in either NanoLetters or Applied Physics Letters.
Figure 1: In this graph, the dashed lines represent the effect on $\Delta G$ of the incorporation of dopant atoms on the face, and solid lines represent incorporation in the bulk. The different colors represent different values of the quantity $\frac{\Delta U}{k_B T}$. 
Optimization and Reliability Studies of PEMFC Electrodes

The long-term goal of this project is to exploit the unique characteristic advantages of nano-structures (particularly Carbon Nanotubes) in order to improve conventionally-made membrane electrode assemblies (MEAs) by optimizing apparent performance and durability. The conventional MEAs use vulcan Carbon Black with pre-deposited platinum catalyst mixed with an Ionomer and painted on Carbon paper. Such a method results in a random network comprised of Carbon, Platinum, Ionomer, and voids which succeeds in facilitating the anodic and cathodic reactions required for an effective PEMFC at three-phase interface sites that gases can reach through the voids. However, the random nature of this configuration limits the electrochemically active surface area (ECSA) within the electrodes, effectively wasting significant amounts of Platinum catalyst which lies inactive in many sites that can not facilitate a reaction as well as limiting the performance of the electrode. One possible solution is using a more organized carbon substrate like a CNT network and applying the Platinum catalyst in a controlled fashion using electrodeposition. This method can optimize the ECSA, increase the proportion of active catalyst to applied catalyst, and improve the overall performance of the cell.

Before the effects of nano-structures in the electrodes can be tested, it is necessary to establish a control by testing MEAs constructed conventionally and to standardize various testing protocols to be used. This also gives the researchers a chance to learn the skills required to construct, test, and analyze MEAs. This is the phase of the project taking place this summer.

In June work started on constructing the conventional MEAs. A procedure was developed to mix the Catalyst ink comprised of vulcan carbon black (already impregnated with Platinum catalyst) and Nafion Ionomer in Isopropyl Alcohol. Subsequently the ink is carefully painted on Carbon paper to distribute the catalyst-ionomer mixture. Allowed to dry, this forms one electrode of the MEA. At this point, the researchers took this opportunity to study the effect of the Platinum catalyst loading on the performance of the electrodes. Since multiple MEAs were to be constructed to effectively develop and learn the procedure, the loadings on each were varied. Finally, the last construction procedure is developed to assemble the full MEAs by heat-pressing a proton exchange membrane sandwiched by two inward facing electrodes. Each MEA is lastly conditioned at different applied voltages in a test rig.

Various tests are to be developed and used to study the performance and reliability of the MEAs constructed. The first was the polarization test which simply runs each cell at certain conditions and records the current resulting from particular voltages over a certain range. The results of this test are shown below.
The conclusion can be drawn that low catalyst loadings on the anode have little effect on performance while the same low loadings on the cathode significantly hinder cell performance. This is interesting because it shows that less (expensive) Platinum catalyst can be used on the anode however adequate loadings are required on the cathode. Also note that loadings can be too high in the cathode as well, reducing the amount of void in the electrode resulting in a cathode flooding and a current drop-off.

Currently, researchers have developed a method of testing the impedance of the cells using potentiostatic electrochemical impedance spectroscopy (EIS) in an in-situ setup; however, tests will not be completed until August 5. Procedures to perform cyclic voltammetry to gain insight into the reliably of the MEAs has been drafted and will be finalized at the commencement of testing in the second week of August. Scanning electron microscopy is the final test researchers intend to perform by the end of August, time permitting. These tests together will provide valuable data on the efficiency and durability of the conventional MEAs but furthermore, they represent standardized testing procedures developed specifically for this long-term project.

In the future, researchers will be working with CNTs to replace the vulcan carbon black as the electron transport network in the electrodes. Protocols for using such materials as well as using electrodeposition to apply Platinum catalyst will need to be developed and practiced before the tests developed this summer can be used to quantify and study any change in performance and reliability. A drastic improvement in both would signify a major step towards a more cost-effective and viable PEMFC.
NUE Project 5:
Student: Lisa Thomanek (Chemical Engineering)  Faculty: J Chen (Chemical Engineering)

Using Density Functional Theory to Calculate binding energies of atomic systems on nanoparticle scale

Throughout the course of the summer, density functional theory (DFT) is used to help examine the binding energies of atomic systems on the nanoparticle scale. For the purpose of this investigation, DFT is, in brief, a quantum mechanical application utilized to investigate the electronic structures of bimetallic surfaces by looking closely at the nanoparticles of a given surface. DFT is a powerful theory that can help to reveal periodic trends in the binding energies of the bimetallic surfaces studied herein. This study has concentrated on many 4-d elements (Ag, Pd, Rh, Ru, Tc, Mo, and Nb), as well as two 3-d elements, Co and Cu, using platinum as the second metallic particle. The p4vasp program helps to illustrate the binding energies of a single bimetallic surface for each of the four configuration sites: atop, bridge, fcc, and hcp. Examinations of all four sites then reveal the most stable configuration site where a nitrogen atom is likely to bind onto a particular surface.

