FORMATION OF THREE-DIMENSIONAL GRAPHENE STRUCTURES BY
CONTROLLED THERMAL ACTIVATION OF POLYMERIC SHAPE MEMORY
SUBSTRATES

BY

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ABSTRACT

This thesis details methodologies for a single-step approach to realise heterogeneous, three-dimensional (3D) texturing of graphene and graphite by using thermally-activated shape-memory polymers as the underlying substrate and the material characterizations thereof. Uniform, large area arrays of textured 3D graphene crumple features can be created on the centimeter scale by controlling simple processing parameters without compromising graphene’s superior mechanical, electrical, and optical properties. In addition, the capability to deterministically pattern graphene and graphite crumples in a spatially selective manner from otherwise flat graphene/graphite is achieved via infrared activation, which has not been previously possible with other methods such as relaxation of mechanically pre-strained elastomers, contraction of solvent swollen hydrogels, or thermal expansion mismatch between the surface film and substrate. The proposed methods will enable facile large-scale topographical and strain engineering of not only graphene and graphite but also other low-dimensional, thin-film and 2D materials such as transitional metal dichalcogenides and furthermore provide a pathway to realizing 3D all carbon-based devices and sensors.
The pursuit of happiness.

-Chris Gardner
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<tr>
<td>3D</td>
<td>Three Dimensional</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
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<tr>
<td>Ar</td>
<td>Argon</td>
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<tr>
<td>CVD</td>
<td>Chemical Vapour Deposition</td>
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<tr>
<td>DI</td>
<td>De-ionized</td>
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<tr>
<td>FET</td>
<td>Field-Effect Transistor</td>
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<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
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<tr>
<td>IPA</td>
<td>Isopropanol</td>
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<tr>
<td>KPFM</td>
<td>Kelvin Probe Force Microscopy</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
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<tr>
<td>PMMA</td>
<td>Poly (methyl methacrylate)</td>
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<tr>
<td>PS</td>
<td>Polystyrene</td>
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<tr>
<td>SCCM</td>
<td>Standard Cubic Centimeters per Minute</td>
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<tr>
<td>SERS</td>
<td>Surface Enhanced Raman Spectroscopy</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
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<tr>
<td>SiO₂</td>
<td>Silicon Dioxide</td>
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<tr>
<td>SRG</td>
<td>Surface Relief Grating</td>
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<td>UV-Vis</td>
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CHAPTER 1: INTRODUCTION

1.1. Graphene

Graphene, a single atomic layer of sp\(^2\)-bonded carbon atoms, has been a material of intensive research and interest over recent years.\(^1,2\) Its combination of exceptional mechanical properties\(^3\), high carrier mobility\(^4\), and thermal conductivity\(^5\), make it a candidate material for next generation electronic, electromechanical and bio-electronic applications. As an example, graphene’s large surface-to-volume ratio due to its atomically thin structure and high sensitivity have enabled ultrasensitive graphene-based field-effect transistor (FET) sensors\(^6\) with single molecule detection limits.\(^7\) Previous advances have already realized numerous indispensable strategies for large-area graphene synthesis\(^8–10\), transferability onto various substrates\(^11\), and device integration. Recent efforts have also focused on controlling graphene’s material properties by altering its shape and geometry. In particular, electrical properties can be modulated via elastic strain engineering whereby localized straining of graphene alters its electronic band structures and induces giant pseudo-magnetism.\(^12–19\)

While mechanical straining of graphene has proven its utility for electronic transport, its usefulness can be even further enhanced by inducing three-dimensionality (3D)\(^20\), whereby textured graphene may serve as a candidate material for 3D electrodes and sensors.\(^21,22\) Notably, physical deformation by texturing graphene amplifies its already large surface area\(^23,24\), thereby increasing the degree of functionalization\(^25,26\) and alters chemical reactivity\(^27\), which is desirable for applications such as for electrode materials in electrochemical cells and supercapacitors.\(^20,28,29\) Novel applications of textured graphene
and graphitic films are also possible such as tunable wettability and optical properties.\textsuperscript{30} In addition, texturing of surface films has been well established as a means to confer flexibility and stretchability to otherwise stiff films and components.\textsuperscript{31}

