Graphene Oxidation Barrier Coating

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Graphene Oxidation Barrier Coating

An Undergraduate Honor’s Thesis
Presented to the Faculty of
University of Colorado at Boulder
In Partial Fulfillment of the Requirements for the
Honor’s Title of Bachelor’s Degree

by
Xu Zhou
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Graphene Oxidation Barrier Coating of Copper

Xu Zhou, B.S.

University of Colorado at Boulder 2011

Since its experimental isolation in 2004, graphene has shown some outstanding properties. We propose that graphene can be used as an oxidation barrier coating and its oxidation resistance weakens at the graphene grain boundaries. Copper is a superior conductor but is easily oxidized in air at room temperature or higher. Using graphene as a coating material may reduce the cost of protecting against oxidation because copper is commonly coated with gold. The goal of the project is to investigate the breakdown of graphene as an oxidation barrier. Specifically, we studied the failure modes of this oxidation barrier coating which oxidations begin at the grain boundaries of the graphene coating. By determining its breakdown locations, additional sealant can be applied to those locations to enhance its oxidation resistance.
BIOGRAPHICAL SKETCH

(Tony) Xu Zhou was born on December 27, 1989 in GuangZhou, China. He attended elementary and middle school in GuangZhou. On September 28th 2005, he moved to US to pursue higher education. He attended Eaglecrest High School in Colorado. After three years of high school, he applied and was accepted to University of Colorado (CU) at Boulder. He then enrolled and studied engineering physics at CU Boulder. Within three years, he was able to complete all degree requirements and plans to graduate in May 2011. During his time at CU, he was introduced to graphene research in May 2009 and started his first research project of producing large graphene film in Scott Bunch’s lab. In May 2010, he joined McElroy’s group to learn more research problem solving, how to become a skillful experimental physicist, and fundamental physics research. Kyle’s research focuses on building STMs and using them to investigate the properties of interesting materials. Recently, he was admitted to the Applied Physics Ph.D. program at Harvard. He plans to pursue his Ph.D. degree in physics at Harvard in fall of 2011.
To my future wife and children
ACKNOWLEDGEMENTS

I still remember the day before I moved into CU Boulder’s dormitory. I told Dylan that I was anxious about the upcoming college life. After three years of studying at the University of Colorado at Boulder, I felt that I have grown more mature and independent. This undergraduate time is probably one of the most important times in my life. At CU, I got my first ever paid job and apartment. It was the first time I worked very hard to accomplish goals, found the major that I am most interested in, and became involved in major science research for the first time. However, the most precious thing is that I have met many people that shaped my life.

For my undergrad research experience, it was an honor to work under supervision of Prof. Scott Bunch and Prof. Kyle McElroy. They both had enormous experience in condensed matter physics. What amazed me the most is their ability to come up with new ideas and solutions within a short moment when encountering problems. They are both phenomenal mentors. I wish one day I could publish Nature and Science papers in my graduate study like them.

I thank Dr. Bunch for giving me a chance to taste what research is like when I asked him in a freshman engineering class that I would like to join his group. A lot of professors wouldn’t like to hire a freshman like me. Before he embraced me, my research position applications had been ignored by many professors. He not only hired me, who was only a newbie in physics and research, but also supervised me closely in every project I worked on. It was my honor as part of the force to assist him in his early research lab. He has impressive communication skills, and I have not seen anyone that
replies emails as quick as he does. It doesn’t matter who the sender is; he always replies
to personal emails. That inspired me a lot, and I see him as my model. Most importantly,
he is the one who led me into the scientific research world.

I met Kyle in solid state physics class, and he was my instructor. Like everybody
else, I had a hard time in the class. That was mostly due to the fact that solid state is a
hard subject and it shouldn’t be only one semester long class. The small reason is that
Kyle has a very different way of thinking. His different way of thinking gives him a very
unique perspective of analyzing situations and problem solving. So to speak, that is what
makes his research successful. After joining his group, I realized how much his unique
thinking is needed in building two complex STMs. I am also extremely impressed by his
sense of humor and how detailed and broad his knowledge outside of physics is.

During completion of my research projects, I was given a helping hand by many
undergrad, graduate students, post-docs, and professors. I thank them. This project can’t
be done without them. Thanks my committee members, Prof. Rishi Raj and John Cumalat,
who are willing to spare their time to evaluate my thesis and thesis defense from their
busy times. Because of Prof. Rishi’s offer, our Bunch group members are able to use this
Raman. Prof. Jun Ye, my research class instructor, gave me good ideas on powerpoint
presentation. Xinghui, Luda, Guillermo, and Steven in Bunch’s lab helped me out
frequently and trained me how to measure mechanical resonators and use an optical
microscope, AFM, and Raman spectroscopy. Nathan from chemistry department helps us
to optimize the CVD recipe. In Kyle’s lab, Jixia and Edie taught me things about STM,
different use of tools, and informed me what physics graduate life will be like; in their
free times, they helped me on GRE problems and we had great discussion on life in
general. I would like to thank my collaborators on the project, Jonah, ChienChung, and Schibli who offered samples from their low pressure CVD system and helped me to come up with new ideas. Professor Rogers trained me on the use of ellipsomter and offered the best help he can.

I want to thank people giving me knowledge and pointing me to the right direction in my career. All my class instructors have been great, so I am equipped with the basic tools and skills. If I didn't take Debra Biasca’s class, I would never be interested in BEC and put my potential advisor's name on my "I like to work with" list in the Harvard application. When I was uncertain about my career, I had career advising from Dr. Bunch, Kyle, Thomas Schibli, Prof. Becker, and Prof. Anderson. I did study abroad in China for the summer of 2010, and that was the best trip ever. The Humanity professor Anja Lange brought studying humanity fun to my science filled life. Because of her, twelve other students and I could travel to China and explore interesting Chinese culture. I could better identify myself after that phenomenal trip. I would like to thank friends that made my trip so enjoyable, Ed, Josh, Deena, Genevieve, Camila, Daniel, Stefan, Logan, John, Chris, Matt, and Cheyenne.

