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Liang, Jiayun

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2024

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Confinement Growth of Materials Through Interface Engineering

By

Jiayun Liang

A dissertation submitted in partial satisfaction of the
requirements for the degree of

Doctor of Philosophy

in

Engineering – Materials Science and Engineering

in the

Graduate Division

of the

University of California, Berkeley

Committee in charge:

Professor Zakaria Y. Al Balushi, Chair

Professor Mark Asta

Professor Kwabena Bediako

Spring 2024

Confinement Growth of Materials Through Interface Engineering

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Jiayun Liang

Abstract

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Doctor of Philosophy in Engineering - Materials Science and Engineering

University of California, Berkeley

Professor Zakaria Y. Al Balushi, Chair

This dissertation explored the innovative avenues for the confinement growth of materials, leveraging both space-confined and area-selective synthesis strategies through a variety of interface engineering approaches. It highlighted the multifaceted roles of the interface during the synthesis process, acting not only as a nanoreactor and/or a physical scaffold to constrain the geometry of the resulting materials, but also setting a specific chemical microenvironment. This environment is instrumental in facilitating the confined nucleation, growth, and stabilization of intermediates or final products, a process pivotal to area-selective synthesis. Towards it, we first focused on the intercalation of large molecules, such as P_2O_5 , through the basal plane of graphene. This process yielded a confined P_2O_5 and/or metal phosphate structure within the graphene/Ge (110) heterointerface, following a two-step mechanism. This mechanism involved the dissociation of P_2O_5 and the subsequent intercalation of its fragments, as corroborated with density functional theory (DFT). The focus was then turned to area-selective synthesis of materials by engineering the surface energy profile at the vacuum-liquid and/or graphene/diamond like carbon (DLC) interface. In one study, a complex surface energy profile was achieved at liquid metal-vacuum interface using Laguerre-gaussian (LG_{pl}) lasers as the heat source, which induced novel Marangoni flow pattern. Marangoni surface flow, and convective flow in bulk liquid metal directed the movement of microparticles within the liquid, demonstrating that careful tuning over the parameters of the LG_{pl} laser (i.e., laser mode, spot size, and intensity of the electric field) allowed for precise control over the structure of the ring-shaped particle assemblies at solid-liquid interface. Finally, this dissertation presented a novel method for tuning the work function of monolayer graphene across a broad temperature range. This was achieved through engineering the graphene-Ga implanted DLC heterointerface, allowing for bipolar tuning (either increase or decrease) of the local work function landscape of graphene up to 500°C. This comprehensive study established a clear link between interface engineering and the confinement growth capabilities of materials, offering new strategies and advanced understanding for confinement materials synthesis.

Acknowledgements

First, I would like to thank Professor Zakaria Al Balushi for giving me the opportunity to join his research group and engage in a series of interesting and highly innovative projects. From him, I have profoundly appreciated the importance of an extraordinary attention to detail and a passion for science in research. Over the past five years, I am fortunate to have been inspired by his enthusiasm for science, especially during those challenging times marked by failures. With his guidance, I have grown into a more independent, more productive, and more skeptical researcher. As I move forward in my future career, I will carry this meticulousness and passion, dedicating myself to each research project ahead.

Also, I'd like to extend my gratitude to those who have supported me throughout my academic journey. Foremost, my appreciation goes to Professor Chunhua Chen and the members of the Chen Lab at the University of Science and Technology of China (USTC), as well as Professor Yadong Yin and the Yin Lab team at the University of California, Riverside (UCR). They offered me my first taste of the science world, generously sharing their knowledge and encouraging me to go for a Ph.D. degree during my undergraduate years. Those days with them never faded in my memory.

Meanwhile, I'd like to acknowledge the tremendous help from my lab mates, including Xiaotian, Healin, Bumjun, Josh, Derick, Jennifer, Elena, and Ayush. Xiaotian, in particular, has been an extraordinary mentor not only to guide me in the experimental and simulation work, but to teach me the quintessential trait of a researcher: the capacity to identify a question and to solve it. And I'd like to thank Healin for mentoring me in fabrication, thereby rounding out my skillset. Healin and Bumjun have been wonderful companions during research and coffee breaks. Our discussions, whether about science or life beyond the lab, have been a source of great enjoyment and inspiration.

Moreover, my research would not have been fruitful without the invaluable contributions of my collaborators. Dr. Cameron Johnson and Dr. Andreas Schmid played a pivotal role in the SPLEEM/LEEM experiments and offered creative insights that pushed our research forward. Dr. Paul Ashby's assistance in KPFM measurements was indispensable. Dr. Xiao Zhao's remarkable experimental skills and insightful feedback on characterization techniques consistently impressed me. Likewise, the support from the scientists at ALS—particularly Dr. Hans Bechtel for nano-FTIR, along with Dr. Chris Jozwiak, Dr. Aaron Bostwick, and Dr. Eli Rotenberg for nano-ARPES—was instrumental to our research. A special acknowledgment goes to Ke Ma and Dr. Matthew Sherburne for their exceptional DFT calculations. Last, I would like to acknowledge our funding resources – Department of Energy (DOE) and Canadian Institute for Advanced Research (CIFAR).

The journey through my Ph.D. would certainly be much less enriching without friends. My heartfelt thanks to Ji, Xin, Jinhong, Xiao, and Hao for standing by my side and sharing in the joy of our accomplishments. Special gratitude is extended to Shiyun, Yaying, and Yue for their unwavering support and care throughout our two decades of friendship.

Last but certainly not least, thanks to my parents for showing me what is 'love', and to Jiawei, with whom I want to practice this love throughout our lifelong journey together. Echoing my favorite saying to my family and friends, "Every moment spent with you was dazzling. Whether the days were fair or not, or just right, every day was beautiful."

Table of Contents

List of Figures.....	v
List of abbreviations and symbols.....	xiii
Chapter 1	1
1.1 Confinement growth of materials and interface.....	2
1.2 Role of interface in confinement growth of materials.....	3
1.2.1 Adsorption, diffusion, and nucleation at the interface.....	3
1.2.2 Geometry confinement in materials synthesis	4
1.3 Current state-of-art for interface engineering on confinement material growth	4
1.3.1 Space-confinement synthesis of materials	4
1.3.2 Area-selective synthesis of materials.....	6
1.4 Motivation and organization of dissertation.....	11
Chapter 2	14
2.1 Introduction	15
2.2 Experimental setup and characterization	16
2.2.1 Chemical vapor deposition (CVD) process for the intercalation of P_2O_5 ..	16
2.2.2 Graphene transfer process.....	16
2.2.3 Materials characterization.....	16
2.3 First Principles Calculation.....	17
2.4 Intercalation of P_2O_5 at the graphene/Ge (110) heterointerface	18
2.5 Chemistry of the graphene/substrate heterointerface after intercalation.....	20
2.6 Mechanism of large molecule intercalation through graphene.....	22
2.7 The impact of the intercalants on the electronic structure of graphene interface	26
2.8 Space-confinement synthesis of metal phosphates at heterointerface.....	33
2.9 Conclusions	35
Chapter 3	37
3.1 Introduction	38
3.2 Finite element simulation setting	39
3.2.1 Framework for coupling the Marangoni effect and fluid flow.....	39
3.2.2 Laser heating setup and conditions.....	48

3.2.3 Particle trajectory	39
3.3 Laser-induced Marangoni flow in liquid gallium.....	41
3.4 Influence of laser-induced Marangoni flow on Brownian and particle assembly	43
3.5 Investigating the interacting forces impacting particle assembly	48
3.6 Tunable laser parameters for particle assembly	53
3.7 Conclusions	59
Chapter 4	61
4.1 Introduction	62
4.2 Experimental setup and characterization	64
4.2.1 Ga ⁺ -FIB patterning on DLC and polymer-free graphene transfer on DLC	64
4.2.2 Polymer-free graphene transfer on DLC.....	66
4.2.3 Anneal and work function quantification in low energy electron microscope (LEEM).....	66
4.2.4 Atomic force microscope (AFM), Kelvin probe force microscope (KPFM), Raman measurements	69
4.2.5 Time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements	70
4.2.6 Scanning tunneling microscope (STM), scanning tunneling spectroscopy (STS), and electron energy loss spectroscopy (EELS) measurements	70
4.2.7 Nano-angle-resolved photoemission spectroscopy (nano-ARPES) measurements.....	71
4.2.8 DFT calculations	71
4.3 Temperature-dependent work function on tuning graphene surface	71
4.4 Temperature-dependent work function on Ga implanted DLC	73
4.5 Interaction between graphene and Ga implanted DLC.....	79
4.6 Structure-dependent electronic transport at the heterointerface	81
4.7 Highly tunable work function landscape of graphene at chosen temperature	86
4.8 Conclusions	88
Chapter 5	90
5.1 Large molecule intercalation through graphene-substrate heterointerfaces... ..	91
5.1.1 <i>In situ</i> experiments for the intercalation process.....	91
5.1.2 Control over the intercalation process through the basal plane of graphene	

.....	92
5.1.3 Expansion of confined metal phosphates family.....	92
5.1.4 Synthesis of phosphorus allotropes at the heterointerface	93
5.2 Light induced surface tension for hierarchical assembly of particles from liquid metals.....	95
5.2.1 Investigation of laser modes and arrangements	96
5.2.2 Particle radius for the assembly	99
5.2.3 Experiments to corroborate simulation results	99
5.3 Area-selective work function tuning in graphene across a broad temperature range through substrate heterointerface engineering.....	100
5.3.1 Area-selective growth of materials on engineered graphene	101
5.3.2 Alternative element for gallium.....	102
5.3.3 Applications for heavily doped graphene and beyond	102
5.4 Conclusions	106
References	108
Appendix A:.....	128
Appendix B:.....	132
Appendix C:.....	135
Appendix D:.....	142

List of Figures

Figure 1.1: Summary of the space-confinement synthesis of materials through interface engineering. (a to c) Scheme for intercalation of molecules through interface for thickness-confined growth at the heterointerface, where intercalants are: (a) single small molecules, (b) multiply small molecules to initialize chemical reactions within the confined heterointerfaces, (c) large molecules, respectively. (d to h) Scheme for hard template assist synthesis approach for geometry-confined synthesis. For the template, the pore shapes and/or arrangement can be flexibly adjusted, such as (d) round-shape, (e) square-shape, (f) triangle-shape, (g) binary-shape, and (h) six-membered ring pore arrangement.	5
Figure 1.2: Summary of major interface engineering strategies for the area-selective growth of materials.	7
Figure 1.3: Schematic for energetic-preferred direction of surface adsorption and diffusion of molecules on interface with engineered surface energy landscape. The direction of surface adsorption and diffusion are highlighted with brown arrows and orange-to-pink arrows, respectively.	10
Figure 2.1: Intercalation of P_2O_5 at the graphene/Ge (110) heterointerface. (a) Configuration of P_2O_5 adsorbed onto pristine graphene calculated from DFT. (b) Schematic of intercalation process through the graphene-substrate heterointerface: (i) decomposition of P_2O_5 into P_x and O_y , (ii) intercalation of P_x and O_y through graphene and formation of P_2O_5 at heterointerface via chemical reactions. (c) SEM highlighting the formation of graphene bubbles (white arrows), with STM image of the graphene lattice on the top surface of the bubble (bottom left inset). (d) SEM-EDS maps of (left) oxygen and (right) phosphorus of the highlighted graphene bubbles in (c). (e) STEM-HAADF cross-section image of a graphene bubble with corresponding STEM-EDS maps of the (f) oxygen, and (g) phosphorus distribution in the bubble.....	18
Figure 2.2: XPS depth profile of graphene/Ge (110) after exposure to P_2O_5. High-resolution XPS spectra collected before the ion sputtering process (black); after the first sputtering cycle (red); after the second sputtering cycle (blue); after the third sputtering cycle (green); after the fourth sputtering cycle (violet) and after the fifth sputtering cycle (yellow) for core-levels of (a) C 1s, (b) Ge 3d, (c) O 1s, and (d) P 2p. In the XPS spectra of Ge 3d, region where the binding energy ranged from 31eV to 35eV is magnified to highlight the intensity change of the germanium oxide.	19
Figure 2.3: Chemistry at the graphene/Ge (110) heterointerface. (a) Near-field white light IR image in a region of the sample containing large graphene bubbles. The white light IR image was the near-field amplitude (S_2) image, which was spectrally averaged over approximately ~ 610 - 1400cm^{-1} by setting the interferometer at the white light position. (b) Nano-FTIR spectral heat map acquired at 50 nm intervals along the black solid arrow in (a). The graphene bubble region is highlighted with white dashed lines and dashed arrow. The collected phase channel (ϕ_2) was normalized to that obtained in a silicon sample using the same acquisition parameters. (c) Comparison between extracted nano-FTIR spectrum of a graphene bubble (top panel, black solid line) and spectrum collected from a reference P_2O_5 sample (bottom panel, red solid line). XPS of C, P and Ge core-levels from graphene on germanium samples (d, e, and f) annealed without an upstream flux of P_2O_5 (i.e., unintercalated sample) and from graphene on germanium samples (g, h, and i) annealed with an upstream flux of P_2O_5 (i.e., intercalated sample).	21
Figure 2.4: Mechanism for intercalation P_2O_5 through the basal plane of graphene. (a) Top view of the four types of point defects in isolated graphene sheets. (b) Adsorption energy of phosphorus pentoxide on pristine and defective graphene monolayers. Within each P_xO_y molecule,	

the atom interacting directly with carbon at the defect site is labeled in parentheses. (c) Calculated energy barrier of bond cleavage for P-O double bond (route 1, labelled as green) and single bond (route 2, labelled as blue) within P_2O_5 in different local environments. (d) Energy and configurational profile of PO molecule penetrating through defects. (e) Energy barrier of P (blue bars) and O (red bars) atoms permeating through defects. 24

Figure 2.5: Intercalation of P_2O_5 molecule through a defect of 9 vacant atoms. (a) A comparison of dimensions of a defect of 9 vacant atoms and P_2O_5 molecule. (b) Energy profile of P_2O_5 intercalation through a 9-vacant-atom defect. The molecule underwent spontaneous dissociation upon contact with the defect site and would require an energy barrier of 7.7eV to desorb and recombine on the opposite side of the graphene monolayer. Top (left) and angled (right) view of the (c) initial, (d) intermediate, and (e) final state configuration of P_2O_5 molecule during intercalation. 25

Figure 2.6: Raman and STS spectrums of graphene after intercalation. Raman spectra of graphene (a) before (*black solid line*) and after (*red solid line*) exposure to an upstream flux of P_2O_5 , (b) Raman 2D versus G peak position of graphene before (*black dots*) and after (*red dots*) exposure to an upstream flux of P_2O_5 . (c) STS dI/dV of intercalated graphene sample. The corresponding phonon scattering gap and Dirac points are highlighted with *green dashed line* and *yellow dashed line*, respectively (Tunneling set point = 200pA, 750mV). Spectra are vertically offset for clarity. 27

Figure 2.7: Raman spectra of the post-intercalated sample in lower frequency range. (a) Ge (110) substrate without exposure to SiP_2O_7 (*black solid line*) and after exposure to SiP_2O_7 (*red solid line*) from 300 to 950 cm^{-1} . (b) Raman spectra of Ge (110) substrate without exposure to SiP_2O_7 from 200 to 500 cm^{-1} 29

Figure 2.8: Projected density of states (PDOS) analysis of carbon atoms in monolayer graphene subject to mechanical deformation: PDOS of an isolated pristine graphene monolayer (top panel) compared to its behavior under mechanical deformation. The middle panel shows PDOS for graphene subjected to biaxial tensile strain of 1% (blue curve) and 4% (orange curve), whereas the bottom panel depicts the PDOS under biaxial compressive strain of 1% (blue) and 4% (orange). The energy in all DOS plots is normalized against the Fermi level. Notably, even at 4% biaxial strain, either tensile or compressive, the electronic structure of graphene monolayer closely resembles that of the undeformed system. 29

Figure 2.9: Projected DOS of graphene on germanium surface. The top panel shows the DOS for carbon atoms in an isolated, free-standing graphene monolayer. The middle and bottom panels present the DOS for carbon atoms in graphene sheet separated from the underlying germanium surface at various distances. 30

Figure 2.10: Projected DOS of graphene in different scenarios. Projected DOS of (a) Pristine graphene sheet without (black) and with (red and blue) adsorbed phosphorous oxide, (b) Graphene with SW- (black), D- (red), and Q-defects (blue) without adsorbed phosphorous oxide. (c) Comparison of p-orbital DOS of graphene with S-defect (black) and with S-defect covalently bound to P atom in chemisorbed P_2O_5 (red). (d) Differential charge density of P_2O_5 covalently bound to S-defect. All wireframe isosurfaces denote charge transfer equivalent to 0.001 $e \cdot Bohr^{-3}$. Blue isosurface represents charge loss and red isosurface indicates charge gain. 32

Figure 2.11: Projected DOS of defected graphene with P_2O_5 adsorbed. 33

Figure 2.12: Confinement growth of indium phosphate at graphene-substrate heterointerface. XPS core-levels of (a) In 3d for 2D indium confined at the graphene-SiC heterointerface before (*black solid line*) and after exposure to P_2O_5 (*blue solid line*). The XPS spectra for a pure In_2O_3 crystal (*red solid line*) is also included as a reference. The range for $InPO_4$ peak position data from

reference¹⁷¹⁻¹⁷² is highlighted in a shaded gray region. (b) P 2p for the confined 2D indium after exposure to P₂O₅.....34

Figure 3.1: Electric field profiles, temperature profiles and resulting particle patterns assembled out of liquid-gallium under different Laguerre-Gaussian (LGpl) laser modes. (a) Schematic highlighting the process of assembling particles out of liquid-gallium using a *LGpl* lasers (laser wavelength, $\lambda=645\text{nm}$ and $w_0=125\mu\text{m}$). When *LGpl* lasers interacted with liquid-gallium, Marangoni flow developed, guiding randomly dispersed tungsten particles (diameter, $dp=20\mu\text{m}$) to assemble at the liquid-solid interface. (b to d) Profile of the electric field on the surface of liquid-gallium under (b) *LG00*, (c) *LG04*, and (d) *LG14* lasers, respectively. An inner and outer ring were observed in the doughnut-shaped electric field profile for (d) *LG14* laser, as highlighted by two *dashed red arrows*. The scale bar for all the electric field profiles is $200\mu\text{m}$. (e to g) Profiles of the electric field (*dashed red lines*) and temperature (*solid black lines*) on the surface of liquid-gallium. (h to j) Resulting particle patterns at the liquid-solid interface for (h) *LG00*, (i) *LG04*, and (j) *LG14* lasers interacting with liquid-gallium. The ring-shaped particle patterns were obtained with (i) *LG04*, and (j) *LG14* laser modes only, creating a “forbidden zone” of assembly, where tungsten particles did not gather which is highlighted by *dashed red lines*. The scale bar for all particle patterns is $200\mu\text{m}$ 42

Figure 3.2: Influence of surface tension gradients of liquid-gallium on the particle motion in the bulk fluid. (a to c) Surface tension profiles of liquid-gallium along the x-axis for (a) *LG00*, (b) *LG04*, and (c) *LG14* lasers ($\lambda=645\text{nm}$ and $w_0=125\mu\text{m}$). (d to f) Convective flow patterns induced by the surface tension gradient (i.e., Marangoni flow) for (d) *LG00*, (e) *LG04*, and (f) *LG14* lasers. For (e) *LG04*, and (f) *LG14* lasers, two additional central vortices were observed in the convective flow patterns in the fluid, as highlighted by *dashed black lines* under the magnified regions (scale bars are $50\mu\text{m}$). The absolute value of the fluid velocity is indicated by the color bar at the bottom. 44

Figure 3.3: The mean-squared displacement (MSD) versus radial position (r) of for particles under different laser mode. (a) *LG00*, (b) *LG04*, and (c) *LG14* lasers ($\lambda = 645\text{nm}$ and $w_0 = 125\mu\text{m}$) when the particle moved near the top surface of liquid-gallium ($z \leq 10\mu\text{m}$, *shaded gray background*). The insets in (a, b, and c) are the particle trajectories (*blue-to-green gradient*) guided by the fluid flow induced under the (a) *LG00*, (b) *LG04*, and (c) *LG14* laser modes, respectively. All particles were released at the same position in the fluid (*blue star*) and finally assembled at the liquid-solid interface (*green star*). 45

Figure 3.4: Impact of the laser mode on the particle pattern assembled out of liquid-gallium. (a, b, and c) Time dependent radial (r) particle count density for 2000 randomly released tungsten particles ($dp=20\mu\text{m}$) in liquid-gallium guided by the convective flow induced by (a) *LG00*, (b) *LG04*, and (c) *LG14* lasers ($\lambda = 645\text{nm}$ and $w_0 = 125\mu\text{m}$). All 2000 particles were released at $t = 0\text{s}$ and all settled at the liquid-solid interface at $t = 0.2\text{s}$. The width of the radial bin for the particle count density profiles was set to $50\mu\text{m}$ 46

Figure 3.5: Impact of the laser spot size on the particle pattern assembled out of liquid-gallium. (a to c) Fluid flow pattern in liquid-gallium under *LG14* laser with the spot size of (a) $75\mu\text{m}$, (b) $100\mu\text{m}$, and (c) $125\mu\text{m}$. Two additional “central vortices” are magnified for clarity (scale bar is $50\mu\text{m}$). The absolute value of the fluid velocity is indicated by the color bar (*red-to-blue gradient*) on the right. (d to f) Density distribution maps (bin size = $50\mu\text{m}$) and corresponding entropy values for particle patterns induced by fluid flow under the *LG14* laser with a spot size (w_0) of (d) $75\mu\text{m}$, (e) $100\mu\text{m}$, and (f) $125\mu\text{m}$. The scale bar for all density distribution maps is $200\mu\text{m}$ 47

Figure 3.6: Statistical analysis of the entropy calculations. Relative change of entropy (left y-axis, *blue box*) and mean squared error of entropy (right y-axis, *black solid line*) for the particle assembly obtained in 10 repeated runs.....48

Figure 3.7: Mechanism for the formation of ring-shaped particle patterns in liquid-gallium under the LG14 laser. (a) Trajectory of a representative particle with effective gravitational force. The particle started near the top surface and settled at the liquid-solid interface (bottom surface). For simplification, only half of the liquid-gallium fluid flow is shown, where the center of liquid-gallium is marked by a solid yellow line. The width of the “forbidden zone” is marked by a double headed dashed black arrow. (b to d) Highlight the forces exerted on the particle when it: (b) moved along the top surface of liquid-gallium, (c) moved towards the liquid-solid interface and (d) before it settled at the liquid-solid interface. The direction of the drag forces (FD) and the effective gravitational force (G_{eff}) are shown on the particle (solid black arrows). The background of the fluid velocity with superimposed streamlines illustrates the fluid dynamics of liquid-gallium in the magnified regions. (e) Trajectory of a representative particle without effective gravitational force. Particle started near the top surface and settled near the periphery of the liquid-gallium boundary. (f to h) Highlight the forces exerted on the particle when it: (f) initially was released into the fluid, (g) moved along the top surface of liquid-gallium, and (h) before it settled around the periphery of the liquid-gallium boundary. The absolute values of the fluid velocity (red-to-blue gradient) and particle velocity (green-to-yellow gradient) are indicated by the color bars on the right side of the figure. 51

Figure 3.8: XY cross-section of the particle assembly with the sticking coefficient of the sidewalls set to unity (LG14 laser mode and $w_0 = 125\mu\text{m}$). The diameter of the particles (dp) were: (a) $25\mu\text{m}$, and (b) $5\mu\text{m}$, respectively. The sidewall is marked with solid black line and highlighted with a dashed black arrow. The scale bar for the particle pattern is $200\mu\text{m}$ 53

Figure 3.9: Summary of the tuning knobs of LGpl lasers to obtain ring-shaped pattern with different degrees of order. (a) Impact of LGpl lasers: entropy of particle patterns ($dp = 20\mu\text{m}$) under different LGpl lasers (LG00, LG04, and LG14, $w_0 = 125\mu\text{m}$, and $E_{max} = 4000\text{V/m}$). The bin size for the calculation of entropy is $50\mu\text{m}$. The entropy as a function of the bin sizes was also shown in the inset. (b) Impact of LGpl laser spot size: entropy of particle patterns ($dp = 20\mu\text{m}$) under LG14 laser ($E_{max} = 4000\text{V/m}$) with spot size of $75\mu\text{m}$, $100\mu\text{m}$, and $125\mu\text{m}$. Bin size for the calculation of entropy is $50\mu\text{m}$. The entropy values at different bin sizes were also shown in the inset. (c) Impact of maximum intensity value of the electric field: entropy of particle patterns under different E_{max} values (LG14 laser and $w_0 = 125\mu\text{m}$). The bin size for the calculation of entropy is $50\mu\text{m}$ for $20\mu\text{m}$ diameter particles (solid black line), and the bin size is $20\mu\text{m}$ for $5\mu\text{m}$ diameter particles (solid red line). Corresponding density distribution maps for selected data points (dashed circles in (c)) are shown. The count of particles in each square grid is indicated by the color bar at the bottom (green-to-white gradient for $20\mu\text{m}$ diameter particles, and blue-to-white gradient for $5\mu\text{m}$ diameter particles). (d) Fluid velocity profile along the solid-liquid interface under E_{max} values. The velocity peaks are marked by dashed black lines. The region of the “forbidden zone” is highlighted in a shaded grey region. E_{max} and temperature maxima (T_{max}) in the liquid-gallium are indicated by the top color bar.....54

Figure 3.10: Particle patterns under different maximum intensity value of the electric field (E_{max}) for particles with a diameter of $20\mu\text{m}$ (LG14 laser mode and $w_0 = 125\mu\text{m}$). (a) $E_{max} = 3500\text{V/m}$, (b) $E_{max} = 3700\text{V/m}$, (c) $E_{max} = 3825\text{V/m}$, and (d) $E_{max} = 4000\text{V/m}$. The scale bar for the particle pattern is $200\mu\text{m}$ 56

Figure 3.11: Entropy of the particle pattern under different maximum intensity value of the electric field (E_{max}) calculated with different bin sizes (LG14 laser mode and $w_0 = 125\mu\text{m}$).

The diameter of the particles (dp) are: (a) 20 μm , and (b) 5 μm , respectively.	56
Figure 3.12: Particle patterns under different maximum intensity value of the electric field (E_{max}) for particles with a diameter of 5 μm (LG14 laser mode and $w_0 = 125\mu\text{m}$). (a) $E_{\text{max}} = 3500\text{V/m}$, (b) $E_{\text{max}} = 3700\text{V/m}$, (c) $E_{\text{max}} = 3825\text{V/m}$, and (d) $E_{\text{max}} = 4000\text{V/m}$. The scale bar for the particle pattern is 200 μm	57
Figure 3.13: Entropy of particle patterns under different E_{max} values (LG14 laser mode and $w_0 = 125\mu\text{m}$) with drag coefficient from Schiller-Naumann model. The bin size for the calculation of entropy is 50 μm for 20 μm diameter particles (<i>solid black line</i>), and the bin size is 50 μm for 5 μm diameter particles (<i>solid red line</i>).	58
Figure 4.1: Surface energy difference ($\Delta\gamma_{GR}$) between doped graphene and un-doped graphene at different temperatures. Two preset temperature values are: (a) 300 $^{\circ}\text{C}$, and (b) 500 $^{\circ}\text{C}$, respectively.	62
Figure 4.2: SRIMS results for Ga distribution in DLC films with varied FIB energy ($EFIB$) and density of a DLC film (ρ_{DLC}). Four typical $EFIB$ were simulated: (a) $EFIB=2\text{keV}$, (a) $EFIB=5\text{keV}$, (c) $EFIB=10\text{keV}$, and (d) $EFIB=30\text{keV}$. Results for $\rho_{DLC}=2.0\text{g/cm}^3$, $\rho_{DLC}=2.253\text{g/cm}^3$, and $\rho_{DLC}=2.9\text{g/cm}^3$ are presented in red, black, and blue bars, respectively.	64
Figure 4.3: XPS spectrums for DLC film and corresponding step height analysis for surface features resulted in the FIB dose studies. XPS of C core-level of DLC films synthesized under voltages of: (a) 500V and (b) 0V in the filtered cathodic vacuum arc deposition system, respectively. Corresponding step height analysis of surface features after different FIB implantation time (x-axis) and FIB currents (solid circles) for: (c) DLC (500V), and (d) DLC (0V), respectively. The $EFIB$ was fixed at 7.5keV for all FIB dose studies. R_{max} predicted with the SRIM model is highlighted with a grey open circle and grey dash line.	65
Figure 4.4: Schematic of the principle for real time imaging in LEEM. Trajectories of incident beam and reflected beam in the magnetic sector filed and objective lens of LEEM are outlined with blue arrow and purple arrow, respectively.	68
Figure 4.5: Scheme for graphene/Ga implanted DLC heterointerface engineering and its impact on temperature-dependent tuning of graphene work function. (a) Schematic depicting the three-step engineering process: (top) the Ga^+ -FIB patterning on DLC, (middle) polymer-free graphene transfer and (bottom) Φ_{GR} engineering through annealing. (b) AFM image of Ga implanted DLC with corresponding central height profile of Ga implanted DLC region. (c) AFM image of graphene on Ga implanted DLC (yellow dash box) and corresponding central height profile of graphene/Ga implanted DLC region. (d) Representative I-V curve for the graphene/Ga implanted DLC sample. (e) KPFM image of graphene on Ga implanted DLC at 25 $^{\circ}\text{C}$ after annealing at 300 $^{\circ}\text{C}$. (f,g,h) Work function mappings of graphene on Ga implanted DLC annealed at 300 $^{\circ}\text{C}$ (f), 420 $^{\circ}\text{C}$ (g), and 500 $^{\circ}\text{C}$ (h), respectively. (i) temperature-dependent $\Delta\Phi_{GR}$ values at various preset T_{anneal}	72
Figure 4.6: AFM and temperature-dependent work function changes of unimplanted DLC. (a) AFM image of DLC before FIB patterning. (b) Temperature-dependent work function evolution in unimplanted DLC. The error bars are magnified by a factor of 10^4 for enhanced visual clarity.	73
Figure 4.7: ToF-SIMS mapping for Ga within DLC layer after different annealing treatments. The depth profiles of Ga distribution in DLC for three different annealing settings were characterized: (a) at room temperature without annealing, (b) post-annealing at 300 $^{\circ}\text{C}$, and (c) post-annealing at 500 $^{\circ}\text{C}$. All the ToF-SIMS characterizations were performed at room temperature. The distribution of C and Ga are presented in blue and red, respectively. For each of the 3D render	

models, it is $5\mu\text{m}\times 5\mu\text{m}$ in x-y plane (top surface) and 50 nm in z-direction.	74
Figure 4.8: Point-to-point normalized intensity for Ga^+ in ToF-SIMS spectra for graphene/Ga implanted DLC after different annealing treatments. graphene/Ga implanted DLC in three conditions were examined: before annealing (blue diamond marks), after annealed at 300°C (orange circle marks), and after annealed at 500°C (green square marks). All the ToF-SIMS characterizations were performed at room temperature.	74
Figure 4.9: Temperature-dependent work function difference and sp^2/sp^3 ratio in Ga implanted DLC. (a to d) Work function mappings for Ga implanted DLC annealed at 300°C (a), 420°C (b), 450°C (c), and 500°C (d), respectively. (e) Temperature-dependent $\Delta\Phi_{\text{DLC}}$ values of Ga implanted DLC at 25°C and after annealing at various preset <i>T_{anneal}</i> . (Right) Change of $\Delta\Phi_{\text{DLC}}$ before and after annealing at different preset <i>T_{anneal}</i> . (f) Raman spectrums for Ga implanted DLC across a temperature range from 25°C to 500°C . Fitting curves for D- and G peak are highlighted in black dash line and black solid line, respectively. (g) Comparison of the intensity ratio $I_{\text{D}}/I_{\text{G}}$ in Raman spectrums between Ga implanted (orange) and unimplanted DLC (blue). Temperature range for $I_{\text{D}}/I_{\text{G}}$ ration enhancement in Ga implanted DLC is highlighted in a light-grey region.....	76
Figure 4.10: Temperature-dependent Raman spectra for unimplanted DLC across a temperature range from 25°C to 500°C. Curve fits for the D- and G peak positions are highlighted in black dash line and black solid line, respectively.	77
Figure 4.11: Cross-section EELS measurements for Ga implanted DLC after different annealing treatments. The cross-section EELS spectra ware collected along the z-direction of Ga implanted DLC for three different annealing settings: (a) at room temperature without annealing, (b) post-annealing at 300°C , and (c) post-annealing at 500°C . For each sample, seven EELS spectra at depth values of: 0nm (top surface of DLC, red line), 2.5nm (orange line), 5nm (yellow line), 7.5nm (grass green line), 10nm (light green line), 15nm (green line) and 20nm (dark green line). The reference EELS spectrum was collected on pristine DLC with a sp^2/sp^3 ratio of 1.5 (black line). The energy window for the intensity integration of π^* and σ^* peaks are highlighted with light yellow and light pink boxes, respectively. All the cross-section EELS characterizations were performed at room temperature.....	77
Figure 4.12: Quantification of the relative amount of sp^2 in Ga implanted DLC after different annealing treatments. The relative amount of sp^2 was quantified along the depth direction of Ga implanted DLC for three different annealing settings: (a) at room temperature without annealing, (b) post-annealing at 300°C , and (c) post-annealing at 500°C	78
Figure 4.13: Temperature-dependent Raman measurements of graphene/Ga implanted DLC heterostructure. (a,b) Raman spectra for graphene/DLC(a) and graphene/Ga implanted DLC (b) across a temperature range from 25°C to 500°C . (c,d) Temperature-dependent evolution of G peak (blue) and 2D peak (orange) in Raman spectra for graphene/DLC (c) and graphene/Ga implanted DLC (d). Temperature-dependent evolution of G peak (blue) and 2D peak (orange) positions for pristine graphene are highlighted in dash line.	79
Figure 4.14: STS measurements of graphene/Ga implanted DLC heterostructure. STS dI/dV measurements across graphene/DLC (blue solid line) and graphene/Ga implanted DLC region (orange solid line) with $V_{\text{modulation}}$ as 5mV. The corresponding Dirac points (V_{D}) are highlighted with black dashed line and red dashed line, respectively.	80
Figure 4.15: Constant-current imaging over different graphene regions. STM images ($I_{\text{tunnel}} = 30\text{ pA}$, $V_{\text{sample}} = 1.0\text{ V}$) depicting the unit cell of graphene were collected over (a) graphene on pristine DLC region and (b) graphene on the Ga implanted DLC region. The scale bar is 1nm. .	80
Figure 4.16: Simulation of Ga precipitation at the heterointerface and its impact on	

electrostatic doping level of graphene. (a) Schematic illustrating the four stages of Ga diffusion with increasing annealing temperature. (b) Variation in the work function of graphene relative to the reference system of graphene on unimplanted DLC, accompanied by visualizations of electron transport from DLC substrate and intercalated Ga to graphene monolayer. Displayed isosurfaces correspond to differential charge transfer of 0.0008 electron/Bohr³, where regions of charge depletion and regions of charge accumulation are highlighted with *blue* and *orange*, respectively. (c) Plot showing the change in the graphene work function (Φ_{GR}) in relation to the increase in Ga-Ga bond length from equilibrium in system P2; (d) with respect to the increase in vertical spacing between Ga and graphene monolayer from equilibrium in systems DLC and P0. 83

Figure 4.17: Variation in structure configuration and electronic properties in graphene with increased Ga presence at the heterointerface. The panels on left depict the projected density of states for graphene, while the right panels illustrate the corresponding heterointerface structures with: (a) single atomic Ga anchored on the Ga implanted DLC surface; (b) single atomic Ga adsorbed onto graphene monolayer; (c) a diatomic Ga cluster under graphene; (d) sub-monolayer triatomic Ga cluster; (e) a Ga monolayer separating graphene from Ga implanted DLC surface; (f) graphene monolayer deposited on Ga (001) surface of bulk metallic Ga. 84

Figure 4.18: Comparison of electronic properties of graphene on DLC substrates with and without implanted Ga ions. (a) Projected density of states of graphene on DLC and on Ga implanted DLC. Visualization of structure and isosurface of differential charge transfer for heterostructures consisting of (b) graphene monolayer on pristine DLC; (c) graphene monolayer on Ga^{implanted} DLC. 85

Figure 4.19: Tuning the work function landscape of graphene with temperature. (a) Work function maps for graphene on Ga implanted DLC annealed at 500°C (left), then cooled to 300°C (right). (b) Work function maps of graphene on Ga implanted DLC annealed at 300°C (left), then held at 300°C (right). (c) Corresponding temperature-dependent $\Delta\Phi_{GR}$ values extracted from (a) and (b). 86

Figure 4.20: Nano-ARPES mappings on array pattern composed of uniform Ga implanted DLC squares. (a) XPS spectrums collected inside (orange) and outside (blue) graphene/Ga implanted DLC region after annealing at 500°C, respectively. (b) Photoemission intensity map for 215µm-by-215µm pattern composed of 81 Ga implanted DLC squares near Ga 3d core level ($E - EF = -20.4\text{eV}$). (c,d) magnified integrated photoemission intensity map of the central region of d (yellow dash box) with $E - EF = -5.6\text{eV}$ (c) and $E - EF = -3.3\text{eV}$ (d), respectively. (e) Energy resolution of the integrated photoemission intensity along dashed arrow in (b), and Ga implanted DLC square regions are highlighted with black dash lines. The spectral integration range for b to e is $\pm 0.3\text{eV}$ 88

Figure 5.1: The structural similarity between Ge (110) and black phosphorus, and the diffusivity and solubility of P in Ge. (a) Top-view structure of Ge (110). (b) Top-view structure of black phosphorus. (c) The intrinsic (left y-axis, black circles) and extrinsic (right y-axis, open squares) diffusivities of P in Ge at different temperatures from reference¹⁴⁴. The temperature-dependent fittings for the intrinsic diffusivity of P in Ge are depicted with solid black lines. Reprinted with permission from Cai et al., Journal of Applied Physics 112, no. 3 (2012). Copyright 2012 AIP publishing. (d) The solubility of P in Ge at different temperatures from reference¹⁴³. Reprinted with permission from Olesinski et al., Bulletin of Alloy Phase Diagrams 6, 262-266 (1985). Copyright 1985 the American Society for Metals. 93

Figure 5.2: Chemical environment and surface morphology for graphene/P₂O₅/Ge (110) after annealing in H₂ at 500°C. Raman spectrum for graphene/P₂O₅/Ge (110): (a) before (*black line*) and (b) after (*red line*) annealing treatment in H₂. (c) High-resolution XPS spectrum for O 1s

showing the existence of C-O bond (*green line*), along with P-O bond (*yellow line*) and P=O bond (*purple line*) for P_2O_5 . (d) SEM image of graphene on Ge (110) surface after post-annealing treatment in H_2 showing small graphene bubbles. The scale bar is 200nm. (e) Nano-FTIR spectrum for small graphene bubble on Ge (110) surface post-annealing treatment in H_2 . IR peaks induced by non-bridging oxygen-P bond (*blue and green solid lines*) and by bridging oxygen-P bond (*purple solid line*) were observed. 94

Figure 5.3: Transverse mode shapes for LGp, l (left), IGp, l (mid), and HGp, l laser (right) modes, respectively. The corresponding p and l are marked at the lower right corner of each panel, adopted from reference^{144, 283}. Reprinted with permission from Bandres et al., Journal of the Optical Society of America A 21, no. 5 (2004): 873-880. Copyright 2004 Optica Publishing Group. 97

Figure 5.4: Marangoni flow patterns in a cuboid liquid influenced by Gaussian lasers. (a to c) Schematic of multiple Gaussian lasers with different arrangements on the liquid surface, including: (a) two lasers arranged off-center along the y-axis. (b) four lasers symmetrically positioned around the center. (c) multiple lasers aligned to form an elliptical-like beam along the y-axis. (d to f) Marangoni flow pattern (highlighted with red arrows) on the liquid surface induced by the laser groups illustrated in (a), (b), and (c), respectively. 98

Figure 5.5: Work function values of possible alternative elements to implant into DLC. Experimental measured work function values adopted from Holzl's work²⁹² (blue circles) and Michaelson's work²⁹³ (orange squares). The work function of graphene (black diamond) was quantified with the low energy electron microscope²⁹⁴. 102

Figure A.1: Schematic for the AP/LPCVD furnace allows for reversible flow during the material growth process. (Left) Schematic for the AP/LPCVD furnace setup, with each pneumatic valve numbered for reference. (Right, top) the solenoid-based control system for the pneumatic valves in this AP/LPCVD furnace setup. (Right, bottom) Summary of the symbols in the schematic representing different valves. 129

Figure B.1: Polymer-free graphene transfer process. (a) The as-cut CVD grown graphene monolayer on Cu foil and the size for each piece is approximately 0.8cm by 1.2cm. (b) The adhesive Al frame window placed atop graphene monolayer. (c) Graphene/Cu sample with Al frame window placed atop floating in the etchant solution (~0.3M sodium persulfate) for Cu etching. (d) Cu was fully etched away after approximately 1 hour. (e) Transfer the graphene together with the Al window frame to the deionized water reservoir using a watch glass. (f) After removing the excess sodium persulfate in deionized water reservoir, the graphene was fished out with a sample and dried out in N_2 box. 133

List of abbreviations and symbols

Abbreviations:

0D	Zero-dimensional
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
AAO	Anodic aluminum oxide
AES	Auger electron spectroscopy
AFM	Atomic force microscopy
ALD	Atomic layer deposition
ARPES	Angle-resolved photoemission spectroscopy
CVD	Chemical vapor deposition
DFT	Density functional theory
DOS	Density of states
EBL	Electron-beam lithography
EDX	Energy dispersive X-ray
EELS	Electron energy loss spectroscopy
EPC	Electron-phonon coupling
FEM	Finite element method
FIB	Focused ion beam
FTIR	Fourier-transform infrared spectroscopy
FWHM	Full width at half-maximum
I-V curve	Reflected intensity-starting voltage curve
KPFM	Kelvin probe force microscopy
LDOS	Local density of states
LEEM	Low energy electron microscopy
LLS	Liquid-liquid-solid
MBE	Molecular beam epitaxy
MM	Mirror mode
MMT	Minimum mirror threshold
MS	Mass spectrometry
PL	Photolithography
PLD	Pulse laser deposition
PVD	Physical vapor deposition
QSE	Quantum-size effect
SEM	Scanning electron microscopy
SERS	Surface-enhanced Raman spectroscopy
STM	Scanning tunneling microscopy
STS	Scanning tunneling spectroscopy
SLS	Solid-liquid-solid
TEM	Transmission electron microscopy
TGA-MS	Thermogravimetric analysis-mass spectrometry
ToF-SIMS	Time-of-flight secondary ion mass spectrometry
vdW	Van der Waals
VLS	Vapor-liquid-solid

XPS X-ray photoemission spectroscopy

Materials:

TMD Transition metal dichalcogenide
GR Graphene
a-C Amorphous carbon
a-C:H Hydrogenated amorphous carbon alloy
ta-C Tetrahedral amorphous carbon
ta-C:H Hydrogenated tetrahedral amorphous carbon alloy
DLC Diamond like carbon

Symbols:

r^* Critical radius for nucleation
 ΔG Free energy change
 ΔG_v Volumetric free energy of target material
 θ Contact angle
 γ_{gf} Surface energy at gas-target material interface
 γ_{gs} Surface energy at gas-substrate interface
 γ_{fs} Surface energy at target material-substrate interface
 d Minimum resolvable distance in Abbe limitation
 λ Wavelength
 NA Numerical aperture
 S Spreading coefficient
 LG_{pl} Laguerre-Gaussian mode
 $\vec{v}$ Fluid velocity
 P Pressure in liquid gallium
 μ Dynamic viscosity of liquid gallium
 $\vec{g}$ Gravitational acceleration vector
 C_p Heat capacity for liquid gallium
 k_T Thermal conductivity of liquid gallium
 $\vec{q}$ Heat flux in liquid gallium
 k_0 Temperature coefficient of surface tension for liquid gallium
 Q_e Electromagnetic heat in liquid gallium
 σ_f Electric conductivity of liquid gallium
 J Current density of liquid gallium
 E Electric field intensity
 z_0 Rayleigh range of the laser
 $E_{0pl}(r, z)$ Amplitude for the electric field distribution of the LG_{pl} laser mode
 Q_P Work done by pressure change in liquid gallium
 α_p Thermal expansion of liquid gallium
 Q_{vd} Viscous dissipation in liquid gallium
 τ Viscous tensor
 $q_{r,net}$ Net outward radiative flux
 ρ_f Density of liquid gallium
 ρ_p Density of tungsten particle

ε	Emissivity of liquid gallium
n_{Ga}	Real part of refractive index for liquid gallium
k_{Ga}	Imaginary part of refractive index for liquid gallium
σ	Stefan–Boltzmann constant
G	Total incoming radiative flux
$\vec{n}$	Unit normal vector
$\vec{F}_D$	Drag force
$\vec{F}_B$	Brownian force
$\vec{F}_G$	Gravitational force
$\vec{F}_{Bouyant}$	Buoyant force
$\vec{u}$	Particle velocity
τ_P	Characteristic time for the particle
k_B	Boltzmann constant
ζ	Vector of independent, normally distributed random numbers with zero mean and unit standard variation
$\vec{u}_c$	Particle velocity when the particle approaches the boundary of the liquid gallium domain
P_0	Possibility for particle-side wall interaction
S_{ref}	Reference entropy value for a completely random particle assembly composed of 2000 tungsten particles
$S_{assembly}$	Entropy value for the specific particle assembly of interest
$\Delta\gamma_{GR}$	Surface energy difference of graphene
C_Q	Quantum capacitance of graphene
v_F	Fermi velocity
E_{FIB}	FIB energy
ρ_{DLC}	The density of a DLC film
R_{max}	The maximum implantation depth of ion in materials
T_{anneal}	Annealing temperature
$\Delta\varphi$	Phase shift
a_0	Step height
Φ_C	Work function of cathode
Φ_{Sample}	Work function of sample

$\Delta\phi$	Work function difference
ϕ_{GR}	Work function of graphene
ϕ_{DLC}	Work function of diamond like carbon
I_{MM}	Mirror mode reflected intensity
I_{LEEM}	Minimum LEEM mode reflected intensity
σ	Gaussian spread of electron energy
V_{MMT}	Voltage corresponding to minimum mirror threshold
$\Delta\phi_{GR}$	Work function difference of graphene
$\Delta\phi_{DLC}$	Work function difference of diamond like carbon
I_G	Peak intensity for G peak
ω_G	Peak position for G peak
Γ_G	Full width half maximum of G peak
Q^{-1}	BWF coupling coefficient
I_D	Peak intensity for D peak
ω_D	Peak position for D peak
Γ_D	Full width half maximum of D peak
ω_{2D}	Peak intensity for 2D peak
V_D	Dirac point
h	Planck constant
ΔE_F	Fermi level shifting

Chapter 1

The role of the interface in materials synthesis

This chapter provides an introduction to the concept of the interface and its roles in current state-of-art confinement growth of materials. Starting with the definition of confinement growth and interface, a detailed review of confined material growth through interface engineering is provided, describing the critical role of interface in confined material synthesis. Following it is a summary of the current limitations remaining in this area, thereby providing the background and motivation for the key concept of this dissertation: new possibilities for the confined material growth of materials through various interface engineering approaches and their mechanisms. Last, an outline for the remainder of the dissertation is provided.

