THE PENNSYLVANIA STATE UNIVERSITY

DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING

CONFINEMENT HETEROEPITAXY: SYNTHESIS AND CHARACTERIZATION OF TWO-DIMENSIONAL METALS

Ana I. De La Fuente Durán

SPRING 2020

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 A. Robinson Associate Professor of Materials Science and Engineering Thesis Supervisor We approve the thesis of Ana De La Fuente Durán:

Date of Signature_____

Joshua A. Robinson Associate Professor of Materials Science and Engineering Thesis Supervisor

ABSTRACT

Ultrathin metal structures have become highly interesting in the field of 2D materials because of their broad range of predicted properties including topological behavior, superconductivity, ferromagnetism, and unique optoelectronic and nonlinear optical properties. However, one of the largest problems presented by the synthesis of 2D metals is the fact that when metals are confined to two dimensions, they become very hard to stabilize and make effectively resistant to oxidation. In this thesis, the process of confinement heteroepitaxy (CHet) is explored as a technique for realizing air-stable, crystalline metals with atomic thicknesses at the epitaxial graphene (EG)/silicon carbide (SiC) interface. Specifically, this work examines the evolution of EG throughout CHet, highlighting the reasons why In intercalation via CHet is successful. The effects of intercalation temperature and variations in the EG are also explored with respect to In intercalation. The development of the CHet process has the potential to broadly impact next generation electronics, photonics, and optoelectronic technologies.

DISCLAIMER: A large portion of this work was completed through National Science Foundation Materials Research Science and Engineering (NSF MRSEC) funding. The findings and conclusions of this work do not necessarily reflect the view of this funding agency.

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ACKNOWLEDGEMENTS

First and foremost, I would like to thank my research advisor Dr. Joshua Robinson for giving me the opportunity to conduct research as a part of his group since my freshman year at Penn State. This experience and the opportunities that have resulted from it have shown me the exciting nature of materials research and greatly impacted my post-graduation plans. Additionally, I would like to thank my graduate student mentor, Natalie Briggs, as well as graduate student Brian Bersch for their guidance and assistance throughout my undergraduate career. Finally, I would like to thank the entirety of the J. A. Robinson research group for being exceedingly welcoming, friendly, and willing to lend a helping hand.

Chapter 1: Literature Review

1.1 Structure and Properties of Epitaxial Graphene

Less than 20 years ago, Konstantin Novoselov and Andre Geim successfully isolated and characterized two-dimensional (2D) carbon through mechanical exfoliation of bulk highly oriented pyrolytic graphite. [1] This isolation of graphene along with the subsequent study of its unique mechanical, electronic, and optical properties triggered a great deal of research into the synthesis and characterization of 2D structures. In the years following the discovery of the remarkable nature of graphene in 2004, the world of materials science has reported many extraordinary examples of the great impact that both size and dimensionality have on overall material properties. Compared to their traditional three-dimensional counterparts, materials with nanometric dimensions shaped into zero-, one-, or two-dimensional structures often exhibit enhanced electronic, chemical, optical, and magnetic properties due to their quantum confinement in up to three dimensions. [2]

Many two-dimensional materials, including graphene, are derivatives of van der Waals solids. Van der Waals solids are lamellar structures with strong covalent bonds in-plane (within layers) and weaker van der Waals bonds out-of-plane (between layers), as can be observed in the common structure of graphite. Because of this extreme anisotropy in binding energies, the exfoliation of a single layer of material can be easily achieved in these kinds of solids.



Figure 1. Cartoon representations of (a) the layered graphite structure and (b) the honeycomb lattice structure of graphene with a unit cell comprising a basis of two atoms. [3]

Despite the fact that Novoselov and Geim exhibited the successful isolation of graphene through what has come to be known as the 'Scotch Tape method' and the relative ease with which that exfoliation method can be accomplished, research into alternative routes for achieving atomic layers of carbon accelerated exponentially after their discovery in 2004. These alternative routes for realizing graphene included variations of the 'Hummers' method, ion implantation, chemical vapor deposition, liquid-phase exfoliation, and epitaxial growth upon a silicon carbide (SiC) substrate. [4] These alternative routes of graphene production quickly became a pertinent topic of research as the 'Scotch tape method' used by Novoselov and Geim could only isolate small of amounts of graphene at a time and proved to be a tedious manual process involving repetitive steps of peeling carbon layers from a highly ordered pyrolytic graphite crystal and sticking them to a substrate using adhesive tape. [4]

Synthesis of monolayer graphene using SiC substrates was first achieved in 1975 and has since shown much greater promise as a method for the large-scale production of graphene. [5] While this technique was realized well before 2004, it remained largely underutilized for producing mono- to few-layer graphene until it underwent a resurgence following the experimental realization of graphene's unique properties. In this method, single crystal SiC substrates are heated to temperatures typically ranging from 1200-1600°C under pressures ranging from ultra-high vacuum to atmospheric. [6] [7] Since the sublimation rate of silicon is higher than that of carbon, as the SiC substrate is heated, excess carbon is left behind on its SiC(0001) surface. The carbon atoms that remain after Si sublimes undergo a $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ epitaxial reconstruction to form an interfacial layer of carbon on SiC. This first carbon layer is commonly referred to as the zero or buffer layer and consists of carbon atoms in a graphene-like honeycomb structure. [8] Heating SiC substrates for increased times at elevated temperatures enables the controlled formation of multiple layers of graphene through continued sublimation of Si from SiC. [7] For the formation of monolayer graphene, the initial interfacial carbon layer is turned into graphene through the desorption of Si atoms. The transformation of the buffer layer into a layer of graphene, therefore, requires the reformation of a new underlying reconstructed buffer layer. Consequently, any additional layers of graphene that are formed through Si sublimation require the reformation of a new buffer layer. [3]



Figure 2. Transmission electron microscopy images and cartoon representations showing a SiC substrate before it is used to grow epitaxial graphene and after EG is grown. [9]

Epitaxial graphene (EG) differs from graphene realized through other methods in a number of ways. However, the primary feature that distinguishes EG from exfoliated graphene is the existence of the aforementioned buffer layer. Although the buffer layer has a honeycomb structure similar to that of free-standing graphene, roughly 30% of the carbon atoms in this layer are covalently bound to the Si in the underlying SiC substrate, preventing the typical electronic structure of graphene from developing. [8] Normally, the electronic structure of graphene is such that there is sp² hybridization between an *s* orbital and the p_x and p_y orbitals in carbon to create σ bonds. The formation of in-plane bonds between sp² orbitals create the characteristic graphene hexagonal planar structure and are responsible for forming a valence band away from the Fermi level. The remaining electron per carbon that sits in the out-of-plane p_z orbital then forms π bonds with neighboring carbon atoms. The delocalized electrons in these partially-filled π bonds are the cause behind the high electronic conductivity observed in graphene as well as the attractive forces between graphene layers that lead to van der Waals bonding.



Figure 3. Models for the σ and π bonds as well as the sp² hybridization characteristic of the graphene honeycomb structure. [10]

Due to its partial covalent bonding and its intrinsic electron doping, however, the buffer layer observed in EG scatters charge carriers in the graphene layers lying on top of it, resulting in a decreased carrier mobility compared to that of free-standing exfoliated graphene and a pronounced n-type conductivity. [8] This n-type conductivity and change in carrier mobility can be attributed to the electron transfer that occurs between the buffer layer and the overlying graphene. Because the Si-face of SiC is negatively charged due to the intrinsic polarization of Si(0001), the interfacial zero layer is positively charged by electrostatic induction, and the graphene lying on top of it is then electrostatically doped with excess electrons. [8] This deviation from the typical electronic structure of graphene, therefore, renders the buffer layer observed in EG electronically inactive relative to the typical properties observed in graphene.