1.2. Graphene Crumples/Wrinkles/Buckles/Ripples

Here, the deterministic and heterogeneous crumpling of graphene and graphite via heat-induced deformation of an underlying polystyrene-based shape memory polymeric substrate is studied.\textsuperscript{32} While graphene inherently exhibits tiny intrinsic ripples in ambient conditions, the goal is to create large and tunable crumpled graphene textures in a deterministic and scalable fashion.\textsuperscript{33} More notably, we demonstrate localized 3D texturing, which enables the creation of a heterogeneous mixture of flat and crumpled morphologies based on graphene/graphite alone via selective infrared irradiation, which has been unattainable with previous methods to date.

Furthermore, systematic investigations of electrical, morphological and materials characterizations are presented for graphene/graphite crumples as they are progressively and selectively generated. This is a new direction compared to previous studies which have exploited either mechanical deformation of flexible polymeric substrates (crosslinked elastomers such as polydimethylsiloxane (PDMS) and polyethylene terephthalate (PET)), solvent induced pre-swollen hydrogels, two/four-point bending setups, or thermal expansion mismatch between the surface material and underlying substrate to yield overall strain and whole surface crumpling of graphene (and also other metallic films) upon relaxation of the pre-strained or pre-swollen substrates.\textsuperscript{30,34–36}
As a simpler, more scalable and spatially selective alternative method distinguishable from previous techniques, we demonstrate textured graphene and graphite by exploiting thermally-induced transformation of commercially available pre-strained polystyrene-based polymeric thermoplastics, which has been previously applied to microfluidic miniaturization, nanowire assembly, and metallic film applications.32,37,38 Specifically, we exploit the large stiffness mismatch between that of graphene/graphite and the underlying oriented polystyrene sheet (PS) to induce large deformations and create global as well as localized 3D crumples in the top graphene/graphite film.
2.1. Synthesis and Transfer of Graphene, Graphite and Graphene-Graphite Heterostructures

Graphene and graphite samples were synthesized using established low pressure chemical vapor deposition (CVD) (Rocky Mountain Vacuum Tech Inc., Korea) techniques on copper (Cu) foils and cobalt-copper (Co-Cu) catalyst thin films on a SiO₂ substrate, respectively (Figure 1). Copper, which has negligible carbon solubility, typically yields 1-3 layers of graphene on the catalyst surface via CVD synthesis whereas Co-Cu catalyst thin film with a higher carbon solubility yields graphite with tunable thicknesses.²¹

Figure 1. Low pressure chemical vapour deposition (CVD) system for graphene and graphite synthesis.

Graphene synthesis was conducted on 99.8% purity, 25 micron thick copper foils (Alfa Aesar, MA) in a methane (100 sccm) and hydrogen (50 sccm) atmosphere at 1050 °C, 520 mTorr for 2 minutes (Figure 2).⁹ Prior to CVD synthesis, the copper foil was annealed in the CVD chamber for ~35 minutes in 150 mTorr hydrogen atmosphere without breaking vacuum.
Figure 2. Typical CVD synthesis parameters and timeline to yield graphene on Cu foil.

It was found that residual graphene forms on the underside of the copper foil from the slight gap that forms between the Cu foil and the underlying supporting quartz holder inside the CVD chamber. This underside graphene presents a nuisance as it tends to disintegrate during subsequent transfer processes but cling onto the desired top side graphene, thus inducing formation of cracks and graphitic particles. To remove the underside graphene prior to subsequent fabrication procedures, the as-grown graphene on the top side of copper foil was spin-coated with a thin layer of PMMA subsequent to CVD synthesis as a physical protective barrier. The Cu foil is then flipped turned upside down and subjected to a gentle oxygen plasma etch to oxide and remove the underside graphene. The top protective PMMA layer is then immediately removed with several rinses in acetone and isopropanol (IPA); a subsequent thermal annealing step may be done to remove any remaining PMMA residue to yield only pristine topside graphene on copper foil. Aside from using a PMMA protective barrier, a custom designed holder also facilitates oxygen plasma removal of the underside graphene by shielding the topside within a small bottom-vented cavity, without the undesirable effects of residue and doping from a polymer or metallic layer (Figure 3).
Figure 3. Custom designed holder for oxygen plasma removal of underside graphene.