1.1 Confinement growth of materials and interface

The properties of a material depend on its structure and composition. Over the past decades, many materials with novel structures and/or composition have been prepared with the wet-chemical synthesis¹⁻², electrochemical synthesis³⁻⁴, chemical vapor deposition (CVD)⁵⁻⁷, and template assisted synthesis⁸⁻⁹. This gives rise to fascinating properties of materials, including superconductivity, electrocatalysis, ferroelectricity, and magnetism to name a few, and consequently boosts the prosperity of semiconductor devices such as diodes, transistors, sensors, microelectromechanical systems, quantum devices and so on¹⁰. Recently, the rapid evolution of modern electronics, for example, the emergence of complex heterostructures¹¹, which take advantage of the unique properties of materials across different dimensions and compositions, present new challenges. Among them, one critical challenge is the confinement growth of materials, aiming to a direct integration of different materials into lateral and/or vertical heterostructures, and such advancements are crucial for the development of next-generation semiconductor devices.

Confinement is a concept stemming from catalysis and surface science, where nanoparticles and/or molecules are restrictedly distributed in a nano-space or on the surface to enhance their catalytic properties. Later, the concept of confinement was introduced into materials science and engineering and applied as the controlled synthesis of materials across a wide scale¹². Accordingly, the confinement growth of materials can be principally categorized into two methodologies: “space-confined synthesis” and “area-selective synthesis”. Space-confined synthesis targets the geometric confinement of materials during synthesis, addressing parameters such as thickness and shape. On the other hand, area-selective synthesis emphasizes the preferential growth of materials on preselected regions of a substrate. To realize the confinement growth of materials, an effective engineering towards the interface, where material synthesis initiates, is necessary.

Herein, an interface is defined as the boundary separating two distinct phases¹³, such as phase α and β . These interfaces can be systematically classified according to the states of α and β into six categories: solid-solid, liquid-liquid, gas-gas, solid-liquid, solid-gas, and liquid-gas interfaces. These interfaces serve as the external surface of materials that interact with the environment, playing a pivotal role in the confinement synthesis of materials. For example, the interface can not only serve as a nanoreactor to constrain the shape and size of materials, but also provides specific chemical microenvironment to promote the confined nucleation, growth and stabilization of intermediates or products. More importantly, the bonding nature of the interface allows one to flexibly engineer the interfacial microenvironment to cater to different demands. At the interface, the structure of both phase α and β discontinues, leading to a different surface bonding configuration compared to that of its bulk phase. This discontinuation results in distinct surface properties that differ from those observed in the bulk materials, including increased reactivity, altered electronic properties and an enhanced sensitivity to the changes in the surface properties upon the surface modification.

Yet, the widespread application of the confined growth of materials is, in part, precluded by the relative lack of interface engineering toolset, especially for the lithography mask-free strategies. Expanding the interface engineering approaches as well as developing a

thorough understanding of interface science are thus essential for advanced material design, material growth, and applications. The following subsection elucidates the critical role that interfaces play in the confinement growth of materials, underscoring their significance in dictating the nucleation sites, growth directionality, and ultimately, the morphological and structural characteristics of the synthesized materials.

1.2 Role of interface in confinement growth of materials

1.2.1 Adsorption, diffusion, and nucleation at the interface

The interface is where precursors and/or reactants undergo adsorption, diffusion, accumulation, and nucleation to initialize the material synthesis. Therefore, the control over the diffusion and nucleation sites at the interface is of great importance for the confinement growth of materials. For adsorbed precursors at the interface, its surface diffusion usually follows a random walk model¹⁴, where molecules transit from one site and another site to find the energy-favored site for subsequent surface incorporation. This diffusion process could be controlled *via* designing the surface energy or morphology (e.g., defect engineering at the interface¹⁵) landscape of the interface, resulting in a directional surface diffusion along the energy gradient to the pre-defined regions.

Moreover, in terms of nucleation control in material growth process, in order to form a stable nucleus at the substrate interface, its radius must exceed the critical radius (r^*) through material accumulation. In heterogeneous nucleation process, the relationship of the free energy change (ΔG) versus nucleus radius can be described by¹⁴:

$$\Delta G(r) = \left[\frac{4\pi}{3} r^3 \Delta G_v + 4\pi r^2 \gamma_{gf} \right] * \left[\frac{2 - 3\cos\theta + \cos^3\theta}{4} \right]$$

where ΔG_v is the volumetric free energy of target material, γ_{gf} is the surface energy at gas-target material interface, and θ is the contact angle from Young's equation as

$$\cos\theta = \frac{\gamma_{gs} - \gamma_{fs}}{\gamma_{gf}}$$

where g, f , and s representing gas, target material, and substrate, respectively. At the critical radius, $\Delta G(r)$ reaches its maximum,

$$\left. \frac{d\Delta G(r)}{dr} \right|_{r^*} = 0$$

This condition yields the critical radius r^* as

$$r^* = -\frac{2\gamma_{gf}}{\Delta G_v}$$

Nucleation, and the consequent material growth, are initialized only in regions of the interface where material supply is sufficient to surpass the critical radius. Therefore, by directing the preferential supply of precursors and/or reactants to regions of interest through lithography mask or mask-free interface engineering strategies, control over

nucleation can be achieved. A more detailed discussion would be included in section 1.3.2.

Furthermore, in some scenarios where material growth occurs within the confined space of a heterointerface, materials can exhibit novel diffusion behaviors attributed to the nano-confinement effects and the intrinsic properties of interface itself¹⁶. One notable example includes the diffusion behavior of water within nanometer-scale slit pores, which has been extensively studied and could serve as a reference for the behavior of numerous other materials. Specifically, water within the carbon-based nanostructures, such as graphene slit pores and carbon nanotubes, has shown significantly low resistance to flow along the walls of these confined spaces¹⁷. Conversely, in geometrically similar structures comprised of different materials, such as h-BN, no significant slippage of water was observed. Additionally, within this confined space, materials may exhibit different adsorption behavior. For example, the CO molecules at graphene/substrate heterointerface were predicted to have a weakened adsorption on the substrate¹⁸. These factors together should also be taken into consideration when designing the confined growth process, especially in the field of space-confined growth.

1.2.2 Geometry confinement in materials synthesis

Additionally, the structure and/or morphology of an interface can act as a template to geometry confinement in materials synthesis. For example, the limited distance at the heterointerface naturally confines the thickness of the target materials, which is usually achieved through interaction, a topotactic insertion process of atoms and small molecules between the layers or at the interfaces of layered materials. Furthermore, the interface can act as a physical scaffold that defines the geometry of the target materials, as exemplified by the hard template assisted synthesis. In this context, the template typically refers to a group of networking porous materials. During the synthesis process, precursors and/or reactants diffuse into the cavities of the template materials, undergo reaction, and grow following the pre-designed morphologies at the template interface. Upon removing the template from the product, the resulting materials retain surface geometries that mirror those of the template, thereby enabling the synthesis of materials with intricate and precisely controlled geometrical features.

1.3 Current state-of-art for interface engineering on confinement material growth

1.3.1 Space-confinement synthesis of materials

As for thickness-confined synthesis of materials, as illustrated in Figure 1.1, intercalation has been extensively validated as an effective method. The intercalation of graphite, for instance, has been remarkable success throughout its 160-year history, giving rise to an extensive family of graphite intercalation compounds (exceeding 100 varieties)¹⁹. These intercalants encompass a diverse range, including alkali metal and/or alloys²⁰⁻²¹, metal halides²²⁻²⁴, acid²⁵⁻²⁷, and others^{19, 28-29}. Meanwhile, the space-confined synthesis of diverse metals (e.g., Ga, In, Al³⁰, Bi³¹, Fe³², Sb³³, Gd³⁴, Pb³⁵, etc. has been achieved through the intercalation of monolayer graphene (Figure 1.1a).

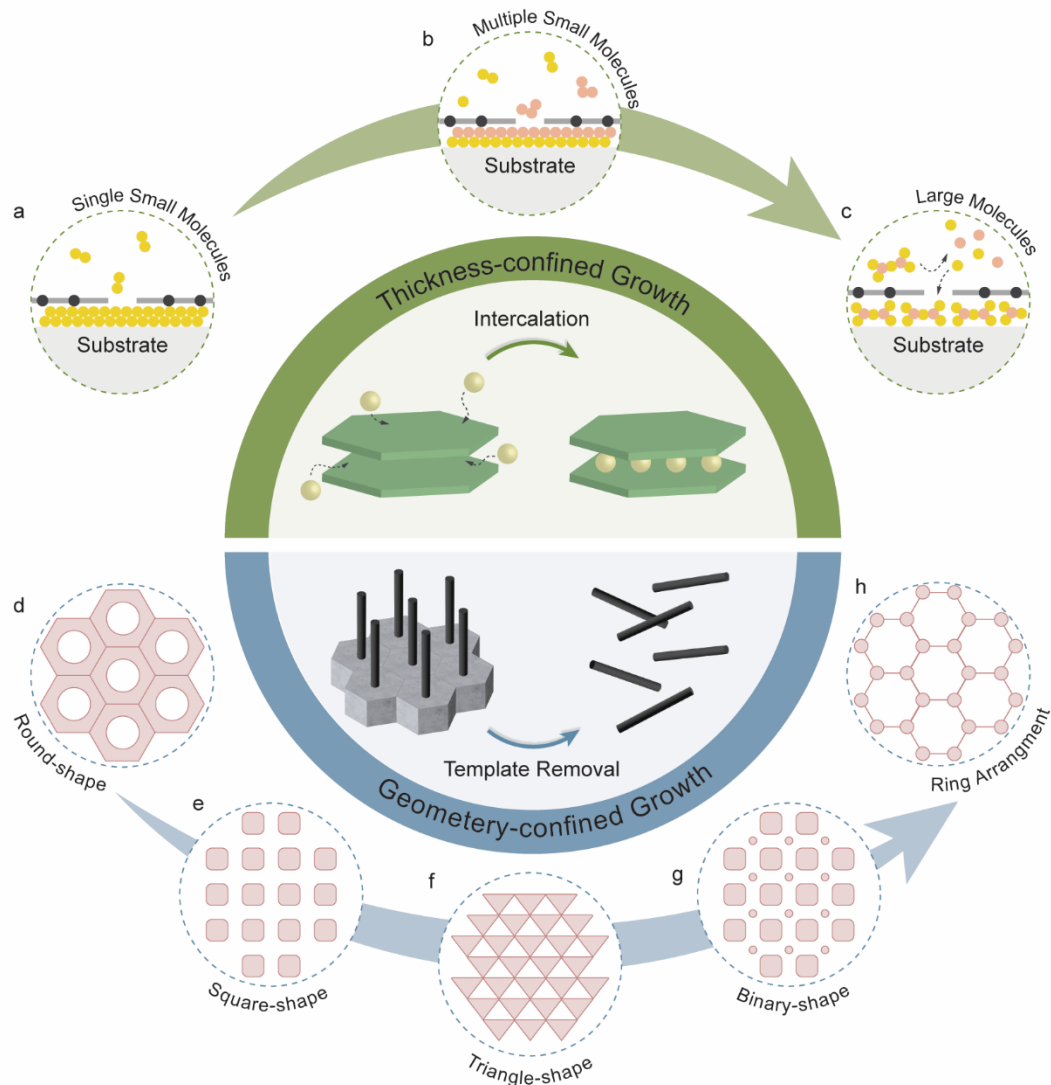


Figure 1.1: Summary of the space-confinement synthesis of materials through interface engineering. (a to c) Scheme for intercalation of molecules through interface for thickness-confined growth at the heterointerface, where intercalants are: (a) single small molecules, (b) multiply small molecules to initialize chemical reactions within the confined heterointerfaces, (c) large molecules, respectively. (d to h) Scheme for hard template assist synthesis approach for geometry-confined synthesis. For the template, the pore shapes and/or arrangement can be flexibly adjusted, such as (d) round-shape, (e) square-shape, (f) triangle-shape, (g) binary-shape, and (h) six-membered ring pore arrangement.

Moreover, except for the metal, ice monolayer in an island like structure was obtained through intercalating water vapor through graphene/mica heterointerface³⁶. Also, space-confined synthesis of layer material - for example, germanene thin layers – succeed at graphene/Ag(111) heterointerface this scenario, a layer exchange mechanism facilitates the diffusion of Ge from the Ge substrate underlying Ag towards the heterointerface, where it subsequently forms germanene³⁷. Recently, chemical reactions within the confined

heterointerfaces of layered materials provides a promising solution to bypass the limitation on the direct intercalation of large molecules through traditional pathways including point defects³⁸⁻⁴⁴, and/or grain boundaries⁴⁵. As shown in Figure 1.1b, individual chemical species or multiple small fragments of the initial state of the molecule would first intercalate through typically available pathways in the graphene lattice, and then recombine at the heterointerface *via* chemical reactions⁴⁶. To date, this strategy has enabled the space-confined synthesis for a diverse array of layer materials (GaN⁴⁷⁻⁴⁹, AlN⁵⁰, MoS₂⁵¹, PtSe₂⁵², Ga₂O₃⁵³, etc.) at graphene/substrate heterointerfaces. Moreover, the wafer bonding in ultra-high vacuum emerged as an alternative strategy. With this approach, monolayer tellurium has been synthesized at the interface of two CdTe wafers⁵⁴.

Furthermore, the confined space at the heterointerface serves as a playground for exploring the novel properties of materials, induced by nanoconfinement effects and the inherent characteristics of the interface materials. This includes enhanced catalytic activity¹⁸, anisotropic dielectric responses¹⁶, and so on. Moreover, the van der Waals (vdW) pressure within vdW layers can reach magnitudes on the order of 1 GPa⁵⁵, potentially changing the structure and thus the properties of synthesized materials. This was illustrated by the phase transition of liquid water to ice at the graphene-mica heterointerface³⁶. Such high vdW pressures also promote material conversion processes within these confined spaces, for instance, the conversion from CuSO₄ to CuO and the conversion from Ca (OH)₂ to CaO have been observed in the interlayer spaces of few-layer graphene⁵⁵. Moreover, the flexible confining surfaces of graphene layers has been demonstrated to have great impact on the relative stability of specific phases of a material. To demonstrate it, the mono-, bi-, and trilayer water were trapped between graphene layers, and it was found that, in this heterostructure, the solid phase of water was energetically favored over its liquid and gas phase counterparts⁵⁶. Intriguingly, the coexistence of ice with liquid water or vapor within this system has been predicted.

Regarding the geometry-confined synthesis of materials, the hard template assisted synthesis approach using anodic aluminum oxide (AAO) along with other templates such as titanium and zirconium oxide is widely utilized. These templates are formed through the anodization of metal in acidic solutions, a process wherein both the pore size and geometry, as well as the thickness of templates can be precisely adjusted by modulating the time for anodization and the applied voltage⁵⁷. This allows for meticulous control over the three-dimensional scales of synthesized products. For example, beyond the commonly observed parallel nanochannels arranged in a close-packed hexagonal pattern (Figure 1.1 d), many novel pore geometries and arrangements have been developed. This includes square and triangular pores⁵⁸ (Figure 1.1 e and f), binary-shape pores⁵⁹ (Figure 1.1 g), branched-pores (e.g., ‘Y’ shaped⁶⁰ and tree-like structures⁶¹), conical pores⁶², and six-membered ring pore arrangement⁶³ (Figure 1.1 h). To date, this versatility has enabled the synthesis of a wide array of materials with well-controlled geometrical attributes⁶⁴ across zero-dimensional (0D, e.g., nanoparticles⁶⁵), one-dimensional (1D, e.g., nanowires⁶⁶, nanotubes⁶⁷, and hybrids of nanowire/nanotube⁵⁹), two-dimensional, (2D, e.g., nano-walls⁶⁸), and three-dimensional (3D, e.g., nano-cones⁶⁹ and nano-dents⁷⁰).

1.3.2 Area-selective synthesis of materials

Significant advances have also been made in the area-selective synthesis of materials, a field that can be broadly categorized into two main strategies: lithography mask and mask-free interface engineering, as summarized in Figure 1.2.

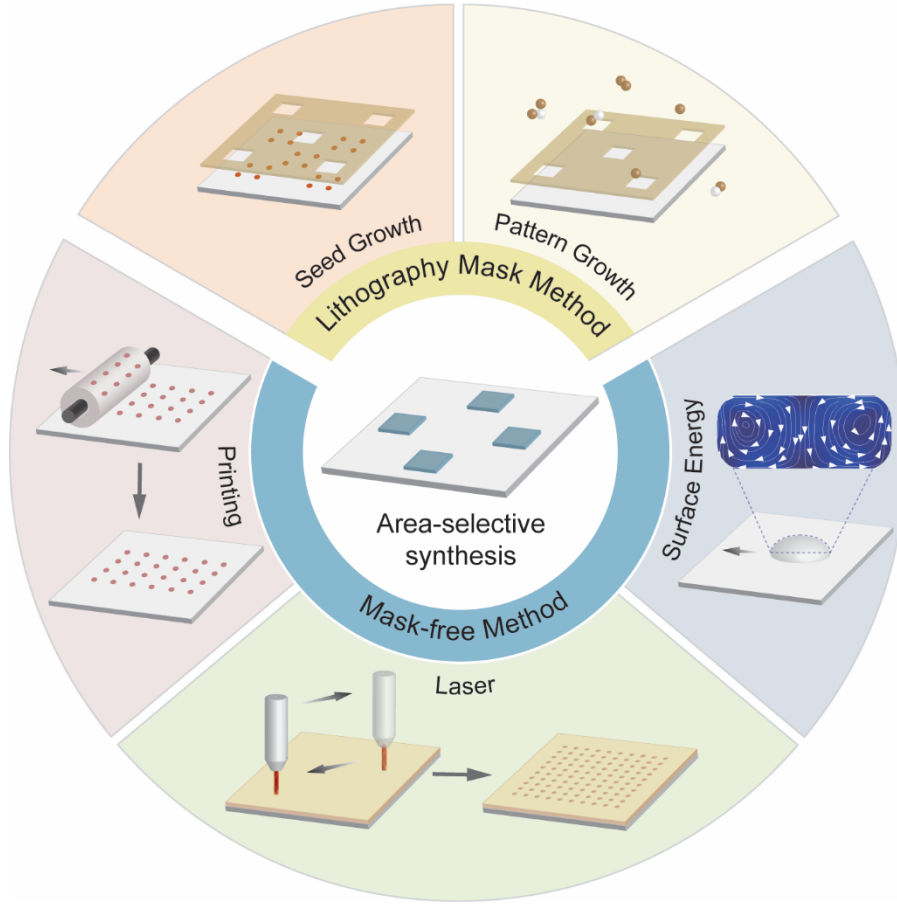


Figure 1.2: Summary of major interface engineering strategies for the area-selective growth of materials.

1.3.2.1 Lithography mask interface engineering strategies

In lithography mask interface engineering strategies, one key step is to create desired patterns onto the resist coating at the substrate interface using light, electron beams or ion beams to modify the properties of the resist. Based on the lithography source, the technique is further categorized into photolithography (PL, utilizing light), electron-beam lithography (EBL, utilizing electron beams), extreme ultraviolet (EUV) lithography, and focused ion beam (FIB) lithography. In the as-created pattern, the minimum resolvable distance (d) between features is constrained by the diffraction limit, also known as the Abbe's resolution limit, and is given by the equation:

$$d = \frac{k_1 \lambda}{2NA}$$

where λ represents the wavelength of the lithography source, and NA is the numerical

aperture of the lithography system. k_1 is a constant depending on the specific resist material⁷¹. The wavelength, λ , can range from micrometer to sub-nanometer, offering a wide spectrum of spatial resolutions suitable for various applications. Following the patterning process, the resist undergoes development; in positive resists, the exposed areas are etched away, while in negative resists, these areas are retained, leaving behind a pattern for material synthesis.

The processes that follow patterning diverge into two primary paths: seeded growth and pattern growth⁷². Seeded growth introduces seeds into the as-created pattern, which lowers the surface free energy barrier at seed sites, thereby preferentially promoting the area-selective material growth. These seeds can be the precursor of the target products, providing essential elements for the synthesis process. For example, pre-patterned MoO_3 reacts with sulfur to form patterned MoS_2 ⁷³. This concept has also been extended to multi-material systems and their heterostructures, such as the formation of WS_2/MoS_2 vertical heterostructure through sulfurizing the pre-defined stacks of W and Mo thin films in a one-step CVD process⁷⁴. Moreover, arrays of foreign nonreactive metal dots, like Au⁷⁵, can act as nucleation sites to support the area-selective growth of materials. For example, owing to the reduced formation energy at MoS_2 -Au interface compared to that at MoS_2 - SiO_2 interface, MoS_2 preferentially nucleated on Au surface, subsequently growing laterally along the SiO_2 interface⁷⁵. Notably, throughout this process, Au maintained its solid state, distinguishing it from the well-known liquid metal-assisted growth observed in nanowires. In contrast, patterned growth allows a stricter confinement of the synthesis area in terms of a control over both the nucleation sites and the geometry of the resultant materials⁷⁶. Due to its fine spatial resolution, the lithography mask interface engineering strategy has widespread applications in both fundamental research and large-scale fabrication, demonstrating its capability to fabricate a variety of materials and their heterostructures with a high complexity. Nevertheless, it is worth mentioning that this technique may introduce contamination to the surface and interfaces of the heterostructures, which could adversely affect the performance of device fabricated.

1.3.2.2 Mask-free interface engineering strategies

Therefore, to address the challenges associated with conventional lithography mask techniques, mask-free interface engineering strategies have been identified as promising alternatives. These strategies include several innovative approaches, each designed to precisely control nucleation sites and thus influence the localized growth of materials without the need for a physical mask.

One such approach involves the interface printing method, where passive or precursor patterns are directly deposited onto the substrate interface. This technique effectively depresses or promotes local material growth by controlling the deposition of these patterns, enabling precise manipulation of nucleation sites⁷⁷⁻⁷⁸. Additionally, laser-assisted growth stands out for its contact-free, catalyst-free, and programmable natures. Laser serves multiple functions. For instance, it can generate specific defect arrays at pre-grown large-scale 2D material – substrate interfaces. These defect arrays act as energetically favorable adsorption sites for precursors, facilitating the localized growth of another 2D material at these sites, thus enabling the formation of mosaic 2D material heterostructures (e.g.,

WSe₂/VS₂⁷⁹). Moreover, a high-power laser can serve as a localized heat source to initialize the patterned growth of materials and their heterostructures, such as WS₂, MoS₂ and their heterostructure⁸⁰. However, it is important to note that e-beam and laser processing can change the surface structure of materials, and excessive power may even damage them⁸¹⁻⁸⁵.

Moreover, upon the evaporation process of nanoparticles solutions, the intermolecular forces⁸⁶ and forces placed on nanoparticles exerted by the surrounding fluid – such as those associate with Marangoni flow⁸⁷ and fluid fluctuations⁸⁸ – facilitate the large scale correlations among nanoparticles and their consequent collective behavior. This process results in the de-wetting assembly of nanoparticles into various patterns, including isolated islands⁸⁸⁻⁹⁰, worm-like domains⁸⁸⁻⁸⁹, ring-like structures⁹¹⁻⁹², spinodal structures⁹³, and cellular networks^{91, 94-95}, exhibiting outstanding selectivity in the spatial distributions of nanoparticles on the substrate. Notably, transitions between these patterns were observed at the different stages of the liquid drying process. For instance, in a homogeneous liquid drying process, disk-like aggregates of nanoparticles dominated at the first stage. These domains subsequently expanded anisotropically across the substrate, forming ribbon-like features, and ultimately coalesced into a single, macroscopic disk. In contrast, the dynamics of the self-assembly process in a heterogeneous drying process were markedly different, with worm-like domains and cellular networks becoming more dynamically preferred⁸⁸. These resulted nanoparticle assembly could later serve as the nucleation sites for the spatial-selective growth of materials.

Additionally, aside from introducing nucleation sites, there is a growing interest in focusing on a more fundamental pathway, that is, manipulating the surface energy profile at the interface, aiming to direct the movement of precursors and/or reactants. Among them, some studies focused on liquid reaction flow-gas interface. One example is the Marangoni flow. Given that liquids with higher local surface tension pull strongly around its surroundings, the resulting shear stress at the two-phase interface gives rise to a rather strong convective motion of the fluid, naturally flowing from regions of low local surface tension to high ones, known as the Marangoni flow. This surface tension gradient in fluids can be induced by several means, for example by adding surface surfactants⁹⁶⁻⁹⁷, tailoring the solute concentration⁹⁸ or developing a temperature gradient on the surface using a variety of heating sources⁹⁹⁻¹⁰¹. Much of the research in this field has been focused on controlling Marangoni flow in transparent hemispherical droplets. In this case, fluid flows away from the apex of the droplet to compensate for the liquid loss at the edges. Particles dispersed in these droplets end up accumulating at the edges, giving rise to the seminal “coffee-ring” effect⁸⁷. By inducing Marangoni flow in the opposite direction, one can suppress the “coffee-ring” effect and achieve a more uniform particle pattern⁹⁶, or even the “reverse coffee-ring” effect¹⁰²⁻¹⁰⁴, where particles accumulate at the center of the droplet upon evaporation. Furthermore, the Marangoni effect has also been observed in opaque liquids, like liquid metals, such as in a variety of crystal growth directional solidification processes¹⁰⁵⁻¹⁰⁸. Such liquid metals have also been used as catalysts during the confinement growth of thin films and nanostructures by the vapor-liquid-solid (VLS,¹⁰⁹⁻¹¹³), liquid-liquid-solid (LLS,¹¹⁴⁻¹¹⁵), and solid-liquid-solid (SLS,¹¹⁶) growth mechanisms of materials.

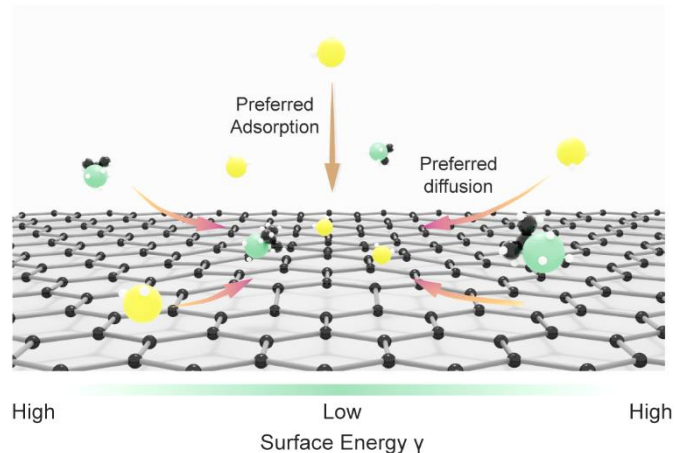


Figure 1.3: Schematic for energetic-preferred direction of surface adsorption and diffusion of molecules on interface with engineered surface energy landscape. The direction of surface adsorption and diffusion are highlighted with *brown arrows* and *orange-to-pink arrows*, respectively.

Meanwhile, other studies investigate the surface energy profile at substrate interfaces, illuminating the energetically preferred zones for adsorption and surface diffusion toward local minima in the surface energy landscape, as depicted in Figure 1.3. The determinants of surface energy – comprising morphology, surface adsorption, and the electronic structure of interface materials¹¹⁷ – play pivotal roles in designing these surface energy profiles. For instance, the surface roughness of the substrate interface can significantly change the effective contact area for the precursors (e.g., liquid droplets containing reactants) and the resultant contact angle. Therefore, through creating etched micropillars with varied pillar width and spacing on a silicon substrate, one can achieve directional transport of liquid droplets along the contact angle gradient¹¹⁸. Moreover, local deformations at the interface, such as steps, wrinkles, and defects, characterized by an abundance of dangling bonds, result in reduced surface energy to facilitate area-selective nucleation and growth¹⁴⁻¹⁵. Furthermore, introducing nanoparticle patterns underneath interfaces, such as those in graphene, allows for a better control over local deformation distributions¹¹⁹. Other strategies to create spatial variations in surface energy include the exposure to different gas environments or surface functionalization with molecules¹²⁰⁻¹²². However, these methodologies might introduce challenges in quality control of the material synthesis, stemming from surface unevenness and potential contamination by foreign molecules at the engineered interface.

Consequently, the electronic structure of the interfaces emerges as a promising avenue for effective platform for area-selective synthesis, while maintaining a flat and clean surfaces. Graphene, in particular, stands out as an ideal playground, owing to its high sensitivity of electronic structure to doping. Research indicates that doped graphene, both p-type and n-type, exhibits lower surface energy compared to its pristine form¹²³. Thus, engineering the local doping levels of graphene can designate specific areas as either energetically preferred or forbidden zones for growth, leveraging well-developed techniques from the

field of area-selective graphene doping, such as lithographically defined gate doping¹²⁴⁻¹²⁸, self-assembly molecules¹²⁹⁻¹³⁰, and laser/e-beam writing^{81-85, 131}, to facilitate confined material growth.

1.4 Motivation and organization of dissertation

Despite the considerable advancements in the confinement growth of materials through interface engineering, challenges persist, warranting a detailed investigation for both space-confinement growth and area-selective growth.

In the context of space-confinement growth, two major limitations stand out. Firstly, from a material standpoint, the diversity in compositions of material heterostructures offer enhanced tunability, and consequently greater potential for both fundamental research and practical applications compared to single material systems. However, the space-confinement growth of these complex structures is particularly challenging due to the size constraints of intercalation pathways at the interface, which limit the incorporation of materials and their precursors. To date, many functional 2D materials have been synthesized using various nanoreactors and reaction precursors. This strategy brings us two promising directions. One is to explore the synthesis of other 2D materials with distinct phases and structures through the careful selection of reaction precursors and nanoreactors. Another is to develop new approaches to bypass the size limitation of the existing intercalation pathways. For example, one can break down the intercalants and/or their precursors into smaller fragments, thereby reducing the intercalation energy barrier and enhancing the efficiency of the intercalation process, as presented in Figure 1.1c. Secondly, from a mechanism standpoint, the processes governing the space-confinement synthesis, particularly in template free approaches, differ substantially from template-assisted synthesis and require further investigation¹². Understanding these mechanisms and growth processes in detail will provide critical insights into the reaction kinetics and thermodynamic processes within confined microenvironments. Such insights are invaluable for the rational design of nanoreactors and reactants, ultimately facilitating the synthesis of targeted products.

For the area-selective growth, despite the success of lithography mask interface engineering in achieving both precise spatial and shape control over target materials, mask-free strategies based on interface energy profile design face notable challenges. Limitations include operation temperatures. Methods on area-selective doping of graphene, including photo-patterned metal nanoparticle, laser patterning, and e-beam irradiation, show promise in heavy graphene doping at room temperature. But they encounter difficulties at elevated temperatures due to enhanced surface diffusion, desorption, and potential structural damages, raising concerns about their stability and efficiency in high-temperature environments. It potentially limits their performance against the stronger thermal fluctuation—and consequently, the control over the synthesis area on the graphene. Additionally, the tunability of surface energy profiles at the liquid reaction flow-gas interface and the control over resultant Marangoni flow patterns require further innovation. So far, Gaussian lasers have only been applied as a heating source to induce Marangoni flow at liquid-solid and liquid-liquid interfaces of transparent liquids¹³². This directional

fluid leads to the particle assemblies such as “coffee-ring” pattern, uniform pattern, and reversed “coffee-ring” pattern. Developing complex particle patterns through the introduction of novel heating sources beyond Gaussian lasers to engineer more complex temperature gradients is crucial.

Thereby, this dissertation explores new possibilities for the confinement growth of materials through various interface engineering approaches, aiming to expand the toolsets of interface engineering and advance corresponding understanding in the growth mechanism. The first work is on space-confinement growth of materials through intercalation, and we investigate the possibility of large molecules intercalation through the basal plane of graphene and present a new mechanism for intercalating large molecules through monolayer graphene to form confined oxide materials at the graphene-substrate heterointerface. Density functional theory (DFT) corroborate the experimental results and reveal the intercalation mechanism, whereby P_2O_5 dissociates into small fragments catalyzed by defects in the graphene that then permeates through lattice defects and reacts at the heterointerface to form P_2O_5 . This process can also be used to form new confined metal phosphates. While the focus of this study is on P_2O_5 intercalation, the possibility of intercalation from pre-dissociated molecules catalyzed by defects in graphene may exist for other types of molecules as well.

We then turn our attention to the area-selective synthesis of materials through designing the interface of the reactant flow and substrate, respectively. In the former case, we studied how directional fluid flow can guide the movement of randomly released microparticles within the liquid and direct the consequent assembly of particle at solid-liquid interface. Herein, the fluid flow of interest is the light induced Marangoni flow in liquid metals (i.e., liquid-gallium) with Laguerre-gaussian (LG_{pl}) lasers as heating sources. It is an effective approach to overcome Brownian forces on particles, giving rise to predictable assemblies with high degree of order. We show that by careful control over the parameters of the LG_{pl} laser (i.e., laser mode, spot size, and intensity of the electric field) can tune the temperature and fluid dynamics of the liquid-gallium as well as the balance of forces on the particle. This in turn can tune the structure of the ring-shaped particle assembly with a high degree of fidelity and can extended for more complex assembly of particles and small-scale solutes.

Ultimately, we designed the surface work function landscape of graphene interface, which can serve as the substrate for area-selective synthesis of varied 2D materials. In this work, we reported a highly area selective scheme for tuning the work function of monolayer graphene across a broad temperature range through graphene- Ga^+ implanted DLC (Ga^+ -DLC) heterointerface engineering. This process enabled bipolar tuning (either an increase or decrease) of the local work function landscape of graphene across the entire temperature spectrum up to 500°C. Remarkably, this synergistic interaction between precipitated gallium clusters and localized DLC reconstruction led to heavy n-doping in graphene, reaching the doping level of $3\sim6.84\times10^{13} \text{ cm}^{-2}$ at 300°C. This surface work function landscape, and the corresponding surface energy landscape of graphene over a broad operating temperature range, can facilitate the selective area growth of materials in various nanofabrication processes. The remainder of this dissertation is organized as follows:

Chapter 2 presents the study of the large phosphate molecule intercalation through graphene-substrate heterointerfaces and the corresponding mechanism.

Chapter 3 describes a finite element simulation study on Laguerre-gaussian laser induced Marangoni for hierarchical particle assembly at liquid-solid interface.

Chapter 4 details the study of area selective and broad temperature work function tuning in graphene through sub-interface engineering.

Chapter 5 summarizes the findings in this dissertation, as well as discussing open questions and potential future work directions.

Chapter 2

Large phosphate molecule intercalation through graphene-substrate heterointerfaces

Intercalation is a process of inserting chemical species into the heterointerfaces of two-dimensional (2D) layered materials. While much research has focused on intercalating metals and small gas molecules into graphene, the intercalation of larger molecules through the basal plane of graphene remains challenging. In this work, we presented a new mechanism for intercalating large molecules through monolayer graphene to form confined oxide materials at the graphene-substrate heterointerface. We investigated the intercalation of phosphorus pentoxide (P_2O_5) molecules directly from the vapor phase and confirmed the formation of confined P_2O_5 at the graphene/substrate heterointerface using various techniques. Density functional theory (DFT) corroborated the experimental results and revealed the intercalation mechanism, whereby P_2O_5 dissociated into small fragments catalyzed by defects in the graphene that then permeated through lattice defects and reacted at the heterointerface to form P_2O_5 . This process can also be used to form new confined metal phosphates (e.g., 2D $InPO_4$). While the focus of this study is on P_2O_5 intercalation, the possibility of intercalation from pre-dissociated molecules catalyzed by defects in graphene may exist for other types of molecules as well. This in-depth study advances our understanding of intercalation routes of large molecules *via* the basal plane of graphene, as well as heterointerface chemical reactions leading to the formation of distinctive confined complex oxide compounds.

