

THE PENNSYLVANIA STATE UNIVERSITY  
MILLENNIUM SCHOLARS PROGRAM

DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

The Synthesis and Characterization of Two-Dimensional Copper via Confinement  
Heteroepitaxy

SYDNI FRITTS  
SPRING 2022

A thesis  
submitted in partial fulfillment  
of the requirements  
for a baccalaureate degree in materials science and engineering

Reviewed and approved\* by the following:

Joshua Robinson  
Professor of materials science and engineering  
Thesis Supervisor

\* Electronic approvals are on file

## Signature Page

This report by Sydni Fritts was reviewed and approved by the following:

Joshua A. Robinson

Professor of Materials Science and Engineering

Professor of Chemistry

Professor of Physics

Research Advisor

Amy Robinson

Associate Professor of Materials Science and Engineering

Associate Head for Undergraduate Education in the Materials Science and Engineering Department

## **Abstract**

Two-dimensional (2D) materials have been a focus of more research in recent years due to its unique properties that are attributed to its structure that is a single atom thick. This physical feature is due to the fact that it is composed of covalent bonding within the layers but the layers themselves are held together by weak van der waal bonding. The weak bonding between the layers allows for separation of the layers leading to dangling bonds after separation. Graphene in two-dimensional form has been researched for its variety of properties when intercalated with other elements. Copper intercalation with graphene is the main focus throughout this research paper due to the fact that its metallic properties increase the catalytic reaction. Experiments were performed to determine the optimal process to yield the most efficient copper intercalation with graphene to achieve the desired properties. Parameters that were changed during the experiments were duration and temperature of the intercalation process and how these changes affect the atomic composition and topological surface. This report will begin with background history on 2D materials including 2D metals and their uses due to their properties as well as motivation and their importance. This will be followed by the process that was conducted in each step of the experiments such as cleaning procedures and what was performed to properly analyze the results. These results of the different experimental parameters will then be shown and discussed to understand their importance in understanding the optimal parameters in intercalating copper with epitaxial graphene.

# Table of Contents

<b>LIST OF FIGURES</b> .....	<b>5</b>
<b>1. INTRODUCTION</b> .....	<b>6</b>
1.1 HISTORY OF 2-DIMENSIONAL MATERIALS .....	6
1.2 ELECTRICAL AND PHYSICAL PROPERTIES OF 2-DIMENSIONAL MATERIALS .....	7
1.3 MOTIVATION .....	7
1.3.1 Applications.....	7
1.3.2 Catalytic reaction.....	8
1.3.3 Metal Oxidation.....	9
<b>2. PROCEDURES</b> .....	<b>10</b>
2.1 SYNTHESIS PROCESS.....	10
2.2.1 Parameters for Intercalation.....	11
2.2 CHARACTERIZATION TECHNIQUES.....	12
<b>3. RESULTS AND DISCUSSION</b> .....	<b>13</b>
3.1 PERSONAL IMPACT ON THE PROJECT .....	13
3.2 OPTIMIZATION 2D CU INTERCALATION.....	13
3.2.1 EG vs Buffer Layer.....	13
3.2.2 Cu Foil's Impact.....	14
3.2.3 Optimal Temperature.....	15
3.2.4 Optimal Duration .....	16
3.3 SURFACE TOPOGRAPHY .....	17
3.4 ATOMIC STRUCTURE AND CHEMICAL ANALYSIS OF 2D CU VIA TRANSMISSION ELECTRON MICROSCOPY .....	18
<b>4. CONCLUSION</b> .....	<b>19</b>
<b>5. FUTURE WORK</b> .....	<b>20</b>
5.1 SELECTIVE AREA INTERCALATION .....	20
5.2 CO AND CO <sub>2</sub> ADSORPTION STUDIES ON 2D CU.....	20
<b>6. REFERENCES</b> .....	<b>21</b>

## List of Figures

Figure 2-1: (a) schematic demonstrating the process of formation of cu intercalation as the elemental metal. To begin, epitaxial graphene (EG) is formed via si sublimation and then treated with O2 plasma to create defects. (b) Schematic demonstrating the experimental setup for intercalation by thermal evaporation of cu onto EG.....	11
Figure 3-1: High-resolution XPS (a) Cu 2p, (b) C 1s, and (c) Si 2p spectra of EG and buffer layer after annealing at .... with Cu precursor. (a) no Cu present in the buffer layer and (c) shows there is more Si in the buffer layer so the buffer layer was not intercalated with Cu while the EG was intercalated with Cu .....	14
Figure 3-2: (a) Optical microscope (OM) image toward the edge of the sample with dark regions throughout. (b) OM image of the center of the sample with more bright areas. (c) Ultra-low frequency (ULF) peak in the bright regions have a higher intensity and shows were Cu is present. There is more cu intercalation present toward the center of the sample since the cu foil is placed beneath the sample toward the center of the sample. ....	15
Figure 3-3: OM images of Cu intercalated onto EG. (a) Image consists of spherical Cu particles that are joined together throughout the sample. (b) Image consists of slim dark vertical lines throughout the sample which are non-intercalated EG. (C) Image consists of Thick dark vertical lines throughout the sample which is non-intercalated EG. Based on these results, 975 C is the optimal temperature for intercalation. Scale bars represent 4 $\mu\text{m}$ . ....	16
Figure 3-4: OM images of Cu intercalated onto EG with a scale bar of 4 micrometers. (a) Image has 57% of the sample intercalated. (b) image has 74% of the sample Intercalated. (c) Image has 82% of the sample intercalated. Using this information, it is concluded that 60min is the optimal time duration for intercalation. The coverage is measured via Imagej software. ....	16
Figure 3-5: High-resolution XPS of (a) O 1s 1, (b) Si 2p 3, (c) Cu 2p 4, and (d) C 1s 2 with different time durations of intercalation. More Cu is present with an intercalation time of 60 min as seen in (c) so 60 min would be the optimal time. ....	17
Figure 3-6: SEM image of Cu intercalation onto EG at 975 C showing Si in the bright areas where charging was occurring on the surface. The dark region throughout the sample is 2D Cu and there are thin diagonal lines from the top right to the bottom left of the image which are the step edges.....	18
Figure 3-7: (a) and (b) are dark field TEM images showing the surface of EG intercalated with cu without a step edge (a) and with a step edge (b). (c) EDS image showing the layers of C, O, Si, and Cu of the intercalated sample. ....	19