To minimize contamination and ensure material compatibility (i.e. solvent free), a direct aqueous solution transfer approach was exploited to apply the pristine centimeter-scale graphene films onto target substrates (PS, SiO$_2$) without the use of a carrier film such as poly(methyl methacrylate) (PMMA) or gold, which differs from conventional techniques.$^{10}$

The resulting topside graphene on copper foil are then carefully floated onto the surface of prepared sodium persulphate (Na$_2$S$_2$O$_8$) etchant solution (Sigma Aldrich, MA) for about half an hour without the use of any carrier film/medium. Complete removal of copper is verified visually and immediately after complete copper dissolution has occurred, the resulting free floating graphene films were then thrice rinse by transferring via a clean glass slide onto DI water surface to remove residual etchant. Commercially available oriented PS sheets (Shrinky Dinks, K&B Innovations, WI) were cleaned with DI water and IPA and used as the target substrate for the free floating graphene (Figure 4).
Figure 4. Centimeter scale graphene transferred onto flexible PS substrate via the direct aqueous solution transfer approach.

Graphite and graphene-graphite heterostructure samples were prepared similarly by CVD synthesis on cobalt and copper thin film catalyst substrates which were deposited via plasma sputtering (AJA International, MA) on a 285nm thermal SiO₂ on Si wafer. Following established techniques, graphite and graphene-graphite heterostructure samples were carefully transferred onto the same aforementioned sodium persulphate solution surface for etching of the catalyst metallic layer with the aid of a spun-on poly(methyl methacrylate) (PMMA) (Sigma Aldrich, MA) carrier top layer film. The graphite and graphene-graphite heterostructures with PMMA film slowly cleaves away from the wafer as the metallic layers are etched and were then subsequently transferred similarly to DI water for cleaning and finally onto clean PS and SiO₂ substrates. The PMMA carrier top layer were finally removed with glacial acetic acid (compatible with PS) and subsequently rinsed in DI water.

Optical microscope image shows heterogeneous graphite cross pattern monolithically connected with a graphene background on a 285 nm SiO₂ wafer (Figure 5).
Graphite features (blue) are ~20 nm thick relative to the graphene background (magenta); the green and yellow hued blotches arise from residual PMMA after acetic acid treatment and may be removed by further rinsing in acid/solvent or thermal annealing.

Figure 5. Heterogeneous graphene-graphite cross pattern.

2.2. Uniaxial vs. Equi-Biaxial/Isotropic/Uniform Texturing

The texturing of graphene and graphite is realized via thermally inducing shrinkage of the underlying PS substrate by heating above the polymer’s glass transition temperature as schematically shown in Figure 6a. The graphene and/or graphite on PS composite were placed in an oven (BINDER, Germany) at temperatures between 105°C to 120°C with varying amounts of induced macroscopic strain achievable by adjusting the duration of heat treatment, which varies between a few minutes to several hours.

The resultant compressive strain due to the deformation of the underlying substrate forms a well-defined crumpled texture from the top graphene/graphite layer without any
prior patterning typically necessary via photo-lithography or nano-imprint-lithography.\textsuperscript{39,40} In general, three texturing schemes were realized (Figure 6b): (1) uniaxial, (2) equi-biaxial/isotropic/uniform and (3) localized.

![Figure 6](image)

In general, three texturing schemes were realized (Figure 6b): (1) uniaxial, (2) equi-biaxial/isotropic/uniform and (3) localized.

Figure 6. Sample fabrication and thermal transformation. (a) Schematic of thermally-induced substrate transformation to induce texturing of surface graphene/graphite. (b) Photograph illustrating difference between untreated sample (original, left) versus samples subjected to uniaxial (middle) and equi-biaxial (right) texturing schemes. Note that as the polymer contracts, there is a corresponding increase in thickness.