Thank you Mom, Dick, and my dad. I know you guys will always support me. Without your supports, I would never be able to finish my undergraduate degree within three years.

Lastly, I would like to thank all my friends. Rhiana, Garrett, Zach, Sonya, and Liz made my college life fun. It is a shame that I later (after the first year) got so busy with my goals that I could no longer hang out with you guys as frequently. I have an
interesting story to tell about Liz because she is a special girl. She rejected a date with me in an unexpected fashion. I’d like to send positive vibes to my previous roommate Zach, so he can work hard and make a change in his life. I hope Mike keeps his dream and moves out of his parents’ house to be independent. I wish my current housemates Dani and Teresa luck, and I would like to see my landlord’s daughter follow my steps to Harvard. My library job supervisor Theresa gave me the best job for a busy student. Two of my best friends, Dylan and Brian, always hang out with me when I go back to Centennial; I have known you two since high school, and I believe our friendship will last forever. Three of my best friends are in college with me, Todd, Trevor, and Tyler; Lately I always have lunches with Tyler and his girlfriend, and dinner with Todd and Trevor. Because of them, I am no longer alone on a meal table; we all made through hard times at CU Boulder; without you guys I couldn’t accomplish this impossible mission within three years. Nikki, sorry I feel bad for letting her complete most of the math project when I was busy with other classes, GRE, and GRE physics tests. I like her stubbornness. She is a special girl; offering her ride and dinner treats degraded her pride. She only focuses on studying and nothing else. I wish her luck on her medical school pursuit even though she sees me like an enemy after I gently asked her out a couple of times. I hope we can shake hands to be friends again the next time we see each other.

Twice without eating for 24 hours, average 6 hours of sleep on weekdays, constantly swamped by homework, lab reports, and lab experiments are undergraduate life experiences deep inside my memory. A new stage awaits in the near future.
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Chapter 1
Introduction

1.1 Introduction

The unique atomic structure of graphene and its impermeability of gas has established graphene as an excellent candidate for oxidation barrier coating of copper\(^1\). However, no research and study has been done on where this coating breaks down. As a result, nobody has a clue about how to improve its oxidation protection for copper. This thesis explores the breakdown of a graphene coating on copper to improve oxidation protection.

1.2 Outline

Before describing the experiment of the project, we review some of the corrosion protections and the basic properties of. We will then describe the methodology of the project, which includes sample preparation and experiment details. Finally, results and discussion are presented.
Chapter 2
Corrosion protection Background

2.1 Copper oxidation background

Copper oxidation limits high thermal and electrical conductivity of the noble metal. Pure copper is chemically active and reacts with oxygen atoms to form an oxide layer even at room temperature\(^2\). The copper oxide has two forms. One form is CuO and the other one is CuO\(_2\). Generally, CuO doesn’t form until enough CuO\(_2\) formed on the surface (Figure 2). It is well understood that the early oxidation kinetics of oxide layer thickness vs. time can be characterized as a linear relationship\(^3\)\(^-\)\(^6\). The early oxidation refers to the growth of oxide layer is primary CuO\(_2\). Similar to oxidation of every other material, the oxide layer has a final thickness at a certain temperature. That is because oxygen needs to diffuse thicker and thicker oxide layer in order to further oxidize the copper. The whole oxidation kinetics must be a linear, and then exponential relationship\(^3\)\(^-\)\(^6\). There are cases reported that CuO and CuO\(_2\) grow together at the same time instead of one after the other. That indicates that oxide layer growth depends on the oxidation environment, temperature, impurity of copper, and so on.
2.2 Metal Corrosion protection background

The history of protecting metal corrosion is long and full. Long ago, people had tried many different methods to protect metals from corrosion in air and solutions. Because metals have high thermal and electrical conductivity values, they are valuable in heat and electrical transmissions. However, metals are frequently utilized in corrosive conditions, so corrosion damages the properties of metal. Hence, a different kind of material is commonly deposited on metals serving as a corrosion protection coating.

One of the common coatings on metal against corrosion is an organic polymer coating. In a recent study of the corrosion protection of iron by organic polymer coating, Stratmann et al. showed that polymer coatings are not sufficient against the diffusion of water and oxygen. In solution, they observed that ions slowly access the iron surface through the defects of the coating. When the ions reach the iron surface, a galvanic element is formed and causes oxygen reduction at the interface between the polymer and iron. During the oxygen reduction, the bonds between polymer and iron surface are broken. Once the polymer coating and iron start detaching, the corrosion protection fails. They concluded that a strong adhesion is needed between organic polymers and metal to be sufficient against corrosive solutions. The weak adhesion between organic polymer coating and metal substrate is probably due to physical coating method such as using a spinner. Nevertheless, the corrosion rate will stay low as long as the polymer adheres to the substrate. For protection against oxygen, the group calculated the diffusion coefficient of oxygen in polymer to be $10^{-8}$ cm$^2$/s. Because the organic polymer is very thin, they claim this rate is too high for thin organic polymer coating to be a sufficient corrosion protection.
In contrast to organic polymer coating on iron, Redondo et al. were able to electrodeposit polypyrrole, a conducting polymer, on a copper substrate using NaH$_2$PO$_4$ solution. To test the corrosion resistance of this conducting polymer, they monitor electrochemical impedance and corrosion resistance of coated copper in NaCl solution. They discovered that the polypyrrole films were electrosynthesized and formed in an overoxidized state. Using Fourier Transform Infrared Spectroscopy, they found that their polymer film was uniform, and strongly adherent to the copper substrate. After 8 days of immersion in 0.1 mol dm$^{-3}$ NaCl solution, the copper remains in original condition and the corrosion resistance still remained but the corrosion protection properties were reduced due to long immersion time. They attribute the sufficient protection to the fact that polymer film is overoxidized and strongly adherent to the copper substrate.