# 1. Introduction

## 1.1 History of 2-Dimensional Materials

Beginning in 2004, two dimensional (2D) materials have made scientists and researchers across the world interested in not only their unique structure but also their physical and electrical properties. They have a thin structure that resembles a piece of paper that is only a single atom in thickness and comes from bulk materials that have a layered like structure [1]. Graphene is the most common type of 2D material because of its electronic and mechanical properties. The planes within graphite are composed of covalent bonds but these planes are stacked and held together by weak van der waal (vdW) bonds. These weak vdW bonds allow the planes to be separated from each other easily without leaving any dangling bonds.

Metallic materials in 2D form create interest due to their variety of electrical, chemical, optical, and physical properties that can be used in many applications [4]. However, there is little research done on metallic 2D materials due to the rapid oxidation that occurs during multiple steps of formation. Another challenge that prohibits the research done on 2D metals is having techniques that can stabilize the material [3]. Ultra-high vacuum (UHV) environments are required during the formation of these materials and still protective capping layers are needed to remove the material to prevent oxidation [3]. In order to prevent oxidation, metallic elements such as copper (Cu) are intercalated with graphene as the graphene creates a protective layer over the Cu. Having this layer of graphene may limit some of the physical, chemical, optical, and electrical properties of the material.

Two-dimensional (2D) materials are created by mechanical exfoliation, liquid exfoliation, chemical vapor deposition (CVD), or solution-based chemical synthesis [2]. Mechanical exfoliation is done by taking a piece of sticky tape and placing it on the surface of the layered material, and then peeling it off. Liquid exfoliation is done by placing the material in a solvent and then using sonication to cause the layers to split apart. Chemical vapor deposition is done by passing gases through a heated furnace where they will react with each other or a substrate to form a thin layer of graphene [2]. Solution-based chemical synthesis is mainly used for large scale production since there are a few ways from performing this such as using high temperature chemical reactions [2].

## 1.2 Electrical and Physical Properties of 2-Dimensional Materials

The main aspect of graphene that has been researched for the purpose of this report are the electrical and physical properties of graphite in 3D and graphene in 2D. Graphite possesses metal and non-metal properties overall. It is flexible but not elastic with a high electrical and thermal conductivity. Graphite also is highly refractory, chemically inert, and has a low adsorption of x-rays and neutrons. These properties are due to graphite's crystalline structure with carbon (C) atoms in a hexagonal arrangement in a planar condensed ring [5]. Graphite is composed of carbon atoms that have three strong covalent bonds within each layer. Each of these atoms are left with a spare electron creating all of these delocalized electrons to be loosely bonded between the layers. Then, these delocalized electrons are free to move together giving graphite its electrical conducting properties. Commercial graphite has a low electrical resistivity of  $5 \times 10^{-6} - 30 \times 10^{-6}$  ohm meters and a high electrical conductivity of about  $10^4$  Siemens per centimeter [5,6].

These important properties are shared with 2D graphene. Graphene has the same hexagonal in plane structure that allows the material to have a high thermal and electrical conductivity. It is actually the best conductor of electricity ever known with macroscopic graphene having electrical conductivity up to 80 milli siemens per meter (mS/m) [7]. Graphene also is chemically inert, highly refractory, and has a low adsorption of x-rays and neutrons.

## 1.3 Motivation

### 1.3.1 Applications

Copper is typically used for electrical equipment such as wiring and motors due to its highly conductive properties of heat and electricity. It is also a highly flexible material which makes it suitable for wiring and electrical connectors. The applications for 2D copper focus in energy generation and storage. A recent study published in 2021 used a green synthesis method for 2D copper nanosheets with minimized transport resistance [11]. Nanosheets maintain electrochemical properties such as having a high capacitance allowing them to be useful in energy storage systems [11]. 2D copper is also used in generating hydrogen gas ( $H_2$ ) which is a

method of energy generation. When copper atoms fill the vacancies, they are shown to steadily increase the rate of H<sub>2</sub> production since its metallic state acted as a co-catalyst [12].

This research supports multiple issues from the Accreditation Board for Engineering and Technology such as sustainability, economic issues, and environmental issues. Graphene has the potential to alleviate the carbon footprint and enhance the current performance of current materials [4]. Examples of this are making lighter packaging, reducing costs and energy consumption due to its properties. Graphene and layered materials are used to improve current solar cell devices to aid in more affordable and clean energy [4]. As research continues and new products are developed and on the market for sale, this will create new employment opportunities to boost the economy and job market. One example of this is the graphene battery that is coming to market currently with faster cycle times and the ability to hold a charge for a longer period of time. Graphene can also be used to aid in removing pollutant gases like nitrogen oxide in large cities by improving current monitoring devices [4]. As more research is conducted on 2D materials and layered materials, there will be more products and devices that will come to market since there is potential for the variety of properties and other uses, the examples listed above are current applications for graphene.

