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Templated Growth of Graphene:
A Novel Method for Efficient Graphene Synthesis

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ABSTRACT

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A novel templated growth process for graphene structures is proposed and demonstrated. Extended, pristine sheets of graphene can be synthesized by additively reacting carbon into a pre-existing graphene sheet which is on a templating substrate through a CVD type process termed “van der Waals templating”. Finding a technologically viable synthesis method for planar graphene has recently become of significant interest with the recent recognition of its unusual electronic properties. Various morphological growth patterns such as “pacman” structures and rounded corners are observed which elucidate interesting features of this growth mechanism, linear sheet growths on the order of 150 nm have been produced.
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**Introduction:**

Since the discovery of carbon nanotubes, the 1-D nature and unique electronic structure of graphene has been appreciated as the origin of their remarkable properties. Graphene serves as a useful model system for exploring nanotube growth mechanisms, and has itself recently gained recognition for potential use in a wide range of applications.\(^1,2,3,4\)

Planar graphene has many remarkable properties including extremely high sheet-strength and the largest diamagnetic response of any bulk room-temperature material,\(^5\) and has shown some indications of nanoscopically controllable ferromagnetism.\(^6\) Graphene has attracted particular attention as being useful for high speed nanoelectronics applications as being geometrically more easily integrable with existing technology\(^7\) but has suffered from a dearth of sample preparation means. Commercially viable applications, particularly electronics, will require reliable large scale production of quality graphene; beyond what current technologies produce.\(^8\)

Despite the increased interest in planar graphene as a technological material, the available means of synthesis are inefficient and impractical for technological applications. Graphene has been prepared for experimental characterization by two primary types of methods: 1) graphite cutting, extraction and micromechanical manipulation techniques, 2) graphene growth methods.

Much of the experimental characterization of graphene employed small graphene pieces extracted from larger graphite samples. Various methods have been used such as rubbing planar graphite,\(^9\) lithographic etching and micromanipulation,\(^10\) and chemically
solubilizing "platelets" from graphite.\textsuperscript{11,12} Micromanipulation and liquid phase chemical techniques have demonstrated usefulness for moving and positioning graphene but cannot provide high precision placement and orientation needed for electronics applications. Highly controlled graphene manipulation will be particularly crucial for graphene electronics since its electronic character depends strongly on the crystallographic axis. This approach is also inherently limited by currently available graphite materials (10 \(\mu\) or smaller).\textsuperscript{13}

Several methods have been reported in the literature for growing graphene materials directly. The most successful technique to date for producing graphene directly and demonstrating its promising electronic properties has been the heteroepitaxial synthesis of graphene materials onto a 6H-SiC substrate by selective evaporation of silicon from the substrate so that the excess carbon remaining assembles into a graphene coating on the surface.\textsuperscript{14} While this approach has demonstrated the potential for high quality electronics devices built from graphene, it has certain inherent limitations which make a more general growth technique desirable for technological applications. Particularly the process requirements for high temperature UHV conditions and strong sensitivity to the quality and surface termination of the single crystal SiC substrate prompt investigations into alternative means of synthesis.

Various other methods to synthesize graphene materials have been explored. These include vertical, free-standing sheets of rumpled graphene fabricated by a plasma CVD method,\textsuperscript{15} polycyclic aromatic hydrocarbons (PAHs) from liquid phase chemistries,\textsuperscript{16}
small graphene sheets nucleated on HOPG using UHV methyl radicals\textsuperscript{17} and graphene sheets have been grown by the catalytic decomposition of carbon precursors on cleaned Ni(111) surfaces under UHV conditions.\textsuperscript{18,19} It is widely recognized, however, that none of these synthesis methods is well suited to producing graphene for technologically scalable integrated circuit applications.

We propose and here report a new approach for synthesizing graphene structures. Here, extended, pristine sheets of graphene have been synthesized by additively reacting neutral carbon species into a pre-existing graphene sheet resting on a templating substrate, HOPG.

**Physical Considerations:**

Many different factors contribute to the observed difficulty of pristine graphene synthesis. The problem of synthesizing graphene sheets is essentially one of homoepitaxially growing a two dimensional material over extended distances in a three-dimensional environment. It is well recognized that the conceptual physical simplicity of high-quality single-crystal homoepitaxy belies the difficulty of its practice. While a crystal lattice grown in quasi-equilibrium at 0 K will be perfect, a real crystal grown at finite temperature will have some entrained defects associated with non-equilibrium fluctuations related to the multiplicity of phase space available. Despite the lattice energy associated with lattice defects and grain boundary mismatches, such defects inevitably nucleate and resist efficient removal from the lattice so that they persist in the lattice despite thermodynamically instability. Furthermore, side reactions of the feedstock...
(particularly prevalent in carbon feedstocks) can lead to the nucleation of materials which are not part of the original crystal lattice. For graphene these can occur both in the feedstock delivery phase and on the non-step-edge surface of the graphene. Due to the relatively large number of states associated with these states over those corresponding to step-edge reactions these are favored by the system geometry and must be suppressed.