Besides single layer coating, double layers coating is commonly used to enhance the corrosion resistance of single layer coating. In this area of study, Mittal et al. recently investigated a double layer coating method to protect carbon steel in corrosive environment. Their study was to find a solution for corrosion of carbon steel inside a heavy water reactor in nuclear power plants. Carbon steel is commonly coated with Fe$_3$O$_4$ inside heavy water reactor. However, at high temperature and under radioactivity transport, corrosion of carbon steel occurs in two simultaneous processes. One is that metal ions from carbon steel are released into water through the grain boundary of Fe$_3$O$_4$. The other one is that oxygen atoms leak onto carbon steel through nano-pores that are created due to lattice mismatch of carbon steel and Fe$_3$O$_4$ coating. To solve these two problems, the group deposited magnesium ferrite (MgFe$_2$O$_4$) on top of Fe$_3$O$_4$ coated carbon steel using pulsed laser deposition (PLD). By measuring the impedance of the
samples in ionic solution, they found MgFe$_2$O$_4$ coated samples have at least 2 times higher impedance than the only Fe$_3$O$_4$ coated samples. They conclude that the MgFe$_2$O$_4$ film serves as a barrier to cover up grain boundaries and nano-pores of Fe$_3$O$_4$, so ions and oxygen atoms are not able to move freely through those areas. Therefore, they found this double layer coating method further prevent corrosion of carbon steel.

2.3 Copper corrosion protection

One of the interesting methods of copper corrosion protection is to coat chromium on copper and copper nickel alloy. Segarra et al. proposed to eletrodeposit Chromium on copper and copper nickel alloy$^{10}$. They oxidized copper alloys with different percentages of nickel at 800 °C under a pure oxygen atmosphere.

They measured weight gain by oxidation with respect to time. According to this data plot, they claimed that a chromium coating can be useful against high temperature copper
oxidation. Chromium oxidation resistance coating is an interesting field but further study needs to be completed to establish its importance in metal corrosion protection.

In the field of polymer coating for corrosion protection of copper, polyaniline (PANI) was studied under various conditions of temperature, humidity, and bias electrical voltage by Brusic et al. Their main focus was to investigate the reduction in corrosion rate of copper with PANI coating in water and acidic solutions. Polyaniline (PANI) refers to a family of polymer. One of the advantages of using PANI coating is that the properties of the polymer can be tuned to suit whatever the application is in need. Thus, the conductivity and solubility of a polymer in PANI can be modified by doping other materials. Therefore, the research group found that PANI could either worsen the corrosion or provide a significant corrosion protection depending on the properties of the polymer which are tunable. For example, in ionic solutions, bare copper exchange ions in the solution and corrode. Then, the aim is to coat copper with low conductivity PANI polymer so that it prevents or significantly slows down the exchange of ions between coated copper and solution. The study is complete in corrosion protection against general corrosive solutions. However, it would be interesting to see how PANI coating protects copper from oxidation in air at various temperatures.

One of the studies on polymer coated copper against air oxidation was done by Itoh et al. They successfully deposited 11-mercapto-1-undecanol HO(CH\textsubscript{2})\textsubscript{11} SH (MUO) on copper. After exposing the polymer coated copper to air for 10 days at room temperature, they found little oxidation on the polymer coated copper with X-ray photoelectron spectroscopy (XPS). However, the study was incomplete in a way that no
higher than room temperature oxidation experiment was done, and the study didn’t cover why air can still diffuse into copper through polymer.

In oxidation protection of copper, one of the promising coatings is silicide coating SiH₄. Cabrera et al. studied how SiH₄ coated copper reacts with air at a temperature range 400 °C-600 °C. They characterized their oxidation protection by measuring the weight gained by the samples at various times. Because the oxidation was performed at a relatively high temperature, the oxide layer grew thick in a short period. They found parabolic rate of weight of bare copper vs. time. For SiH₄ coated copper, they found the weight of coated copper vs. time has an approximately linear relationship. The rate of weight gain of coated copper is 72 times smaller than that of uncoated copper. This could be a decent low temperature oxidation protection below 400 °C. However, they could have done other measurements to back up their claim that SiH₄ is an effective corrosion protection coating for copper.

Li et al. studied oxidation and protection for copper using alloy thin films. They evaporated TiN layer, Si₃N₄ layer, and copper film alloying with Ti, Pd, Cr, and Al on copper on top of SiO₂ substrate. The oxidation resistance was characterized by measuring the resistance over original resistance of the sample vs. time. For TiN coating, they oxidized the samples at 300 °C and compare oxidation resistance between TiN and oxidized TiN. To test Si₃N₄ layer, they systematically characterize the oxidation resistance at various temperatures. On a plot of resistance ratio vs. temperature, all alloy coatings were compared in oxidation protections responding to temperature rise up to 400 °C. Conclusively, all the coatings reduce the oxidation rate of copper to some extent but no microscopic study was done on the failure modes of each coating.
The most common corrosion protection coating for copper is gold plating\textsuperscript{15-18}. Gold plating copper is important in producing electronic connectors. Because copper has the 2\textsuperscript{nd} highest electrical conductivity value among metals, it is often used in electrical circuits and connectors. Thus, it can provide the least energy loss in electricity transmissions. Nevertheless, it easily corrodes in pollutant atmosphere and oxidizes easily. There are many corrosion protection coating candidates. Gold stood out among them because gold is a very chemically stable metal and can diffuse into copper surface in coating process. Thus, gold coating is strongly coupled with copper so little room is left for corrosive atoms to diffuse into. Geckle et al. studied gold plated copper in an environment that containing chlorine, hydrogen sulfide, and nitrogen oxide\textsuperscript{19}. They observed corrosion on the base substrate of copper, and the corrosion layer on copper increases in thickness with increased exposure time. They suspect that corrosive gas diffused through gold layer at defects of the gold.