This chapter is adopted from Jiayun Liang *et al* 's work entitled "Elucidating the Mechanism of Large Phosphate Molecule Intercalation Through Graphene-Substrate Heterointerfaces" from reference⁴⁶, with permission to reproduce it in this dissertation from the co-authors. In this work, the DFT calculation was performed and analyzed by Ke Ma and Dr. Matthew Sherburne.

2.1 Introduction

One promising strategy for space-confinement growth of materials at interface is through intercalation, a topotactic insertion process of organic and/or inorganic chemical species (i.e., atoms, small molecules, etc.) between the interfaces and heterointerfaces of two-dimensional (2D) layered materials. Intercalation can occur through the exposed side edges of a 2D layered bulk crystal and/or through its basal planes¹³³. In the latter case, for example, in monolayer to few-layer graphene, the intercalation pathways are typically point defects³⁸⁻⁴⁴ and/or grain boundaries⁴⁵. However, the intercalation of molecules through the basal plane of monolayer graphene that are significantly larger than the lattice parameters of graphene remain challenging. This is because the size and energy barrier for intercalation inhibits the permeation of such large molecules¹³⁴⁻¹³⁵. The ability to intercalate large molecules could further expand the toolsets for subsurface and heterointerface engineering of 2D layered materials, and therefore enrich the material choices available for the fabrication of heterostructures and intercalation compounds used in energy storage, optoelectronics, thermoelectric, catalysis, etc¹³⁶⁻¹³⁸.

Towards it, chemical reactions enabled by confinement to the heterointerfaces of 2D layered materials provide a pathway to circumvent the limitation on intercalating large molecules directly through the basal plane. In most cases, however, chemical species are individually introduced in a sequential manner when intercalating graphene. This is done to prevent pre-reactions in the vapor phase between the individual elements prior to intercalation. Such pre-reactions usually lead to the formation of clusters at defect sites on the graphene surface, rather than intercalating through the lattice itself and forming a compound at the heterointerface.

In this work, we report a mechanism of vapor phase intercalation of large molecules through the heterointerface of monolayer graphene to form confined oxide materials underneath graphene with a chemical composition that resembles the initial state of the large intercalant molecule itself. Unlike prior work where chemical species and/or elements are sequentially introduced into the heterointerface, single molecules are introduced directly into the vapor phase for intercalation through the basal plane. This mechanism was revealed by investigating the intercalation of phosphorus pentoxide (P_2O_5) molecules directly from the vapor phase to form P_2O_5 at a graphene-substrate heterointerface. The formation of confined P_2O_5 was confirmed using a variety of chemical analysis and spectroscopic techniques as well as microscopic surface, and cross-sectional imaging. Density functional theory (DFT) was used to corroborate experimental results and to deduce the mechanism for the intercalation of P_2O_5 molecules through the basal plane of graphene. First, P_2O_5 dissociated into small fragments (e.g., P_x , O_y , etc.) when interacting with the graphene surface. These small fragments consistently showed lower energy barriers for intercalation through defects commonly observed in the graphene lattice. Once the small fragments intercalated, they reacted at the heterointerface to form P_2O_5 . We showed that the intercalation of P_2O_5 at the graphene/substrate heterointerface can tune the electronic structure of the graphene overlayer through strain and charge transfer. In addition, we showed that this process can also be used in the formation of new confined metal phosphates by intercalating P_2O_5 into a graphene/substrate heterointerface initially containing confined 2D indium metal to form $InPO_4$. Although this study focuses on the

intercalation of P_2O_5 , the concept of intercalation from pre-dissociated molecules catalyzed by defects in graphene could be possible in other classes of molecules. Ultimately, this study provides an important insight for advancing the understanding of intercalation pathways of large molecules through the basal plane of graphene as well as heterointerface chemical reactions to form unique confined complex oxide compounds.

2.2 Experimental setup and characterization

2.2.1 Chemical vapor deposition (CVD) process for the intercalation of P_2O_5

The intercalation process was performed at 1 atm in a single zone furnace under argon flow. Two kinds of samples were used in this study: transferred CVD graphene (Graphenea) onto cleaned Ge(110) substrates (MTI Corp.), and 2D indium samples intercalated at graphene-SiC(0001) heterointerface, as reported by Rajabpour et al.³⁰. SiP_2O_7 (Saint-Gobain Inc.) was utilized to produce an upstream flux of P_2O_5 to the samples. First the center of the furnace was set to 950°C at a ramping rate of 55°C/min (stage-I) and then dwelled at 950°C for 45 mins (stage-II). In stage-II, the measured temperature for the sample and SiP_2O_7 was 600°C and 950°C, respectively. Samples were then naturally cooled down to room temperature under argon flow. (More details about the furnace setup in **Appendix A**)

2.2.2 Graphene transfer process

1cm by 1cm CVD-grown monolayer graphene on polymer film (Graphenea) was placed into deionized water slowly and detached from the supporting polymer film underneath. Afterwards, a clean Ge (110) substrate was then introduced into deionized water and fished the graphene from below, followed by 30-mins dry in air and another 1-hour heating treatment at 150°C on a hotplate. Later, graphene-Ge (110) sample was kept in low pressure environment ($\sim 10^{-3}$ torr) overnight and annealed at 450°C in N_2 atmosphere for 2 hours.

2.2.3 Materials characterization

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were performed on a Thermo Fisher Scios 2 dual-beam microscope. The cross-section samples of graphene bubbles for transmission electron microscopy (TEM) analysis were prepared using a focused ion beam (FIB) Zeiss NVision 40 FIB-SEM. The target location was extracted from the specimen and attached to a copper FIB grid using a conventional FIB milling and lift-out procedure. The high-angle annular dark-field (HAADF) image and scanning transmission electron microscopy (STEM)-EDS mappings on the cross-section of graphene bubbles were collected with a Thermo Fisher Scientific Talos 200X operated at 200kV. HAADF was performed with a spot size less than 1 nm with a convergence semi-angle of 10.5 mrad. Furthermore, X-ray photoelectron spectroscopy (XPS) spectra and depth profiles were carried out in a Thermo-Fisher K-Alpha Plus XPS system and in Kratos Axis Ultra DLD system using a monochromatic Al $K\alpha$ source ($h\nu = 1486.6$ eV). Raman measurements were performed on a Renishaw inVia system with a 488nm laser (maximum power at 100mW). Scanning tunneling microscope (STM) was performed in a closed-cycle RHK Pan Scan Freedom SPM system in UHV ($\sim 1 \times 10^{-10}$ mbar) at a base temperature of 10K. dI/dV measurements were taken using a built-in digital lock-in amplifier operating at 1.3156kHz with a 10-mV excitation amplitude. Moreover, nano-Fourier transform infrared spectroscopy (nano-FTIR) of the graphene bubbles was performed on a commercial scattering-type scanning near-field optical microscope (s-

SNOM) setup (Neaspec Inc.) and the collected spectra were normalized to that obtained on a silicon sample using the same acquisition parameters. Nano-FTIR of the P₂O₅ reference sample was performed on a synchrotron infrared light-based nano-spectroscopy (SINS) setup (Innova, Bruker) (beamline 5.4, Advanced Light Source, Lawrence Berkeley National Laboratory).

2.3 First Principles Calculation

DFT calculations were performed using generalized gradient approximation (GGA) with Vienna *Ab initio* Simulation Package. The Projector-Augmented-Wave (PAW) method was used and Grimme's DFT+D2 was applied to better account for the Van der Waal's interaction between graphene monolayer and absorbed species¹³⁹. Kinetic energy cutoff was set at 500eV, and the global convergence criterion for breaking electronic SC-loop was chosen to be 5×10^{-5} . A vacuum space of 22Å was applied on top of the graphene sheet to best model the isolated state of a monolayer. Γ point sampling was used throughout all calculations. For relaxations and nudged elastic band (NEB) calculations, a grid of $5 \times 4 \times 1$ was used. To obtain density of states (DOS), a grid of $9 \times 9 \times 1$ was adopted for best precision.

When simulating the dissociation of phosphorous oxide molecules and hetero atom intercalation through defected graphene monolayer, climbing image nudged elastic band (CI-NEB) calculations were performed to determine the most probable reaction route¹⁴⁰. Such a process involves three steps. First, the most stable initial and final configurations were obtained by structural relaxation. Then a CI-NEB calculation with 6-8 intermediates was conducted to find a most realistic energy path connecting the two configurations. Lastly, the two intermediates closest to the maxima on energy profile were used as initial and final configurations for another NEB calculation of 3-4 images to precisely determine the geometry and energy profile of intermediate states. To accurately model P₂O₅ dissociation reactions of complex potential energy surface, multiple plausible chains of images were generated, and NEB calculations were performed for each. The energy profile of all chains was examined and the pathway exhibiting the lowest energy barrier was identified as the most probable route for the reaction.

Four types of intrinsic defects of graphene were studied *via* DFT. Stone-Wales defects (denoted as SW-Defects in Figure 2.4a) were created by rotating a single pair of carbon atoms by 90 degrees to form adjacent pairs of pentagonal and heptagonal rings. The formation of Stone-Wales defects did not involve the introduction or removal of any atoms. Single vacancy defect (denoted as S-Defect in Figure 2.4a) was formed when a single carbon atom was removed from a hexagon ring in graphene monolayer. In response to the removal of a single atom, the structure near the vacancy underwent Jahn-Teller distortion to minimize total energy, leading to a decreased separation between carbon atoms near the vacancy. Similarly, double vacancy defects (D-Defects in Figure 2.4a) were formed through the loss of two adjacent carbon atoms in pristine monolayer graphene. Lastly, quadruple vacancy defects (Q-Defects in Figure 2.4a) were produced by removing one carbon atom and its three nearest neighbors from the hexagon, resulting in a total of four missing atoms.

2.4 Intercalation of P_2O_5 at the graphene/Ge (110) heterointerface

The physical size of phosphorus pentoxide (P_2O_5) can be deduced from our DFT calculated ground state structure when adsorbed onto the surface of pristine graphene (Figure 2.1a). This molecule consists of two main phosphorus bonds with oxygen. The P-O single bond (denotated as oxygen bridging), has a bond length of 157-159pm, and the P=O double bond (denotated as oxygen terminal) has a bond length of 143.2-144.5pm¹⁴¹. When intuitively comparing the physical size of the molecule to the lattice parameter of graphene, intercalation through the basal plane appears to be unlikely. Our DFT calculations revealed that the intercalation of P_2O_5 molecules in their native state through graphene could only occur if large pores formed by the removal of 9 carbon atoms. The formation of such large pores in graphene is, however, energetically unfavorable¹⁴². In fact, other theoretical studies have predicted large energy barriers for permeation of many atoms and molecules through pristine graphene¹³⁴⁻¹³⁵.

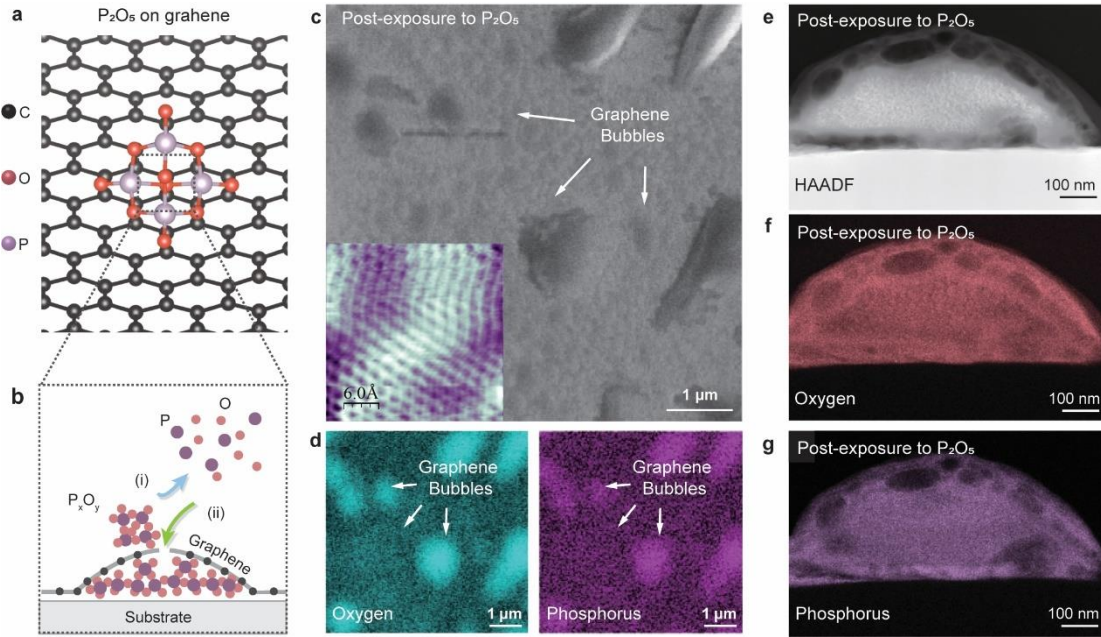


Figure 2.1: Intercalation of P_2O_5 at the graphene/Ge (110) heterointerface. (a) Configuration of P_2O_5 adsorbed onto pristine graphene calculated from DFT. (b) Schematic of intercalation process through the graphene-substrate heterointerface: (i) decomposition of P_2O_5 into P_x and O_y , (ii) intercalation of P_x and O_y through graphene and formation of P_2O_5 at heterointerface via chemical reactions. (c) SEM highlighting the formation of graphene bubbles (white arrows), with STM image of the graphene lattice on the top surface of the bubble (bottom left inset). (d) SEM-EDS maps of (left) oxygen and (right) phosphorus of the highlighted graphene bubbles in (c). (e) STEM-HAADF cross-section image of a graphene bubble with corresponding STEM-EDS maps of the (f) oxygen, and (g) phosphorus distribution in the bubble.

In our case, we experimentally showed that it was possible to intercalate P_2O_5 through monolayer graphene transferred onto germanium substrates without the need of large pores to serve as intercalation pathways. In our studies, germanium was used as a substrate due

to the limited solubility¹⁴³ and low diffusivity¹⁴⁴ of phosphorous into germanium, allowing to fully capture and study the formation of P_2O_5 at graphene/Ge(110) heterointerfaces. To intercalate P_2O_5 , we prepared monolayer graphene on germanium substrates which were then annealed downstream of SiP_2O_7 at 950°C. At such temperatures, the decomposition of SiP_2O_7 produced an upstream flux where P_2O_5 is the predominant gas-phase species, as supported by previously reported experimental and computational evidence¹⁴⁵⁻¹⁴⁷. P_2O_5 then impinged onto the surface of graphene downstream and subsequently intercalates into the heterointerface (Figure 2.1b). A more detailed discussion of the mechanism is included in the following sections.

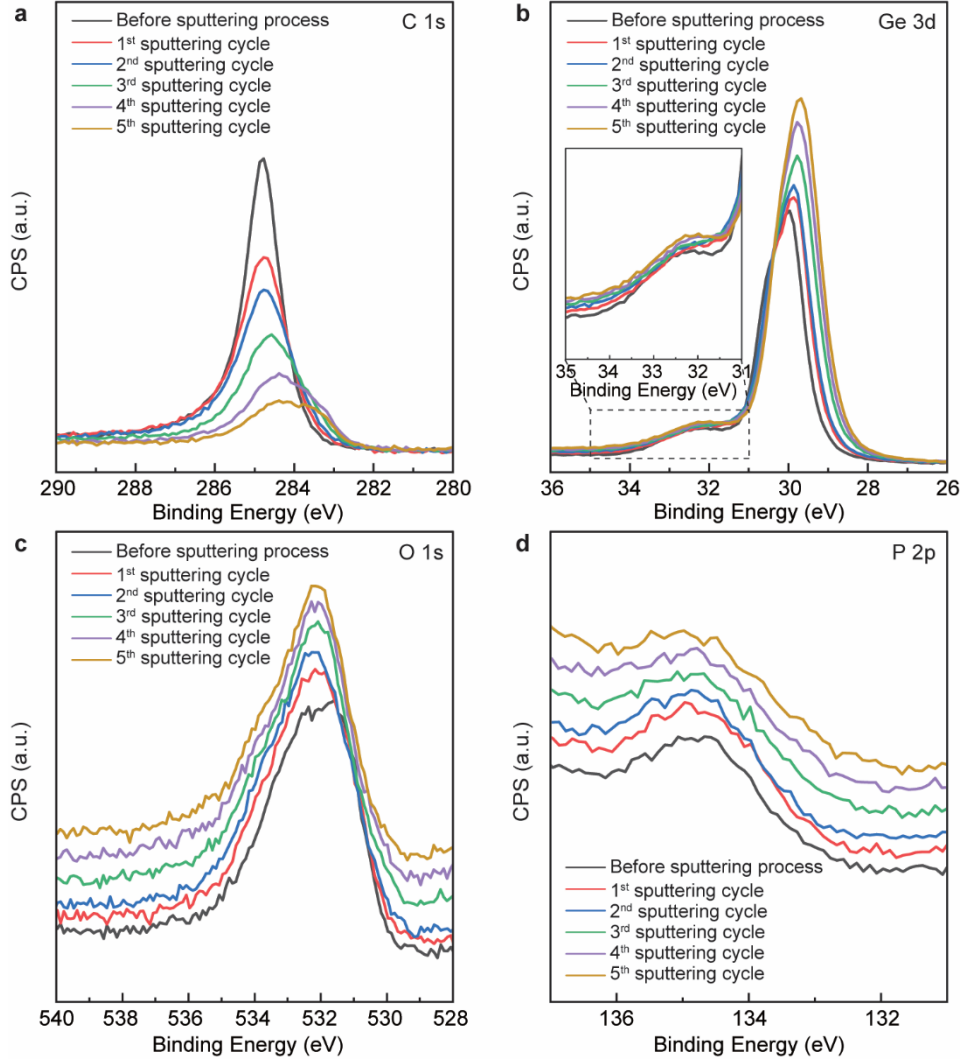


Figure 2.2: XPS depth profile of graphene/Ge (110) after exposure to P_2O_5 . High-resolution XPS spectra collected before the ion sputtering process (black); after the first sputtering cycle (red); after the second sputtering cycle (blue); after the third sputtering cycle (green); after the fourth sputtering cycle (violet) and after the fifth sputtering cycle (yellow) for core-levels of (a) C 1s, (b) Ge 3d, (c) O 1s, and (d) P 2p. In the XPS spectra of Ge 3d, region where the binding energy ranged from 31eV to 35eV is magnified to highlight the intensity change of the germanium oxide.

As shown in Figure 2.1c, many bubbles appeared on the surface of graphene after exposing samples to a flux of P_2O_5 (*white arrows* in scanning electron micrograph, SEM). From scanning tunneling microscopy (STM) imaging of the bubble surface (Figure 2.1c, *inset*), the characteristic hexagonal lattice of graphene was clear. This suggested that not only was the graphene surface free of large pores, but also highlighted that the bubbles themselves were “graphene bubbles” containing subsurface material. Such graphene bubbles were prevalent in many intercalation studies of monolayer to few-layer graphene in the literature^{134, 148}. Upon further inspection of the surface using energy dispersive spectroscopy (EDS), strong phosphorus and oxygen signals confined to the graphene bubbles were observed (Figure 2.1d). This implied the formation of phosphorus oxides within the bubbles themselves. The distribution of the phosphorus and oxygen in the graphene bubbles were further corroborated in sample cross-sections. In Figure 2.1e, a representative high-angle annular dark field scanning transmission electron microscope (HAADF-STEM) image of a graphene bubble was shown. The EDS cross-section elemental maps of the bubble (Figure 2.1f and g) also revealed strong oxygen and phosphorus signals. The atomic fractions of oxygen and phosphorus in the graphene bubble were 55.06% and 15.52%, respectively. This elemental distribution was further corroborated within x-ray photoelectron spectroscopy (XPS) depth profiles of the sample, facilitated by repeated ion sputtering (Figure 2.3). During the ion sputtering process, the graphene surface was first etched. This resulted in a rapid decrease in the C 1s core-level peak intensity (Figure 2.3a). The peak intensities for the Ge, O, and P core-levels increased upon sputtering of graphene (Figure 2.3, b to d), which served as additional evidence on the confinement of phosphorus oxide at the graphene/Ge(110) heterointerface after exposing samples to a flux of P_2O_5 .

2.5 Chemistry of the graphene/substrate heterointerface after intercalation

Moreover, the chemical environment of phosphorus oxide within the graphene bubbles was investigated using nano Fourier-transform infrared spectroscopy (nano-FTIR). A near-field white light IR image of a region of the sample containing graphene bubbles, spectrally averaged over $\sim 610 - 1400 \text{ cm}^{-1}$, was highlighted in Figure 2.3a. Spectral points in the range associated with vibrational modes associated with the phosphorus and oxygen functional groups were acquired at 50 nm intervals across a graphene bubble (*black arrow*). This was plotted in Figure 2.3b as a near-field phase (φ_2) heat map, which was related to the local absorption spectra of the material, and therefore, useful for determining the chemical environment of the intercalant¹⁴⁹⁻¹⁵⁰. Figure 2.3c highlighted a comparison between two nano-FTIR spectra. The top panel (*black solid line*) was the extracted phase spectrum at the center of the graphene bubble in Figure 2.3b, while the bottom panel (*red solid line*) was a spectrum collected from a reference sample of P_2O_5 using high-resolution synchrotron-based nano-FTIR measurements. Evident in Figure 2.3b and the top panel of Figure 2.3c were three characteristic IR bands localized to the graphene bubble. These bands were assigned as the P-O-P bending mode ($940 - 970 \text{ cm}^{-1}$), the P-O bridging mode ($1060 - 1125 \text{ cm}^{-1}$), and the P=O terminal oxygen stretching modes ($1135 - 1235 \text{ cm}^{-1}$)¹⁵¹. The intensity of the P=O bond in the heat map (Figure 2.3b) reached a maximum at the center of the graphene bubble. More importantly, these peaks well matched the P_2O_5 reference sample in Figure 2.3c (bottom panel), and therefore supported phosphorus oxide

that was confined at the graphene/Ge (110) heterointerface from the cross-section micrograph in Figure 2.1g was P_2O_5 .

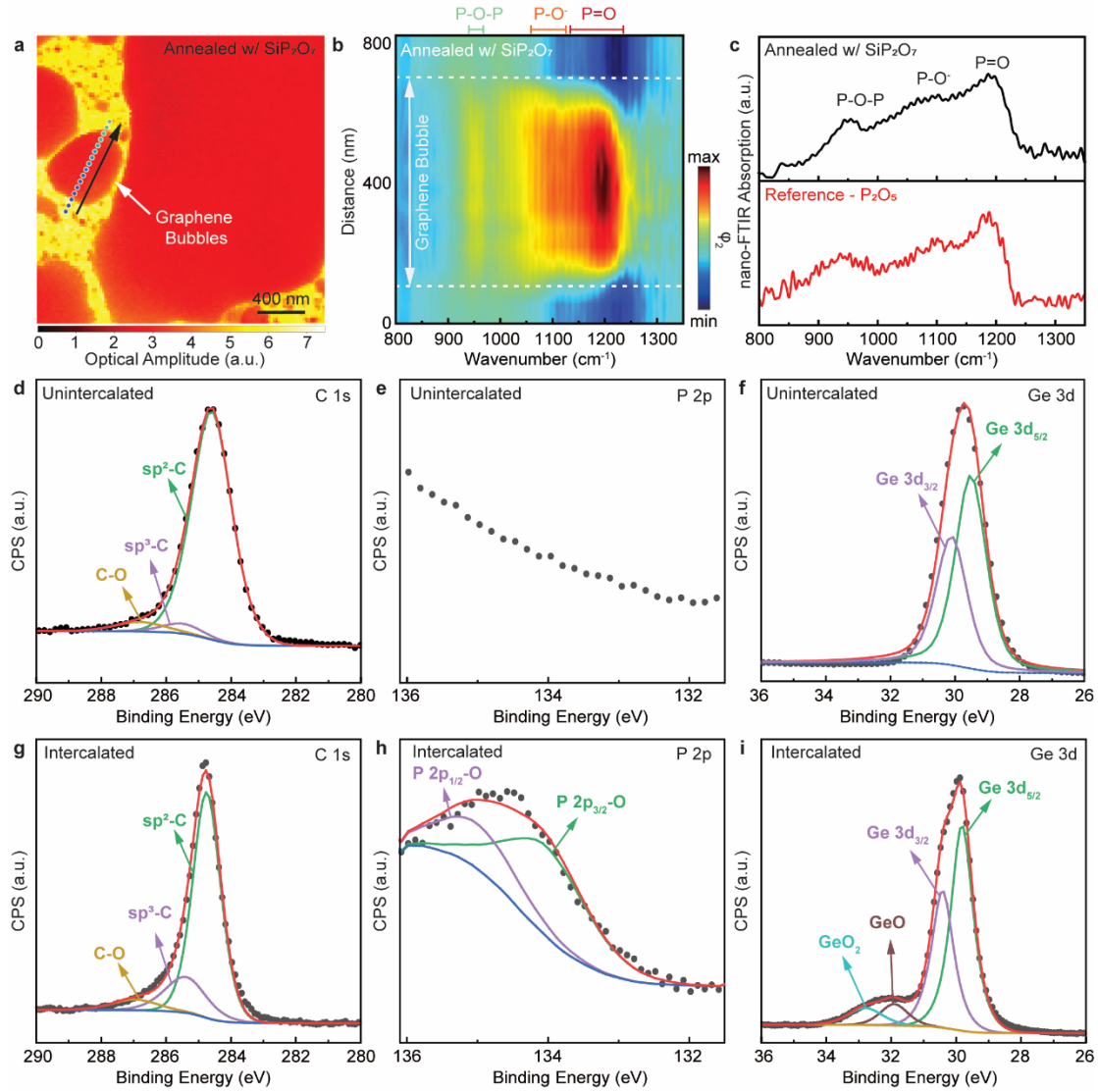


Figure 2.3: Chemistry at the graphene/Ge (110) heterointerface. (a) Near-field white light IR image in a region of the sample containing large graphene bubbles. The white light IR image was the near-field amplitude (S_2) image, which was spectrally averaged over approximately ~ 610 - 1400cm^{-1} by setting the interferometer at the white light position. (b) Nano-FTIR spectral heat map acquired at 50 nm intervals along the *black solid arrow* in (a). The graphene bubble region is highlighted with *white dashed lines* and *dashed arrow*. The collected phase channel (ϕ_2) was normalized to that obtained in a silicon sample using the same acquisition parameters. (c) Comparison between extracted nano-FTIR spectrum of a graphene bubble (top panel, *black solid line*) and spectrum collected from a reference P_2O_5 sample (bottom panel, *red solid line*). XPS of C, P and Ge core-levels from graphene on germanium samples (d, e, and f) annealed without an upstream flux of P_2O_5 (i.e., unintercalated sample) and from graphene on germanium samples (g, h, and i) annealed with an upstream flux of P_2O_5 (i.e., intercalated sample).

Furthermore, a comparative XPS study between non-intercalated and intercalated samples was also performed to further deduce the chemical bonding information at the graphene/Ge (110) heterointerface. Figure 2.3, d to f were XPS core-level spectra collected from samples that were annealed without an upstream flux of P_2O_5 , while the XPS core-levels in Figure 2.3, g to i were from samples annealed downstream to a flux of P_2O_5 . In the non-intercalated samples, the sp^3/sp^2 carbon ratio, extracted from the C 1s core-level, was $\sim 4\%$ (Figure 2.3d), and neither phosphorus oxides (Figure 2.3e) nor germanium oxides (Figure 2.3f) could be detected in those samples. However, in intercalated samples, the sp^3/sp^2 carbon ratio increased to $\sim 7.7\%$ (Figure 2.3g). Such an increase in sp^3 bonded carbon within the non-intercalated samples is likely due to the formation of additional point defects in the graphene lattice. These defects could have resulted from the intercalation process itself and/or due to the enhanced hybridization of the graphene with the underlying intercalants. Moreover, a strong phosphorus oxide peak, whose binding energy was associated with P_2O_5 (135eV, Figure 2.3h), further corroborated its formation¹⁵². Also, from the Ge 3d core-level, the intercalated P_2O_5 appeared to oxidize the germanium substrate, resulting in characteristic peaks for GeO and GeO₂ that were observed between the binding energies of 31 – 33eV (Figure 2.3i). These combined results allude to a strong affinity of oxygen from P_2O_5 to the underlying germanium substrate, and perhaps provides an additional driving force in the intercalation process with the aid of point defect and/or grain boundaries in the graphene lattice as a pathway for intercalation through the basal plane of graphene⁴³.

2.6 Mechanism of large molecule intercalation through graphene

To gain a deeper understanding into the mechanism by which phosphorus pentoxide P_2O_5 (or molecular formula P_4O_{10}) intercalated through the basal plane of graphene, we first examined the adsorptive properties of these molecules on five different graphene systems, consisting of pristine graphene and four graphene lattice defect configurations (Figure 2.4a). This survey was performed to factor in different interaction parameters of distinct chemical environments on the intercalation process. The configurational space of the adsorptive states (chemisorption *vs.* physisorption) was thoroughly explored by including a multitude of initial interacting geometries for both P_2O_5 and P_4O_{10} on each of the different graphene lattice defect configurations (Figure 2.4b). As summarized in Table 2.1, covalent interactions with graphene occurred exclusively in the chemisorption of P_2O_5 onto graphene defect sites, whereas in pristine graphene, P_2O_5 interacted weakly *via* van der Waals (vdW) forces. In comparison, interactions between the more stable P_4O_{10} molecule with all graphene systems were vdW in nature. In the case of covalent bonding between P_2O_5 adsorbents and graphene, P atoms consistently demonstrated a higher affinity towards graphene. This was shown by the greater adsorption energy of P_2O_5 to graphene through the P atom (denoted by $P_2O_5(P)$ in Figure 2.4b). In contrast, initial configurations of P_2O_5 approaching graphene with its O atom (designated by $P_2O_5(O)$) either relaxed to drastically different interaction geometries to allow bond formation between carbon and phosphorous or had a much lower total adsorption energy when compared to $P_2O_5(P)$. The only exception was $P_2O_5(O)$ chemisorbed to S-defects, in which both O and P atoms bonded covalently to the graphene defect site. Such trends can be rationalized by the fulfillment of covalency and increase charge transfer stabilization of carbon atoms at defects when

bonding to less electronegative P atoms in P_2O_5 .

Table 2.1: Summary of absorption mechanisms of P_2O_5 and P_4O_{10} on pristine and defected graphene monolayer. The notation (P) denotes that the molecule is binding or approaching graphene primarily through the phosphorous atom, while (O) represents adsorption primarily through the oxygen atom.

Adsorption Mechanism	$P_2O_5(P)$	$P_2O_5(O)$	$P_4O_{10}(P)$	$P_4O_{10}(O)$
Pristine Graphene	vdW	vdW	vdW	vdW
SW-Defect	Covalent	Reaction	vdW	vdW
S-Defect	Covalent	Covalent	vdW	vdW
D-Defect	Covalent	vdW	vdW	vdW
Q-Defect	Covalent	Reaction	vdW	vdW

Pristine graphene has been predicted to be impermeable to most gaseous species under non-extreme conditions^{134-135, 148}, and the presence of defects is thus the precondition for P_2O_5 intercalation. A quantitative description of intercalation through defects was complicated by the competition between diffusion and bonding with carbon atoms at defect sites. This gave rise to three different energy profiles corresponding to distinct pathways¹⁵³. To address these complexities, we employed a case-by-case strategy by calculating the penetration barriers for fragments of P_2O_5 of varied size and chemistry based on calculated and experimental evidence from the literature¹⁴⁷. Based on experimental evidence of P_2O_5 confinement at the graphene/Ge (110) heterointerface, the intercalation of molecular P_2O_5 in its entirety was first investigated. Point defects of various sizes were examined, with the largest created by removing 9 adjacent carbon atoms in an isolated graphene sheet (Figure 2.5). In all scenarios, P_2O_5 decomposed into fragments solvated by carbon atoms at defect sites. Notably, the energetic profile of P_2O_5 permeating through large defects showed a negative reaction coordinate energy curve with small intermediate energy barriers as a result of the bonding of the fragmented P_2O_5 molecule onto the defect site. Despite this negative reaction coordinate energy curve, a barrier of at least 7.7eV was still present for fragments to desorb from the defect and diffuse into opposite sides of the monolayer graphene (i.e., intercalate).

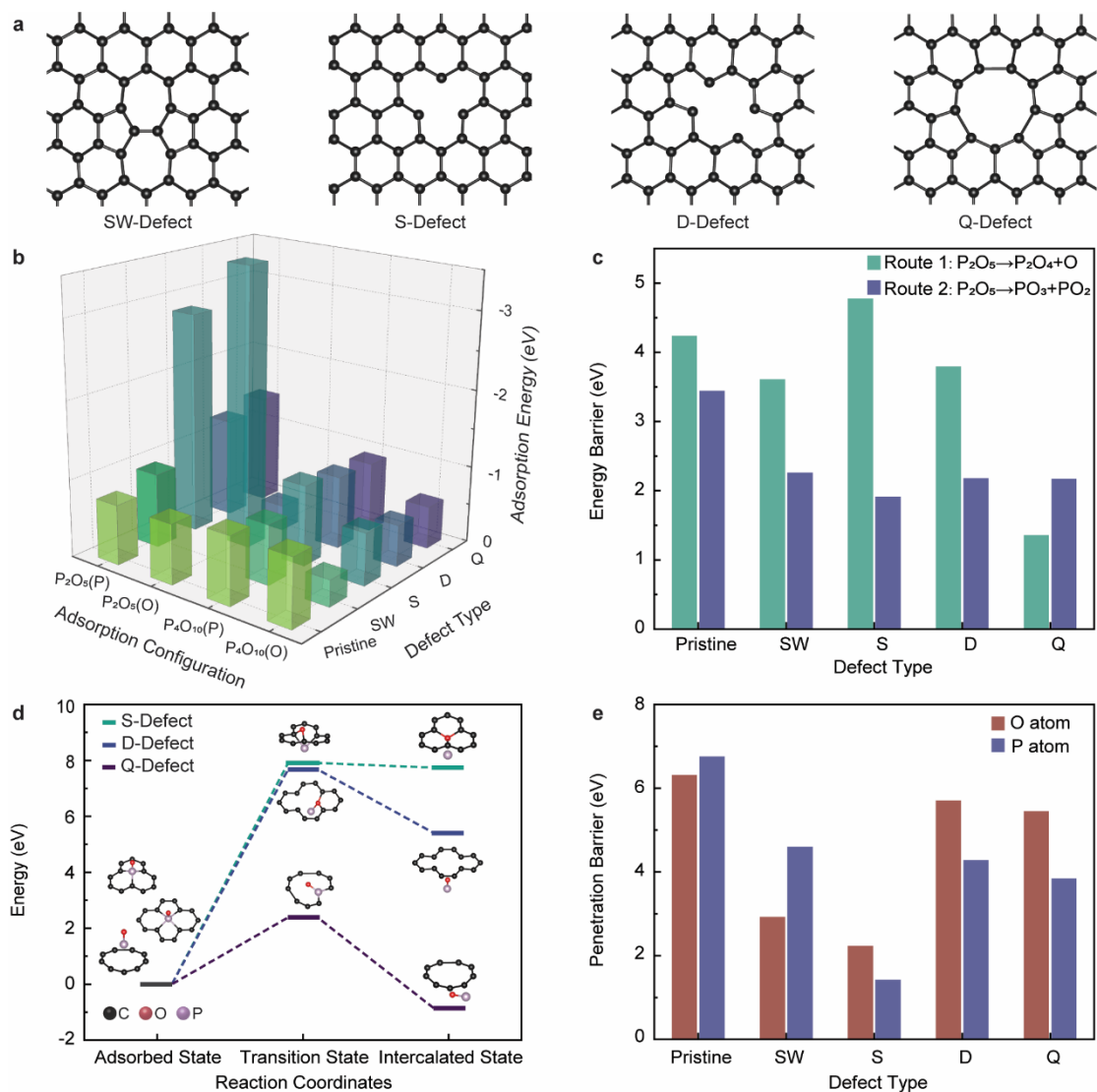


Figure 2.4: Mechanism for intercalation P_2O_5 through the basal plane of graphene. (a) Top view of the four types of point defects in isolated graphene sheets. (b) Adsorption energy of phosphorus pentoxide on pristine and defective graphene monolayers. Within each P_xO_y molecule, the atom interacting directly with carbon at the defect site is labeled in parentheses. (c) Calculated energy barrier of bond cleavage for P-O double bond (route 1, labelled as *green*) and single bond (route 2, labelled as *blue*) within P_2O_5 in different local environments. (d) Energy and configurational profile of PO molecule penetrating through defects. (e) Energy barrier of P (*blue bars*) and O (*red bars*) atoms permeating through defects.

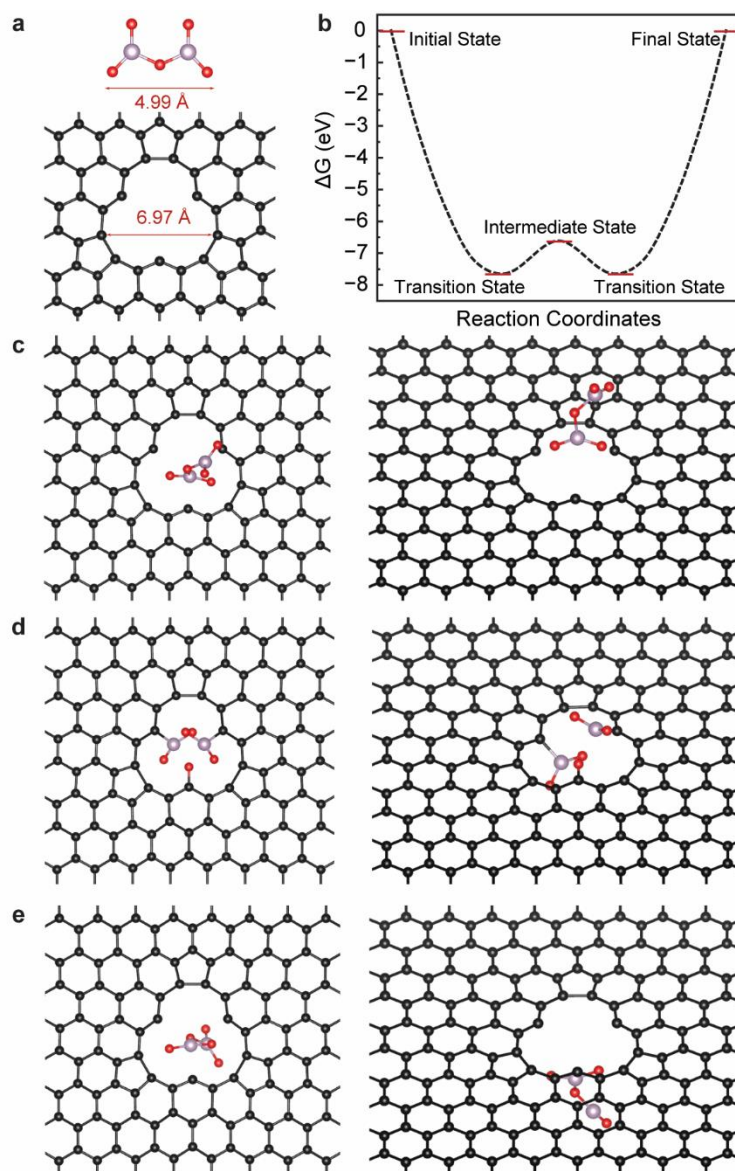


Figure 2.5: Intercalation of P_2O_5 molecule through a defect of 9 vacant atoms. (a) A comparison of dimensions of a defect of 9 vacant atoms and P_2O_5 molecule. (b) Energy profile of P_2O_5 intercalation through a 9-vacant-atom defect. The molecule underwent spontaneous dissociation upon contact with the defect site and would require an energy barrier of 7.7eV to desorb and recombine on the opposite side of the graphene monolayer. Top (*left*) and angled (*right*) view of the (c) initial, (d) intermediate, and (e) final state configuration of P_2O_5 molecule during intercalation.