### **1.3.2 Catalytic reaction**

A catalytic reaction is a chemical reaction between the catalyst and a reactant that ultimately form intermediates that allow each other to react more quickly to form the final product. Catalysis is the process of increasing the rate of these chemical reactions. Copper is used in industry as a catalyst during the process of water-gas shift reactions, partial oxidation of methanol, converting esters to alcohols, and hydrogenation of oils along with many other uses [13]. Typically, in copper based catalytic reactions water dissociates fully to oxygen and hydrogen or water that firsts couples with carbon monoxide dissociates however, a study published in 2016 demonstrated how the catalytic reaction changes drastically with ambient conditions such as pressure [13].

With the addition of defects or other functional groups in graphene, the chemical properties cause graphene to have a high potential of catalytic support [10]. Graphene appears

useful when it comes to supporting catalytic reactions due to this high electron mobility. For catalysis, typically a noble metal catalyst is used a physical mechanical support as well as providing charge transfer [10]. In this report, copper is used as the main element being intercalated with graphene to analyze changes in the catalytic reactions.

### **1.3.3 Metal Oxidation**

Metal oxidation occurs when an ionic chemical reaction occurs on a metal's surface with the presence of oxygen causing electrons to move from the metal to the oxygen molecules. When negative oxygen ions enter the metal, an oxide surface is then created. In copper, the oxidation process occurs in three steps. First, copper oxidizes to copper oxide, then cupric sulfide, and then copper carbonate [14]. The changes chemically begin simply with the presence of oxygen which then turns into sulfur and finally with the addition of carbon, hydrogen, and oxygen. The chemical reactions that occur not only have an impact on the material visually, but it also impacts its physical properties.

Copper oxide crystallizes in a cubic structure and is commonly used in paints for glass and porcelain as a semiconductor for photocells, and antifouling paint for boats and ships. It has a high melting point of 1,232 degrees Celsius (C) and is insoluble in water with effective controls over corrosion [15]. While there are many uses for copper oxides, one of the main attractions of copper is lost, electrical conductivity. Through the copper oxidation process, a protective coating is formed over the metal to prevent further corrosion which hinders the electrical conductivity [16]. Mechanical properties can also be affected by reducing the compressive strength as well. For this research report, the electrical properties of copper wanted to be maintained and this can be done by protecting the copper layer prior to any oxidation.

For our research, we used the Chet process which allows for 2D copper to form at the silicon carbide (SiC) surface with a protective layer of epitaxial graphene (EG). The metal layers adjacent to the SiC surface are covalently bonded to silicon (Si) while there is vdW bonding at the interface between EG and the top-most layer of copper metal [3]. Graphene creates a barrier between the copper metal and oxygen (O) due to the particle size and surface area while strengthening the bonding on the surface between the coating and the metal substrate to block water particles [17]. The SiC interface is important because it essentially acts a template during intercalation to induce the hexagonal structure in the 2D metals [3]. The SiC and EG interface

potentially drives intercalation due to the high energy at the surface which allows for copper atoms to pass more freely [3]. 2D materials typically are directly interfaced with the neighboring materials such as SiC which plays a dominant role in determining mechanical and physical properties due to the high surface area to volume ratios [18]. The SiC and EG interface allows there to be more research for other 2D materials due to its ability to stabilize bulk materials in its 2D form. The mechanism that is allowing this stabilization process to occur is unclear, but another main benefit is improved uniformity. Intercalation is the insertion of atoms or molecules within the layers of the host material which aids in the stabilization process [3].

There are a few methods that can be done to do intercalation such as vapor, liquid, and electrochemical-based approaches. Vapor intercalation is what was performed for this report and is when graphene and an intercalant source, such as copper, are heated in a furnace at a specified temperature, pressure, and duration of time. The quantity that is intercalated by the graphene is dependent on the distance the intercalant is with the graphene while in the furnace. Liquid intercalation occurs by exposing the graphene host to an intercalant gas or by submerging graphene in a solution where time, temperature, and concentration of the intercalant in the solvent alters the final properties [3]. In electrochemical intercalation, graphene anodes are placed in solutions with strong acids that allow the intercalant uptake to be controlled by the electrode voltage [3]. EG layers may separate from the SiC substrate they are grown on due to the intercalating species on the EG and SiC substrate [3].

## 2. Procedures

### 2.1 Synthesis Process

Epitaxial graphene growth was performed directly on the SiC substrates through a high-temperature silicon sublimation process. The SiC wafers are diced along the (0001) face to prepare the individual wafer [3]. A buffer layer is then formed on the substrate by heating the substrate above 1500 C under pressure from an ultra-high vacuum [3]. EG is formed similarly but must be heated above 1800 C. This results in the sublimation which is the silicon atoms from the SiC surface turning from a solid to a gas. On the Si face of the SiC, the remaining carbon becomes reconstructed, and the buffer layer is formed consisting of carbon atoms in a hexagonal structure with 1/3 of the carbon atoms covalently bonded to the silicon on the SiC

surface [3]. Additional carbon layer is stabilized As this occurs, additional Si sublimation occurs and form epitaxial graphene (EG )on the SiC surface [3].

There are multiple steps involved with the SiC substrate prior to the EG growth because the surface of the substrate impacts the growth greatly. The SiC wafers are annealed in hydrogen (H<sub>2</sub>) which etches the surface and remove sub-surface damage caused by the wafer polishing process. he copper precursor of Cu foil is used which is cleaned prior to intercalation. Cu foil cleaning is a crucial step to ensure that there are no particles on the surface so that there is an even intercalation. The Cu foil is hand shaken in acetic acid to remove the native oxide layer. This will slow the evaporation of Cu which will help to avoid CuO from forming. The copper passes through the SiC lifting the initial layer of carbon from the substrate forming graphene layers that are physically and electrically decoupled from the substrate but show improved carrier transport when compared to as-grown EG layers [3].

