On the Cover (from left to right):

1. Simulated high angle annular dark field and annular bright field images of AlN. (see R. Kumar et al., page 13);

2. Ruthenium crystal on a sample holder connected to two tantalum wires and a thermocouple. (see S. Balgooyen et al., page 1);

3. Micro fluidic device with a pink strip of cured PtOEPK lying on the center to detect the presence of oxygen. (see K. Chen et al., page 7).
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Introduction

Dear Colleagues,

welcome to the sixth edition of the Journal of Undergraduate Research at the University of Illinois at Chicago (UIC). After nearly twelve months of hard work from our authors, referees and the journal’s editorial staff, we have finally completed this edition, which contains 10 outstanding papers from undergraduate students who performed their research over the last year at UIC. Several papers are part of the National Science Foundation (NSF) Research Experience for Undergraduates (REU) site in the Departments of Chemical and Biomedical Engineering. I would especially like to thank Professor C. G. Takoudis and Dr. G. Jursich for heading this effort here at UIC.

The continued success of the journal is, of course, due to the great research that is being performed by our undergraduate students in the Colleges of Liberal Arts & Sciences, as well as Engineering. To further increase the awareness of our Journal in the Science and Engineering community not only here at UIC, but also nationwide, we invite every undergraduate student performing research during the semester or over the summer, to submit his/her work to the Journal for publication.

Last but not least, I also want to thank the editorial assistant, Keenan Avers, for his outstanding work and help in putting together the sixth volume of this Journal. Keenan recently finished his undergraduate career here at UIC and has moved on to graduate school. We wish him all the best!

Robert F. Klie
Nanoscale Physics Group

May 2013
Selective Oxidation of Ammonia on Ruthenium to Form p(2 x 2) Nitrogen Layer

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Oxidation of ammonia was used to prepare a p(2 × 2) nitrogen layer on the Ru(0001) surface as verified by temperature-programmed desorption (TPD) and low energy electron diffraction (LEED). The process takes place in an ultra-high vacuum (UHV) chamber. The surface is precovered with oxygen and then exposed to ammonia at low temperature. Upon heating, the ammonia is oxidized to form water, which desorbs at low temperature to leave a nitrogen covered surface. The resulting layer can be used in a variety of surface chemical studies, including a hydrogenation reaction, which is an important part in the study of the Haber-Bosch process, in which ruthenium is used as a catalyst.

Introduction

Heterogeneous catalysis is an important part of industrial processes. One important heterogeneous catalytic reaction is the Haber-Bosch process (depicted by Equation 1), which is the synthesis of ammonia.

\[ \text{N}_2(g) + 3\text{H}_2(g) \leftrightarrow 2\text{NH}_3(g) \] (1)

This reaction provides the ammonia that is used in fertilizers and is essential to life. In 2010, a total of 131,000,000 metric tons of ammonia was produced worldwide.\(^1\) Industrially, an iron-based catalyst is used in this process because it is relatively inexpensive. However, this catalyst requires high pressure and temperature conditions. Ruthenium is known to be a better catalyst but its high cost makes it unsuitable for industrial applications.\(^2\) For this reason, it is beneficial to study the details of the process over ruthenium (the ideal process) so that a more efficient yet still inexpensive catalyst may be proposed.

An important part of ammonia synthesis is the hydrogenation of nitrogen. To study this process, an ordered nitrogen layer needs to be prepared on the ruthenium surface. One way to do this is through oxidation of ammonia, as shown by Equation 2:\(^3\)

\[ \text{NH}_3\text{ads} + \text{O}_{\text{ads}} \rightarrow \text{N}_{\text{ads}} + \text{H}_2\text{O} \] (2)

Oxydehydrogenation of ammonia can be performed over ruthenium by pre-covering the surface with oxygen and then introducing ammonia. Ammonia is known to desorb from oxygen covered ruthenium near 175 K, H\(_2\) is known to desorb near 375 K, and N\(_2\) near 750 K.\(^4\) The importance of these temperatures is that somewhere between 375 K and 750 K, solely nitrogen will be on the surface of ruthenium. The adsorption structure of the nitrogen can be identified by low-energy electron diffraction (LEED).

This method of oxidation of ammonia has been studied on several metal surfaces, including platinum. In the study of Pt(111), it was found that the formation of an atomic nitrogen layer depended on both the amount of oxygen and ammonia. The ideal exposures for the gases were 2.0 L of O\(_2\) and 0.4 L of NH\(_3\)\(^5\) (1 Langmuir = 10\(^{-6}\) Torr for 1 second). Along with the products and reactants of Equation 2, the study also found desorption of NO in some of the trials with NH\(_3\) exposures of less than 0.4 L. Also at a lower exposure of NH\(_3\), they found a second peak for molecular oxygen (desorption peak for recombinative oxygen after N\(_2\) has desorbed), which implies that not all of the oxygen was consumed in the process. The maximum amount of surface nitrogen was found at the ideal conditions above. It was confirmed to be a well-structured p(2 x 2) nitrogen layer using Auger electron spectroscopy (AES) and LEED. The nitrogen layer can also be hydrogenated (using an exposure of H\(_2\)) and the resulting N-H stretch in the RAIR spectrum was observed.\(^5\)

Nitrogen layers can also be prepared on ruthenium by plasma discharge of N\(_2\)\(^6\) or dissociative adsorption of NH\(_3\),\(^7\) but since the sticking coefficient of nitrogen on ruthenium is so small (10\(^{-12}\)),\(^8\) a large exposure of gas is required, which elevates the pressure in the chamber and makes these methods impractical.

The presence of atomic nitrogen on ruthenium would be an ideal condition to further study the details of the
Haber-Bosch process since the dissociation of N\textsubscript{2} is the rate limiting step of the reaction under realistic industrial conditions. The desired outcome of this study is an atomic layer of nitrogen on the ruthenium crystal after performing the oxydehydrogenation of Equation 2 in a UHV (ultra-high vacuum) chamber and stopping the heating before N\textsubscript{2} desorbs from the ruthenium surface. This nitrogen layer may be further used to study its hydrogenation to form NH. From this, the reaction temperature and kinetics of the process may be found. If the NH is found to be stable, it can be hydrogenated to NH\textsubscript{2}. Through this type of study, it may be determined if surface NH\textsubscript{3} can be formed by hydrogenating atomic N on Ru(0001). This method has been used previously to study the hydrogenation of N on platinum.

**Experimental Methods**

A Ru(0001) crystal is used in this study in a UHV chamber equipped with a Hiden HAL 201/3F quadrupole mass spectrometer (QMS) for temperature-programmed desorption (TPD), an ion gun for sputtering, a Bruker IFS 66 v/s Fourier transform infrared (FTIR) spectrometer for reflection-absorption infrared spectroscopy (RAIRS), and LEED optics. The crystal is spotwelded to two short tantalum wires for resistive heating up to 900 K. It can also be heated to higher temperatures (up to 1500 K) by using electron beam heating from a thoriated tungsten filament adjacent to the sample. The electrons emitted by the heated filament are accelerated to the sample by positively biasing the sample to 600 V. The chamber is pumped by a turbomolecular pump backed by a mechanical pump to keep the pressure around 1 \times 10^{-10} Torr. Gases are let into the system through a variable leak valve connected to a gas manifold.

**Cleaning the Sample**

The crystal was cleaned with two cycles of Ar\textsuperscript{+} ion sputtering and annealing. The first cycle was sputtering at 1 kV followed by annealing to 1500 K for 30 seconds. The second cycle was sputtering at 0.5 kV followed by annealing to 850 K for 1 min. The pressure of the argon in the chamber during sputtering was 5 \times 10^{-5} Torr. The sample was rotated 5 degrees every 2 minutes for 15-16 minutes to ensure uniform sputtering. One of the main purposes of this procedure is to eliminate any carbon impurities on the surface. If there were any carbon on the surface, an introduction of oxygen in the chamber would oxidize the carbon, forming CO. In order to prove the absence of carbon impurities after cleaning, the sample was saturated with oxygen and TPD data was taken (heating rate of 2 K/sec). This data is used to check for the existence of a recombinative CO peak.

**Formation of Nitrogen Layer**

After cleaning, the sample was cooled down to 150 K using liquid nitrogen. It was annealed to 600 K to remove any residual CO and was then cooled down to around 90 K. Varying amounts of O\textsubscript{2} were introduced to the chamber (0.2 L, 0.5 L, 1 L, 2 L, 5 L) at the beginning of each trial. Time was allowed to let the pressure decrease and equilibrate. 5 L of ammonia was then put on the crystal and the pressure was again allowed to decrease. TPD data was taken (heating rate of 2 K/sec, ranging from 150 K to 950 K) to find the amount of O\textsubscript{2} that is enough to saturate the surface. This data was also used to find the temperature at which everything except nitrogen desorbs. This was the temperature used in the next part of the experiment. The following desorption products were monitored in the TPD data: H\textsubscript{2} (m/z = 2), NH\textsubscript{3} (m/z = 17), H\textsubscript{2}O (m/z = 18), N\textsubscript{2}/CO (m/z = 28).
FIG. 4: TPD data for masses 28, 14, and 12 to distinguish N\textsubscript{2} from CO. Data was taken with a pre-covering of 2 L of oxygen and exposure of 5 L of ammonia, both at 89 K.

CO (not from the carbon impurities), adsorbed from either the residual gases in the vacuum chamber or deliberately dosed onto the surface, will desorb from ruthenium at 350-450 K\textsuperscript{10} so this will appear in the data whether the sample is clean or not. The recombinative CO that is formed from the oxidation of carbon impurities on the surface begins to desorb at around 530 K.\textsuperscript{11} Shown in Figure 2, the absence of recombinative CO desorption from an oxygen-saturated surface indicates the cleanliness of the surface. Cleaning with two cycles of sputtering and heating was done before every experiment to ensure that there was no residual carbon interfering with the reactions.

The first set of experiments tested the production of nitrogen with varying amounts of oxygen on the surface. The surface was pre-covered with oxygen and then 5 L of ammonia was put on the surface. Both gases were put on the surface at 90 K because the sticking coefficient is higher at low temperatures.\textsuperscript{8} The sample was heated while TPD data was taken. The TPD data of mass 28 from these experiments are shown in Figure 3.

As the amount of oxygen increases, the desorption temperature of nitrogen decreases (as shown by the dotted line) and the intensity of the peak increases slightly, meaning more nitrogen is being formed. The peaks at 425-475 K are due to background CO, which is an irrelevant part of this experiment (CO is always present in the background). In the data with no oxygen added, there is a small peak at 625 K. This represents the small amount of recombinative CO. The data with oxygen are not suspected to have much or any recombinative CO. This is proven by monitoring mass 12 with TPD. Mass 12 corresponds to the carbon atom fragment of CO. A mass 12 peak aligning with a mass 28 peak indicates desorption of CO. There is a small peak for mass 12 at 625 K when there is no pre-covering of oxygen, but is absent when there is a pre-covering of oxygen.

Peaks for molecular oxygen (m/z = 32) are not seen in the data from this experiment. This is because the
heating used for TPD data collection (resistive heating) only reaches a temperature of 950 K. Molecular oxygen is expected to desorb from the surface around 1500 K and was not able to be seen within the parameters of this experiment.

Peaks are attributed to nitrogen in the same manner. Both mass 12 and mass 14 are monitored to distinguish CO peaks from \( \text{N}_2 \) peaks in the mass 28 data. An example is shown in Figure 4.

The data above proves that the mass 28 peak around 430 K can be attributed to CO (since it aligns with a mass 12 peak) and the mass 28 peak around 540 K can be attributed to \( \text{N}_2 \) (since it aligns with a mass 14 peak). The mass 14 peak around 375 K aligns with molecular ammonia desorption and is not associated with mass 28.

Another way to prove that reaction 2) is occurring is by monitoring mass 18 in TPD to discern any water being produced. Mass 18 was observed after ammonia was put on the surface both with and without oxygen. The results are shown in Figure 5.

Without a pre-covering of oxygen, there should be no water forming because there should not be any presence of oxygen in the chamber. However, there is a small peak around 180 K when there is no oxygen present. This is attributed to water in the background gases that adsorb to the surface at 88 K. However, the mass 18 peak for the oxygen-precovered surface is significantly larger than that without oxygen, suggesting that water is being produced in the reaction. The presence of a distinct peak for both water and nitrogen is a strong indicator that reaction (2) is indeed occurring since both products are present.

The structure of the nitrogen layer was observed using LEED. To prepare the sample for LEED, the procedure for TPD was followed. The only difference being that the heating was stopped just before the nitrogen desorbs (~ 457 K). This ensures that everything but nitrogen desorbs. Figure 6 shows the desorption data for all the components of Equation 2. It is clear that at ~ 457 K, only nitrogen should remain on the surface. The small \( \text{NH}_3 \) peak at ~ 700 K is likely from ammonia desorption from the sample holder. After the sample was cooled back down to 90 K, the LEED picture was taken and compared to a LEED picture of a clean Ru(0001) crystal.

Figure 7 compares the LEED picture from the clean Ru(0001) surface with that of the N covered surface. The latter shows additional spots indicative of a p(2 \( \times \) 2) LEED pattern from the atomic nitrogen layer. The weakness of the spots could be caused by a low coverage of the atomic nitrogen layer. It has been shown that 5 L exposure of \( \text{NH}_3 \) produces less than 0.05 monolayers (ML) of nitrogen on Ru(0001). Oxygen pre-coverage of the surface does increase the amount of desorbed \( \text{N}_2 \), as shown in Figure 3, but not by much. Therefore, the amount of nitrogen produced on the surface is likely much lower than the saturation amount. However, the observation of a p(2 \( \times \) 2) LEED pattern still proves the N layer to be well structured. Figure 7(c) shows what a well structured p(2 \( \times \) 2) layer should look like. The additional spots are aligned with those of the ruthenium crystal and are symmetric. Figure 7(b) shows that the LEED of the N layer also has these properties.
Conclusion

This study used TPD and LEED to prove the formation of an atomic nitrogen layer on ruthenium resulting from the oxidation of ammonia. Ammonia is known to decompose on Ru(0001) into atomic nitrogen and hydrogen, which desorb as N$_2$ and H$_2$ at 800 and 400 K, respectively. However, when the surface is pre-covered with oxygen, the nitrogen desorption peak is lowered in temperature and increased in intensity, indicating that the presence of adsorbed oxygen facilitates NH$_3$ decomposition on Ru(0001) and decreases the activation energy required for N$_2$ desorption. These results have been corroborated by other research. An exposure of 2 L of oxygen was found to be enough to saturate the surface. Without oxygen, the desorption temperature was around 915 K; with 2 L of oxygen, the desorption temperature was around 540 K. The assignment of mass 28 desorption at $\sim$ 550 K to N$_2$ instead of CO is supported by the observation of mass 14 (N) and the absence of mass 12 (C) at the same temperature. In addition, the observation of water desorption at $\sim$ 180 K confirms the production of water from reaction (2). The LEED data showed the presence of a well ordered p(2 × 2) N layer. This method of nitrogen layer formation is effective and credible.

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Funding from the National Science Foundation grant # 1062943 is gratefully acknowledged. Without the provided resources, this research would not have been possible. The help of Professors Christos Takoudis and Gregory Jursich and Mr. Arman Butt for managing the REU program, “Novel Advanced Materials and Processing with Applications in Engineering” is also gratefully acknowledged.

Analyzing the behavior of normoxic and hypoxic cells through the use of microfluidic devices

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Current cellular exposure to atmospheric normoxic (21%) oxygen concentrations have been proven to be physiologically inaccurate since the human body only ranges between 1%-13% in the body. We wish to observe how human mesenchymal stem cells (hMSCs) and human lung microvascular endothelial cells (HLMVECs) interact with one another and their behavior when exposed to either hypoxic (defined as being less than normoxic) or atmospheric normoxic concentrations. The cells were grown and cultured on microfluidic devices - a relatively cheap and easily fabricated method of experimental testing that can lend itself to mass production and cellular analysis techniques. The analyses mainly focus on quantifying the amount of hypoxia-inducible factor-1 (HIF-1) present in the cells - this factor is responsible for activating countless transcription factors within the cell. Overall, these methods and tests have provided evidence to the fact that hypoxic conditions increase cellular growth, migration, proliferation, and growth factor production by almost two times.