Graphene also has materials specific characteristics which particularly impede useful sheet growth beyond those associated with the problems of homoepitaxy of reduced dimensionality. Carbon's three different bond hybridizations have different kinetic reactivities. Though graphene (sp2-bonded, planar hexagonal carbon lattice) is thermodynamically favored, quasi-stable sp1 and sp3 structures are also possible. Sp1 hybridized bonds are significantly more reactive than sp2 so that if sp1 sites exist at the edge of the graphene, these structures will dominate carbon incorporation. Adatom, vacancy and contaminant (e.g. oxygen) defects favor sp3 configurations sites. Once a defect has been enclosed in the lattice the annealing time is much longer so that enclosure around such a defect effectively seals it into the lattice.

Furthermore, graphene lattice edges show a strongly enhanced chemical stability over standard sp2 bonds. This occurs to such a degree that HOPG edges exposed to air is observed to retain some fraction of unoccupied sites rather than react with atmospheric species. Its origin is debated; however, the empirical fact of this stability indicates that defect structures at the graphene edge will dominate if the growth is rate-limited by the step-edge reaction.
Solution:

These difficulties can be solved by: 1) providing a template surface for growth, 2) delivering feedstock gas at a rate lower than the defect annealing rate, 3) suppressing the tendency of the system to nucleate carbonaceous materials: step-edge chemistry must dominate.

1) A non-reactive template such as a continuous sheet of graphene underlying the growing graphene layer applies a Lennard-Jones type potential to the growing edge. This potential increases the energetic cost of all deviations from a pristine graphene sheet and geometrically reduces the space of favorable states available for growing materials to be included in the lattice. The non-reactive character of the substrate ensures that it does not stabilize non-sp2 bonds in the growing graphene. This idea is illustrated in Fig. 1.

![Figure 1: The bottom lattice is the van der Waals template and the top lattice represents graphene grown onto the green lattice, solid features indicate extra atoms in the lattice as an linear edge dislocation and an add dimer. Such dislocation defects are some of the candidates for the observation of "crinkled" morphologies in this type of graphene growth as seen in figures 3 & 5. The edge dislocation has an associated energy cost of 16 eV and an add dimer has an energy cost of ~4-5 eV with respect to an unstrained lattice. The for the edge dislocation shown ~13% of this is due to substrate interaction, for the add dimer only ~4% of this energy is due to substrate interaction. These energies are calculated using the Lennard-Jones potential shown in Fig. 2.][1]

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2) Carbon can add to the graphene edge in a variety of different configurations. Furthermore, configurations not corresponding to the growth of pristine graphene are more kinetically reactive than those which are. Therefore if the carbon feedstock is supplied at a higher rate than defects can be annealed out of the edge\(^2\) then growth will be dominated by reaction at defect sites, resulting in the growth of a highly defective carbon lattice.

Suppression of this tendency is accomplished through a combination of high graphene temperatures to speed annealing and low feedstock partial pressures to limit the rate of feedstock delivery to the growing edge. Etchants can also be selected to attack defects preferentially.
3) Nucleation is suppressed by maintaining the system at a low sooting potential through maintaining the feedstock at low partial pressures and low temperatures while maintaining the growing edge at high temperatures.

The anomalous stability of a graphene step-edge suggests other possibilities for increasing step-edge reactivity. Whether stabilization occurs by localization\textsuperscript{18} or delocalization\textsuperscript{23}, these possibilities suggest methods for the direct activation of graphene edge reactivity. Excitation of the $\pi \to \pi^*$ transitions in graphene can be used to localize and heat electrons within the lattice\textsuperscript{24} for delocalization induced stability. For stabilization through localization via novel free-radical structures chemical activation can be achieved through direct excitation of these structures (o-benzyne-like and carbene-like sites).

In standard parlance, "homoepitaxy" refers to growth of material onto a planar surface (2D) thus extending the material volumetrically (3D). The extended growth of graphene is conceptually equivalent to homoepitaxy with a reduced dimensionality: that is, it is the growth of a material onto a linear surface (1D) extending the material as a sheet (2D). As such this process has the added difficulty that this two dimensional epitaxy occurs in a three dimensional space.