In a recent paper by Ruoff’s group, graphene was proposed to be an oxidation barrier coating for copper\textsuperscript{1}. They demonstrated that graphene grown on copper using Chemical Vapor Deposition (CVD) protects the metal surface up to 4 hours in air at 200 °C. In their study of graphene as an oxidation barrier coating, they used Scanning Tunneling Microscope (SEM), Raman spectroscopy, and X-ray Photoelectron Spectroscopy (XPS) to characterize coated and uncoated samples. After 4 hours of annealing graphene coated samples in air at 200 °C, they observed no noticeable Raman signal change in the graphene films. As a result, graphene was able to protect metal substrate and remain the same throughout the oxidation process. However, every
oxidation barrier coating must break down at some point. They suspect that graphene grain boundary is where the oxidation resistance is the weakest.

2.4 Conclusions of the chapter

Many different methods have been developed to prevent corrosion of metals such as single layer coating, double layer coating, metal alloying coating, and so on. Studies have shown that break down of corrosion coatings commonly occurs at grain boundary and defects of the coatings. The adhesion of the coating and metal also plays an important role in effectiveness of the coating against corrosion. For noble metal copper protection, there are many coating candidates that have shown excellent protections but the studies of where breakdown and failure modes of the coatings are absent.

Chapter 3
Graphene background

3.1 Introduction

Nanotechnology has been a fast growing science field in the 21st century. One fascinating nano-material is graphene. Graphene is a single atomic layer of carbon atoms. It was the first time experimentally observed in 2004 by Andre Geim and Kostya Novoselov who were recently awarded a Nobel Prize for. Graphene is one of the known carbon materials but it possesses unique, fascinating properties. It is a stable 2-D material in ambient conditions. Since its discovery, graphene has been shown to be the
thinnest and strongest material ever tested, it is a zero band gap semiconductor and a superior thermal conductor. This background section reviews the basic properties of graphene.

3.2 Dimensionality

First of all, graphene is the first known 2-D material. Before the discovery of graphene, there were no known crystals with a dimensionality of 2. That is what made graphene unique. For example: Bucky ball \( \text{C}_{60} \) is the representative of dimensionality 0. The carbon nanotube, discovered in 1991, is the representative of dimensionality 1. In addition, most materials are 3-D. Graphene looks like a plane, with carbon atoms in a honeycomb pattern lattice\(^3\). It is the thinnest material in the world. Its thinness was verified by Geim and Novoselove’s group, using atomic force microscopy (AFM)\(^{21,22}\).

In addition to graphene’s dimensionality, Geim and Novoselov claimed graphene was the “mother” form of carbon\(^{21,22}\). This claim shows the importance of graphene among other carbon materials. In fact, graphene can form any carbon material with a hexagonal atomic structure. For example, 3-D graphite is composed of stacked graphene layers. 1-D materials, such as carbon nanotubes, are cylinder shaped. Nanotube researchers picture graphene as a nanotube that has been cut length-wise and
unrolled. However, it is more logical to think of the 1-D nanotube as what you get if you roll graphene into a cylinder even though nanotubes were discovered first. In the dimensionality 0 case, a graphene sheet is folded until it produces a sphere. This sphere, known as bucky ball C_{60}, is made of sixty carbon atoms. This also means the graphene sheet used to make the sphere needs to contain 60 carbon atoms. Nevertheless, graphene cannot be used to form diamond because diamond has a cubic crystal structure rather than hexagonal atomic structure.

3.3 Mechanical properties

After its dimensionality was revealed, mechanical properties of graphene were measured. Before graphene, diamond was known as the strongest material because the basic atomic structure of diamond was triangular. However, the hexagonal atomic structure of graphene displayed enormous strength. To measure graphene’s mechanical properties, Lee’s group\(^2\) measured the breaking strength to be 42 (N m\(^{-1}\)). This value is the highest value ever measured and 200 times that of steel.

3.4 Electronic properties

Another fascinating property of graphene is its electronic properties. According to Geim and Novoselov, a single graphene stack acted as a semi-conductor with zero band gap\(^2\). A single layer of graphene was observed to be a conductor with minimum conductivity of the order of \(e^2/h\) per change carrier, where \(e\) is the electronic charge and \(h\) is Planck’s constant. This conductivity was predicted by a number of theories\(^2\).
The electronic conductivity of graphene is high, and graphene has superior thermal conductivity as well. One of the research groups that measured the thermal conductivity of graphene was the Balandin group\textsuperscript{25} at the University of California. At room temperature, they measured the thermal conductivity of graphene in the range of $4.84 \times 10^3$ to $5.30 \times 10^3$ W/m K, an extremely high thermal conductivity value. Most metals for example, have conductivities ten times less than that of graphene.

### 3.6 Optical properties

The optical properties of graphene are interesting in terms of graphene’s transparency and light absorption. Its optical properties were measured by Novoselov and Geim\textsuperscript{26}. The transmittance of white light in graphene was expected to be high. That is because Kovoselov and Geim had previously observed graphene film on a silicon substrate to be almost transparent\textsuperscript{20-22,27,26}. In this experiment, graphene was suspended over a hole. White light was then directed downward, through the hole. A light detector was built on the other side of the hole to collect the transmitted light. Novselov and Geim found that about 2.3\% of the light was lost in the process. Thus, graphene absorbed only 2.3\% of the light.