From this we ascertain that intercalation is only possible from significantly smaller molecular fragments of P_2O_5 . Developed from these findings, we proposed a mechanism involving three consecutive steps of realistic energy barriers to intercalate P_2O_5 through the basal plane of monolayer graphene. First, chemisorbed P_2O_5 decomposed into atoms or small molecular fragments. The resulting species then intercalated separately through point defects and then reacted underneath graphene monolayer to form P_2O_5 at the confined

heterointerface. Describing such processes with a full network of reaction pathways would require a dedicated theoretical effort and is beyond the scope of this study, but two modes of P-O bond cleavage representing the initial steps of two probable pathways were investigated to exemplify our hypothesis. As illustrated in Figure 2.4c, route 1 involved cleaving the P=O double bond to remove one terminal oxygen from the molecule, while route 2 described the fragmentation of P_2O_5 into PO_2 and PO_3 by cleaving the single bond between P and bridging O. Energy barriers for both reactions were shown in Figure 2.4c. Evidently, with the exception of S-defect in route 1, all four types of point defects exhibited catalytic activities towards decomposition of P_2O_5 . These findings were consistent with the results of adsorption state calculations, as covalent interactions and charge transfer between the defects and adsorbed molecules weaken the intramolecular bonds. Having substantiated the possibility of catalytic dissociation of adsorbed P_2O_5 at defect sites, we then calculated the energetics of smaller fragments intercalating through point defects. Phosphorous monoxide (PO), the simplest oxide of phosphorous, was chosen as the subject of this part of the study. Given the positive correlation between a molecule's size and the energy barrier required for its penetration through point defects, we posited that the simulation of PO provided a baseline for the minimum energy barrier applicable to the diffusion of any potential phosphorous oxide molecules through the monolayer. In the focused reaction coordinate diagram (Figure 2.4d), we presented the energy of three key configurations: the adsorbed state, where PO molecule adsorbed to the defect site; the transition state, where the molecule penetrated halfway through the defect; and the intercalated state, in which PO has permeated through the monolayer but has not yet desorbed or reconfigured itself to the lowest-energy absorption geometry. The energy difference between the transition and adsorbed states indicated the minimum energy barrier required for PO molecules to intercalate. Similar to P_2O_5 , PO could not permeate through pristine graphene or Stone-Wales (SW) defects without introducing defects of larger sizes. When penetrating through S- and D-defects, the molecule decomposed into individual atoms, with the rate limiting step having an energy barrier as high as 8eV. On the other hand, PO was surprisingly permeable at Q-defects. It diffused through Q-defect without further fragmentation, with a barrier of approximately 2eV, comparable to the energy required to break down chemisorbed P_2O_5 . Finally, to compare atomic phosphorous and oxygen diffusing through the four different types of defects in graphene (Figure 2.4e), we performed calculations on (4×6) graphene supercells and incorporate results for D- and Q-defects from the work by Song *et. al*¹⁵³. Remarkably, while point defects enabled both species to intercalate with reduced energy barriers, the energy barrier for individual atoms to penetrate through D- and Q-defects were higher than those for the PO molecule fragments. This observation reiterated the complexity of the interaction process through graphene point defects that cannot be generalized into a single step process.

2.7 The impact of the intercalants on the electronic structure of graphene interface

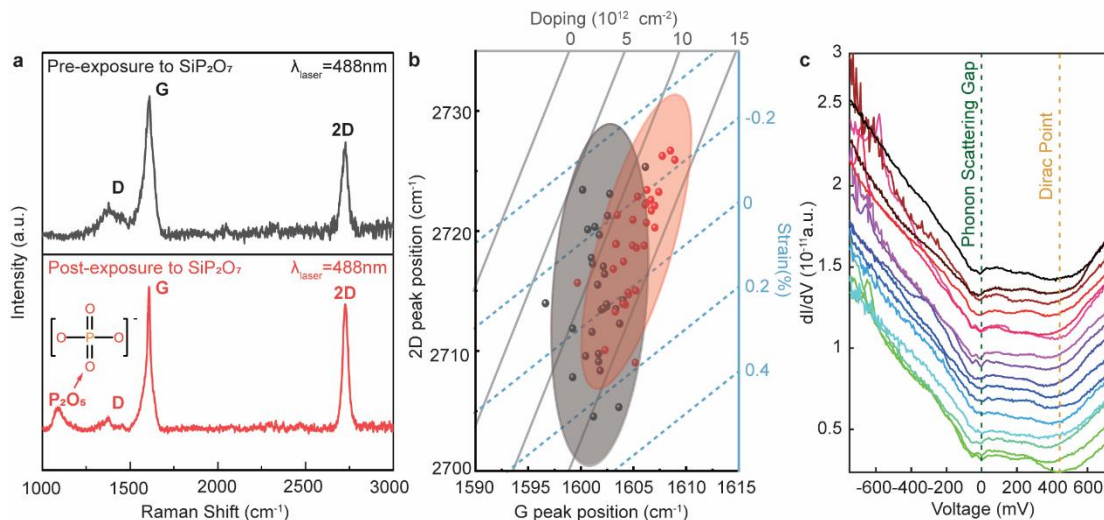


Figure 2.6: Raman and STS spectrums of graphene after intercalation. Raman spectra of graphene (a) before (*black solid line*) and after (*red solid line*) exposure to an upstream flux of P₂O₅, (b) Raman 2D versus G peak position of graphene before (*black dots*) and after (*red dots*) exposure to an upstream flux of P₂O₅. (c) STS dI/dV of intercalated graphene sample. The corresponding phonon scattering gap and Dirac points are highlighted with *green dashed line* and *yellow dashed line*, respectively (Tunneling set point = 200pA, 750mV). Spectra are vertically offset for clarity.

Graphene inherits highly delocalized π -electrons. Any modification to the spatial extent of the charge density of these π -electrons or tilt of the π -orbitals leads to significant changes to the physical properties of graphene¹⁵⁴⁻¹⁵⁷. For example, electronegative or electropositive intercalants confined underneath graphene will lead to charge transfer and doping. This in turn influences the spatial extent of the π -electron charge density and thus the Fermi level of graphene. Moreover, intercalants, such as those confined in graphene bubbles, can also lead to straining of the graphene lattice¹⁵⁸⁻¹⁶⁰. This will also change the π -orbital tilt and charge density in graphene and thus its Fermi level. Therefore, it is expected that the confinement of large P₂O₅ molecules at the graphene/Ge (110) heterointerface would lead to significant changes to the physical properties of graphene itself. In our case, we showed that charge transfer occurs from graphene to P₂O₅, resulting in p-type doping of the graphene layer. Raman spectroscopy was used to assess changes in the G and 2D peak positions. In Figure 2.6a, we compared the Raman spectra between non-intercalated and intercalated samples. After intercalation process, both G and 2D peaks blue-shifted after the intercalation process, resulting from changes in strain and doping of graphene due to intercalation¹⁶¹⁻¹⁶². Besides the typical G, 2D and D peaks of graphene, a new Raman peak, approximately at 1100cm⁻¹, was observed (Figure 2.6a, *red solid arrow*). This vibrational mode was associated with a $[PO_4^-]$ unit in the P₂O₅ cage-like structure, and in our case was activated *via* charge transfer from graphene to the intercalated P₂O₅¹⁶³. The observation of this vibrational mode in Raman, together with the symmetric stretch of bridging oxygen P-O-P bond (Figure 2.7), further corroborated the formation of the P₂O₅ non-planar cage-like structure at the graphene/substrate heterointerface after intercalation of phosphorous oxide fragments as suggested from our DFT calculations. Furthermore, it is possible to deconvolute the effects of charge transfer and strain on the doping level of

graphene by performing a correlation analysis of the G (ω_G) and 2D (ω_{2D}) peak positions between the non-intercalated and intercalated samples (Figure 2.6b)¹⁶⁴. According to the model developed by Lee *et al*¹⁶⁴, for p-type doped graphene, each datapoint $\mathbf{P}(\omega_G, \omega_{2D})$ in $\omega_{2D} - \omega_G$ plot can be represented as $\mathbf{OP} = a\mathbf{e}_{strain} + b\mathbf{e}_{hole-dope}$, where $\mathbf{O}$ ($\omega_G=1582\text{cm}^{-1}$, $\omega_{2D}=2700\text{cm}^{-1}$) stands for unstrained and undoped graphene¹⁶⁵. The slope of $\Delta\omega_{2D}/\Delta\omega_G$ for tensile strain and hole doping effects in graphene was set as 2.2 and 0.7, respectively. By plotting $\omega_{2D} - \omega_G$ lines under different hole doping levels (*blue dash lines* in Figure 2.6b) and tensile strain level (*grey solid lines* in Figure 2.6b), the hole doping level and strain of our system can be extracted from the $\omega_{2D} - \omega_G$ plot. In the intercalated samples, a 12% increase in the hole doping level of graphene was observed when compared to the non-intercalated samples. This was further corroborated from scanning tunneling spectroscopy (STS) dI/dV measurements of the intercalated graphene surface (Figure 2.6c). The dI/dV curves were collected on the graphene surface in a line scan with a step of $\sim 1.1\text{nm}$. The slope of the dI/dV curve is proportional to the local density of states (LDOS) of the sample at the tunneling site. Two local minima were observed in all dI/dV curves, that is, one at $V = 0$ which is the phonon scattering gap (*green dashed line*), and the another at the Dirac point where the LDOS of graphene reaches its minimum (*yellow dashed line*)¹⁶⁶. From Figure 2.6c, the Dirac point up-shifts to +425 mV (*yellow dashed line*) with respect to the Fermi level ($V = 0$) after intercalation, indicating P_2O_5 led to p-type doping of graphene. Moreover, the point defect density (n_D) can be estimated with the I_D/I_G ratio. Considering that our I_D/I_G ratio before and after annealing process was no greater than 0.13 (low defect density regime), the point defect density can be calculated as below¹⁶⁷:

$$n_D = \frac{(1.8 \pm 0.5) \times 10^{22}}{\lambda_L^4} \times I_D/I_G$$

where λ_L is the wavelength for the excitation laser in Raman measurement, and the unit for n_D is cm^{-2} . I_D/I_G is 0.122 and 0.127 before and after the exposure to SiP_2O_7 , respectively. Given that λ_L was 488nm in our study, the corresponding estimated point defect density values were $(3.8 \pm 1.1) \times 10^{10} \text{cm}^{-2}$ before and $(4.0 \pm 1.1) \times 10^{10} \text{cm}^{-2}$ after the exposure to SiP_2O_7 , respectively.

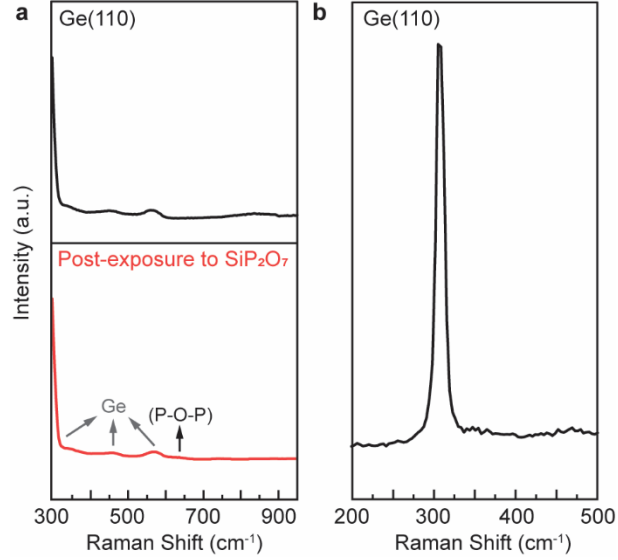


Figure 2.7: Raman spectra of the post-intercalated sample in lower frequency range. (a) Ge (110) substrate without exposure to SiP₂O₇ (black solid line) and after exposure to SiP₂O₇ (red solid line) from 300 to 950cm⁻¹. (b) Raman spectra of Ge (110) substrate without exposure to SiP₂O₇ from 200 to 500cm⁻¹.

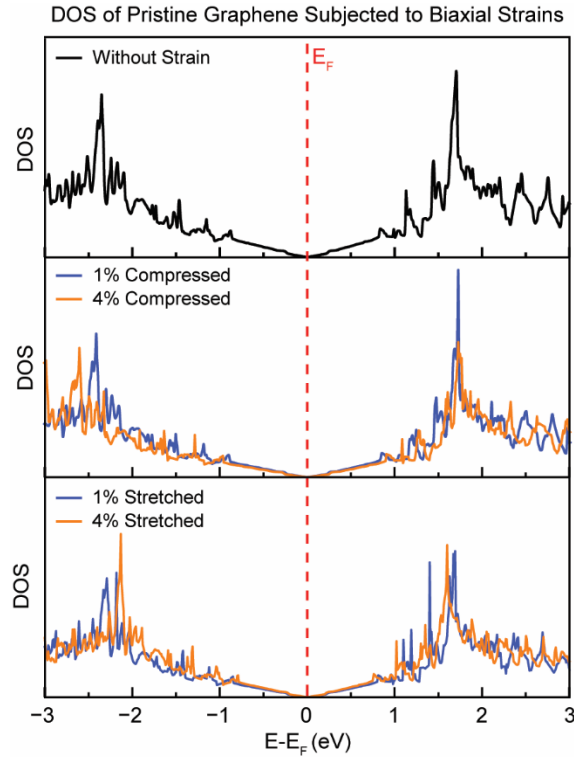


Figure 2.8: Projected density of states (PDOS) analysis of carbon atoms in monolayer graphene subject to mechanical deformation: PDOS of an isolated pristine graphene monolayer (top panel) compared to its behavior under mechanical deformation. The middle panel shows PDOS for graphene subjected to biaxial tensile strain of 1% (blue curve) and 4% (orange curve), whereas

the bottom panel depicts the PDOS under biaxial compressive strain of 1% (blue) and 4% (orange). The energy in all DOS plots is normalized against the Fermi level. Notably, even at 4% biaxial strain, either tensile or compressive, the electronic structure of graphene monolayer closely resembles that of the undeformed system.

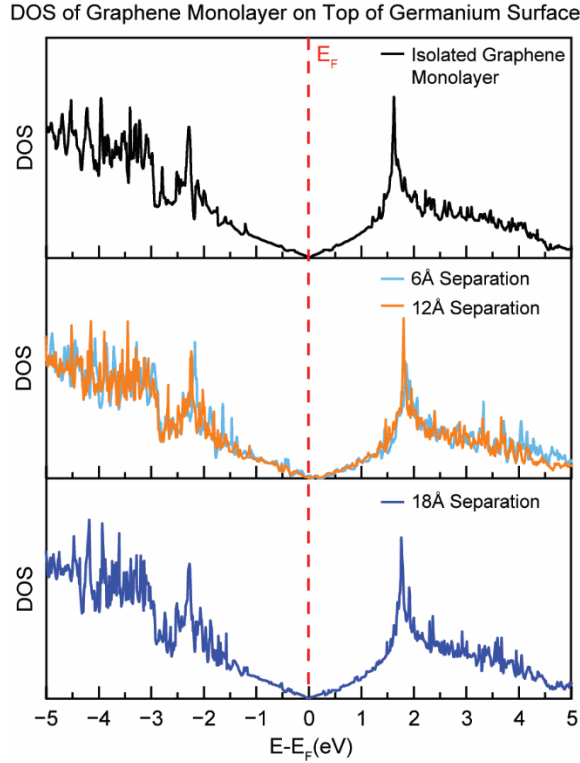


Figure 2.9: Projected DOS of graphene on germanium surface. The top panel shows the DOS for carbon atoms in an isolated, free-standing graphene monolayer. The middle and bottom panels present the DOS for carbon atoms in graphene sheet separated from the underlying germanium surface at various distances.

DFT calculations were also performed to investigate the origins of the observed conductive properties of graphene after intercalation. Given that graphene transferred onto germanium substrates could be subjected to strain¹⁶⁸⁻¹⁷⁰, the impact of possible deformation on the electronic structure of monolayer graphene was studied. Our density of states (DOS) calculations based on (4×8) supercells of graphene suggested that the electronic structure near Fermi level did not undergo significant change, despite an increase in the overall system energy with respect to the increased strain. While compressive and tensile stress led to horizontal stretches and compression of the total DOS, respectively, the overall electronic structure near the Fermi level did not vary (Figure 2.8). We observed that both pristine and deformed graphene behaved as semimetals. As a result, strain alone did not significantly contribute to the experimentally observed p-type conductive properties in Raman and STS measurements. While non-uniform strain and formation of bubbles on the graphene monolayer could cause variations in the distance between graphene and underlying germanium substrate, the impact of the germanium surface on the electronic structure of graphene became negligible when the separation reached $\sim 2\text{nm}$ (Figure 2.9).

Notably, even in regions where the graphene monolayer was only a few angstroms distant from the top layer of the germanium surface atoms, the presence of germanium still did not induce semiconducting behavior in graphene. Similarly, while the exposure to P_2O_5 caused changes in DOS of graphene far above and below the Fermi level, the overall electronic properties of pristine graphene with adsorbed molecules remained semi-metallic, with characteristic converging overlap between the bottom of the conduction band and the peak of valence band (Figure 2.10a).

Moreover, to elucidate the effect of point defects on altering the bulk conductivity of graphene, the partial DOS of carbon atoms away from the defect sites were also calculated. As shown in Figure 2.10b, graphene with SW-defects had a conduction band overlapping the valence band at Fermi level, implying semi-metallic behaviors similar to pristine graphene. On the contrary, systems with missing carbon atoms all developed bandgaps and distinct electronic states near the Fermi level. Graphene with S-defects still behaved as a semimetal but developed a gap in its conduction band just less than 0.2eV above the Fermi level. In the case of graphene with D-defects, the bandgap played an even more noticeable role, as it lied right above the Fermi level, separating the valence band from the conduction band. In systems with Q-defects, the bandgap appeared to widen even further, positioning the Fermi level about 0.4eV above the top of the valence band and 0.7eV below the bottom of the conduction band. Nevertheless, the enlarged bandgap did not render the system semi-conductive. A new, albeit small, state emerged within the band gap and crosses the Fermi level, causing the system to behave more like a metal. Finally, we found that systems whose carbon atoms at defect sites formed covalent bonds to adsorbed P_2O_5 fragments underwent substantial changes in their electronic structure due to charge transfer between graphene and adsorbed molecules. DOS of carbon atoms in defected graphene bond to P_2O_5 was illustrated in Figure 2.11. In all defected systems, the presence of chemisorbed molecules served to enlarge the bandgap and enhance the states in the bandgap, with $P_2O_5(P)$ chemisorbed to S-defect being the most notable case (Figure 2.10c). A summary of these effects was also listed in Table 2.2. To visualize the loss of electron density in the graphene π -orbitals when P_2O_5 was covalently bonded to the graphene defect sites, differential charge calculations were employed (Figure 2.10d). This change in electron charge density was equivalent to hole-doping of the graphene monolayer, which was consistent with our experimental observations.

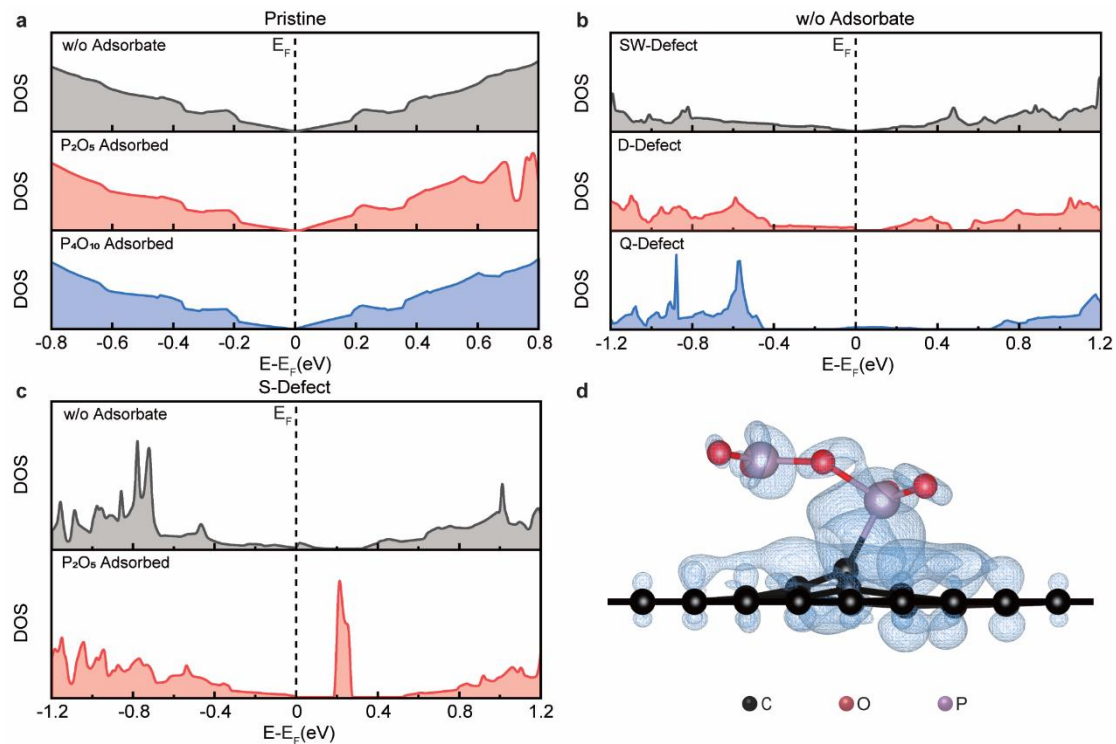


Figure 2.10: Projected DOS of graphene in different scenarios. Projected DOS of (a) Pristine graphene sheet without (*black*) and with (*red and blue*) adsorbed phosphorous oxide, (b) Graphene with SW- (*black*), D- (*red*), and Q-defects (*blue*) without adsorbed phosphorous oxide. (c) Comparison of p-orbital DOS of graphene with S-defect (*black*) and with S-defect covalently bound to P atom in chemisorbed P_2O_5 (*red*). (d) Differential charge density of P_2O_5 covalently bound to S-defect. All wireframe isosurfaces denote charge transfer equivalent to $0.001e \cdot \text{Bohr}^{-3}$. Blue isosurface represents charge loss and red isosurface indicates charge gain.

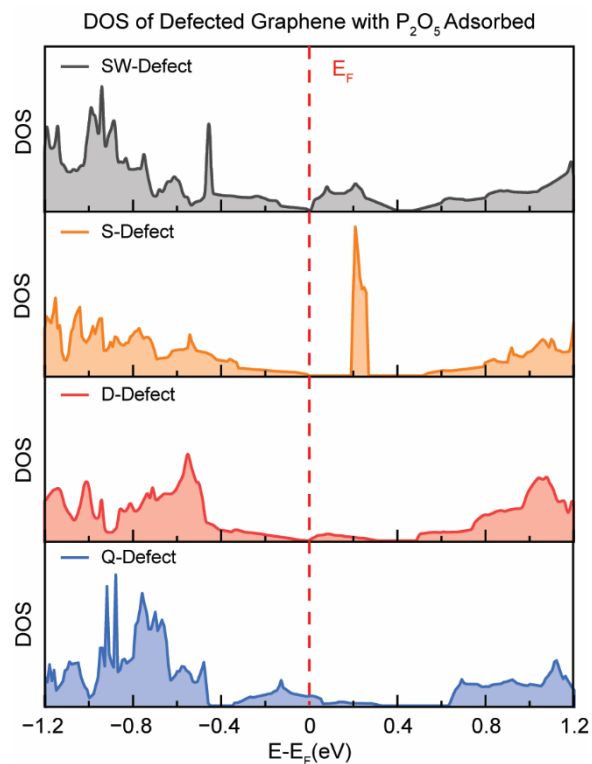


Figure 2.11: Projected DOS of defected graphene with P_2O_5 adsorbed.

Table 2.2: Conductive properties of pristine and defected graphene sheets exposed to P_2O_5 molecules.

	Without Absorbate	$P_2O_5(P)$	$P_2O_5(O)$
Pristine Graphene	Semimetal	Semimetal	Semimetal
SW-Defect	Semimetal	Semimetal	Semimetal
S-Defect	Semimetal	P-type	P-type
D-Defect	P-type	Semimetal	P-type
Q- Defect	Metal	Metal	Metal

2.8 Space-confinement synthesis of metal phosphates at heterointerface

Although phosphorus has limited solubility¹⁴³ and diffusivity¹⁴⁴ into germanium, our XPS analysis of the Ge 3d core-level revealed that the intercalation of P_2O_5 led to chemical

reaction with the germanium substrate. This could have been possible from the intercalated oxygen fragments themselves and/or the affinity of $\text{P}_2\text{O}_5(\text{O})$ to bond with germanium (Figure 2.3i). To further elucidate other chemical reactions of the intercalated fragments of P_2O_5 that could take place at graphene-substrate heterointerfaces, we showed that this process could also be used to form confined metal phosphates by intercalating P_2O_5 into a graphene/substrate heterointerface initially containing 2D metals to form indium phosphate as the example in this study.

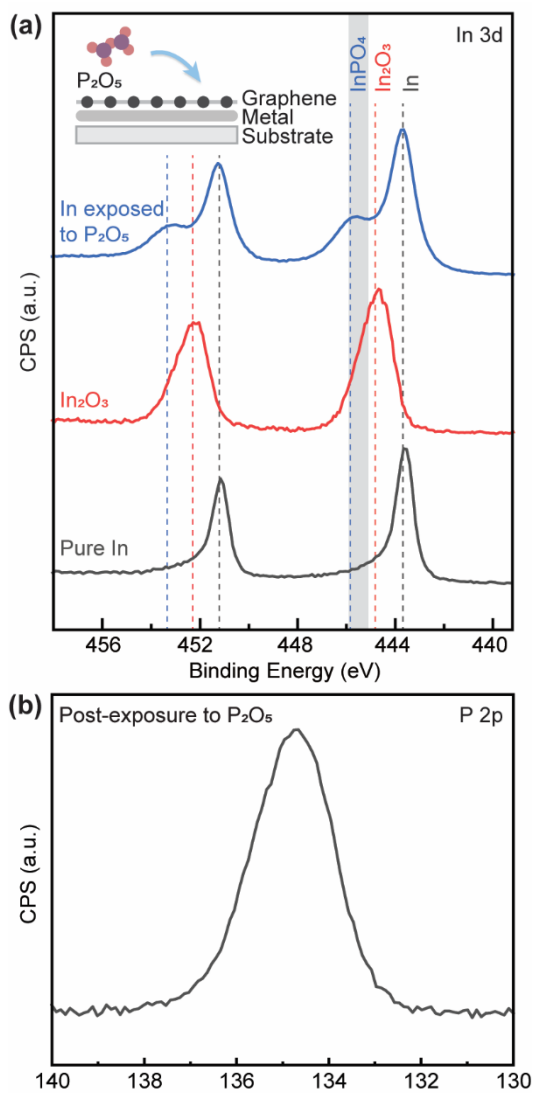


Figure 2.12: Confinement growth of indium phosphate at graphene-substrate heterointerface. XPS core-levels of (a) In 3d for 2D indium confined at the graphene-SiC heterointerface before (*black solid line*) and after exposure to P_2O_5 (*blue solid line*). The XPS spectra for a pure In_2O_3 crystal (*red solid line*) is also included as a reference. The range for InPO_4 peak position data from reference¹⁷¹⁻¹⁷² is highlighted in a shaded gray region. (b) P 2p for the confined 2D indium after exposure to P_2O_5 .

Indium phosphate, specifically InPO_4 , is a wide bandgap insulator ($E_g = 4.5\text{eV}$)¹⁷³ with excellent dielectric properties that initially gain interest as a gate material for InP formed *via* surface oxidation¹⁷⁴⁻¹⁷⁷. However, the formation of dimensionally confined indium phosphates remains largely unexplored, thus impeding a more comprehensive understanding of its physical properties and potential applications. In our case, we demonstrated the successful formation of confined indium phosphates by intercalating P_2O_5 into a graphene-SiC heterointerface initially containing confined mono- to bilayer indium also formed by intercalation^{30, 178}. We identified the composition of the confined indium phosphate at heterointerface by investigating the In and P core-levels using high-resolution XPS (Figure 2.12, a and b, respectively). In Figure 2.12a, we compared the core-levels of In 3d, before (*black solid line*) and after (*blue solid line*) intercalation of P_2O_5 to the graphene/substrate heterointerface containing 2D indium, to the In 3d core-level of a pure In_2O_3 reference sample (*red solid line*). In addition to the typical peaks for indium metal (*black dashed line*), the XPS spectra exhibited new peaks around 445.8eV and 453.3eV in the intercalated sample (*blue dashed line*). These two new peaks were up-shifted by 1.1eV from the peak position of the In_2O_3 reference (*red dashed line*)¹⁷⁹. Furthermore, a strong phosphorus signal was detected in samples intercalated with P_2O_5 . (Figure 2.12b) Therefore, based on these observations, we can exclude the formation In_2O_3 in the P_2O_5 intercalated samples. Further inspection and comparison of our XPS core-level spectra to previous reported XPS of indium phosphates suggested that the peaks at 445.8eV and 453.3eV were the In 3d core-levels associated with P-O-In $3d_{3/2}$ and P-O-In $3d_{5/2}$ bonding, respectively. Although the phase of the confined indium phosphate at the graphene/substrate heterointerface was likely in the form of InPO_4 , $\text{In}(\text{PO}_3)_3$ and other metastable oxide phases could also form at such confined spaces^{53, 171-172} and therefore of important investigation in future studies.

2.9 Conclusions

In this chapter, we have demonstrated that large molecules, such as P_2O_5 , can permeate the basal plane of graphene and intercalate into the heterointerface. This was evident from the strong phosphorus and oxygen signals that were detected underneath the graphene surface from spectroscopic measurements (EDS, nano-FTIR, XPS, Raman, STS) and microscopic cross-sectional imaging and analysis in TEM. Although the physical size of the molecule is larger than that of the graphene lattice, fragments of the molecule could intercalate through typical pathways in the graphene lattice. This was revealed by calculating the penetration barriers for fragments of P_2O_5 of varied size and chemistry through pristine and defected graphene of different configurations. The complexity of the interaction process of large molecules through the basal plane of graphene could not be generalized into a single step process. However, a two-step mechanism, based on realistic permeation energy barriers, was proposed for the intercalation of P_2O_5 : (i) P_2O_5 first dissociated into small fragments (e.g., P_x , O_y , etc.) catalyzed by point defects in the graphene lattice; (ii) these fragments once intercalated can chemically react at the confined graphene/substrate heterointerface forming a condensed phase that chemically resembles the initial state of the molecule. It has been shown that the intercalation of P_2O_5 at the graphene/substrate heterointerface could effectively tune the doping level of graphene *via* charge transfer. Moreover, the intercalated P_2O_5 (and/or its fragments) can also act as reactants and further

contribute to other interfacial reactions, for example, the conversion of 2D indium into 2D indium phosphate at the heterointerface between graphene and SiC. Although our findings only focus on indium phosphates, our results demonstrate the potential of this approach for the conversion of other metals (e.g., Ga, Al, etc.) and alloys. Furthermore, spatial control over the distribution of defects, such as localized irradiation using plasma processing¹⁵, can promote the selective area intercalation and of metals and/or alloys under specific regions of graphene. While the focus of this study is on P₂O₅ intercalation, the possibility of intercalation from pre-dissociated molecules catalyzed by defects in graphene may exist for other types of molecules as well. This in-depth study advances the comprehension of intercalation routes of large molecules *via* the basal plane of graphene, as well as heterointerface chemical reactions leading to the formation of distinctive confined complex oxide compounds.

Chapter 3

Light induced surface tension for hierarchical assembly of particles from liquid metals

In this chapter, light induced Marangoni flow in liquid metals (i.e., liquid-gallium) with Laguerre-gaussian (LG_{pl}) lasers as heating sources and the resulting hierarchical particle assembly was studied. We showed that by carefully engineering surface tension gradients in liquid-gallium using non-gaussian LG_{pl} lasers, the Marangoni and convective flow that developed in the fluid drove the trajectory of randomly dispersed particles to assemble into 100 μ m wide ring-shaped particle assemblies. Careful control over the parameters of the LG_{pl} laser (i.e., laser mode, spot size, and intensity of the electric field) can tune the temperature and fluid dynamics of the liquid-gallium as well as the balance of forces on the particle. This in turn can tune the structure of the ring-shaped particle assembly with a high degree of fidelity. The use of light to control the motion of particles in liquid metals represents a tunable and rapidly reconfigurable approach to spatially design surface tension gradients in fluids for more complex assembly of particles and small-scale solutes. This work can be extended to a variety of liquid-metals, complementary to what has been realized in particle assembly out of ferrofluids using magnetic fields.

This chapter is adopted from Jiayun Liang and Zakaria Al Balushi's work entitled "Light-Induced Surface Tension Gradients for Hierarchical Assembly of Particles from Liquid Metals" from reference¹⁸⁰, with permission to reproduce it in this dissertation from the co-author.

3.1 Introduction

Achieving control over the motion of particles in fluids is important to realize the high degree of perfection needed in the area-selective growth processes of nano-to-macroscale objects at the liquid-solid interface¹⁸¹⁻¹⁸⁴. An important force that must be taken into consideration in the assembly of such particles is Brownian motion¹⁸⁵⁻¹⁸⁷. One approach to reduce the impact of Brownian on particles dispersed in liquids is controlling the fluid flow near the liquid-solid interface to facilitate the precursors supply to specific areas at the interface, for example, by taking advantage of the Marangoni effect¹⁸⁸⁻¹⁸⁹. Laser heating is useful in engineering this fluid flow¹⁹⁰⁻¹⁹¹ and can be tuned through a variety of parameters, including wavelength (λ), spot size (w_o) and the profile of the electric field. This makes lasers highly accessible as rapid and reconfigurable heating sources for engineering temperature gradients in fluids. So far, the use of non-Gaussian lasers to engineer more complex temperature gradients in transparent or opaque liquids has been largely unexplored.

Herein, we modeled the light-matter interaction of laser heating sources to spatially structure surface tension gradients on liquid metals to therefore control the motion and assembly of particles *via* the Marangoni effect. In this work, Laguerre-Gaussian (LG_{pl}) lasers were utilized to engineer surface tension gradients and induced Marangoni flow. Here, p and l are radial and azimuthal index numbers for the LG_{pl} laser, respectively. The LG_{pl} lasers are selected because compared to a Gaussian laser, they operate in higher-order transverse modes which determines the intensity distribution in the cross-section of the laser beam, where higher-order transverse modes lead to a higher complexity in this intensity distribution. Therefore, LG_{pl} lasers allow for more degrees of freedom in the design of the temperature gradient and thus Marangoni flow patterns. Liquid-gallium is used as a model liquid metal because of its low melting point, high boiling point and relatively low vapor pressure over a wide temperature range¹⁹². Furthermore, liquid-gallium does not form compounds with many elements (e.g., tungsten, silicon, germanium, carbon etc., Table 3.1) and therefore useful in a variety of crystal growth processes^{110, 193-195}. In this work, a ring pattern assembly of tungsten particles out of liquid-gallium was realized by strategically choosing the radial and azimuthal index numbers as well as beam conditions for the LG_{pl} laser interacting with the surface of liquid-gallium. The assembled ring-shaped particle patterns were preferentially formed because of unique fluid flow vortices that formed within the bulk of liquid-gallium, essentially creating a “forbidden zone” of assembly. This allows one to specifically structure assembled particle features between the “coffee-ring” and “reverse coffee-ring” effects. The perfection of the assembly is quantified by assessing the entropy of these patterns, which improved with the existence of significant drag forces on the particles that could overcome Brownian motion of the particles due to Marangoni flow.

Table 3.1: Summary of elements that do not form compounds with liquid gallium stable above the energy hull cutoff¹⁹⁶⁻²⁰²

H	He	Be
B	C	Ne

Al	Si	Ar
Zn	Ge	Kr
Cd	In	Sn
Xe	W	Hg
Tl	Pb	Bi

3.2 Finite element simulation setting

3.2.1 Framework for coupling the Marangoni effect and fluid flow

In this study, liquid-gallium was placed with cylindrical boundary conditions to simplify the model and avoid the influence of surface curvature on surface tension at the two-phase interface. The steady-state Marangoni flow pattern in liquid-gallium induced by the Laguerre-Gaussian laser mode was simulated by coupling the laminar flow, heat transfer in the fluid and electromagnetic wave using a combination of finite element method solver packages (COMSOL Multiphysics®). Herein, the laminar flow in liquid-gallium was governed by the Navier-Stokes equation:

$$\rho_f \vec{v} \cdot \nabla \vec{v} = -\nabla P + \nabla \cdot \left[\mu (\nabla \vec{v} + (\nabla \vec{v})^T) - \frac{2}{3} \mu (\nabla \cdot \vec{v}) \vec{I} \right] + \rho_f \vec{g}$$

where ρ_f is the density of liquid-gallium, $\vec{v}$ is the fluid velocity, P is the pressure in liquid-gallium, μ is the viscosity of liquid-gallium, and $\vec{g}$ is the gravitational acceleration vector. The heat transfer in the fluid was coupled to the movement of the fluid by combining $\vec{v}$ and P . The heat transfer in liquid-gallium was described with the conservation of energy given by:

$$\rho_f C_p \vec{v} \cdot \nabla T + \nabla \cdot \vec{q} = Q_e + Q_p + Q_{vd}$$

$$\vec{q} = -k_T \nabla T$$

where C_p is the heat capacity and k_T is the thermal conductivity of liquid-gallium, respectively. Moreover, the temperature gradient that developed on the surface of liquid-gallium induced shear stresses at the gas-liquid interface giving rise to Marangoni flow:

$$\left(-P \vec{I} + \mu (\nabla \vec{v} + (\nabla \vec{v})^T) - \frac{2}{3} \mu (\nabla \cdot \vec{v}) \vec{I} \right) \vec{n} = k_0 \nabla_t T$$

where $\vec{v}$ is the velocity of the fluid and k_0 is the temperature coefficient of surface tension of the fluid. In the case of liquid-gallium, this k_0 is negative²⁰³.

3.2.3 Particle trajectory

Particle trajectories were simulated under steady state fluid flow. A random distribution of 2000 neutrally charged tungsten particles were consistently released in the liquid-gallium for fair comparison. The particle trajectory was simulated based on Newton's second law:

$$\frac{d(m_p \vec{u})}{dt} = \vec{F}_D + \vec{F}_B + \vec{F}_G + \vec{F}_{Bouyant}$$

where $\vec{F}_D$ is the drag force from the fluid flow, $\vec{F}_B$ is the Brownian force, $\vec{F}_G$ is the gravitational force, and $\vec{F}_{Bouyant}$ is the buoyant force. Here, the drag force from the fluid

flow ($\vec{F}_D$) was given by:

$$\vec{F}_D = \frac{m_p(\vec{u} - \vec{v})}{\tau_p}$$

where $\vec{u}$ is the velocity of particle, $\vec{v}$ is the velocity of fluid flow, and τ_p is the characteristic time for the particle. The amplitude of the Brownian force ($\vec{F}_B$) was given by²⁰⁴:

$$\vec{F}_B = \zeta \sqrt{\frac{6\pi k_B \mu T d_p}{\tau_p}}$$

where k_B is the Boltzmann constant and ζ is a vector of independent, normally distributed random numbers with zero mean and unit standard variation as indicated in COMSOL. For the sticking probability of the particles at the liquid-solid interface was set to 50% (bottom side of liquid gallium). When particle stuck on the boundary:

$$\vec{u} = \vec{0}$$

otherwise, the particle would bounce elastically back into the fluid:

$$\vec{u} = \vec{u}_c - 2(\vec{n} \cdot \vec{u}_c)\vec{n}$$

where $\vec{u}_c$ is the particle velocity when the particle approaches the boundary of the liquid gallium domain. At all other boundaries of liquid gallium, the particles would bounce back elastically. To guarantee the accuracy of the simulated particle trajectories, the time step was set to the characteristic time of the particle (τ_p , See **section 3.5**)

In our simulation model, gravitational, buoyant, Brownian, and drag forces were applied to the particles. For the boundary conditions, all particles bounced back elastically, except at the liquid-solid interface where assembly of particles could occur (bottom side of liquid-gallium). For the liquid-solid interface, a sticking probability of 50% was included in our models, otherwise the particle would be able to bounce back into the fluid elastically. To simplify the calculations, the heat transfer between particles and liquid-gallium was neglected due to the low concentration of particles in the fluid ($<10^{-15}$ mol/L). Also, the particles were not interacting with each other. All the physical parameters and the corresponding values in our simulation were summarized in Table 3.2.

Table 3.2: Parameters for finite element model²⁰⁵⁻²⁰⁶

Parameter	Physical Meaning	Value
k_0	Temperature coefficient of surface tension for liquid gallium	$-6.6 \times 10^{-5} \text{ N}/(\text{m} \cdot \text{K})$
C_p	Heat capacity for liquid gallium	$381.072862 \text{ J}/(\text{kg} \cdot \text{K})$
ρ_f	Density of liquid gallium	$5592 \text{ kg}/\text{m}^3$
ρ_p	Density of tungsten	$1930 \text{ kg}/\text{m}^3$

	particle	
k_T	Thermal conductivity of liquid gallium	$8.0844 \text{ W}/(\text{m} * \text{K})$
α_p	Thermal expansion of liquid gallium	3.0762
μ	Dynamic viscosity of liquid gallium	$0.64288 \text{ mPa} * \text{s}$
σ_f	Electric conductivity of liquid gallium	$7.1 \times 10^6 \text{ S}/\text{m}$
n_{Ga}	Real part of refractive index for liquid gallium at 645nm	$n = 1.57434 + 6.38 \times 10^{-4} * (\text{T} - 273.15)$
k_{Ga}	Imaginary part of refractive index for liquid gallium at 645nm	$k = 7.48476 + 2.46 \times 10^{-3} * (\text{T} - 273.15) + 2.18 \times 10^{-6} * (\text{T} - 273.15)^2$
ε	Emissivity of liquid gallium at 645 nm	$\varepsilon = 0.0771 + 6.852 \times 10^{-5} * \text{T}$

3.3 Laser-induced Marangoni flow in liquid gallium

To illustrate the uniqueness of using a laser to structure the surface tension gradient and therefore convective flow patterns in liquid metals, the interaction of LG_{pl} lasers ($\lambda=645\text{nm}$ and $w_o=125\mu\text{m}$, Figure 3.1) onto the surface of liquid-gallium with 2000 randomly dispersed tungsten particles with diameter (d_p) of $20\mu\text{m}$ was investigated. As illustrated in Figure 3.1a, the interaction of the laser would induce Marangoni flow for the hierarchical assembly of these randomly dispersed particles at the liquid-solid interface.

