Chemical Vapor Deposition Growth and Density Functional Theory Calculations of Trilayer Graphene

A thesis presented in partial fulfillment of the requirements for a degree of the Master of Science in Nanotechnology from The Royal Institute of Technology (KTH)

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Abstract
Density functional theory was employed to investigate the energetics of ABA, ABC, and intermediary stacked phases for both pristine and s-triazine functionalized graphene trilayers. The energy of the ABC-stacked phase relative to the pristine ABA-stacked ground state showed a 94% increase when s-triazine was adsorbed to the graphene surface, confirming previous studies of the ability of s-triazine to facilitate the ABC to ABA phase-transition. This work is outlined in an enclosed publication titled “Trilayer Graphene as a Candidate Material for Phase Change Memory Applications.”

Subsequently, low-pressure CVD was used to synthesize single-crystal graphene trilayers of up to 200 µm, the largest reported thus far. The defect density, stacking density, and morphology of the CVD-grown graphene trilayers are evaluated using Raman spectroscopy. The layers are also shown to be directly discernable as-grown on copper substrates using dark-field optical microscopy even without contrast oxidation of the copper film, representing a quick and reliable method for their identification. Slow-etching of the graphene yielded well-aligned, hexagonal domains further indicating the high-quality, single-crystalline of the graphene.
Acknowledgements

First I would like to offer my sincerest thanks to my supervisors during this project: Professors Ostling, Maruyama, and Rong, all of whom have my utmost gratitude for their constant guidance, support and supervision.

Next, I would like to thank my colleagues and coworkers, both at The Royal Institute of Technology and the University of Tokyo, whose fruitful discussions lead to much academic and personal growth, and inspired much of the work done here.

Finally, I would like to thank the friends and family who supported this academic journey in two of the foremost academic institutions in both Asia and Europe.

I would also acknowledge and give thanks to the numerous academic initiatives and their outstanding support staff that made this thesis possible: the USTEP Global Exchange program at the University of Tokyo, the JASSO for awarding me the scholarship for short-term stay in Japan, and the KTH Opportunities Fund, whose endowment also facilitated this trip.
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1. Introduction

1.1. A Historical Perspective of Graphene

Graphene’s debut as the first truly two-dimensional material shifted the paradigm of the scientific community and opened up an entirely new field of research into two-dimensional homo- and hetero-structures, which now also includes such contenders as phosphene, silicene, and hexagonal boron nitride (hBN).

In the strictest sense of the word, graphene is a single atom thick (or corrugated) sheet of carbon atoms Sp2 bound in a hexagonal structure. Its existence was first hypothesized in 1946 by Canadian physicist Philip Russell Wallace, who denounced the possibility of its existence on thermodynamic baseis[1]. Nearly half a century later, in 2004, physicists Andre Geim and Konstatin Novoselov succeeded in isolating graphing for the first time using the now ubiquitous exfoliation process from hyper-pure graphite[2]. In 2011 these two co-discoverers were jointly awarded the Nobel Prize for their efforts, largely in fact to the materials exemplary physical properties in addition to the exciting new fields of two-dimensional material research that it helped instigate.

2.2 Physical Properties of Graphene

A key driver for graphene research both in academia and industry is the ease with which methods to produce superior quality graphene at low costs are progressing. Many graphene research applications have already approached the theoretically projected limits of this material, including room temperature electron ballistic transportation lending it an electron mobility of $2.5 \times 10^5$ cm$^2$V$^{-1}$s$^{-1}$[2]. Thanks to its strong Sp2 bonds, its Young’s modulus has a theoretical limit approaching 1 TPa and its yield strength nears 130 GPa[3]. Graphene also has numerous unique surface properties, including a high hydrophilicity, high impermeability, and a large specific surface area[4]. These physical properties have lead graphene to gain mounting importance in numerous industries including: electronics, structural reinforcement, catalytic chemistry, and corrosion protection.

2.3 Industrial Prospects of Graphene

The aforementioned superior properties of graphene have led to many industry collectives being initiated to further graphene research, with the goal of industrial adaptation. The European Union has allocated a 1 billion Euro fund to the Graphene Flagship, a graphene industrial adaptation initiative headquartered at the Chalmers University of Technology in Goteborg, Sweden[5]. Similar initiatives include a $350 million initiative for industrialized adoption of graphene technologies in Korea and a 50 million GBP initiative by Britain to facilitate graphene commercialization[6].

The majority of the funding in such initiatives is allocated to researching and commercializing ways for graphene to replace silicon in the semiconductor industry, due to the exceptionally high mobility of its charge carriers, the problem being that single layer graphene is both gapless, and as of yet, difficult to dope, making it unsuitable for the immediate replacement of silicon.
Another problem with the adoption of graphene in electronics is the painstaking layup: while silicon technology can be masked, doped, grown and etched with acceptably high yields thank to highly developed, well-established integrated planar technologies, no such developed technologies yet exist for graphene, leading to the need for the highly inefficient and oftentimes inefficient, manual individual placement and testing of graphene sensors and transistors[7].

2.4 Properties of ABA and ABC Stacked Graphene Trilayers

Graphene trilayers are capable of existing in an ABA-stacked “Bernal” stacking order and an ABC-stacked “rhombohedral” stacking order[8-11]. These two stacking orders represent two thermodynamically-stable phases that even naturally-occurring graphitic materials assume, with ABA comprising roughly 85% and ABC comprising the remaining 15%[8, 12-14]. Attempts at fabricating and subsequently characterizing graphene trilayers has generally yielded mixed results[15, 16]: exfoliated layers from graphite are generally of superior quality to their chemically synthesized counterparts[17], and efforts are constantly being made to improve the quality of chemical vapor deposited graphene as compared to exfoliated graphene[18].

From a stereo-chemical perspective, ABA phase possesses interlayer symmetry, while the ABC phase does not, leading to distinct differences and strong coupling between the thermal[12, 19, 20], optical[14, 21, 22], magnetic[13, 19], and electronic[2-4] properties of the two phases.

Of particular interest are the differences in electronic transport properties between the phases. While ABA-stacked trilayer graphene behaves as a zero-bandgap semimetal[17, 23], a bandgap can be opened in semiconducting ABC-stacked graphene trilayers through the application of an electric field[23]. Bandgaps of up to 250 meV have been opened in ABC graphene trilayers, while even at large displacement fields, ABA trilayer graphene remains semimetallic[23]. The difference in conductivities resulting from the band modulatiion of ABA and ABC graphene trilayers in a double gated structure have been confirmed even at relatively high temperatures of up to 120 K, by virtue of inelastic phonon scattering[10].

The thermodynamic stability of the two phases, together with the discrepancy in their electronic properties could be utilized in creating a phase-change memory device, should a reversible pathway between ABA and ABC stacked graphene be found[24], and more importantly, should consistent methods for the production and layup of high-quality graphene trilayers be attained, which this thesis strives to address.