### 3.7 Impermeable properties

Graphene membranes are impermeable to gases, and it can support pressure differences larger than one atmosphere. Bunch et al. were able to suspend graphene membranes on a well in an oxidized silicon wafer\textsuperscript{28}. By vacuuming the air out of the hole and pressurizing the membrane from outside with different gases, the membrane starts to bulge downward due to unequal pressure. Their studies showed that gases eventually leak...
into the hole, not through graphene membrane but the silicon oxide the membranes are supported on. In the background chapter, the experimental results by Ruoff’s group on graphene oxidation resistance were reviewed. The oxidation resistance results give a macroscopic view on graphene’s impermeable properties\(^1\). The large graphene film produced by CVD has a size on the center meter scale; in contrast, the graphene membrane studied by Bunch et al has a size on the micro meter scale. The study by Bunch et al indicates that graphene coating should be the strongest oxidation resistance on a single crystal domain, so the breakdown likely occurs at the boundary of single graphene crystal domains.

### 3.8 Conclusions of the chapter

These basic properties of graphene attracted attention from scientists and engineers. Scientists want to learn these basic properties more in depth, and engineers are brainstorming potential applications of graphene. Currently, potential applications have been promoted that use the basic properties of graphene. For example, graphene switches are expected to replace silicon-made transistors in computer chips. Electronics companies have considered producing touch screens using graphene. This is because graphene is transparent, good at conducting of electricity, and rapidly dissipates heat. Paul McEuen’s group at Cornell University considers graphene as a thin, stiff membrane, so they built an electromechanical resonator using it\(^29\). For the purpose of our research, the impermeable properties are important for us to know.
Chapter 4
Sample preparation

The fabrication of graphene is still a challenge. A common fabrication method is exfoliation known as the “scotch tape method.”\textsuperscript{20,27} The disadvantage of the scotch tape method is the limited size of the graphene film produced. Since our work requires a large area of graphene, we use a different method to coat graphene on copper. This section explains that method.

The method we used is called chemical vapor deposition (CVD)\textsuperscript{30,31}. CVD was developed to solve the limited size problem of the scotch tape method. CVD is commonly used to produce materials other than graphene such as diamond, silicon, polycrystalline, and carbon nanotubes. The basic idea of CVD is to flow gas, which contains carbon atoms, over the top of a substrate. CVD occurs when the gas is heated to the temperature at which the chemical bonds of the gas break up. Once the carbon atoms are free from their chemical bonds, they form a thin layer of graphene on the surface of the substrate. So far, nickel and copper are the only known substrates that attract carbon atoms and facilitate the growth of graphene.

Our apparatus (Figure 5) has a transparent quartz tube going through a furnace. One end of the tube is connected to a flow controller that lets gas flow through at a fixed flow rate. The other
end of the tube is connected to a fumehood where waste gases are contained. These gases are: Argon (Ar), Methane (CH₄), and Hydrogen (H₂). The argon acts as a gas carrier that reduces the concentration of other gases and maintains gas flow in the CVD system. Argon is used because it is a noble gas that does not react with other substances. Methane bonds break up at 1000 degrees Celsius, and its carbon atoms grow graphene. The third gas, hydrogen, is chosen to re-react with the left-over carbon atoms. Only a tiny portion of the carbon atoms forms graphene; the rest react with hydrogen to become gas and flow out to the fumehood.

To make graphene, we open one end of the quartz tube and load copper substrates inside. We also ensure that the substrates are inside the furnace. The coating process of graphene to copper consists of three phases: heating phase, growth phrase, and cooling phase. Argon gas is used to clean out the air inside the tube. We then start the flow of argon gas and heat up the furnace to 1000 degrees Celsius. This process is known as the heating phase. When the temperature of the furnace reaches 1000 degrees, we insert methane and hydrogen into the quartz tube. This process is known as the growth phase. Near 1000 degrees Celsius, the methane bonds break up, so a tiny amount of carbon atoms form graphene on the copper surface. After the growth phase, the tube is slid out so that the samples cool down. This is known as the cooling phase where only argon is flowing and the other gases are turned off. As soon as the furnace cools to room temperature, we stop the flow of argon and unload the samples from the tube. Graphene is now coated on the copper substrate. The experimenter needs to vary the parameters of the CVD method such as flow rates of gases in the different phases, growth temperature, and growth time in order to find the recipe that produces uniform, large scale of graphene.
Nevertheless, some defects appear on the graphene sheet using the CVD method. Optimizing the growth recipe is the key to reducing the amount of disorders and defects.

In a number of experiments, large grains of graphene are essential. Generally, a single grain of graphene with defects is a complete single crystal of graphene. The graphene grains grow in the CVD growth phase. When carbon atoms start growing on copper surface, enormous amount of carbon sheets reside at random locations and expand its area (Figure 6).

Eventually, the grains meet up one another and form grain boundaries. In microscopic scale, the graphene grown on top of copper is not a single sheet of carbon atoms but many small single layer graphene sheets connecting together. To grow large grains of graphene, we add a vacuum pump at the end of the quartz chamber in the CVD setup. The purpose of it is to keep low pressure in the chamber during CVD process. Therefore, the number of spots for carbon atoms reside and expand is gradually reduced. In other words, the probability for carbon atoms to stick onto copper surface decreases. This is the same idea for ultra-high vacuum pumping; the idea is that the lower pressure, the less
chance for air molecules to stick on surface. This low pressure CVD (LPCVD) is generally used to grow large grain sized graphene\textsuperscript{30}.