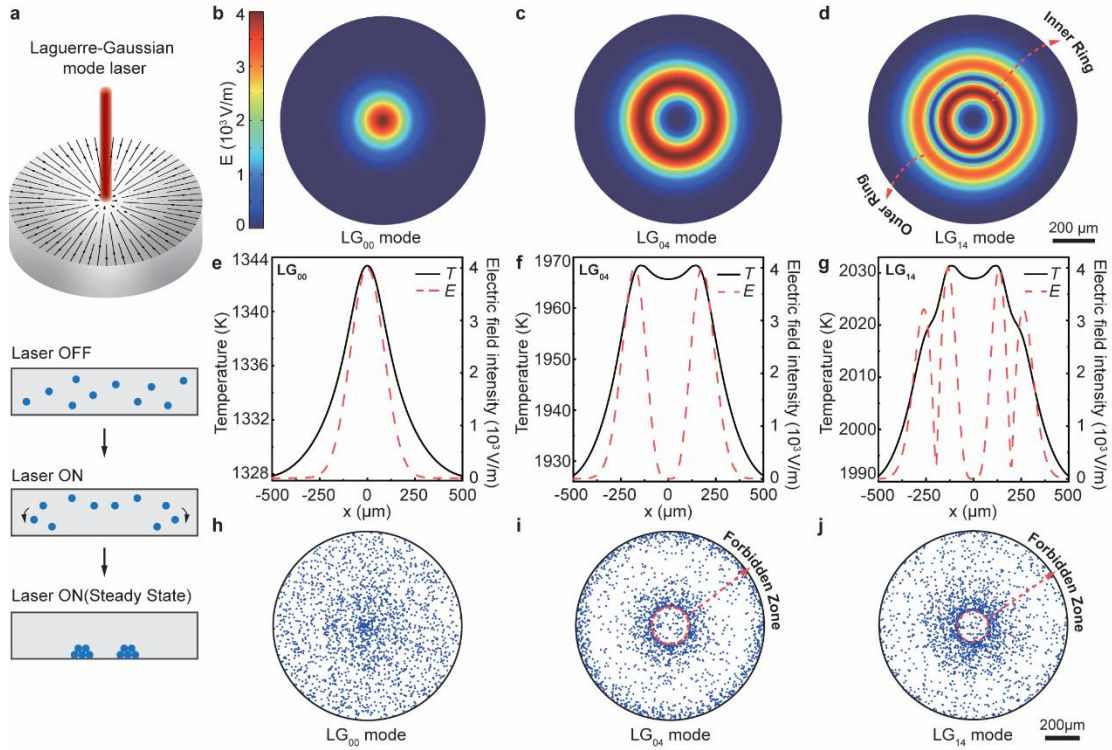


Figure 3.1: Electric field profiles, temperature profiles and resulting particle patterns assembled out of liquid-gallium under different Laguerre-Gaussian (LG_{pl}) laser modes. (a) Schematic highlighting the process of assembling particles out of liquid-gallium using a LG_{pl} lasers (laser wavelength, $\lambda=645\text{nm}$ and $w_o=125\mu\text{m}$). When LG_{pl} lasers interacted with liquid-gallium, Marangoni flow developed, guiding randomly dispersed tungsten particles (diameter, $d_p=20\mu\text{m}$) to assemble at the liquid-solid interface. (b to d) Profile of the electric field on the surface of liquid-gallium under (b) LG_{00} , (c) LG_{04} , and (d) LG_{14} lasers, respectively. An inner and outer ring were observed in the doughnut-shaped electric field profile for (d) LG_{14} laser, as highlighted by two *dashed red arrows*. The scale bar for all the electric field profiles is $200\mu\text{m}$. (e to g) Profiles of the electric field (*dashed red lines*) and temperature (*solid black lines*) on the surface of liquid-gallium. (h to j) Resulting particle patterns at the liquid-solid interface for (h) LG_{00} , (i) LG_{04} , and (j) LG_{14} lasers interacting with liquid-gallium. The ring-shaped particle patterns were obtained with (i) LG_{04} , and (j) LG_{14} laser modes only, creating a “forbidden zone” of assembly, where tungsten particles did not gather which is highlighted by *dashed red lines*. The scale bar for all particle patterns is $200\mu\text{m}$.

To reveal the relationship between the LG_{pl} laser and the Marangoni flow, three different LG_{pl} lasers (i.e., LG_{00} , LG_{04} , and LG_{14}) were investigated. The electric field distribution (E) on the surface of the liquid-gallium was shown in Figure 3.1, b to d. Unlike the Gaussian distribution of the electric field with the LG_{00} laser (Figure 3.1b), the electric field distribution of the LG_{04} and LG_{14} lasers were doughnut-shaped (Figure 3.1, c and d, respectively). That is, the peak intensity of the electric field was not at the center of the surface of liquid-gallium (Figure 3.1, e to g, *dashed red lines*). Unlike the single electric field ring maximum in the LG_{04} laser seen in Figure 3.1c, the LG_{14} laser contained two ring maxima in the electric field distribution over the surface of liquid-gallium. These rings

were labeled as “inner” and “outer” rings in Figure 3.1d (*dashed red arrows*). The interaction of these lasers with liquid-gallium led to electromagnetic heating of the surface. The surface temperature profiles of liquid-gallium due to the interaction of these three LG_{pl} lasers were also illustrated in Figure 3.1, e to g. Since the intensity of the electromagnetic heating was proportional to the square of the strength of the electric field, the surface temperature profiles of liquid-gallium were composed of single (Figure 3.1e), double (Figure 3.1f), and quad (Figure 3.1g) temperature maxima for the LG_{00} , LG_{04} , and LG_{14} lasers, respectively. Though the maximum intensity values of the electric field were equal for the LG_{00} , LG_{04} , and LG_{14} lasers ($4 \times 10^3 \text{ V/m}$), due to the variation in the electric field distribution between these three lasers, the amount of electromagnetic heating and therefore resulting temperature maxima of liquid-gallium using each laser differed. This strong dependance of the electromagnetic heating of liquid-gallium on the electric field of the laser highlights the ability to engineer a variety of unique temperature gradients in liquid-gallium with a high degree of versatility.

Moreover, the temperature gradient that developed on the surface of liquid-gallium induced shear stresses at the gas-liquid interface giving rise to Marangoni flow. Over time, the randomly dispersed tungsten particles picked up drag forces and followed the convective flow streamlines within the bulk of the liquid-gallium. Finally, these particles assembled at the liquid-solid interface into a variety of patterns which depended on the conditions of the LG_{pl} laser. The resulting particle patterns were highlighted in Figure 3.1, h to j. Figure 3.1h showed randomly distributed tungsten particles across the solid surface when the LG_{00} laser was used as a heating source. However, when the LG_{04} , and LG_{14} lasers were utilized, ring-shaped particle patterns were assembled out of the liquid-solid interface as shown in Figure 3.1i and 3.1j for the LG_{04} , and LG_{14} lasers, respectively. The use of the LG_{04} , and LG_{14} lasers essentially created regions where particles could not assemble on the solid surface. These regions were referred to as the “forbidden zone” which formed due to unique vortices that developed within the flow pattern in the bulk of liquid-gallium.

3.4 Influence of laser-induced Marangoni flow on Brownian and particle assembly

The pattern of the assembled particles observed in Figure 3.1, h to j were highly dependent on the electric field distribution and the consequentially developed surface tension gradients when the LG_{00} (Figure 3.2a), LG_{04} (Figure 3.2b), and LG_{14} (Figure 3.2c) lasers interacted with the surface of liquid-gallium. To understand the origin of the “forbidden zone”, the Marangoni and resulting convective flow patterns within the depth of liquid-gallium, as a function of the laser, were investigated (Figure 3.2, d to f). Fluid flow induced by the LG_{00} laser (Figure 3.2d) led to the formation of two vortices, allowing liquid-gallium to recirculate from the center to the periphery of the bulk. However, the formation of two additional vortices within the center of the convective flow pattern (i.e., “central vortices”) were prominent when the LG_{04} (Figure 3.2e) and LG_{14} (Figure 3.2f) lasers interacted with liquid-gallium. A substantial enhancement in the velocity of the fluid could also be seen in Figure 3.2e and f. This enhanced fluid velocity would strongly dictate the trajectory of the particles dispersed in the fluid. This was evident in Figure 3.3, a to c, which highlighted the mean-squared displacement (MSD), for particles moving near the surface of liquid-gallium ($|z| \leq 10\mu\text{m}$) as a function of the LG_{pl} laser.

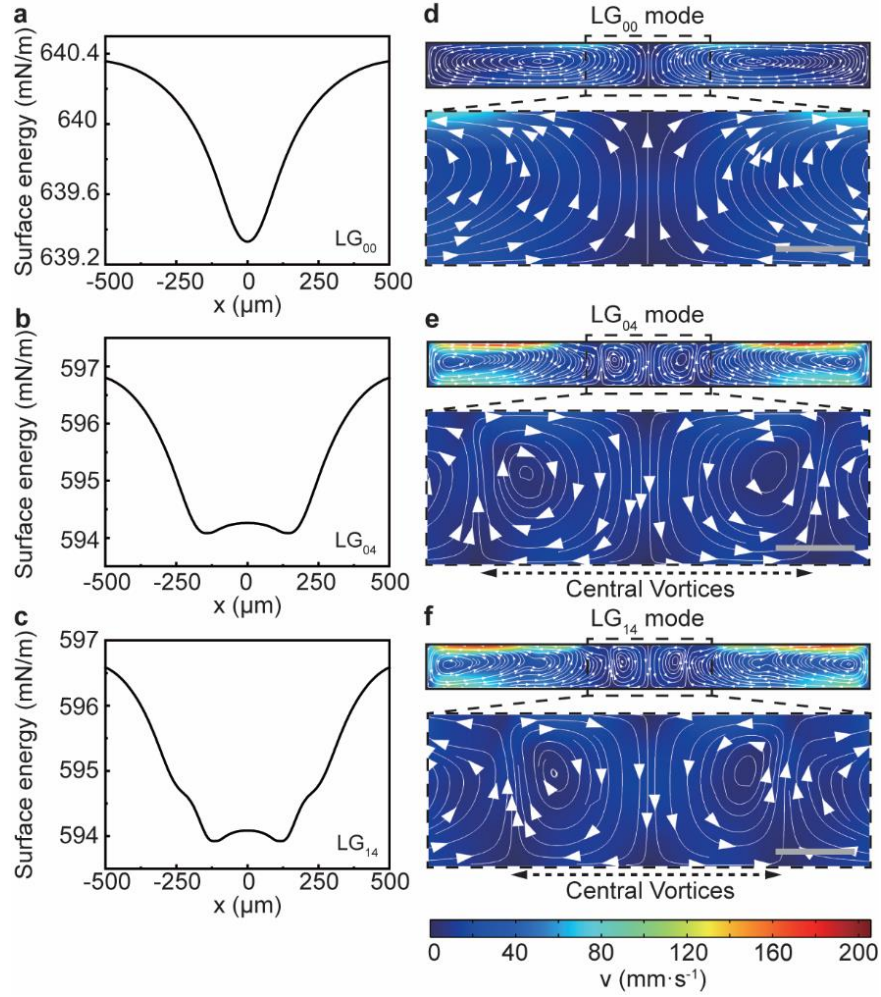


Figure 3.2: Influence of surface tension gradients of liquid-gallium on the particle motion in the bulk fluid. (a to c) Surface tension profiles of liquid-gallium along the x-axis for (a) LG_{00} , (b) LG_{04} , and (c) LG_{14} lasers ($\lambda=645\text{nm}$ and $w_0=125\mu\text{m}$). (d to f) Convective flow patterns induced by the surface tension gradient (i.e., Marangoni flow) for (d) LG_{00} , (e) LG_{04} , and (f) LG_{14} lasers. For (e) LG_{04} , and (f) LG_{14} lasers, two additional central vortices were observed in the convective flow patterns in the fluid, as highlighted by *dashed black lines* under the magnified regions (scale bars are $50\mu\text{m}$). The absolute value of the fluid velocity is indicated by the color bar at the bottom.

The mean-squared displacement ($MSD(\tau_p)$) for the particle trajectory was given by:

$$MSD(\tau_p) = \langle [\vec{r}(t + \tau_p) - \vec{r}(t)]^2 \rangle$$

where $\vec{r}$ is the position of the particle at time t and τ_p is the time step for the simulation. For all the datasets presented in Figure 3.3, the time step was set as the characteristic time of the particle, i.e., for $20\mu\text{m}$ -diameter tungsten particles, τ_p is $6.72 \times 10^{-4}\text{s}$. The corresponding xz trajectory of the particles was also included as insets in Figure 3.3, a to c. In the case of the LG_{04} (Figure 3.3b) and LG_{14} (Figure 3.3c) lasers, the peak of the MSD shifted further away from the center of liquid-gallium compared to the LG_{00} laser (Figure 3.3a). Since the values of the MSD reflected the dynamics of the surrounding fluid, the

emergence of these new “central vortices” with outward flow would ultimately play a key role in preventing particles from remaining at the center of the fluid.

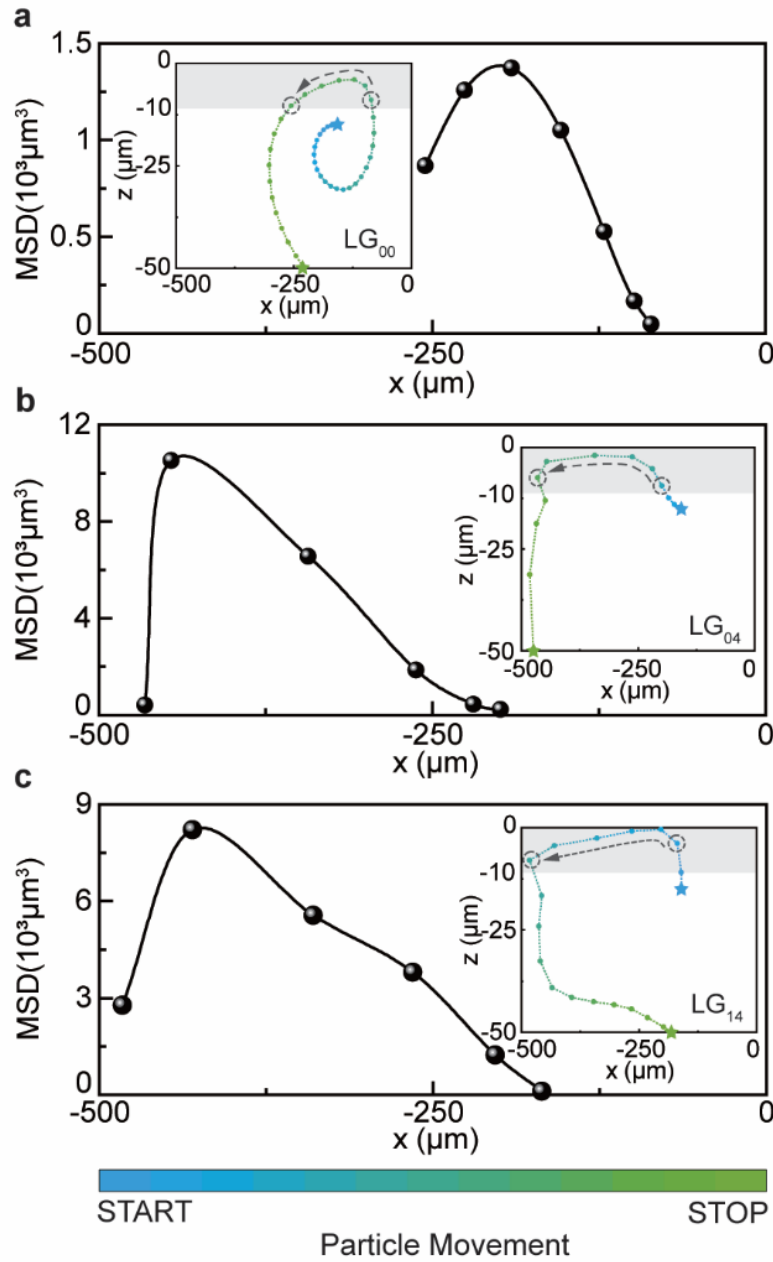


Figure 3.3: The mean-squared displacement (MSD) versus radial position (r) of for particles under different laser mode. (a) LG_{00} , (b) LG_{04} , and (c) LG_{14} lasers ($\lambda = 645\text{nm}$ and $w_o = 125\mu\text{m}$) when the particle moved near the top surface of liquid-gallium ($|z| \leq 10\mu\text{m}$, shaded gray background). The insets in (a, b, and c) are the particle trajectories (blue-to-green gradient) guided by the fluid flow induced under the (a) LG_{00} , (b) LG_{04} , and (c) LG_{14} laser modes, respectively. All particles were released at the same position in the fluid (blue star) and finally assembled at the liquid-solid interface (green star).

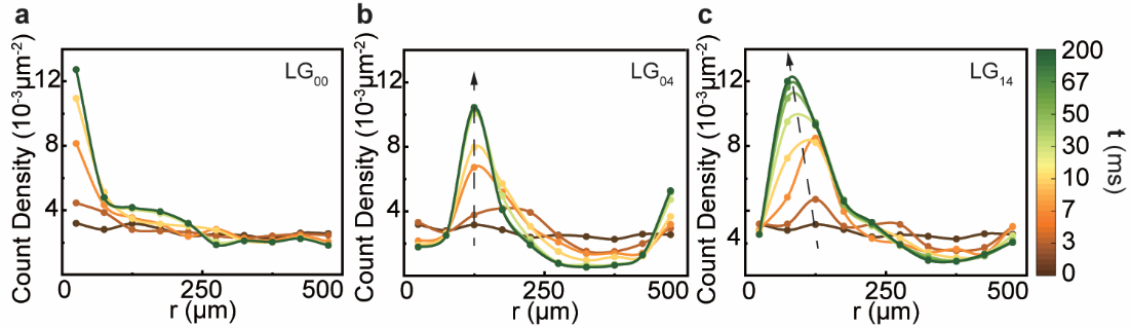


Figure 3.4: Impact of the laser mode on the particle pattern assembled out of liquid-gallium. (a, b, and c) Time dependent radial (r) particle count density for 2000 randomly released tungsten particles ($d_p = 20\mu\text{m}$) in liquid-gallium guided by the convective flow induced by (a) LG_{00} , (b) LG_{04} , and (c) LG_{14} lasers ($\lambda = 645\text{nm}$ and $w_o = 125\mu\text{m}$). All 2000 particles were released at $t = 0\text{s}$ and all settled at the liquid-solid interface at $t = 0.2\text{s}$. The width of the radial bin for the particle count density profiles was set to $50\mu\text{m}$.

The spatial extent of the “central vortices”, and therefore the “forbidden zone”, was smaller in the LG_{14} laser compared to that in the LG_{04} laser. This was due to the existence of the “inner” and “outer” rings in the electric field distribution as alluded to in Figure 3.1d. More broadly, the influence of the “central vortices” on the spatial extent of the “forbidden zone” can be further supported by assessing the time dependence of the radial (r) particle count density of 2000 randomly released tungsten particles ($d_p = 20\mu\text{m}$, Figure 3.4, a to c). When particles were initially released ($t = 0\text{s}$), the particle count density across the radial direction of the liquid-solid interface were very close to each other, oscillating around $3.15 \times 10^{-3} \mu\text{m}^{-2}$ with a mean-squared error of $0.27 \times 10^{-3} \mu\text{m}^{-2}$. Over time, the particle count density at $r \leq 50\mu\text{m}$ in LG_{00} increased (Figure 3.4a), while in LG_{04} and LG_{14} it decreased (Figure 3.4, b and c). At $t = 0.2\text{s}$, the particle count density for the LG_{14} laser around the central region of the liquid-solid interface was $2.55 \times 10^{-3} \mu\text{m}^{-2}$ (Figure 3.4c, *solid green line*), which was an 80% reduction in the particle count density when compared to the LG_{00} laser ($12.73 \times 10^{-3} \mu\text{m}^{-2}$, Figure 3.4a, *solid green line*). Also, as time increased, the peaks in the particle count density also increased (Figure 3.4, b and c, *dashed black arrows*). The peak positions for the LG_{04} and LG_{14} lasers, were at $r = 125\mu\text{m}$ and $75\mu\text{m}$ from the center of the liquid-solid interface, respectively. This elucidated why a smaller diameter in the “forbidden zone” was observed in the LG_{14} laser when compared to LG_{04} laser (Figure 3.1, i and j, respectively). Therefore, the existence of ring features in the electric field distribution in the LG_{pl} laser allows one to spatially control the extent of the central vortices, and by controlling other parameters of the laser beam itself could further tune the extent of the “forbidden zone”.

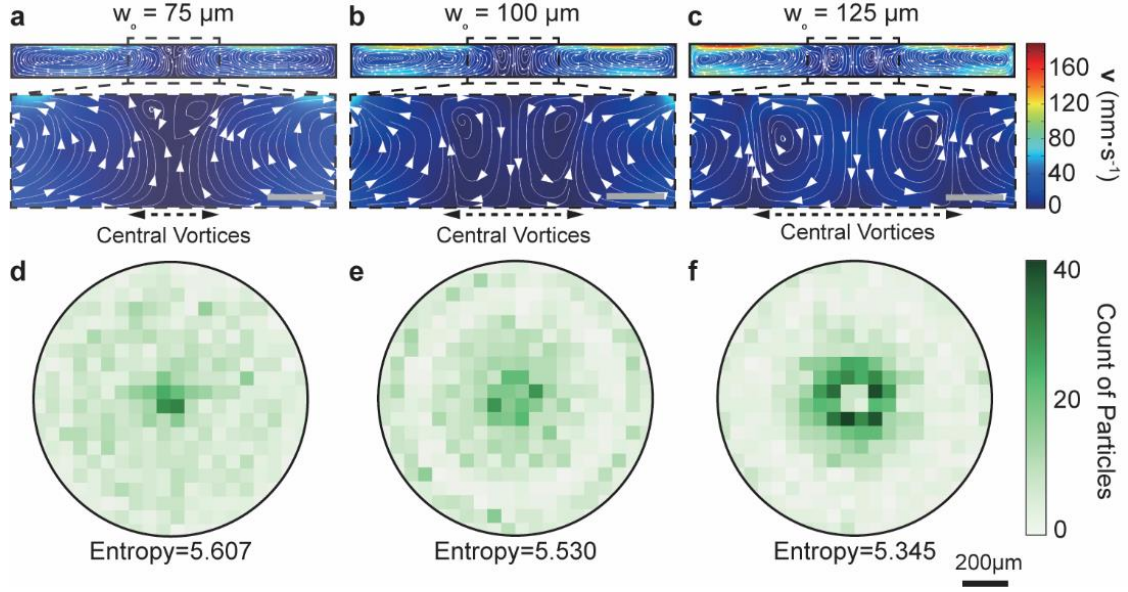


Figure 3.5: Impact of the laser spot size on the particle pattern assembled out of liquid-gallium. (a to c) Fluid flow pattern in liquid-gallium under LG_{14} laser with the spot size of (a) 75μm, (b) 100μm, and (c) 125μm. Two additional “central vortices” are magnified for clarity (scale bar is 50 μm). The absolute value of the fluid velocity is indicated by the color bar (*red-to-blue gradient*) on the right. (d to f) Density distribution maps (bin size = 50μm) and corresponding entropy values for particle patterns induced by fluid flow under the LG_{14} laser with a spot size (w_o) of (d) 75μm, (e) 100μm, and (f) 125μm. The scale bar for all density distribution maps is 200μm.

Moreover, the significance of the central vortices on particle assembly at the liquid-solid interface was further corroborated by investigating the effect of the LG_{14} laser spot size (w_o) on fluid flow. Evident in Figure 3.5a was the fluid flow that results from the interaction of a 75μm LG_{14} laser with liquid-gallium. At this spot size, the spatial extent of the central vortices in the fluid was rather negligible. However, as the w_o increased to 100μm (Figure 3.5b) and 125μm (Figure 3.5c), the appearance of the “central vortices” was substantial, which increased in extent with increasing w_o . The absence of a fully developed central vortex in Figure 3.5a allowed for particles to freely circulate at the center of the liquid. In this case, particles that would assemble out of the liquid-solid interface would have a lower degree of order from the particle density maps as a function of w_o (Figure 3.5, d to f). To highlight this, we introduced the concept of entropy to quantify this degree of order from the particle density maps. To calculate the entropy for different particle assemblies, we equally divided the particle pattern into $(\frac{1000}{n})^2$ square lattices (i.e., “bin”) of size n and counted the number of particles in each bin. Here, the entropy for the patterns was defined as:

$$S = - \sum_{i=1}^{\left(\frac{1000}{n}\right)^2} \frac{N_i}{2000} \ln \frac{N_i}{2000} \quad (1)$$

where N_i is the number of particles in the i^{th} bin. To test the reproducibility of our calculations, we repeated each simulation 10 times and compared the entropy for the particle assembly obtained in different runs. A series of bin sizes were utilized for entropy calculation to avoid the impact of the bin size on the entropy results. As shown in Figure 3.6, no matter the size of the bin utilized, the relative entropy difference was less than 0.8% and the mean squared error was less than 0.6%, supporting the reproducibility of our calculations.

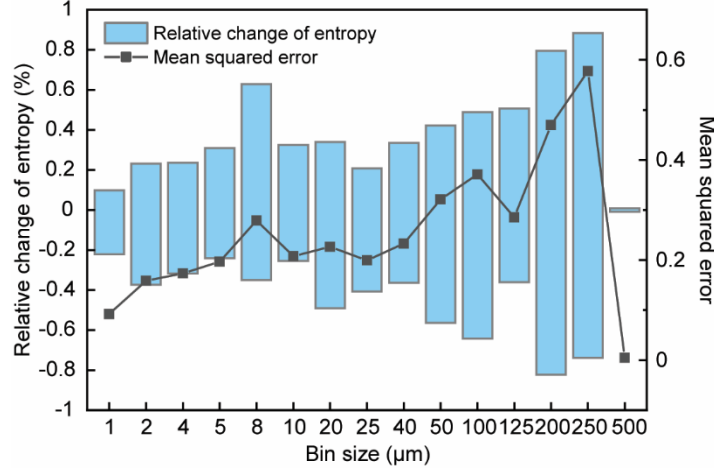


Figure 3.6: Statistical analysis of the entropy calculations. Relative change of entropy (left y-axis, blue box) and mean squared error of entropy (right y-axis, black solid line) for the particle assembly obtained in 10 repeated runs.

A decrease in the value of entropy alludes to a higher degree of order in the particle distribution maps. As the w_o increased from $75\mu\text{m}$, to $100\mu\text{m}$ and to $125\mu\text{m}$, the value of entropy was reduced from 5.607, 5.530 and 5.345, respectively (Figure 3.5, d to f). This means that the $125\mu\text{m}$ w_o for the LG_{14} laser had the highest degree of order as reflected in the well-defined ring feature of the assembled particles seen in the distribution map in Figure 3.5f. Interestingly, it can be observed that 54.2% of the particles preferred to gather around the “forbidden zone” of the solid surface. This was because as the w_o increased, the fully developed central vortices repelled particles from entering the central region of the fluid. This showed that the drag forces on the particle can significantly overcome Brownian forces to assemble patterns with a high degree of order.

3.2.2 Laser heating setup and conditions

The major heating source is by electromagnetic heating which was given by:

$$Q_e = \frac{1}{2} \text{Re}(\vec{J} \cdot \vec{E}^*) = \frac{1}{2} \text{Re}(\sigma_f \vec{E} \cdot \vec{E}^*)$$

where σ_f is the electrical conductivity and J is the current density of the liquid-gallium. In our models, the electromagnetic sources were three different Laguerre-Gaussian laser modes (i.e., LG_{00} , LG_{04} , and LG_{14} laser modes, propagating in the z-direction) which were

described by:

$$E_{p,l}(r, z) = E_{0p,l}(r, z) \frac{1}{\sqrt{1 + \frac{z^2}{z_0^2}}} \exp \left[-\frac{r^2}{w_0^2(1 + \frac{z^2}{z_0^2})} - ikz - ik \frac{r^2}{2z(1 + \frac{z_0^2}{z^2})} + i \arctan\left(\frac{z}{z_0}\right) \right]$$

where z_0 is the Rayleigh range of the laser and $E_{0p,l}(r, z)$ is the amplitude for the electric field distribution of the LG_{pl} laser mode.

For LG_{00} laser mode:

$$E_{00,0}(r, z) = E_0$$

For LG_{04} laser mode:

$$E_{00,4}(r, z) = E_0 \times \left[\frac{\sqrt{2}r}{w(z)} \right]^4 \times \exp \left[4 \times \left(i\phi + i \arctan\left(\frac{z}{z_0}\right) \right) \right]$$

For LG_{14} laser mode:

$$E_{01,4}(r, z) = E_0 \times \left(\frac{\sqrt{2}r}{w(z)} \right)^4 \times \left[5 - \frac{2r^2}{w^2(z)} \right] \times \exp \left[4 \times i\phi + 6 \times i \arctan\left(\frac{z}{z_0}\right) \right]$$

$$w(z) = w_0 \sqrt{1 + \frac{z^2}{z_0^2}}$$

$$\phi = \text{atan2}\left(\frac{y}{x}\right)$$

Furthermore, the work done by pressure change in liquid-gallium (Q_p) was given by:

$$Q_p = \alpha_p T \vec{v} \cdot \nabla P$$

where, α_p is the coefficient of thermal expansion of liquid gallium. The viscous dissipation in liquid gallium (Q_{vd}) was given by:

$$Q_{vd} = \tau : \nabla \vec{v}$$

where τ is the viscous tensor. At the boundary of liquid-gallium, radiation heating from the liquid-gallium to ambient (air) is taken into consideration. The net outward radiative flux ($q_{r,net}$) was given by:

$$q_{r,net} = \varepsilon(e_b(T) - G) = \varepsilon(n^2 \sigma T^4 - G)$$

$$\vec{n} \cdot \vec{q} = q_{r,net}$$

where ε and n are the emissivity and refractive index of liquid-gallium at 645nm, respectively. σ is the Stefan–Boltzmann constant and G is the total incoming radiative flux. $\vec{n}$ is the unit normal vector.

3.5 Investigating the interacting forces impacting particle assembly

To gain a deeper understanding on how particles gathered around the periphery of the “forbidden zone” when the LG_{14} laser ($w_0 = 125\mu\text{m}$) was utilized, the interacting forces on the moving particles in the fluid were investigated. Evidently, the synergy between the Marangoni flow and the effective gravitational force on the particle was responsible in driving the formation of the ring-shaped patterns. This effective gravitational force (G_{eff}) was given by:

$$G_{eff} = G_p - F_{buoyant} = \frac{\pi}{6}(\rho_p - \rho_f)gd_p^3$$

where G_p , $F_{buoyant}$ and d_p are the gravitational force, the buoyant force, and the diameter of the particle, respectively. Since the density of the tungsten particle (ρ_p) is higher than that of the fluid (ρ_f), the direction of the G_{eff} points vertically downwards. The drag force (F_D) from the Marangoni flow and/or convective flow around the particle was given by:

$$\vec{F}_D = \frac{m_p(\vec{u} - \vec{v})}{\tau_p}$$

where $\vec{u}$ is the velocity of particle, $\vec{v}$ is the velocity of fluid flow. The characteristic time for the particle (τ_p) was expressed by:

$$\tau_p = \frac{4\rho_p d_p^2}{3\mu C_D Re_r}$$

where μ is the dynamic viscosity of liquid gallium and Re_r is the relative Reynolds number of particles in the flow. C_D is the drag coefficient coupling the velocity of a particle to the surrounding fluid velocity. Relative Reynolds number (Re_r) was calculated with:

$$Re_r = \frac{|\vec{u} - \vec{v}|d_p\rho_f}{\mu}$$

And the relationship between C_D and Re_r is:

$$\begin{cases} C_D = \frac{24}{Re_r}, & Re_r < 1 \text{ (Stokes model)} \\ C_D = \frac{24}{Re_r}(1 + 0.15Re_r^{0.687}) & 1 < Re_r < 1000 \text{ (Schiller – Naumann model)} \end{cases}$$

Considering the Re_r was less than 1 for most of the time steps in our simulations, if not otherwise specified, results shown in this work was simulated with drag coefficient derived from Stokes law ($C_D = \frac{24}{Re_r}$). And the characteristic time for the 20 μm and 5 μm tungsten particles is $6.72 \times 10^{-4}\text{s}$ and $4.2 \times 10^{-4}\text{s}$, respectively.

The motion of a representative particle moving through the fluid could be seen in Figure 3.7a with magnified snapshots of this motion with the interacting G_{eff} and F_D forces superimposed in Figure 3.7, b to d. In Figure 3.7a, the particle picked up drag forces near the surface due to the Marangoni flow. However, before it reached the sidewalls (Figure 3.7b), it moved downwards due to the gravitational force. The particle then continued to be guided by the convective flow of the fluid while slowly nearing the bottom of the liquid-solid interface (Figure 3.7c). The velocity of the fluid approached zero near the boundary of the “forbidden zone” because the sum of fluid flow directions cancelled each other out (Figure 3.7d). Hence, when particles approached this boundary, the gravitational force on the particle dominated its trajectory. As a result, the particle slowly settled around the periphery of the “forbidden zone”, forming the well-defined ring-shaped pattern seen in Figure 3.5f.

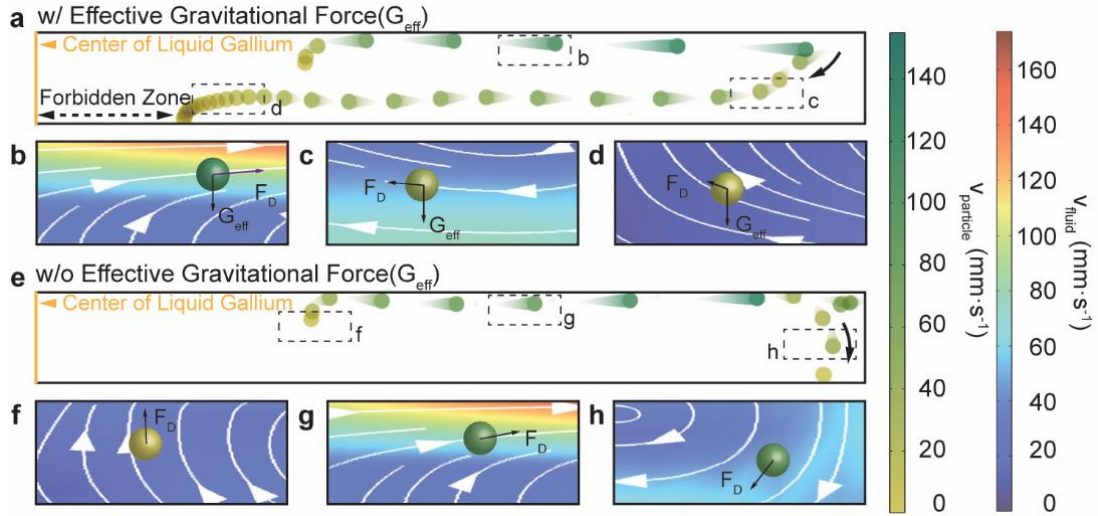


Figure 3.7: Mechanism for the formation of ring-shaped particle patterns in liquid-gallium under the LG_{14} laser. (a) Trajectory of a representative particle with effective gravitational force. The particle started near the top surface and settled at the liquid-solid interface (bottom surface). For simplification, only half of the liquid-gallium fluid flow is shown, where the center of liquid-gallium is marked by a *solid yellow line*. The width of the “forbidden zone” is marked by a *double headed dashed black arrow*. (b to d) Highlight the forces exerted on the particle when it: (b) moved along the top surface of liquid-gallium, (c) moved towards the liquid-solid interface and (d) before it settled at the liquid-solid interface. The direction of the drag forces (F_D) and the effective gravitational force (G_{eff}) are shown on the particle (*solid black arrows*). The background of the fluid velocity with superimposed streamlines illustrates the fluid dynamics of liquid-gallium in the magnified regions. (e) Trajectory of a representative particle without effective gravitational force. Particle started near the top surface and settled near the periphery of the liquid-gallium boundary. (f to h) Highlight the forces exerted on the particle when it: (f) initially was released into the fluid, (g) moved along the top surface of liquid-gallium, and (h) before it settled around the periphery of the liquid-gallium boundary. The absolute values of the fluid velocity (*red-to-blue gradient*) and particle velocity (*green-to-yellow gradient*) are indicated by the color bars on the right side of the figure.

To further elucidate the role of the gravitational force on the particle pattern formation, a comparative study on the motion of the particles without effective gravitational forces ($G_{eff} = 0$) was performed. As seen in Figure 3.7e, when a particle initially picked up the drag force due to the Marangoni flow (Figure 3.7f), it continued to be guided by the fluid flow near the surface until it neared the sidewalls of the liquid-gallium (Figure 3.7g). There the particle had a much higher probability to strike the sidewall because of the absence of gravitational forces. Due to the boundary conditions set in this model, this particle would ultimately bounce off the sidewall back into the fluid (See **section 3.2.3**). The particle then continued to be guided by the recirculating convective flow pattern of the fluid (Figure 3.7h), finally settling at the liquid-solid interface around the sidewall boundaries.

Moreover, the influence of the sidewall boundary conditions on the particle motion and particle pattern formation at the liquid-solid interface was also investigated. Despite setting the sticking coefficient of the sidewalls to unity (i.e., all particles that strike the sidewall will stick), remanence of a ring-shaped particle pattern was still observed for particles with diameter of $20\mu\text{m}$ (Figure 3.8a). More importantly, when the particle diameter was reduced to $5\mu\text{m}$, less particles struck the sidewalls, giving rise to a more well-defined ring-shaped pattern (Figure 3.8b). This was because the probability of impacting the side wall was reduced with decreasing particle size. A particle can only interact with the sidewall when the distance between the particle and the sidewall is no more than the radius of the particle itself. Based on this assumption, the probability for the particle-sidewall interaction (P_0) with different particle size can be given by:

$$P_0 = \frac{\pi(d_f^2 - (d_f - d_p)^2)}{\pi d_f^2} = \frac{2d_f d_p - d_p^2}{d_f^2} \quad (2)$$

where d_f is the diameter of the liquid gallium ($1000\mu\text{m}$ in our model). The probability of the particle-sidewall interaction for $20\mu\text{m}$ diameter particles was 3.96% while for $5\mu\text{m}$ diameter particles, the probability dropped down to 0.998%. Therefore, these results clearly demonstrated that the gravitational force on the particles reduced the particle-sidewall interaction, promoting the formation of a ring-shaped pattern assembly, where the degree of order for the pattern can be further improved through careful tuning of the parameters of the laser itself.

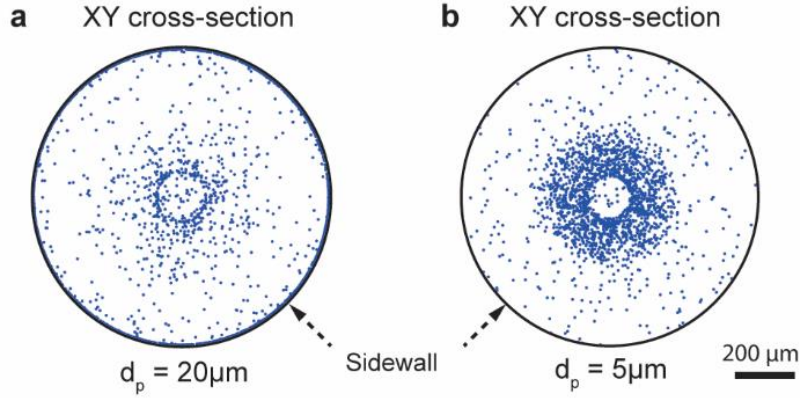


Figure 3.8: XY cross-section of the particle assembly with the sticking coefficient of the sidewalls set to unity (LG_{14} laser mode and $w_0 = 125\mu\text{m}$). The diameter of the particles (d_p) were: (a) $25\mu\text{m}$, and (b) $5\mu\text{m}$, respectively. The sidewall is marked with *solid black line* and highlighted with a *dashed black arrow*. The scale bar for the particle pattern is $200\mu\text{m}$.

3.6 Tunable laser parameters for particle assembly

Our results showed that LG_{pl} lasers could be effectively used to engineer the temperature and surface tension of liquid metals to create unique Marangoni flow patterns in the fluid. Although only a ring-shaped pattern assembly was demonstrated in this study, the use of non-Gaussian lasers could more broadly be a simple yet powerful approach to realize hierarchical assembly of particles and other small-scale solutes from liquid metals through appropriate scaling and laser parameter tuning. Therefore, in Figure 3.9, a to d, we summarized what were deemed the most important and tunable parameters of LG_{pl} lasers to design ring-shaped particle assemblies with varying degrees of order. In Figure 3.9a, the influence of the LG_{pl} lasers on the entropy of the ring-shaped pattern were highlighted. These results showed that regardless of the bin size applied to calculate the particle density maps per LG_{pl} laser (Figure 3.9a, inset), the LG_{14} laser led to particle assemblies with the lowest entropy values when compared to the LG_{00} and LG_{04} lasers. Also, as evident in Figure 3.9b, enlarging the w_0 of the LG_{14} laser mode was beneficial in improving the degree of order in the ring-shaped pattern assembly independent of the bin size used to calculate the entropy.