2.5 Phase Transition between ABA and ABC-Stacked Graphene Trilayers

There is general consensus in the scientific community that the predominance of the ABA phase in comparison with ABC phase is due to the slightly larger cohesive energy of the ABA stacking order[25]. Despite this, there are very few reports of induced phase transition from ABC-stacked trilayer graphene to ABA-stacked trilayer graphene[26, 27], although the reverse phase transition has been successfully executed via a highly localized displacement field from an STM tip[28]. The lack of a reversible pathway between the two phases hinders the adaptation of graphene trilayers for hypothetical memory applications.
2.6 This Work: Combined Computational and Experimental Studies into the Thermodynamics and Fabrication of Graphene Trilayers

Graphene trilayers are unique in being the first stacking number capable of expressing commensurate stacking having interlayer symmetry in the case of ABA-stacked “Bernal” phase and interlayer asymmetry in the case of ABC-stacked “rhombohedral” phase. Despite the fact that both these stacking orders are thermodynamically stable and naturally occurring in graphitic materials, and that the ABA stacking order is more thermodynamically stable, there are very few reports of induced phase transition from the ABC stacking order to the ABA stacking order. One reported pathway for the induction of ABC to ABA phase transition in graphene trilayers is through the decoration of trilayer graphene with the aromatic molecule s-triazine.

Comparing the formation energies of pristine and s-triazine decorated graphene trilayers calculated using \textit{ab initio} DFT calculations elaborates on how this organic molecule facilitates the phase transition from ABC to ABA stacked trilayers. These theoretical studies are succeeded by an attempt to synthesize and characterize well-ordered ABA and ABC stacked trilayers using alcohol precursor low pressure chemical vapor deposition at the Maruyama-Chihashi Laboratory of the Mechanical Engineering Department in the University of Tokyo.

These unique and understudied properties of graphene trilayers spurred the initial investigation and resulting publication summarized in the subsequent section “Trilayer Graphene as a Candidate Material for Phase Change Memory Applications” wherein the formation energy of pristine and s-triazine decorated trilayer graphene are compared to better understand the role of this admolecule in altering the energy landscape of graphene trilayers and facilitating the transition from ABC stacking to ABA stacking.
2. Trilayer Graphene as a Candidate Material for Phase Change Memory Applications

In light of the previous introduction on graphene in general and trilayer graphene in particular, this section is intended to summarize the scientific premise, findings, discussion, and conclusion of a publication titled “Trilayer Graphene as a Candidate Material for Phase-Change Memory Applications” done as a collaborative work in the scope of this thesis, as addended to this work in the Appendix section of this thesis and published in the online scientific periodical MRS Advances.

3.1 Computational Objective

The objective of this research project was to use ab initio density functional theory calculations to map the formation energies of different spatial orientations of graphene trilayers between and including the ABC and ABA orientations, both with and without an adsorbed triazine molecule to better understand the effect of this molecule on the overall energy of the triazine-trilayer graphene system.

By doing so, we aimed to shed more light on the previous findings of Zhang et al.[26] who found that adsorbing s-triazine to the surface of mixed ABA and ABC trilayers exfoliated from kish graphite lowered the thermally-activated phase transition from the ABC stacking order to the ABA stacking order from above 1200°C to a much more accessible 100°C. Using ab initio techniques of their own, they attributed this pronounced difference in energy required to induce the ABC to ABA phase transition to a qualitative increase in the energy difference between the ABA and ABC phases resulting from the accumulation of triazine molecules along the boundaries between the ABA and ABC phases, which the group postulated could encourage these wrinkled regions to relax in favor of increasing the overall ABC phase content.

3.2 Computational Methodology

Using the open source DFT software package Quantum Espresso[29] and the crystal structure visualization package Xcrysden[30], we modeled 4×4 supercells of both pristine and triazine-adsorbed graphene trilayers in ABA and ABC and intermediary stacking orientations at 1/8th carbon-carbon bond length intervals.

A total of 96 carbon atoms was simulated for the graphene trilayers. Despite their larger computational overhead, Hamann, Schluter, Chiang and Vanderbilt (HSCV) non-conserving pseudopotentials[31] were used due to the high accuracy of these pseudopotentials in the simulation of formation energies in graphene and graphitic systems. A plane-wave periodical boundary condition was used, with a cut-off energy of 130 Ry.

The reciprocal lattice was sampled with a k-point mesh finesse of 4×4×1, packed in Monkhorst[32] geometry. The open source long range interaction model used was the second revision of the van der Waals density functional (vdW-DF2). In placing the triazine atop the topmost layer of the graphene trilayers, said triazine was placed in a cross orientation at a distance of 3.16Å, as determined by C Chang et al., who used ab initio techniques in comparing
organic molecular dopants to find molecularly adsorbed species that had high adsorption energy and surface interaction with the underlying graphene[33].

### 3.3 Computational Results and Discussion

Using the aforementioned DFT techniques it was shown that the addition of triazine to the ABC trilayer graphene system increased the formation energy of the system by 94% relative to the ABA phase as shown in Figure 1.

![Figure 1](image_url)  
**Figure 1** Energy Difference between ABA and ABC phase graphene trilayers with and without triazine

To find this formation energy for the ABC trilayer graphene, the formation energy of s-triazine was first calculated. Next, the energy of the pristine graphene layers in different stacking orientations were also calculated. Finally, the formation energy of the analogous graphene-triazine layers were also calculated. The triazine formation energy was subtracted from the energy of the formation energy of the triazine-graphene systems and compared against the formation energy of the pristine graphene, once as a difference and again as a quotient.

Special care was taken to ensure as little triazine-triazine interaction as possible between the infinitely repeating supercells resulting from the periodical boundary condition by making these
super cells as large as possible without incurring too steep a computational cost by choosing the 4×4 supercell.

This sheds some light regarding the results reached by Zhang et. al. who experimentally demonstrated that the addition of this admolecule lowered the thermal energy barrier for the transition of ABC phase graphene trilayers back to the ABA phase. As the energy of the ABC phase increases due to the addition of this admolecule, it becomes more energetically favorable for the graphene trilayers to transition back to the ABA phase which becomes pronouncedly lower in energy.

To better understand this results a charge density difference map upon the addition of triazine to graphene trilayers was conducted to show regions of charge accumulation and depletion upon the addition of this admolecule, as shown in Figure 2.

This resulting figure shows that the triazine induces a highly localized dipole in the topmost layer of trilayer graphene, which could destabilize this layer in a similar fashion to the application of a highly biased STM tip.