Chapter 5

Oxidation experiment

The CVD method coats the graphene on top of a copper substrate. The samples are ready to undergo oxidation after CVD. To see graphene’s oxidation resist, controlled experiments need to be done, so bare copper samples and graphene coated samples are oxidized together. The goal is to observe the difference between bare copper samples and graphene coated samples at various times of oxidation and temperatures in air. The layout of samples is shown (Figure 7):

Figure 7 bare copper samples(bottom) and graphene coated samples (top)
A set of bare copper and graphene coated samples are flattened by using glass slides compression and placed on an aluminum block. The reason of using an aluminum block is that aluminum is a good thermal conducting material. Thus, by moving the whole sample stud inside the oven, samples will be uniformly heated up to the desired temperature at the same time. In the oxidation process, a pair of bare copper and graphene coated copper is taken out from time to time. That indicates that temperature of air inside oven will drop whenever a pair of samples is taken out but the aluminum block keeps the samples strongly coupled with the oven so that the air cycling has little effect on the temperature of samples.

To obtain a uniform temperature environment, an oven with enclosed glass case is used (Figure 8).
The oven is able to connect to gas cylinders or obtain a vacuum environment through valves on the top. However, for our purpose, the valves are open to allow air flow inside to oxidize the samples. Before loading the samples in, the temperature of the oven needs to be set by turning the knob on the bottom. It takes a while for the oven to heat up the inside environment. A thermal couple inside indicates the temperature of the inside environment, so samples are loaded in once it reaches the desired temperature. By recording the time or using a stopwatch, pairs of samples can be taken out at designated times.
Chapter 6
Brief Introduction to Ellipsometry

Thin films deposit is commonly used to serve as additional layer on a substrate. There are a number of spectroscopies and surface analysis techniques developed to characterize these thin film deposits. One of the most important characterizations is thickness of the thin film. If the thin film is not very thick and the substrate surface reflects light well, then the interaction between light wave and thin film substrate can be an effective way to measure thickness of the thin film. An ellipsometer is one of the instruments that accurately measure thickness of a thin film on a reflective material. In ellipsometry, polarized light is irradiated onto a sample surface which has a set of unknown real and imaginary refractive index values (Figure 9).

![Figure 9 principle of ellipsometry](image)

This set of complex index of refraction \((n, k)\) is known as the optical constants of a material. By convention, complex index of refraction is defined as:

\[ N = n + ik \]
When polarized light interacts with a surface of unknown optical constants, reflected light will be reemitted with a new state of polarization. The difference in polarization between incoming light and outgoing light is the key to solve the optical constants \((n, k)\) of this surface. If the surface is a thin film, the thickness of the layer can be computed from that. The raw data an ellipsometer measures are \((\psi, \Delta)\). The \((\psi, \Delta)\) measured from ellipsometry are defined from the ratio of reflection coefficients in two different polarizations,

\[
p = \tan(\psi)\exp(i\Delta) \equiv \frac{r_p}{r_s} \tag{1}
\]

where \(r_p\) is the reflection coefficient for p-polarization, and \(r_s\) is the reflection coefficient for s-polarization. The electrical fields in p-polarization and s-polarization are perpendicular to each other. \(\psi\) can be seen as the amplitude and \(\Delta\) can seen as the phase of the ratio of two polarization reflection coefficients. The ellipsometry we use is called a spectroscopic ellipsometry. What it does is to sweep the light over the visible light range, and measures \((\psi, \Delta)\) and \((n, k)\) at each wavelength. The thickness of the oxide layer of copper can be calculated by,

\[
d = \frac{i}{2\left(\frac{n_o - n_i}{\lambda_o - \lambda_i}\right)} \tag{2}
\]

where \(i\) is the number of complete cycles from \(\lambda_o\) to \(\lambda_i\), if it sweeps through 8 wavelengths, then \(i\) is 8. \(n_o\) and \(n_i\) are the refractive index values of Cu oxide film at the wavelengths of \(\lambda_o\) and \(\lambda_i\).
Chapter 7
Data results and discussion

7.1 Study of oxidation barrier effectiveness

The first major case we investigated was oxidation at 120 °C. In this case, we use ellipsometry to characterize the thickness of the oxide layer, so extra sample polishing was needed. Before the CVD growth, copper samples were polished so that they were at least semi-mirror shiny. This process later helped ellipsometer detect better light signal reflected off the samples. The optical images were used to characterize the oxidation (Figure 10)
Before the oxidation, the graphene coated sample looks shinier than the bare copper samples. As I mentioned before, copper surface forms a thin oxide layer even at room temperature, so it looks dimmer. In the CVD process, hydrogen gas would remove that thin oxide layer from the room temperature reaction, then graphene grows directly above the copper surface. Plus graphene is transparent, so graphene coated samples has the shininess from pure copper. As the oxidation progresses, bare copper samples react with oxygen molecules in the air and oxidize. They color changes from reddish brown to orange, dark orange, purple, gray, and then golden. These color phases shifts indicate that the thickness of the oxide layers increases as oxidation time increases. In contrast, graphene coated samples did not have any noticeable color change after 17 hours. However, by 42.5 hours, graphene coated samples start to turn orange and oxidize. From
the last two graphene coated samples, one can tell they are changing color toward orange. The edges of graphene coated samples are oxidizing more severely than the middle areas.

To further characterize the same set of samples, we did ellipsometry on these samples. Ellipsometer gives the information about the reflectivity of the surface and the change of polarization of the light. From these information, the thickness (Figure 11) of the copper oxide layer on the samples were calculated by the ellipsomtry program.