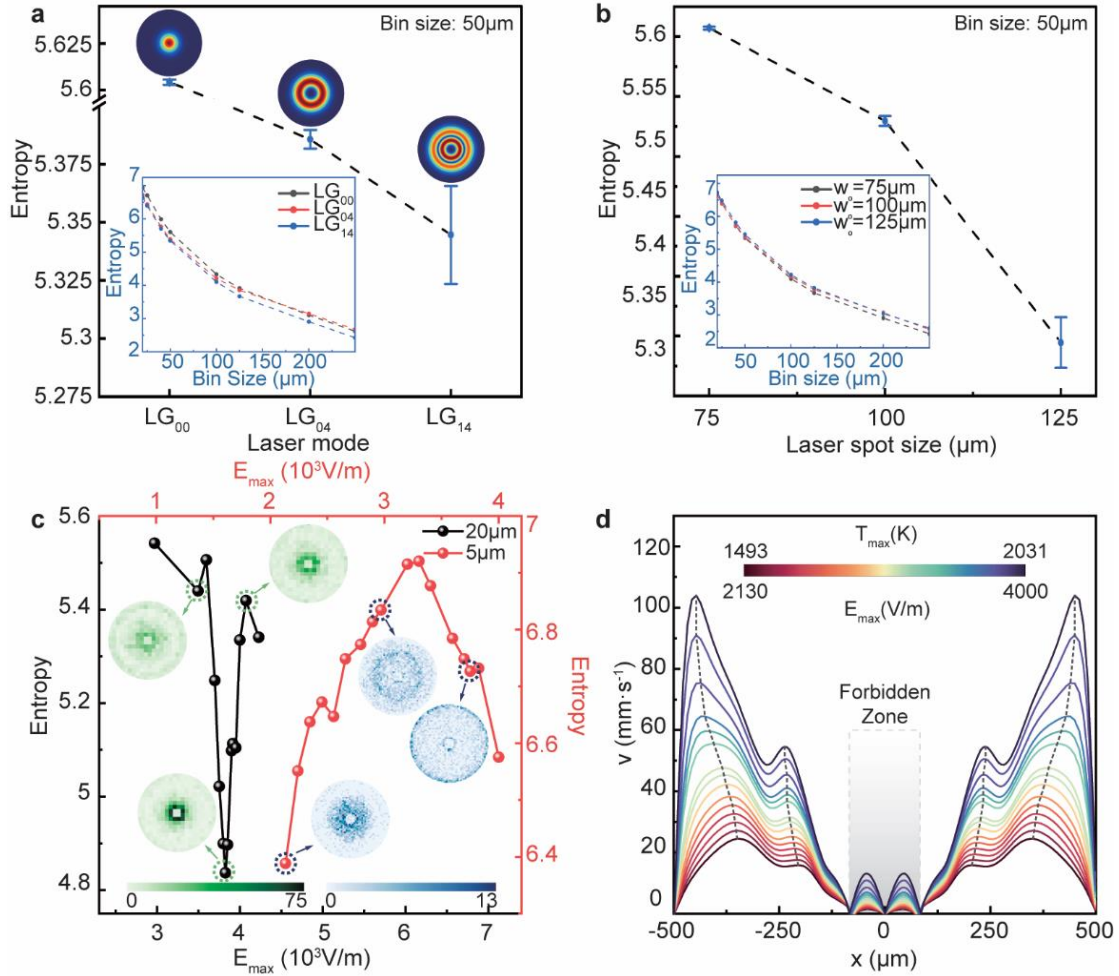


Figure 3.9: Summary of the tuning knobs of LG_{pl} lasers to obtain ring-shaped pattern with different degrees of order. (a) Impact of LG_{pl} lasers: entropy of particle patterns ($d_p = 20\mu m$) under different LG_{pl} lasers (LG_{00} , LG_{04} , and LG_{14} , $w_0 = 125\mu m$, and $E_{max} = 4000V/m$). The bin size for the calculation of entropy is $50\mu m$. The entropy as a function of the bin sizes was also shown in the inset. (b) Impact of LG_{pl} laser spot size: entropy of particle patterns ($d_p = 20\mu m$) under LG_{14} laser ($E_{max} = 4000V/m$) with spot size of $75\mu m$, $100\mu m$, and $125\mu m$. Bin size for the calculation of entropy is $50\mu m$. The entropy values at different bin sizes were also shown in the inset. (c) Impact of maximum intensity value of the electric field: entropy of particle patterns under different E_{max} values (LG_{14} laser and $w_0 = 125\mu m$). The bin size for the calculation of entropy is $50\mu m$ for $20\mu m$ diameter particles (solid black line), and the bin size is $20\mu m$ for $5\mu m$ diameter particles (solid red line). Corresponding density distribution maps for selected data points (dashed circles in (c)) are shown. The count of particles in each square grid is indicated by the color bar at the bottom (green-to-white gradient for $20\mu m$ diameter particles, and blue-to-white gradient for $5\mu m$ diameter particles). (d) Fluid velocity profile along the solid-liquid interface under E_{max} values. The velocity peaks are marked by dashed black lines. The region of the "forbidden zone" is highlighted in a shaded grey region. E_{max} and temperature maxima (T_{max}) in the liquid-gallium are indicated by the top color bar.

Another important parameter that could be controlled in the laser was the maximum

intensity value of the electric field (E_{max}). This allows one to tune the electromagnetic heating of the surface of liquid-gallium. This was highlighted in Figure 3.9c for both 20 μm (*solid black line*) and 5 μm (*solid red line*) particle sizes that assembled out of the liquid-gallium using a LG_{14} laser. The resulting particle density maps that were shown as insets in Figure 3.9c contained the same number of particles for each electric field condition. For the case of the 20 μm particle size, the entropy values were larger at lower values of the electric field. This was due to the reduced velocity and temperature of the fluid, and therefore drag forces on these 20 μm particles. Interestingly, when increasing the electric field, the entropy values of the ring-shaped particle assembly first decreased to a minimum and then rapidly increased. To quantify the enhancement of the degree of the order, we set the entropy for a completely random particle assembly composed of 2000 tungsten particles as the reference value (S_{ref}). In a completely random particle assembly, the possibility for a particle to assemble at different positions is the same. Therefore, with a 50 μm bin size, the entropy for a completely random particle assembly was given by:

$$S_{ref} = - \sum_{i=1}^{400} \frac{5}{2000} \ln \frac{5}{2000} = 5.9915 \quad (3)$$

Therefore, the reduction in entropy (ΔS) was given by:

$$\Delta S = \frac{S_{ref} - S_{assembly}}{S_{ref}} \quad (4)$$

where $S_{assembly}$ is the entropy for the specific particle assembly of interest. S_{ref} and $S_{assembly}$ were calculated with the same bin size. The reduction in entropy at the entropy minimum for these 20 μm particles, 19.26% from randomly distributed particles, stood for the highest degree of order in the ring-shaped particle assembly seen for 20 μm particles using a LG_{14} laser. As evident in the particle density map at $E_{max} = 3825\text{V/m}$ (Figure 3.9c, *green map* inset), 70.1% of the particles gathered around the “forbidden zone” which led to this high degree of order and more detailed particle maps were included in Figure 3.10. No matter the bin size used for the calculation of entropy, the highest degree of order in the ring-shaped particle assembly was always achieved at $E_{max} = 3825\text{V/m}$ (Figure 3.11a).

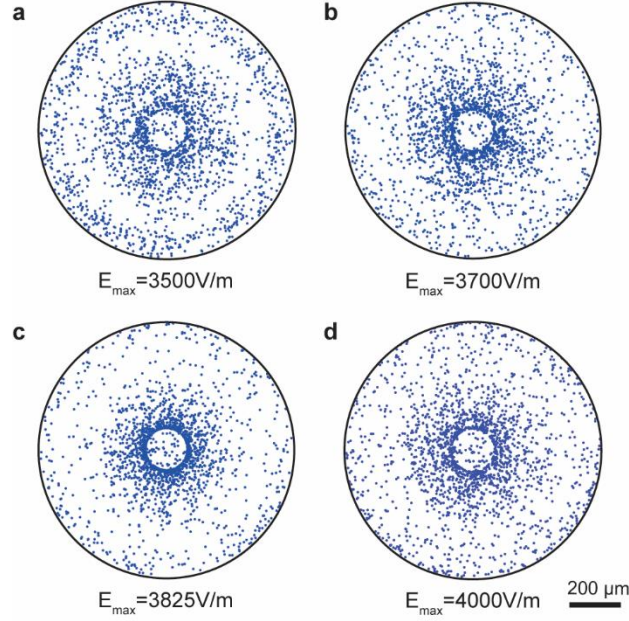


Figure 3.10: Particle patterns under different maximum intensity value of the electric field (E_{max}) for particles with a diameter of 20 μm (LG_{14} laser mode and $w_0 = 125 \mu\text{m}$). (a) $E_{max} = 3500 \text{ V/m}$, (b) $E_{max} = 3700 \text{ V/m}$, (c) $E_{max} = 3825 \text{ V/m}$, and (d) $E_{max} = 4000 \text{ V/m}$. The scale bar for the particle pattern is 200 μm .

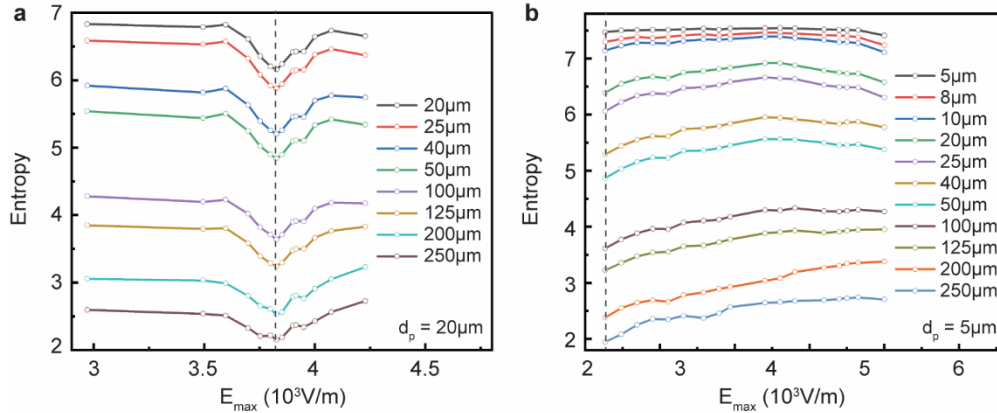


Figure 3.11: Entropy of the particle pattern under different maximum intensity value of the electric field (E_{max}) calculated with different bin sizes (LG_{14} laser mode and $w_0 = 125 \mu\text{m}$). The diameter of the particles (d_p) are: (a) 20 μm , and (b) 5 μm , respectively.

Furthermore, with the smaller 5 μm particle size (red line, Figure 3.9c), a minimum entropy value in the ring-shaped pattern was achieved at even lower values of electric field when compared to the 20 μm particle ($E_{max} = 2130 \text{ V/m}$, Figure 3.9c and Figure 3.11b). It was expected that a further reduction in the electric field for the 5 μm particle size seen in Figure 3.9c would further reduce the entropy value and more detailed particle maps were included in Figure 3.12. This was because the competition between the drag and gravitational forces

on the particles, as seen in Figure 3.7, ultimately dictated the degree of order of the ring-shaped pattern. Since the ratio between the drag forces and the gravitational force is proportional to d_p^{-2} , this ratio will increase significantly as the particle size is reduced. Therefore, to improve the entropy of patterns produced with smaller particle sizes, the magnitude of this drag force must be reduced. This could be simply done by lowering the electric field intensity as corroborated in Figure 3.9c when comparing this effect on both the 20 μm and 5 μm particle sizes.

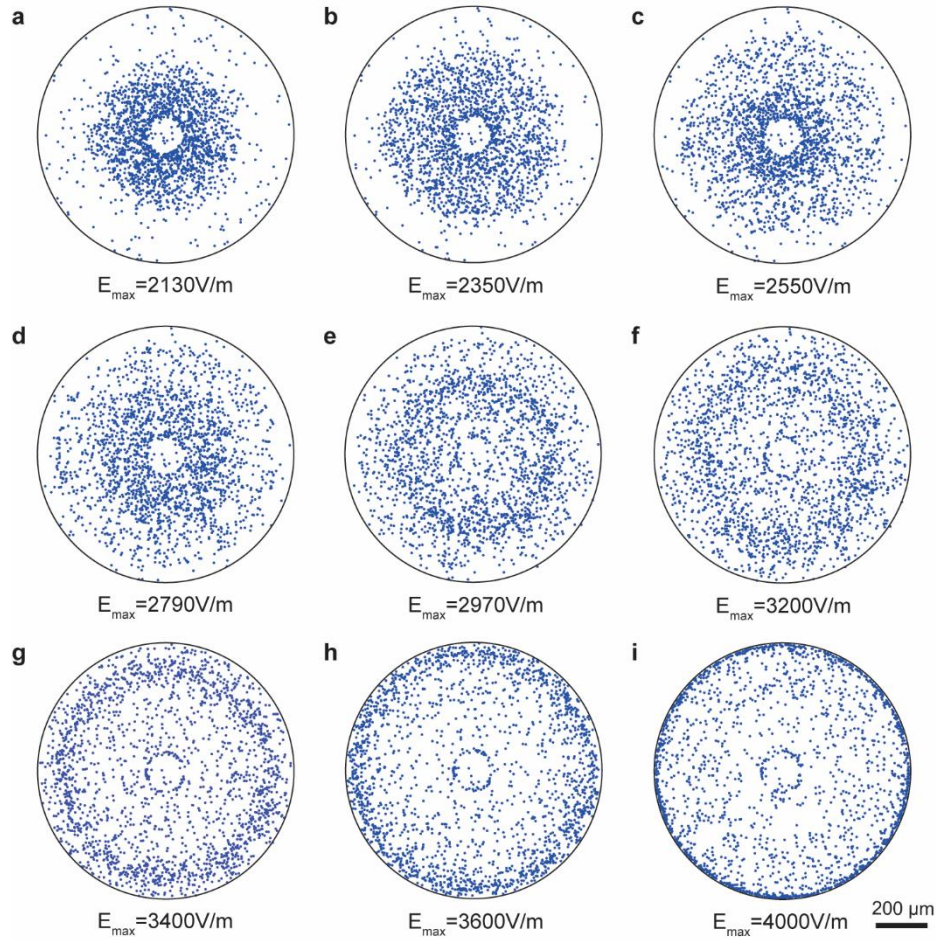


Figure 3.12: Particle patterns under different maximum intensity value of the electric field (E_{max}) for particles with a diameter of 5 μm (LG_{14} laser mode and $w_0 = 125\mu\text{m}$). (a) $E_{max} = 3500\text{V/m}$, (b) $E_{max} = 3700\text{V/m}$, (c) $E_{max} = 3825\text{V/m}$, and (d) $E_{max} = 4000\text{V/m}$. The scale bar for the particle pattern is 200 μm .

To further investigate the influence of the drag coefficient on particle assembly, a comparative study between the drag coefficient derived from the Schiller-Naumann model was performed. For both the Stokes and Schiller-Naumann models, a ring-shaped particle pattern was observed, and the trend of entropy changes with the electric field intensity was consistent. The only difference between the two models lied in the E_{max} corresponding to the entropy minima, which was higher in the case of the Schiller-Naumann model ($E_{max} = 3950\text{V/m}$, Figure 3.13) compared to Stokes law ($E_{max} = 3825\text{V/m}$) for 20 μm particles.

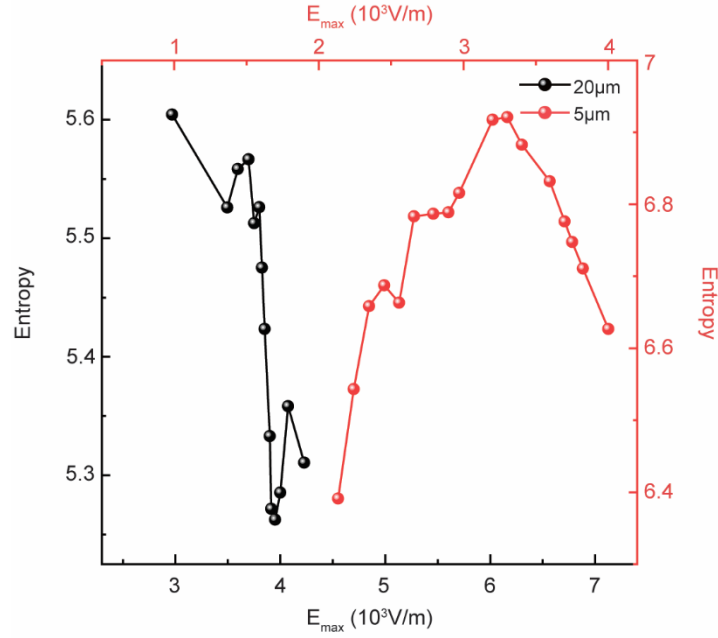


Figure 3.13: Entropy of particle patterns under different E_{max} values (LG_{14} laser mode and $w_0 = 125\mu\text{m}$) with drag coefficient from Schiller-Naumann model. The bin size for the calculation of entropy is $50\mu\text{m}$ for $20\mu\text{m}$ diameter particles (*solid black line*), and the bin size is $50\mu\text{m}$ for $5\mu\text{m}$ diameter particles (*solid red line*).

Moreover, it was not only possible to control the extent of the “forbidden zone” through careful choice of the radial and azimuthal index numbers of the LG_{pl} laser, but it was also possible to control the particle dispersion-width of the ring-shaped assembly by tuning the velocity of the fluid with the electric field of the laser. Here the particle dispersion-width was qualitatively defined as the radial distance from the boundary of the “forbidden zone” to the boundary of the liquid-gallium domain wall. The velocity profiles of the fluid as a function of the LG_{14} laser electric field intensity at the liquid-solid interface was shown in Figure 3.9d. At the boundary of the “forbidden zone” (Figure 3.9d, *shaded grey region*), the velocity of the fluid dropped to zero. Outside of the “forbidden zone”, undulated fluid velocity profiles can be seen. As the electric field intensity of the laser increased, the absolute value for the fluid velocity also increased. This also shifted the fluid velocity maxima away from the center of liquid-gallium (Figure 3.9d, *dashed black lines*). In this case, the drag forces on the particles would also increase with electric field, making them harder to assemble around the boundary of the “forbidden zone”. Consequently, particles would be able to assemble out of the liquid-gallium before reaching the boundary of the “forbidden zone”. This would result in a larger dispersion-width in the ring-shaped particle assembly. However, if the fluid velocity becomes too high, the drag forces would dominate the motion of the particles, where particles will prefer to circulate within the convective flow pattern of the fluid at longer time scales, making them more likely to strike the sidewalls. Under this case, particles would gather around the periphery of the liquid-gallium domain wall (Figure 3.12h). Therefore, to obtain a tighter ring dispersion-width, the intensity of the electric field should be kept at a moderate value to maintain a moderate ratio between the drag and gravitational forces as seen in Figure 3.7a.

3.7 Conclusions

In this chapter, we have demonstrated that light induced surface tension gradients have proven useful in not only controlling fluid flow of opaque liquids, but also directing the trajectory of dispersed particles within the bulk of liquid gallium, which was commonly dictated by Brownian forces. Overcoming Brownian motion is imperative to realize the controllable movement of solutes within the bulk of liquids, and thus to achieve a predictable spatial assembly with a high degree of order, complementary to what has been realized in particle assembly out of ferrofluids using magnetic fields²⁰⁷⁻²⁰⁹. Our results highlighted that assemblies with different degrees of order can be formed by engineering Marangoni flow in liquid-gallium using LG_{pl} lasers, which represented a tunable approach to design particle assemblies out of liquid metals. We found that the synergy between the drag forces on the particle from convective flow of the fluid and the effective gravitational force were responsible for limiting the influence of Brownian forces on the particle's motion in the fluid, therefore resulting in the formation of unique ring-shaped particle assemblies at the liquid-solid interface with a high degree of tunability. Careful control over the parameters of the LG_{pl} laser (i.e., laser mode, spot size w_o , and intensity of the electric field E_{max} etc.) could tune the temperature and fluid dynamics of the liquid-gallium as well as the balance of forces on the particle, which in turn could tune the structure of the ring-shaped particle pattern between the “coffee ring” and “reverse coffee ring” effects. This was a result of prominent “central vortices” within the convective flow of the bulk liquid that creates a “forbidden zone” of assembly at the liquid-solid interface. A striking example of this was when 70.1% of randomly dispersed tungsten particles in liquid-gallium under the LG_{14} laser mode ($d_p = 20\mu\text{m}$, $w_o = 125\mu\text{m}$ and $E_{max} = 3825\text{V/m}$) gathered around the periphery of the “forbidden zone” at the liquid-solid interface, forming a $100\mu\text{m}$ wide ring-shaped particle assembly that was smaller than the beam size of the laser itself.

Although this study has focused on the interaction of lasers with liquid-gallium, this approach can be extended to other liquid metals, such as mercury (Hg), indium (In), tin (Sn), etc., or eutectic metal alloy systems, such as Galinstan, field's metal, etc. The variety of liquid metals that are available with different melting points, surface tension – temperature relationships, viscosities, solubilities and reactivities will further expand the design space for creating complex material designs from a variety of elements and particle structures dissolved and/or dispersed in these fluids across different length scales from the bottom-up. Additionally, our approach extends beyond the specific pairing of liquid gallium and tungsten particles and can be applied across a diverse array of liquid metals and particles that do not alloy or react during the assembly process. In our study, the combination of liquid gallium and tungsten serves as an exemplary case, elucidating the underlying scientific principles while also ensuring the computational feasibility of large-scale simulations. The characteristic time for the particles, which dictates the time step for our time-dependent simulations, is $6.72 \times 10^{-4}\text{s}$ for particles with a $20\mu\text{m}$ diameter, and $4.2 \times 10^{-5}\text{s}$ for those with a $5\mu\text{m}$ diameter. Consequently, each simulation on average requires around two days to complete. It is anticipated that simulations involving lighter elements and/or smaller particle sizes would demand significantly more time, thereby incurring higher computational costs. Nonetheless, the scientific principles illustrated in

this work are expected to be applicable across various scale sizes. Meanwhile, the use of a common laser as a heating source to develop Marangoni flow in liquid metals opens the possibility of achieving rapid spatial switching in the design of the temperature gradients on the liquid metal, and therefore the surface tension gradients. The modularity of this fabrication process could potentially allow for an on demand spatial control over the precipitation of solutes out of the liquid metal, such as that seen in crystal growth processes of nanostructures, like the VLS mechanism²¹⁰⁻²¹¹. This can be done by altering the input of the laser beam shape and profile of the electric field using spatial light modulators and other appropriate optical components. This chapter is adopted from Jiayun Liang *et al* 's work¹⁸⁰ entitled “Light-Induced Surface Tension Gradients for Hierarchical Assembly of Particles from Liquid Metals”.

Chapter 4

Spatially structuring the surface energy of graphene through selective interface engineering

Central to surface energy profile design of graphene is finely tuning the electronic properties of graphene with excellent area selectivity over wide temperature ranges. Traditional approaches like chemical doping and electrostatic gating struggle with high carrier density, whereas alternatives like photo-patterned metal nanoparticles encounter limited thermal stability. Here, we report a method for area-selective graphene work function tuning with Ga^+ implanted diamond like carbon, effective from 25°C to 500°C. This technique enables bipolar work function tuning and heavy n-doping graphene ($3\text{--}4.6 \times 10^{13} \text{ cm}^{-2}$) at 300°C. Further DFT calculations reveal the pivotal role of diffusion and intercalation of sub-monolayer Ga in achieving high levels of electrostatic doping. Also, this platform allows for achieving different graphene work functions at the same temperature. Furthermore, a complex engineered pattern can be designed to cater for different purposes, significantly expanding the applications of graphene as substrate for area-selective material growth.

In this work, the DFT calculation was performed and analyzed by Ke Ma and Dr. Matthew Sherburne, and this work is reproduced in this dissertation with permission from the collaborators.

4.1 Introduction

An intriguing characteristic of graphene is its reduced surface energy upon both p-type and n-type doping compared to pristine graphene¹²³. Thereby, the work function difference can be converted into the surface energy difference ($\Delta\gamma_{GR}$) using the following equation:

$$\begin{aligned}\Delta\gamma_{graphene} &= \gamma_{doped\ GR} - \gamma_{undoped\ GR} \\ &= -\frac{1}{2}C_Q(\Delta\Phi_{GR}) * \Delta\Phi_{GR}^2\end{aligned}$$

where C_Q is the quantum capacitance of graphene²¹²,

$$C_Q = \frac{2e^2k_BT}{\pi(\hbar v_F)^2} \ln \left[2 \left(1 + \cosh \frac{e\Delta\Phi_{GR}}{k_BT} \right) \right]$$

where v_F is the fermi velocity. The derived $\Delta\gamma_{GR}$ for a series of graphene work function difference ($\Delta\Phi_{GR}$) at 300 °C and 500 °C are depicted in Figure 4.1, a and b, respectively. As previously discussed in **section 1.3.2.2**, this $\Delta\gamma_{GR}$ can drive the preferential adsorption and diffusion of materials towards or away from the Ga implanted regions, thereby designating these zones as either favorable or unfavorable for material growth.

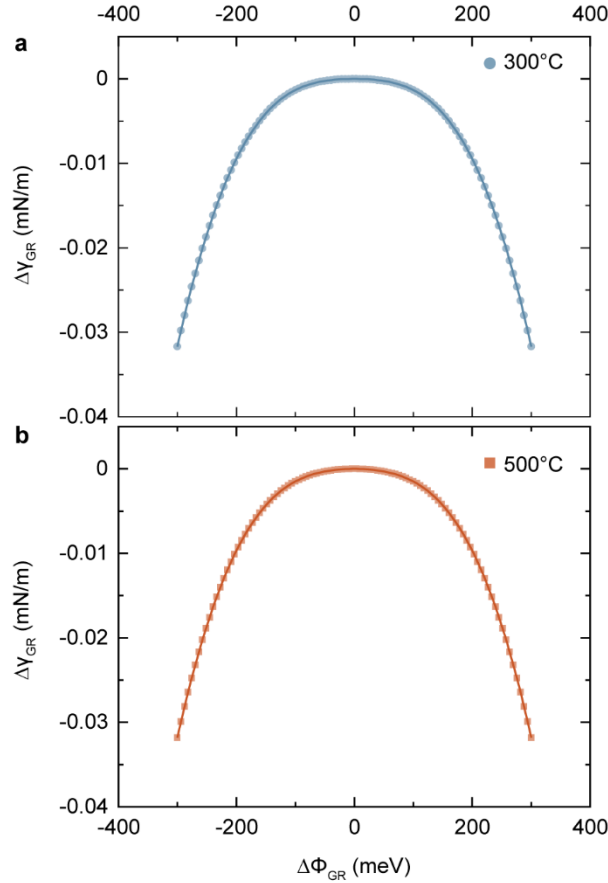


Figure 4.1: Surface energy difference ($\Delta\gamma_{GR}$) between doped graphene and un-doped graphene at different temperatures. Two preset temperature values are: (a) 300°C, and (b) 500°C,

respectively.

Towards it, central to the design of the surface energy landscape of graphene is the precise engineering over its electronic structure, aiming for high carrier concentrations combined with area selectivity across extensive temperature ranges. This will enhance the applicability of graphene in high-temperature environments, for example, during the area-selective material growth process. Traditional methods of chemical doping such as dopant substitution²¹³⁻²¹⁵ or surface functionalization²¹⁶⁻²¹⁷ have been extensively studied but shown to be constrained by dopant solubility limit, induced structural disorder, and impaired charge mobility²¹³⁻²¹⁵. Non-invasive electrostatic doping techniques such as lithographically defined gates¹²⁶⁻¹²⁸ and self-assembly of functionalized molecules^{129-130, 218-219} allowed area selective carrier tuning but struggle to achieve high carrier density. Recent efforts including laser/e-beam patterning^{81-85, 131, 220}, have shown promise in surpassing carrier density limitations ($>3 \times 10^{13} \text{ cm}^{-2}$ ¹³¹). However, structural damage such as defects in graphene from laser and e-beam exposure^{81-85, 131, 220} raised concerns about the effectiveness of the area selectivity in material growth process. In this scenario, precursors may preferentially adsorb and diffuse to the beam-induced defects rather than the targeted region¹⁵. Also, these methods were predominantly assessed at room temperature and their performance at high temperature environment remains unclear.

To address these challenges, a process to spatially control the doping of graphene, especially at elevated temperatures, is crucial. Our strategy involves the use of Ga implanted diamond-like carbon (DLC), leveraging the immiscible nature of Ga-C system²²¹, such as DLC and graphene. DLC is an amorphous carbon structure with significant $\text{sp}^3\text{-C}$ bonding²²²⁻²²³. The rich $\text{sp}^3\text{-C}$ bonding in DLC gives rise to many properties similar to those of diamond, including the seminal mechanical hardness and chemical inertness²²⁴. These properties together allow for the preservation of an ultra-flat DLC surface after the Ga implantation and benefit the subsequent graphene transfer process. Usually, according to the sp^2/sp^3 ratio and the incorporation of hydrogen, DLC can be categorized into amorphous carbon (a-C) and its hydrogenated alloys (a-C:H), tetrahedral amorphous carbon (ta-C) and its hydrogenated alloys (ta-C:H), and so on. Notably, DLC used in this dissertation was in ta-C form. Ga can be implanted into DLC through Ga^+ -focused ion beam (FIB) or *via* a nano-implanter in predetermined regions, effectively inducing the conversion from $\text{sp}^3\text{-C}$ to $\text{sp}^2\text{-C}$ within the DLC²²⁵. The resultant electron-rich surface environment, facilitated by the local structure reconstruction in DLC and the Ga precipitation upon heating, thereby addressing the crucial demands of high carrier density and spatial precision under varying thermal conditions. Also, the DLC substrate underneath facilitates a higher carrier mobility in graphene²²⁶⁻²²⁷. Furthermore, the insolubility of Ga in graphene plays a vital role in preserving the structural integrity of graphene²²⁸.

Here, we described a highly area selective platform for tuning the work function of monolayer graphene (Φ_{GR}) across a broad temperature range through graphene-Ga implanted DLC heterointerface engineering. We controlled the $\text{sp}^3\text{-to-sp}^2$ conversion within DLC and the precipitation of Ga by varying annealing temperatures from 25°C to 500°C. This process enabled a bipolar tuning (either an increase or decrease) of the local

work function landscape of graphene across the entire temperature spectrum up to 500°C. Remarkably, the synergistic interaction between precipitated Ga sub-monolayer and localized DLC reconstruction led to heavy n-doping in graphene, reaching the doping level at the order of $3\text{-}6.84 \times 10^{13} \text{ cm}^{-2}$ at 300°C. Specifically, after annealing at 300°C, the work function of graphene atop Ga implanted DLC was -0.962 eV lower than the pristine graphene, which was estimated to induce a decrease of 1.043 mN/m in graphene surface energy at 300°C. This innovative platform paves the way for significant potential in developing high-performance graphene-based devices²²⁹⁻²³⁰ and probing the intrinsic physics of heavily doped pristine monolayer graphene²³¹⁻²³⁷. Furthermore, the work function engineered graphene can act as an ideal playground to explore the dynamic process of area-selective material growth with a wide temperature spectrum.

4.2 Experimental setup and characterization

4.2.1 Ga⁺-FIB patterning on DLC and polymer-free graphene transfer on DLC

50nm-thick hydrogen-free DLC was deposited on Si wafer with a filtered cathodic vacuum arc deposition system from Kim Lab in Korea Institute of Materials Science (KIMS). The following Ga⁺-FIB patterning on DLC layer was performed with a FEI SCIOS 2 LoVac Dual Beam FIB. The voltage and current for the Ga⁺-FIB is 7.5kV and 0.23nA, respectively.

For further reference on the optimization of FIB conditions to cater to the need of varied applications, the main takeaways from the stopping and range of ions in matter (SRIM) simulation and FIB dose study conducted on DLC films are summarized in the following subsections.

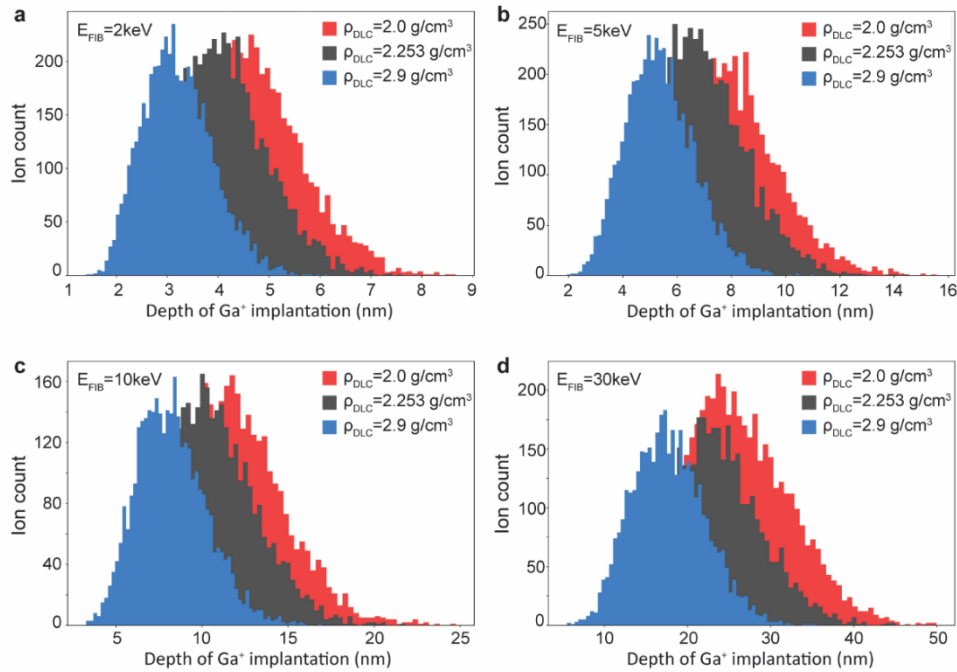


Figure 4.2: SRIMS results for Ga distribution in DLC films with varied FIB energy (E_{FIB}) and density of a DLC film (ρ_{DLC}). Four typical E_{FIB} were simulated: (a) $E_{FIB}=2\text{keV}$, (a)

$E_{FIB}=5\text{keV}$, (c) $E_{FIB}=10\text{keV}$, and (d) $E_{FIB}=30\text{keV}$. Results for $\rho_{DLC}=2.0\text{g/cm}^3$, $\rho_{DLC}=2.253\text{g/cm}^3$, and $\rho_{DLC}=2.9\text{g/cm}^3$ are presented in red, black, and blue bars, respectively.

4.2.1.1 SRIM simulation analysis

To investigate the implantation depth of Ga ions within DLC film under varying experimental conditions, a series of SRIM simulations were conducted. These simulations explored the effects of FIB energy (E_{FIB}) ranging from 2keV to 30keV and examined the density of a DLC film (ρ_{DLC}) at three presentative values²³⁸ (2.0 g/cm³, 2.253 g/cm³, 2.9 g/cm³). The results summarized in Figure 4.2 suggested that an increase in E_{FIB} , or a decrease in ρ_{DLC} , led to larger implantation depth of Ga ions within DLC film. A mathematical model was further developed to describe the maximum implantation depth (R_{max}) of Ga ions in DLC film as a function of E_{FIB} and ρ_{DLC} :

$$R_{max} = 10.642 \times E_{FIB}^{0.6488} / \rho_{DLC}^{0.946}$$

where the units for R_{max} , E_{FIB} , and ρ_{DLC} are nm, keV, and g/cm³, respectively. This model predicted that the E_{FIB} used in our experiment, 7.5keV, would give rise to a R_{max} for Ga ions in DLC film spanning from approximately 20.4nm ($\rho_{DLC}=2\text{g/cm}^3$) to 14.4nm ($\rho_{DLC}=2.9\text{g/cm}^3$).

4.2.1.2 FIB dose study on DLC films

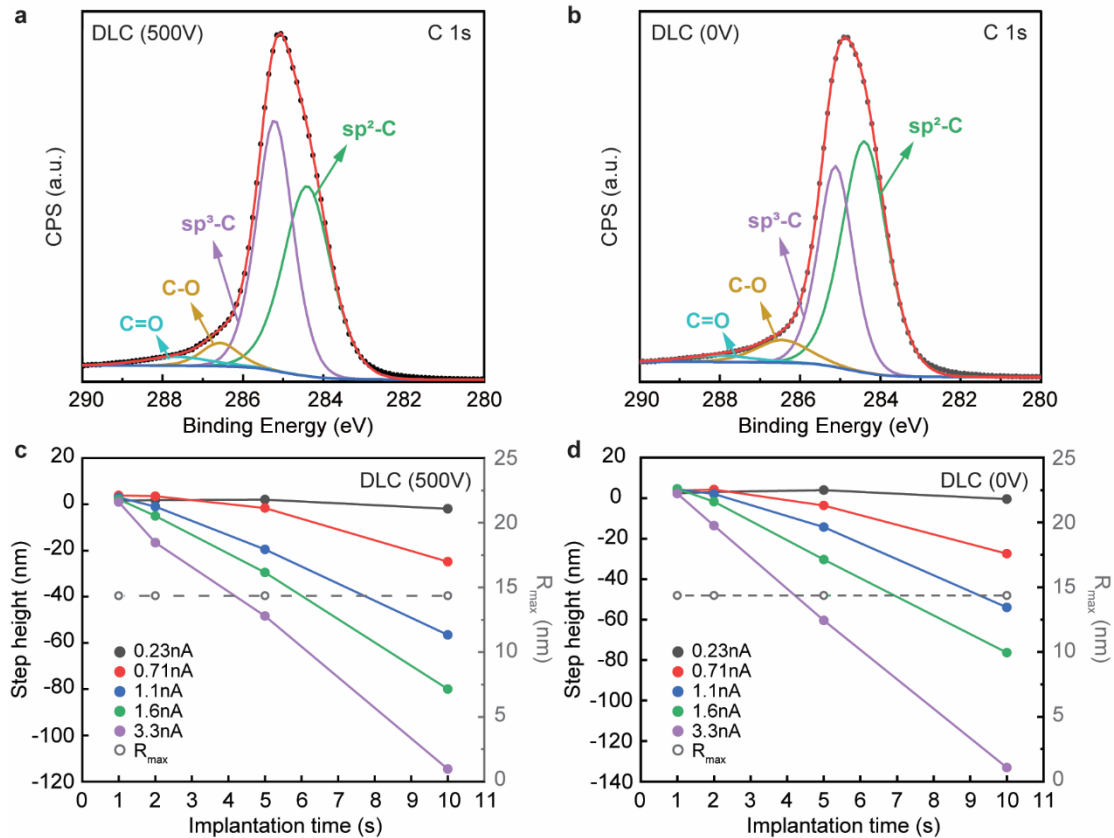


Figure 4.3: XPS spectrums for DLC film and corresponding step height analysis for surface

features resulted in the FIB dose studies. XPS of C core-level of DLC films synthesized under voltages of: (a) 500V and (b) 0V in the filtered cathodic vacuum arc deposition system, respectively. Corresponding step height analysis of surface features after different FIB implantation time (x -axis) and FIB currents (*solid circles*) for: (c) DLC (500V), and (d) DLC (0V), respectively. The E_{FIB} was fixed at 7.5keV for all FIB dose studies. R_{max} predicted with the SRIM model is highlighted with a *grey open circle* and *grey dash line*.

In a further investigation, a series of FIB dose studies were performed to probe the change in the surface morphology of DLC films after Ga^+ implantation. Three different variables – FIB implantation time, FIB current, and sp^2/sp^3 ratio of DLC film– were investigated in these experiments. The XPS C1s spectra for two different DLC films, synthesized under voltages of 500V and 0V in the filtered cathodic vacuum arc deposition system, respectively, revealed significant differences in their sp^2/sp^3 ratios (Figure 4.3, a and b). While DLC (500V) exhibited a sp^2/sp^3 ratio of 3, DLC (0V) exhibited a sp^2/sp^3 ratio of 1.5. The finding from subsequent dose studies, incorporating variations in FIB current and FIB implantation time, were summarized in Figures 4.3, c and d. And the size of the implanted region was fixed to $5\mu m \times 5\mu m$. The Ga^+ implantation fluence was proportional to the product of varied FIB current and implantation time. It was observed that a hill-like structure corresponding to the positive step height dominated at low Ga^+ implantation fluences, and then transitioned to a valley-like structure (i.e., negative step height) at higher Ga^+ implantation fluences. The physics behind this structural evolution was that both ion-induced sp^3 -to- sp^2 conversion and sputtering effect existed in DLC thin film²²⁵. While the former led to a volume increase due to the increasing sp^2 -C bonding, the latter consistently physically removed the top-most layer of DLC thin film. Notably, for DLC(0V) under a FIB current of 0.23nA and a FIB implantation time of 10s, a feature with a step height of -0.47nm was formed, indicating a nearly balanced effect of ion-induced sp^3 -to- sp^2 conversion and sputtering. To maintain the quality of subsequently transferred graphene atop Ga implanted DLC and ensure its contact with the underlying DLC, a hill-like surface feature with small step height would be beneficial. Therefore, unless specified otherwise, the experiments presented in the subsequent sections used DLC (0V) and the FIB process were conducted under a FIB current of 0.23nA and an implantation time of 5s.

4.2.2 Polymer-free graphene transfer on DLC

To avoid polymer residue affecting the work function quantification, a polymer free graphene transfer method adopted from Lu *et al*²³⁹ was employed. A CVD-grown monolayer graphene on Cu foil (Graphene Factory) was used for transfer and its Cu side was treated with O_2 plasma to remove the carbon residues. To support the graphene during the transfer, a frame window consisting of adhesive Al foil was placed on the graphene side and the sample then floated on a $\sim 0.3M$ sodium persulfate solution for Cu etching. After the Cu was fully etched away, graphene together with the Al window frame was carefully transferred to a deionized water reservoir to remove the salt residue and this step was repeated twice to ensure complete removal of excess sodium persulfate salt. Lastly, the sample went through a high vacuum (10^{-6} torr) annealing treatment at $220^\circ C$ to enhance the adhesion of graphene to DLC. (More details in **Appendix B**)

4.2.3 Anneal and work function quantification in low energy electron microscope

(LEEM)

The as-prepared graphene/pristine DLC, graphene/Ga implanted DLC, pristine DLC and Ga implanted DLC samples were outgassed around 150°C in ultra-high vacuum, and last until the chamber pressure stabilized back to 5×10^{-9} torr. After cooling back to 25°C, the samples were annealed in LEEM chamber (10^{-9} - 10^{-8} torr, Elmitec LEEM III microscope) to *in situ* quantify the sample work function at specific annealing temperature (T_{anneal}) ranging from room temperature to 500°C. The ramping rate of annealing is approximately 11°C/min.