In the case of uniaxial texturing, boundary conditions are applied whereby two ends of the PS sheet are held stationary in order to restrict shrinkage in that particular longitudinal direction (i.e. only lateral width decreases) by securing the ends with a custom-made aluminum clamp fixture (Figure 7). In the case of equi-biaxial shrinkage, the constraints were removed and the sheet was allowed to freely shrink uniformly in all directions by simply laying on a clean glass slide.
Figure 7. Custom designed aluminum clamp fixture for uniaxial texturing. The transparent PS sheet is shown placed on a glass slide and constrained on two ends, fixed freestanding between two aluminum clamps.

To characterize the amount of deformation, the macroscopic strains are defined as:

\[
\% \text{ strain} = \frac{l_o - l_i}{l_o}
\]

where \( l_o \) and \( l_i \) represent a given linear sample dimension (width for uniaxial) before and after the thermal treatment, respectively (i.e. a reduction from 15 mm to 4 mm is equivalent to a strain of \(~73\%)\). Note that existing literature presents a variety of confusing definitions to describe strain especially in the context of elastomers including, percentage compaction, percentage of relaxed/recovered restrain, etc. For the sake of clarity, we maintain the typical engineering convention that the strain should be denoted as the ratio of linear length change going from the original flat/relaxed state of the graphene to the crumpled state over that of the original length in the flat/relaxed state.
2.3. Localized Thermal Texturing via Selective Infrared Irradiation

Locally and heterogeneously patterned graphite crumplings were realized by concentrating a 20-watt infrared source (HawkEye Technologies, CT) with a spot size of \(\sim 5\) mm onto the backside of PS sheet, opposite from the graphene/graphite surface (Figure 8, Figure 9a).

![Figure 8](image)

Figure 8. Infrared setup for localized patterning. Photograph (a) shows the experimental setup of IR emitter used for localized patterning of PS with an accompanying IR thermal image (b) showing a concentrated irradiation spot size of \(\sim 5\) mm on a 15 mm wide PS sheet. Infrared thermal images of the IR setup and process were taken with a thermal camera (T400, FLIR, OR).

The distribution of heterogeneous flat and crumpled graphene/graphite regions were visualized with optical microscopy in dark field transmission and reflection modes (Axio Imager M2m, Carl Zeiss, Germany) (Figure 9b). It is well established that even single layer graphene is clearly visible on precisely tuned thicknesses of SiO\(_2\) substrate.\(^{41,42}\) Similarly, when placed on flat PS, there is a noticeable contrast difference between the graphene and bare PS areas (Figure 4). More evidently, upon crumpling, there exists
significant amount of light scattering which makes the crumples very visible, especially in dark field illumination mode (Figure 9b).

Figure 9. Localized texturing of graphene/graphite. (a) Schematic shows localized pattern texturing by subjecting selective areas to IR irradiation. The affected area with induced crumples is clearly visible in a dark field optical microscope image (b) due to enhanced light scattering of the crumpled structures as compared and flat graphene/graphite (interface shown as dotted line). SEM images show lack (c) and presence (d) of crumples on either sides of the interface. Wide area SEM image (Figure 18) shows continuity of graphite film from flat to crumpled area with no obvious material defects.
CHAPTER 3: MATERIAL CHARACTERIZATION

3.1. Morphology Characterization of Crumpled Graphene and Graphite Films

To systematically investigate the evolution of graphene crumple (i.e., geometry, roughness and coherence of the crumple) as a function of macroscopic compressive strain (i.e. amount of PS shrinkage), analysis was done through scanning electron microscope (SEM) and atomic force microscope (AFM) images in addition to optical microscopy.

SEM images show the development of linear crumple akin to that of surface relief gratings (Figure 10 for graphene, Figure 11 for graphite (~5nm thick)) with a concomitant observable increase in wrinkle alignment and coherence for the uniaxial case as the resultant strain progressively increase. For the equi-biaxial case, on the other hand, patterns resembling checkered structures are developed (Figure 10 lower right).\textsuperscript{43,44} SEM images (S-4800, Hitachi, Japan) were obtained for graphene samples after being sputtered with 2.5 nm of AuPd to improve imaging contrast and minimize charging of the PS substrate; graphite and graphene-graphite heterostructure samples were imaged as-is.
Figure 10. SEM images of uniaxially (18%, 46%, 71%) and equi-biaxially (58%, bottom-right panel) textured graphene.