In order to counteract the electronic effects of the intrinsic electron doping and covalent bonding in the buffer layer of EG, it is desirable to physically and electronically decouple the buffer layer from the SiC substrate to form what is known as quasi-free-standing epitaxial graphene (QFEG). [8] This type of graphene exhibits an improved carrier transport and mobility that can be compared to the outstanding properties observed in exfoliated graphene. A common way to form QFEG is through a hydrogenation step, where an EG sample is annealed at high temperatures in the presence of pure hydrogen gas. This hydrogenation permits hydrogen atoms to intercalate to the EG/SiC interface and passivate the dangling bonds at the face of SiC(0001), thus decoupling the buffer layer to form QFEG. In general, breaking and saturating the covalent bonds between the buffer layer and SiC substrate is required to realize the desirable properties observed in QFEG, and this can be achieved via the intercalation of atomic species to the EG/SiC interface, not limited strictly to hydrogen.



Figure 4. Side view models for (a) the $(6\sqrt{3} \times 6\sqrt{3})R30^\circ$ reconstruction of SiC(0001) ("zero or buffer layer") and (b) epitaxial monolayer graphene. After hydrogen intercalation (c) the buffer layer and (d) monolayer graphene are decoupled from the substrate. [8]

1.2 Intercalation

In a broad sense, intercalation is the insertion of ions, atoms, or molecules into the interplanar spaces within a lamellar structure without the destruction of the host's layered bonding network. Stacking order, bond distances, and occasionally even bond direction can be changed after intercalation, but the overall characteristic lamellar identity of the host must be preserved. [11] Intercalation, as a phenomenon, was formally discovered over 150 years ago. Since its discovery, intercalation has been utilized to create materials that can be used as superconductors, catalysts, high-energy density battery electrodes, lubricants, membranes, and organic reagents. [11]

Graphite intercalation has been a topic of interest since 1841, when the first paper on H₂SO₄ graphite intercalation compounds was published. As previously mentioned, the common structure of graphite consists of two-dimensional carbon sheets that are stacked and weakly bonded to each other through van der Waals interactions. The covalent bonds between the carbon atoms within the graphene sheets are composed of strong σ bonds between in-plane sp² hybridized orbitals. The weak, out-of-plane van der Waals interactions between the layers of graphene arise from the remaining electron per carbon atom that enters a delocalized orbital of p- π symmetry. Because of the nature of this physical and electronic structure, graphite can react with a large variety of intercalants to form lamellar compounds in which the planar graphene is preserved. These compounds are frequently formed by direct combination of the chosen intercalant and graphite with suitable control of pressure and temperature, but they may also be formed in the presence of appropriate solvents. [11] The specific stacking that occurs when graphite is used for intercalation can vary and is differentiated through stages. Stage 1

corresponds to one layer of graphene between intercalant atoms, stage 2 corresponds to two layers of graphene between intercalant species, and so on.



Figure 5. Schematic illustration of Rüdorff and Daumas–Hérold models for the staging mechanism of guest species intercalated into graphite. [12]

With respect to their applications, graphite intercalation compounds (GICs) can be divided into five general categories: highly conductive materials, electrode materials in batteries, catalyzers for organic synthesis, materials for storage and isotope-separation of hydrogen, and others (e.g. thermal energy storage materials). [13] The applications for GICs are largely determined by their respective properties. While intercalant molecules and atoms play a large role in the ultimate properties observed in a GIC, a number of experiments have also proven that the host graphite has definite and quantifiable effects on the functions of the resulting GIC. For example, in order to obtain high electrical conductivity in AsF₅ graphite intercalation compounds, high crystallinity is necessary in the host graphite. Because carbon and graphite materials have various structures and textures, they can readily yield a wide range of properties when used as hosts for the intercalation of the same atoms/molecules. [13] Therefore, the selection of the structure and texture of the host material is very important not only to obtain a specific functionality, but also to attain a higher degree of stability of GICs in order to manipulate them in air. [13] Most GICs are not stable in air, water, or organic media, and techniques to stabilize them have to be developed in order to fully leverage their broad range of properties and possible applications.

After 2004, when interest in graphene was at an all-time high, the interest in intercalation and its impacts on material properties shifted from applications in bulk layered materials like graphite to being studied in two-dimensional systems. Graphene, specifically, became a material of interest for these studies for two major reasons. Firstly, studying intercalation in graphene allowed scientists to revisit and further understand the mechanisms through which graphite intercalation compounds achieved their unique properties (e.g. superconductivity). [14] Secondly, graphene intercalation was of particular interest because intercalation became a proposed strategy to overcome one of graphene's biggest drawbacks: its nonexistent band gap (pictured in Figure 6). Despite the fact that graphene boasts unparalleled charge carrier mobilities, a room temperature quantum Hall effect, plasmon amplification, and a spin relaxation between 10 and 100 μ m, its potential applications in the world of next-generation nanoelectronics are hugely limited by the fact that it is missing a band gap. [14]



Figure 6. Schematic illustration of (a) the honeycomb lattice of graphene and its Brillouin zone, where the Dirac cones are located at the K and K' points, and (b) the electronic dispersion seen in graphene. The missing gap between Dirac cones indicates that graphene has a zero band gap. [15]

To overcome this obstacle, several different routes of functionalization have been studied including methods like the patterning of graphene using templates, the cutting of graphene nanoribbons, and the additional deposition of different atomic species. [8] However, among all the attempted functionalization methods, the intercalation of a variety of elements and molecules has proven to be the most efficient method to impact and modify the band structure of graphene. [14] In diverse material systems, intercalation permits a graphene layer to decouple from its corresponding substrate. This can be seen when H, Ge, and Pd (among other elements) are used to decouple the epitaxial graphene buffer layer from its SiC substrate, when Au intercalation is used to achieve decoupling for graphene/Ni(111), or when O intercalation is used for decoupling graphene/Ru(0001) systems. [8] However, most studies regarding the effects of intercalation on graphene functionalization have been performed in the EG/SiC system.

In general, EG/SiC is favorable for intercalation studies because of how well epitaxial graphene is suited for intercalation. As previously mentioned, hydrogen intercalation is very common in the EG/SiC system, and it can be achieved relatively easily through several layers of high-quality EG. [16] However, for a wide variety of atoms that are larger than hydrogen, intercalation may be best achieved through EG that is defective. Defects in EG can serve as "windows" for intercalant atoms to go through in order to reach the EG/SiC interface. These defects in the EG can be inherent to the system, such as graphene grain boundaries and wrinkles, or they can be deliberately generated in the graphene prior to intercalation. [17] For the species that cannot effectively intercalate through high-quality (low defect density) EG, defects can be introduced into the EG in order to facilitate intercalation over large areas. An example of intentional defect generation is the use of O₂/He plasma to create carbon vacancies in the

graphene. In addition to the formation of the aforementioned "windows" in the graphene, the use of plasma can also passivate vacancy-edge C atoms to create species like C–O–C that can further aid the intercalation process by binding to intercalant atoms more strongly than C atoms in pristine graphene. [18] By drawing intercalant atoms to the EG surface, these passivated species can help to promote intercalation as well. As will be shown in this work, plasma-treated EG layers can be utilized to realize large-area, two-dimensional In.

As can be seen in Table 1, a large variety of intercalants have been used in the EG/SiC system to achieve p-type, n-type, as well as charge neutral graphene. [19] Depending on the thicknesses of the elemental layers at the EG/SiC interface, both p- and n-type graphene can be achieved with the same element as has been observed with intercalated Ge and Au. With most of the intercalant elements seen in Table 1, intercalation through EG used an initial deposition step, where metal atoms (e.g. Co, Pt, Fe, and Au) are deposited onto the surface of EG via thermal evaporation, E-beam evaporation, sputtering, or molecular beam/Knudsen cell deposition. [19] To actually achieve the intercalation through the EG, the EG/SiC samples were annealed at temperatures greater than or equal to 600°C under UHV conditions after the deposition step was completed. [20] [21] [22] [23] Using in situ characterization techniques such as low-energy electron diffraction, low-energy electron microscopy, angle-resolved photoemission spectroscopy, and XPS is relatively easy, making the investigation of intercalated structures at the EG/SiC interface fit for this synthesis approach. [19]