This procedure was designed to tune the work function of graphene, employing a LEEM for real-time, *in situ* analysis. Distinct from conventional electron microscopy techniques such as scanning electron microscopy (SEM) and transmission electron microscopy (TEM), LEEM utilizes a low energy electron beam with energies ranging from 0 to 50eV as the imaging source. This offers LEEM two pivotal advantages, making it ideal for investigation over the morphological and electronic structures of solid surfaces.

Firstly, electron scattering is highly surface sensitive, a consequence of the short inelastic mean free path nature of low energy electrons in solids. Secondly, the reflectivity of these electrons is significantly enhanced, by orders of magnitude over their high energy counterparts. This increase in electron reflectivity is attributed to the diminished forward scattering effects, reduced momentum transfer, and a decrease in the distribution of elastically scattered electrons across permissible diffraction conditions. Collectively, these attributes give rise to unparalleled capabilities of LEEM in delivering high-resolution and surface-sensitive imaging in real time.

4.2.3.1 Principles for real time imaging with LEEM

Central to the generation of LEEM imagery is the production and manipulation of low-energy electron beams. As illustrated in Figure 4.4, electron emission is initiated at a cathode, subsequently accelerated to a typical microscope potential (12-20keV). The incident beam is then focused by lenses, converging at a crossover point situated in the back focal plane of the objective lens. Here, the beam is further focused to infinity and decelerated to a preset incident energy. A homogeneous electric field established between the objective's final electrode and the sample surface facilitates the final deceleration phase, giving rise to the low energy electrons. Upon interaction with the sample surface, these electrons are reflected, subsequently re-accelerated to the microscope potential, and deflected by a magnetic section field into the imaging column where they are separated from the incident beam. Image acquisition is then executed through a high-resolution, high-dynamic-range CCD camera.

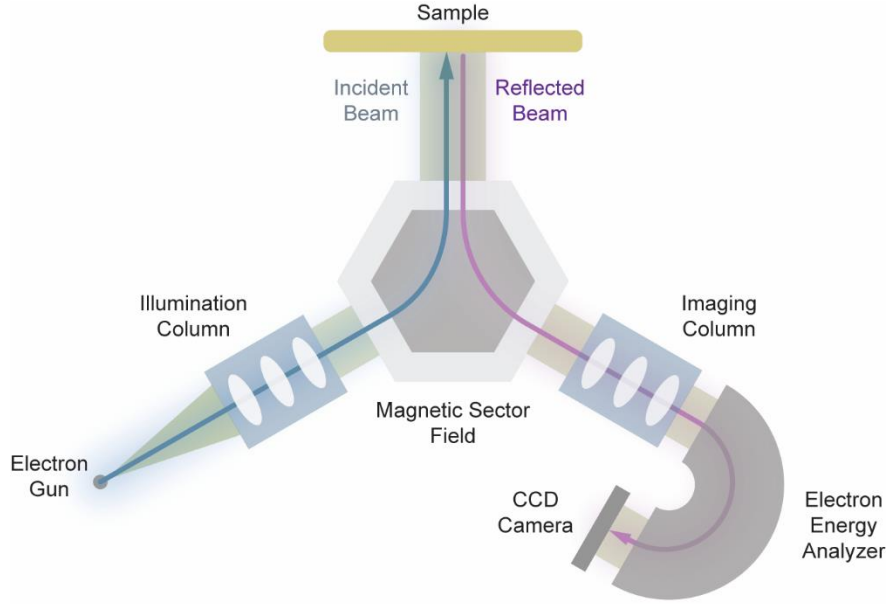


Figure 4.4: Schematic of the principle for real time imaging in LEEM. Trajectories of incident beam and reflected beam in the magnetic sector field and objective lens of LEEM are outlined with *blue arrow* and *purple arrow*, respectively.

The energy of the incident beam demarcates two principal imaging modes in LEEM: the Mirror Mode (MM) and LEEM Mode, with a detailed discussion in **section 4.2.3.2**. In the LEEM mode, the image contrast reveals the surface properties of a solid. Most of the contrast observed, namely amplitude and phase contrast, originate from variations in reflected electron intensity and phase of the electron wave upon interacting with sample surface, respectively. And amplitude contrast depends on incident electron energy, the surface structure, and composition of a solid surface. In the phase contrast, the two best-known examples are atomic step contrast and quantum-size contrast²⁴⁰. Step contrast arises from the path length difference traversed by electron waves reflecting off terraces flanking a step, yielding a characteristic phase shift, as given by below:

$$\Delta\phi = \frac{2\pi}{\lambda} a_0$$

where the λ is the electron wavelength and a_0 is the step height. Additionally, the quantum-size contrast is associated with the quantum-size effect (QSE) in electron reflectivity, for example, at the thin film – substrate interface. In this scenario, the QSE interference periodically modulates the reflected intensity both as a function of film thickness and electron wavelength²⁴¹. Therefore, the quantum-size contrast is widely utilized in LEEM to determine the thin film thickness in real time.

4.2.3.2 Error function fitting on intensity-voltage curve for work function measurements

Depending on the beam energy, incident electrons will interact with the sample surface differently. Usually, it is contingent upon the relative work function of cathode (Φ_c) in

LEEM and the sample (Φ_{sample}). The difference between these work functions, denoted as work function difference ($\Delta\Phi$):

$$\Delta\Phi = \Phi_{sample} - \Phi_c$$

In instances where the incident electron energy is lower than $\Delta\Phi$, all the electrons will be completely reflected, hallmarking the mirror mode with its characteristic high surface reflectivity. The transition from mirror to LEEM mode occurs at the minimum mirror threshold (MMT), where the incident electron energy aligns with $\Delta\Phi$. This gives rise to a sharp decrease in surface reflected intensity as electrons start to interact with the sample surface and get partially reflected.

Accordingly, the sample work function, for example, Φ_{GR} and Φ_{DLC} in this chapter, can be derived from reflected intensity - starting voltage curve (I-V curve), pinpointing the voltage corresponding to the MMT. This voltage, V_{MMT} is extracted through an error function fit, using the following equation from Jobst *et al* 's²⁴²:

$$I = \frac{I_{MM} - I_{LEEM}}{2} \cdot \text{erfc}\left(\frac{V - V_{MMT}}{\sqrt{2}\sigma}\right) + I_{LEEM}$$

where

$$\text{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-r^2} dr$$

I_{MM} and I_{LEEM} are the mirror mode reflected intensity and the minimum LEEM mode reflected intensity, respectively, alongside a Gaussian spread of electron energy, σ . The fitting process based on Python iteratively optimized V_{MMT} to minimize the sum of squared residuals (More information see **Appendix C and D**). All error values were estimated based on a linear approximation to the error function around the optimum. The Φ_{sample} was then extracted from:

$$\Phi_{sample} = eV_{MMT}$$

Notably, the Φ_{GR} and Φ_{DLC} values were extracted from the center of the region of interest away from the boundary of Ga implanted DLC region to avoid artifacts induced by work function variations and step height. This approach ensures a clear, sharp transition in the normalized I-V curve, as illustrated in Figure 4.5d, thus providing a precise estimate of V_{MMT} , and subsequently, Φ_{sample} .

Other common methods for extracting V_{MMT} , for example, defining V_{MMT} as the corresponding voltage value when I/I_{MM} decreases from unity to a critical value (e.g., 0.9)²⁴³ and dual linear fits²⁴⁴ to determine work function from the intersection point, involves predetermined critical values or dual linear fitting region, but these can introduce subjective errors absent in the error function fitting method adopted in our study.

4.2.4 Atomic force microscope (AFM), Kelvin probe force microscope (KPFM), Raman measurements

AFM and KPFM mappings were conducted by Asylum Jupiter Atomic Force Microscope. Temperature-dependent Raman measurements of both graphene/DLC and DLC samples

were performed on a Witec alpha300R Raman spectrometer employing 532nm light at 15mW and the spectral accuracy is 1cm^{-1} . Samples were heated at a rate of 11°C and allowed to dwell for at least 5 minutes at every temperature set-point (from 50 to 500°C with a step of 50°C). For each temperature, 36 separate spectral acquisitions in the same location were acquired and each individual integration utilized a collection time of 5s.

4.2.5 Time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements were conducted using a combined setup of a TOF.SIMS⁵ instrument (ION-TOF GmbH, Münster, Germany) and an integrated *in situ* scanning probe microscope (NanoScan, Switzerland) at Shared Equipment Authority of Rice University. The area for ToF-SIMS characterization was $150\times 150\mu\text{m}^2$, using a Bi_3^{++} beam at 30keV and 0.1pA with a raster of 1024×1024 to create the detailed 3D depth profile. During these measurements, a charge neutralization was made using an electron flood gun, while the charge effects were adjusted with a surface potential. The time for each cycle was set at $70\mu\text{s}$, which corresponds to $m/z = 0 - 415$ amu mass range. For the sputtering process, a $300\times 300\mu\text{m}^2$ area was bombarded with a Cs^+ beam at 2keV and 110nA. The operation mode of the beams was set to be non-interlaced, alternating 1 analysis cycle and 3 frames of sputtering followed by a pause of 5s for the charge compensation.

The MCs_n^+ ($n=1, 2$) depth profile using was also employed to enhance the interpretation of the data, particularly beneficial for quantifying alloys and identifying ion compounds. This technique utilizes a cesium primary beam for sputtering, enabling the detection of MCs^+ or MCs^{2+} cluster ions, where M represents the element of interest. The use of MCs^+ and MCs^{2+} cluster ions in ToF-SIMS analysis is advantageous for minimizing matrix effects and enables the identification of both electronegative and electropositive elements and compounds²⁴⁵⁻²⁴⁹.

4.2.6 Scanning tunneling microscope (STM), scanning tunneling spectroscopy (STS), and electron energy loss spectroscopy (EELS) measurements

All STS/STM measurements were conducted using a Createc GmbH scanning probe microscope, which was operated in an ultrahigh vacuum environment ($< 2\times 10^{-10}$ mbar) at liquid helium temperatures ($< 6\text{K}$). For the measurements, etched tungsten or platinum iridium tips were used. To refine the shape of the tip apexes, they were indented onto a gold substrate before use. STM imaging was carried out in a constant-current mode, with a voltage bias applied to the samples under examination. For STS measurements, a lock-in amplifier was employed, set to a resonance frequency of 683Hz and a modulation amplitude of 5mV.

Prior to the EELS measurements, the cross-sectional Ga implanted DLC samples were prepared in a FEI Helios 660 focused ion beam system, where an *in situ* lift out was performed with Ga^+ focused ion beam. To protect the region of interest, a thick amorphous was deposited over it with electron beam deposition. And the milling voltage started with 30kV, which was gradually reduced to 2kV, aiming to minimize damage to the sidewalls and thin down the sample for electron transparency. To further reduce the surface damage caused by Ga^+ during the FIB process, the TEM samples were polished using an Ar ion

beam in a PIPS II system (manufactured by Gatan), employing a 300eV beam for 90s. Following this preparation, the samples were analyzed using dual-EELS on a dual aberration-corrected FEI Titan³ G2 60-300 S/TEM operated at 300kV.

4.2.7 Nano-angle-resolved photoemission spectroscopy (nano-ARPES) measurements

The nano-ARPES measurements were conducted at the MAESTRO beamline 7.0.2.2 of the Advanced Light Source. The sample was inserted into the ultrahigh vacuum environment and annealed for several hours at 150°C for several hours and 200°C for 30 mins to remove atmospheric adsorbents from the surface prior to measurement at a temperature of approximately 20 K. The photon beam was focused to a beam spot of approximately 1 μ m with a capillary reflective optic from Sigray. Photoemission was measured with a Scienta R4000 analyzer, and a photon energy of 100eV was used. Spatial maps were made by raster scanning the beam across the sample and collecting photoemission spectra at each spatial point.

4.2.8 DFT calculations

Ab initio calculations were conducted within the framework of DFT using the Vienna *Ab initio* Simulation Package (VASP 6.4)²⁵⁰⁻²⁵¹ to investigate the structural and electronic properties of graphene/Ga implanted DLC heterointerface. Plane-wave basis and Projector Augmented-Wave (PAW) formalism were applied²⁵²⁻²⁵³. Generalized Gradient Approximation (GGA) and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional were used for all calculations²⁵⁴. To accurately represent van der Waals interactions between graphene monolayer and underlying DLC substrates, Grimme's DFT-D3 method was incorporated in the simulations²⁵⁵. A plane-wave energy cutoff of 550 eV was implemented, along with a convergence criterion of 5×10^{-5} for structural relaxations and 10^{-6} for self-consistent field (SCF) electronic calculations.

The heterointerface model consists of pristine monolayer graphene placed atop co-periodic DLC or Ga implanted DLC slabs, derived from their respective optimized bulk structures. Exposed, undercoordinated carbon atoms on slab surfaces were passivated with hydrogen atoms to reflect the realistic surface conditions²⁵⁶⁻²⁵⁷. The supercell setup features a across-sectional dimension of approximately 7.5×8.5 Å, containing about 120 carbon atoms in a DLC slab of thickness over 10 Å, 24 atoms in graphene monolayer, and a variable number of Ga atoms depending on the specific configuration. A vacuum space of 20 Å was applied on top of the heterostructure, and dipole correction was applied in the z-axis for all heterointerface calculations to mitigate interference from periodic images of the supercell²⁵⁸. For structural optimization, the Brillouin zone was sampled using a Γ -centered k-grid of $7 \times 7 \times 1$. For electronic structure analysis such as density of states and differential charge transfer, a finer KPOINTS setting of $11 \times 11 \times 1$ was employed to ensure precision.

4.3 Temperature-dependent work function on tuning graphene surface

The engineering of graphene/Ga implanted DLC heterointerface to achieve temperature-dependent tuning on graphene work function, illustrated in Figure 4.5a, involved a three-step process: (i) the Ga⁺-FIB patterning on DLC, followed by (ii) polymer-free transfer of graphene and (iii) Φ_{GR} engineer through annealing in high vacuum (see **section 4.2.1** to

4.2.3). After Ga^+ -FIB patterning, a sharp square feature with a 4 nm step height was formed (Figure 4.5b). Owing to the inherent robustness of DLC, its surface remained flat post-patterning, thereby facilitating subsequent graphene transfer. The root-mean-square (RMS) surface roughness values measured before and after patterning exhibited slight variations—321.0pm and 337.4pm inside and outside the Ga implanted DLC region, respectively, compared to 131.7pm initially (Figure 4.6a). Following graphene transfer atop the Ga implanted DLC region, the step height increased to 4.7nm (Figure 4.5c). For *in-situ* mapping of temperature-dependent Φ_{GR} , we employed LEEM, a characterization technique uniquely sensitive to the graphene surface. The measurement was based on the I-V curve, where the incident electrons were totally reflected (mirror mode) off the sample surface until their energy aligned with the sample work function. As the electron energy increased, partial reflection of electron (LEEM mode) occurred, marked by a sharp dip in surface reflected intensity²⁵⁹ (Figure 4.5d). Through fitting the curve with an error function (see **section 4.2.3.2**), we could obtain Φ_{GR} mappings with high spatial resolution ($\sim 10\text{nm}$) and accuracy.

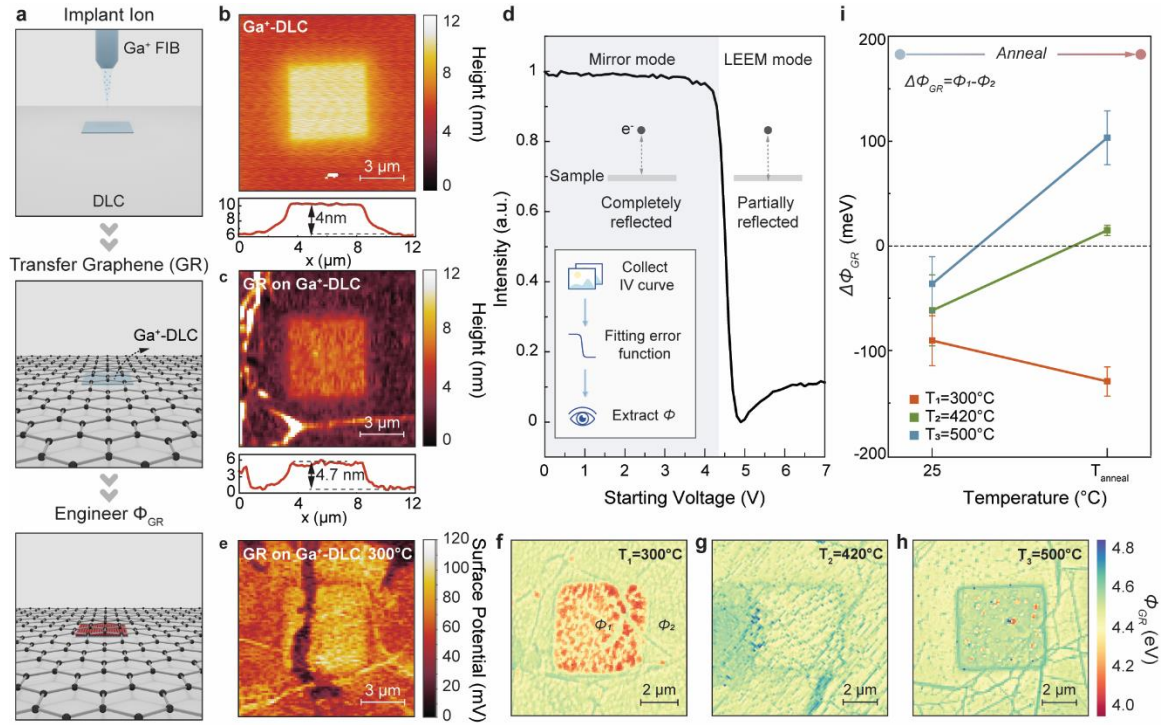


Figure 4.5: Scheme for graphene/Ga implanted DLC heterointerface engineering and its impact on temperature-dependent tuning of graphene work function. (a) Schematic depicting the three-step engineering process: (*top*) the Ga^+ -FIB patterning on DLC, (*middle*) polymer-free graphene transfer and (*bottom*) Φ_{GR} engineering through annealing. (b) AFM image of Ga implanted DLC with corresponding central height profile of Ga implanted DLC region. (c) AFM image of graphene on Ga implanted DLC (*yellow dash box*) and corresponding central height profile of graphene/Ga implanted DLC region. (d) Representative I-V curve for the graphene/Ga implanted DLC sample. (e) KPFM image of graphene on Ga implanted DLC at 25 °C after

annealing at 300°C. (f,g,h) Work function mappings of graphene on Ga implanted DLC annealed at 300°C(f), 420°C(g), and 500°C(h), respectively. (i) temperature-dependent $\Delta\Phi_{GR}$ values at various preset T_{anneal} .

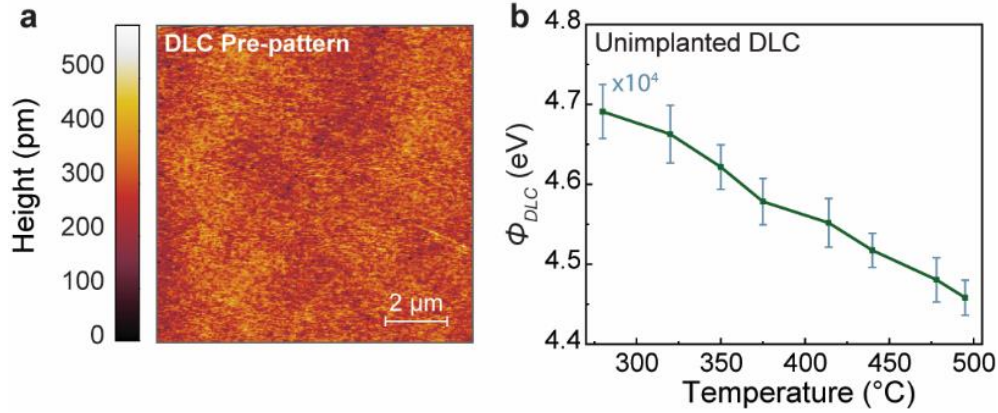


Figure 4.6: AFM and temperature-dependent work function changes of unimplanted DLC. (a) AFM image of DLC before FIB patterning. (b) Temperature-dependent work function evolution in unimplanted DLC. The error bars are magnified by a factor of 10^4 for enhanced visual clarity.

Before annealing at 25°C, as shown in Figure 4.5i, the graphene work function on Ga implanted DLC region (Φ_1) was lower than in the unimplanted region (Φ_2). This difference, $\Delta\Phi_{GR} = \Phi_1 - \Phi_2$, varied from -36.26 ± 25.93 meV to -90.52 ± 23.90 meV, primarily due to surface adsorption of gas molecules (e.g. H_2 , O_2 , N_2 , CO_2 with a partial pressure level of 10^{-9} to 10^{-10} torr) and adventitious carbon across different experiments. Upon heating to various preset annealing temperatures (T_{anneal}), Φ_{GR} changed and $\Delta\Phi_{GR}$ exhibited distinct behavior at different T_{anneal} . Notably, at 300°C, $\Delta\Phi_{GR}$ remained negative, as evidenced by KPFM and LEEM measurements. When cooled down to room temperature from the annealing treatment at 300°C, the surface potential map (Figure 4.5e) indicated a higher potential within the Ga implanted DLC region compared to the unimplanted region, with a difference of 31.9 ± 4.6 mV. This surface potential value represented the work function difference between the sample surface and the KPFM tip (constant during scanning, and higher than the sample work function), suggesting a lower Φ_{GR} on the Ga implanted DLC region. Furthermore, *in-situ* work function measurement at 300°C through LEEM corroborated this, showing a $\Delta\Phi_{GR}$ of -129.48 ± 13.84 meV (Figure 4.5f). This discrepancy in $\Delta\Phi_{GR}$ transitioned from a negative to positive around a threshold of approximately 420°C, yielding a $\Delta\Phi_{GR}$ of 13.84 ± 4.90 meV (Figure 4.5g). At higher T_{anneal} , such as 500°C, $\Delta\Phi_{GR}$ became increasingly positive, reaching 103.20 ± 25.70 meV (Figure 4.5h). The change of $\Delta\Phi_{DLC}$ while increasing T_{anneal} was summarized in Figure 4.3i, and all error values were estimated based on a linear approximation to the error function around the optimum²⁴² (see section 4.2.3.2).

4.4 Temperature-dependent work function on Ga implanted DLC

Due to the immiscible nature of Ga-C system, upon heating, the implanted Ga would diffuse towards the surface. The depth profiles of Ga distribution in DLC at various annealing temperatures were presented in Figure 4.7. In the un-annealed samples, majority

of Ga remains embedded within the DLC matrix, with only a marginal quantity presented on the surface—a result of thermal effects and ion injection during the Ga^+ -FIB implantation process²⁶⁰ (Figure 4.7a). However, as the annealing temperature increased, Ga diffused, accumulated, and precipitated at the graphene/Ga implanted DLC heterointerface (Figure 4.7b). At 500 °C, the Ga concentration graphene/ Ga implanted DLC heterointerface was an order of magnitude higher than that in the pre-annealed samples, with minimal Ga retention within the DLC matrix (Figure 4.7c and Figure 4.8).

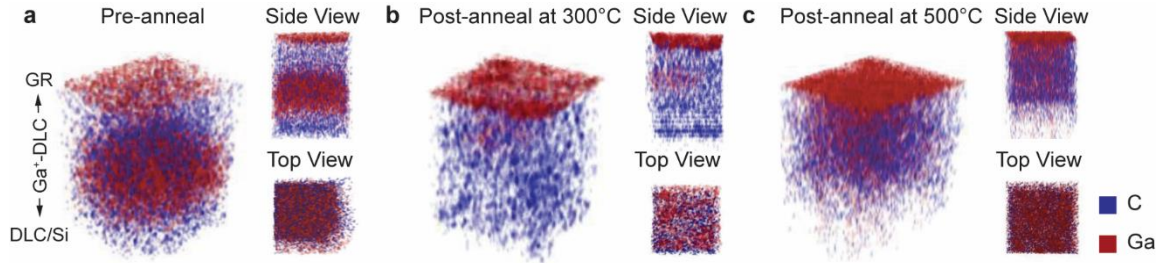


Figure 4.7: ToF-SIMS mapping for Ga within DLC layer after different annealing treatments. The depth profiles of Ga distribution in DLC for three different annealing settings were characterized: (a) at room temperature without annealing, (b) post-annealing at 300°C, and (c) post-annealing at 500°C. All the ToF-SIMS characterizations were performed at room temperature. The distribution of C and Ga are presented in *blue* and *red*, respectively. For each of the 3D render models, it is 5 μm ×5 μm in x-y plane (top surface) and 50 nm in z-direction.

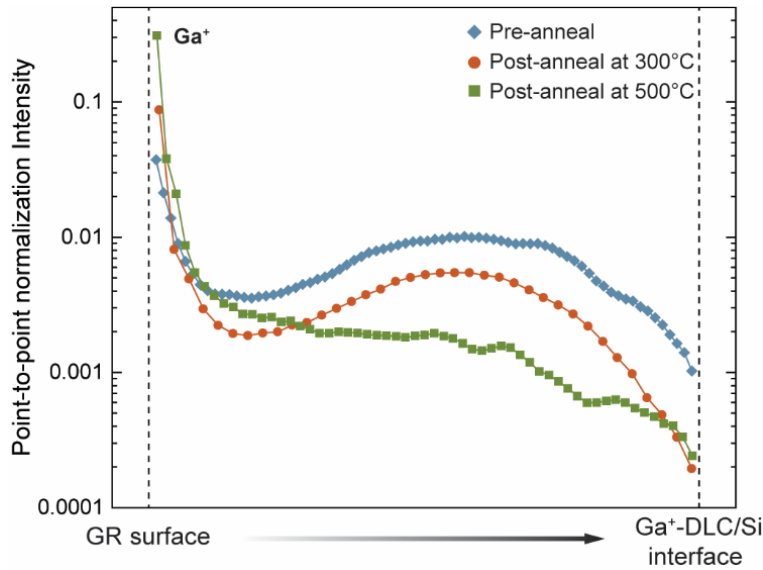


Figure 4.8: Point-to-point normalized intensity for Ga^+ in ToF-SIMS spectra for graphene/Ga implanted DLC after different annealing treatments. graphene/Ga implanted DLC in three conditions were examined: before annealing (*blue diamond marks*), after annealed at 300°C (*orange circle marks*), and after annealed at 500°C (*green square marks*). All the ToF-SIMS characterizations were performed at room temperature.

The diffusion of Ga within DLC could then greatly change the local environment of the heterointerface, and consequently the graphene work function. Therefore, to elucidate the

underlying physics of temperature-dependent work function tuning of graphene, we investigated the temperature-dependent work function of DLC (Φ_{DLC}), both in Ga implanted and unimplanted samples. In the unannealed sample, the work function in the Ga implanted DLC region (Φ_3) was lower than in unimplanted region (Φ_4), varying from -233.26 meV to -674.09 meV, which was also attributed to surface adsorption of gas molecules and adventitious carbon. As shown in Figure 4.6b, the work function of pristine DLC decreased with increasing T_{anneal} . Similarly, under increasing T_{anneal} Φ_4 for the unimplanted DLC region also decreased, while Φ_3 for the Ga implanted DLC region first decreased then rise. The difference in Φ_{DLC} between Ga implanted region and unimplanted region was denoted as $\Delta\Phi_{DLC}$. And the temperature-dependent change in $\Delta\Phi_{DLC}$ was similar to that observed in the graphene/Ga implanted DLC heterointerface. Specifically, at 300°C, $\Delta\Phi_{DLC}$ was negative (-458.79±4.90 meV, Figure 4.9a). It then transitioned to positive between 420°C ($\Delta\Phi_{DLC} = -49.72\pm9.85$ meV, Figure 4.9b) to 450°C ($\Delta\Phi_{DLC} = 150.55\pm17.75$ meV, Figure 4.9c). At higher temperatures, such as at 500°C, it remained positive ($\Delta\Phi_{DLC} = 143.72\pm15.00$ meV, Figure 4.9d). The transition of $\Delta\Phi_{DLC}$ from negative to positive values with increasing T_{anneal} was illustrated in Figure 4.7e. Additionally, the relative change of $\Delta\Phi_{DLC}$ before and after annealing at different preset T_{anneal} became increasingly positive at higher temperature values. Specifically, annealing at 300°C led to a more negative relative change in $\Delta\Phi_{DLC}$ (-225.53±5.99 meV), while at 500°C, there was a significant shift in the relative change of $\Delta\Phi_{DLC}$ towards a positive value (817.8±45.55 meV). The value of $\Delta\Phi_{DLC}$ was similar to the change in $\Delta\Phi_{GR}$ observed in the graphene/Ga implanted DLC heterointerface, indicating the charge transfer at that heterointerface.

Furthermore, we collected temperature-dependent Raman spectra on both Ga implanted (Figure 4.9f) and unimplanted regions (Figure 4.10) to probe the local structural reconstruction in the DLC film. Two characteristic peaks of DLC, the D peak (~1350cm⁻¹) and G peak (~1600cm⁻¹), were observed in the Raman spectra. Deconvolution of these peaks allows quantitative analysis of the sp²/sp³ ratio in DLC using I_D/I_G ratio in Raman spectra. Specifically, we adopted a Breit-Wigner-Fano (BWF) fit for the G peak and a Lorentzian fit for the D peak²⁶¹. The BWF fit is given as below:

$$I(\omega) = \frac{I_G [1 + 2(\omega - \omega_G) / Q\Gamma_G]^2}{1 + [2(\omega - \omega_G) / \Gamma_G]^2}$$

where I_G and ω_G are the peak intensity and peak position for G peak, respectively. Γ_G is the full width half maximum (FWHM) of G peak and Q^{-1} is the BWF coupling coefficient.

The Lorentzian fit is given as below:

$$I(\omega) = \frac{I_D \left(\frac{\Gamma_D}{2}\right)^2}{(\omega - \omega_D)^2 + \left(\frac{\Gamma_D}{2}\right)^2}$$

where I_D and ω_D are the peak intensity and peak position for D peak, respectively. Γ_D is FWHM of D peak. A higher I_D/I_G indicates an increased the sp²/sp³ ratio in the DLC film²⁶¹. Notably, even in the pre-annealed sample, the Ga implanted region showed a higher

sp^2/sp^3 ratio compared to the unimplanted region (Figure 4.9 g). With increasing temperature, the implanted region took on graphitic (sp^2) order, as evident at 400°C where a saddle point between the D and G peaks appeared. In contrast, the unimplanted region exhibited a much less pronounced ordering with temperature, except for 500°C, where annealing-induced graphitization initialized²⁶².

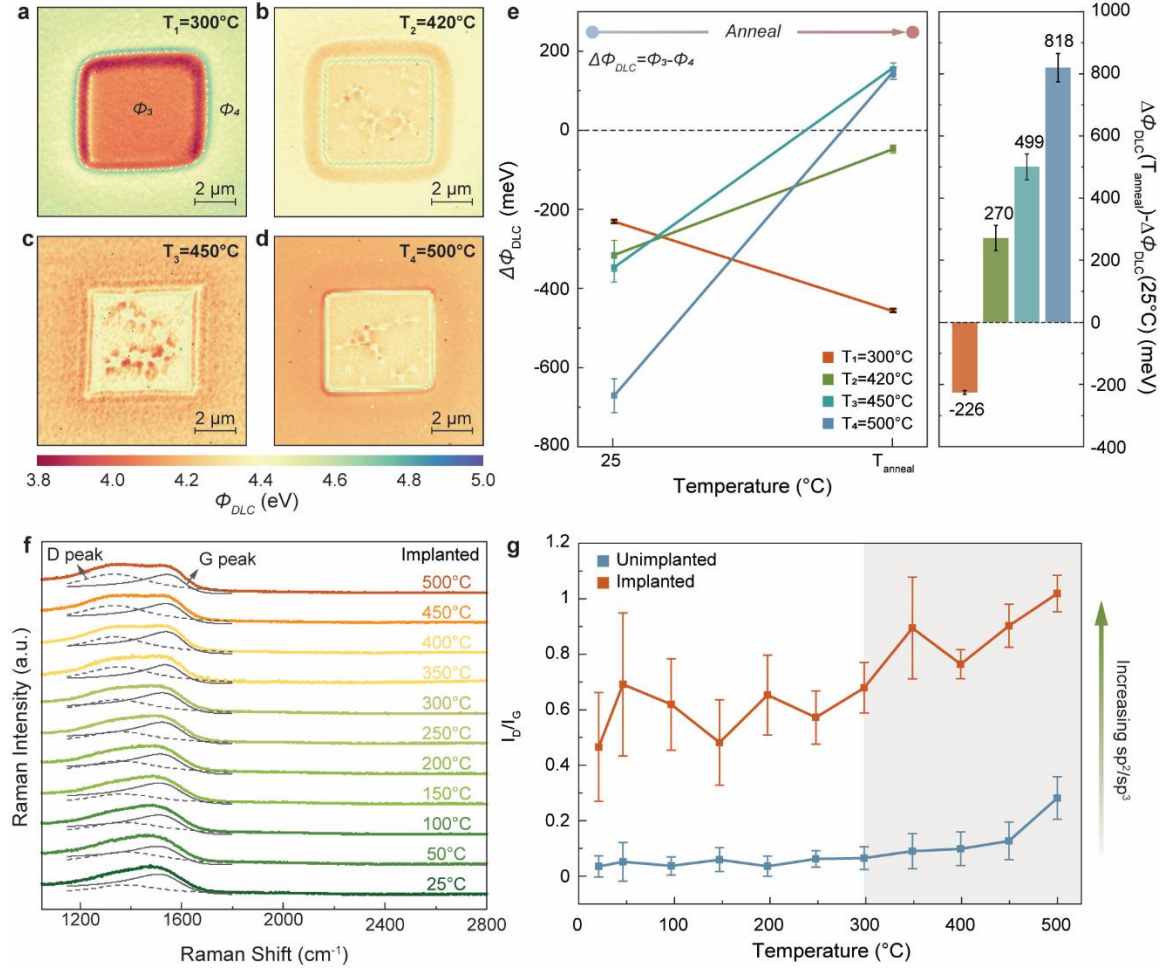


Figure 4.9: Temperature-dependent work function difference and sp^2/sp^3 ratio in Ga implanted DLC. (a to d) Work function mappings for Ga implanted DLC annealed at 300°C (a), 420°C (b), 450°C (c), and 500°C (d), respectively. (e) Temperature-dependent $\Delta\Phi_{DLC}$ values of Ga implanted DLC at 25°C and after annealing at various preset T_{anneal} . (Right) Change of $\Delta\Phi_{DLC}$ before and after annealing at different preset T_{anneal} . (f) Raman spectrums for Ga implanted DLC across a temperature range from 25°C to 500°C. Fitting curves for D- and G peak are highlighted in black dash line and black solid line, respectively. (g) Comparison of the intensity ratio I_D/I_G in Raman spectrums between Ga implanted (orange) and unimplanted DLC (blue). Temperature range for I_D/I_G ration enhancement in Ga implanted DLC is highlighted in a light-grey region.

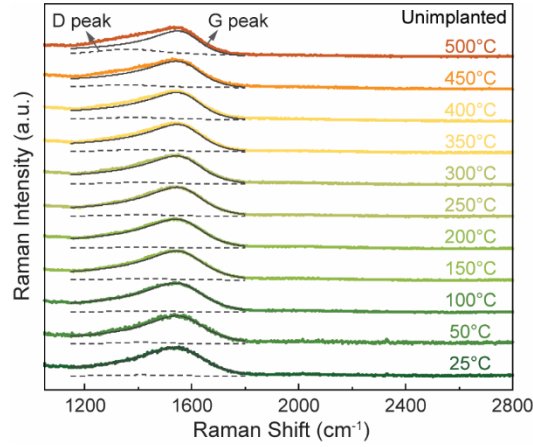


Figure 4.10: Temperature-dependent Raman spectra for unimplanted DLC across a temperature range from 25°C to 500°C. Curve fits for the D- and G peak positions are highlighted in *black dash line* and *black solid line*, respectively.

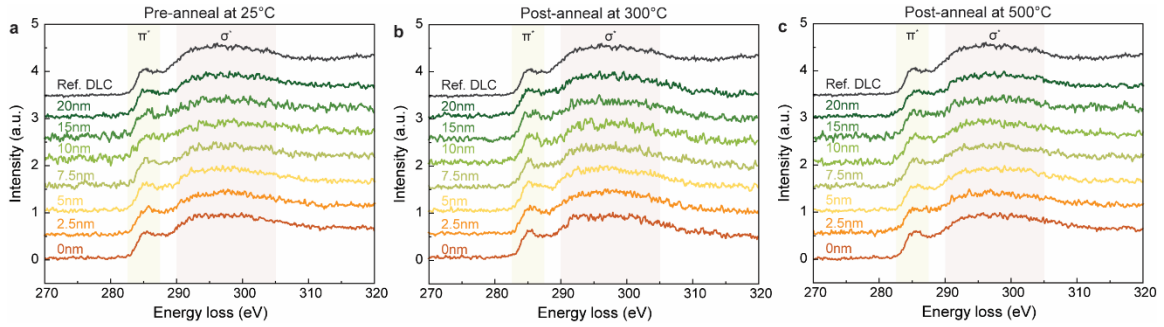


Figure 4.11: Cross-section EELS measurements for Ga implanted DLC after different annealing treatments. The cross-section EELS spectra were collected along the z-direction of Ga implanted DLC for three different annealing settings: (a) at room temperature without annealing, (b) post-annealing at 300°C, and (c) post-annealing at 500°C. For each sample, seven EELS spectra at depth values of: 0nm (top surface of DLC, *red line*), 2.5nm (*orange line*), 5nm (*yellow line*), 7.5nm (*grass green line*), 10nm (*light green line*), 15nm (*green line*) and 20nm (*dark green line*). The reference EELS spectrum was collected on pristine DLC with a sp^2/sp^3 ratio of 1.5 (*black line*). The energy window for the intensity integration of π^* and σ^* peaks are highlighted with *light yellow* and *light pink boxes*, respectively. All the cross-section EELS characterizations were performed at room temperature.

Further investigation into the temperature-dependent evolution of local sp^2/sp^3 ratio in Ga implanted DLC was conducted with cross-section EELS measurements. Evident in Figure 4.11 were two characteristic peaks, π^* (~285.4eV) and σ^* (~295eV) peaks, across Ga implanted DLC samples which underwent varied annealing treatments: without annealing (Figure 4.11a), annealing at 300°C (Figure 4.11b), and annealing at 500°C (Figure 4.11c), respectively. The π^* peak is associated with the $1s \rightarrow \pi^*$ transition in carbon, whereas the σ^* peak relates to the $1s \rightarrow \sigma^*$ transition²⁶³. Thereby, the intensity ratio between the π^* and σ^* peaks (I_{π^*}/I_{σ^*}) enables the quantification of sp^2/sp^3 ratio in Ga implanted DLC, where

a stronger π^* peak suggests an increase sp^2/sp^3 ratio. Towards it, a two-windows method²⁶⁴ was used, where I_{π^*} and I_{σ^*} were integrated within an energy range highlighted with *light yellow* and *light pink boxes* in Figure 4.11, respectively. It's critical to note that the accuracy of the calculate sp^2/sp^3 ratio heavily relies on the integration range for π^* peak²⁶⁴. Drawing parallels between our EELS spectra—specifically in terms of the shape of spectra and peak positions—and those reported by Bruley et al²⁶⁴, we adopted to their optimized integration parameters to ensure the accuracy in the quantification process. For π^* peak, integration was performed within a 4eV energy window centered at 285.4eV. And for σ^* peak, a 10eV energy window from 295eV to 305eV was adopted. The relative amount of sp^2 in Ga implanted DLC was calculated with²⁶³:

$$\frac{sp^2_{Ga^+-DLC}}{sp^2_{ref}} = \frac{I_{\pi^*,Ga^+-DLC}}{I_{\pi^*,Ga^+-DLC} + I_{\sigma^*,Ga^+-DLC}} / \frac{I_{\pi^*,ref}}{I_{\pi^*,ref} + I_{\sigma^*,ref}}$$

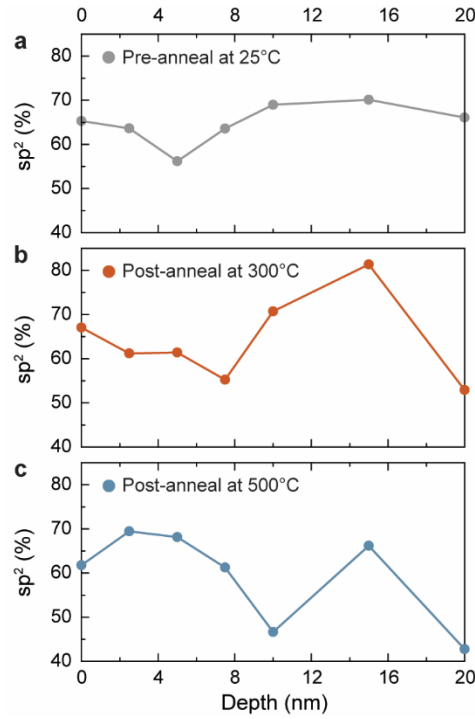


Figure 4.4.12: Quantification of the relative amount of sp^2 in Ga implanted DLC after different annealing treatments. The relative amount of sp^2 was quantified along the depth direction of Ga implanted DLC for three different annealing settings: (a) at room temperature without annealing, (b) post-annealing at 300°C, and (c) post-annealing at 500°C.