Introduction

The current standard for cell culture involves sterile hood techniques and incubation in order to promote proper cell growth in vitro, but ignores the fact that oxygen concentrations within the human body are much lower than that of the atmosphere - varying from 1% in the cartilage to 7% in the bone marrow to 10-13% in the arteries, lungs, and liver. Thus, cells cultured under atmospheric conditions may not behave effectively during in vitro tests. Recent studies have begun to acknowledge this fact, and there has been testing done on tissue cultures of hMSCs under hypoxia with 1% oxygen. While these studies have shown that hypoxia indeed affects the differentiation and cellular growth of hMSCs, they are inconclusive as to whether or not this effect is beneficial or negative.

Further studies must be done to address the amalgamation of cells and oxygen concentrations in the human body. In order for in vitro experiments to be as physiologically relevant as possible, they must also take into account the fact that cells in the body are neighbored by other types of cells which also may be exposed to different oxygen gradients. Specifically, the following studies aim to look at these effects on wound healing. When a surface wound occurs, some of the cells within the wound may be exposed to normoxic conditions which still neighbor hypoxic cells - differing cells in hypoxic or normoxic conditions will be adjacent to each other. We aim to observe the exact effect of different oxygen concentrations on cellular growth.

In the following studies, hMSCs and HLMVECs were seeded and allowed to signal each other as they reached confluence. hMSCs were chosen due to their role in angiogenesis. Both cells are important during wound repair - hMSCs can differentiate into structural cells necessary for wound repair while HLMVECs provide the angiogenesis needed for proper regeneration. Wound repair is especially crucial to study due to it being one of the main focal points in the tissue engineering field. Using a novel microfluidic design, both cell types could be grown inside a microfluidic device while also being exposed to different oxygen concentrations. The devices can thusly mimic more natural conditions and also work easily with standard cell culture techniques - it is relatively inexpensive and also easy to collect cells for cellular analysis (western blotting, quantitative polymerase chain reaction (qPCR), immunofluorescence). The following experiments explore the process of microfabrication as well as the effects that different permutations of oxygen concentration and cell type can have on cell growth, proliferation, migration, and growth factor formation. Specifically, it will look at the presence of hypoxia-inducible factor-1 (HIF-1), which is the master regulator of hypoxic vascular responses and activates countless transcription factors that promote angiogenesis and cellular growth. For qPCR, quantities of glucose transporter 1 (GLUT1) were analyzed within the cells and normalized with glyceraldehydes 3-phosphate dehydrogenase (GADPH). GLUT1 aids in the transportation of glucose throughout the body. It is hypoxia responsive and affected by HIF-1 activity. GADPH is a non-hypoxia affected transcription factor that needed to be quantified in order to compare with the amount of GLUT1 present.
FIG. 1: a) The microfluidic device was composed of four layers: (1) a foundation layer, (2) the microfluidic network so that oxygen could flow across the surface of the devices, 3) the gas permeable membrane so that the oxygen could diffuse to the cells on top, and (4) the well to keep the cells and media within a confined area. b) Oxygen from tanks would be inserted at the (a) inlets and travel across half the devices before exiting the (b) outlets. (c) The cells would reside within the well.

Methods

Microfabrication

The microfluidic devices were designed by combining four differing layers of polydimethylsiloxane (PDMS) - which is a silicone elastomer used in soft lithography - the bottom foundation, the microfluidic network, the gas permeable membrane, and the well to contain the cells (Figure 1). An important detail to note was that the bottom foundation will either be composed of a glass slide or PDMS strips. The glass slides were necessary to perform immunofluorescence tests while the PDMS foundations were needed for PCR and Western Blotting.

The well and network parts first needed to be designed through photo lithography. SU-8 was spun onto a silicon wafer and placed on a hotplate at 65 °C for 5 minutes and then 95 °C for 60 minutes. The wafer was placed under an ultraviolet (UV) light with a UV resistant mask over it. The mask had open areas designating the design of the respective layer for the device, and these open areas were consequently cross-linked once exposed to the UV light for a set amount of time. These wafers would then be put on a hotplate again at 65 °C for 5 minutes and then 95 °C for 25 minutes, and then placed on a shaker in a solution of SU-8 developer to wash off all non cross-linked SU-8. The resultant mold would be placed in a petri dish and covered with PDMS (soft lithography) and cured at 85 °C for 60 minutes. The PDMS was created at a 10:1 ratio of pre-polymer and curing agent (Sylgard 184 kit, Dow Corning). The cured pieces were cut out and bonded through oxygen plasma treatment. More in depth details on the fabrication process can be found in a previously published paper by S. C. Oppegard and D.T. Eddington.

Device Functionality

After a sufficient amount of devices were created, one of them needed to be tested to ensure proper functionality. The device was attached to two gas tanks, one for each inlet. The three combinations of gas tested were 1) both inlets at atmospheric 21% oxygen, 2) both inlets at hypoxic 0% oxygen gas, and 3) one inlet at 0% and one at 21% (dual conditions). Using the program Meta-morph, the device was viewed under a microscope with a moving platform. The device was calibrated and multiple pictures were taken across the device while the gas was flowing through them. The camera took pictures of fluorescence given off by platinum(II) octaethylporphine ketone (PtOEPK), which naturally fluoresces but is quenched in the presence of oxygen. Thusly, the side exposed to atmospheric concentrations should fluoresce at a lower intensity than that of the hypoxic condition. The PtOEPK was spun on a silicon wafer with a PDMS layer and then cured at 85 °C. Strips of it were cut off and place on the device (Figure 2).

Cell Culture

hMSCs and HLMVECs were cultured and passaged (P9-12) in Endothelial Cell Based Medium-2 (EBM-2) and MEM Alpha Medium (MEM-α), respectively. When
enough devices were completed, the devices were autoclaved for 30 minutes at 121 °C and then seeded. The seeding procedure first involved removing the media from the cultures and exposing them to a two-time 5 mL wash of Dulbecco’s Phosphate Based Saline (DPBS) and then 4 mL of trypsin-CDTA. The cells were momentarily incubated to allow the enzyme to detach them and then 6 mL of the respective media was added to neutralize the trypsin. The solution was centrifuged to pellet the cells and the supernatant aspirated. The cells were resuspended in 1-4 mL of their respective media and counted. For the devices, a total of approximately one million cells per device were seeded and then allowed to grow.

**Experimental Setup**

After devices became fully confluent with cells, plastic tubing was attached to the inlets and led out of the incubator. The tubing was connected to a rotometer - responsible for managing air flow - which subsequently was attached to a gas tank (either 0% or 21%). With multiple devices, we were able to test a variety of conditions. The HLMVECs were run for 24 hours, and the MSCs were run for 20 hours based off previous research.3

**Immunofluorescence Tests**

Immunofluorescence tests can only be performed on devices with a glass foundation, due to the application of 4% paraformaldehyde to fix the cells to the device. The device was first exposed to a 3x PBS wash before the 4% paraformaldehyde. They were then washed with 0.2% Tx-100 (triton) in PBS for 10 minutes and another PBS wash was applied before incubating the device with anti-HIF-1α antibody overnight. A 3x Tris-Buffered Saline and Tween 20 (TBST) wash was performed and then the device was incubated with the secondary antibody for two hours at room temperature. Finally, after a 3x TBST wash, the device was stained with 4',6-diamidino-2-phenylindole (DAPI; a fluorescent stain with a 0.4 µL:2 mL ratio of Hoechst 33342 trihydrochloride trihydrate:blocking buffer). The cells could then be imaged with a microscope to detect fluorescence.

**Quantitative Polymerase Chain Reaction (qPCR)**

To prepare the cells for PCR, the media was aspirated off and the device was given a 2x PBS wash. We then cut the device into 3 equal pieces and added 300 µL of a 50 µL:5 mL ratio of mercapto-ethanol to lysis buffer to each piece. The cells were scraped off and transferred to DNA/RNA free tubes. Then, the DNA was converted to cDNA using a high-capacity cDNA reverse transcription kit and then left in a warm bath. 2.5 µL of each set of cDNA was then added to a SYBR Green template, which consists of 12.5 µL master mixture (AB4309155), 1.25 µL of forward primer, 1.25 µL of reverse primer, and 7.5 µL dH2O. The DNA was then placed in a PCR machine for actual analysis.

**Results**

**Device Functionality**

Proper functionality was observed throughout the devices as shown in Figure 3. The results were calibrated to display the percentage of oxygen concentration detected by the PtOEPK. They show that when both inlets are inserted with the same gas (either 0% or 21%), the device received an almost uniform distribution of that respective concentration across the network. Also, when the left inlet was inserted with 0% and the right inlet with 21% (dual conditions), the PtOEPK successfully detected the proper concentrations on their respective halves.

**Immunofluorescence**

The cells were viewed under a microscope under the proper fluorescence wavelengths to view cells (Figure 4). Pictures were taken of the cells on both the hypoxic and normoxic sides of the devices through HIF-1 staining and show an increase in HIF-1 production in hypoxic conditions. Further studies must be done to quantify these values and compare them to other results. GLUT1 staining
FIG. 4: Images of a device showing the HIF-1 staining of a) hypoxic conditions and b) normoxic conditions. The two show that there is a higher amount of HIF-1 production in hypoxic conditions. Further analysis must be done to quantify this amount.

FIG. 5: GLUT1 staining images in a) hypoxia and b) normoxia. The hypoxic hMSCs show an increase in GLUT1 production, which correlates to an increase in HIF-1 production as well as cellular proliferation, migration, and growth. was also performed (Figure 5) on MSCs, showing a larger amount of GLUT1 production in the hypoxic conditions as compared to those in normoxic conditions.

qPCR

The DNA within the cells were amplified through PCR until the amount of DNA reached a certain threshold \((C_t)\). The numbers were normalized by calculating \(2^{\Delta C_t}\), in which \(\Delta C_t = (C_t \text{ of GADPH}) - (C_t \text{ of GLUT1})\). These newly calculated numbers were then divided by the average of the \(2\Delta C_t\) values for the normoxic devices in order to normalize them. The subsequent graph outputs the amount of GLUT1 as a ratio to the other devices, with the normoxic devices set to 1 (Figure 6).

Discussion and Future Work

Through the various tests and continual assembly line production of microfluidic devices, we can safely conclude that our devices perform at their intended functionality and can be fully utilized for their intended usage. Any gas that is inputted at the inlets will properly flow through its respective half of the device, exposing that half of the cells to a specific oxygen concentration.

An important issue to note with the devices is that roughly 10-20% of completed devices are dysfunctional due to faults in the PDMS curing or bonding issues. Further testing must be done to solve this problem. The images that have been collected pertaining to the amount of HIF-1 in those cells show that there is a difference in the quantity of HIF-1 and GLUT1 between the hypoxic and normoxic sides of the devices. Further analysis must still be done on the HIF-1 and GLUT1 images to fully quantify the amount of transcription factor that is present. The qPCR results show that a fully hypoxic device outputs about twice as much GLUT1 (which correlates to more cellular activity) as a fully normoxic device, and also gives us evidence that the cells will grow faster and proliferate more on the hypoxic side of a dual condition device.

Conclusion

Overall - although further tests must still be performed - e can safely conclude that culturing cells under hypoxic conditions definitely increases transcription factor production, which consequently should lead to an increase in cellular growth, proliferation, and migration. These results show that our novel microfluidic design can properly deliver differing gas concentrations the cells on each half of the devices. Both cell lines respond by up-regulating HIF-1 in hypoxic conditions. These findings will greatly affect future cell culture procedures worldwide due to the
need to accurately mimic human physiology. The results show that cells respond positively when exposed to 0% hypoxic conditions, and we should make use of this in the future.

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6 (2009).
7 R. Lam, M. Kim, and T. Thorsen, Analytical Chemistry 81, 5918 (2009).
Analysis of Al$_x$Ga$_{1-x}$N nanowires through simulated methods of scanning transmission electron microscopy and electron energy-loss spectroscopy

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Al$_x$Ga$_{1-x}$N nanowires have promising applications for ultraviolet light emitting diodes (LEDs). However, these nanowires are not typical p-n junction semiconductors, but rather rely on varying concentrations of Al versus Ga to produce electron hole pairs. More information on the atomic structure is needed to better understand the properties of these nanowires. In this study, Al$_x$Ga$_{1-x}$N nanowires were imaged using scanning transmission electron microscopy (STEM) and compared to computer simulated STEM images to obtain physical information on the nanowires. Electron energy-loss spectroscopy (EELS) and FEFF9 computer simulations were also performed to better understand the structural and chemical properties of the nanowires. Results from these simulations showed that changes in the chemical ordering of the nanowires were responsible for changes in intensity and resolution in the images. These intensity and resolution trends were not a result of interface effects. This will help to further characterize nanowires in the future.

**Introduction**

Advances in nanotechnology over the past few decades have been driven by a greater understanding of the materials used to create new devices. Electron microscopy provides a means to obtain information necessary to understand structural, chemical and electrical properties of materials. Specifically, the scanning transmission electron microscope (STEM) allows for unprecedented spatial resolution of both heavy and light elements, providing more detailed information on atomic structure. STEM techniques will be used to help obtain physical and chemical information on Al$_x$Ga$_{1-x}$N nanowires, a new material with applications in ultraviolet light emitting diodes (LEDs). The Al$_x$Ga$_{1-x}$N nanowires examined were previously presented in $^2$. Each nanowire is graded in composition from $x = 0$ to $x = 1$ and back to $x = 0$ with a quantum well of primarily GaN in the center. This produces Ga rich regions at the ends of the nanowires and Al rich regions surrounding the quantum well as shown in Figure 1. The change in composition from Al to Ga produces electron hole separation, creating a p-n junction without the need of a dopant material as found in traditional semiconducting materials. $^2$

STEM provides information about a specimen on the atomic scale. Electrons are accelerated from a source, such as a tungsten cold field or LaB$_6$ emitter, towards the specimen. These electrons are focused prior to reaching the specimen by an electro-magnetic lens which alters the electric and magnetic fields that the incident electrons travel through. The electrons converge on the specimen and then scatter through the specimen. Two different detectors are placed below the specimen to obtain signals for imaging: a high angle annular dark field (HAADF) detector and an annular bright field (ABF) detector. HAADF imaging collects electrons scattered at high angles from the central beam and provides good z-contrast images. ABF imaging collects electrons that are scattered at low angles to the central beam and is useful in imaging lighter elements. $^3$ In using the HAADF and ABF detectors, nanowire images can give information on the composition and structure by observing nitrogen contrast and resolution as well as intensity changes from the atoms. These details help describe what the composition of a specific region of the nanowire might be.

In order to verify the composition, multislice STEM image simulations were performed. $^4$ This method involves dividing a continuous specimen into discrete atomic layers. Each layer has a different group of atoms with a certain atomic potential energy associated with the slice. The code calculates the transmission wave func-
tion as it passes through each individual layer. Most crystalline materials are sliced in repeating units according to the stacking sequence of the material. However, as the crystals produced have more complicated structures, each layer must be generated individually instead of repeating layers through a sample.  

In addition to STEM imaging, electron energy-loss spectroscopy (EELS) also helps characterize atomic scale structures. This technique allows for better understanding of chemical and electronic properties of materials by bombarding the specimen with monoenergetic electrons. These incident electrons interact with the specimen and collide inelastically with the specimen electrons, causing the incident electrons to lose energy. This lost energy is directly dependent on the material that the incident electrons travel through. The energy value changes as the specimen's composition changes from one element to another. This characteristic energy value can be recorded as a function of the number of incident electrons losing that energy, known as an EEL spectrum. In an EEL spectrum, elemental regions are differentiated by their energy peaks and the overall shape of the spectra.  