The term "Van der Waals epitaxy" is often used to describe a process of heteroepitaxy where the epitaxial substrate interacts with the grown material only or primarily via van der Waals interactions. The SiC growth method of graphene is this type of process. The process herein described uses a van der Waals interaction with a substrate to template a
reaction which occurs at the growing edge of a two dimensional material. Thus this process differs from standard van der Waals epitaxy in requiring the conjunction of van der Waals epitaxy type guidance of a two dimensional homoepitaxial process of adding carbon into an existing step edge. Therefore the name “van der Waals templating” is chosen to describe this process. The action of the van der Waals template is to change the energetic stability of defect states in the growing material, thus making defect states even less thermodynamically favorable rather than to provide a surface for true epitaxy.

This method is distinctive from previous methods in several aspects. As with the plasma CVD method, this process adds carbon into a graphene edge from gaseous feedstock. However, graphene synthesized by this method is highly defective and distorted. Van der Waals templating eliminates this problem by providing an additional geometric constraint on the growth. As with UHV methyl radical growth, this method uses an HOPG substrate to template the grown material; however, this method provides mechanism for growing extended graphene materials whereas the methyl radical has only been observed to nucleate new graphene sheets. Unlike SiC based synthesis of graphene, this process generates a graphene layer from freshly deposited material so that the van der Waals template plays no direct role in the synthesis except by being flat and inert.

**Experimental Methods:**

All experiments were performed in a one inch diameter quartz tube furnace at temperatures from 800-1100°C. A strong tendency toward higher quality graphene growth and fewer side products was observed with increasing temperatures.
Graphene growth has been obtained using carbon feedstocks of several classes: hydrocarbon, alcohol and ketone species have all produced graphene sheet growth. The best results have been obtained with ethanol. It is thought that the OH group carried by the ethanol reduces the sooting potential of the system and provides an etchant which reduces the tendency to grow defective material. Ultra pure argon was used as a diluent carrier gas for the feedstock. Water has been added to the system to act as an etchant species during growth. Feedstocks containing water show graphene growth at higher pressures but show higher nucleation and defect rates.

Ethanol feedstock partial pressures from 5-20 mTorr have shown high quality graphene growth. The process shows extreme sensitivity to low levels of contamination. Such contamination can be overwhelmed by using higher feedstock partial pressures with premixed etchant species (such as water) to dominate the system reaction; oxygen in particular is believed to be deleterious, possibly in relation to its ability to attack at non-step edge sites in graphene and participate in non-hexagonal structures and out-of-plane bonding geometries. Low levels (<2 mW/cm²) of 254 nm illumination showed no affect on the morphology or deposition rate of the grown material.

Characterization of grown material was performed by AFM, STM, and XPS and Raman. Figures depicted here are from AFM surface scans which measure the height of the grown material. XPS and Raman characterization both showed signal indistinguishable from pristine (as-cleaved) HOPG. All AFM characterization was performed with a
Veeco Nanoscope IIIa in tapping mode using a silicon cantilever probe. STM confirmed the data obtained by AFM but did not provide new information.

**Results and Discussion:**

This method has been observed to produce graphene growth from preexisting step edges with low rates of nucleation. Material grown from single step edges or few step edges together (up to 4) tends to grow high-quality planar material. The growth of graphene layers is most conclusively demonstrated by observing the alteration in the relative positions of step-edges before and after growth. An upper bound for reactivity is calculated based on feedstock gas flux per observed linear sheet growth. On the order of 1:1000 carbon feedstock atoms which collide with a step edge from the gas phase are added into the lattice. Since this calculation does not take into account surface diffusing carbon feedstock it may underestimate the reaction probability. This rate indicates a highly selective reaction process must occur for graphene to grow by this process.

Graphene grown by this method shows several morphological features not observed in as-cleaved HOPG which give insight into the process’ growth dynamics.

Growth extending outward from a preexisting step-edge without other superstructural feature is termed “sheet” growth. Some growth conditions are observed to grow material with a topographical roughness much greater than as-cleaved HOPG giving it a “crinkled” appearance. Growth extending from a pre-existing edge will occasionally develop a spiral structure corresponding to growth around a screw dislocation. Growth of
circular graphene structures which are not derived from a preexisting graphene edge and which are single graphene layers in height has been observed, these are termed platelets. Structures resembling a circle with a wedge missing have been observed to form at growing edges, these are termed “pacman” morphologies (after the shape of the video-game character). Non-graphene carbon has also been observed to grow under certain conditions and is termed “nodular carbon” due to the morphological shapes it takes. These various morphological features are illustrated in Fig. 3-6.

