Graphene-BN Heterostructures: An In-Plane Transistor

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I. INTRODUCTION

Abstract-- Graphene-Boron Nitride (G-BN) heterostructures can lead to the realization of nanoscale electronics that will be smaller than the dimensional limit—14 nanometers—of silicon transistors and provide higher mobilities. However, the grapheneboron nitride heterostructure although self-insulating, cannot function as a transistor alone due to not having a second conducting pathway. Thus, the utilization of the graphene-boron nitride heterostructure within a side gated FET would require two G-BN flakes to randomly nucleate together. In contrast, the growth of a graphene ribbon around the BN ribbon if fabricated, would allow for a single flake to act as a side gated FET. In order to grow such a G-BN-G heterostructure, the hydrogen etching of BN at high processing temperature must be overcome, which means the use of methane as a carbon precursor for graphene growth is no longer a viable option. As a result, benzoic acid will be studied in the following report as a potential carbon source to synthesize the outer graphene ribbon due to its low thermal breakdown temperature with present showing that hydrogen etching of BN has been reduced.

The graphene field effect transistor (FET) has gained a lot of attention over the recent decade for its high carrier mobility-the ease with which electrons can flow through the crystalline lattice due to its honeycomb lattice, effectively reducing the collision and scattering rates between conducting electrons and fixed carbon atoms. This high mobility along with graphene being a two dimensional atomically thin material has led to the conclusion that graphene could replace the silicon transistor in future nanoscale sensors and circuits because lithographic patterning is reaching its miniaturization limit. However, in order for graphene to truly replace silicon as the transistor material of choice, graphene must be engineered in a way that converts the zero bandgap semiconductor into a true semiconductor with a distinct bandgap. This will allow graphene to have a distinct on and off state within its electronic structure, which is the basis for modern binary coding and memory storage.

Therefore, researchers have begun to look into graphene nanoribbons because theorists have shown that by using density functional analysis, graphene will develop a bandgap when the cross sectional width approaches length scales beneath ten nanometers [1]. At such small length scales, any charge traps at the interface between graphene and silicon dioxide will greatly reduce the carrier mobility of the graphene ribbon therefore boron nitride—a 2-D atomically thin large bandgap dielectric-is currently being studied as an eventual replacement of silicon dioxide as the transistor gating material. Boron Nitride-a structurally and chemically compatible material to graphene-has a complete valence shell due to the ionic bonding between the boron and nitrogen atoms that make up its honeycomb lattice, which means that it has no charge traps [2] due to dangling bonds like silicon dioxide. This has led to the formation of the Graphene-Boron Nitride (G-BN) heterostructure that can serve as a template for the possible chemical vapor deposition (CVD) of a graphene ribbon around the boron nitride ribbon.

The main obstacle for the realization of this outer graphene ribbon is the hydrogen etching reaction of BN at temperatures exceeding 800°C [3]. This eliminates the most common carbon source for graphene growth, which is methane, because its thermal decomposition requires temperatures in excess of 1000°C at atmospheric pressure. Thus, the primary objective of my research is to design CVD growth parameters that test the viability of benzoic acid whose pyrolytic composition temperature is 550°C [4] as a potential carbon source that may allow the growth of the graphene ribbon without the adverse hydrogen etching of the boron nitride ribbon template.

II. Background

3.1 Graphene-Boron Nitride Interface:

The coupling of graphene to its isostructural insulator, boron nitride, results in an interfacial structure that has an equivalent electronic structure to that of the bandless semiconductor, graphene. This is the result of an edge potential that arises from bonding the respective atoms of both structures together. In order to form the G-BN heterostructure, boron nitride's atoms at the interface have to exchange electrons with the carbon atoms of graphene either by accepting (forms stable bonding states) or donating (forms unstable antibonding states) electrons. This phenomena is determined by which atom the edge terminating carbon atoms of graphene bind to within boron nitride. If it is a boron to carbon terminating bond, then a full bonding state will occur, but if the terminating bond is carbon to nitrogen, then an antibonding state will appear [5]. This mix of bonding states at these interface produces the aforementioned edge potential that bends the discreet valence and conduction bands that initially arises within graphene from the quantum confinement of the G-BN edge states to a common point fixed at zero electrons volts, which is the Dirac point of pristine graphene with zigzag edges [6]. Therefore, the crystallographically aligned boron nitride ribbon with that of its graphene template cannot form a bandgap within graphene. The BNRs can however protect the sensitive edge states of graphene through passivation, which preserves the graphene edge states within its wide band gap. 3.2 Graphene Nanoribbon Bandgap Theory:

Due to the cross sectional width of graphene nanoribbons having to approach length scales beneath 10 nanometers in order for a bandgap to appear [1] within their electronic structure, their edge geometry—orders of magnitude larger—will dramatically affect both the mechanism by which the bandgap develops and the width of the resulting bandgap. Current theories on bandgap formation and size are based on density functional analysis, which utilizes the zigzag and armchair edge geometries of hexagonal graphene flakes and full graphene sheets to center the computational calculations. The current model of zigzag graphene nanoribbons (ZGNRs) depicts bandgap formation as a result of the staggered sublattice potential that is created from the magnetic ordering of the electrons. In contrast, a nanoribbon of armchair edge geometry (AGNR) will develop a bandgap from the effects of quantum confinement and increased electron transfer between the edge atoms from atomic bonding length changes [6]. The important feature of such bandgap formation mechanisms is that the width of the bandgap is dependent upon the cross sectional width of the nanoribbon because of quantum confinement effects. For example, the bandgap increases and oscillates with a decrease in nanoribbon width for zigzag and armchair graphene nanoribbons respectively [7]. This allows for tunable bandgap transistors or diodes made of semiconducting graphene nanoribbons that could eventually lead to nanoscale circuitry and sensors. 3.3 Hydrogen Etching Reaction

Although both graphene and boron nitride prefer to attach to the edges of one another before nucleating on the exposed copper surface [5], both materials are highly susceptible to anisotropicdirectional dependent-hydrogen etching at temperatures below their normal growth temperatures using methane and ammonium borane as their respective precursors. Anisotropic hydrogen etching occurs by reversing the growing reaction using residual atomic hydrogen to cleave the carbon-carbon bonds of graphene and the boron-nitrogen bonds of boron nitride to regenerate precursory compounds such as methane, BH_x and NH_x. For graphene, the most efficient hydrogen etching takes place at temperatures near 800°C with a steady decline in the percent area etch for temperatures that either exceed or fall beneath this optimal zone [8]. This drop off in

graphene etching efficiency at lower temperatures is the result of not having enough energy to overcome the activation barrier needed to break the carbon bonds of the zigzag edge while the exothermic nature of this hydrogen etching reaction would make exceedingly high temperatures unfavorable for this reaction.

In contrast, the hydrogen etching of boron nitride at temperatures lower than 900°C occurs mainly along crystal edges and grain boundaries. When temperature reaches above 950°C, a significant amount of anisotropic etching can now occur within the interior of boron nitride crystals, which results in the formation of triangular etched holes along the zigzag direction [3]. The hydrogen etching reaction that occurs in both materials is dependent upon the copper substrate because it allows for atomic hydrogen to adsorb and diffuse into the crystal centers and interfaces of the graphene-boron nitride heterostructure. Thus, the realization of a continuous graphene-boron nitride-graphene nanoribbon heterostructure will be unattainable if the growth substrate material and growth temperature do not reduce this hydrogen etching effect significantly.

IV. Materials and Methods 4.1 Atmospheric Pressure Chemical Vapor Deposition

Chemical vapor deposition (CVD) utilizes the pyrolytic decomposition of compounds to expose their constituent atoms to a metal substrate that catalyzes the reordering of the atoms into complex nanomaterials of various single crystalline geometries. These pyrolytic decomposition reactions often occur at temperatures in excess of 500°C in order to supply enough thermal energy to break the atomic bonds of the compounds within the precursor gas. Atmospheric pressure (760 torr) CVD is utilized over low pressure (1 mtorr) CVD for single crystal growth of graphene and boron nitride due to highly reproducible hexagonal and triangular morphologies that are seen respectively when grown under atmospheric pressure compared to the irregular flowerlike shape grains associated with low pressure CVD growths [5]. The well aligned edge structure of both graphene and boron nitride individual grains will prove beneficial in their utilization as templates for growing boron nitride ribbons and graphene ribbons that will assume their crystallographic orientations. The general CVD setup used in the lab is a horizontal tube wall furnace that flows gases through a one inch quartz tube that can be heated up to 1100°C by external wall heaters. The gas flows are controlled by programmable flow controllers that release carrier gases-gases that facilitate the movement of sublimated solid or bubbled liquid precursory gases through the system-or precursor gases themselves at flow rates of standard cubic centimeter per minute (sccm). The unwanted byproducts of the thermal decomposition of the precursors are carried off into an external exhaust system in order to avoid exposure to harmful gas compounds such as carbon monoxide.

4.2 Methane

Methane will be used for the initial hexagonal graphene flake because its thermal breakdown at temperatures in excess of 1000°C is well defined within the field of chemical vapor deposition growth of 2-D atomic graphene. Methane (CH₄) decomposes as series of four dehydrogenation events on the surface of the copper substrate, which involves the cleavage of a single hydrogen by overcoming a one to two electron volt activation barrier each time. This requires a lot of thermal energy and is not energetically favorable consequently the partially dehydrogenated species will reconnect with each other before complete dehydrogenation of methane to create intermediate hydrocarbon species such as C_2H_2 [9]. These intermediate hydrocarbon species require less energy to form on the copper surface compared to CH dissociation and act as the nucleating species for surface limiting graphene growth on the copper surface. Hence, the initial hexagonal graphene ring will be grown from a methane precursor in order to have a high crystallinity with sharply defined edge structure to ensure that the boron nitride will grow with a uniform crystallographic orientation from this graphene template.