### 3.4 Computational Conclusions

The addition of s-triazine can be shown to locally polarize the topmost layer of the graphene trilayers, leading to the increase in the formation energy of ABC phase graphene trilayers by 94% relative to ABA phase graphene trilayers. The induction of this localized dipole can be considered analogous to the application of a localized electric field using an STM tip. By studying the graphene-trizine interaction more closely, it may be possible to find more effective ways to induce reversible ABA-ABC phase transition between these two phases. The detailed work summarized here can be found in Appendix 1 in of this thesis.
3. CVD Growth of Trilayer Graphene

Following the uncovering of this significance of the molecule s-triazine in raising the energy of ABC-stacked trilayer graphene relative to ABA-stacked graphene, attempts are made to synthesize and experimentally quantify graphene trilayers using low pressure chemical vapor deposition (LP-CVD) with ethanol as the carbon source.

3.1. Chemical Vapor Deposition

Alcohol catalyzed CVD of graphene provides a reproducible and customizable platform for the growth of single crystalline graphene flakes having different morphologies[16, 34-36]. The general process involves the high temperature thermolysis of a carbon precursor at the surface of a suitable substrate in the presence of a reducing atmosphere. In the case explored in this thesis, the carbon source is ethanol, the high temperature for thermolysis is set to 1065°C (15-20°C below the 1085°C melting point of copper), the substrate is high-purity commercial copper foil (Nilaco Corp., CU-113303), and the reducing gas is 3% H₂ diluted in Ar.

3.1.1. Overview of CVD Process

An overview of the final recipe found in this work follows, succeeded by a detailed explanation of each step:

Commercial copper foil (Nilaco Corp., CU-113303) was successively sonicated in HCl, DI-water, and IPA for 10 minutes each. The cleaned foil was then left to oxidize on a hot plate at 250°C for 1 hour. After oxidation, the foil was crimped in the shape of a pocket enclosure and loaded into the quartz tube of a home-made CVD reaction chamber that was evacuated to 15 Pa. The reaction chamber was heated to the target temperature of 1065°C under a constant flow rate of 300 square centimeters per minute (sccm) of 3% H₂ diluted in Argon throughout the reaction. A butterfly valve was used to maintain the total pressure within the quartz tube at 280 Pa for the duration of the growth procedure. After reaching the target temperature of 1065°C, the copper foil was left to anneal for one additional hour under constant flow of Ar/H₂. After the annealing process was completed, a constant flow of 0.016 sccm ethanol vapor was introduced to induce the graphene growth. Growth times (as measured from start of the introduction of the ethanol vapor) were fixed at 6 hours, leading to hexagonal graphene single crystals roughly 0.5 mm across with large, discernable bilayer and trilayer regions. Upon completion of the growth step, the furnace was turned off and the quartz tube bearing the graphene-impregnated copper films was cooled using a fan for 30 minutes under the flow of 300 sccm Ar gas to prevent the collapse of the copper pockets. Immediately after synthesis and cooling, the pocket was opened and subjected to a contrasting oxidation on a hotplate at 250°C for 1 minute to discern the regions of the copper films with graphene (which did not oxidize) from those without graphene, which developed a colorful film of copper oxide. The regions bearing continuous graphene film were then transferring using the wet-etching PMMA transfer process as detailed later in this work.

3.1.2. Choice of Ethanol as the Carbon Source

Thermally evaporated ethanol vapor serves as a suitable carbon source for the chemical vapor deposition of graphene on copper and nickel substrates, although it is not as popular a carbon
source for graphene CVD as methane due to the complex interplay between the resulting thermolysis radicals of ethanol as compared to the simpler and more straightforward deposition of methane [22, 24, 29, 30]. Gas phase ethanol thermally decomposes at temperatures above 750°C into ethylene and water, with the ethylene further reacting to form acetylene[37, 38], a well-established precursor for carbon nanomaterials including graphene and carbon nanotubes:

<table>
<thead>
<tr>
<th>Ethanol Decomposition Products</th>
<th>Reaction Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_2H_5OH$</td>
<td>$\Delta$ $C_2H_4 + H_2O$</td>
</tr>
<tr>
<td>$C_2H_4$</td>
<td>$\Delta$ $C_2H_2 + H_2$</td>
</tr>
</tbody>
</table>

Other ethanol decomposition products suspected to contribute to the graphene CVD reaction based on chemical kinetic simulations[37] include CH$_4$, CO, H$_2$, CH$_3$OH and CH$_2$O. The oxygen atom of ethanol contributes an etching effect during the CVD growth of graphene[39]. This etching effect is vital in the healing of defects and filling of vacancies during the graphene CVD process[40] and is also the reason why hydrogen is introduced during the reaction.

### 3.1.3. Choice of Copper as Target Substrate

Copper and nickel are the substrates of choice for the chemical vapor deposition of graphene due to their catalytic effect in the breakdown of carbon precursors such as methane and ethanol, the ease of etching and consequently the transfer of graphene from these substrate materials to others following graphene growth, and the low cost of both of these materials[41]. Copper is chosen over nickel due to the low solubility of carbon in copper (4.8 ppm at 1000°C [42]), which prevents the absorption and subsequent surface segregation of carbon from bulk copper, leading to a surface-dominated graphene CVD process with better control over multilayer formation.

### 3.1.4. Copper Foil Pre-oxidation

Pre-oxidation of the copper foil prior to folding and crimping the enclosure was done to form a thin copper oxide layer, limiting the nucleation density during growth[43, 44]. Without such a retardant to nucleation, large, merged regions of graphene form on the copper surface during CVD, making it difficult to discern the morphology of the resulting flakes. Oxidized and unoxidized copper films are shown side by side in the following Figure 3.
In addition, there is evidence that the pre-oxidation and subsequent reduction of the copper oxide layer during graphene deposition enables the in situ synthesis of copper nanoparticles on the surface, which serve as sites for the initial nucleation and consequent growth of the graphene flakes.\cite{45, 46} Evidence of these aggregate nucleation sites can often be seen in optical microscopy images of the copper foil after graphene growth as shown in Figure 4 below:

![Figure 3 Unoxidized (Left) versus Oxidized (Right) Copper Foil](image)

Figure 3 Unoxidized (Left) versus Oxidized (Right) Copper Foil

The copper foil in this work was oxidized for 1 hour at 240°C on a hotplate to achieve full, homogenous coverage with copper oxide, as confirmed visually.

![Figure 4 Black aggregate in the center of graphene flake signifying nucleation point](image)

Figure 4 Black aggregate in the center of graphene flake signifying nucleation point
3.1.5. Cu Enclosure
An enclosure which improves the morphology of the grown graphene can be formed by folding a copper foil in half and crimping the three remaining edges, by rolling the copper foil in a tubular structure, or by stacking two layers of copper foil atop one another prior to CVD growth [28, 34, 35]. The folding and crimping technique is the simplest and most reproducible of the three and is consequently selected in this work.

![Folded copper enclosure for CVD](image)

A typical copper pocket is shown in the above Figure 5. The improvement in morphology accompanying the usage of these enclosures can be attributed to the elimination of possible SiO₂ contamination from the quartz tube, the lower and more steady flux of the carbon source to the inner copper surfaces, and the reduction in carbon source partial pressure.