Intercalant	Intercalation Pressure	Intercalation Temperature (°C)	Deintercalation Temperature (°C)	Majority Carrier Type	E_D relative to E_f ($E_f=0$) (meV)
Н	600 Torr atmospheric	600 - 1200		р	100
Li	UHV	290 - 330 350 360	500	n	-650900 -1000 -1400
Ν		500			
0	Atmospheric	250 600 750		р	
F		200 800	1200	p neutral	790 0
Na	UHV	180		n	
Si	UHV	750 800	1000	n	-260 -300
Ca		350			
Mn	UHV	600	1200	n	-300
Fe	UHV	600		n	-250
Со	UHV	650 - 800			
Cu	UHV	600 700	800	n	900 850
Ga	50 Torr	550, 675			
GaN _x	50 Torr	550, 675			
Ge	UHV	720	800	p, n	
Pd	UHV	>700	900	neutral	
Sn	UHV	850	1050		
Eu	UHV	800 120 – 300	1050	n	
Yb	UHV	500		n	1500
YbO _x	UHV	500, 260		n	400
Pt	UHV	900		n	-150
Au	UHV	800 - 1000		p, n	100 -232 -850
Pb	UHV	675		р	100

 Table 1. EG/SiC Intercalation Conditions (Temperature, Pressure) and Resulting Graphene Carrier Type. [19]

Gas-phase precursors can be used to achieve elemental intercalation at the EG/SiC interface as well, as can be demonstrated with H₂, O₂, air, and NH₃. [17] [8] [24] [25] Though the gas-phase precursors are not deposited onto the surface of EG in the way that metals are, gas phase precursors are similar in the way that they are thought to adsorb onto the EG surface and subsequently diffuse through the graphene layers. Unlike the UHV conditions that are used to anneal EG/SiC samples for metal intercalation, atmospheric pressures can be used for the intercalation of gaseous precursors. [8] [24] [25]

In addition to the previously mentioned precursors, plasmas, metal-organics, molten baths, and other molecular precursors have also been used to enable intercalation. [26] [27] These different precursor varieties have been used to intercalate H, Ga, Ca and F. Nevertheless, these sorts of precursors remain largely unstudied.





Overall, EG/SiC intercalation is most commonly done under UHV conditions. [19] However, achieving intercalation at the EG/SiC interface can be done through alternative methods that do not depend on a UHV environment. Most relevant to this thesis is the method of heating metal-organic or solid metallic precursors together with EG/SiC samples in a tube furnace. For the intercalation of non-refractory metals with melting temperatures that are near or below 900°C, this heating approach is effective. The heating of the metallic precursors to temperatures that are near or above their elemental melting temperatures can result in vapor pressures that are great enough to achieve intercalation through EG. The use of compound precursors may be useful and necessary for the intercalation of refractory metals that have very high melting temperatures. The utilization of compound precursors is more complicated than the use of metallic precursors because melting temperature is not the only factor that has to be taken into consideration. In addition to melting temperature, other factors such as decomposition chemistry, relative constituent vapor pressures, and vapor transport characteristics have to be considered.

1.3 Properties of Two-Dimensional Metals

As previously mentioned, a great number of two-dimensional materials have shown a large range of exceptional material properties due to their quantum confinement along one dimension. A majority of the 2D structures that have been extensively studied are held together in-plane by strong covalent bonds and connected out-of-plane by van der Waals forces. This type of layered structure facilitates the confinement of these solids to two dimensions, making 2D materials that are derived from van der Waals solids relatively easy to realize. Because of their inherent differences in structure, 2D materials held together through metallic bonding have remained largely unexplored. Throughout this thesis, the term '2D metals' will be used to refer to films of metal atoms that are only a few atomic layers thick (<5). Beyond this defined thickness, metals will be considered to be three-dimensional. Compared to their covalently-bound, van der Waals solid counterparts, metallically bound materials prefer bonding in three dimensions to form close-packed structures, not bonding in two dimensions to form layered structures. [29] This, in turn, renders 2D materials with metallic bonding harder to achieve and effectively stabilize.

Nevertheless, materials with flexible, metallic bonding have the potential to establish a new class of 2D materials with novel properties that have a number of possible applications. Within the last decade, there have been some notable breakthroughs in this area. For instance, Zheng et al. reported the synthesis of ultrathin hexagonal Pd which exhibited promising properties for applications in photothermal therapy. [30] In a different application, nanostructures of 2D Pd nanosheets were used for ultra-fast hydrogen sensing. [31] In addition to advancements seen with 2D Pd, Jin et al. successfully made atomically thin Au nanosheets that can be applied as transparent and conducting electrodes for next-generation electronics. [32] More recently, single-atomic-layered Rh nanosheets were successfully realized and demonstrated outstanding catalytic activities. [33] Two-dimensional honeycomb configurations of Sn have also been shown to have topological insulating behavior with a very large bandgap, enhanced thermoelectric performance, and topological superconductivity. [34] In a similar configuration, Hf has been shown to have unique ferromagnetic properties. [35] Overall, atomically thin metal structures have become highly interesting in the 2D materials field due to their potential for uses in biosensing, imaging, catalysis, and quantum and optoelectronic technologies.

However, one of the largest problems presented by the synthesis and stabilization of 2D materials that are metallically bonded, aside from the fact that metals prefer close-packed configurations, is the fact that metals are innately more reactive than their 2D semiconducting or insulating counterparts. Very few metals effectively resist oxidation when exposed to air, and when metals are confined to two dimensions, they become even harder to stabilize without the use of encapsulation methods or ultra-high vacuum (UHV) environments. [18] The need to implement encapsulation methods or UHV technologies for the synthesis and stabilization of 2D metals has, to date, greatly limited their practical integration and use in their many potential applications. Much like the aforementioned GICs, in order to fully leverage the broad range of unique properties that are possible with 2D metals, a technique for attaining a higher degree of stability in various media and a specific functionality for these materials is necessary. The confinement heteroepitaxy (CHet) process discussed in this thesis is a technique for realizing metals with atomic thicknesses that are air-stable and crystalline.

1.4 Synthesis and Characterization of Two-Dimensional Metals

i. Synthesis

2D metals, as they are defined in this thesis, are primarily synthesized through the use of molecular beam epitaxy (MBE). Among the variety of potential physical or chemical vapor deposition techniques, MBE is considered to be one of the best methods for achieving high-purity, low-defect, crystalline, and atomically flat metal films that are only a few atoms thick. In MBE, a target or targets are slowly heated to obtain sublimation of the desired material that will reach the substrate and be deposited mono-atomically. Owing to the low deposition rate, there will be an epitaxial growth of the layers, thus yielding a much smoother film. [36] The largest

drawback for the MBE process, however, is that it depends on a UHV environment, meaning that the 2D metals that result from MBE cannot be practically integrated into any devices that are exposed to air. This presents a need for an alternative method of realizing 2D metals.

CHet is a technique that can be utilized to realize atomically thin metals that are crystalline, like those synthesized via MBE, but also air-stable, unlike those achieved through other methods. Unlike the most commonly implemented EG intercalation methods mentioned in Section 1.2, CHet achieves metal atom intercalation at the EG/SiC interface through the use of plasma-treated EG and high pressure (~700 Torr) thermal evaporation. For CHet, epitaxial graphene is grown from 6H-SiC and is subsequently treated with an oxygen plasma that generates defects in the graphene. The samples of plasma-treated EG are then placed into a tube furnace together with metallic precursors that are vaporized onto the EG surface at high temperatures (typically \geq 700°C). The graphene defects generated by the oxygen plasma serve as entry points for the metal atoms to intercalate to the EG/SiC interface. Throughout CHet, the graphene defects change, and these changes can be best observed via a variety of different characterization techniques.

ii. Characterization

Raman spectroscopy is a characterization technique that relies on a monochromatic light source to measure the inelastic scattering interaction between light and matter. [37] By shining a laser of a given frequency on a sample and measuring the intensity of scattered light, Raman spectroscopy can provide information about a sample's atomic mass, composition, bond strengths, and structure/crystallinity. This is because the light source used in this characterization technique causes vibrations within a material that occur at frequencies that are related to the previously mentioned material characteristics. These atomic/molecular frequencies are related to specific sample characteristics through Stokes and anti-Stokes scattering. [38] Stokes scattering refers to the creation of an atomic vibration when the energy of the light source causes an electronic vibration. Once the electron returns to a lower energy level, a photon with a lower frequency than that of the incident laser photon is emitted. The photon will have a lower frequency because some of the excitation energy was lost in the atomic vibration. Inversely, in anti-Stokes scattering, when the excited electron returns to a lower energy level, the photon that is emitted has a higher frequency than that of the incident photon. This is because atoms/molecules that result in anti-Stokes scattering start in an already excited energy level. Since not many molecules exist in an excited energy state before the absorption of radiation, Stokes-scattered radiation tends to have a higher intensity. In a typical Raman spectrometer, the scattered radiation is passed through a number of filters to reduce noise from any unwanted vibrations and then analyzed by a spectrometer for resolving the incoming signal. Usually, the data that is gathered from Raman spectroscopy is plotted as intensity vs. wavenumber (cm⁻¹).