A useful tool to verify EELS data is a real space multiple scattering code called FEFF9. Similar to the Kirkland code, FEFF9 is a simulation technique that calculates the atomic potentials of a specimen. The phase shifts of the incident electrons are also calculated based on the specimen matrix and energy losses are calculated and quantified. For each of these scattered paths, relative amplitudes are calculated and the simulated EELS spectra are created.

This report focuses on simulating STEM images and EELS through the Kirkland code and FEFF9 simulations. Representative crystals based on the gradation of the nanowires are constructed and used for the simulations. The simulated and experimental results are compared to see whether or not the simulations accurately predict the structural and chemical properties of the nanowires. This will help in the future to characterize the composition of Al and Ga along each layer of atoms in the nanowires and verify the target growth of the nanowires.

**Experimental Procedures**

**STEM Imaging and EELS**

All STEM imaging was performed on a JEOL JEM-ARM 200CF with a cold field emission gun (CFEG) operated at 200 kV. The electron probe had spherical aberration correctors to allow for spatial resolution down to approximately 65 pm. Four detectors were used with the microscope: high and low angle annular dark field (HA/LAADF), annular bright field (ABF) and a Gatan EELS system. Imaging was performed with a convergence angle of 22 mrad and a probe current of 10.5 pA. These images were all taken on the [100] zone axis. These parameters are well within the resolution power necessary to resolve Ga from N and Al from N, so observable contrast differences, especially in ABF, are expected.

STEM images were taken of single, isolated nanowires. These nanowires were tilted to a low index zone axis to avoid imaging artifacts. HAADF, LAADF and ABF images were taken of the nanowires near the top and bottom of the samples and at the edge of the quantum well. The HAADF inner detection angle was set to 90 mrad, giving ABF an inner detection angle of 11 mrad, or half of the convergence angle. EELS data were also taken at six different points in the nanowire to show spectra at different Al versus Ga concentrations.

**Kirkland and FEFF9**

Simulated STEM images were created using the Kirkland code discussed earlier. The Kirkland code requires the position of each atom in the specimen being imaged. This was done by creating models of the nanowires using Crystal Maker software. Pure GaN, pure AlN, a single graded structure and a double graded structure were the samples created for simulated STEM, as shown in Figure 2. The two pure samples were created to verify pure regions in the nanowires and the two graded structures were created to model the nanowire itself. The single graded structure varied in composition along the imaging direction and the double graded structure varied in composition along the imaging direction and along the imaging face. All atomic positions for each of the samples were then recorded into a script file to be entered into the Kirkland code. The Kirkland code also required basic STEM probe parameters and thermal vibration amplitudes of the atoms which were matched to real STEM imaging conditions. Each sample was imaged 15 times from the front face of the sample at intervals of 1 nm and imaged again at the back face of the specimen. HAADF and ABF images were taken at each thickness interval.

FEFF9 simulations were performed in addition to performing EELS as a comparison to the experimental data. The ATOMS program was used to obtain the input file necessary to run the FEFF9 program. This input file contained the atoms used, their positions, space group, lattice parameters, and other imaging parameters. Pure GaN and pure AlN were simulated from one shell to ten shells of atoms to show convergence in the calculations. The polarization direction was set to [100] for each sample.

**Results and Discussion**

**Structural Characterization**

The Kirkland code, when finished, created 15 HAADF and ABF images. The first image was taken at the front face of the nanowire and every 1 nm into the nanowire
FIG. 2: Computer generated crystals created to find atom positions for Kirkland code. All Ga atoms are green, Al atoms red and N atoms blue; a) Pure GaN; b) Pure AlN; c) Single graded structure; d) Double Graded structure

FIG. 3: Pure GaN simulated STEM images; a) HAADF; b) ABF

thereafter. In Figure 3, the N of the pure GaN sample is not visible in the HAADF image. However, the N in the pure AlN sample in Figure 4 is visible in the HAADF image. Both ABF images show N, but the AlN has a better resolution of the N atoms. This is caused by the Z dependence on the intensity in STEM images. Since $Z_{\text{Ga}} = 31$ and $Z_{\text{N}} = 7$, the Ga intensity dominates the image in GaN. In the AlN sample, $Z_{\text{Al}} = 13$ so the Al does not dominate the intensity and both atoms are visible. In addition, the Ga sites in Figure 3 are larger than the Al sites in Figure 4, showing the change in size between the two atoms.

Simulated STEM images of the single graded structure also show the change in intensity between Al regions and Ga regions. In Figure 5, the composition in both images changes gradually from Ga rich on the left to Al rich on the right. In the HAADF image, the Al rich side has less intense Ga/Al sites than the Ga rich side, showing a clear change in intensity as the composition changes. In the ABF image, the N sites become clearer towards the Al rich side and the Ga/Al sites become smaller towards the Al rich side.

Simulated STEM images of the double graded structure helped confirm the trends shown in the previous three structures. In Figure 6, the Al rich region for each image is the top left corner and the composition changes both horizontally and vertically towards the Ga rich region in the bottom right corner. The HAADF image shows more intense Ga/Al sites on the Ga rich side and less intense Ga/Al sites on the Al rich side. The N sites are more distinct in the ABF image on the Al rich side and the size of the Ga/Al sites gets smaller towards the Al rich side. The changes in both the HAADF and ABF images occur moving across a row and up a column, showing the varying composition in both directions.

All of the trends discussed in the four simulated images match the trends observed in the experimental STEM images. Figure 7 shows a STEM image in the quantum well region of one of the nanowires. The quantum well is composed of primarily GaN and the region above the quantum well is primarily AlN. The Ga rich region is more intense overall than the Al rich region and the Ga sites are larger than the Al sites. The N tails in both re-
FIG. 6: Simulated STEM image of double graded crystal 15 nm into the sample; a) HAADF; b) ABF

FIG. 7: Experiment STEM HAADF image near quantum well displaying separation of Al-rich and Ga-rich areas

FIG. 8: EEL spectra at different locations within the nanowire with an HAADF image of the nanowire labelled at the six spectral points

FIG. 9: FEFF9 results for pure GaN and pure AlN calculated at the tenth shell

EEL spectra were taken from six different locations within the nanowire shown in Figure 8. Each site has a different Al and Ga concentration as seen by the change in intensity in the HAADF image of the nanowire. The singular peak shown in the first spectrum, a Ga-rich site, and the three peaks in the third spectrum, an Al-rich site, match previous X-ray data taken from similar $\text{Al}_x\text{Ga}_{1-x}\text{N}$ samples. This confirms the overall shape of the spectra.

The FEFF9 code resulted in ten different spectra for both pure GaN and pure AlN, from the first shell to the tenth shell for each sample. The GaN sample converged after the seventh shell and the AlN sample converged after the sixth shell. Figure 9 shows the two samples after the tenth shell, where the AlN sample is shifted vertically for viewing purposes. In comparison to the experimental results, the AlN sample looks very similar. The three dominant peaks at about 401, 405, and 408 eV respectively match the three peaks shown in the third spectra in Fig 8. The drop off after these peaks also remains consistent with experiment. The GaN sample has two peaks, one at about 402 eV and one at 404 eV. This, however, is not consistent with experiment which showed one broad peak in the first spectra in Figure 8. The plateau after the larger peak in the simulated spectra is consistent with the rest of the experimental spectra.

The main issues that arose from performing the FEFF9 simulations were controlling the parameters required in the input file. The shell range values that control the number of shells taken into account for electron scat-
tering were set to the shell number and the shell number plus about 0.7 (10.0 and 10.7 for the tenth shell). This value was used to make sure that the bounds on the shell included the entire shell, but changing these range of values may provide different spectra results. In addition, the number of atoms used in each shell was larger than that used in another experiment at the University of Washington, which could mean that the defined shells are not matched exactly to prior experiments. These factors should be taken into consideration for future experiments.

Conclusion

In the simulated STEM images, N contrast was clearer in the Al rich regions and the N atoms had a higher resolution. Al sites were also less intense and smaller in size than the Ga sites. In the FEFF9 simulations, pure AlN spectra showed similar trends to experimental data, having three distinct peaks and leveling off after these peaks. The pure GaN spectra however showed a secondary peak that was unexpected, while the rest of the spectra matched experimental data. Overall, the simulated results showed that changes in the chemical ordering of the nanowires were responsible for changes in intensity and resolution in the images. These intensity and resolution trends were not simply a result of interface effects within the nanowires.

Future work will begin with graded structures for FEFF9 simulations to obtain spectra at varying Al and Ga concentrations. This will be useful in comparing to experimental EEL spectra in which the composition at the spectral points is unknown. In addition, the input parameters of FEFF9 will be experimented with to find the best results. Finally, more STEM images and EELS data will be obtained and the simulated data found will help characterize the nanowires structurally and chemically. This data will help to verify the target growth of the nanowires.

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6 M. Moreno, K. Jorissen, and J. Rehr, Micron 38, 1 (2007).
Anatase Phase, Hydrophilicity, and Thickness of Thermally Oxidized TiO$_2$ Layer on Titanium-V Alloy

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Surface modification of titanium implants has been a large focus of recent research. Thermal oxidation is a technique used to diffuse oxygen into the surface of a material. This process forms an oxide layer. By varying the thermal oxidation temperature, the crystal structure of the TiO$_2$ layer can be changed from anatase to rutile at temperatures of 300 to 600 °C. The crystal structure of anatase has been shown to resemble hydroxyapatite, a mineral involved in bone growth. Fourier transform infrared spectroscopy (FTIR) and goniometry are used to analyse the anatase concentrations created at 24, 300, 375, and 450 °C. It was found that hydrophilicity increases on rough samples as oxidation temperature increases. Also, a peak shift from anatase to rutile is seen as annealing temperatures increase in the range of 300 to 600 °C. Greater relative anatase formation is seen at 300 and 375 °C. The shift to rutile begins to occur at 450 °C and continues to 600 °C.

Introduction

The goal of this experiment is to modify the implant surface such that it promotes osseointegration. Osseointegration is the progression of the bone-implant interface adhesion, which occurs when the natural bone connects to the implant surface. If this connection forms quickly, the implant has a greater possibility of remaining embedded, increasing the chance of success. However, without this connection, the implant becomes loose, loses functionality, and may become infected, leading to costly revision surgery.

Titanium is a popular metal in the world of implants due to its excellent biocompatibility, low density, high ductility, corrosion resistance, atoxicity, and mechanical resistance. It is used mostly for dental and orthopedic implants. Commercially pure titanium does not have a tensile strength as high as some other implant materials, such as cobalt-chromium. Ti6Al4V, a widely used titanium alloy, contains 6 w.t.% aluminum and 4 w.t.% vanadium. The combination of aluminum and vanadium with titanium makes the material stronger than the commercially pure titanium. Thus, this alloy is used with increasing frequency for dental and orthopedic purposes. It is possible that Ti$_6$Al$_4$V can become cytotoxic when aluminum and vanadium ions dissociate from the bulk into neighboring tissues. This occurrence and the low wear resistance of Ti$_6$Al$_4$V make surface modification necessary for improved osseointegration. Sandblasting and acid-etching are techniques used to create a micro-rough surface. This roughened surface improves osseointegration by increasing the surface area for cellular attachment. Titanium forms an oxide layer (TiO$_2$) naturally, but it is advantageous to form an oxide layer under controlled conditions so that properties such as thickness and crystalline structure of the oxide layer can be controlled. Moreover, the varying oxide properties can be tested for superior osseointegration. The TiO$_2$ layer is advantageous because it increases biocompatibility and corrosion resistance.

Hydroxyapatite is a mineral found in the body that has been shown to enhance bone growth both naturally and when coated on implant surfaces. In its anatase phase, TiO$_2$ has been found to assist in bone adhesion due to the similarities of its crystal structure to hydroxyapatite. The crystal structure of apatite aligns better with anatase than with rutile. In previous research, an anatase titanium nanotube surface has been shown to support cell growth better than an amorphous layer. As concentrations of anatase increase relative to rutile or amorphous, superior osseointegration is expected.

Thermal oxidation is a method used to diffuse oxygen into surfaces to create an oxide layer. It has been shown that both the roughness and thickness of the oxide layer increase with oxidation time. Thickness of the surface has also been shown to increase with the temperature to which the sample is exposed. Thermal oxidation was chosen over other techniques for various reasons. The oxide layer created is more conformal to surface topography than that obtained through chemical vapor deposition (CVD) and physical vapor deposition (PVD). Due to the diffusion mechanism, the oxide layer conforms to
the roughness created by sandblasting and acid etching. Also, thermal oxidation is more time efficient when compared to atomic layer deposition (ALD). For example, depositing a 30 nm thick layer would take 16 hours at reported 0.3 Å/cycle/minute as opposed to one hour for thermal oxidation at ambient conditions and 550 °C. Additionally, there is no precursor needed for thermal oxidation unlike CVD, PVD, and ALD. Because no precursor is needed and thermal oxidation is time efficient, this will result in less contamination and lower cost.

**Materials and Methods**

A Single-zone Quartz Furnace (Lindberg, S#848040) was used to oxidize the Ti6Al4V samples at different temperatures. The oxidation tube was made of quartz. The furnace facilitated the diffusion of oxygen into the surface at atmospheric air and ambient pressure. A fan was used to maintain airflow through the oxidation tube, thus continually diffusing oxygen into the titanium surface.

Four samples annealed at different temperatures were surface modified and tested with Fourier Transform Infrared Spectroscopy (FTIR, Nicolet. S#ADU9700221) and a Goniometer (Rame-Hart NRL CA. M#100-0, S#2067). The control samples were oxidized at the ambient temperature of 24 °C, thus the sample was not annealed. This was expected to create a TiO2 layer in the amorphous phase. The other three annealing temperatures were 300, 375, and 450 °C. Two additional samples were made and thermally oxidized at 525 °C and 600 °C. These two samples were done to probe a probable peak shift towards rutile in an FTIR scan. Anatase phase has been shown to form between the thermal oxidation temperatures of about 250-500 °C. The amount of anatase is expected to be greater towards the middle of this range. Therefore, the thermally oxidized samples at 300-450 °C were expected to contain varying concentrations of anatase.

Ti6Al4V samples (Mac-Master Carr, Elmhurst, IL, USA) of 15 mm diameter and 1 mm thickness had their surfaces modified before thermal oxidation. To create the smooth samples, eight samples were polished using a polishing wheel (Ecomet Polisher/Grinder, Buehler LTD, Evanston, IL, USA) with Special Silicon Carbide Grinding Paper for Metallography Wet or Dry (#320, #400, #600, #800). Buehler, 0/1102), Diamond Polishing Paste (Buehler, 9-Micron, 487597), MetaDi Fluid (Buehler, 499594), and Colloidal Silica Polishing Suspension (MasterMet. Buehler, 40-6370-064). To create the rough samples, eight samples were sandblasted (Renfert Sandblaster) with 165-micrometer diameter alumina (Al2O3) particles and acid-etched with sulfuric acid and a 1:1 ratio of hydrogen peroxide that was 30 w.t.% solution by water. The rough samples were then sonicated in deionized water. Before thermal oxidation, each sample (rough and smooth) was washed with deionized water for 30 seconds and then dried with nitrogen gas. Additional rough samples were made for a continuation of this experiment to measure the cell viability of the thermally oxidized samples at the four temperatures.

Once thermal oxidation was complete and the sample cooled to room temperature, the sample could then be characterized. An Ellipsometer (J.A. Woollam Co. M-44) was used to measure the thickness of the oxide layer. Due to the multiple suboxides that are created in addition to TiO2, such as TiO and Ti2O3, ellipsometry can only provide an approximate thickness. Therefore, to supplement the ellipsometric data, the color of the sample was also taken into account. Previously, the correlation between color and oxide thickness has been investigated as shown in Table 1. FTIR was used to measure chemical composition, to test for impurities and to determine the relative amounts of amorphous, anatase, and rutile TiO2. A Goniometer was used to measure the water contact angle (WCA), a measure of hydrophilicity. Previous research has shown that increasing oxidation temperatures increases surface roughness, which increases the hydrophilicity of the surface. To a limitation, surfaces that are more hydrophilic have been shown to increase cell growth. Anatase structure, oxide thickness, and surface roughness have all been shown to affect cellular response and thus need to be taken into account when interpreting future cell test results.