Figure 11. SEM images of flat (0%) and uniaxially (23%, 47%, 73%) textured graphite.
Occasionally, sparse cracks are observable (Figure 12), which confirms that crumple formation occurs on an otherwise flat PS substrate and that the 3D crumpled structures are not intrinsic to the PS substrate itself. Even after crumpling, the graphene film remains mostly continuous under high macroscopic compressive strains with a few characteristic cracks that develop during heat treatment which are entirely contained within the film (i.e. crack does not originate from the graphene edge but rather begins and terminates within the film).

Figure 12. SEM image of interface between crumpled graphene (58%) and PS substrate at a particular location showing one of the few sparse cracks that developed during heat treatment, revealing the flat underlying PS substrate.

Atomic force microscopy (AFM) topography data were recorded in tapping mode (MFP-3D, Asylum Research, CA) using a tip with tip radius of \( \leq 10 \) nm and high aspect ratio (7:1), and second order flattened to remove scanning artifacts. Root mean square (RMS) roughness and area percent (projected topography area over scan area) data were calculated using IGOR Pro (WaveMetrics, OR). AFM topography 3D render shows increasing graphene crumple coherence, roughness and alignment as macroscopic compressive strain increases (Figure 13).
Figure 13. Surface topography of uniaxially textured graphene crumples for macroscopic compressive strain of (a) 18\% to (b) 30\%, (c) 58\%, (d) 70\%. Vertical full-scale: 100 nm, 2x2 µm area.

The derived topography data (Figure 13 and Figure 14) shows monotonic increase in the root mean square (RMS) roughness as the macroscopic strain increases. The average RMS roughness of graphene crumples reaches up to \(~8\) nm with a macroscopic compressive strain of \(~70\%) (Fig. 2c). Note that the measured RMS roughness values are limited by the inherent resolution of AFM tips (Tap300Al-G, Budget Sensors, Bulgaria) used to characterize graphene crumples due to their ultrafine and close-packed nature.
Figure 14. RMS roughness of graphene crumples increases monotonically with macroscopic compressive strain. Error bars represent one standard deviation.

The effect of film thickness on crumpling of multilayer graphene (or graphite) was studied for graphite films (average thickness of ~5 nm) synthesized using Co-Cu catalyst thin-film that were textured in the same manner. SEM images (Figure 11) and AFM topography renders (Figure 15) clearly show development of increasing density and height of crumples as a function of macroscopic compressive strains.
Figure 15. Surface topography of uniaxially textured graphite crumples for macroscopic compressive strain of (a) 23% to (b) 47%, (c) 58%, (d) 73%. In addition to increasing crumple height/roughness and alignment as strain increases, bifurcation or hierarchical wrinkling is observed for large strains. Vertical full-scale: 800 nm, 2x2 µm area.

Notably, bifurcation leading to hierarchical wrinkling is evident in the AFM topography render for large strains, whereby a secondary crumple periodicity (of larger wavelength and amplitude) develops along with the original, finer crumple pattern (Figure 15d). As with graphene, the graphite crumpled shows monotonically increasing RMS roughness and also area percent (defined as effective projected area over nominal scanned area) with larger macroscopic compressive strains (Figure 16).
Figure 16. RMS roughness and area percent of graphite crumples increase monotonically with uniaxial strain. The error bars represent one standard deviation.

3.2. Morphology Characterization of Crumpled Graphene-Graphite Heterostructures

The unique aspect of thickness controlled crumpling behavior is further substantiated by investigating monolithic crumpling of heterogeneous graphene-graphite patterns. A film containing symmetrical cross patterns of graphite monolithically connected to a graphene background was synthesized via CVD (Figure 5). Upon uniaxial texturing of the pattern, the originally symmetrical cross-shaped graphite feature (inside white dotted line) is deformed uniaxially into an asymmetric pattern reflecting the degree of shrinkage (~70% macroscopic strain, inside black solid line) (Figure 17). A difference in crumple topography between that of graphene (surrounding the cross pattern) (Figure 17b) and that of graphite (inside the cross pattern) (Figure 17c) is clearly observable.
Furthermore, the monolithic interface is well preserved between crumpled graphene and graphite.