Figure 8. Schematic illustration of (a) Stokes and anti-Stokes Raman scattering with respect to energy changes and (b) where the different scattering types lie on a typical Raman spectrum. [39]

For the effective characterization of the 2D metals achieved at the EG/SiC interface, it is important to analyze the EG spectra that can be obtained through Raman spectroscopy. The Raman spectra for EG can provide a lot of valuable information about the number of layers,

structure, doping, and defect density in the graphene. In a typical EG spectra, there are three Raman-active modes that are the most important, and they correspond to the D, the G, and the 2D peaks. The D peak in the spectra can be indicative of the defect density in a given EG sample, meaning that following the oxygen plasma treatment used on the EG/SiC substrates for CHet, the D peak should increase in intensity relative to as-grown EG. The G peak in the spectra corresponds to the zone-center longitudinal optical phonon. [40] The two-phonon 2D peak corresponds to the double resonant excitation of two phonons close to the K point in the Brillouin zone. [41] It has been demonstrated by Ferrari et. al that the shape of the 2D Raman peak may serve as a way to distinguish mono-, bi-, and few-layer graphene from each other. [30]



Figure 9. Representative Raman spectra for monolayer epitaxial graphene (1LG) and bilayer epitaxial graphene (2LG). The D, G, and 2D bands can be seen in both. [42]

Scanning electron microscopy (SEM) is a characterization technique that is used to image samples through the use of a focused electron beam. [43] As the electrons from the electron beam interact with the surface of a given sample, secondary electrons, backscattered electrons, and characteristic X-rays are produced and then collected by the detectors in the electron microscope. Those collected electrons and X-rays can provide information about a sample's surface topography and composition. The acceleration voltage of the focused electron beam and the density of the material in a sample will determine the penetration depth of the incident electrons. For this thesis, secondary electrons were primarily used for the imaging of the surface of samples produced through CHet.

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive characterization technique that is based on the photoelectric effect, which states that the shining of light on a surface causes the emission of electrons. [44] XPS can provide very valuable quantitative information about the elemental composition and the chemical and electronic states of the elements in a material by measuring the kinetic energy and number of the electrons that escape from the surface of the sample (10-100 Å) when the sample is irradiated by a beam of X-rays. For this work, XPS is utilized for the analysis of the changes in bonding that happen in the C atoms of the epitaxial graphene as it goes through the different steps in the CHet process, as well as the detection of elemental metals once intercalation is complete.

1.5 Engineering Considerations

Throughout the research process, it is important for engineers and scientists to consider any issues related to monetary requirements, the environment, sustainability, health and safety, manufacturability, and social and political impacts that may be involved in a given project. For the work included in this thesis, there were many considerations made with regards to health and safety, economic requirements, and environmental issues. While a large portion of the experimental procedures involved in this work did not pose great physical threat, there were still measures taken to make sure everyone in any given lab space was safe and aware of any potential risks. For example, when cleaning substrates and working with highly corrosive materials (i.e. Nanostrip), proper personal protective equipment was utilized and beakers were always worked with in the fume hood. Before and after being used, the Nanostrip was carefully stored in an acid cabinet and any contaminated glassware was thoroughly rinsed and cleaned. With respect to the environment, proper waste management practices were always employed, and no solvents or solutions were poured down the drain after being utilized.

Additionally, monetary expenses for this work were carefully considered. Monetary expenses encompass anything from the use of characterization equipment, the purchase of raw materials, and the expense of maintaining and fixing equipment. For example, when two tube furnaces became inefficient with for the execution and progression of this research, careful planning was done such that the two tube furnaces could be replaced with four new ones at the lowest possible cost without sacrificing quality and safety. This was to ensure productivity for this and other related projects while maintaining a sense of financial awareness and responsibility.

Chapter 2: Experimental Procedures

2.1 Cleaning SiC Substrates

Prior to epitaxial graphene growth via silicon sublimation, a thorough cleaning of the SiC substrates is necessary to remove any unwanted particulates from the Si(0001) surface that could impact the subsequent growth of graphene. The cleaning process is started with the sonication of the SiC substrates in an acetone bath and an isopropyl alcohol bath for ten minutes each at room temperature. The SiC substrates are then transferred into deionized (DI) water and rinsed thoroughly. After rinsing, the substrates are further cleaned by being placed in Nanostrip (90%

sulfuric acid, 5% peroxymonosulfuric acid, $\leq 1\%$ hydrogen peroxide) at 80°C for twenty minutes for the removal of organic particles. Finally, the substrates are extensively rinsed (~10 times) in DI water to remove any traces of Nanostrip and dried using an N₂ gun.

2.2 Epitaxial Graphene Synthesis

A 6H-SiC substrate is used to grow epitaxial graphene in a hot-zone graphite furnace shown in Figure 10 via the silicon sublimation process outlined in Section 1.1. Typically, four 1x1 cm SiC substrates are placed in a crucible such that the SiC(0001) side of the SiC is face-up and then loaded into the furnace. The furnace is heated to a temperature of 1500°C at a rate of 100°C/min in 10 % hydrogen (where the total flow of gas is 500 sccm with argon). The SiC is left at 1500°C for 30 minutes in order to help remove any damage associated with the micromechanical polishing processes performed on the SiC. [45] After this annealing step, the system is cooled to 850°C, the hydrogen gas is pumped out of the furnace, and argon is reintroduced to pressurize the system to 500-700 Torr. The pressure is chosen depending on the thickness desired for the EG, where a higher growth pressure translates to thinner graphene due to lower amounts of silicon sublimation. For the EG growth, the furnace temperature is elevated to 1800°C and maintained for 10 minutes. During those 10 minutes, the Si sublimes from the SiC(0001) and the C reconstructs as discussed in Section 1.1.



Figure 10. (a) Picture of the graphite hot zone furnace used for EG growth. (b) Schematic drawing of the 6H-SiC polytype. Schematic drawings of the (c) Si face and the (d) C face on SiC. [10]

2.3 Plasma Treatment of Graphene

As previously discussed in Section 1.2, defect generation in epitaxial graphene can help to facilitate the intercalation of a large variety of elements to the EG/SiC interface. For this work, plasma treatments are the primary method implemented for the generation of defects in EG. In a simplified explanation, a plasma is created when enough energy is added to a gas such that electrons are freed from their atoms or molecules and then allowed to coexist with the ionized gas that was created. During a plasma etch, a controlled mixture of gases is turned into a plasma that is then shot at a sample to physically or chemically remove material. The impacts of a plasma etch will be largely dependent on a number of parameters including gas composition, substrate bias, temperature, pressure, etc. The plasma treatments for facilitating intercalation do not require deep material removal, so the plasma treatments are completed using a Tepla M4L plasma etch tool, using O_2 /He plasma with a 150/50 sccm ratio under a pressure of 500 mTorr and 50 W power for 60 seconds.

2.4 Atom Intercalation via Thermal Evaporation

Intercalation via thermal evaporation of metal precursors is completed in a horizontal quartz tube (1 inch diameter) furnace system built by members of the Robinson research group. The pressure controller used is an MKS 600 Series Pressure Controller with an MKS Baratron temperature regulated capacitance manometer (10-1000 Torr). This system employs an Edwards XDS-10 dry scroll vacuum pump and MKS1179C mass flow controllers for each of the two gas supplies: H₂ and Ar. In order to set the gas flow in the system to desired parameters, an MKS 247D four channel flow controller power supply and readout is used. A picture of the STF-1200 furnace along with its additional components can be seen in Figure 11. This furnace set up was the one used for the majority of this work.