<table>
<thead>
<tr>
<th>Oxidized TiO2 Layer Thickness (nm)</th>
<th>10-25</th>
<th>25-40</th>
<th>40-50</th>
<th>50-80</th>
<th>80-120</th>
<th>120-150</th>
<th>150-180</th>
<th>180-210</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Golden</td>
<td>Purple</td>
<td>Deep Blue</td>
<td>Light Blue</td>
<td>Yellow</td>
<td>Orange</td>
<td>Purple</td>
<td>Green</td>
</tr>
</tbody>
</table>

Table I: Colors of Oxide Layer After Anodic Oxidization. This shows the relationship between oxide layer color and thickness.

**Results and Discussion**

**Goniometry**

The Goniometer was used to measure the water contact angle. It was used on the smooth and rough samples. Results of the tests can be seen in Figure 1. At 375 °C, the rough sample is missing due to experimental error. It was determined from this error that the samples should not be washed prior to testing with the Goniometer because this makes the sample superhydrophilic, making the differences in hydrophilicity between samples impossible to detect. The smooth samples show a slight decrease in the water contact angle as the temperature increases.

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Table II: This shows the various temperatures at which smooth samples were thermally oxidized and the estimated thicknesses of the oxide layers based on the observable colors.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>24</th>
<th>300</th>
<th>375</th>
<th>450</th>
<th>525</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observed Color</td>
<td>None</td>
<td>None</td>
<td>Slight Gold</td>
<td>Golden</td>
<td>Yellow</td>
<td>Purple-blue</td>
</tr>
<tr>
<td>Estimated TiO$_2$ Thickness (nm)</td>
<td>$&lt;10$</td>
<td>$&lt;10$</td>
<td>$10 &lt; x &lt; 25$</td>
<td>$10 &lt; x &lt; 25$</td>
<td>$80 &lt; x &lt; 120$</td>
<td>$150 &lt; x &lt; 210$</td>
</tr>
</tbody>
</table>

but the trend is not significant. The rough samples exhibit a clear trend, increasing in hydrophilicity as the oxidation temperature increases. This agrees with previous research.\textsuperscript{22} It can also be seen that at a higher oxidation temperature (450 °C), the rough sample is more hydrophilic.\textsuperscript{22} According to this data, a micro-rough surface oxidized at 450 °C would be more hydrophilic than a smooth or rough sample oxidized at a lower temperature.

Color Characterization

Color characterization was conducted to supplement spectro-ellipsometric data. Observations of color were referenced from the literature (Table I). Table II shows the estimated oxide layer thickness based on color observations. According to these estimations, the thickness of the oxide layer increases with temperature at which the samples were annealed. Samples do not show a color change until 450 °C. The exponential increase in thickness seen at 600 °C agrees with literature results.\textsuperscript{3}

Figure 2: FTIR spectra for 300 (blue), 375 (magenta), 450 (red), 525 (green), and 600 °C (black). The increasing height of the TiO$_2$ peaks (found from 800-850 cm$^{-1}$) indicates an increasing thickness of TiO$_2$ with increasing furnace temperature. Annealing was done for 5 hours to each sample. This graph aligned properly as seen by the alignment of the CO$_2$ peaks at 667 cm$^{-1}$.

Fourier Transform Infrared Spectroscopy

FTIR spectroscopy was done for the smooth samples treated at temperatures from 300-600 °C. The smooth control sample at 24 °C was used as the background for the FTIR data. Figure 2 shows a match scale version of the FTIR data. The main peak between 830 and 870 cm$^{-1}$ is representative of TiO$_2$. The amplitude and area of the peak correlates with the intensity of the FTIR scan. This intensity is representative of TiO$_2$ thickness. Thus, the higher the peak, the thicker the TiO$_2$ layer. It can be seen that the height of the peak increases with annealing temperature. The peak at 300 °C is shortest and the peak at 600 °C is tallest. This is, as previous research has stated, the thickness of the oxide layer increases with annealing temperature (Figure 2).\textsuperscript{3}

A close-up of the TiO$_2$ peak from Figure 2 can be seen in Figure 3. The most prominent peak is TiO$_2$, which is made up of both anatase and rutile phases. The anatase and rutile peaks are indistinguishable, but the relative amounts of anatase compared to rutile can be seen through the shift in the TiO$_2$ peak. Anatase has been reported at 870 cm$^{-1}$ and 550 cm$^{-1}$ and rutile at 830 cm$^{-1}$. At lower temperatures (300 and 375 °C), the TiO$_2$ peak is closer to 870 cm$^{-1}$ (anatase). At higher temperatures (450, 525, and 600 °C), the peak can be seen closer to 830 cm$^{-1}$ (rutile). This suggests the shift of the peak from anatase to rutile as annealing temperature increases. Anatase can also be seen at 550 cm$^{-1}$ for 300 and 375 °C. This further indicates the formation
samples, surface hydrophilicity increases with oxidation temperature: this was not found for smooth samples. Through FTIR spectroscopy, it was shown that anatase exists in the range 300 - 450 °C as the primary crystalline structure. The shift from anatase to rutile was found to mostly take place between 450 - 600 °C in the FTIR spectra.

For future work, more samples and more temperatures should be tested to further investigate the precision of the anatase to rutile shift. Also, using X-Ray Diffraction (XRD) or deconvolution of the FTIR spectra would allow for better observation of the individual crystal structure peaks. In a continuation of this project, Santiago Tovar will continue with cell culture assay. He will relate the characterizations done in this experiment to the cell assay results.

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Introduction

Since the invention of the steam engine coal has been an extremely important resource to humans. Steam engines were used for industry and mechanization, railways, and ships long before liquid fuels such as diesel had been developed. Humans still rely heavily on coal for the generation of electric power. Approximately 49% of electric power generation in the United States is fueled by coal.\(^1\) In South Africa 93% of generated power comes from coal and in Poland the figure is 87%.\(^1\) Mankind’s phenomenal reliance on coal for electricity causes concern among environmentalists across the globe who lament the negative effects of coal combustion. Because coal is mostly comprised of nitrogen, sulfur, carbon, and oxygen, the combustion of coal produces nitrous oxides, sulfur oxides, and carbon dioxide. Nitrous oxides catalyze the formation of low-altitude ozone which causes shortness of breath, and is a component of smog, a dirty, irritating mixture of pollutants.\(^2\) Sulfurous oxides react with water in the body to form sulfurous acid and can cause severe respiratory harm when inhaled.\(^3\) They can also react with water in the air and precipitate as acid rain which damages buildings, infrastructure, and plant life.\(^4\) Carbon dioxide is not poisonous but it can suffocate in sufficient concentrations. All of these gases contribute to the Greenhouse Effect.\(^5\) Many nations now have “Clean Air” laws that regulate allowable emissions of pollutants. Our motivation for this research is to retard the rate of carbon dioxide pollution to the atmosphere without significantly affecting the rate of power generation of a coal-fired power plant.

Carbon Capture technologies are divided into pre-combustion capture technologies and post-combustion capture technologies. Pre-combustion capture systems partially burn fuel to create a gas stream of carbon monoxide and hydrogen gas. The carbon monoxide is reacted with steam to form carbon dioxide which is separated from the system while the hydrogen gas is used in the plant to generate heat. This is an effective system but can not be retrofitted to a plant.\(^6\) Post-combustion capture systems can take many forms including cryogenic separation of carbon dioxide, separation by passing gas through polymer membranes, adsorption of carbon dioxide, and physical and chemical absorption. Cryogenic separation liquefies flue gas which is fed to a distillation column where the CO\(_2\) is removed. This process is extremely expensive as it requires extreme cooling, compression, and expansion steps.\(^7\) Separation by polymer membranes is largely untested and current systems are unreliable.\(^7\) Adsorption systems require large equipment and therefore large operating costs to handle the large flow of flue gas.\(^6\) Physical absorption systems perform best with high concentrations of CO\(_2\), but require that systems be built to withstand high pressures.\(^6\) In large-scale applications this factor can be prohibitively expensive. Chemical absorption is the most understood of these technologies and there have been many experimental reports involving its practice.\(^6,8-11\) We believe that a chemical absorption system has the ability to be quickly implemented in an existing power plant because the process has been extensively studied and is well understood.

A model of an actual coal-fired power plant was developed in ASPEN Plus for use in this project. Each solvent absorption system had to be scaled up to match the magnitude of flows in the power plant model. The flue gas stream of the power plant was split into two equal-flow streams and a solvent absorption model was attached to each flue. Different solvents were never used in the same flow sheet. In this way six different power plant models, each using a different chemical solvent and each flow sheet having two absorption systems, were developed. The total heating requirements of the newly attached systems were determined for each flow sheet and compared to the power output of the power plant and compared to the percentage of carbon dioxide removed from the flue gas by the system. The solvent of choice will have the lowest heating requirements and will remove the highest percentage of carbon dioxide from the flue gas.
FIG. 1: ASPEN Plus model of the absorption system to be attached to the flue gas stack of the power plant for Chemical 194. All tested chemicals had a model similar to this one.

Methods

Many solvent chemicals were invented at the Vishwanmitra Research Institute for application in a chemical absorption carbon capture system. Each chemical was given an identification number to protect its chemical structure. When a chemical is chosen for implementation in a real process it will be patented and its properties will be released. Of the invented chemicals, candidate chemicals for this project were identified as having moderately high boiling points (480 K - 500 K) and as having relatively low energy requirements (determined as the amount of heat required to remove one tonne of CO\textsubscript{2} from saturated solvent, here being between 1.5GJ/tonne and 2GJ/tonne). Chemicals 194, 195, 196, 197, 198, and 202 were selected as being suitable for the project. Each solvent had an absorption system developed in ASPEN Plus Process Modeling similar to Figure 1. Liquid solvent enters through the stream SOLIN-5 and is mixed with the flue gas, FG-5, in the absorption column ABS-5. Nitrogen gas is removed from the system through stream CG-5 and the remaining compounds are passed through a pump and a heat exchanger before entering stripping column STR-5. Solvent leaves the bottom of the column and is recycled to the beginning of the process. Water and carbon dioxide leave STR-5 in the top stream CO\textsubscript{2}. The water and the carbon dioxide are then flashed and separated. The carbon dioxide is pressurized and stored. Each of the six solvents had an absorption system developed that was similar to this process.

Before the systems could be connected the model’s inputs had to be scaled to match the effluents of the power plant. To scale up the solvent models the input variables in stream 2CCSTR-5 had to be removed. Stream SOLIN-5 had to have the mol fractions of its components specified. The internal vapor and liquid flow estimates for blocks ABS-5 and STR-5 were deleted. The mol fractions of the components in stream FG-5 had to be altered to match the composition of the flue gas in the power plant. The flow of flue gas in a split stream was 12.35 kmol/sec with compositions $X_{\text{H}_2\text{O}}=0.034$, $X_{\text{Ar}}=0.009$, $X_{\text{CO}_2}=0.147$, $X_{\text{O}_2}=0.037$, $X_{\text{N}_2}=0.773$. The mol fractions of the salvation model inlet were slowly scaled up while keeping the sum of all mol fractions in the stream within 0.1 % of 1. After each alteration to the compositions the simulation would have any results present purged and the simulation would be run anew. If the simulation then did not converge the previous set of mol fractions were restored, the model was run, and another attempt at altering the compositions was made. If the simulation did converge then new estimates for stage temperature, stage liquid composition, and stage vapor composition were generated for blocks ABS-5 and STR-5 in ASPEN Plus. This process was repeated until the compositions of stream FG-5 matched that of the flue gas to the power plant model, listed above. After the compositions of FG-5 and the flue gas matched and new estimates for stage temperature, stage liquid composition, and stage vapor composition were generated the Manipulated Variable Limits in Design Spec DS-1 were multiplied by the mol-flow per time of the split flue stream and divided by the mol-flow per time of the absorption system model. The mol-flow of stream SOLIN-5 was multiplied by this quantity as well. The mol-flow of stream FG-5 was then changed to the mol-flow of the split flue stream in the power plant model. The simulation was then run and after it converged a final set of estimates were generated for stage temperature, stage liquid composition, and stage vapor composition of blocks ABS-5 and STR-5. The absorption system was then imported to the power plant model twice. Both streams leaving the flue gas splitter were deleted and each absorption system had its FG-5 stream attached to the splitter. The inputs for these newly connected FG-5 streams were deleted. The previous two streams that had been leaving this splitter were deleted, having been replaced by the flue inlets to the carbon dioxide absorption systems.

After the systems were attached to the power plant the Henry Component ID as well as the Property Specifications in the power plant model with the attached absorption systems had to be changed to DEA. Each model would converge when the simulation was run after being constructed in this way.

The power output of the plant was determined by Design Specification D-PWROUT. The heating require-
FIG. 2: The horizontal axis shows the amount of CO$_2$ (kmol) removed per second. The vertical axis is the combined heating requirement of the attached absorption systems as defined in the Introduction. From left to right the points are chemicals 195, 196, 198, 197, 202, and 194.

Results

The data found from the simulations are reported in Table I. The second row reports the power consumption of a single absorption system attached to the power plant. Since the systems were attached in duplicate the value in row two is doubled and reported as the "Overall Power Consumption" in row three. The value in row three is reported as a percentage of the total power output of the power plant, reported in row four, and is given in row five. The total amount of CO$_2$ removed by both absorption systems in a simulation is reported in row six as the "Overall CO$_2$ Removed" and reported as a percentage of the total CO$_2$ in the power plant’s flue gas.

The most important data from the simulations are the percent of CO$_2$ removed from the flue gas and percentage of power output used by the combined absorption systems. The minimum and maximum percentages of CO$_2$ removed are 63.5% and 75.6%, respectively. The minimum and maximum percentages of the power plant’s used power output are 8.96% and 17.5%, respectively. Of the chemicals tested, Chemical 194 uses the least amount of power for its combined absorption systems and captures the most amount of CO$_2$ from the flue gas.

Figure 2 plots the six tested chemicals with the amount of CO$_2$ removed per time on the horizontal axis and the energy requirement per second of the combined absorption systems on the vertical axis.

<table>
<thead>
<tr>
<th>Chemical Number</th>
<th>194</th>
<th>195</th>
<th>196</th>
<th>197</th>
<th>198</th>
<th>202</th>
</tr>
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<tr>
<td>Power Consumption (Individual)</td>
<td>30</td>
<td>58.7</td>
<td>51.4</td>
<td>47.7</td>
<td>52.2</td>
<td>32.5</td>
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<tr>
<td>Overall Power Consumption</td>
<td>60</td>
<td>117</td>
<td>103</td>
<td>95.4</td>
<td>104</td>
<td>65</td>
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<tr>
<td>Power Output of Plant</td>
<td>670</td>
<td>670</td>
<td>670</td>
<td>670</td>
<td>670</td>
<td>670</td>
</tr>
<tr>
<td>Percentage of Power Output Used</td>
<td>8.96</td>
<td>17.5</td>
<td>15.4</td>
<td>14.2</td>
<td>15.5</td>
<td>9.7</td>
</tr>
<tr>
<td>Overall CO$_2$ Removed</td>
<td>2.38</td>
<td>2</td>
<td>2.06</td>
<td>2.12</td>
<td>2.1</td>
<td>2.14</td>
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<tr>
<td>CO$_2$ Flow Rate in Un-split Flue Gas</td>
<td>3.15</td>
<td>3.15</td>
<td>3.15</td>
<td>3.15</td>
<td>3.15</td>
<td>3.15</td>
</tr>
<tr>
<td>Percentage of CO$_2$ removed</td>
<td>75.6</td>
<td>63.5</td>
<td>65.4</td>
<td>67.3</td>
<td>66.7</td>
<td>67.9</td>
</tr>
</tbody>
</table>

Discussion

As we can see from Table I, the absorption systems for chemical 194 and chemical 202 consume between half as much and a third as much energy as the other absorption systems. Chemical 202 also removes 67.9% of carbon dioxide gas entering the system and chemical 194 removes 75.6% of incident carbon dioxide. Chemical 194, having the lowest operating requirements and the highest rate of removal of carbon dioxide among our six candidate solvents, is the best chemical solvent among the tested solvents to be implemented in a carbon capture absorption system. Chemical 202 would be the secondary choice for implementation in such a system.