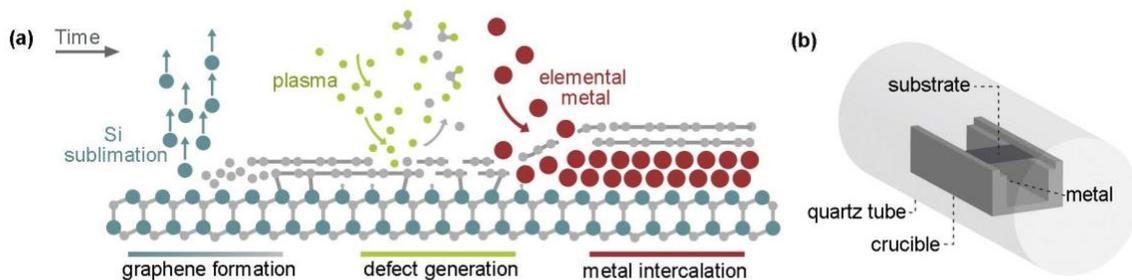


FIGURE 2-1 [3]: (A) SCHEMATIC DEMONSTRATING THE PROCESS OF FORMATION OF CU INTERCALATION AS THE ELEMENTAL METAL. TO BEGIN, EPITAXIAL GRAPHENE (EG) IS FORMED VIA SI SUBLIMATION AND THEN TREATED WITH O<sub>2</sub> PLASMA TO CREATE DEFECTS. (B) SCHEMATIC DEMONSTRATING THE EXPERIMENTAL SETUP FOR INTERCALATION BY THERMAL EVAPORATION OF CU ONTO EG.

### 2.2.1 Parameters for Intercalation

When beginning the intercalation process, an empty Cu annealing tube was placed in the CHet furnace and then the system was put under vacuum. An empty tube is annealed prior to adding the sample in to ensure that the system is free from other containments or particles. The system was then tested to ensure that the pressure does not increase more than 5 mTorr/min to ensure that the leak is minimal. The furnace is then heated at 1050 C for 60 minutes (min) with a

pressure of 700 torr and an Ar flow rate of 200 standard cubic centimeter per minute (sccm). Once the system is fully cooled, the tube is removed after increasing the pressure of the system so that it is at room pressure. The crucible with the Cu foil and the SiC substrate on top is placed in the Cu annealing tube in the furnace system. The system is put under vacuum again followed by having an Ar flow rate of 20 sccm. The system is tested again to make sure that the pressure does not change more than 5 millitorr per minute and then Ar is set to a flow rate of 200 sccm for 10 minutes. Finally, the sample was annealed at 925 C for 60 minutes at a pressure of 700 torr with an Ar flow rate of 50 sccm.

## 2.2 Characterization techniques

Scanning electron microscopy (SEM) produces an image of the sample by scanning the surface with a focused beam of electrons. The electrons are reflected off of the surface by interacting with the atoms in the sample which then produces various signals which contains information about the surface topography and composition of the sample. These images were acquired using a Verios G4 with the accelerating voltage of 2 keV to analyze the images.

Atomic force microscopy (AFM) consists of a high-resolution scanning probe that has a sharp tip. This probe creates an image by raster scanning across the surface of the sample line by line which then creates a 3D image of the surface. The measurements were acquired using a Bruker Dimension Icon microscope in the PeakForce tapping mode with a Scanasyst-air probe at scan rates of 0.7-1 hertz and a peak force set point of ~1 nanonewton.

Raman spectroscopy analyzes a sample by using light to create a molecular vibration and then interpreting this interaction. Through this process chemical composition, crystallinity, and molecular interactions are able to be determined. The measurements were performed using as Horiba LabRam microscope with a wavelength of 532 nanometers. The spectra are acquired by collecting data twice with a 15 second accumulation time using a 300 grooves/mm grating, and then averaging the data.

Transmission electron microscopy (TEM) is a method to determine features of materials on a nanoscale such as grain boundaries, defects, particles, atomic structure, and compositional elements in detail. This is done by a beam of electrons traveling through a vacuum in the column of the microscope and this beam passes through the sample and will either scatter or hit a

fluorescent screen at the bottom of the microscope [19]. The images were collected using an FEI Talos F200X microscope with a dark-field high-resolution technique.

X-ray photoelectron spectroscopy (XPS) is used to analyze a material's surface chemistry and can measure elemental composition. A solid surface is irradiated with a beam of x-rays and then the kinetic energy of the electrons emitted from the top 1-10 nanometers of the material are measured [20]. These measurements were collected with a Physical Electronics Versa Probe III with a monochromatic Al K $\alpha$  X-ray source and a concentric hemispherical analyzer. High-resolution spectra were observed with a pass energy of 29 eV for C 1s and Cu 2p regions and 55 eV for O 1s and Si 2p regions.

Energy dispersive spectroscopy (EDS) is used to determine the chemical composition of a material by having a single crystal that adsorbs energy from incoming x-rays which then yields free electrons that become conductive which produce an electrical charge bias [21]. The data was collected using the superX EDS system which consisted of 4 detectors.

## 3. Results and Discussion

### 3.1 Personal Impact on the Project

SiC wafer cleaning for the EG growth and Cu foil cleaning for 2D Cu intercalation were performed by me. I also performed the intercalation experiments and following the experiments I had done characterization analysis through the use of SEM, AFM, and Raman. Other characterizations, such as XPS and TEM, were performed by our group members or collaborators. Throughout the experiments we had the goal of determining the optimal conditions to have maximum 2D Cu coverage underneath at the EG/SiC interface.