Figure 11. Picture of the STF-1200 horizontal tube furnace system used for a majority of the intercalation work.

The intercalation of metal atoms to the EG/SiC interface is performed by placing a 1×1 cm plasma-treated EG/SiC substrate in a custom-made alumina crucible such that the EG side of the substrate faces towards the crucible. Roughly 30-60 mg of In powder (Alfa Aesar, 325 mesh, 99.99%) are placed in the crucible directly below the EG/SiC substrate. After the metal powder and the substrate are placed in the crucible, the crucible is loaded into the horizontal tube furnace. The quartz tube is then evacuated until it reaches pressures around 5 mTorr. Once the furnace reaches that pressure, the leak rate is checked by closing off the access of the vacuum pump to the quartz tube for 5 minutes and checking how much the pressure increased in the system over that time. Intercalation runs are only completed if the furnace leak rates were ≤ 5 mTorr/min. This is done in an attempt to avoid atmospheric gases entering the furnace while the intercalation process is happening in order to prevent the oxidation of the metals held within. Once the desired leak rate is confirmed, the tube is pressurized with Ar to 700 Torr at a flow rate of 50 sccm. As 700 Torr is reached, the furnace is heated to 600-800°C at a ramp rate of 20°C/min. For the intercalation step, the furnace is held at the desired temperature for 30 minutes, and then cooled to room temperature through the use of fans.



Figure 12. (a) Illustration of the CHet intercalation process. (b) Schematic drawing of the substrate and metal precursor loaded into a crucible and then quartz tube. [19]

The temperature at which the intercalation is performed is determined by the intercalant metal that will be used. The most important factors to consider for the determination of the process temperature are the melting temperature of the metal and the vapor pressure of said metal at any given temperature. It is possible to calculate the vapor pressures of liquid metals and the sublimation pressures of solid metals at any temperature from the specific heats of the solid and liquid, the heat of fusion, the melting point of the metal, and the vapor pressure of the liquid or the solid at one temperature (usually melting temperature is chosen for this). [46] The equation used to calculate this vapor pressure is as follows [47]:

$$\log(p) = A + \frac{B}{T} + C\log(T) + \frac{D}{T^3}$$

In this equation, p is pressure, T is temperature, and the A, C, and D values are simple functions of the specific heat and entropy of the solid or liquid metal, and of the molecular weight of the gaseous metal. B is a constant determined by one value of the pressure at one temperature, where melting temperature and pressures are typically used. This equation reproduces the observed vapor pressures to an accuracy of ± 5 % or better.

For solid indium metal, the values of A, B, C, and D are 5.991, -12548, 0, and 0, respectively. Given the values of these constants, it is possible to then calculate and plot the appropriate sublimation/vapor pressures of In at a range of temperatures. A plot for In can be seen in Figure 13. However, it is worth noting that a similar plot can be obtained for any metal once the constants for the aforementioned equation are known.



Figure 13. Plot displaying the increase in the vapor pressure for In as temperature is increased.

A temperature for intercalation is chosen such that the resulting vapor pressure of the metal precursor allows for a great enough number of metal atoms to reach the EG surface and adhere. Once those metal atoms are adhered to the plasma-treated EG, they can then intercalate through the defects in the graphene to reach the EG/SiC interface. If the vapor pressure at a given temperature is not high enough, the area for successful intercalation will be small and patchy.

2.5 Characterization Settings

Raman spectroscopy measurements are performed using a Horiba LabRam Raman system with a laser wavelength of 488nm at a power of 4.6 mW. Spectra are acquired with an integration time of 30 seconds and a confocal hole of 50, using a 600 grooves/mm grating.

Scanning electron microscope images are obtained using a Leo 1530 Field Effect Scanning Electron Microscope using a 5.00 kV acceleration voltage and an in-lens detector.

X-ray photoelectron spectroscopy measurements are carried out with a Physical Electronics Versa Probe II equipped with a monochromatic Al K_{α} X-ray source (hv=1486.7 eV) and a concentric hemispherical analyzer. High resolution spectra are obtained over an analysis area of 200 µm at a pass energy of 29.35 eV for C 1s, Si 2p, Ga 3d, and Ga 2p regions. O 1s regions are collected with a pass energy of 46.95 eV. The acquired spectra are fitted Lorentzian line shapes, and the asymmetric graphene peak fit is derived from exfoliated highly oriented pyrolytic graphite and H-intercalated EG reference samples. Spectra are charge referenced to this graphene peak in C 1s corresponding to 284.5 eV. A U 2 Tougaard background was used to fit XPS spectra. [48]

Chapter 3: Results and Discussion

The work discussed in this section was a result of great teamwork and collaboration. The EG/SiC samples used for this thesis were largely grown by Shruti Subramanian and Chengye Dong, and the plasma-treatment step was executed by Dr. Brian Bersch. Natalie Briggs was a massive contributor to this work as well. She collected the TEM images and the XPS data seen in this thesis and also completed all of the subsequent XPS data analysis that was so crucial to our collective understanding of CHet and its resulting samples. For this thesis, this author was responsible for completing the In-intercalation step for all resulting samples and for collecting the Raman spectra and the SEM images used to analyze the EG/2D-metal/SiC structure.

3.1 Evolution of Epitaxial Graphene through CHet

Throughout the confinement heteroepitaxy (CHet) process, the epitaxial graphene on the EG/SiC substrates was characterized using Raman spectroscopy and XPS. The characterization of the EG in its as-grown, plasma-treated, and post-intercalation states was vital for elucidating the changes that occurred in the graphene as it was impacted by the different steps involved in CHet. In Figure 14, the Raman spectra for EG at the different stages of CHet can be seen.



Figure 14. Raman spectra for epitaxial graphene as it goes through the CHet process. The Raman spectra correspond to (a) as-grown, pristine EG, (b) EG treated with O_2 /He plasma, (c) EG post In intercalation. The added table shows the changes in relative peak intensities.

When looking at the Raman signature of EG at the different steps throughout the CHet process, it is clear that the graphene goes through significant changes. One of the most important metrics to consider when characterizing EG in Raman is the I_D/I_G ratio. [49] As previously mentioned, the D peak signature can provide valuable information regarding the defect density in a sample of EG. When its magnitude increases with respect to the G peak, this can be a sign that the graphene is highly defective. [50] As can be observed in Figure 14, when comparing a pristine, as-grown sample of EG to a plasma-treated sample, the I_D/I_G ratio increases by a factor of ~11. Through the plasma-treatment step, the I_D/I_G ratio has been shown to increase by a factor as large as 15, which is indicative of the formation of highly defective EG post plasma-treatment. [18] Additionally, the manifestation of the D' mode in the form of a shoulder on the G peak is indicative of C vacancies in the graphene. [49] This result was expected, as the plasma treatment is meant to engineer defects into the EG of the EG/SiC substrates to be used for intercalation.

As is also evident in Figure 14, when comparing a plasma-treated EG sample to an Inintercalated EG sample, it can be observed that the I_D/I_G ratio decreases drastically, and that the D peak intensity returns to values that are comparable to those seen in pristine EG. While the change in ratio in and of itself might not offer valuable insights on the inherent state of the EG because of the fact that the I_G increases so drastically after metal intercalation, the decrease in I_D suggests that the graphene is in some way modified as metal intercalation occurs. [51] [52] Although the cause of the D mode suppression is not evident, it is hypothesized that during the intercalation process, the EG heals or re-grows to confine the metal atoms at the EG/SiC interface. [53] [54] Work done by Natalie Briggs for her 2020 dissertation 'Novel Synthesis of 2-Dimensional Group III and IV Metals and Binary Compounds' has also helped to highlight the fact that the I_D is not decreased to the same degree when the plasma-treated EG is annealed in a tube furnace without the presence of a metal intercalant, suggesting that the metal precursors play a role in potentially catalyzing the re-growth or the healing of EG. [48]