The Effect of Different Geometries on Percolation in Two Dimensions

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Using the model simulation developed by Weddell and Feinerman, this study found results for the percolation threshold as a function of aspect ratio for rectangle shaped holes and then compared these results to Weddell’s elliptical ones. We developed a slightly different experimental set-up than Weddell, proving that this method for collecting percolation data is repeatable and valid. The percolation threshold for both shapes has been found to exhibit a similar trend - as aspect ratio decreases, percolation threshold increases. At small aspect ratios, when both shapes are almost indistinguishable lines, the percolation threshold results are very similar. For larger aspect ratios, the differences in percolation threshold are much greater. More shapes need to be considered, but these results imply that there exists a point at which the aspect ratio of a shape does influence the percolation threshold.

Introduction

Percolation describes the movement of a fluid across a porous material. The phenomenon pervades our everyday life, but it requires complicated measures to quantify. Percolation theorist, Peter Kleban writes, “Although percolation is... arguably the simplest model... the ease of formulation of the model is in the other sense deceptive, tending to conceal its inherent complexity.” Percolation as a field has implications to the studies of not only soil physics and geology, but also biology. Agricultural scientists interested in studying the flow of water carrying nutrients through soil would use percolation models. So too, would geologists interested in fluid flow through micro-fractures in rocks. Doctors modeling the diffusion of drugs through the bloodstream have considered fractal and percolation cluster formations.

The specific quantity of interest in this study is the percolation threshold, \( p_c \). It is the smallest pathway across which fluid can flow. In more measurable quantities, it means the critical fraction of area for which a medium can still be electrically or thermally conductive. It is of interest because it can relate thermal and electrical conductivity, or a medium’s diffusion constant, to a single quantity of area through which electrons or fluid can flow.

In our experiment, we cut pores on a region until there exist no pathways which current could flow across. Through experimental measurements of current across a percolated region and a proxy region, which represents an equivalent amount of area remaining across the percolated region, we can determine a value for \( p_c \). In this specific study, random networks of 1500 rectangle shaped pores of variable aspect ratios were created. Aspect ratio is the ratio of a rectangle’s length to width. Rectangles of aspect ratio 0.0125, a long stick, to 1.000, a perfect square, were cut. We want to look at rectangles especially, because experimental research for the shape has not been done before to our knowledge. We measured how the changing aspect ratio for rectangles affects the percolation threshold, and then compared our results to the previous experimental ellipse results of Weddell et. al.

In the next section, we will discuss the framework for our percolated systems and describe, in a more mathematically explicit fashion, how the percolation threshold was calculated. Then, the physical set-up for our electrical model will be described. Lastly, we will present our results for the percolation threshold with respect to changing aspect ratio, discuss the data’s relationship to elliptical results, and cite possible sources of error.

Experimental Design and Procedure

In order to create a percolation pattern, we used the computing program MATLAB. Rectangles of specified aspect ratios were randomly generated and oriented using the program. MATLAB continues to arrange shapes beyond the point at which any current could flow across the percolated square (left square in Figure 1). The code also allows us to change the number of cuts made. In this study, the number of cuts was kept constant at roughly 1500 cuts. (According to percolation theory, the number of cuts should not affect the value of the percolation threshold obtained. We will return to discuss the significance of a finite cut number in the conclusion.)
Figure 1: Sample AutoCAD design for overlapping rectangles of aspect ratio 0.2500. The percolated region is on the left, and the effective area display is on the right.

MATLAB outputs a random system of pores to a script file, which the drafting program, AutoCAD, reads. From AutoCAD, we can output a design, for example the one shown in Figure 1, to our Universal 100 Watt CO$_2$ laser, which cuts the design into a sheet of Mylar with aluminum coating. The CO$_2$ laser cuts a few rectangles of a specified aspect ratio on the first square, our percolated region, and across the second, the laser will remove the effective amount of area for each series of cuts (right square in Figure 1). (Precisely, the effective area square is updated every time 1% or more of the area on the percolated sheet has been decreased.) Thus, this second square reflects the appropriate amount of area remaining across the percolated square.

The percolation threshold, the quantity our study focuses on, is the critical percentage of area that must remain for electrical conduction to take place. We can determine this critical fraction using the definition of resistance and looking at the change in current across our effective area region. First, in Equations 1 and 2 we use the definition of resistance. They describe the initial and final resistances, $R_0$ and $R_r$ respectively, across our effective display area. Below, $\rho$ is a constant for the resistivity of our conductive sheet, $L$ is the constant length across which we are measuring current, and $\tau$ is the constant thickness of our conductive sheet. $H_0$ is the original height of the effective area square, and $H_r$ is the height of the area remaining of that same square when the first square has been fully percolated.

\[
R_0 = \frac{\rho L}{\tau H_0} \quad (1)
\]

\[
R_r = \frac{\rho L}{\tau H_r} \quad (2)
\]

The percolation threshold is a ratio of area across the effective area side, when no current is flowing across the first square, to the initial area (see Equation 3):

\[
p_c = \frac{H_r L}{H_0 L} = \frac{H_r}{H_0} \quad (3)
\]

Using Equations 1, 2, and 3, the percolation threshold can be expressed in terms of resistances $R_0$ and $R_r$. In our experiment, a constant voltage was applied as current was measured across both squares. Using Ohm’s Law, we can express the percolation threshold in terms of currents $I_0$ and $I_r$ (see Equation 4).

\[
p_c = \frac{\rho L / \tau R_r}{\rho L / \tau R_0} = \frac{R_0}{R_r} = \frac{I_r}{I_0} \quad (4)
\]

Electrical Model

The design of the electrical model used is nearly the same as Weddell’s setup. The apparatus consists of an aluminum baseplate, which has a layer of double-sided adhesive sheet and a thin layer of conductive aluminum Mylar placed flat on top. Our model, unlike Weddell’s, can fit two runs of data, and features more space on the sides of both the percolated and effective area squares. These edges contribute some resistance, which we take into account for our calculation of the percolation threshold. The conductive sheet is divided into two squares of the same area, which are our percolation and effective area regions. At the same time as the laser is cutting both sheets, the current is measured with alligator clips on two brass rods placed across each square. Not only are the brass rods used to measure the current across both regions, but they also hold the Mylar in place. The brass rods used are secured in place with acrylic fixtures and nylon screws (which will prevent an electrical short,
unlike Weddell’s metal screws). In this model, as shapes are cut across the first square, we eliminate possible pathways for electrons to flow. So as we measure current across both squares, the current decreases to zero (resistance becomes infinite) across the percolated square. (This can be seen in Figure 2, a representative of typical raw data.)

Results

Figure 2 shows typical results from a single trial. You can see as the laser continues to cut the conductive Mylar, the current across the percolated square reaches zero (dashed), while the current measured across the effective area square (solid) steadily decreases.

As more cuts are made, the difference between the bond probability (the current percentage of area remaining) and the percolation threshold should approach zero. This means that the natural log of that difference should approach negative infinity. In Figure 3 below we can see that the \( \ln(p - p_c) \) slowly decreases at first, but then steeply decreases as more and more cuts are made. From 3750 seconds on, the \( \ln(p - p_c) \) becomes undefined (approaches negative infinity) as \( p \) becomes slightly less than \( p_c \). This also shows where the percolation threshold has been reached.

Table 1 features the results of our experiment. For each aspect ratio, 3-6 different patterns of roughly 1500 rectangular shapes were cut and the average percolation threshold is listed below. The \( \pm \) value listed is the standard deviation found for the multiple measurements taken at each aspect ratio. The percolation threshold has been calculated using Equation 3 and our experimentally measured values for current. These experimental results for rectangles are compared to elliptical results in Figure 4 below.

Discussion

Many control tests were run in order to replicate the results of Weddell et al. We collected 5 runs of data for 1000 circle cuts and found an average \( p_c \) of 0.34 \( \pm \) 0.073, close to the theoretical value Xia and Thorpe cite, 0.33, and Weddell’s value, 0.36. From this result, we can conclude that this experimental method is repeatable and valid.

The process of creating a percolated system is random, so it inherently will produce slight deviations for our results. By creating multiple distinct patterns for

| Aspect Ratio | Percolation threshold for rectangles (\( \pm \) STD) | Percolation threshold for ellipses
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0000</td>
<td>0.498 ( \pm ) 0.078</td>
<td>0.351</td>
</tr>
<tr>
<td>0.7000</td>
<td>0.533 ( \pm ) 0.046</td>
<td>0.392</td>
</tr>
<tr>
<td>0.6000</td>
<td>0.492 ( \pm ) 0.039</td>
<td>0.414</td>
</tr>
<tr>
<td>0.2500</td>
<td>0.563 ( \pm ) 0.024</td>
<td>0.588</td>
</tr>
<tr>
<td>0.1000</td>
<td>0.697 ( \pm ) 0.113</td>
<td>0.723</td>
</tr>
<tr>
<td>0.0125</td>
<td>0.969 ( \pm ) 0.008</td>
<td>0.923</td>
</tr>
</tbody>
</table>

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shapes of the same aspect ratio, and averaging the percolation threshold for each of those trials, we can try to determine the most appropriate value. For results with initially high standard deviations, more measurements of the threshold were taken to try to more accurately define the value. For example, the standard deviations for our percolation thresholds at aspect ratios 1.0 and 0.1 are relatively large. The percolation threshold for these aspect ratios could be more accurately determined by collecting more data. Results show a relatively low value for the percolation threshold at an aspect ratio of 0.6000. This is likely due to a statistical error.

Additionally, there may be a slight error due to the finite number of cuts each trial used. Theoretically, \( p_c \) shouldn’t change for the number of cuts, but it seems reasonable to think that the \( p_c \) will become more precise for a larger number of smaller cuts.\(^6\) Though it also seems reasonable to think that at some point, an increasing number of cuts won’t begin to significantly affect \( p_c \) measurements, due to the finite percolation region we are considering. More research should be conducted to describe how the number of cuts affects the percolation threshold.

Errors beyond statistical errors are very hard to measure. The error found in Weddell’s previous experimental result was attributed to a underestimating of the kerf of our laser, where kerf is the width of a laser’s cut. A MATLAB code was developed that arranged rows of circles a specified width apart. When no current was measured across the region, we knew the distance between each row was the same as the kerf of the laser. We have precisely found the kerf to be 114 microns, so we believe we have little error associated with the laser, unlike Weddell’s results.\(^1\)

It is seen in Figure 4, that generally, for rectangle shaped holes, the percolation threshold increases as the aspect ratio decreases. This is a trend that ellipses also exhibit.\(^1\) This result is explained by Weddell as being due to the fact that holes that are nearly lines will still block the current from flowing, but have much smaller area as compared to circles or squares.\(^1\) At small aspect ratios, the percolation thresholds for ellipses and rectangles are close to each other. This makes sense because at an aspect ratio of 0.0125, both rectangles and ellipses are very thin and appear to be nearly the same shape. At larger aspect ratios, the difference between percolation threshold values for rectangles and ellipses is more significant because these shapes are more distinct. This result seems to suggest that there is a value of the aspect ratio at which the shape’s geometry seems to uniquely affect the measured percolation threshold. (Our best guess for this value would be somewhere around an aspect ratio of 0.5000.)

Conclusion

This study verifies that the experimental method Weddell and Feinerman have developed is indeed valid. We have repeated circle results and found a \( p_c \), not only close to Weddell’s result, but also consistent with prior published theoretical values. Our results for rectangle shaped holes exhibit a very similar trend as our elliptical results as the aspect ratio approaches zero, the percolation threshold approaches one. At small aspect ratios, we find our rectangle results in close agreement with elliptical data. The most significant observation we can make looking at our data is that for some critical aspect ratio, the percolation thresholds for rectangles begin to differ from ellipses (around roughly 0.5000). Future work could be done trying to more precisely pinpoint the aspect ratio at which the percolation threshold begins to deviate. Also more work could include looking at different shapes, such as triangles.

Acknowledgements

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Introduction

Traditionally, ferroelectric and ferromagnetic materials have been used for actuators, optoelectronic devices, capacitors, information storage devices, and sensors. However, recently, multiferroic materials, materials which demonstrate both magnetic and ferroelectric properties, have piqued great interest. This unique combination of ferromagnetic and ferroelectric ordering means these materials have a wide range of potential uses for which standard ferromagnetic and ferroelectric materials are not ideally suited. In multiferroic materials, electric polarization can be used to influence ferromagnetic polarization, thereby manipulating magnetization and ferromagnetic ordering. Multilayer heterostructures of these materials are of particular interest, because they allow for control of electron spin polarization which has a number of applications in the area of magnetic sensors and devices. Further research into and development of these novel heterostructures could demonstrate unusual uses only appropriate for these materials. It is believed that the end result of this research will be the realization of multicomponent multiferroic systems which afford electrical control of magnetism.

Contemporary research in this area has focused on thin film, hetero-epitaxial bilayers, of ferromagnetic (FM) and antiferromagnetic (AFM) materials. These bilayers exhibit three distinctive phenomena which merit further research: exchange bias (EB), exchange enhancement (EE), and exchange coupling (EC). Exchange bias is a shift of the hysteresis loop of a material along the field axis, in the case of FM/AFM, specifically La$_{0.7}$Sr$_{0.3}$MnO$_3$ and SrRuO$_3$ bilayers in the positive direction. Exchange enhancement is an augmentation of the coercive field of the ferromagnetic layer as a result of exchange interaction. Finally, exchange coupling is an interaction between the spin states of the atoms in between the ferromagnetic and antiferromagnetic layers; it is the base effect that allows for EB and EE. These phenomena are extremely important in the development of multiferroic bilayers.

The pairing of ferromagnetic lanthanum strontium manganite oxide (La$_{0.7}$Sr$_{0.3}$MnO$_3$, LSMO), with multiferroic, ferroelectric bismuth ferrite (BiFeO$_3$, BFO) has merited considerable study. On its own LSMO possesses a high Curie Temperature of 370 K and interesting colossal magneto resistance properties which are active at and above room temperature making it an ideal candidate for research. LSMO is a rare earth manganite which, with hole doping, becomes a member of an intriguing family of conductive and ferromagnetic materials which have potential uses as memory materials, sensors, and as electrodes in ferroelectric films. Similarly, BFO has been the subject of research because it is ferroelectric and anti-ferromagnetic with a high Curie temperature of ~ 537 K and a high Neel temperature of ~ 640 K. The combination of a high Curie and Neel temperature allows for coupling of magnetic and electrical orders at high temperatures making BFO a promising material for the development of multiferroic technologies; the most prominent being tunnel junction devices based on thin films of BFO. Studies on bilayers of BFO and LSMO are advantageous, especially when compared to earlier studies focusing on bilayers of transition metal anti-ferromagnetic alloys and metallic ferromagnets, because they are both perovskites and have similar lattice parameters, 0.396 nm for BFO and 0.387 nm for LSMO. This allows for very close control of film growth, ensuring the multilayers are epitaxial which is integral to the investigation of the exchange effects.
between the ferromagnetic and anti-ferromagnetic layers. Additionally, bilayers are grown on substrates that possess a perovskite structure to further ensure uniform crystalline structure throughout. The most commonly used substrates are Lanthanum Aluminate (LaAlO$_3$) and Strontium Titanate (SrTiO$_3$)$^3$.