### 3.2 Optimization 2D Cu Intercalation

#### 3.2.1 EG vs Buffer Layer

The buffer layer is composed of covalent bonds between only some of the C atoms and underlying Si atoms which can make it challenging to be uniformly intercalated. Figure 3-1 is high-resolution XPS images where it is observed that the buffer layer consists of C and Si but no Cu while the EG had Cu present after intercalation.

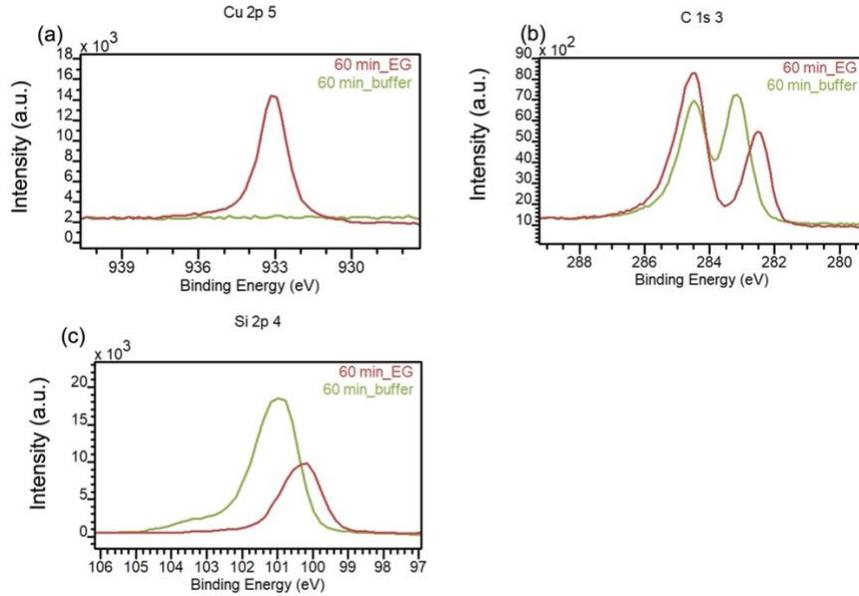


FIGURE 3-1: HIGH-RESOLUTION XPS (A) CU 2P, (B) C 1S, AND (C) SI 2P SPECTRA OF EG AND BUFFER LAYER AFTER ANNEALING AT 975 C WITH CU PRECURSOR. (A) NO CU PRESENT IN THE BUFFER LAYER AND (C) SHOWS THERE IS MORE SI IN THE BUFFER LAYER SO THE BUFFER LAYER WAS NOT INTERCALATED WITH CU WHILE THE EG WAS INTERCALATED WITH CU

### 3.2.2 Cu Foil's Impact

While making sure that the Cu foil is cleaned properly, its placement under the sample also is important for the intercalation process. The results of the intercalation the center of the SiC wafer are different compared to the edge of the SiC wafer. Figure 3-2 (c) shows the bright regions of the samples are intercalated as seen by the ultra-low frequency (ULF) Cu peaks [ref max Wetherington paper- 2-dimensional polar metals: a low-frequency Raman scattering study]. The ULF peak appears with the presence of metal, and in this case, Cu. The center of the SiC wafer is shown in Figure 3-2 (b) which has more bright regions rather than dark regions which shows that most of the sample is intercalated. The edge of the sample shown in Figure 3-2 (a)

has more dark regions when compared to the center of the sample showing that the edge of the sample has less intercalation.

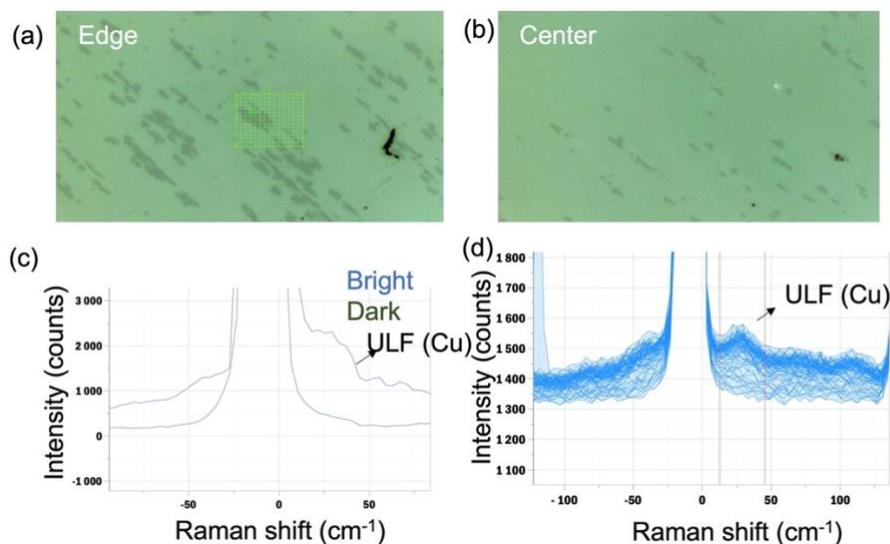


FIGURE 3-2: (A) OPTICAL MICROSCOPE (OM) IMAGE TOWARD THE EDGE OF THE SAMPLE WITH DARK REGIONS THROUGHOUT. (B) OM IMAGE OF THE CENTER OF THE SAMPLE WITH MORE BRIGHT AREAS. (C) ULTRA-LOW FREQUENCY (ULF) PEAK IN THE BRIGHT REGIONS HAVE A HIGHER INTENSITY AND SHOWS WHERE CU IS PRESENT. THERE IS MORE CU INTERCALATION PRESENT TOWARD THE CENTER OF THE SAMPLE SINCE THE CU FOIL IS PLACED BENEATH THE SAMPLE TOWARD THE CENTER OF THE SAMPLE.