3.1.6. Annealing of Copper Film
The annealing of the copper film is a well-established process known to improve the quality of CVD-grown graphene by eliminating grain boundaries, releasing mechanical stress, and smoothing the surface of copper prior to deposition[16, 47, 48]. The following Figure 6 compares the same copper surface on the inside of the pocket before and after the annealing process prior to the growth step. The parallel equidistant lines in the left image are indicative of mechanical cutting which inadvertently leads to mechanical stresses arising in the material. The figure on the right shows that the induced recrystallization and growth of copper crystals at the surface, yielding a more relaxed surface conducive to single-layer graphene growth.
There exists a tradeoff in improvement of the copper surface through annealing and the annealing time, with annealing times typically ranging between 40 minutes and 1 hour, after which, improvements are nominal in comparison with the required energy input. Copper films were annealed for 1 hour at 1065°C prior to the start of the ethanol vapor in an inert Argon atmosphere.

3.2. **Trends in the CVD Parameter Space**

Extensive work has been done on the synthesis and characterization of carbon nanomaterials using ethanol as the carbon source by the Maruyama-Chihashi group at the University of Tokyo Department of Mechanical Engineering [19-24]. Group member Xiao Chen and collaborators found a regime where single-crystal domains of Bernally-stacked graphene bilayers of sizes exceeding 450 µm could be synthesized by modulating the ethanol mass flow rate and the total pressure within the CVD reaction chamber during graphene growth [24]. The group found a narrow window for the growth of this bilayer graphene by limiting the reaction pressure to 450 Pa and using a moderate ethanol mass flow rate of 0.06 square centimeters per minute (sccm) [24]. In exploring the parameter space of alcohol catalytic CVD for graphene growth, it was found that lower total pressures and ethanol flow rates resulted in the growth of well-ordered graphene multilayers [24], providing a starting point for the investigation of parameters suitable for the growth of graphene trilayers.

3.2.1. **Ethanol Flow Rate**

In investigating the CVD parameter space to find a regime for trilayer graphene growth the most critical parameter for evaluation was deemed the ethanol vapor pressure, as it directly contributes to the size and morphology of the resulting graphene flakes being both the carbon source and an etchant for the graphene. The ethanol flow rate was varied between 0.016 and 0.16 sccm keeping the rest of the parameters constant: a total pressure of 450 Pa and an Ar/H₂ flow rate of 300 sccm for 6 hours, the results of which are discussed in subsequent sections.

3.2.2. **Total Pressure**

To determine the effect of total pressure on the morphology of the grown graphene, the total pressure within the reaction chamber was varied between 280-500 Pa keeping the ethanol flow rate fixed at 0.06 sccm, the Ar/H₂ flow rate fixed at 300 sccm, and the time fixed to 6 hours.
The effect of total pressure becomes very pronounced in determining the morphology of the trilayer graphene; a higher pressure shows a clear, discernable trend towards single layer graphene, whereas lower pressures were more facilitative to multilayer growth as detailed in the result section.

3.2.3. Temperature
Previous work has shown that the allotropes of CVD carbon are highly dependent on the deposition temperature. For example, deposition temperatures of approximately 400°C always result in amorphous carbon, whereas higher temperatures showing a clear trend towards multilayer and subsequently, single layer graphene[48]. The conventional growth temperature as established by the previous work of group member Xiao Chen is 1065°C, 15°C below the melting point of copper.

3.2.4. Time
Time is a straightforward factor on the overall morphology and coverage of graphene: longer times resulted in larger flake sizes, larger coverage, as well as more single crystal and multilayer nucleation. The time was fixed in these experiments at 6 hours, mostly as a matter of convenience, but also to accommodate as large a number of growth runs as possible. Heating to the target temperature of 1065°C was done linearly over one hour using a programmable temperature controller to ensure a steady and reproducible rate of input heating.

3.3. Contrasting Oxidation of Copper
Thermally annealing the graphene-bearing copper foil following growth allows for the direct facile detection and optical characterization of the graphene flakes[49]. In this work, graphene-bearing copper foils are oxidized on a hot plate for 30 seconds at 240°C, as shown in Figure 7. The graphene-covered regions retain their original color because they block atmospheric oxygen from reaching the copper surface, whereas the uncovered regions are oxidized and become visibly darker[49]. This makes it easy to discern the flake size and morphology of the grown graphene using optical techniques such as bright and dark field microscopy, or Raman spectroscopy, as-grown on copper.
3.4. **Graphene Transfer**

The useful applications of CVD graphene as grown on a conductive substrate such as copper are limited, including surface passivation [43] or plasmonic photodetection [50]. The facile transfer of the graphene flakes to another substrate such as silicon or quartz while preserving the quality of the graphene is thus an important post-growth step to graphene CVD. Using a supportive poly(methyl methacrylate) (PMMA) layer, graphene can be transferred to such target substrates with minimal deterioration of the as-grown quality [7, 51, 52].

The method employed in this work involves first spin-coating the graphene-bearing copper film with 1% PMMA in anisole at 3000 RPM for 60 seconds. The coated samples are then left to bake on a hot plate at 140°C for 5 minutes. Samples are then floated, uncoated side down, on a 1M FeCl₃ solution to etch away the copper, while leaving the graphene adhered to PMMA film. Using a watch glass or shallow plastic petri dish, the films are gently scooped up and floated on a 30% HCl solution in deionized (DI) water for 30 minutes to leech any residual heavy metal ions [15, 51]. The samples are then floated on DI water twice, for 30 minutes each to rinse the films of any residual HCl. The films are then transferred to a silicon or quartz target substrate that has been ultrasonicated in acetone, IPA, and water for 5 minutes each and left to dry overnight. Finally, the PMMA is resolved by submerging the samples in acetone for 30 minutes. This same technique can also be used for transfers to TEM grids for subsequent characterization.

4. **Characterization**

4.1. **Raman Spectroscopy**

Raman spectroscopy is a fast, high spatial resolution, nondestructive tool for probing the fundamental properties of graphene, including layer number, defect density, stacking order, as well as electronic and thermal transport properties of this material [53, 54].

Figure 7 Visible contrast in bright-field optical image between bare oxidized copper and graphene flake after contrasting oxidation
The process relies on the so-called “Raman inelastic scattering” of monochromatic laser light in the visible, near infrared, or near ultraviolet regions of the electromagnetic spectrum. The light induces phonon inelastic scattering processes in graphene leading to a shift in a very small percentage of incoming photons to either higher or lower energies, which can then be measured using a photodetector[55].