Using the p4vasp program, numerous calculations were compiled in order to determine each bimetallic surface’s highest binding energy, and determining in which configuration site this occurs. Each of the elements studied were examined on a surface and sub-surface interface, imitating a bimetallic surface and using platinum as the second metallic element of the system. The bimetallic surfaces were then initially run in p4vasp to obtain optimal binding energies for each of the slabs. A single nitrogen atom was then added to each surface in four different configuration sites: atop, bridge, fcc, and hcp. For example, for the bimetallic surface Rh-Pt-Pt (111), the surface before any nitrogen atom is illustrated in Figure 1. Figure 2 illustrates configuration site of the optimal binding energy for the Rh-Pt-Pt (111) bimetallic surface.
Calculations were run again using p4vasp. A comparison of the results for all four configuration sites yielded the optimal binding energy required to bond a nitrogen atom to a given bimetallic surface, and in which configuration site such bonding is expected to occur. For the Rh-Pt-Pt (111) surface, Figure 2 shows the optimal binding energy was determined as the hcp site. A summary of the results for the bimetallic surfaces were then compiled, found in Table 1, indicating which configuration site was most stable for each of the bimetallic surfaces, for both the surface and sub-surface interfaces.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Configuration Site</th>
<th>Binding Energy (Kcal/mol)</th>
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</thead>
<tbody>
<tr>
<td>Co-Pt-Pt</td>
<td>hcp</td>
<td>-127.5026</td>
</tr>
<tr>
<td>Pt-Co-Pt</td>
<td>hcp</td>
<td>-83.6860</td>
</tr>
<tr>
<td>Cu-Pt-Pt</td>
<td>fcc</td>
<td>-86.5525</td>
</tr>
<tr>
<td>Pt-Cu-Pt</td>
<td>hcp</td>
<td>-93.1493</td>
</tr>
<tr>
<td>Rh-Pt-Pt</td>
<td>hcp</td>
<td>-127.8234</td>
</tr>
<tr>
<td>Ru-Pt-Pt</td>
<td>hcp</td>
<td>-147.9017</td>
</tr>
<tr>
<td>Tc-Pt-Pt</td>
<td>hcp</td>
<td>-160.0123</td>
</tr>
<tr>
<td>Pt-Tc-Pt</td>
<td>hcp</td>
<td>-90.3569</td>
</tr>
<tr>
<td>Mo-Pt-Pt</td>
<td>hcp</td>
<td>-160.8357</td>
</tr>
<tr>
<td>Nb-Pt-Pt</td>
<td>hcp</td>
<td>-166.3053</td>
</tr>
<tr>
<td>Pt-Nb-Pt</td>
<td>hcp</td>
<td>-74.9198</td>
</tr>
</tbody>
</table>

Table 1: Summary of results for each of the bimetallic surfaces studied gathered thus far.
While Table 1 cannot give any indication of a periodic trend in binding energies, future work expects to calculate the d-band centers for all of these bimetallic surfaces. A plot could then be constructed to examine binding energy trends for these elements. Furthermore, binding energy calculations for the 5-d elements should be examined, and d-band center calculations should be completed as well. This data can then be added to the aforementioned plot to give a more comprehensive understanding of periodic trends in bimetallic surface binding energies.
NUE Project 5:

Student: Ivor Fazlik (Electrical Engineering)  Faculty: James Kolodzey

Developing Lab modules for the NUE program for Nanostructure Characterizations

During the summer of 2010 I have been working under Dr. Kolodzey in accordance with Dr. Shah. Through the NUE program funded by NSF I was encouraged to participate in some hands-on lab or research work that would tie in with the ever increasing popularity of nanotechnology. Thus far in the program there have been two real foci as to what kind of work I've been doing.