As of yet, researchers know very little about how complex interfacial phenomena between layers of the film affect magnetic properties.$^{1,6,7}$ It is necessary to understand how local types of interference at layer boundaries including diffusion of chemical species, deviations from stoichiometry, and lattice mismatch resulting from different lattice parameter between the FM and AFM layer effect bilayer properties in order to fully characterize these heterostructures and utilize them in novel technologies.$^{6,7}$ This paper reports on experiments to determine how varying bilayer parameters effect interfacial interactions. First, the substrate on which the bilayers are grown will be varied between LaAlO$_3$ and SrTiO$_3$. Second, the thickness of the BFO and LSMO layers will be varied to determine which components of the bilayer dominate in interfacial interaction. Finally the order in which the layers are deposited will be varied in order to fully characterize component interaction. These experiments will hopefully serve as the basis for future research into the magnetic interaction of LSMO and BFO bilayers.

Films will be grown using Pulsed Laser Deposition and will be characterized by transmission electron microscopy (TEM), x-ray reflectivity (XRR) and diffraction (XRD) techniques, and x-ray photoelectron spectroscopy (XPS). Pulsed laser deposition is used because it is ideal for the deposition of complex oxides as it preserves stoichiometry and can be performed in the presence of a background gas such as O$_2$, ensuring proper film growth.$^8$ Transmission electron microscopy probes the local crystal structure, and provides evidence about the crystalline phase of the film and alignment between layers of the film. X-ray reflectivity and diffraction techniques are used for analysis as they provide a detailed electron density profile which can be used to judge film characteristics, the most important being the crystallinity of the whole film, the thickness of the FM and AFM layers, lattice mismatch, and diffusion of one component into another. Finally, XPS probes the composition of certain areas of the surface of the film, and can be used to determine the changes in stoichiometry between the target material and the deposited layer.

Materials and Methods

5 mm × 5 mm × 0.5 mm silicon, quartz, LaAlO$_3$ (100), and SrTiO$_3$ (100) substrates with one side polished, and a miscut of $0^\circ$ manufactured by CrysTec were used in all experiments. BiFeO$_3$ and La$_{0.7}$Sr$_{0.3}$MnO$_3$ rotating rod targets, manufactured by Kurt J. Lesker, were used in all experiments. These targets were constructed from pre-synthesized oxide powders using a low stress powder compression technique. Pulsed laser deposition was carried out using a pulsed KrF excimer laser with an output wavelength of 248 nm and a pulse duration of 15 ns.

Before beginning film deposition, the growth rate of perovskite films on a perovskite substrate in the available PLD setup was determined. LaAlO$_3$, Silicon, and Quartz substrates were layered on one another so as to form steps. Layering substrates on top of another means portions of the substrate surface are protected from depositing material and no film forms there, and at the boundary between the protected and unprotected surface a plateau forms, which can be measured in order to determine the thickness of the deposited film. The substrates were then mounted on the deposition stage. A sanded and polished LSMO target was mounted in the vacuum chamber. The chamber was sealed and vacuum pumped until the pressure reached 5*10$^{-4}$ torr. The substrates were heated to 650$^\circ$ C over a period of 30 minutes and the target was pre-ablated for 500 pulses. Once the substrate reached the target temperature background O$_2$ gas was introduced at a pressure of 10$^{-2}$ torr and 12,000 pulses of LSMO were deposited with a shot frequency of 5 Hz and a laser fluence of 1.5 J cm$^{-2}$. The distance between target and substrate was 4.5 cm. Following the deposition, vacuum was reestablished and the substrate was allowed to cool to room temperature over 1.5 hours. The substrates were removed, separated, and sonicated in acetone and methanol to wash off any adhesive. Film thickness was measured using a stylus profilometer and divided by the number of pulses to determine the growth rate, which was 0.014 nm/pulse. This growth rate can be applied to all substrates and targets as only perovskite type materials are used and all deposition parameters are held constant.

For the actual depositions, targets were sanded and polished at room temperature and substrates were sonicated for 5 minutes in acetone, then 5 minutes in methanol. Substrates were affixed with silver paint glue either directly to the deposition stage, or on a rotating sample mount that allowed for deposition on multiple substrates without breaking vacuum. Targets were pre-ablated for 500 pulses at a pressure of 5*10$^{-4}$ torr. Substrates were heated to 650$^\circ$ C over a thirty minute period. High temperatures insure epitaxial film growth; the slow heating prevents the buildup of thermal stresses which could damage the substrate. The substrate was held at 650$^\circ$ C for the entire deposition process. Once the ablation temperature was reacted O$_2$ gas was introduced at a pressure of 10$^{-2}$ torr, this pressure that was maintained throughout deposition. The laser was pulsed at a frequency of 5Hz with a laser fluence of 1.5 J cm$^{-2}$. The distance between target and substrate was 4.5 cm. Following deposition, the O$_2$ supply was removed and pressure lowered to 5*10$^{-4}$ torr. The substrate was then cooled to room temperature over a period on 1.5 hours, again to insure no damage due to thermal stressing. Substrates were removed from the setup, excess glue was sanded away and the samples were cleaned and stored.
<table>
<thead>
<tr>
<th>Thickness</th>
<th>Pulses for</th>
<th>Thickness</th>
<th>Pulses for</th>
<th>Order of layers on substrate (bottom/top)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSMO (nm)</td>
<td>LSMO Deposition</td>
<td>BFO (nm)</td>
<td>BFO Deposition</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>150</td>
<td>10,580</td>
<td>BFO</td>
</tr>
<tr>
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<td>10,580</td>
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<td>BFO</td>
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<td>200</td>
<td>14,100</td>
<td>150</td>
<td>10,580</td>
<td>BFO/LSM/O</td>
</tr>
<tr>
<td>250</td>
<td>17,630</td>
<td>150</td>
<td>10,580</td>
<td>BFO/LSM/O</td>
</tr>
<tr>
<td>150</td>
<td>10,580</td>
<td>0</td>
<td>0</td>
<td>LSMO</td>
</tr>
<tr>
<td>150</td>
<td>10,580</td>
<td>150</td>
<td>10,580</td>
<td>LSMO/BFO</td>
</tr>
<tr>
<td>150</td>
<td>10,580</td>
<td>200</td>
<td>14,100</td>
<td>LSMO/BFO</td>
</tr>
<tr>
<td>150</td>
<td>10,580</td>
<td>250</td>
<td>17,630</td>
<td>LSMO/BFO</td>
</tr>
</tbody>
</table>

TABLE I: Listing of films Deposited. Two sets of the following films were deposited one on LaAlO$_3$ and one on SrTiO$_3$ for future analysis. For a detailed listing of the films deposited see Table I.

X-ray diffraction and reflectivity measurements were performed on the manufactured samples using the Rigaku-ATXG diffractometer at the NU X-Ray Facility. For XRD analysis the diffractometer was in the slit collimation geometry with S1 set to 0.5 mm (h) x 2 mm (v) and S2 set to 0.01 mm (h) x 2 mm (v) S3 and R were replaced with a soller slit so only peaks from the film, not the substrate, were seen. Omega was locked at 0.5° and 2Theta was scanned from 20° to 60°. For XRR the diffractometer was in the GE111 Crystal geometry with S1 set to 0.5 mm (h) x 2 mm (v), S2 set to 0.01 mm (h) x 2 mm (v), S3 set to 0.2 mm (h) x 5 mm (v), and R = 0.2 mm (h). The incident beam flux was $2.1 \times 10^6$ photons/sec. The step size for our scans was 0.001°. Data was fit using the Motofit package available within IGOR thin film analysis software.

TEM imaging and XPS analysis were performed by outside technicians. A TEM sample was made from the 150 nm BFO LaAlO$_3$, and was analyzed by Riad Alzghier of the Laboratory for Oxide Research and Education (LORE). XPS analysis was performed on 150 nm BFO SrTiO$_3$ films.

Results

The TEM images in Figure 1A demonstrate that BFO films deposited by PLD are highly crystalline. The structure of the BFO film and the LaAlO$_3$ substrates is highly ordered. There are no visible grain boundaries in the film or substrate so it is possible that this is a single crystal film. This observation is supported by the electron diffraction pattern shown in Figure 1B which indicates that there is only one crystalline phase in the BFO layer. Additional TEM analysis indicates that the BFO layer is approximately 300 nm thick, twice the anticipated thickness. This may be a result of measuring growth rate only with LSMO, it was assumed that this value could be applied to BFO as BFO and LSMO have the same perovskite structure however TEM data demonstrates otherwise. It is important to note that TEM data is highly localized, and only samples a small portion of the surface, therefore, on the whole, film characteristics may deviate from the results pictured here.

XRD analysis indicates that 9 of the 16 films deposited are amorphous as is the case for the 150 nm LSMO 150 nm BFI LaAlO$_3$ film in Figure 2B, and five are nanocrystalline as with the 150 nm BFO SrTiO$_3$ film shown in Figure 2D. Nanocrystalline films have very small crystalline domains, on the order of 5 nm to 10 nm. There were two films that demonstrated crystalline order however. Figure 2C shows that the 150 nm BFO SrTiO$_3$ film is nanocrystalline in agreement with the TEM data for that film (Figure 1). Finally, the 150 nm BFO 150nm LSMO SrTiO$_3$ film, XRD data shown in Figure 2A, is the highest quality film deposited. There is a sharp diffraction pattern

FIG. 1: A) is a normal contrast image of the 150 nm BFO LaAlO$_3$ film. B) is an electron diffraction pattern for the 150 nm BFO LaAlO$_3$ film.
Table II: Size of crystallites in nanocrystalline films

<table>
<thead>
<tr>
<th>Film</th>
<th>θ (radians)</th>
<th>B(2θ) (radians)</th>
<th>Crystallite Width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>150 nm BFO SrTiO₃</td>
<td>0.263</td>
<td>0.111</td>
<td>5</td>
</tr>
<tr>
<td>150 nm LSMO SrTiO₃</td>
<td>0.256</td>
<td>0.0803</td>
<td>8</td>
</tr>
<tr>
<td>150 nm BFO 150 nm LSMO LaAlO₃</td>
<td>0.265</td>
<td>0.111</td>
<td>5</td>
</tr>
<tr>
<td>200 nm BFO 150 nm LSMO SrTiO₃</td>
<td>0.259</td>
<td>0.0986</td>
<td>6</td>
</tr>
<tr>
<td>250 nm LSMO 150 nm BFO SrTiO₃</td>
<td>0.254</td>
<td>0.116</td>
<td>5</td>
</tr>
</tbody>
</table>

To further analyze the nanocrystalline the Scherrer Equation, shown below, was used to determine the size of the crystallites.

\[
B(2θ) = \frac{K\lambda}{L\cosθ}
\]

\[B(2θ) = \text{Peak Width (radians)}\]  
\[\lambda = 0.1542 \text{ nm}\]  
\[L = \text{Crystallite Width (nm)}\]  
\[θ = \text{d-spacing (radians)}\]  
\[K = \text{Scherrer Constant (Assumed to be 1)}\]

The Scherrer Equation relates peak width, B(2θ), to crystallite size, L. After analyzing the data in Table II, it was determined that the crystallites in the nanocrystalline samples range in size from 5 nm to 8 nm approximately. The average crystallite size is 5.8 nm, rather large crystallites for nanocrystalline films. However, these values are tentative estimates, as the data has not been corrected to account for peak widening resulting from instrumentation, and not the film itself.

To determine if the poor structure of the films was a result of the deposition process a new 150 nm BFO SrTiO₃ sample was deposited using an alternate deposition process. The deposition temperature and pressure and the cooling/annealing temperature and pressure were changed. In this case the substrate was held at 670°C during deposition, and the O₂ background pressure was held at 2*10⁻² Torr. When deposition finished the oxygen background pressure was increased to 700 Torr. The sample was then cooled to 390°C and held at that temperature for 1 hour to anneal, an additional step to ensure oxygen was not diffusing out of the film. Following annealing the film was removed from the PLD setup and analyzed via XRD as shown in Figure 3. The resulting data had no clear features indicating it might be amorphous and of lower quality than the original film. To further understanding of what was going on this new film was subsequently analyzed by XPS, these results will be discussed later.

XRR did not afford much valuable information. The films were too rough to accurately model the extremely fine oscillations at high Q values seen in Figure 4. Of particular interest is the gradual decline in R which is very indicative of a high roughness film. Additionally the intensity of the X-rays used for XRR analysis was particularly low washing out R oscillations which are usually very prominent, but are barely visible in the XRR data. As a result this model does not provide accurate thickness information since the roughness was too high and the films were possibly too thick. Finally the most accurate model includes a high density, high roughness surface layer. This is not unphysical as the samples could not be fully cleaned before analysis as washing might have damaged the films. The upper layer is likely a combination of organic residue and possibly silver particles from
the adhesive used to attach the substrate to the deposition stage which remained on the surface after sonication. However, as of yet the fit is not of sufficient quality to draw specific conclusions.

XPS analysis confirmed shown in Table IV confirms that using the original deposition procedure, the stoichiometry of the deposited film roughly matched the stoichiometry of the starting target material. In spite of this, there is an observed iron deficiency in the sample prepared using the new technique described earlier. This discrepancy needs to be studied further to realize stoichiometric films. It is possible this deficiency caused the new sample to appear amorphous in the XRD data in Figure II. XPS is a surface sensitive technique, only sampling the top several nanometers of a film so it is possible that stoichiometry deviations may not persist as the sampling depth is increased.

### Conclusion/Discussion

In conclusion, while the films deposited were not epitaxial there is evidence that several of the films are highly crystalline. However there were a number of amorphous and nanocrystalline samples indicating problems during deposition. In order to identify the problem, an alternative experimental procedure was used to deposit a film to test this hypothesis, but the resulting film had abnormal stoichiometry deviations and no conclusions could be drawn. It was observed that PLD in an O$_2$ background preserves stoichiometry when depositing complex oxides. Finally, XRR data indicated films have high roughness and the model is incapable of providing accurate thickness data.

It is clear that the deposition process for LSMO and BFO has to be optimized to realize epitaxial growth. It is believed that low film quality is a result of the diffusion of oxygen out of LSMO and BFO during cooling. The formation of oxygen vacancies in the film results in the creation of multiple crystalline phases and may even result in metal precipitates like iron or bismuth. It would be advantageous, in the future, to experiment with raising oxygen pressure during cooling. This new procedure was attempted, but the resulting film was not suitable for use due to an iron deficiency. It may also be worthwhile to check the stoichiometry of the targets used as they are old and have been used multiple times. It is possible there are defects in the targets which are affecting the structure of the deposited films.

To close, while epitaxial multilayers of BFO and LSMO were not successfully deposited several key points were confirmed. Pulsed Laser deposition is capable of preserving stoichiometry and producing crystalline growth when depositing complex oxides. In the future it will be possible to refine deposition parameters to ensure epitaxial growth. One just needs to continue manipulating the O$_2$ background pressure and deposition and annealing temperatures and times. Additionally, in the future the targets used for deposition should be examined to ensure damage to the starting material is not affecting the deposited films. This study will provide guidance for future experiments using multilayers of BFO and LSMO.

### Acknowledgements

The financial support from the National Science Foundation, EEC-NSF Grant # 1062943 is gratefully acknowledged. The authors would like to thank Professors Jurisch and Takoudis for organizing the REU Program.