4.3 Ammonia Borane

The boron nitride ribbon precursor will be ammonia borane (NH₃BH₃), which is an air stable solid derivative of borazine. Ammonia borane has a high BN content (80.4 wt. %) that upon thermal dehydropolymerization at temperatures exceeding 60°C reduces to borazine and aminoborane [10]. These compounds can then absorb on the copper surface where another thermally induced polymerization event takes place to generate polyborazylene at 600°C. Polyborazylene is then further dehydrogenated to form thin films of hexagonal-BN at temperatures greater than 700°C [10]. In the experimental CVD process, both the thermally activated polymerization and dehydrogenation occur at the same time since boron nitride is grown at either 1030°C or 1057°C, which can leave residues of non-reacted polyborazylene on the copper surface. However, the amount of polyborazylene on the copper surface will only be trace amounts since the boron nitride growth temperature far exceeds the limit to convert polyborazylene into crystalline hexagonal-BN that

take the form of triangles when grown via atmospheric pressure chemical vapor deposition (APCVD).

4.4 Benzoic Acid

Pyrolytic decomposition of organic compounds such as benzoic acid involves using thermal energy to break the bonds within their chemical structure to acquire smaller molecules such as CO₂ and shorter chained/ringed organic molecules such as benzene. Upon heating up benzoic acid past 550°C, a complete decarboxylation—removal of carbon dioxide-in vacuum occurs within ten minutes if the sample mass is approximately 3.6 mg [4] yielding one benzene molecule based on the stoichiometry of the proposed decarboxylation reaction. The now exposed benzene can be further broken down by dehydrogenation-removal of molecular hydrogen-reactions near the copper surface that acts as the catalysis for the surface limiting growth of graphene. However, the CO₂ secondary product of the pyrolytic decarboxylation of benzoic acid has been found [11] to etch away exposed boron nitride at process temperatures in excess of 900°C. This carbon dioxide etching reaction occurs due to the stronger electronegative oxygen ion pulling away the positively charged boron ion from its ionic bond with nitrogen in order to form boron trioxide, carbon monoxide, and molecular nitrogen. As a result, if graphene growth from benzoic acid can occur at temperatures below 800°C, then the boron nitride will not be etched away by either the carbon dioxide byproduct or by molecular hydrogen that is flown into the system in order to prevent the oxidation of the copper foil by trace oxygen impurities within the argon carrier gas. 4.5 APCVD Growth Recipes

In order to look at the interplay between the carbon dioxide etching reaction and the hydrogen etching reaction of the graphene-BN heterostructure during the growth of a possible third graphene ribbon grown from a benzoic acid precursor, a continuous and discontinuous growth of all three rings were designed and tested. A continuous growth without a cooling period between the formations of the boron nitride ribbon at temperatures exceeding 1000°C and the graphene ribbon around 800°C would be carbon dioxide etching dependent because the hydrogen would be used to facilitate the new graphene growth on the copper surface. However, a discontinuous growth with a cooling period in between boron nitride growth and the later graphene growth using benzoic acid will be hydrogen etching dependent since no carbon dioxide is being produced until the growth temperature is below the carbon dioxide etching temperature.

To test the nature of both growth mechanisms, the initial hexagonal graphene flake and boron nitride ribbon growths were kept constant while the cooling period-no benzoic acid flow into the system—was adjusted over a set of time intervals from 0 to 300 seconds as the system was cooled down to 800°C for a benzoic acid graphene growth period of ten minutes that started when benzoic acid was introduced into the system. The initial hexagonal graphene flakes were grown under a reduced nucleation environment due to exposing the copper foil to oxygen impurities within the 500 sccm (standard cubic centimeter per minute) argon gas flow up to 950°C without the presence of hydrogen gas [12]. This reduced nucleation in the graphene flakes will allow for the surface area needed to grow the boron nitride ribbon and possibly a subsequent

graphene ribbon from the exposed edges of the individual hexagonal graphene grains.