The first task I have done is the creation of various Nanotech Lab Modules to be used in a future lab course on nanomaterials at the University of Delaware. The labs will feature the characterization of samples such as fullerenes, polystyrene, and magnetite using instruments such as SEM, TEM, DLS and SLS. Aside from these more nano-focused lab modules there are also more basic modules that tend themselves towards EE a bit more. It is not yet clear which of these will be used in the actual course. The course may be a one or three credit course.

The second aspect of my work has been in regards to the setup and logistics of the CVD system. The CVD or Chemical Vapor Deposition system should soon be online thanks to various tasks that needed to be done. As of this moment, we have ran hydrogen through the system to test pressures and baked-out the system to remove moisture. In addition various logistical tasks have been done such as learning of the control software by myself for future endeavors and construction of piping diagrams of the various gas lines. These vital diagrams will aid other users of the system in its operation. The system should be ready to grow samples to investigate new alloys of silicon, tin, carbon, and germanium very soon. We hope that once the system is up and running it will offer a good alternative to the MBE or Molecular Beam Epitaxy currently being used by Dr. Kolodzey's team to grow the needed samples.
NUE Project 6:
Student: Teodor Stanev (Physics) Faculty: B Walker (Physics)

**Thermal Conductivity Measurement of Nanocomposites by Picosecond Thermoreflectance Technique**

For thermoelectrics, one of the most important measurements is the thermal conductivity measurement as a function of temperature. Even though we have a setup which allows us to measure the thermal conductivity at temperatures up to 75°C, the reproducibility of this method is of concern. Under the ances of Barry Walker in the Physics Department we are putting together a thermal conductivity measurement system using picosecond thermoreflectance technique. In this method, thin films deposited on transparent substrates are characterized for their thermal conductivity using the picosecond thermoreflectance method under the rear heating-front detection configuration. The Figure 1 shows the setup for the experiments.

![Picosecond thermoreflectance measurement setup](image)

**Fig. 1:** Picosecond thermoreflectance measurement setup.

In this setup a Ti/Sapphire laser is used with 76 MHz repetition rate and the wavelength is 776 nm. The spot diameter of heating beam is 50 μm. The average pulse energy is 0.4 nJ/pulse. The pulse beam is split by a polarizing beam splitter cube with 90% pulse beam heating the sample surface and 10% of the probe beam detecting the reflectance change on the back of the surface as...
the film temperature changes due to laser heating. Both beams are configured to be on the same spot on the specimen and confirmed by charge coupled device camera’s. The configuration of the beams allows the reflectance signal from the probe beam to be detected by the photodiode at different delay times. The reflectance values are fitted with by $\gamma$ and $\tau_i$ and $\tau_f$ parameters which are multiplication coefficient of the heat source, rate of temperature decrease, and heat diffusion time across the film, respectively.

$$\tau_i = \frac{1}{\alpha^2 k_f} \quad \tau_f = \frac{d^2}{k_f} \quad \gamma = \frac{b_f - b_s}{b_f + b_s}$$

The temperature response of film surface is characterized by $\gamma$ and $\sqrt{t_i/\tau_f}$ and changing $\gamma$ parameter.

$b_f =$ Thermal effusivity of film

$b_s =$ Thermal effusivity of substrate

$k_f =$ Thermal conductivity of the film

$\alpha =$ absorption coefficient of the film.

$$T_{RF} = \Delta T \sqrt{\frac{\tau_f}{\tau_i}} \exp\left(\frac{t}{\tau_i}\right) \sum_{n=-\infty}^{\infty} \gamma^n \left(2n - 1\right) \sqrt{\frac{\tau_f}{\tau_i}} \text{erfc}\left(\frac{2n - 1}{2} \sqrt{\frac{\tau_f}{\tau_i}} + \sqrt{\frac{t}{\tau_i}}\right)$$

Once the temperature change and the absorption coefficient of the thin film is found the thermal conductivity of the film can be calculated according to this formula;

$$D * C = Q / dTrf, \quad K = \alpha DC$$

$K :$ Thermal conductivity

$Trf :$ Rear surface temperature

$D :$ Thermal diffusivity of the film

$C :$ heat capacity of the film

$d :$ film thickness

$D \ & \ C$ values are not necessarily needed to be known to determine the relative change in the thermal conductivity as a function of the temperature.

The setup is now ready and we already have done preliminary measurements on a TiO$_2$-Ge thin film.