The most prominent features in the Raman spectra of mono- and few layer graphenes are the G band a Raman shift of 1582 cm\(^{-1}\), the G’ (otherwise known as the 2D) band at a Raman shift of around 2700 cm\(^{-1}\) and the D band at 1350 cm\(^{-1}\) [53, 54, 56]. The G peak, characteristic for all sp\(^2\)-bonded carbon materials, results from the highest-frequency vibrations of the E\(_{2g}\) phonon branch in the dispersion relation of graphene. The D-peak is the result of the breathing modes of the graphene hexagonal rings and requires defects for its activation. Finally, the 2D peak is the 2\(^{\text{nd}}\) order overtone of the D-peak and does not require the presence of defects to manifest[53, 54, 56].

![Raman spectra](image)

**Figure 8** Typical Raman spectra of Mono- (Blue) Bi- (Red) and Tri- (Green) layer graphene

Raman spectroscopy in this work was done on a Renishaw inVia confocal Raman microscope using a 488 nm laser for excitations. All samples were transferred to a silicon substrate using the aforementioned PMMA-mediated transfer process prior to characterization. A typical Raman spectrum spanning the all wavenumbers between the G-peak and 2D-peaks are shown in the above Figure 8.

### 4.1.1. Layer number identification

Raman spectroscopy is a powerful tool in identifying the number of layers of graphene samples through evaluation of the 2D peak shape and intensity[56]. An binary test for identifying graphene as single or multilayer involves the deconvolution of the 2D peak: while single layer graphene has a single Lorentzian 2D peak, commensurately-stacked multilayers have 2D peaks that can be split into multiple components[56]. The layer number of CVD-grown graphene is also discernable in the ratio of the G peak intensity to the 2D peak intensity I(G)/I(2D), which shows a consistent upwards trend as the number of graphene layers increases[57].

### 4.1.2. Defect density quantification

The quantification of defect density in graphene using Raman spectroscopy is straightforward: an increase in the intensity of the D peak is indicative of an increased defect density, as this mode is only Raman-permitted in the presence of defects[58, 59]. Further assertions regarding the density and the nature of the defects can be made based on the ratio of the intensities between the D and D’ peaks I(D)/I(D’)[45, 46], but as the relative intensity of the D peak in the graphene grown in this
work is less than 0.1% of the 2D peak, it can be generally assumed that the graphene produced in this work has few defects as discussed in the results section.

4.1.3. Stacking order determination

The 2D vibrational mode in graphene is sensitive to both the acoustic properties and electronic structure of this material, making it a good indicator of the stacking order[8]. Consistent differences discernable between the ABA and ABC stacking orientations include a widening and asymmetry of the 2D peak for ABC stacking as compared to ABA stacking[60].

The difference in the 2D peak fingerprint of the two stacking orientations persists regardless of the laser excitation energy used to induce Raman scattering or doping, making the 2D peak a reliable indicator of the stacking order in few-layer graphenes[8]. In this work, the spectral width of the 2D peak in commensurately-stacked regions of trilayer graphene transferred to silicon are compared to assess the possibility of different stacking orders in these regions.

It warrants noting that there are other methods for the determination of the stacking order of trilayer graphene whose instrumentation is beyond the scope of this work, including IR spectroscopy, ultra-low wavenumber shear-mode Raman spectroscopy, selective area electron diffraction relative spot intensity, and high resolution transmission electron microscopy. These methods collectively can be used to form a determinate picture of the stacking order of graphene, but were unavailable at the time of this study[21, 61, 62].

4.2. Dark Field Optical Microscopy

Previous works report the presence of conformal, striped ridges forming on copper foil wherever graphene is grown via CVD on this target substrate[63-65]. Kong and collaborators used dark field optical microscopy to quickly identify CVD grown graphene on copper[64].

The improved contrast of graphene-bearing copper regions as compared to non-graphene bearing regions can be attributed to the increased roughness of these graphene-bearing striped regions, which leads to increased Rayleigh scattering of light through the copper step beneath these rougher regions. The intensity of Rayleigh scattering is proportional to the sixth degree of the size of scattering feature, making it highly sensitive to even small changes in surface roughness, as given by the relationship:

\[
I \propto \frac{D^6}{\lambda^4 \left(\frac{n^2}{n^2 + 2}\right)} \left(1 + \cos^2 \theta\right)I_0
\]

Where \(\lambda\) is the the wavelength of light used for illumination, \(D\) is the diameter of the scattering particle (in this case, an indicator of the surface roughness), \(I_0\) is the incident light intensity, \(n\) is the refractive index of the particle, and \(\theta\) is the scattering angle[66]. The correlation between \(I\) and \(D^6\) is what leads to this high variation in reflected light intensity with different roughness.

A direct correlation between the step height and the number of graphene adlayers was also demonstrated, showing that this technique can be used to identify graphene multilayers as grown on copper, as shown in Figure 9.
Work done by Zhang and collaborators shows that these stripes form as a result of the release of the internal stress of copper while shrinking and cooling following CVD[65]. Such direct identification on copper for graphene is demonstrated in this work as being an effective means of discerning graphene single layers from bilayers and multilayers prior to transfer.

Figure 9 Typical dark-field optical microscopy image obtained in this work showing well-ordered multilayer graphene

5. Results and Discussion

Graphene flakes with a mean total size of 650μm and trilayer regions approaching 200μm were synthesized using the optimized growth conditions summarized below:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol Flow Rate (Partial Pressure)</td>
<td>0.016 sccm (0.015 Pa)</td>
</tr>
<tr>
<td>Argon/Hydrogen Flow Rate (Partial Pressure)</td>
<td>280 sccm (8.5 Pa)</td>
</tr>
<tr>
<td>Total pressure</td>
<td>280 Pa</td>
</tr>
<tr>
<td>Temperature</td>
<td>1065°C</td>
</tr>
<tr>
<td>Growth Time</td>
<td>6 hours</td>
</tr>
</tbody>
</table>

These conditions were found through the systematic exploration of the CVD parameter space, first by sweeping the ethanol flow rate between 0.016 and 0.16 sccm while fixing all other parameters, then by sweeping the total pressure between 280 and 500 Pa, again while fixing all other parameters. The corresponding pressures from the measured flow rates can be calculated using the following formula:

\[ P_{gas} = \frac{F_{Gas}}{F_{total}} \times P_{Total} \]
Where $P_{\text{Gas}}$ is the partial pressure of the gas being calculated, $F_{\text{Gas}}$ is the corresponding flow rate of the gas in question, and $P_{\text{Total}}$ is the total pressure in the reaction chamber during growth.

The relation between the partial pressures of ethanol to hydrogen is visualized in the following Figure 10, a chart of the explored parameter space:

![Summary of Explored Parameter Space](image)

**Figure 10** Parameter space explored during the course of thesis work. Effect of pressure, ethanol flow rate are evaluated.

The exploration of the ethanol flow rate effect is represented by the dotted horizontal line having circular markers to delineate individual growth conditions. The blue dashed line with square markers represents experiments done to determine the effect of total pressure on graphene growth. Finally, the diamond at the far lower left of the plot signifies the optimized growth condition achieved for yielding trilayer growth.