120°C oxidation growth rate comparison

The oxidation rate of bare copper is approximately linear at these times. In the literature, the oxidation of the bare copper is linear respect to time until the oxide layer becomes too thick for air to diffuse into at the same rate. Usually, the oxide layer is not considered too
thick until CuO starts to grow instead of CuO$_2$. The oxide layer thickness didn’t start from the origin because the uncoated copper samples already got slightly oxidized in the air before the oxidation experiment. The ellipsometry result backs up the assumptions made in the previous optical images analysis. As expected, graphene coated samples didn’t get oxidized in early times but oxidize at around 1000 minutes (17 hours).

Although no noticeable color change in graphene coated sample at 17 hours, the ellipsometry is much more sensitive to detect the oxide layer thickness. According to the plot, graphene coated samples are oxidized at a linear rate as well. However, this growth rate of coated samples is 5-6 times slower than that of uncoated samples.

After investigating samples macroscopically, we could tell that graphene coating breaks down eventually and turned attention to details why graphene coated samples oxidize and where the oxygen molecules leak through graphene layer to copper surface. Two likely spots that air leak through are the defects of the graphene layer and the grain boundaries of graphene layer.

The most likely breakdown location is along graphene grain boundary (Figure 12).

![Figure 12 CVD graphene grain boundary in TEM, figure adapted from Huang et al. 2011](image)
The graphene grain mismatch along the grain boundary\textsuperscript{32} is likely target for oxygen molecular to sneak in and oxidize copper. To investigate this issue, large grains of graphene are needed on copper using LPCVD.

### 7.2 Oxidation of samples with graphene flakes

We grew graphene flakes on copper so that the grains are not connecting to each other. By controlling the time of growth in LPCVD process, we are able to stop the growth of graphene grains before they expand large enough to connect one another along grain boundaries (Figure 13). The oxidation experiment was performed at 190 °C in air (Figure 14).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure14.png}
\caption{Bare copper samples after oxidation at 190 °C in air}
\end{figure}
Figure 14 SEM image of copper with graphene flakes (large space in between grains) before oxidation

SEM image shows that the dark regions are graphene flakes, and gray regions are the bare copper surface. As we originally planned, the spacing between graphene patches is big. Every single graphene patch is randomly located at local field. In addition, various shapes of the patches indicate that direction graphene grains expand is also arbitrary. This also verifies the qualitative explanation of how graphene grains are formed on copper substrate. We chose to take SEM images of the samples because we might not have seen anything graphene flakes under optical microscope without grain boundaries connected. If oxygen only moves around the graphene grains to oxidize copper, then we should expect graphene covered regions to be pristine at the early oxidation times. Eventually, we expect oxygen start oxidizing areas under graphene flakes.
After 30 minutes of oxidation, the bare copper samples changed the color to orange (Figure 13). We were expecting to see bare copper regions change to orange color in the graphene flakes coated samples. As the results shown, the regions in the gaps indeed changed to orange color, thus it indicates that those regions formed oxide layer. However, the copper regions under the graphene flakes are still pristine and shiny, which indicates that these regions are not oxidized. We could clearly see the flakes under the color contrast.
After 4 hours of oxidation, we couldn’t see the much color contrast. We don’t see much color contrast because the bare copper samples at 4 hours have golden color (Figure 13). So the bare copper regions at the gaps of graphene flakes have the gold color too. In the graphene covered copper regions, they are still shiny and pristine except some thin dark lines and dark black spots are formed. We suspect that dark lines and black spots are due to the oxidation underneath. It is likely that oxygen leak through the defects of the graphene flakes and oxide those dark areas. It is also possible that the black spots are dusts since we are not able to tell if they are on the top or underneath the graphene flakes.

Figure 16 4 hours of oxidation optical images of magnification 40X (left) and 100X (right)
From the results of 37 hours oxidation, the bare copper regions have become black. The graphene covered regions are still shiny and pristine. An interesting fact is that we don’t see the small black spots shown in the previous optical images of 4 hours oxidation although we cannot conclude that the dark spots were the dust or dirty contaminates sticking on the surface. However, the dark lines are still present and increased in amount. We couldn’t see any pattern that the dark lines tended to grow at although the lines tended to orientate in one direction (horizontal direction in the images). One might notice that oxygen didn’t oxidize the graphene covered regions as much as one expected. That is probably because the bare copper area is large enough for oxygen to oxidize uniformly, so regions under graphene are left out because they are better protected than bare copper regions. For the dark lines, we suspect that they can be the root where oxygen enters the graphene covered regions.
7.4 Oxidation of samples with closely spaced grains

After we showed results of graphene grains with big space between them, we studied graphene flakes on copper so that the grains have barely enough space between each other (Figure 17).

Comparing to the samples from the previous section, this set of samples has little spaces in between graphene grains. This SEM image shows a further progress of graphene grains growth. The longer time growth allows graphene grains almost entirely connect to one another.
The optical images of this set of samples are similar to ones of large grain gap samples at 30 minutes of oxidation except the gaps between grains are smaller in this case. Notice on the 40 X image that the machining lines are still on the copper surface. There is a line cutting across the machining line. Don’t get confused with machining line or graphene grain boundary. The line across the machining line is the grain boundary of copper. If the copper sample is annealed for a long time, a single copper crystal can grow to a size larger than 1 cm² area.
By 13.5 hours of oxidation, the black clouds started appearing on the clean graphene grains. We noticed these black clouds are aside of gaps between grains. The most probable answer to explain this phenomenon is that air has leaked through the gaps and oxidizes the copper surface radially outward. It is unlikely that the black clouds are the dust. That is because they tend to locate along the gaps and are circular shaped, which contradicts the general fact that dust randomly sticks onto the sample surface. At the same time, the dark thin lines are present as we see from the samples with large copper gaps.
After 23 hours of oxidation, the areas under graphene have been darkened to a considerable degree. This result is very different to what happened to samples after 37 hours oxidation with large gap between grains. We claim that bare copper area in this case is not large enough for oxygen to oxidize uniformly, so regions under graphene are no longer left out even though they are better protected than bare copper regions.