Figure 17. Heterogeneous crumples via graphene/graphite thickness variation. (a) SEM image of heterogeneous graphene-graphite cross pattern subjected to ~70% strain uniaxial texturing (dotted white outline indicates original cross dimensions prior to texturing, solid black outline shows dimensions after texturing). The background graphene (b) exhibits noticeably smaller crumples than the thicker graphite (c) region inside the cross pattern. Figure 5 shows the optical microscope image of original flat cross pattern on a SiO\textsubscript{2} substrate.

3.3. Localized Infrared Thermal Treatment Morphology

A novel aspect and unique advantage of this heat induced texturing approach is the ability to locally pattern graphene/graphite crumples via spatially selective concentrated IR irradiation and the resultant shrinking of the PS substrate (Figure 18).
Figure 18. Optical microscope image (a) of locally textured graphite shows region affected by IR irradiation. Low magnification SEM image (b) corroborates continuity and gradient of crumplfes with the largest crumplfes bring developed nearest to the IR focal spot (to the right). Higher magnification of the left region ((c), father from IR spot) shows flat graphite whereas the right region ((d), closest to IR) shows large, dense crumplfes. Large scale (tens of microns) random wrinkles in left portion of (b) are due to folds generated during solution transfer of graphite with PMMA onto a PS and subsequent removal of PMMA in glacial acetic acid. Wide-field SEM image was compiled using Adobe Illustrator (Adobe Systems, CA).
As opposed to previously reported approaches which relied on lithographic pre-patterning of the substrate or multi-step fabrication of a metal-film layer after graphene transfer\textsuperscript{45}, we are able to apply this direct patterning approach immediately after the film of interest (i.e., graphene/graphite) has been transferred to the target PS substrate, without any additional pre- or post-processing steps. At the junction of the heat affected area, the presence (or absence) of crumples is clearly noticeable. High magnification SEM images at both regions show the lack and presence of crumples in the native (Figure 18c) and IR-affected regions (Figure 18d), respectively. This approach clearly demonstrates a simple, single-step, direct patterning of 3D graphene or graphite crumples without any additional prior patterning or post fabrication.

3.4. Raman Characterization

Raman spectroscopy is one of the most ubiquitous techniques to characterize carbon-based nanomaterials.\textsuperscript{46} Graphene exhibits the most intense Raman features at two locations, the G peak at around 1580cm\textsuperscript{-1} and the G’ or 2D peak around 2700cm\textsuperscript{-1} with the precise locations dependent on a variety of factors such as substrate affects, doping, strain, excitation wavelength etc.\textsuperscript{47} Likewise, defects and edges in graphene contribute to a D peak at around 1350cm\textsuperscript{-1}.

Raman spectroscopy characterization was conducted to confirm the presence and quality of graphene subsequent to synthesis and transfer onto the PS substrates and following heat treatment. Comparing the Raman spectra between that of flat and crumpled graphene further shows the integrity of graphene crumples even as compressive strain
increases (Figure 19 and Figure 20). Raman spectra were captured using a 633 nm laser (InVia microPL, Renishaw, UK) at 1800/mm grating, 10% laser output and 10 second accumulation to minimize sample heating affecting the polymeric substrate.

Figure 19. Raman spectroscopy of uniaxially strained graphene crumples (71%, blue). Inset shows 2D peak position for flat (on SiO$_2$ [black] and PS [red]) and crumpled (71% [blue]) graphene. Spectrum is flattened against a broad PS baseline spectra (PS peaks preserved) and normalized to the highest peak.

As a control, we identify the position of the characteristic 2D peak for a control graphene sample transferred in the same manner onto a 285 nm SiO$_2$ substrate compared with that of graphene on flat and strained PS (Figure 19 inset). We observed a consistent blue shift of the 2D band as the macroscopic compressive strain increases, consistent with earlier literature.$^{48}$
Figure 20. Raman spectroscopy confirms presence of graphene for equi-biaxially (58%) textured graphene crumples. Spectrum is flattened against a broad PS baseline spectra (PS peaks preserved) and normalized to the highest peak.