### 5.1. **Effect of Ethanol Flow Rate**

#### 5.1.1. **Total Size**

The mean diameters of the graphene flakes grown at 450 Pa, 300 sccm Ar/H₂ and 1065°C for 6 hours as a function of ethanol flow rate are represented below. Each measurement is taken from one vertex to the opposite vertex of a well-etched, 6-lobed graphene flake, with at least 15 measurements being weighed for each flow rate:
A clear upwards trend in the size of the total size of the graphene flakes as the ethanol flow rate is increased is observable as shown in Figure 11, although the extent of this increase is debatable if the outlying 0.16 sccm condition is omitted. The slower increase in the flake size between 0.016 sccm and 0.1 sccm is more convincing, considering the dual etching and growth effect of this carbon source mentioned before.

5.1.2. Morphology
The increase in ethanol vapor pressure also lead to more dispersion and less nucleation and growth of the graphene multilayers, indicating that a high ethanol flow rate is unfavorable for the deposition of such well-ordered graphene multilayers as can be seen in the comparison between the 0.06 and 0.16 sccm ethanol mass flow samples.

While the multilayer nucleation and growth is concentrated around the center of the graphene flake in the case of an 0.06 sccm flow rate of ethanol, this nucleation and growth of multilayers is more dispersed and smaller in size in the case of the higher, 0.16 sccm ethanol flow rate. This could possibly be attributable to an increase in etching effect at higher flow rates, destabilizing the nucleation and growth of graphene multilayers, indicating that a lower flow rate is more favorable for the intended goal of trilayer growth.

5.2. Effect of Total Pressure
Increasing the total pressure had the predictable effect of increased etching of the primary graphene flakes and decreased multicore nucleation and growth as can be seen in the comparison between samples grown at 450 Pa versus those grown at 500 Pa, shown in Figure 12:
All other growth parameters are kept constant: the ethanol flow rate was fixed at 0.06 sccm, the Ar/H₂ flow rate was fixed at 300 sccm, and the time and temperature were fixed to 6 hours and 1065°C respectively.

Increasing the pressure from 450 Pa to 500 Pa can be clearly seen to decrease the 6-fold hexagonal symmetry of the primary graphene flake and suppress the nucleation and growth of multilayers on this flake, as can be seen in Figure 13. This could be attributed to the lingering of the etching gases, both hydrogen and those resulting from ethanol thermal decomposition, leading to an enhanced etching effect of the graphene flakes. This makes it favorable to decrease the total pressure of the CVD reaction to favor multilayer growth.

5.3. Further Decreasing Ethanol Flow Rate and Total Pressure
From the trends established for the effects of ethanol flow rate and total pressure, the pressure and flow rates were further decreased to encourage trilayer growth. The ethanol flow rate was lowered to 0.032 and subsequently, 0.016 sccm, while the pressure was decreased to 300 and subsequently 280 Pa.

5.4. The 0.032 sccm Ethanol Growth Condition and Twist Angle
The first growth condition tested was an ethanol flow rate of 0.032 sccm and a total pressure of 300 Pa. The optical microscopy images before and after transfer are shown below:
The immediate effect of depositing well-ordered hexagonal primary flakes and adlayers can be seen, although the adlayers are consistently shown to exhibit a twist angle of approximately 30°, seen in Figure 14. Previous work has shown that twisting arises to alleviate high strain energy during simultaneous nucleation of the primary flake and the accompanying multilayers and suggests that a lower flow rate could mitigate this twisting effect and lead to the deposition of commensurate, ABA or ABC-stacked layers[67].

5.5. Emergence of Increased Surface Roughness in Large Adlayers

An interesting image artifact arose beginning from this 0.032 sccm ethanol growth condition: a darker, hexagonal shadow in the center of the majority of graphene flakes observed on copper. The contrast of these darker regions increased dramatically when observed using dark-field microscopy imaging, shown in Figure 15:

The bilayer region is clearly discernable from the monolayer region due to an increase in surface roughness. It is interesting to note that the orientation of the surface roughness is also altered between the two regions. After confirming that this effect was indeed the result of adlayer-copper interaction by comparing to existing literature, consequent growth runs were thus subjected to dark field optical imagery to discern the presence of graphene multilayers.
5.6. Approaching the Ideal Growth Condition for Trilayer Graphene

The flow rate is next lowered to 0.016 sccm, and the pressure is lowered to 280 Pa to further encourage commensurate multilayer growth, hereby referred to as “the optimized condition”. A typical sample is imaged in Figure 16, showing this condition using both bright and dark field microscopy:

![Figure 16](image)

**Figure 16** Bright (left) and Dark (right) optical microscopy imagery of a graphene flake from the 0.016 condition. The scale bar is 200µm.

Large suspected bilayer and trilayer regions become discernable by dark field optical microscopy as seen in the following Figure 17:

![Figure 17](image)

**Figure 17** Dark field optical microscopy image of large multilayer graphene regions

These regions are also confirmed after transfer, shown in Figure 18 below:
Figure 18 Multilayer graphene flake with large trilayer region

Image analysis of the albedo of the dark field images using the image analysis software Fiji[68] shows that the suspected trilayer regions comprise at least 15% of the overall multilayer composition of the total surface area of the grown graphene.

5.7. Evidence of Single Crystallinity
To better understand the mechanism of wrinkle formation during cooling, samples were left to anneal for 10 hours following growth. A minute amount of oxygen leakage during this prolonged annealing process lead to the aligned, hexagonal etching of the graphene flakes, shown in Figure 19 below:

Figure 19 Long range order in etching of optimized condition graphene flakes
The long range order exhibited by these etched regions allude to the monocrystalline nature of the grown graphene flakes, although additional confirmation through selective area electron diffraction is necessary to conclusively ascertain the mono-crystallinity of the graphene.