After reaching 950°C, the copper foil was annealed for 30 minutes at 1057°C under a flow of 500 sccm Ar and 30 sccm H₂, which prevented any further oxidation of the copper foil. Methane was then allowed to enter the CVD system at a minimal flow rate between 1.75 and 2 sccm for a ten minute growth period keeping both the hydrogen and argon flow rates fixed at 30 and 500 sccm respectively. Once the 10 minute methane graphene growth period was completed, a magnetic holder containing an ammonia borane pellet was slid to a heat zone-7.7 centimeters away from the furnace-from a cool zone—17.5 centimeters away from the furnace. This initiated the growth of hexagonal boron nitride by sublimating the ammonia borane pellet within the temperature range of 60°C to 70°C. The first two minutes of the five minute growth period involved preannealing the ammonia borane pellet under a flow of 1.75 sccm CH₄, 500 sccm Ar, and 30 sccm H₂ in order to ensure the formation of a sharp interface between the graphene flake and boron nitride ribbon [5]. After the two minute preanneal, the CH₄ was shut off and the hydrogen flow rate was reduced to 20 sccm for the final three minutes of the boron nitride ribbon growth period. The procedure at this point then changes based on the cooling down period described above to test the effects of the carbon dioxide etching reaction due to an early exposure of benzoic acid at temperatures above 900°C and the hydrogen etching reaction due to a late exposure of benzoic acid at temperatures below 900°C. The hydrogen flow rate remained fixed at 20 sccm till the benzoic acid growth period where it was then raised back to 30 sccm to facilitate graphene growth on the copper surface.

4.6 Microscopic Analysis

Once the growths used to test the generation of a graphene-boron nitride-graphene heterostructure by varying the temperature at exposure of benzoic acid into the CVD system were finished, the resulting product was analyzed using a combination of optical and atomic force microscopy on copper foil. Standard optical microscope images—micron resolution were able to show if graphene and boron nitride had been produced due to the optical contrast that resulted from oxidizing the exposed copper foil regions on a hot plate set to 200°C. The regions that are not covered by either graphene or boron nitride would turn red under oxidizing conditions while the protected regions that are covered by one of the two aforementioned materials would appear white.

Atomic Force Microscopy (AFM) nanometer resolution—was then utilized to check for the development of a third graphene ring by using the phase image that was produced by scanning over the surface of the G-BN-G heterostructure. The phase image monitors the phase lag between the signal that drives the cantilever within the AFM to oscillate and the cantilever output signal [13], which is effected by the elasticity, adhesion, and friction of the material surface. Graphene, boron nitride, and copper will produce different colors within the phase image based on the different phase lags that results when the cantilever scans over their respective rings within the G-BN-G heterostructure.

V. Experimental Results



Figure 1: Optical Image of a Discontinuous Growth with a 300 second delay between Graphene Ribbon Growth and Boron Nitride Formation Figure 3: Optical Image at 20 um zoom of a Continuous Growth with no delay between Graphene Ribbon Growth and Boron Nitride Formation





Figure 2a and 2b: AFM Z-Sensor (Height) Images of a Discontinuous Growth with a 300 second delay between Graphene Ribbon Growth and Boron Nitride Formation with the left image being a 30 um scan and right image being a zoomed in 8 um scan Figure 4: Optical Image at 10 um zoom of a Benzoic Acid Precursor Grown Hexagonal Graphene Flake that occurred at a growth temperature of 875°C



Figure 5a and 5b: AFM Z-Sensor (Height) Images of a Continuous Growth with no delay between Graphene Ribbon Growth and Boron Nitride Formation with the top image being a 30 um scan and the bottom image being a zoomed in 10 um scan Figure 6a and 6b: AFM Images of a Continuous Growth grown from a second graphene flake with no delay between Graphene Ribbon Growth and Boron Nitride Formation with the top image being a 66 um Phase image and the bottom image being a 66 um Z-Sensor (Height) image

VI. Discussion and Conclusion

As we can see by the optical and AFM images, the discontinuous growth results in a discontinuity between the original graphene flake and the outer graphene ribbon while the continuous growth results in a nearly seamless transition between the rings without the loss of the boron nitride middle template. This could have been the result of the primary etching reaction in the discontinuous growth mechanism being hydrogen etching by molecular hydrogen that can diffuse more easily through the copper substrate and attack the original grapheneboron nitride interface. However, in the continuous growth the hydrogen gas is being used also to facilitate the growth of the benzoic acid graphene at high temperatures as a consequence, the primary etching reaction is now the carbon dioxide byproduct of the benzoic acid thermal decomposition. Carbon dioxide diffusion through the copper substrate is an order of magnitude lower than hydrogen, thus it is unlikely that enough CO2 will be able to diffuse through the growing benzoic acid graphene and the boron nitride to the original boron nitride-methane graphene interface to attack it. The end result will be an intact graphene-boron nitride heterostructure with graphene grown on the expose substrate around it for the continuous growth of benzoic acid graphene after the boron nitride ribbon formation.



Figure 7: Diffusion of Hydrogen, Steam, Carbon Monoxide, and Carbon Dioxide through Copper at 700°C from Transactions of the American Institute of Mining and Metallurgical Engineers Copyrighted in 1919

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