The Raman D-to-G peak ratio does not show any changes as compressive strain increases, which demonstrates that the material integrity of graphene is preserved and suggests that deformation of graphene is highly elastic in both uniaxial and equi-biaxial cases.

Additionally, to substantiate that the localized patterning via IR irradiation does not in fact contribute to additional intrinsic graphene defect formation, we consider the intensity of the D peak before and after 20 seconds of IR irradiation for graphene on a flat 285nm SiO$_2$ substrate (Figure 21). Note that the spectra are almost identical, and there is
no increase in the intensity or broadening of the D peak upon 20 seconds of IR irradiation, which is still significant longer than the typical irradiation time for localized texturing (~5s).

Figure 21. Raman spectra of graphene on SiO$_2$ before (black) and after (red) 20 seconds of focused IR irradiation. Spectra are normalized to show the same 2D peak intensity.

Due to the vicinity of the G peak to the background peaks of PS and the susceptibility of G peak position to doping effects, we consider the 2D peak position as an indicator of the intrinsic amount of strain developed inside the crumples. Up to a macroscopic uniaxial strain of 66.9%, the 2D peak position (as fitted by a single Lorentzian function) blue shifts from ~2636cm$^{-1}$ to ~2653cm$^{-1}$ (Figure 22). Considering estimates of a -64cm$^{-1}$/% blue shift arising from intrinsic uniaxial compressive strain, the ~17cm$^{-1}$ blue
shift measured here would correspond to an intrinsic strain of ~0.27% which is on the same order of magnitude with previously reported values for compressively wrinkled graphene ribbons.\textsuperscript{34,35}

![Graph showing Raman 2D peak position as a function of uniaxial macroscopic strain.](image)

Figure 22. Raman 2D peak position as a function of uniaxial macroscopic strain. Error bars represent one standard deviation from 10 spot measurements at arbitrary locations.

3.5. Electrical Characterization

Electrical sheet resistance characterization was performed by progressively crumpling graphene with simultaneous 4-point probe electrical characterizations. Measurements were conducted using a linear four-point probe head (RM3-AR, Jandel Engineering, UK) on the lowest probe pressure dial setting in order to minimize contact
and puncture damage to the sample. No significant changes in the sheet resistance (1.2-1.8 kΩ/□) were observed up to the maximum attainable 73% macroscopic compressive strain (Figure 23) when characterized with the linearly spaced measurement probes oriented along the same direction of the crumples (Figure 23 inset). The sheet resistance values obtained are consistent with those reported for flat graphene transferred onto similar commercially available polymeric substrates.49

![Graph showing sheet resistance vs strain](image)

Figure 23. Four-point probe measurement on graphene crumples as compressive strain increases shows no significant corresponding change in sheet resistance, indicating that graphene integrity is preserved. Inset shows probe measurement orientation with respect to crumple direction. The error bars represent one standard deviation.

The small increase and fluctuation in sheet resistance is attributed to physical damage from repeated probe contact and also successive environmental exposure during each heat treatment step necessary to increase the strain.
To further substantiate that the texturing will not adversely affect the electrical properties, two terminal resistance measurements were also conducted to find the change in linear resistance perpendicular to the direction of the crumpled ridges. The linear resistance increases only moderately, which may be contributed from successive environmental exposure and probe contact (Figure 24).

![Normalized two-terminal resistance as macroscopic uniaxial strain increases.](image)

*Figure 24. Normalized two-terminal resistance as macroscopic uniaxial strain increases.*
CHAPTER 4: CONCLUSION AND FUTURE WORK

The herein presented results clearly show the capability to easily create 3D crumpled structures from otherwise flat, 2D graphene and graphite using simple convective heat treatment and IR irradiation through a non-linear buckling process.\textsuperscript{34,50} Not only are the different bulk morphologies tunable, but also demonstrated is the ability to form deterministic patterns by varying induced strain direction and strain amount, film thickness, and localized shrinkage. This shape-memory polymer substrate induced crumpling of graphene/graphite has several key advantages over earlier works.