Beyond the alterations in the I_D and the I_D/I_G ratio, it is important to also consider the changes observed in the G and 2D Raman bands. After In intercalation, it can be observed that the I_G in the EG Raman signature increases by a factor of ~3 when compared to the I_G of asgrown EG. The cause of this increase is not fully understood; however, it may be attributed in part to the aforementioned healing and re-growth of EG that occurs during the intercalation step. Another potential contributor to the enhancement of the I_G is the fact that the EG transitions from as-grown, where it is still partially attached to the SiC substrate because of its buffer layer, to quasi-free-standing due to the layers of metal atoms at the EG/SiC interface that decouple the buffer layer from the SiC. [55] [40] In addition to forming QFEG, the presence of the metal atoms at the EG/SiC interface may also increase I_G via plasmon enhancement and charge transfer. [56] [57]

Considering the 2D band specifically, In intercalation leads to an increase in I_{2D} typically by a factor ranging between 1 and 2 when compared to the I_{2D} values observed in as-grown EG. Also, as can be seen in Figure 14, the 2D peak for the In intercalated EG sample is redshifted (shifted to the left) by about 20 cm⁻¹ compared to the peak in as-grown EG. This redshift observed in EG may be because of a variation in the number of EG layers, as this peak position is greatly impact by the EG layer number. [41] However, it is possible that the shift is caused by a strain-relief in the graphene that occurs as the metal atoms at the EG/SiC interface eliminate the partial bonding that occurs between the buffer layer and the underlying SiC. [55]

In conjunction with the information gained from Raman spectroscopy, the XPS data gathered for EG/SiC samples as they went through the CHet process played a critical role in

expounding the evolution of the bonding within EG and between the EG and the SiC substrate as the EG sample goes from as-grown, to plasma-treated, to metal-intercalated. For understanding the changes in bonding that happen within the graphene, consideration of the C 1s peak is most crucial. Looking at the C 1s region for as-grown EG/SiC in Figure 15, it is evident that the primary contributions to the overall peak's shape are the C 1s peaks that stem from the C atoms in SiC, the C atoms in graphene, and the C atoms that are partially bonded to the SiC in the buffer layer. Because those are all of the components that should be present in a pristine EG/SiC sample, this peak shape is generally an expected result.



Figure 15. (a) XPS spectra showing the C 1s region for as-grown EG/SiC, O₂/He plasma-treated EG/SiC, and Ga-intercalated EG/SiC. The buffer layer component is shown in red. (b) XPS spectra of (b) the C 1s region and (c) the In 3d region for In-intercalated EG/SiC. [18]

After an EG sample is plasma-treated with O₂/He plasma, the C 1s region changes shape because of the features that result from C–OH and/or C–O–C bonding as well as C=O bonding. These bonds result in C 1s peaks located at approximately 286.7 eV and 288.2 eV, which provide the additional shoulder on the left of the overall C1s region, at lower energies than the buffer layer peak. [58]

Following intercalation for both Ga and In, the C 1s region shows a complete split between the graphene and SiC C 1s peaks. This is due to the fact that intercalation decouples the buffer layer from SiC, thereby eliminating the buffer layer component from the C 1s region. [59] In addition to eliminating the buffer layer C 1s contribution, intercalation also eliminates the carbon-oxygen bonding components, which suggests that the C vacancies in the defective, plasma-treated graphene are eliminated during intercalation. This can be concluded because the carbon-oxygen bonds are a result of the passivation of vacancy-edge C atoms. Once the vacancies are eliminated, the vacancy-edge C atoms are eliminated as well, meaning that the need for passivation via bonding to oxygen species is no longer necessary. Another notable change in the C 1s region for EG/SiC samples post-intercalation is the shift in the SiC C 1s peak to lower binding energies by approximately 0.7–2.0 eV. The presence of metal atoms at the EG/SiC interface results in a change in the charge transfer or interfacial dipole between SiC and EG caused by the decoupling of the buffer layer, and this change results in the aforementioned shift. [60] This shift, in addition to the presence of the metallic In 3d peaks in XPS, confirms the presence of In at the EG/SiC interface.

3.2 Temperature Study for In Intercalation

As already mentioned, the temperature at which the intercalation step is executed in the furnace plays a key role in how successfully the metal atoms intercalate. In order to find the temperature range that best suited In intercalation, a temperature study was completed using similar samples of plasma-treated EG. In order to start at temperatures that were higher than the

In melting temperature (~156°C), the intercalation step was completed at temperatures ranging from 400 to 800°C for this study. As can be seen in the SEM images in Figure 16, the overall area of the lighter colored regions in the EG/SiC samples increased between 400 and 600°C and did not seem to improve between 600 and 800°C. Because the electrons that were being detected were secondary electrons, the contrast in the SEM images alone cannot lead to any valuable conclusions about whether the lighter colored regions correspond to an intercalated area or not. However, because of additional studies completed in conjunction with Auger electron spectroscopy, it is reasonable to correlate the lighter colored regions in the SEM images to the metal-intercalated areas within the EG/SiC sample.



Figure 16. SEM images captured for EG/SiC samples after In intercalation executed at (a) 400°C, (b) 500°C, (c) 600°C, (d) 700°C, and (e) 800°C, showing that lateral intercalation area increased from 400 to 600°C and did not noticeably change between 600 and 800°C.

In order to further compare relative intercalation area for different temperatures, XPS data was collected for the EG/SiC samples that were intercalated at varying temperatures. As

discussed in Section 3.1, one of the most important regions to consider in XPS for the intercalated EG/SiC samples is the C 1s. When comparing the C 1s region for the samples produced at different temperatures in Figure 17, the characteristic peak splitting that occurs between the graphene and the SiC can be observed across all samples. However, there are clear deviations in the sample that was intercalated at 400°C. In this sample, the SiC C 1s peak is weak and there is a marked shoulder on the graphene C 1s peak as well. Given the information that was gathered from additionally analyzing the Si 2p peak for the 400°C sample, it is likely that the peak corresponding to SiC in the C 1s was suppressed because of the fact that there was a large component of SiO₂ bonding. The shoulder on the graphene peak, which corresponds to the buffer layer bonding to the underlying SiC (~283.6 eV), is indicative of nonuniform metal intercalated at 500°C is likely indicative of the same thing to a lesser degree. This quantitatively confirms what can be observed qualitatively in the SEM images.



Figure 17. XPS spectra for (a) the C 1s region and (b) the metallic In 3d region of the EG/SiC samples that were used for In intercalation at temperatures ranging 400-800°C.

XPS spectra for the metallic In 3d regions were also collected for the EG/SiC samples In-intercalated at different temperatures. Because the spot size for the acquisition of this data was 200 μ m, it is likely that the data collected within this area included some mixture of areas that were successfully intercalated and areas that were not. As is evident in Figure 17, all of the samples exhibit metallic In 3d peaks. However, it can be observed that the overall In signal measured for EG/SiC samples intercalated at temperatures $\geq 600^{\circ}$ C was greater than the signal observed for the samples intercalated at both 400 and 500°C, with the 400°C sample showing the weakest signal. The lower intensity of the metallic In 3d peaks observed for the samples intercalated at lower temperatures is indicative of partial intercalation. This is because the lower signal suggests that a smaller fraction of the spot size consisted of successfully intercalated In compared to what is observed in the samples intercalated at higher temperatures.

3.3 Impacts of Graphene Variation on In Intercalation

While variations in temperature play a large role in how fully a metal intercalates to the EG/SiC interface, another key factor to consider in CHet is the nature of the host EG/SiC system. In order to better understand and highlight the effects that the overlying graphene has on the resulting intercalated sample, a study on the impacts of variations within the graphene was completed. There are many variations that can be made to the EG in the EG/SiC system, including the number of EG layers, the defect density within those layers, the kind of bonding that happens at C vacancies as a result of the gases used in the plasma-treatment, graphene step width, and more. For this study, the graphene was varied by the number of layers and relative defect density, and as such, the intercalation process was completed with EG/SiC samples

consisting of pristine and plasma-treated few layer EG (FLEG) and pristine and plasma-treated buffer layer (BL) samples.