### 3.2.3 Optimal Temperature

Different surface features and elemental composition can be observed when observing EG on SiC that is intercalated with Cu at different temperatures. Image 2 below shows the optical microscopy (OM) image in Raman of the sample intercalated at 925 C. Diagonal lines from the top left to the bottom right are observed which is commonly observed on SiC substrates so it can be seen that there is not much Cu intercalated into the surface. Image 3 shows the sample that was intercalated at 975 C, and it also has a few faint small dark lines throughout the sample which are the EG/SiC substrate and areas of the sample that are not intercalated. The sample that was intercalated at 1000 C is shown in Figure 3-3 where beading on the surface is seen. The beading on the surface is likely Cu particles that did not end up getting intercalated into the EG due to the high temperature the intercalation was performed at. With a higher annealing temperature, more Cu evaporates but there may not be enough time for the

intercalation to occur before another Cu particle joins to them. This likely occurs because the Cu on the EG surface can reduce the system's energy by either intercalating at the interface to satisfy the Si dangling bonds or by forming spherical particles on the surface. It was concluded that the intercalation that was ran at 975 C had the most even intercalation of Cu into the EG based off of the OM images shown in Figure 3-3 since there were few dark spots and exposed SiC as well as no grouping of the Cu particles.

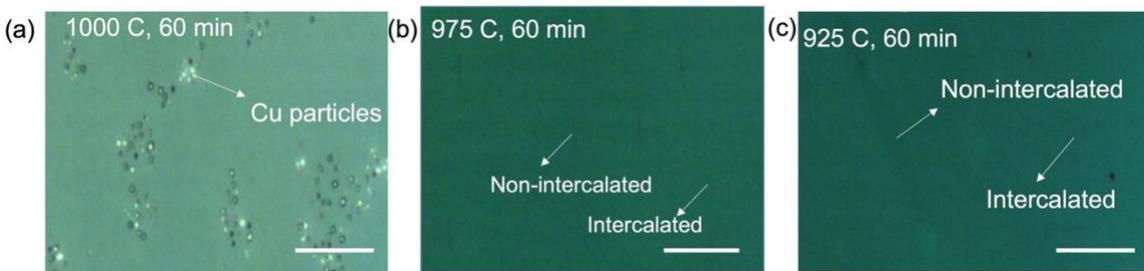


FIGURE 3-3: OM IMAGES OF CU INTERCALATED ONTO EG. (A) IMAGE CONSISTS OF SPHERICAL CU PARTICLES THAT ARE JOINED TOGETHER THROUGHOUT THE SAMPLE. (B) IMAGE CONSISTS OF SLIM DARK VERTICAL LINES THROUGHOUT THE SAMPLE WHICH ARE NON-INTERCALATED EG. (C) IMAGE CONSISTS OF THICK DARK VERTICAL LINES THROUGHOUT THE SAMPLE WHICH IS NON-INTERCALATED EG. BASED ON THESE RESULTS, 975 C IS THE OPTIMAL TEMPERATURE FOR INTERCALATION. SCALE BARS REPRESENT 4  $\mu$ M.

### 3.2.4 Optimal Duration

To determine the optimal duration that the samples should be intercalated at, all parameters except for time were held constant and the intercalation temperature was 950 C. The dark areas on the OM images shown in Figure 3-4 below are areas of the sample that are not intercalated while the bright regions are where the sample is intercalated, confirmed via Raman spectroscopy. Based on this, it is observed that the optimal intercalation time is 60 minutes since 82% of the sample is intercalated with that duration, measured via Imagej software.

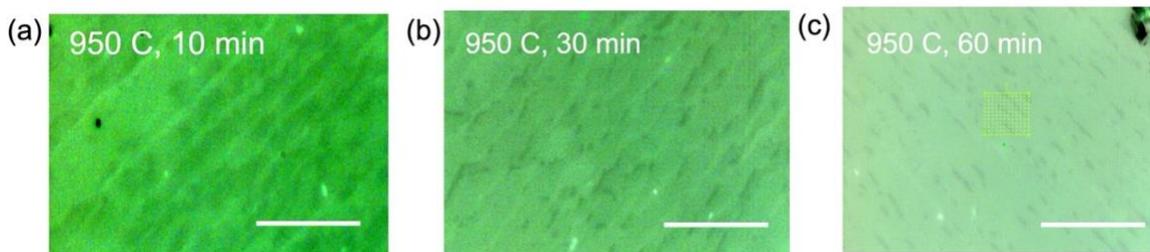


FIGURE 3-4: OM IMAGES OF CU INTERCALATED ONTO EG WITH A SCALE BAR OF 4 MICROMETERS. (A) IMAGE HAS 57% OF THE SAMPLE INTERCALATED. (B) IMAGE HAS 74% OF THE SAMPLE

INTERCALATED. (C) IMAGE HAS 82% OF THE SAMPLE INTERCALATED. USING THIS INFORMATION, IT IS CONCLUDED THAT 60MIN IS THE OPTIMAL TIME DURATION FOR INTERCALATION. THE COVERAGE IS MEASURED VIA IMAGEJ SOFTWARE.

Figure 3-5 is the XPS data of Cu intercalation on EG with different durations. Figure 3-5 (d) shows that all time durations have very similar amounts of carbon present. As seen in Figure 3-5 (b), there is less silicon present when intercalated for 30 min and 60 min when compared to being intercalated for 10 min and 120 min. Through this, it is observed in Figure 3-5 (c) that there is more Cu present after 60 min of intercalation which would yield a more effective intercalation.