5.8. **Raman Spectroscopy of the Optimized Condition**

The Raman spectra of trilayer regions of the graphene samples were imaged and compared with mono- and bilayer regions on the same flake. A typical sample and the accompanying Raman spectra for mono, bi, and trilayer graphene are shown below in Figure 20:

**Figure 20** Typical Raman spectrum for mono- (black), bi- (blue), and tri- (red) layered graphene.

The spectra shown in the lower inset of the above Figure 20 agree well with those previously found in literature: there are clearly discernable G peak at 1580 cm\(^{-1}\) and a clear 2D peak around 2700 cm\(^{-1}\). This 2D peak can be seen to exhibit a slight blue shift as the layer number increases from monolayer graphene to trilayer graphene with the monolayer graphene having a local maximum at 2695 cm\(^{-1}\), the bilayer graphene having a maximum at 2700 cm\(^{-1}\), and the trilayer
graphene having a maximum at 2705 cm⁻¹. The 2D peak exhibits the expected broadening as the number of layers increases, seen in Figure 21:

![Figure 21](image)

**Figure 21** Close-up of the 2D Peak for mono- (black) bi- (blue) and tri- (red) layer graphene

The relative intensity $I(G)/I(2D)$ also increases as expected as the layer number increases:

<table>
<thead>
<tr>
<th>Layer Number</th>
<th>$I(G)/I(2D)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monolayer Graphene</td>
<td>0.235</td>
</tr>
<tr>
<td>Bilayer Graphene</td>
<td>0.833</td>
</tr>
<tr>
<td>Trilayer Graphene</td>
<td>1.243</td>
</tr>
</tbody>
</table>

It is worth noting that relative peak intensity $I(G)/I(2D)$ for the bilayer and trilayer graphene is considerably higher than the expected, possibly indicating the presence of a strain or twist effect. This high relative peak intensity for the suspected trilayers is consistent across multiple flakes, and lies falls between the peak intensity for bilayer and tetralayer graphene, further confirming this graphene as trilayer. The quality of the graphene is also confirmed from the weakness of the D-peak intensity for all three layer numbers, which would otherwise register at around 1350 cm⁻¹ as seen in Figure 22 below:

![Figure 22](image)

**Figure 22** Close up of the D-Peak region for mono- (black) bi- (blue) and tri- (red) layer graphene
5.9. Discerning the Stacking Order

A deconvolution of the 2D peak of from the trilayer graphene yielded 6 well-differentiated Lorentizian peaks, seen in Figure 23:

<table>
<thead>
<tr>
<th>Curve Index</th>
<th>Centre</th>
<th>Width</th>
<th>Height</th>
<th>Area</th>
<th>ChiSq</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2663.73</td>
<td>28.8017</td>
<td>155.014</td>
<td>7013.06</td>
<td>1.16769</td>
</tr>
<tr>
<td>2</td>
<td>2686.08</td>
<td>31.3379</td>
<td>456.136</td>
<td>22453.5</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2700.66</td>
<td>29.616</td>
<td>1436.79</td>
<td>66840.4</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2717.77</td>
<td>27.3463</td>
<td>1085.18</td>
<td>46614.6</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2731.71</td>
<td>23.2037</td>
<td>985.618</td>
<td>35924.1</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2744.52</td>
<td>18.5334</td>
<td>505.55</td>
<td>14717.7</td>
<td></td>
</tr>
</tbody>
</table>

Figure 23 Deconvolution of the 2D peak
This fingerprint is consistent with the trilayer regions of other graphene flakes. The consistent width, equispaced distancing and consequent symmetry of the deconvoluted peaks suggests the presence of ABA stacked trilayer graphene. The existence of a peak explicitly at the centroid of 2700 cm\(^{-1}\) is especially indicative, although additional confirmation using IR spectroscopy or selective area electron diffraction is necessary to confirm the stacking order, especially in light of the anomalous I(G)/I(2D) ratio for the suspected trilayer graphene.

6. Conclusion

In summary, DFT calculations were used to investigate the energetics and charge density difference of ABA, ABC, and intermediary stacking orientations for pristine and s-triazine functionalized trilayer graphene. The addition of s-triazine to the graphene surface led to a 94% increase in the relative energy of the ABC-stacking orientation as compared to ABA, explaining the experimentally observed facilitation of the ABC-ABA transition.

Subsequently, systematic investigations of LP-CVD of graphene using alcohol carbon source yielded an optimized condition for the growth of well-ordered graphene multilayers, a large fraction of which were trilayers with sizes approaching 200\(\mu\)m. Dark field optical microscopy was demonstrated to be capable of discerning more than one graphene adlayer directly on copper for the first time. A consistent, if anomalously high I(G)/I(2D) ratio. The quality of the grown graphene was assessed using Raman spectroscopy, and the D peak was found to be negligible. The 2D peak of the Raman spectrum for the trilayer graphene was deconvoluted, but no clear stacking order could be discerned.

The 2D fingerprint was reminiscent of twisted graphene, but it too anomalous to be determinately considered as such. Additional work using the aforementioned characterization tools of HR-TEM, SAED, IR spectroscopy and shear-mode Raman spectroscopy are need to conclusively determine the stacking order of this graphene to pave the way for its adaptation in electronics applications.
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Figure 15 Observable change in contrast due to roughness of graphene flakes on copper. The scale bar is 200μm

Figure 16 Bright (left) and Dark (right) optical microscopy imagery of a graphene flake from the 0.016 condition. The scale bar is 200μm

Figure 17 Dark field optical microscopy image of large multilayer graphene regions

Figure 18 Multilayer graphene flake with large trilayer region

Figure 19 Long range order in etching of optimized condition graphene flakes

Figure 20 Typical Raman spectrum for mono- (black), bi- (blue), and tri- (red) layered graphene

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Figure 22 Close up of the D-Peak region for mono- (black) bi-(blue) and tri- (red) layer graphene

Figure 23 Deconvolution of the 2D peak
8. Bibliography


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9. Appendix: Trilayer Graphene as a Candidate Material for Phase Change Memory Applications
Trilayer Graphene as a Candidate Material for Phase-Change Memory Applications

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MRS Advances / Volume 1 / Issue 20 / January 2016, pp 1487 - 1494
DOI: 10.1557/adv.2016.237, Published online: 05 April 2016

Link to this article: http://journals.cambridge.org/abstract_S2059852116002371

How to cite this article:
Mohamed M Atwa, Ahmed AlAskalany, Karim Elgammal, Anderson D Smith, Mattias Hammar and Mikael Östling (2016). Trilayer Graphene as a Candidate Material for Phase-Change Memory Applications. MRS Advances, 1, pp 1487-1494

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Trilayer Graphene as a Candidate Material for Phase-Change Memory Applications

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ABSTRACT

There is pressing need in computation of a universal phase change memory consolidating the speed of RAM with the permanency of hard disk storage. A potentiated scanning tunneling microscope tip traversing the soliton separating a metallic, ABA-stacked phase and a semiconducting ABC-stacked phase in trilayer graphene has been shown to permanently transform ABA-stacked regions to ABC-stacked regions. In this study, we used density functional theory (DFT) calculations to assess the energetics of this phase-change and explore the possibility of organic functionalization using s-triazine to facilitate a reverse phase-change from rhombohedral back to Bernal in graphene trilayers. A significant deviation in the energy per simulated atom arises when s-triazine is adsorbed, favoring the transformation of the ABC phase to the ABA phase once more. A phase change memory device utilizing rapid, energy-efficient, reversible, field-induced phase-change in graphene trilayers could potentially revolutionize digital memory industry.

INTRODUCTION

As the semiconductor industry continues to push the limits of Moore’s law, fabricating transistors that are smaller, faster, and more energy-efficient than ever before, a new bottleneck in computation has arisen in the form of data storage and retrieval speed. Universal memory, corroborating the fast, non-linear data retrieval of RAM, with the retention and storage density of hard disk drives has thusly become a research topic of increasing importance in both academic and industrial contexts¹–³.