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**TABLE IV: XPS Results for original 150 nm BFO SrTiO$_3$: Proper Stoichiometry Observed**

<table>
<thead>
<tr>
<th>Peak</th>
<th>Position (ev)</th>
<th>FWHM (ev)</th>
<th>Raw Area (CPS)</th>
<th>RSF</th>
<th>Atomic Mass Conc. (%)</th>
<th>Atomic Conc. (%)</th>
<th>Mass Conc. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi 4f</td>
<td>156</td>
<td>2.767</td>
<td>1302850</td>
<td>9.140</td>
<td>208.98</td>
<td>21</td>
<td>68</td>
</tr>
<tr>
<td>Fe 2p</td>
<td>708</td>
<td>4.572</td>
<td>378805.0</td>
<td>2.957</td>
<td>55.846</td>
<td>19</td>
<td>17</td>
</tr>
<tr>
<td>O 1s</td>
<td>527</td>
<td>3.162</td>
<td>318230.0</td>
<td>0.780</td>
<td>15.99</td>
<td>60</td>
<td>15</td>
</tr>
</tbody>
</table>

Tunability of Atomic Layer Deposition of Yttria-Stabilized Zirconium Oxide for use in Solid Oxide Fuel Cells

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Thin films of yttria-stabilized zirconium oxide (YSZ) were successfully deposited using atomic layer deposition (ALD) for use in solid oxide fuel cells (SOFCs). YSZ was deposited on p-Si(100) by ALD using Tris(isopropyl-cyclopentadienyl)yttrium and tris(dimethylamino)cyclopentadienylzirconium [ZyALD] as metal precursors and ozone as oxidant. The normalized ALD cycle ratio of yttria cycles / total cycles used in making these films was varied to investigate the tunability of this process. Spectral ellipsometry was used to measure the thickness of the films. X-ray photoelectron spectroscopy (XPS) analyses were used to evaluate the composition and binding environments of as-deposited YSZ films. The normalized cycle ratio and the yttrium atomic percentage (Y atoms / metal atoms) have a linear relationship with a strong correlation, implying excellent tunability for this process. The binding environment analyses determine the oxidation state of the metals and show that decreasing the cycle ratio decreases the extent of yttrium hydroxidation.

Introduction

Solid Oxide Fuel Cells (SOFCs) show great potential for future energy generation\(^1\). SOFCs are more efficient and have better stability than other types of fuel cells, but generally operate at very high temperatures (750-1000 °C)\(^2\). The electrolyte of SOFCs must conduct ions between the electrodes but not conduct electricity. The high operating temperatures of SOFCs are due to the high temperatures required by the solid electrolytes to conduct ions. One way to reduce the operating temperature of SOFCs while maintaining functionality is to make the electrolyte thinner\(^1\). A very thin electrolyte reduces the resistance of the electrolyte, allowing the SOFC to be operated at lower temperatures. This work seeks to create a thin layer of yttria-stabilized zirconia (YSZ) for use in electrolytes of SOFCs and to investigate factors affecting the development of these thin films.

YSZ films have been regarded as one of the leading components for enabling future fabrication of intermediate temperature SOFCs (ITSOFCs). Also, YSZ has been widely investigated as a traditional electrolyte for SOFCs because of its high ionic conductivity and low electronic conductivity\(^3\). This films of YSZ have been deposited using many physical vapor deposition techniques such as electron beam evaporation\(^4\), laser ablation\(^5\), and plasma spraying\(^5\).

In addition to the techniques mentioned above, YSZ thin films have also been deposited using atomic layer deposition (ALD). ALD is a modified type of chemical vapor deposition (CVD) in which gas phase reactants are introduced one at a time. Excess reactants are purged after each exposure, leaving a monolayer of reactant on the substrate. This monolayer then reacts with the other gas-phase reactant to create solid product on the substrate. Growth of film per cycle is generally constant\(^6\), which allows deposition of highly conformal, thickness-controlled films\(^7\). ALD is of particular interest for use in development of SOFCs due to its ability to control thickness to the sub-monolayer level. ALD can also be used to deposit composite materials or ternary oxides by alternating cycles of each component or oxide\(^7\). It is this feature of ALD that makes its use suitable for the deposition of YSZ, a ternary oxide.

Others have used ALD to deposit YSZ. Zirconium with cyclopentadiene and methyl groups have been used as a zirconium precursor in the ALD of YSZ\(^8,9\). These precursors yielded high growth rates but carbon and hydrogen impurities\(^8,9\). ZrCl\(_4\) has also been used as a zirconium ALD precursor, but has been shown to leave chlorine impurities\(^3,8\). Y(thd)\(_3\) has been used as a yttrium precursor for ALD of YSZ\(^3,8,9\), however it has also been found to leave carbon impurities\(^3\). The use of tris(dimethylamino)cyclopentadienylzirconium
in ALD of Zirconium oxide has been investigated to some extent\textsuperscript{10}, but its use in YSZ deposition has not been fully explored. The use of this and tris(isopropyl-cyclopentadienyl)yttrium as zirconium and yttrium precursors, respectively, for ALD of YSZ has not to date been extensively investigated.

The composition of a thin film of YSZ is very important if it were to be used as the electrolyte of a SOFC. As a composite, film composition of YSZ can be largely controlled by varying the number of yttria cycles to zirconia cycles, or the cycle ratio. However, the composition of the film is not exactly the cycle ratio because less than one monolayer of material is deposited per cycle due to steric hindrance. In this study, the relationship between the ratio of yttria cycles : zirconia cycles and the final composition of the film is determined. Impurities from the above precursors are also investigated.

**Experimental**

Tris(isopropyl-cyclopentadienyl)yttrium and tris(dimethylamino)cyclopentadienylzirconium were the yttrium and zirconium precursors, respectively. UV radiation of oxygen gas (99.999% purity) immediately upstream of the reactor was used to generate the ozone (1000 ppm ozone), which was used as the oxidizing agent. Argon (99.999% purity) was used as a carrier for the metal precursors and as a purge gas.

A custom-built hot wall reactor was used, shown schematically in Fig. 1. The base pressure of the reactor was 2.67 Pa (20 mTorr) and the base temperature of the reactor was 25-450 °C. The reaction chamber was kept at 66.7 Pa (500 mTorr) and 270 °C. The yttrium precursor was kept at 110 °C, the zirconium precursor was kept at 50 °C, and each line from the precursor to the reaction chamber was kept 20 °C higher than the respective precursor bubbler. During a yttria cycle, yttrium precursor was pulsed for 8 s and purged for 10 s. Ozone was pulsed for 1 s and also purged for 10 s. Zirconium precursor was pulsed for 5 s per cycle, with purge and ozone pulse times the same as with the yttria cycle.

Samples were grown on p-type Si(100) wafers (15 mm x 20 mm). Wafers were cleaned using a 1:1:5 solution of \( \text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O} \) for 15 min, then rinsed with deionized water to remove any organic residues. Wafers were dried under \( \text{N}_2 \) then dipped in 1% HF for 10 s, rinsed with deionized water, and dried again under \( \text{N}_2 \). This process was performed to reduce the native oxide layer on the silicon surface. Samples were made with yttria cycles : zirconia cycles of 1:7, 1:2, and 1:1.

Thickesses of samples was analyzed using a spectral ellipsometer (J.A. Woollam Co., Inc., model M44). Compositional analysis was performed using high-resolution X-ray photoelectron spectroscopy (XPS) (Kratos Analytical Ltd., Kratos AXIS-165). This XPS uses a monochromatic Al K\( \alpha \)(1486.6 eV) X-ray source which operates at 10 mA and 15 kV.

**Results and Discussion**

All samples were found to be 14 nm thick using spectral ellipsometry. The thickness was highly uniform across all samples.

XPS data can be found in Figure 2. Before calibration, yttrium 3d peaks can be found at a binding energy of 156-157 eV, zirconium 3d peaks can be found at 179-180 eV, and oxygen peaks can be found at 528 eV. These values are consistent with other XPS data of YSZ\textsuperscript{11}. As the cycle ratio decreased (number of yttria cycles decreased with respect to zirconia cycles), the intensity of the yttrium 3d peaks decreased and amount of zirconium increases.

Using the XPSPEAK software, the atomic fractions of yttrium and zirconium (Y atoms / total metal atoms and Zr atoms / total metal atoms respectively) were deter-
mined from the XPS data. The yttria atomic fraction was compared to the normalized cycle ratio (yttria cycles / total cycles) to determine the tunability of this process. For a cycle ratio of 1:1, it was found that 53.2% of the metal atoms in the film were yttrium. At a cycle ratio of 1:2, 35.6% of the metal atoms in the film were yttrium, and at a cycle ratio of 1:7, this number was 13.1%. This data is highly consistent with other research on the ALD of YSZ\cite{12,13}. Figure 3 shows the correlation between atomic yttrium fraction and normalized cycle ratio. The line of best fit has slope of 1.071 ± 0.008 and an intercept of -0.002 ± 0.003 and a correlation value of 0.9999. This shows that changing the cycle ratio changes the amount of zirconium and yttrium in a linear manner.

The peak position in the XPS data was calibrated using the carbon peak location using the XPSPEAK software. The location of our calibrated peaks are also consistent with literature\cite{11}. The calibration allowed the zirconium 3d and yttrium 3d peaks to be fitted using component peaks using this software. Figure 4 shows the yttrium 3d peaks and their component Y$_2$O$_3$ and YOH peaks. The intensity of the yttrium peaks, and therefore the amount of yttrium, decreases with decreasing cycle ratio. The intensity of the YOH peak also decreases with decreasing cycle ratio. The entirety of the yttrium peak for the sample with cycle ratio of 1:7 was perfectly fitted by only a Y$_2$O$_3$ peak, making the addition of a fitted YOH unnecessary; this implies the yttrium peak in this sample is entirely Y$_2$O$_4$. Figure 5 shows zirconium 3d peaks and their component ZrO$_2$ peaks. The amount of zirconium increased with decreasing cycle ratio. All of the zirconium peaks were able to be fitted using only ZrO$_2$ peaks, meaning that all of the zirconium in the film is in the form of zirconium oxide.
Conclusions

When the cycle ratio is decreased, there are a greater total number of zirconia cycles than at higher cycle ratios, making the sample have more zirconia when the cycle ratio is low. The total number of yttria cycles decreases with decreasing cycle ratio, so it is expected that the amount of yttrium in the sample decreases as cycle ratio decreases.

The strong correlation between metal composition and cycle ratio implies that this ALD process is highly tunable. The cycle ratio can be changed to accurately change the composition of the film. The highly tunable nature of this process is most likely due to the consistency of the ALD reactor used as well as the efficacy of the precursors.

It was also found that decreasing the cycle ratio decreased the amount of YOH. The last cycle in these films was always zirconia, therefore the higher the cycle ratio, the more zirconia cycles were on top of the last yttria cycle. As yttrium forms YOH when exposed to air, YOH was most likely prevented from forming at lower cycle ratios by these additional zirconia layers between the yttrium in the last yttria cycle and the air.

Acknowledgments

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Atomic Layer Deposition of Cerium Oxide for Potential Use in Solid Oxide Fuel Cells

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With the growing need for sustainable energy, solid oxide fuel cells are an attractive alternative for power generation since they are efficient and environmentally friendly. However, required high operating temperatures limit their widespread use. The two ways to reduce the operating temperature of solid oxide fuel cells is to decrease the thickness of the electrolyte and to use new materials that have lower ion resistivities. In this study, both methods were employed. Currently, yttrium stabilized zirconium is the material used in solid oxide fuel cells as the electrolyte, and in this study cerium oxide was examined to be a potential replacement. To decrease the thickness of the electrolyte, thin films production techniques can be used. One technique for making thin films is atomic layer deposition, also known as ALD, which uses alternating saturative surface reactions. ALD creates films that have good conformality, are pin-hole free, and thickness is easily controlled. In this study, the atomic layer deposition of cerium oxide was studied for potential use in solid oxide fuel cells as the electrolyte and anode. The optimum precursor temperature was found to be 130 °C and the water pulse length was found to be 55 msec. The ALD window, which is the temperature range of ideal ALD growth, was determined to be 210 to 280 °C, the surface was saturated when at least four plugs of precursor pulses were used in the procedure, and the growth was linear at 1.2 Å/cycle.

Introduction

With the rising need for sustainable energy, fuel cells are an attractive alternative for power generation and are now becoming practical for wide spread use. Fuel cells are generally characterized by the material that the electrolyte is made of. Examples include alkaline fuel cells, PEM fuel cells, and solid oxide fuel cells. With no nitrogen oxides, sulfur oxides, or hydrocarbon emissions, very little CO₂ emissions, high efficiency, and fuel flexibility, solid oxide fuel cells are a sustainable power source for high power applications. However, solid oxide fuel cells have very high operating temperatures- in the range of 800 to 1000 °C. The high operating temperatures forces the cells to have long heat up and cool down periods, and the materials that a cell can be made of is currently limited since the thermal expansion coefficients for cell layers must be close.

There are three parts of a solid oxide fuel cell- the anode, the cathode, and the electrolyte which is made of a solid inorganic oxide. As seen in Fig. 1, the fuel, which is hydrogen gas or a hydrocarbon such as methane, biogas, or landfill gas, enters at the anode. The fuel is reformed into hydrogen and carbon monoxide either at the anode or before entering the cell. On the cathode side, air containing oxygen enters, and oxygen is reduced to oxygen ions which then travel though the electrolyte. Once the ions reach the anode, they react with the fuel to produce carbon dioxide and water. The electrons move from the anode to the cathode through an external circuit where they can perform electrical work.

There are two ways to lower operating temperatures. The first is to change the materials that the electrolyte is made of to a material with a lower ion resistivity, and the second is to decrease the thickness of the cells electrolyte which lowers the ion resistivity. A way to decrease the thickness of the electrolyte is by making the components of the cell out of thin films. There are multiple ways of creating thin films including physical vapor deposition which is a purely physical process, and chemical vapor deposition, a chemical process frequently used in the semi-conductor industry. Chemical vapor deposition includes atomic layer deposition which is a technique for creating thin films with control down to the atomic level.

There are many benefits of using atomic layer deposition over other thin film manufacturing techniques. ALD (atomic layer deposition) creates highly uniform and pinhole-free films, and the process is reproducible. Another benefit is that the reaction is self-limiting- once all of the saturation sites are filled, the reaction is complete which means that the exact stoichiometric ratios do
not need to be known. The film thickness is also easily controlled by the number of cycles. Atomic layer deposition is also insensitive to small temperature changes during the process when operating in the ALD window which is the temperature range in which ALD behavior is nearly ideal. Below this range, condensation or incomplete reactions may occur and above this range decomposition or desorption may occur.

ALD creates films by using alternating saturative surface reactions between a precursor, a coreactant, and the surface. The process is cyclic with each cycle containing four steps. The first step is to pulse the first precursor into the reactor using an inert carrier gas, and the precursor saturates the surface. Once enough time has been allowed for all sites to be filled, the first purge takes place. In this step, an inert gas is pulsed through the reactor to remove the excess of the precursor so it does not react with the coreactant in the vapor phase. Once the reactor has been evacuated, the coreactant is pulsed into the chamber where it reacts with the surface to complete the first monolayer. To finish the cycle, the reactor is purged again. Cycles are performed until the film is at the desired thickness. This process can be viewed in Fig. 2.

In this study, atomic layer deposition was used to create cerium oxide for use in solid oxide fuel cells as the anode and electrolyte. Cerium oxide is a valid replacement for yttrium doped zirconium (better known as YSZ), which is currently used as the electrolyte in solid oxide fuel cells, because the ion permeability of cerium oxide is higher at lower temperatures than YSZ. Previous studies creating cerium oxide using ALD have taken place using β-diketonates ligands as precursors. The precursor being used was tris(i-propylclopentadienyl)cerium and the coreactant was water. Tris(i-propylcyclopentadienyl) cerium was used because it reacts with water and β-diketonates ligands do not. The goals were to find the optimal ALD conditions for the growth of cerium oxide including the ALD window, the saturation curve, and the linear growth dependence.

Materials and Methods

The custom-built hot wall reactor was brought to 0.18 Torr by a vacuum pump and was brought to the desired temperature by a heating coil that surrounded the quartz tube that held the sample. The system contained three precursor vessels and deionized water in an ice bath as the coreactant. Nitrogen gas was the carrier gas.

FIG. 1: Fuel is fed to the anode of the solid oxide fuel cell where it is reformed to hydrogen and carbon monoxide while oxygen is feed to the cathode. Electrons provided from the half-cell oxidation reaction at the anode travel through an external electrical circuit to the cathode to reduce oxygen to oxygen ions which flow through the electrolyte.