Sheet growth is universally observed to grow rounded features from preexisting sharp corners; platelets form circular or nearly circular graphene sheets. These observations indicate that this growth process shows very little selectivity in crystallographic axis under the growth conditions tested. Only in spirals have angular growth features been occasionally observed.

Crinkled sheet growth is believed to be the result of the growth of graphene with a high density of structural defects, such as add dimers, edge dislocations or sp3 bonded structures. These topological defects create strained regions in the lattice causing it to protrude upward (as it cannot protrude downward). However, the underlying template ensures that the growing material maintains an essentially planar morphology. These defects are observed to cluster in their formation as indicated in figure 3 with crinkled and smooth regions forming. While it is known that topological defects exert mutual potentials within the lattice, the exact physical basis for this observed clustering remains unclear. STM observation of these structures failed to resolve atomic...
characteristics of this growth morphology. This may be attributed to electronic
disruption by sp3 type defects or to the lattice disorder creating a lack of clear α and β
sites with respect to the underlying lattice.28

Figure 3: This AFM scan displays various morphologies of graphene growth: sheet growth, spiral
growth and platelet growth are all clearly visible. As indicated, various regions of the sheet
growth are pristine while other sections of growth from the same extended edge are crinkled.
Spirals are observed to grow 3-10+ times faster than linear sheet growth. The fast growth
of screw dislocations is commonly observed in crystal formation for a variety of
materials. It may be due to the rapid growth of spiral morphologies that angular (quasi-
hexagonal) features, indicating a preferred crystallographic growth direction,
ocasionally occur in spiral growth and not in linear sheet growth.
Pacman features are formed when a new sheet of graphene nucleates atop a preexisting sheet of graphene at a growing step edge. When this occurs the growth is retarded where the two step edges are in contact and largely unaffected elsewhere. Therefore the nucleated sheet grows back away from the growing edge in a semicircular fashion just as it does during platelet growth and the preexisting edge which is not in contact with the nucleated layer grows linearly out unimpeded. However, the retardation of growth at the contact region leads to a wedge shaped region missing from the growth of both the nucleated and preexisting graphene. The origin of this retardation is uncertain. Two mechanisms are immediately plausible: competition for carbon feedstock or lip-lip
interactions between the edges which reduce the edge reactivity. Pacman with various wedge angles and various wedge depths have been observed, sometimes within a single sample; suggestive of a lip-lip controlled growth mechanism.

![Image: A pacman feature is observed on the edge of crinkled sheet growth.](image)

Figure 5: A pacman feature is observed on the edge of crinkled sheet growth.

Nodular carbon is observed to form at the tops of spirals and at features composed of many step edges together. Presumably this morphology occurs when there are bond structures available to stabilize non-graphene growth of carbon and when pristine (without available bonds) substrates are not present to template the graphene growth. At multi-step features both of these conditions are met: there is no substrate present and lip-
lip interactions$^{29,30,31}$ will allow for the stabilization of non-planar bonding configurations and lattice restructuring.$^{32}$

![Image of nodular carbon formation](image)

**Figure 6:** Nodular carbon is observed to form primarily at the tops and sides of spirals where many step-edges are clustered together and where no efficient surface exists to template the carbon growth.

This process shows promise for further development in this vein as well as elucidating some of the basic nature of the dynamics of carbon reaction into the graphene lattice. Various morphological features are suggestive of the nature by which this growth occurs and the low growth rate with respect to feedstock delivery rate suggests that the reaction is highly selective while the isotropic growth observed indicates that this selectivity is not strongly correlated to lattice direction.
Conclusion:

These initial observations suggest a number of directions by which this method could be extended. It is coincidental that an edge of HOPG serves as the nucleation site for the extended growth of graphene. Graphene could also be grown by this same conceptual method using graphene seed sheets deposited on substrates other than HOPG which would support this type of growth. Highly inert substrates supporting van der Waals templating provide ideal candidates: inert metals and liquid metal substrates as well as inherently planar materials like hexagonal boron nitride provide obvious choices. Furthermore, it should be recognized that the concept of templated growth naturally extends beyond the strictures of gas-phase CVD and could be applied to PAH-like syntheses in the liquid phase to grow extended graphene sheets onto inert substrates.


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Zhang, X, Kun, J., Sharma, P., & Yakobson, B. An Atomistic and Non-classical Continuum Field Theoretic Perspective of Elastic Interactions between Defects (Force Dipoles) of Various Symmetries and Application to Graphene. *Journal of the Mechanics and Physics of Solids*, (Accepted for Publication)