First, the simplicity of thermal processing allows deterministic tunability of crumple morphology and density over a large range of macroscopic strains via simple processing parameters. Furthermore, this novel thermal deformation mechanism allows spatially controlled texturing via direct local patterning for the first time. Second, our proposed approach provides a simple and robust platform for studying the texturing and strain engineering of a wide range of other novel 2D atomic-layer materials of recent interest, such as silicene, germanane, hBN, MoS\textsubscript{2}, and other transition metal dichalcogenides.\textsuperscript{51–53} Finally, the ubiquity, scalability, and low cost of shape-memory polymers and the accompanying thermal processing offers a pathway that is conducive to large-scale manufacturing of textured graphene-based flexible devices, circumventing costly lithographic pre-patterning and post-pressing deposition steps required in traditional wrinkle-forming techniques.

Through various characterization techniques such as SEM, Raman spectroscopy and four-point probe measurements, we deduce that graphene’s integrity has been
preserved during increasing compressive strains and that there has been little plastic deformation or damage due to the crumpling and buckling process. Nonetheless, there is still a variety of characterization techniques which merit further exploration for this unique material configuration and may elucidate any unique physics intrinsic to the local regions of the crumpled structures (e.g. apex versus trough of the crumpled).

As the periodicity and roughness of the crumpled structures are sub-wavelength to conventional spectroscopic techniques such as UV-Vis-NIR, FTIR, actively research is being pursued for near-field characterization techniques such as near-field scanning optical microscopy (NSOM) and other scanning probe derivative thereof such as apertureless AFM-FTIR and AFM-Raman. Preliminary results from AFM based near-field apertureless IR spectroscopy shows contrast in amplitude and phase shift of the scattered light between not only the graphene and PS substrate but also to features internal to the crumpled structures (Figure 25). Further investigation at finer resolution and over a larger spectrum of excitation may elucidate any potential plasmonic effects.
Figure 25. Optical amplitude (left) and phase shift (right) of near-field AFM-based IR spectroscopy on crumpled graphene on PS substrate at 1100 cm\(^{-1}\) (9.09 µm) (top) and 1600 cm\(^{-1}\) (6.25 µm) (bottom). Images courtesy of T. Gokus, Neaspec GmbH.

In addition to near-field optical characterization, analogous scanning probe based electrical characterization techniques such as Kelvin probe force microscopy (KPFM) and scanning microwave impedance microscopy (sMIM) may elucidate any induced localized electrical inhomogeneities. These high resolution techniques will be able to determine the localized surface work function and distribution of localized capacitance and resistance changes, respectively. Further complementary AFM characterization with specific probe
selection will also allow for force and tribological studies not only on the graphene structures themselves, but also indirectly the underlying graphene and PS interface interactions (adherence versus delamination).

In conclusion, this thesis demonstrates the facile, single-step, controlled texturing of graphene and graphite into 3D crumpled structures via thermally induced transformations on an oriented PS substrate. It is shown here that the 3D texturing of both graphene and graphite can be modulated by varying simple processing parameters, and that the material integrity of graphene and graphite was maintained even up to induced macroscopic compressive strains as large as \( \sim 70\% \). Furthermore, texturing of monolithic graphene-graphite patterns were demonstrated and showed that continuous interfaces were preserved between graphene and graphite crumpled regions, which is promising for all carbon-based flexible devices. More notably, the deterministic, spatially localized 3D patterning of graphene/graphite crumpled regions is proven which enables creation of a mixture of flat and crumpled heterogeneous morphologies based on graphene/graphite alone without substrate pre-patterning or any post-processing material deposition.

The presented approach can be readily extended to a variety of other 2D materials (such as MoS\(_2\) and other dichalcogenides), and is much more amenable to large scale manufacturing of 3D crumpled structures as compared to previously reported methods.\(^{51-54}\) This simple patterning approach would enable monolithic integration of flat and textured graphene/graphite to realize mechanically robust and flexible advanced 3D devices and sensors in the future.\(^{55}\) Preliminary studies have already shown promising results for this crumpled graphene material platform to be effective for surface enhanced Raman
spectroscopy (SERS) applications and also morphological influence on surface cultured cells due to its unique structure.
REFERENCES


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