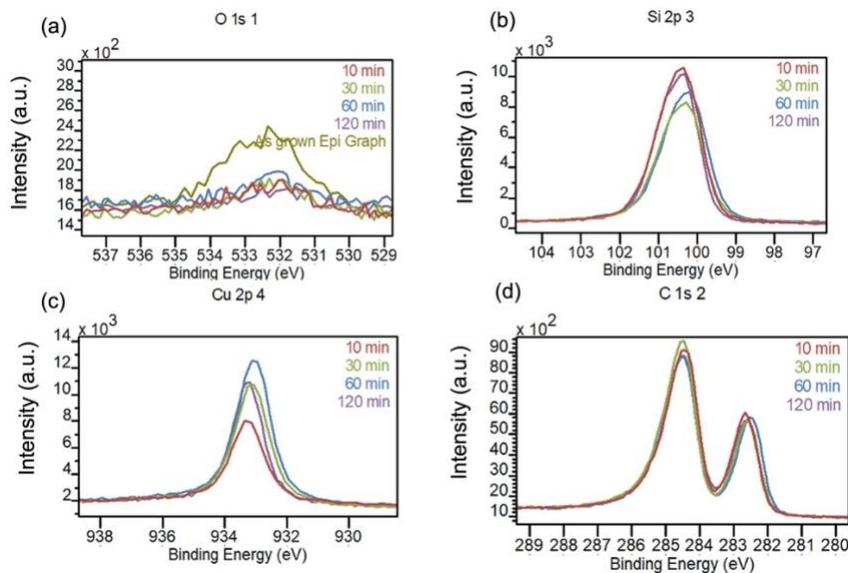


FIGURE 3-5: HIGH-RESOLUTION XPS OF (A) O 1s 1, (B) SI 2P 3, (C) CU 2P 4, AND (D) C 1s 2 WITH DIFFERENT TIME DURATIONS OF INTERCALATION. MORE CU IS PRESENT WITH AN INTERCALATION TIME OF 60 MIN AS SEEN IN (C) SO 60 MIN WOULD BE THE OPTIMAL TIME.

### 3.3 Surface Topography

The surface of Cu intercalated EG at 975 C is shown through SEM imaging shown in Figure 3-6 below. The areas of the sample that are bright are SiC which appear bright due to charging on the surface. The dark region that covers much of the sample is 2D Cu which shows that the sample is evenly intercalated throughout. There are step edges throughout the sample that run diagonally, and these step edges are not intercalated with Cu which is why they appear bright. Some of the dark spherical areas may be particles on the surface. These results show that

intercalation at 975 C leads to an even intercalation which would make it the optimal temperature for intercalation. Ideally, if the sample was fully intercalated, it would be dark throughout the whole sample.

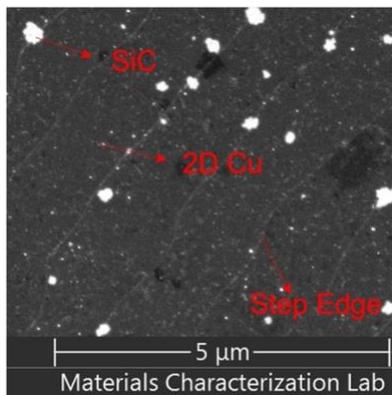


FIGURE 3-6: SEM IMAGE OF CU INTERCALATION ONTO EG AT 975 C SHOWING SI IN THE BRIGHT AREAS WHERE CHARGING WAS OCCURRING ON THE SURFACE. THE DARK REGION THROUGHOUT THE SAMPLE IS 2D CU AND THERE ARE THIN DIAGONAL LINES FROM THE TOP RIGHT TO THE BOTTOM LEFT OF THE IMAGE WHICH ARE THE STEP EDGES.

### 3.4 Atomic Structure and Chemical Analysis of 2D Cu via Transmission Electron Microscopy

Dark field imaging is performed by illuminating the sample with light and the light is then scattered by the sample which then creates the image. The bright areas in TEM are heavier elements and, in this case, it is Cu since Cu atoms are heavier than C, O, and Si. In Figure 3-6, the step edges appeared dark because they are not intercalated with Cu, and this is shown in Figure 3-7 (b) as it is observed on the slope there are no bright areas. Figure 3-7 (a) shows Cu at the interface as there is a bright region evenly throughout the SiC interface. These step edges consist of thicker graphene and current flows through these non-intercalated and thinner graphene regions from EG to SiC since there is a much lower resistance causing the step edges to not be intercalated. The corresponding EDS images are shown in Figure 2-7 (c) which provide

the elemental composition. It can be observed that C is present throughout the sample, Si is predominately present farther from the interface, and Cu is only present at the interface.