As is evident in Figure 18, there are significant visual differences between the varied EG/SiC samples after In-intercalation. When comparing the as-grown samples to their plasmatreated counterparts, it is evident that the largest change happened between the FLEG samples. The as-grown FLEG sample clearly exhibits partial intercalation, with lighter colored regions that are patchy and oddly shaped, whereas the plasma-treated FLEG sample exhibited nearly full intercalation. Another notable difference between these samples is the fact that the plasmatreated sample seemingly accrued In particulates on its surface, which can be seen as the small white dots/chunks that are gathered along the vertical lines in Figure 18c. This accumulated In on the sample surface may be attributed to the fact that the oxygen bonds that are created to passivate vacancy-edge C atoms facilitate intercalation by favorably adhering to and interacting with metal atoms. While not as drastic as what can be observed with the FLEG samples, a similar difference can be observed between the as-grown and plasma-treated BL samples, where the plasma-treated sample had a few In chunks on its surface. Compared to the FLEG samples, however, the BL samples proved harder to visually characterize with respect to relative In intercalation area because of their morphology. Nevertheless, the plasma-treated BL sample does have a more uniform appearance with respect to contrast, which might suggest that it was more successful with intercalation.



Figure 18. SEM images of In-intercalated samples with varied EG. The images display relative differences in intercalation between (a) as-grown, few layer EG, (b) as-grown buffer layer, (c) plasma-treated, few layer EG, and (d) plasma-treated buffer layer.

Much like what was done for the temperature study, XPS data was gathered for all four intercalated samples in order to better quantitatively understand the role that different capping graphene layers play in the resulting EG/2D-metal/SiC structure. Looking at the C 1s region for the different samples in Figure 19, it is evident that there was a great variation within the resulting intercalated samples. When comparing both as-grown samples to their plasma-treated counterparts, it is clear that the full C 1s peak split only occurs with the FLEG and BL samples that were plasma-treated. Both the as-grown FLEG and as-grown BL samples show a shoulder on the graphene peak that corresponds to the buffer layer bonding to the underlying SiC (~283.6 eV). The presence of this shoulder suggests that the intercalation in both of these samples ended up being partial, such that the buffer layer was not fully decoupled by the presence of In atoms.

Another notable deviation from what is expected of the C 1s region for intercalated EG/SiC samples is the very weak SiC C 1s peak observed in the as-grown FLEG. When looking at the Si 2p region for that specific sample, it shows a much larger Si^{2+}/Si^{3+} component than the other samples, suggesting that the SiC C 1s peak may be so weak because of a change in bonding for Si atoms near the EG/SiC interface.



Figure 19. XPS spectra for (a) the C 1s region and (b) the metallic In 3d region of the pristine and plasma-treated variations of few layer EG and buffer layer samples used for In intercalation.

Comparing the metallic In 3d region in the XPS spectra for the different samples, it is evident that the sample with the most intercalated metallic In is the plasma-treated FLEG sample. The as-grown counterpart to this sample showed the weakest signal overall, which is unsurprising because of the pristine nature of the few layers that comprise the sample. Graphene does have inherent defects that can allow for intercalation in its as-grown state; however, because the FLEG samples have more than one graphene layer that metal atoms have to intercalate through, it is less likely that they will make it to the EG/SiC interface.

When looking at the In 3d region for the BL samples, it is evident that both show noticeable shoulders at higher binding energies, with the plasma-treated BL sample actually exhibiting a stronger peak at the higher binding energy than at the energy that corresponds to metallic In. This peak observed in the plasma-treated BL sample corresponds to the binding energy of In in In₂O₃ (~444.8 eV), which is also the source of the shoulder in its as-grown counterpart. [58] The strong presence of an oxide component in the BL samples can be attributed to the fact that the buffer layer, once decoupled from the SiC substrate, only constitutes one layer of what is most likely defective graphene. This graphene is not an effective capping layer for the EG/2D-metal/SiC structure as it more easily allows oxygen atoms through, ultimately allowing for the oxidation of the metal at the EG/SiC interface. The plasma-treated BL sample exhibited stronger signs of oxidation because of the fact that its plasma-treatment compounded the defects that would already be present in the QFEG once the BL was decoupled by the metal atoms. The additional defects only further facilitated the oxidation of the In film post-intercalation.

3.4 Material Structure

In conjunction with the studies completed above, which primarily relied on Raman spectroscopy, SEM, and XPS in order to optimize and better understand the metal intercalation process as it is executed via CHet, other characterization techniques were used to highlight the structure that is formed at the EG/SiC interface once the metal is intercalated. One of the techniques used to image the cross section of the EG/2D-metal/SiC samples was scanning transmission electron microscopy (STEM).

Based on what can be observed in the cross-sectional STEM images in Figure 20, it is clear that the CHet process is successful at intercalating metal atoms to the EG/SiC interface, but that the underlying SiC can play a critical role in how uniform and undisrupted the resulting metal film is. When metals are intercalated via CHet, the resulting metal film at the EG/SiC interface tends to favor being 1-3 atoms thick. In the case of indium, the metal film prefers to be between 1-2 atom layers thick. However, as can be seen in Figure 20b, the metal film can reach a thickness of up to 4 atom layers. At this thickness though, the blurriness that can be observed in the top layers of the In film may suggest that they are not as structurally stable as those layers that are closer to the substrate and bonded to the underlying SiC. Additionally, the metal film can fluctuate in thickness at the step edges in the SiC. While the In metal film tends to remain a uniform thickness when it spans a SiC terrace region, once it reaches a step, it may either be disrupted or increase in thickness near the step edge. Based on what can be observed in the STEM images, when a SiC step consists of multiple atomic steps, the metal film will become discontinuous. When the step is smaller, however, the metal film may simply become thicker near the edge, returning to its normal thickness after spanning a distance slightly over 10 nm.



Figure 20. Cross-sectional STEM images showing In-intercalated EG/SiC that resulted in (a) 2 atomic layers of In and (b) 4 atomic layers of In. (c) Cross-sectional STEM image showing a disrupted film of In at a large step in the underlying SiC. (d) Cross-sectional STEM image showing increased thickness of In at a smaller step in SiC.

Another characterization technique that was used to characterize the EG/2D-metal/SiC cross section was energy dispersive X-ray spectroscopy (EDS). This particular technique was helpful in confirming that the elemental metal film at the EG/SiC interface was indeed In and that it was not oxidized. When comparing the STEM image of the sample that was used for EDS maps, it is easy to correlate the components of the EG/2D-In/SiC structure to their respective elements. Looking at the In and O EDS maps, it is evident that the bright layer of indium atoms below the graphene are not oxygen-rich, suggesting that the In film is metallic and not oxidized. When looking at the final image in Figure 21, it is also evident that the structure that is seen in STEM is in fact a SiC substrate, followed by a thin layer of In atoms, confined by epitaxial graphene, which are all capped by SiO₂ for the purposes of characterization in STEM and EDS.



Figure 21. (a) Cross-sectional STEM image showing In-intercalated EG/SiC sample. (b-f) EDS maps of In, O, C, Si for the same EG/2D-In/SiC sample shown in (a).

Chapter 4: Summary and Conclusion

For this thesis, the intercalation of indium metal to the EG/SiC interface was explored through the process termed confinement heteroepitaxy (CHet). For understanding the mechanisms through which the CHet process progresses, one of the most valuable studies completed as a part of this thesis was the study on the evolution of epitaxial graphene (EG) as it undergoes the different steps in CHet. For this study, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) were the primary characterization tools that were used. The Raman and XPS spectra collected for EG samples in their as-grown, plasma-treated, and Inintercalated states were able to highlight characteristic changes that happen within the EG/SiC system. Compared to what is observed in pristine as-grown EG, the Raman I_D/I_G ratio for plasma-treated EG increased by about $11\times$. This suggests that the plasma-treatment step, which is absolutely crucial to the success of CHet, results in highly defective EG and thereby facilitates precursor atom adhesion and intercalation. When compared to each other, the XPS spectra for the C 1s region observed for as-grown and plasma-treated EG also show notable characteristic differences. After an EG sample is plasma-treated with O₂/He plasma, the C 1s region changes shape because of the features that result from C–OH and/or C–O–C bonding as well as C=O bonding. When combining this information with the information gathered from the Raman spectra, it is reasonable to conclude that the defects generated by the O₂/He plasma-treatment are C vacancies and C vacancy-edge atoms that are passivated by carbon-oxygen bonds.