7.5 Oxidation of samples with graphene grains connected

Using LPCVD, a set of graphene coated samples with large grain domain is obtained. If the grains are big enough, an optical microscope is enough to see them. Optical microscope images are used to characterize the bare copper and graphene coated copper from LPCVD (Figure 22).
Originally, the bare copper foil taken out of the product case shows only the machining lines, a result of manufacture of thin copper foils. After LPCVD of bare copper, the machining lines are still noticeable. However, some small transparent grains are noticeable. By adjusting the focus and lighting of optical microscope, the graphene grain boundaries are clearly there. Since these optical images are taken in 20X magnification, the grain sizes vary from 10 μm to 20 μm. The grains are connected to each other with no gap in between.

This set of graphene coated samples was also oxidized for different times in air at 190 °C. We expect to see oxidation begins along the graphene grain boundaries. Perhaps oxidations also start at the defects on a single graphene grain. Optical microscopic images are captured for each sample at different times.

Figure 22 comparison between bare copper (left) and graphene coated copper (right)
In the 40X image, the machining copper lines are still there but the cracks take place along the grain boundaries. From the dark lines, many small patches or grains clearly emerge in the optical images. Their sizes vary between 10 and 20 μm. That is the size variation we see in the figures before oxidation. After 30 minutes of exposure to air at 190°C, we claim that oxygen molecules leak through the grain boundaries and react with copper to form dark copper oxide. It is expected that the cracks extend and become wider as the oxidation continues.

The optical microscope images of samples after 10 hours oxidation are captured. Images are captured at the same magnifications of 40X and 100X, so direct comparison can be made (Figure 24).
In comparison with the images at 30 min oxidation, the crack lines are longer and wider. Evidently, more oxygen molecules get inside of graphene layer and further oxidize the copper surface. As the oxidation time involves, the crack lines grew like tree roots extending deeper and broader in the soil.

The optical microscope images of samples after 35 hours oxidation are captured. Images again are captured at the same magnifications of 40X and 100X, so direct comparison can be made with the previous images (Figure 25).
In comparison with the previous two oxidation times, the crack lines still exist but there are many dark regions start showing up because oxygen has completely gotten under those graphene grains and oxidize the local areas entirely.

To quantitatively characterize the oxidation, Raman spectroscopy is used to see difference between before and after oxidation. Raman spectroscopy measures the vibration modes of the material. Before the oxidation, the Raman signal is shown (Figure 26).
The two peaks are the signals from graphene’s vibration modes\textsuperscript{33}. Generally, if there is only graphene on a silicon wafer, then two peaks should start at the same level. The peak on the left is referred as “G-peak”, and it is usually located at 1580 cm\textsuperscript{-1} Raman shift. The peak on the right is referred as “2-D peak”, and it is usually located at 2700 cm\textsuperscript{-1} raman shift. However, since we have copper underneath graphene, the peaks signals are added on top of the raman signal of copper.

The Raman results are taken on samples after 4 hours of oxidation. We specifically focus the Raman laser on center of a graphene grain where has not yet oxidized (Figure 27).
We are able to focus the laser beam with a microscope camera to a spot size around 10-15 μm. The Raman signals of the spot are shown below:

**Figure 27** focus laser beam on clean graphene grain

**Figure 28** Raman signal on clean graphene grain after 4hrs of oxidation
As expected, the shapes of the Raman signals (Figure 28) do not change much from the signals (Figure 26) from the samples before oxidation except that intensity scale can be different. To verify whether the graphene had more defects after oxidation, we looked at the Raman signal at 1350 cm$^{-1}$. It is known that if a CVD grown graphene has amount of defects proportional to the height of the peak at 1350 cm$^{-1}$ which referred as “D Peak.” According to our Raman signals before and after oxidation, there is not a noticeable D peak at 1350 cm$^{-1}$. This indicates that LPCVD has produced high quality graphene film, and graphene grain has no defects emerge from oxidation, which is the results that Ruoff’s group observed$^1$.

Conclusions of the chapter

The low pressure chemical vapor deposition (LPCVD) allowed us to grow large grains of graphene on copper, we are able to study where the graphene coating breaks down. A sequence of samples has been studied. Controlling the growth time of LPCVD, we are able to three sets of samples with large gaps, little gaps, and no gaps between graphene grains. In each case, the results clearly show that air get around the graphene patches and through the gaps or graphene boundaries to oxidize copper surface. So if we have a graphene film coated copper entirely, the breaks down of the coating first occur along the graphene grain boundaries. From the optical images, we could tell that the area along the graphene grain boundaries got oxidized first.
Chapter 8

Conclusions and Future Work

Graphene has demonstrated many unique characteristics. It is the thinnest and strongest 2-D material. Additionally, this material possesses superior thermal and electrical conductivity. Graphene is transparent, and this could lead to a large range of applications in electronic devices. In this paper, we proposed another potential application using graphene as oxidation barrier coating for copper. CVD was introduced as a way to deposit graphene on copper. We demonstrated that graphene dramatically decreased the oxidation rate of copper. We also verified that air leaked through graphene grain boundaries to oxidize copper surface. This indicates the future of the application. To produce effective graphene oxidation barrier coating, the larger grain size, the more effective graphene can protect copper from air. The other potential work is to stitch up the graphene boundaries by depositing another thin layer of coating on top of graphene coating. If the graphene oxidation protection increases by covering up grain boundaries, then it opens up many more corrosion protection applications. For example, graphene coating can be transferred to metals other than copper, so it becomes a corrosion protection coating for many other materials.
References (Nature Journal Style)