Current candidates for universal memory include spin-torque transfer RAM (STT-RAM)⁴, oxide-resistance phase change memory (PCM)³ and flash memory. Each suffer shortcomings that limit their potential as universal memory devices: STT-RAM lacks low dynamic energy⁵, requiring inconveniently large current densities (~1-10 mA)² to switch memory states. Existing PCMs suffer from phase drift³, limiting the number of read-write cycles they can endure (~50,000 operations⁵). The need for a universal memory grows ever more pressing as innovations in processing power continually overtake those in data storage and retrieval²,³.

Trilayer graphene (TG) assumes one of two stable stacking orientations, corresponding to two different phases: a Bernal, ABA-stacked phase and a rhombohedral, ABC-stacked phase⁶. These two phases have different electrical properties by virtue of their electronic configurations: ABA-
TG behaves as a zero-bandgap semi-metal due to symmetry about the middle layer. Meanwhile, ABC-TG behaves as a semiconductor, and exhibits a bandgap in the presence of large electric fields due to its interlayer asymmetry.

Previous experimental and theoretical work done by Xu et al. and Taut et al. showed a pathway between ABA and ABC stacked graphene layers on highly oriented pyrolytic graphite using scanning tunneling microscopy (STM) imaging at room temperature and first-principle calculations. They identified a low-energy barrier (1.1 meV/atom) no-overlap direction for carbon top-layer motion to induce the ABA to ABC phase change.

Subsequent experimental work done by Yankowitz et al. showed the possibility of inducing ABA to ABC phase-change in single TG graphene flakes by traversing a potentiated STM tip over the localized strain soliton separating ABA and ABC-stacked regions. They also alluded to the possibility of inducing a similar phase-change using global electric fields, a perquisite to TG usage in phase-change memory devices.

A significant hurdle to the utilization of ABA/ABC-TG as a programmable material is the difficulty of inducing the reverse phase transition from ABC to ABA in unmodified TG. Even at 1200°C, ABC-TG was found not to revert to ABA-TG, despite the common belief that ABA-TG is the more thermodynamically stable of the two phases. However, by decorating TG with 1,3,5-triazine, Zhang et al. were able to lower the transition temperature for ABC-TG to ABA-TG to a more accessible 100°C, which they attributed to an increase in the energy difference between the two phases, which renders this reverse transition more favorable.

Motivated by these findings, we use ab initio methods to evaluate the energetics and examine the charge density distribution contours of a direct, ABA-ABC transition with and without adsorbed triazine and divest the feasibility of lasting, reversible ABA-ABC phase change in TG.

**METHODOLOGY**

We model and simulate pristine and triazine-decorated 4×4 TG supercells comprised of 96 carbons each using Quantum Espresso and Xcrysden crystal structure visualization package. Hamann, Schluter, Chiang and Vanderbilt (HSCV) non-conserving pseudopotentials as downloaded from The Electronic Laboratory were used for the subsystem atomic species. A plane-wave basis set with a cutoff of 130 Ry was selected. The Brillouin zone is sampled with a...
4x4x1 Monkhorst-Pack k-point grid and Methfessel-Paxton smearing of 0.0037 Ry\textsuperscript{19}. The van der Waals density functional (vdW-DF2) was used\textsuperscript{20-22}.

The triazine was placed 3.16Å above the topmost graphene layer in the cross position, a spacing and orientation previously investigated by C Chang et al.\textsuperscript{23} who used DFT to compare molecular dopants in yielding the highest adsorption and maximal surface interaction with graphene \textsuperscript{23}.

![Triazine doping](Image)

Figure 2 ABA trilayer graphene with adsorbed Triazine molecule adsorbed on the topmost layer.

Previous work by Xu et al.\textsuperscript{6} has shown there to be two possible real-space pathways between ABA and ABC: the first passing through a no-overlap position wherein the topmost layer does not directly coincide above the middle layer, and the second passing through an overlap ABB position, wherein the topmost layer does coincide above this middle layer.

The topmost graphene layers of the pristine and triazine-decorated TGs were shifted from the ABA to ABC stacking order in increments of 1/8\textsuperscript{th} bond length, once through the overlap position, and again through the no overlap position.

**RESULTS AND DISCUSSION**

Carrying out DFT calculations on the systems described in the methodology section, we attained the total energies of isolated triazine, ABA-TG, ABC-TG, and transitionary stacking orders. ABA-TG in both the pristine and triazine-decorated cases was taken as a datum by subtracting the ABA-TG system’s total energies from the respective transitionary states and the ABC-TG phases.
Figure 3 System total energy versus displacement for pristine trilayer graphene and Triazine decorated trilayer graphene, with the energy of ABA configuration of Triazine decorated trilayer graphene as a reference.

Figure 3 shows the rendered energies across the displacement of the top most layer in both the overlap and no-overlap directions, for both pristine and triazine decorated graphene. All energies were referenced with respect to the energy of ABA triazine decorated graphene.

It is evident that there is a negligible energy difference between the ABA and ABC stacking orders in both the triazine decorated and pristine cases. The ABA and ABC states are shown to be separated by a symmetrical energy barrier along the no overlap pathway. The overlap position is seen to have the highest energy of any of the states.
Figure 4 Change in system’s total energy at each displacement position starting from ABA stacking and passing through the non-overlap configuration.

A charge density difference contour for the ABC-TG phase was conducting after it was found that triazine-decoration yielded a nearly 100% increase in energy in the TG. The adsorption of triazine was found to induce a dipole in the topmost graphene layer of the TG, the charge destabilizing effects of which may explain why it renders the ABC to ABA transition more attainable. The lower two layers were found to be negligibly affected. The moment of this dipole and its magnitude are to be further investigated in upcoming studies.
CONCLUSIONS

Using ab initio methods, we investigated the energetics and charge density difference contours of the ABA-ABC phase change in both pristine and triazine-decorated TG to better understand how reversible ABA-ABC phase change may be induced. We show that the addition of triazine lead to a nearly 100% increase in energy in the triazine-decorated case. This energy increase might be attributed to the system’s total energy of a dipole between the adsorbed triazine and the topmost graphene layer of TG.

As this DFT only comprises the calculation of enthalpies calculation at 0K, additional calculations using nudged elastic band theory and dispersion relations are planned to determine the entropic energy contribution to this phase transition. More extensive investigation of the energy landscape along different real-space pathways is required.

ACKNOWLEDGMENTS

The computations were performed on resources provided by the Swedish National Infrastructure for Computing (SNIC) at the PDC center for high-performance computing, KTH as well as NSC at Triolith.

This publication is part of Ahmed AlAskalany's research work at KTH, thanks to a Swedish Institute scholarship.

Both of the first two authors contributed equally to this work.
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