Following the intercalation step, the Raman and XPS spectra once again provided valuable information to elucidate the nature of the final EG/2D-metal/SiC structure. While the I_D/I_G ratio drastically decreased relative to plasma-treated samples, it may not be a valuable metric to judge changes inherent to the overlying EG because of the fact that the I_G increased by

roughly $3\times$ after intercalation. Nevertheless, compared to plasma-treated samples, the raw I_D for the In-intercalated samples decreased drastically, suggesting that EG is modified by the intercalation process. Because the I_D can be indicative of defect density, the decreased intensity may suggest that the intercalation process can serve to heal or catalyze the re-growth of EG to effectively encapsulate the metal atoms at the EG/SiC interface. The XPS spectra in the C 1s region for intercalated samples exhibited a complete C 1s peak split between graphene and SiC, with an eliminated buffer layer component. This suggests that metal intercalation successfully decouples the buffer layer from the SiC substrate.

In addition to the studies focused on the evolution of EG, a temperature study was completed for the final step of CHet, which is the step revolving around atom intercalation via thermal evaporation. Because CHet relies on the vapor pressure of the precursor metal to be great enough to facilitate atom adhesion to the defective EG surface and the subsequent intercalation through those defects, it was important to explore a range of temperatures for the thermal evaporation of In metal powder. For this study, intercalation was completed on multiple plasmatreated few layer EG (FLEG) samples at temperatures ranging from 400-800°C. This study showed that the lateral area of In intercalation increased between 400 and 600°C, but remained relatively equal between 600 and 800°C. Intercalations completed for In following this study were completed at 800°C.

As well as exploring the effects of temperature on intercalation, the impacts of variations in the EG were also studied. While there are a great number of changes that can be made to EG, the samples that were used for this work were as-grown FLEG, plasma-treated FLEG, as-grown buffer layer (BL), and plasma-treated BL. These samples were chosen with the purpose of studying the impacts of the number of layers and the relative defect density in EG. The sample that exhibited the worst overall intercalation was the as-grown FLEG sample, suggesting that the plasma-treatment step is crucial for the realization of a fully intercalated metal at the EG/SiC interface. While both of the BL samples exhibited relatively good intercalation in both XPS and SEM, they also showed the highest levels of oxidation, suggesting that a greater number of healed EG layers play a large role in the effective encapsulation of the metal atoms. While multiple layers of graphene may not be entirely necessary, this study conclusively exhibited that the decoupled buffer layer is not enough to provide a barrier to oxygen atoms, thereby rendering those samples no longer air-stable.

In order to visualize the cross-section of the EG/2D-In/SiC structure, scanning transmission electron microscopy (STEM) and energy dispersive X-ray spectroscopy (EDS) were utilized. The STEM images captured for an In-intercalated sample confirmed that an In film with a thickness that was most often around 2 atomic layers was confined at the EG/SiC interface, though the thickness of the In film did reach up to 4 atomic layers. These images also served to display the fact that the underlying SiC can impact the uniformity of the intercalated metal film. If the metal film reaches a step in the SiC that is too large (several atomic units of SiC), it may become discontinuous. Conversely, if the metal film reaches a step that is smaller, it may increase its thickness near the step edge. The EDS maps collected for an In-intercalated sample confirmed the presence of In at the EG/SiC interface without the presence of oxygen, suggesting that the metal film confined at the interface was truly metallic.

Overall, in this work, CHet was proven to be a reliable, relatively easy-to-achieve method for realizing two-dimensional indium metal at the EG/SiC interface without concern for oxidation when exposed to air. With this as a basis, there are many things left to be explored within the specific area of 2D In and within the larger world of CHet.

Chapter 5: Future Work

As already mentioned, ultrathin metal structures have become highly interesting in the 2D materials field due to their broad range of predicted properties such as topological behavior, superconductivity, ferromagnetism, and unique optoelectronic and nonlinear optical properties. Because CHet facilitates the realization of 2D metals in a method that prevents their characteristically rapid oxidation and enables their stabilization at the 2D limit, there are many potentially interesting directions and applications that can be pursued.

One of the potential research directions in which CHet could be pushed forward is the further exploration of the different materials that can be stabilized as 2D allotropes of their usual 3D form at the EG/SiC interface. While this thesis was focused on the intercalation of In metal, CHet has also been utilized to achieve 2D forms of elemental Ga, Sn, Ag, Pb, Cu, a Ga/In alloy, and InN_x and GaN_x compounds. The synthesis of a variety of different 2D metals and materials that exhibit various ranges of magnetic, plasmonic, and superconducting properties at this interface via CHet may facilitate their implementation in applications such as quantum spintronics or surface-enhanced sensing.

Aside from the creation of different 2D materials at the EG/SiC interface, there are a variety of avenues that remain to be investigated further within the realm of the CHet process itself. Although this thesis limitedly explored the effects of the intercalation temperature and the nature of the graphene layer on the overall success of intercalation for an In metal powder precursor, there are many studies left to be completed revolving around the different steps involved in CHet including the effects that temperature and graphene may have on varied precursors with different melting temperatures and chemistries.

For improving the general understanding of the role that the defects in the graphene layer of the EG/SiC substrates play in the intercalation of a variety of elements, it would be worthwhile to complete the plasma-treatment step with a set of different gas mixtures. For this thesis, the plasma-treatment step was completed using an O₂/He gas mixture, and this in turn resulted in the formation of C vacancies whose edge atoms were passivated by a variety of carbon-oxygen bonds. Because those vacancies and the bonds that are created because of them have proven to be so essential to the success of CHet, it would be interesting to explore the effects that different plasma chemistries may have on the formation of defects and passivation bonds. Also, as a part of this study, the investigation of the role that different bonds created on the EG surface play in aiding the intercalation of different materials/precursors may be useful, not only for better understanding the role of defects, but for developing a way to predict which plasma chemistries and treatment times may prove to be most effective for the realization of different 2D materials at the EG/SiC interface. This would ultimately improve the efficiency and quality of creating the EG/2D-material/SiC structure.

Within the final intercalation step of CHet, there remain a variety of things left to study as well. Aside from the obvious temperature studies that must be completed when a different precursor is used in the intercalation step, there are number of factors that have yet to be thoroughly explored. One of the factors that has not yet been truly studied in the context of CHet is the amount of time at which the intercalation step is executed. Studying the effects of time on intercalation with materials that have already proven to be relatively easy to intercalate (i.e. In) may help to elucidate the way in which intercalation progresses in the EG/SiC system. Because In has proven to be the easiest metal to intercalate, it may be interesting to observe the way in which atoms migrate at the EG/SiC interface dependent on the amount of time that a sample is left in the tube furnace in the presence of its precursor. This would further our understanding of the intercalation step in CHet and may be useful for making CHet more efficient as precursors and materials are changed. This time factor may prove to be especially important for materials that are not as easy to intercalate because they have a higher melting temperature or low vapor pressures, and understanding it may enable the intercalation and stabilization of a broader variety of materials via CHet.

Beyond the experimental synthesis considerations that can be explored for CHet, there are also a great number of avenues to explore in the realm of the EG/2D-metal/SiC structure properties and its potential applications. Because the potential applications for these materials systems are so varied, it may be more productive to focus only on one of the applications for which the EG/2D-In/SiC structure may be particularly useful.

Due to the asymmetry that is inherent in the EG/2D-metal/SiC systems, they could prove to be uniquely well-suited for nonlinear optical (NLO) applications. As is discussed in more detail in Natalie Briggs's previously mentioned dissertation, 2D metals realized via CHet exhibit a gradient in bonding character. The bottom-most layer of the metal is covalently bound in an epitaxial configuration to the underlying SiC substrate. As the thickness of the confined metal increases, the layers that are closer to the overlying EG exhibit a more metallic bonding character. [48] As a result of this gradient, 2D In is polar in nature and exhibits second harmonic generation peaks and $\chi^{(2)}$ values that are significantly higher than the current state of the art, thus rendering it more promising as a material for NLO technologies. [48] In the realm of NLO technologies, the exploration of light-matter interactions in 2D In for applications in metasurfaces would be both very interesting and unique, due to the extreme optical properties observed in 2D In.

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