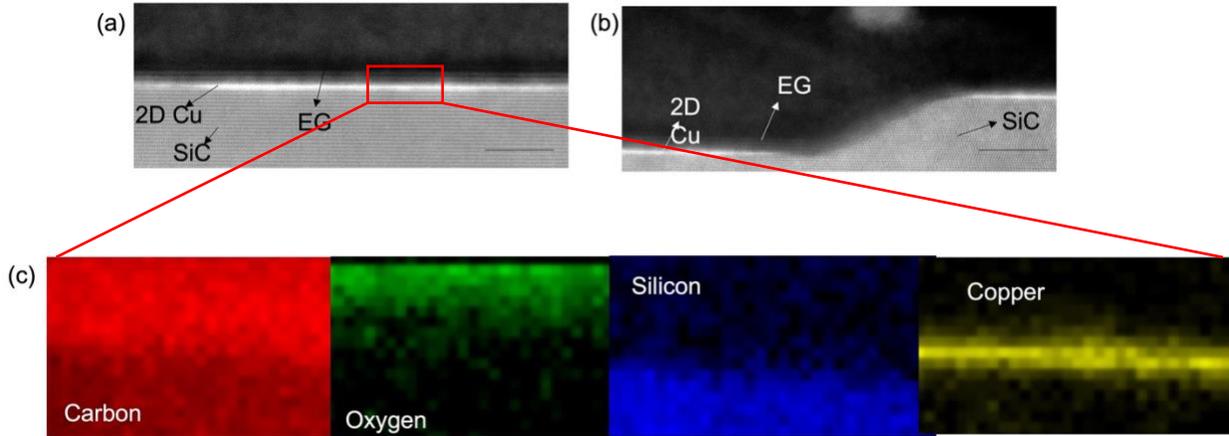


FIGURE 3-7: (A) AND (B) ARE DARK FIELD TEM IMAGES SHOWING THE SURFACE OF EG INTERCALATED WITH CU WITHOUT A STEP EDGE (A) AND WITH A STEP EDGE (B). (C) EDS IMAGE SHOWING THE LAYERS OF C, O, SI, AND CU OF THE INTERCALATED SAMPLE.

## 4. Conclusion

Based on the studies above, it is concluded that defects must be made in the EG to allow for intercalant particles to be adsorbed into the surface. The intercalant such as Cu foil must be thoroughly cleaned to allow for proper evaporation and the Cu foil should be positioned directly underneath the SiC wafer without physically touching it. Higher temperatures lead to more Cu particles being evaporated but not adsorbed by EG while lower temperatures lead to less intercalation because less Cu particles are being evaporated. A duration of intercalation that is 10 min or 120 min will yield the least amount of Cu in the sample while 60 min is the optimal duration. Optimal parameters would be intercalating at 975 C for 60 min at 700 torr to yield the best coverage of 2D Cu underneath EG.

## 5. Future Work

### 5.1 Selective Area Intercalation

Moving forward, modifying the EG growth process such as patterning of the EG layers could allow for selective area intercalation. Previous studies have shown that metal intercalation in patterned EG is possible but there will be oxidation around the EG edges. This oxidation would be that largest challenge but if this were successful this would allow for more controlled and precise intercalation in terms of thickness and composition. One method of preventing oxidation would be to grow EG on modified SiC substrates where there are regions with larger numbers of EG layers.

### 5.2 CO and CO<sub>2</sub> Adsorption Studies on 2D Cu

Carbon monoxide (CO) and carbon dioxide (CO<sub>2</sub>) adsorption on 2D Cu has been studied heavily in recent years [ref]. The general concept would be to convert CO<sub>2</sub> into multi-carbon hydrocarbons due to copper's catalytic properties. To do this, there would need to be even intercalation of Cu on the EG interface, and the CO and CO<sub>2</sub> would need to be able to penetrate the graphene surface above the Cu.

## 6. References

- [1] Prasad, S; Mishra, R; Gupta, S; Prasad, S. Introduction, History, and Origin of Two Dimensional (2D) Materials. *ResearchGate* (2021), p. 4
- [2] 2D Materials: An Introduction to Two-Dimensional Materials. *Ossila* (2022), p.1
- [3] Briggs, N. Novel Synthesis of 2-Dimensional Group III and IV Metals and Binary Compounds. *The Pennsylvania State University* (2020)
- [4] Graphene for a Sustainable Future. *Graphene Flagship* (2022)
- [5] Graphite (C)- Classifications, Properties & Applications. *AZoM* (2002)
- [6] Yemata,T; Xu. J. Conducting Polymer-Based Thermoelectric Composites. *Hybrid Polymer Composite Materials, Vol 4* (2017)
- [7] Köhne, M. Can Graphene-Based Conductors Compete with Copper in Electrical Conductivity? *Bosh Research Blog* (2021)
- [8] What's the Real Difference Between Graphene and Graphite? *TechInstro* (2022)
- [9] Galatzer-Levy, J. Graphene: like diamonds or coal, a carbon with amazing potential. *UIC Today* (2015)
- [10] Zurutuza, A; Urien, A; Torres, E. Graphene for Catalysis. *Graphenea* (2022)
- [11] Turker, F. Synthesis of Non-layered 2D Insulators at the EG/SiC Interface via Confinement Heteroepitaxy and the Investigation of Vertical Charge Transport across 2D Tunnel Barriers. *The Pennsylvania State University* (2022)
- [12] Ganguly, P; Harb, M; Cao, Z. 2D Nanomaterials for Photocatalytic Hydrogen Production. *ACS Energy Lett* (2019)
- [13] Eren, B; Zherenetsky, Z; Patera, L. An Atomic-Level Understanding of Copper-Based Catalysts. *Advanced Light Source* (2016)
- [14] Wieder, H; Czanderma A. The Oxidation of Copper Films to CuO. *American Chemical Society* (1962)
- [15] Zhang, K; Min Suh, J; Hyung Lee, Tae. Copper oxide-graphene oxide
- [16] Whetzel, J. The Effects of Oxidation on Copper. *Sciencing* (2018)
- [17] How Do the Properties of Graphene Protect Against Rust? *Alltimes Coatings* (2020)

- [18] Liu, X; Harsam, M. Interface Characterization and Control of 2D Materials and Heterostructures. *Advanced Materials- Wiley* (2018)
- [19] Transmission Electron Microscopy. *Nottingham University* (2022)
- [20] XPS Surface Analysis of Materials Ranging from Metals to Polymers. *Thermo Fisher Scientific* (2022)
- [21] Goodge, J. Energy-Dispersive X-Ray Spectroscopy (EDS). *University of Minnesota-Duluth* (2017)