FIG. 2: A single cycle of atomic layer deposition: the introduction of the precursor, the purging of the precursor, the introduction of the coreactant, and the purging of the coreactant and the byproducts.
and the purge gas for the system. The precursors were introduced into the reactor using plugs which are short pulses of precursor lasting for a set amount of time.

A pulse time of 55 msec of water followed by a purge time of 22 s was used for all experiments for finding the ALD window, the saturation curve, and the linear growth. In order to avoid cold spots in flow pattern which would cause the precursor to condense in the line, the temperature of the precursor was set at 130 °C, the precursor valve at 140 °C, the precursor leg at 150 °C, and the manifold at 155 °C for all experiments. 130 °C was chosen as the precursor temperature because above that temperature an excess of precursor was entering the reactor chamber and condensing on the wall and below 130 °C the vapor pressure of tris(i-propylcyclopentadienyl cerium) decreases too low for deposition. Each experiment for finding the ALD window used the condition of fifty cycles made of six plugs of precursor pulsing per cycle.

After deposition, the substrates’ thicknesses were measured by a spectral ellipsometer (JA Woollam Co., Inc. model M-44).

For each experiment, the substrate was a 1cm x 1 cm silicon wafer cleaned by standard RCA-1 treatment. The native silicon oxide layer was reduced to 8 to 10 Åusing two percent hydrofluoric acid solution. The substrates were washed in ultrapure deionized water and dried with nitrogen gas.

Results and Discussion

At first, a precursor temperature of 140 °C was used which yielded high growth rates as seen in Fig. 3. It was determined that there was excess precursor in the reactor due to the darkening of the quartz tube that contained the sample during deposition as one can see in Fig. 4. To prevent precursor from being wasted, the precursor temperature was reduced to 130 °C, and condensation of the sample onto the quartz tubes wall no longer occurred.

Experiments were continued with a precursor temperature of 130 °C, a reactor temperature of 250 °C, and a water pulse of 50 msec which yielded the results seen in Fig. 5. It was discovered that not every water pulse was being delivered which explained the inconsistencies in the data points. The length of the water pulse was increased to 55 msec to ensure all experiments were repeatable.

To find the ALD window, for each experiment, the conditions described above in the Materials and Methods section were used. As seen in Figure 6, the ALD window was found to reach 280 °C. Above this tempera-
Decomposition occurs above 280 °C which gives an increased growth rate.

For the experiments that were used to determine that saturation curve, the conditions described in the Materials and Methods section were used. The reactor was at a temperature of 250 °C, and each experiment consisted of 50 cycles. As seen in Fig. 7, at four plugs of precursor pulse, the growth rate of cerium oxide stabilizes.

Cerium oxide was deposited at various thicknesses by varying the number of cycles between 10 and 400 cycles using five plugs of precursor pulsing and the conditions as described in the Materials and Methods section of this paper. The growth followed a linear trend with a growth of 1.2 Å/cycle as seen in Fig. 8. The coefficient of linear determination is 0.9954 which indicates that the process is extremely linear.

Conclusions

In this study, the optimum atomic layer deposition conditions were found. The precursor temperature was found to be 130 °C and the optimum water pulse length 55 msec for atomic layer deposition of cerium oxide. In this study, the ALD window was determined to be 210-280 °C, whereas in previous studies, it was indicated that the ALD window did not exist for this system. When the number of plugs of precursor pulsing was varied, it was determined that deposition occurs optimally at four plugs of precursor pulsing and higher. It was also determined that atomic layer deposition of cerium oxide follows a linear trend with an average growth rate of 1.2 Å/cycle. This is comparable to work using the same precursor and plasma enhanced atomic layer deposition which gave a growth rate of 0.35 Å/cycle. Future work involves using this information to create yttrium doped cerium films for use as the electrolyte and nickel doped cerium films for use as the anode in solid oxide fuel cells.

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4 S. George, Chemical Reviews 110, 111 (2010).
Flow of Carbon Nanotubes under pressure driven conditions through microchannels

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In this work, the flow characteristics of carbon nanotube (CNT) suspensions through microchannels under a pressure gradient have been observed. The suspensions of CNTs were made using sodium dodecylbenzenesulfonate (NaDDBS) as a surfactant. Flow rate of wax intercalated Carbon Nanotubes were also investigated, which will be extended for studying heat transfer characteristics of these nanoencapsulated Phase Change materials (PCMs) under a constant heat flux at the walls of the microchannel.

Introduction

Carbon nanotubes (CNTs) show promise for future applications in the technology field as well as offer a platform for research. They have been used in electronic applications as a three-terminal switching device as a bridge across two electrodes and have also been shown to be useful in biomedical applications as an effective tool for transporting therapeutic molecules. Carbon nanotubes can be attractive for its application in microelectronic cooling by encapsulating phase change materials (PCM) into CNT’s. Microelectronic devices have become more complex and the issue of system designing has become more intricate along with reduction in system weight and dimensions. This has raised the chances of thermal failures in devices as electronic packing designers aim mostly in the cooling section, like getting rid of a bulky fan. It is now more common to use liquid coolant to flow through the micro electronic systems and cool directly or indirectly with the liquid coolant. Use of PCM’s stands out as one the most promising methods of indirect cooling because the PCMs take up heat when changing phase. PCMs like hydrated salts, paraffin waxes are being used as heat storage materials for houses in air conditioning. PCMs like wax can be encapsulated in carbon nanotubes and the suspension of wax filled CNTs can be flown through microelectronics using microchannels as coolant. Such suspension can take up heat from the heated system and can store some of heat due to melting of wax. Nano-encapsulated PCMs are expected to work better than bulk PCMs as the characteristic time of heat transfer (~ 10⁻⁷ s) in comparison to bulk. Besides, nano-encapsulation also allows to “tweak” the temperature range in comparison to bulk. But the biggest problem lies in organization of flow of the suspension through microchannel because CNTs are hydrophobic and do not disperse properly in water to flow the suspension at a high pressure, viscous loss is unavoidable leading to poor efficiency of such system. So, for use of the very promising nanoencapsulated PCMs, the biggest challenge so far was to make stable CNT suspension and detailed understanding of its flow characteristic to optimize the amount of CNT and wax into the system without causing any or minimizing viscous losses. Using the flow characteristics of the intercalated CNTs, it will be seen how the suspension absorbs heat in a microelectronic system by making a prototype of it with a constant heat flux condition.

Theory

The Poiseuille equation gives the flow profile of a fluid through a cylindrical pipe with a circular cross section. In this work, by using microchannels with 256 µm diameter, the continuum approach is still valid. So, for the no-slip boundary condition, Poiseuille equation is still valid. The velocity distribution of flow through circular tubes is given by:

\[ v_z = \frac{1}{4\mu} \frac{dP}{dz} a^2 \left( 1 - \frac{r^2}{a^2} \right) \]  

where \( r \) is the radius of the fluid element, \( a \) is the radius of the microchannel, \( \mu \) is the viscosity of the fluid, and \( dP/dZ \) is the pressure gradient. Figure 1(b) gives the fully developed velocity distribution of laminar flow through a cylindrical channel. To obtain a relationship between the volume flow rate, \( Q \), and the pressure, we consider the flow through a cylindrical channel with a circular cross section (Figure 1(a)) and the volume flow rate is:
Figure 1: a) Flow through a cylindrical channel with circular cross section showing fluid flowing through the channel with a constant heat flux. b) Velocity distribution of flow through a channel. The velocity at the wall is zero due to friction and the maximum velocity is at the center.

\[ dQ = v_z (2\pi r) dr \tag{2} \]

where \( v_z \) is the velocity along the length of the tube and \( r \) is the radius of the fluid, and \( 2\pi r dr \) is the differential area (Figure 1(a)). By integrating this expression over the entire radius of the microchannel, the theoretical volumetric flow rate is given by the Poiseuille formula:

\[ \dot{Q}_{\text{theoretical}} = \frac{\pi a^4 \Delta P}{8\mu L} \tag{3} \]

where \( L \) is the length of the microchannel (m), and \( \Delta P \) is the change in pressure (Pa).

Experimental Section

Materials and Preparation

Carbon Nanotubes (CNT), PR24XTLHT-AM, were obtained from Pyrograf Products Inc. The CNTs were on average 10 \( \mu \)m in length and had a diameter of 70 nm. The average aspect ratio of the CNTs was 200. NaDDBS (Mw=348.48 Da) was obtained from Sigma-Aldrich. The Circular metal microchannels, 256 \( \mu \)m diameter, were obtained from McMaster-Carr. CNT weight percentage varied between 0.01 wt%-1 wt%. The stable suspension of CNTs in water was made along with NaDDBS as the surfactant. The ratio of concentration of CNTs to NaDDBS was 1:10. For preparation of the CNT suspension, 19 mL of water was added to the CNTs and sonicated for 30 minutes. Once dissolved, 1 mL of the NaDDBS was added to the CNT suspension and then was sonicated for 16-24 hrs. After sonication, bubbles were removed using a syringe to avoid clogging in the channel. For the preparation of wax intercalated CNTs, the method of self-sustained diffusion was followed: \[ \text{a wax solution was made using benzene as a solvent.} \tag{16} \]

3 g of CNTs were added to the wax solution and sonicated for 30 min or until a homogenous solution was prepared. The wax intercalated into the CNTs through self-sustained diffusion. Then, benzene was added to the deposit and sonicated for 3 min to rinse any solute the may have been on the outside of the CNTs. The dispersion was then filtered through a syringe filter and then prepared as discussed above.

Experimental Setup

The experimental setup is provided in Figure 2. Air comes through the air line and pushes the oil on top of the CNT suspension chamber once the two way valve is opened. Oil pushes the CNT suspension out through the microchannel and into a 100 mL beaker. Oil was used because air creates flocculation of the system, and the CNTs would be unable to flow through the microchannel. Two cameras were setup to take images of experiment. One camera was placed to take images of the pressure gauge and attached stopwatch. The other camera was placed to take images of the 100 mL beaker. Both cameras captured images simultaneously approximately 30 seconds apart. The pressure is read from the pressure gauge and the theoretical flow rate is calculated. The CNT suspension flowed out of the microchannel into a 100 mL beaker.

Results and Discussion

For flow through microchannels, a stable suspension of CNTs is needed. To produce a stable suspension sodium dodecyl benzene sulfonate (NaDDBS) was used as a surfactant because CNT’s do not disperse well in polar solvents like water. Carbon nanotubes have high aspect rations and high flexibilities result in tight entanglement and close packing. The poor solubility and hydrophobicity stem from strong Van-der-Waals attraction energy between the nanotubes when they are closely packed. Dispersion of CNTs in the desired medium can be achieved through ultra-sonication or shear mixing or using chemical ways like surface functionalization with acids. These sometimes lead to surface fracture or the
use of surfactants to modify surface characteristics toward individual tube wetting and prevention of agglomeration. Surfactants generally consist of two parts: the head group which gets adsorbed onto the surface and the tail which allows the medium to wet the surface. Surfactants like NaDDBS are useful because it has been one of the most efficient surfactants to produce a stable suspension of CNTs in water.\textsuperscript{14,16} The benzene group in NaDDBS allows better dispersion because of $\pi$ stacking interaction of the benzene ring on the CNT surface which enhances adsorption.\textsuperscript{14} The suspension was made using a combination of mechanical (ultra-sonication) and chemical (surfactant) ways. Ultra sonication allows the CNT bundles to exfoliate and helps the surfactant adsorb onto the surface.\textsuperscript{17} The set up did not have any pressure regulators, so the pressures were different in consecutive trial of experiments so experiments were first run with water using the current setup to test the validity of the Poiseuille flow. The experimental flow rate was calculated by the following equation:

$$\dot{Q}_{\text{experimental}} = \frac{\Delta V}{\Delta t} \quad (4)$$

Where $\Delta V$ is the change in volume ($m^3$) and $\Delta t$ is the change in time (seconds). The volume change was found and was used to calculate the experimental flow rate. Figure 3(a) suggests that experimental flow rates are nearly identical with theoretical prediction. This verifies the validity of the setup. Different concentrations were used to explore the system and after adding surfactant, the experimental flow rate was found to be 1.4-1.6 times higher than the theoretical flow rate.

The viscosity of the surfactant solution, measured using LV-II+ cone and plate Brookfield viscometer, was approximately 1 cp. This shows that the increase was not a cause of lower viscosity. The increase in flow rate can be explained by the existence of slip occurring at the wall\textsuperscript{19} and it is attributed to the formation of nanobubbles caused by the surfactant. To explain the existence of slip it was mentioned that the slip occurs because the fluid is rolling over these nanobubbles resulting in the invalidation of the no-slip boundary condition. As explained in the experimental section, during sonication of the surfactant solutions, bubbles were observed. The surfactant piles up at the wall during flow and helps degassing and formation of nano bubbles.

Volumetric flow rates of CNT suspensions with added surfactant were measure at different pressure drops and the results are shown in Figure 4. The results show that the flow rate of the CNT suspension was 1.2-1.8 times higher than the theoretical flow rate.

Next, CNT suspensions intercalated with wax were used. Observations of the wax-intercalated CNTs were done using JOEL JEM 3010 Transmission Electron Microscopy (TEM). The image shown in Figure 5 reveals the presence of wax in the CNT bore.

Volumetric flow rates of wax intercalated CNT suspensions with added surfactant were measured at different pressure drops and the results are shown in Figure 4. The results show that the flow rate of the CNT suspension was 1.2-1.8 times higher than the theoretical flow rate.
Figure 4: Flow rate of different concentrations of CNT suspension: a) 0.1% b) 0.3% c) 0.6% d) 1%. The connected line is the theoretical flow rate and the scattered points are the experimental flow rate.

Figure 5: TEM images of CNTs intercalated with wax.

6. The system was unable to perform beyond 0.7 wt% of wax intercalated CNT concentration because many agglomerates still remained even after 24 hours of sonication which clogged the entry of the microchannel. The results show that the wax intercalated CNTs flow rate was 1.4-2 times higher than the theoretical flow rate under the same pressure gradient.

In all the CNT flow tests, the experimental flow rate was higher than experimental flow rate due to the surfactant. Wax filled CNTs show a higher flow rate than CNT suspension. This is because CNTs has a hydrophobic surface, and when intercalating wax there is always a thin layer of wax remaining on the outside surface of the CNTs which make them more hydrophobic. When the nanotubes come close to the wall, air surrounding the nanotubes causes slip. Other observations were that at higher pressures, the experimental flow rate was much greater than theoretical flow rate. Henry’s Law states that for infinite dilution, the solubility of a gas is directly proportional to the pressure of the gas. As we go down the channel, the pressure decreases resulting in desolubilization of the dissolved gas causing in formation of nanobubbles which are stabilized by the surfactant. According to reference [19], the slip length for a circular channel can be described as:

\[
\frac{Q_{\text{experimental}}}{Q_{\text{theoretical}}} = 1 + \frac{4\lambda}{a}
\]  

Where \(a\) is the radius of the channel and \(\lambda\) is the slip length. Figure 6 shows the slip length of the different percentages of CNTs as well as wax intercalated CNTs measured using Equation 5. We have seen that as the percentage of CNT increases, the slip length also increases.

Conclusion

In this work it has been shown that CNT suspensions can flow through microchannels up to 1 wt% under pressure driven conditions. The results show that even at high weight percentages, the flow rate is much faster than the predicted flow rate, allowing for more CNT to be flowed at a lower pressure drop. The same can be said for wax intercalated CNTs as it has shown a higher flow...
Figure 7: a) Average effective slip length vs. concentration for suspensions of CNTs. b) Average effective slip length vs. concentration for wax intercalated CNTs.

rate at the same pressure drop. We hope to continue working on experiments that use the flow characteristics of the wax intercalated CNTs in the heat transfer experiment and calculate the heat transfer coefficient. We are planning to vary the different concentrations of wax intercalated CNTs and measure the heat transfer coefficient at each concentration, and therefore mimicking a microelectronic application. This is a cost effective way than other liquid coolants and will also eliminate the need of cooling fans that are currently in some computers.

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