Intriguingly, the relative amount of sp^2 was not uniform in Ga implanted DLC (Figure 4.12) and reached its peak in the Ga-rich areas. This observation was well aligned with previous *in situ* TEM study, which suggested that a sp^2 -rich shell would preferentially form around Ga nanoparticles²⁶⁵, where Ga was in direct contact with carbon and thereby facilitated the graphitization. Notably, for Ga implanted DLC without annealing, a broad peak from 10nm to 15nm was observed. No significant peak shifting was observed after annealing treatment

at 300°C, aligning with the findings in the depth profiles of Ga distribution in DLC film (Figure 4.8). Yet, the peak value sharply increased from 70.1% to 81.3%, indicating that Ga trapped within the DLC facilitated the local graphitization of DLC. Upon annealing at a higher temperature, such as 500°C, a noticeable shift in the peak for the relative amount of sp² towards the DLC surface was found, where the peak was 2.5~5nm from the DLC surface. This shift was attributed to Ga diffusion during annealing, as depicted in Figures 4.7 and 4.8. The accumulation of Ga near the DLC surface resulted in an increased concentration of local sp²-carbon compared to other regions.

4.5 Interaction between graphene and Ga implanted DLC

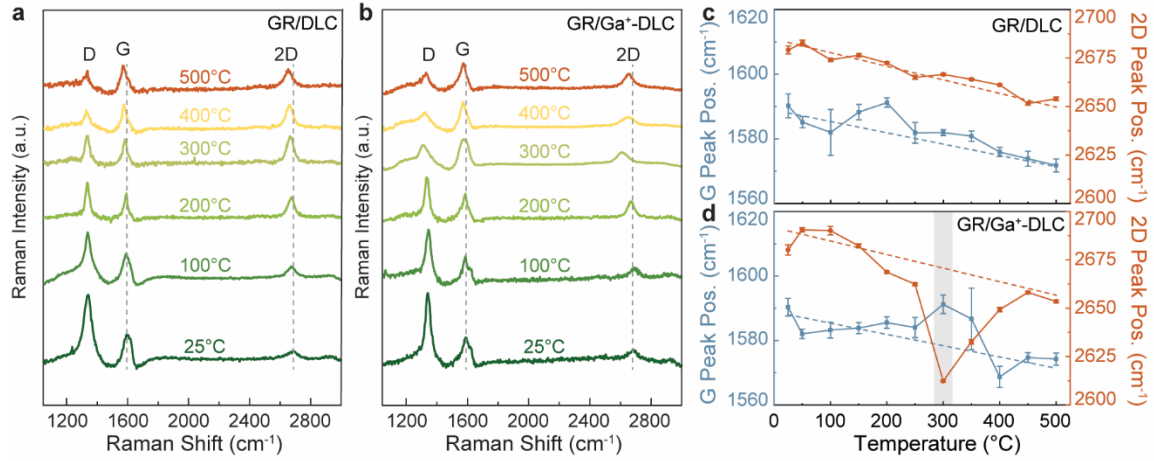


Figure 4.13: Temperature-dependent Raman measurements of graphene/Ga implanted DLC heterostructure. (a,b) Raman spectra for graphene/DLC(a) and graphene/Ga implanted DLC (b) across a temperature range from 25°C to 500°C. (c,d) Temperature-dependent evolution of G peak (blue) and 2D peak (orange) in Raman spectra for graphene/DLC (c) and graphene/Ga implanted DLC (d). Temperature-dependent evolution of G peak (blue) and 2D peak (orange) positions for pristine graphene are highlighted in *dash line*.

Furthermore, heavily n-type doping of graphene was achieved even at 300 °C. Temperature-dependent Raman spectrums for graphene atop both unimplanted (Figure 4.13a) and Ga implanted DLC (Figure 4.13b) were collected to determine the electron concentration in graphene by analyzing the shifts in the G (ω_G) and 2D (ω_{2D}) peak positions. The dashed lines depicted in Figure 4.13c and Figure 4.13d represented the temperature-dependent evolution of the G and 2D peak positions for pristine graphene, adopted from Abudula *et al*'s work²⁶⁶. According to the temperature-dependent Raman measurements on pristine graphene monolayer, which was first annealed in Ar to minimize the impact of air on graphene in ambient environment and then cooled down to room temperature, temperature-dependent ω_G and ω_{2D} could be described with the following equations:

$$\omega_G(T) = -0.035 * T + 1597.3$$

$$\omega_{2D}(T) = -0.070 * T + 2704.5$$

where the units for Raman peak position and temperature are cm^{-1} and K, respectively. Notably, for the graphene/Ga implanted DLC heterostructure, a substantial shift in both G and 2D peaks were detected at 300 °C. These shifts could be attributed to strain and doping effects in graphene¹⁶⁴. However, given that the evolution of G and 2D peak positions in both graphene/DLC and graphene/Ga implanted DLC heterostructures consistently aligned with that of pristine graphene²⁶⁶, we could infer that the influence of strain was negligible. By using the G and 2D peak positions of pristine graphene at 300 °C as references, the observed peak shifts in the graphene/Ga implanted DLC heterostructure were solely attributable to doping, resulting in G and 2D peak shifts of 12.8 cm^{-1} and -58.4 cm^{-1} , respectively. Incorporating these doping-induced shifts into the G and 2D peak positions at room temperature yielded a G peak at 1603.2 cm^{-1} , correlating to an electron concentration of $3 \times 10^{13} \text{ cm}^{-2}$, and a 2D peak at 2621.7 cm^{-1} , corresponding to an electron concentration of $4.6 \times 10^{13} \text{ cm}^{-2}$ ²⁶⁷.

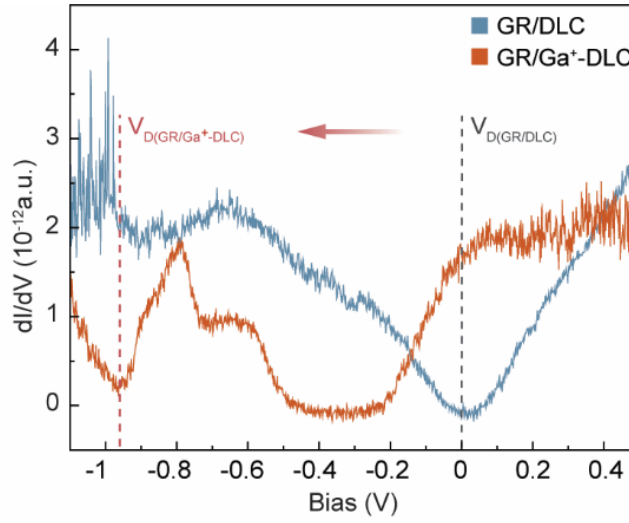


Figure 4.14: STS measurements of graphene/Ga implanted DLC heterostructure. STS dI/dV measurements across graphene/DLC (blue solid line) and graphene/Ga implanted DLC region (orange solid line) with $V_{\text{modulation}}$ as 5mV. The corresponding Dirac points (V_D) are highlighted with black dashed line and red dashed line, respectively.

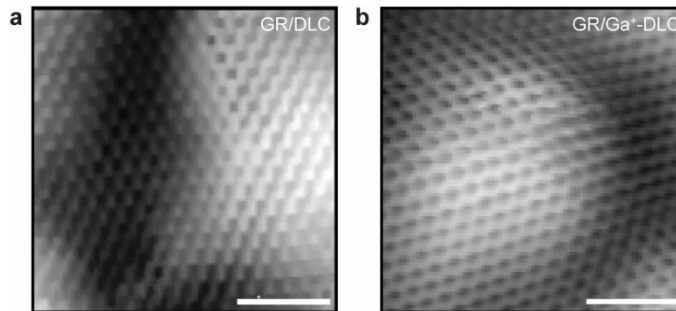


Figure 4.15: Constant-current imaging over different graphene regions. STM images ($I_{\text{tunnel}} = 30 \text{ pA}$, $V_{\text{sample}} = 1.0 \text{ V}$) depicting the unit cell of graphene were collected over (a) graphene on pristine DLC region and (b) graphene on the Ga implanted DLC region. The scale bar is 1nm.

Comparative STS dI/dV measurements across the graphene/DLC and graphene/Ga implanted DLC regions further corroborated this high electron concentration. The dI/dV curve was proportional to the local density of states (LDOS) of the sample at the tunneling site. For graphene/DLC region, the Dirac point (V_D) – indicative of the minimum LDOS of graphene – was observed at $V = 0$ (Figure 4.14, *black dash line*). Contrastingly, a more intricate dI/dV curve was observed in graphene/Ga implanted DLC region, marked with two distinct local minima. The first minimum located around $V = -0.35\text{mV}$ corresponds to the phonon scattering gap¹⁶⁶. The second minimum, the shifted V_D from graphene Fermi level, was at the $V = -0.962\text{V}$ (Figure 4.14, *red dash line*), confirming the n-type doping of graphene. Based on the equation for Fermi energy²⁶⁸, the carrier density (n) is:

$$n = \frac{4\pi|\Delta E_F|^2}{(h v_F)^2}$$

where h is the Planck constant and v_F is the graphene Fermi velocity, the electron density in graphene/Ga implanted DLC region was $6.84 \times 10^{13} \text{ cm}^{-2}$ with a Fermi level shifting (ΔE_F) of -0.962eV . The Raman and STS evidence together demonstrated the successful achievement of heavily n-doped graphene, with an electron density on the order of $3\text{--}6.84 \times 10^{13} \text{ cm}^{-2}$ from the sample that was annealed at 300°C . Additionally, a ΔE_F of -0.962eV was estimated to induce a decrease of 1.043mN/m in graphene surface energy from the sample that was annealed at 300°C .

Additionally, the local structural change for graphene/Ga implanted DLC heterointerface was probed with STM measurements. The honeycomb lattice structure of graphene was clearly observed across the STM images on graphene/DLC (Figure 4.15a) and graphene/Ga implanted DLC (Figure 4.15b), confirming the well preservation of the graphene structure using our work function engineering platform.

4.6 Structure-dependent electronic transport at the heterointerface

The mechanism underlying experimentally observed evolution in the graphene electronic properties in response to the graphene/Ga implanted DLC heterostructure's thermal history was studied by computational simulations focusing on the structure-property relation at this heterointerface. As Raman shifts indicated negligible strain in graphene across all applied temperatures (Figure 4.13, c and d), the impact of annealing-induced Ga redistribution and structural changes within DLC emerged as the focal points in our investigation. Results from depth profiling (Figure 4.7, a to c) and temperature-dependent Raman measurements (Figure 4.9g) indicated three vital structural modifications after annealing: the changing sp^2/sp^3 ratio within Ga implanted DLC, diffusion, precipitation and accumulation of the Ga at graphene/Ga implanted DLC heterointerface. To decouple and assess the influence of each of these variations, computational models were developed to simulate different stages of Ga diffusion through Ga implanted DLC structure. To mirror the ion-induced π character enhancement in Ga implanted DLC observed in Raman measurements (Figure 4.9g), our simulations included three sets of surface models representing DLC substrates with decreasing proportion of saturated (sp^3) bonds (39%, 20%, and 14%). For each set of systems, we examined both isolated DLC structure and that paired with a graphene monolayer. DFT calculations revealed a modest 0.27eV

increase in DLC surface work function as the sp^2/sp^3 ratio decreased from 39% to 20%, but a negligible difference of 0.04eV between structures of 20% and 14% sp^3 compositions. Crucially, analysis focusing on electronic properties of graphene atop these DLC structures demonstrated that changing internal hybridization within DLC exerted minimal impact on graphene work function, with a difference of less than 0.05eV between all three cases. This finding underscored the marginal influence of sp^2/sp^3 ratio in DLC on the electronic structure of graphene, aligning seamlessly with the experimentally observed behavior of graphene/DLC with varying temperatures (Figure 4.13c).

To explore the influence of Ga redistribution in the Ga implanted DLC we constructed a series of systems to reflect the experimentally observed thermally driven diffusion of Ga within the bulk of DLC and its precipitation into the graphene-DLC heterointerface (Figure 4.16a). Computational models emulating this progression were shown in Figure 4.16b, Figure 4.17 and Figure 4.18 to illustrate the initial reference case, the intermediate states of Ga precipitation (Figure 4.16b), and the final state of a graphene on multi-layered Ga slab (Figure 4.17f). Comparison of these systems provided important insights into gallium's role in electrostatically doping graphene. Initially, the presence of Ga in the bulk of Ga implanted DLC exhibited negligible impact on graphene's electronic properties, with a mere 4meV deviation in work function noted between graphene on pristine and Ga-implanted substrates. This was further corroborated by a close match in the projected density of states for atoms in graphene within both DLC and Ga implanted DLC systems (Figure 4.18a). A marked transformation in graphene electronic structure emerged as Ga began to diffuse towards the heterojunction. Notably in the sub-monolayer regime, with the introduction of a single Ga atom confined on DLC surface (P0 in Figure 4.18b) resulted in a significantly greater decrease in graphene work function by 84meV. This was likely due to enhanced charge transfer as evidenced by a discernible differential charge isosurface. The alteration of the graphene work function by single atomic Ga culminated when the atom detached from the substrate surface and diffused into the heterointerface. Energy-minimized configuration of this scenario (P1) featured diffusion of single atomic Ga from Ga implanted DLC surface towards strong adsorption onto graphene monolayer, resulting in a minimal Ga-graphene separation of mere 2.2Å. The strong n-type electrostatic doping of graphene due to Ga adsorption manifested itself in a drastic reduction in graphene's work function by 421meV, an extensive charge density accumulation in graphene conjugated π orbitals (Figure 4.16b), and a notable shift of Fermi level by more than 1eV above V_D deep into the conduction band (Figure 4.17b). This negative doping of graphene by sub-monolayer single atomic Ga was consistent with previously documented behaviors of Ga and other metal adsorbates on graphene²⁶⁹⁻²⁷¹.

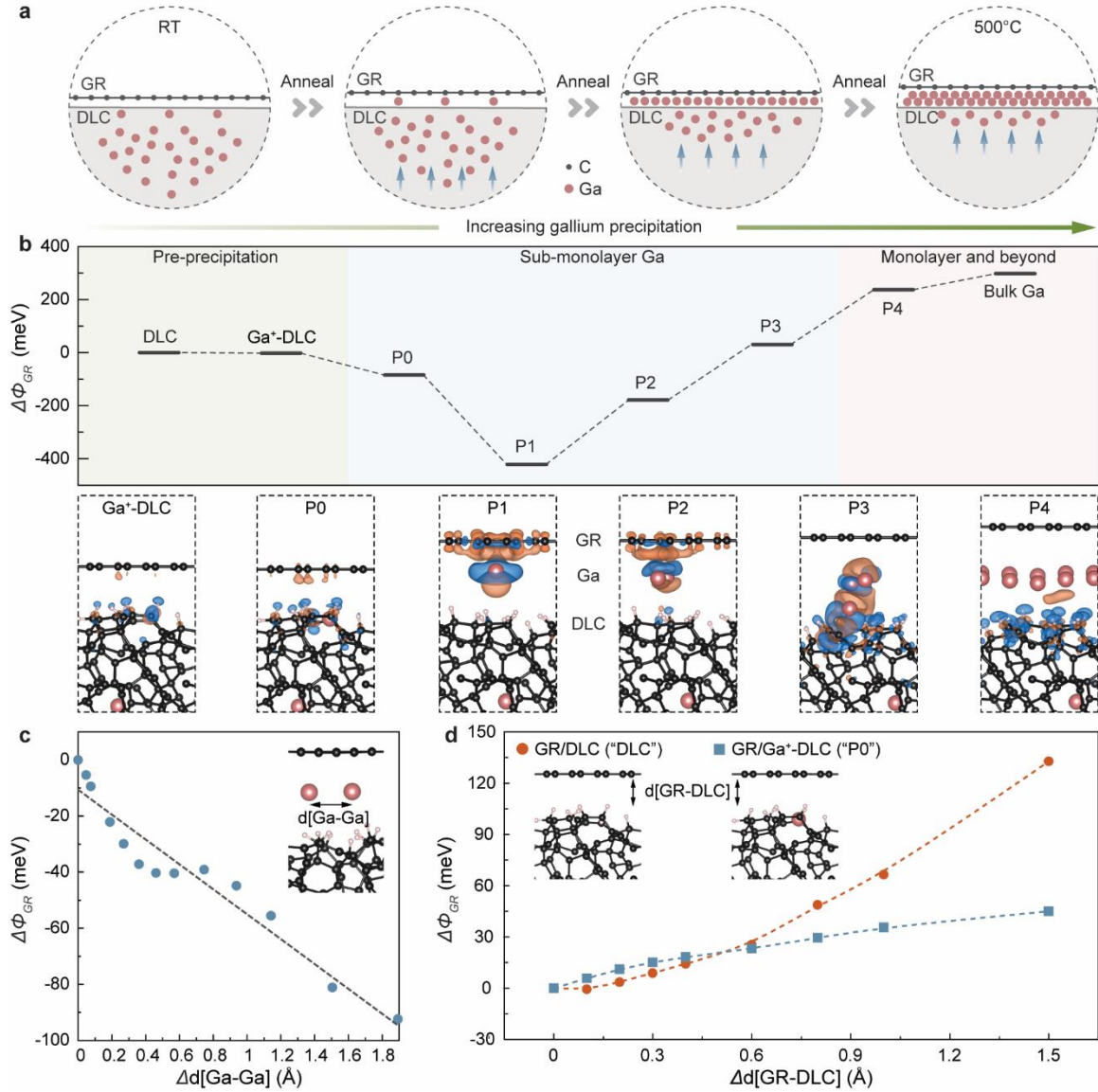


Figure 4.16: Simulation of Ga precipitation at the heterointerface and its impact on electrostatic doping level of graphene. (a) Schematic illustrating the four stages of Ga diffusion with increasing annealing temperature. (b) Variation in the work function of graphene relative to the reference system of graphene on unimplanted DLC, accompanied by visualizations of electron transport from DLC substrate and intercalated Ga to graphene monolayer. Displayed isosurfaces correspond to differential charge transfer of 0.0008 electron/Bohr³, where regions of charge depletion and regions of charge accumulation are highlighted with *blue* and *orange*, respectively. (c) Plot showing the change in the graphene work function (ϕ_{GR}) in relation to the increase in Ga-Ga bond length from equilibrium in system P2; (d) with respect to the increase in vertical spacing between Ga and graphene monolayer from equilibrium in systems DLC and P0.

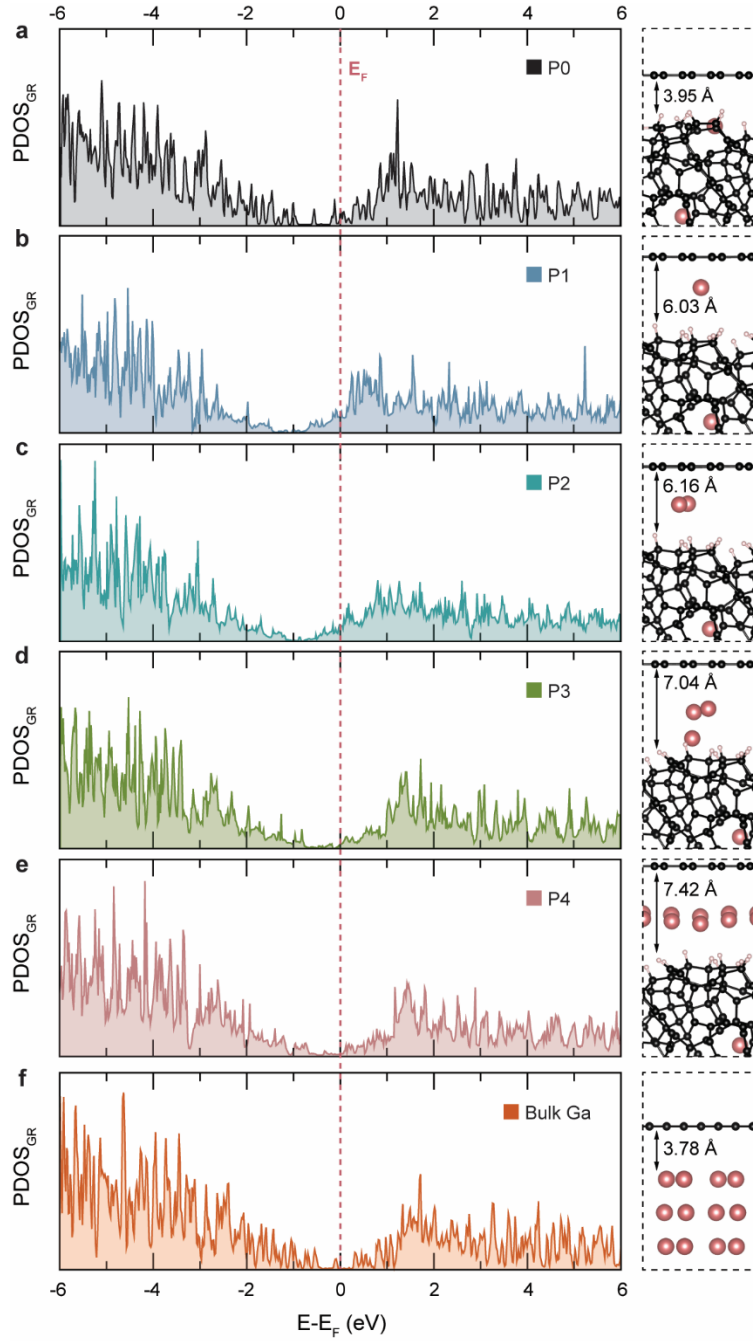


Figure 4.17: Variation in structure configuration and electronic properties in graphene with increased Ga presence at the heterointerface. The panels on left depict the projected density of states for graphene, while the right panels illustrate the corresponding heterointerface structures with: (a) single atomic Ga anchored on the Ga implanted DLC surface; (b) single atomic Ga adsorbed onto graphene monolayer; (c) a diatomic Ga cluster under graphene; (d) sub-monolayer triatomic Ga cluster; (e) a Ga monolayer separating graphene from Ga implanted DLC surface; (f) graphene monolayer deposited on Ga (001) surface of bulk metallic Ga.

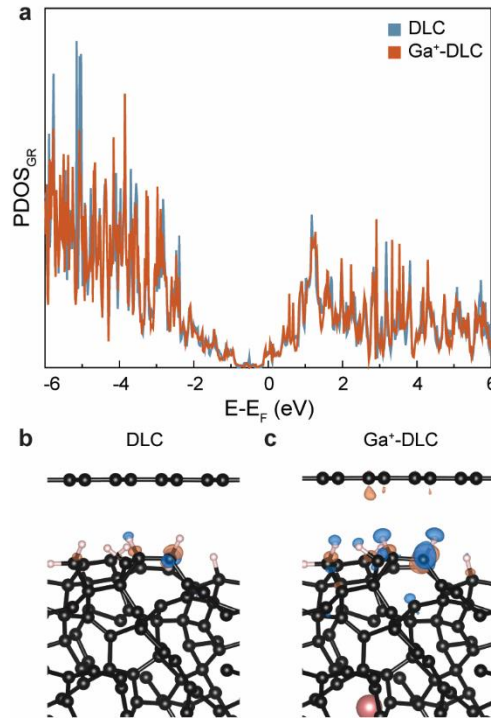


Figure 4.18: Comparison of electronic properties of graphene on DLC substrates with and without implanted Ga ions. (a) Projected density of states of graphene on DLC and on Ga implanted DLC. Visualization of structure and isosurface of differential charge transfer for heterostructures consisting of (b) graphene monolayer on pristine DLC; (c) graphene monolayer on Ga^{implanted} DLC.

Further investigations into heterointerface featuring Ga clusters consisting of 2 and 3 atoms (P2 and P3) revealed a non-monotonic relationship between sub-monolayer Ga concentration and doping levels in graphene. Geometric relaxations presented an increase in spacing between Ga implanted DLC and graphene monolayer (Figure 4.17, b to e) and reposition of Ga closer to Ga implanted DLC substrate surface with increasing size of Ga cluster. Notably, charge transfer from Ga cluster to graphene decreased sharply with each additional Ga atom in the cluster at the heterointerface. The work function of graphene in the presence of 3 sub-monolayer of Ga reverted to a level comparable to that of graphene atop pristine DLC. When the amount of Ga at heterointerface was further increased to simulate an entire metallic monolayer, the work function of graphene elevated to approximately 248meV above the reference (“Bulk Ga” in Figure 4.16b and Figure 4.17). This evolution corroborated conclusions from previous studies on changing doping strength in graphene with different configurations of dopant clusters²⁷¹⁻²⁷³, and provided a mechanistic insight correlating the monotonic increase in Ga distribution at the heterointerface, with bipolar tuning of the spatial contrast in the graphene work function controlled by annealing temperature as seen experimentally.

We then explored the influence of Ga clustering on electrostatic doping of graphene *via* comparative studies on the precipitation geometry and bonding environment of Ga. Contrary to prior hypotheses emphasizing the proximity between Ga and graphene as the

principal determinant of charge transfer²⁷¹, our results revealed the critical influence of inter-Ga atomic distances. Static calculations were performed to investigate the effect of increasing Ga-Ga separation within the diatomic cluster without changing vertical distances between Ga and graphene. The results demonstrated a consistent reduction in graphene work function (Figure 4.16c), signifying a continuous enhancement in charge transfer from Ga to graphene in response to widening inter-Ga separation (Δd). Remarkably, extending the Ga-Ga bond length by less than 60% led to a notable reduction in graphene's work function by roughly 100meV. In contrast, increasing vertical spacing between graphene and Ga atom anchored on Ga implanted DLC surfaces (P0) prompted only marginal changes in graphene's electronic properties, with a shift in work function not exceeding 30meV (Figure 4.16d). Moreover, such alteration in graphene electronic properties could primarily be ascribed to distance-dependent electrostatic interactions between graphene and DLC substrate. Comparative analyses applying equal vertical displacements to graphene on pure DLC indicated that for graphene with heterointerfaces depleted of Ga atoms, an increase in its separation from DLC surface engendered more pronounced changes in its work function than in cases where graphene was separated from substrates with surface-bound Ga. Such sharp comparison confirmed the marginal influence of graphene-Ga vertical spacing in modulating charge transfer and implied the potential capability of Ga in stabilizing electronic behaviors of overlying graphene monolayer against variations in spacing at the heterointerface.

4.7 Highly tunable work function landscape of graphene at chosen temperature

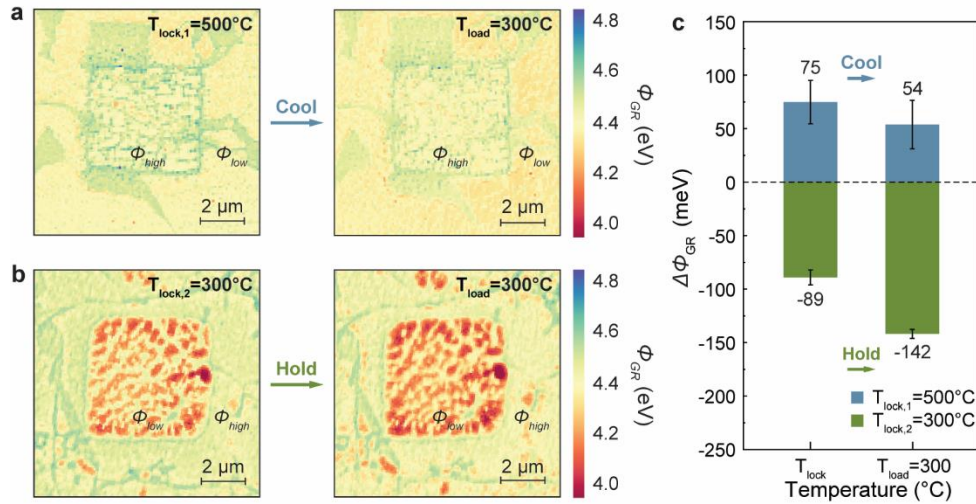


Figure 4.19: Tuning the work function landscape of graphene with temperature. (a) Work function maps for graphene on Ga implanted DLC annealed at 500°C (left), then cooled to 300°C (right). (b) Work function maps of graphene on Ga implanted DLC annealed at 300°C (left), then held at 300°C (right). (c) Corresponding temperature-dependent $\Delta\Phi_{GR}$ values extracted from (a) and (b).

This innovative graphene platform, leveraging the aforementioned mechanism, enables distinct graphene work function landscape at the same temperatures. Specifically, by obtaining a targeted work function difference at a predetermined temperature (T_{lock}), this

difference can be maintained at a different temperature (T_{load}). This capability was demonstrated in Figure 4.19, a and b: after annealing at 500°C for 1.5 hours, the graphene work function on the Ga implanted DLC region was higher than that on the unimplanted region, achieving a $\Delta\Phi_{GR}$ of 74.80 ± 20.20 meV. This $\Delta\Phi_{GR}$ persisted even after rapid cooling to 300°C and subsequent annealing for another hour, with a $\Delta\Phi_{GR}$ of 53.66 ± 22.71 meV. In contrast, initial annealing at 300°C for 1.5 hours resulted in a lower graphene work function on the Ga implanted DLC region ($\Delta\Phi_{GR}$ of -89.21 ± 7.00 meV), which remained lower after additional 1-hour-anneal at 300°C ($\Delta\Phi_{GR}$ of -141.91 ± 4.24 meV) (Figure. 4.19c). This approach effectively decoupled the work function difference from temperature constraints, enabling the realization of a broad range of $\Delta\Phi_{GR}$, available from negative to positive, at one temperature with a same pattern.

Beyond temperature versatility, the complexity of our Ga implanted DLC pattern can be enhanced to cater to diverse applications using Ga implanted DLC squares as building block. Towards it, a FIB pattern was created using the serial patterning mode to guarantee the consistency of FIB implantation time, and therefore the surface morphology (e.g., height and area) across different Ga implanted DLC squares (More details in **Section 4.2.1.2**). For instance, a $215\mu\text{m}\times215\mu\text{m}$ FIB pattern containing 81 Ga implanted DLC squares were designed for demonstration. And nano-ARPES revealed consistent photoemission spectra across these squares after annealing treatment at 500°C with well defined, sharp borders. Representative XPS spectra taken within the squares and outside the squares are shown in Figure 4.20a. The clear peak structure around $E - E_F = -20.4\text{eV}$, attributed to the Ga 3d core levels, was observed within the Ga implanted DLC squares, indicative of uniform Ga precipitation throughout these regions (Figure 4.20, b and c). A detailed nano-ARPES analysis within a central region (*yellow dash box* in Figure 4.20b) showed the spatial distribution of photoemission intensity inside and outside the Ga implanted DLC squares at higher resolution (Figure 4.20, c and d). A notable transition in photoemission intensity was observed as the energy level $E - E_F$ from -7eV to -3eV , aligning with the appearance of DLC XPS peak near -3eV (Figure 4.20a). Specifically, photoemission intensity near $E - E_F = -3\text{eV}$ was stronger outside the squares, and the strong peak may be attributed to DLC electronic features, which are attenuated by the Ga overlayer in the squares, resulting in the reversed contrast (Figure 4.20d). Given the acute sensitivity of nano-ARPES to local electronic structures, this consistency of photoemission intensity across different Ga implanted DLC squares spanning various energy levels suggested a very similar local band structure within these regions (Figure 4.20e). These findings collectively indicated limited lateral bulk diffusion of Ga within the DLC, ensuring the tight confinement of Ga within the designated implanted region. In this way, each Ga implanted DLC square will induce similar change in graphene work function through charge transfer at heterointerface. Leveraging this consistency, we can design intricate patterns using Ga implanted DLC squares as building blocks to obtain varied work function landscapes of graphene at chosen temperature, tailored to specific needs in different area selective material growth process.

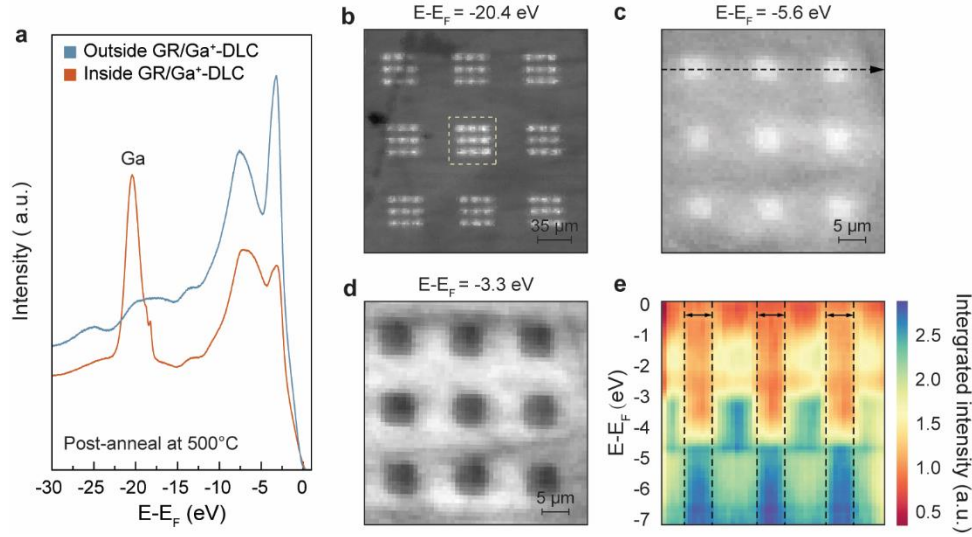


Figure 4.20: Nano-ARPES mappings on array pattern composed of uniform Ga implanted DLC squares. (a) XPS spectra collected inside (orange) and outside (blue) graphene/Ga implanted DLC region after annealing at 500°C, respectively. (b) Photoemission intensity map for 215μm-by-215μm pattern composed of 81 Ga implanted DLC squares near Ga 3d core level ($E - E_F = -20.4\text{ eV}$). (c,d) magnified integrated photoemission intensity map of the central region of d (yellow dash box) with $E - E_F = -5.6\text{ eV}$ (c) and $E - E_F = -3.3\text{ eV}$ (d), respectively. (e) Energy resolution of the integrated photoemission intensity along dashed arrow in (b), and Ga implanted DLC square regions are highlighted with black dash lines. The spectral integration range for b to e is $\pm 0.3\text{ eV}$.

4.8 Conclusions

In this chapter, we have demonstrated a highly controllable and area-selective platform employing Ga implanted DLC films to precisely engineer graphene work function across a broad temperature spectrum. The work function difference between graphene atop Ga implanted DLC and unimplanted DLC can be fine-tuned in both magnitude and polarity, offering exceptional spatial control of the doping level in graphene from ambient temperatures up to 500 °C. Notably, annealing at 300°C resulted in a negative $\Delta\Phi_{GR}$, which transitioned to positive around the threshold temperature of approximately 420°C. This $\Delta\Phi_{GR}$ remained positive at a higher T_{anneal} such as 500°C. The temperature-dependent evolution in $\Delta\Phi_{GR}$ was attributed to the thermal-induced diffusion of Ga within the bulk DLC, and its subsequent precipitation at the graphene/Ga implanted DLC heterointerface. Upon this diffusion process, Ga was found to catalyze a local change in the sp^2/sp^3 ratio within DLC. This led to a structural change in DLC, and consequently, a temperature-dependent work function evolution for DLC similar to that for graphene atop Ga implanted DLC. Remarkably, a heavily n-doped graphene was achieved at 300 °C, exhibiting an electron density at the order of $3\text{-}6.84 \times 10^{13}\text{ cm}^{-2}$, as estimated from G and 2D peak shifts in Raman measurements and V_D shifting in STS dI/dV measurements. A ΔE_F of -0.962 eV would be estimated to induce a decrease of 1.043 mN/m in graphene surface energy at 300°C.

Further DFT calculations revealed the critical role of Ga diffusion and the formation of

sub-monolayer Ga in achieving such high doping levels in graphene. Conversely, variations in the sp^2/sp^3 ratio within the DLC exerted minimal impact on graphene work function, across three ratios examined (39%, 20%, and 14%). Additionally, Ga within the bulk of Ga implanted DLC had negligible impact on the electronic properties of graphene. The introduction of a single Ga atom at the graphene/Ga-implanted DLC interface significantly reduced the work function of graphene, which could be further diminished as Ga detached from the DLC surface and migrated into the interface. However, with increased Ga precipitation, the charge transfer from Ga clusters to graphene decreased sharply with each additional Ga atom at the heterointerface. The graphene work function difference reached its maximum (+248meV) when an entire Ga monolayer formed.

We then showed that our platform could create different graphene work function landscapes at the same temperature, depending on the specific annealing settings. Moreover, using this Ga implanted DLC squares as building blocks, complex FIB patterns could be designed to support various area-selective material growth processes. A very similar local band structure was observed across these Ga implanted DLC squares. Consequently, each Ga implanted DLC square could induce similar change in graphene work function and thereby its surface energy. Moreover, XPS revealed limited lateral bulk diffusion of Ga within the DLC, ensuring the tight confinement of Ga within the designated implanted region. These factors together enhanced the area selectivity in the material growth process through engineering the surface energy profile of substrate interface. This capability not only establishes a foundational platform for exploring the complex physics of heavily doped graphene at high temperature, but opens new pathways for exploring the dynamic process of area-selective material growth across a wide temperature range.

Chapter 5

Conclusions and suggestion for future work

This chapter captures the principal findings of this dissertation and suggests potential avenues for advancing the research frontier of the body of work presented. The investigation of confinement growth of materials through interface engineering approaches has elucidated the pivotal role of interface in material synthesis, which advances the proficiency and versatility in manipulating the structure-property of the materials that reside at these interfaces but also the materials that leads to the formation of such heterointerfaces (i.e., graphene) through proximity effects. To further our understanding and control over material growth processes, extending and refining the interface engineering techniques delineated in this dissertation is suggested.

5.1 Large molecule intercalation through graphene-substrate heterointerfaces

In this work, we explored that large molecule intercalation through graphene-Ge (110) heterointerface offered a novel pathway on circumventing the size constraints inherited in traditional basal-plane intercalation methods. Utilizing phosphorus pentoxide (P_2O_5) as a prototypical large molecule, this study provided an alternative intercalation route that potentially broadens the scope of materials amenable to such processes.

Firstly, the post-intercalation surface morphology and element distribution at the graphene-Ge (110) heterointerface was investigated, confirming the successful intercalation of P_2O_5 through the graphene interface. Then, nano-Fourier transform infrared spectroscopy (nano-FTIR) and X-ray photoelectron spectroscopy (XPS) analyses of the as-formed graphene - attributable to the intercalation - provided critical insights into the chemical reactions that can occur at such heterointerface. Notably, P_2O_5 gave rise to increasing sp^3 bonded carbon in graphene, likely indicative of the intercalation-induced modifications and/or the enhanced hybridization of the graphene with the underlying intercalants. Furthermore, the oxygen from the intercalated P_2O_5 exhibited a strong affinity to the germanium substrate, hinting to complex interfacial chemical dynamics.

Density Functional Theory (DFT) calculations proposed a two-step mechanism for the intercalation of P_2O_5 molecules through graphene-Ge (110) heterointerface, beginning with its dissociation into small fragments upon interaction with graphene defects. These fragments, with lower energy barriers for permeation, intercalated through common-observed intercalation pathways (point defects, line defects, and grain boundaries) to reach the heterointerface, where they re-assembled into P_2O_5 . Regarding the potential applications of this intercalation process, we showed that the intercalated P_2O_5 molecules could not only p-type dope the graphene layer through strain and charge transfer, but also facilitated the formation of confined metal phosphates at graphene-substrate heterointerfaces. These results together provided an important insight for advancing the understanding of intercalation pathways of large molecules through the basal plane of graphene as well as heterointerface chemical reactions to form unique confined complex oxide compounds. The insights garnered here not only deepen our comprehension of the underlying physical chemistry but also offer several directions for extending this work.

5.1.1 *In situ* experiments for the intercalation process

A two-step mechanism was proposed for the P_2O_5 interaction through graphene-Ge (110) heterointerface involving the fragmentation of P_2O_5 and the intercalation of the consequent small fragments. To elucidate this theory, an *in situ* experiments monitoring the gas phase environment change during the intercalation process is essential. Towards it, possible methodologies include time-resolved mass spectrometry (MS) to monitor gas-phase environment change during intercalation process, or a thermogravimetric analysis-mass spectrometry (TGA-MS) measurement from room temperature to 1000°C using a graphene monolayer with SiP_2O_7 powder on top as the sample. Such studies are beneficial for dissecting the P_2O_5 dissociation pathways and identifying the resultant products for each step, thereby solidifying the theoretical framework underpinning this research. Furthermore, by comparing the bonding energy of varied phosphorus-oxygen bonds derived from the MS measurements with the DFT calculation results, we can further

optimize the DFT results, and this theoretical framework may possibly provide guidance for many other large molecule intercalations.

5.1.2 Control over the intercalation process through the basal plane of graphene

The study of P_2O_5 interaction through graphene-Ge (110) heterointerface revealed the significance of graphene defects in facilitating the initial stages of intercalation (see **Chapter 2**). Specifically, these defects served to lower the energy barriers associated with P_2O_5 dissociation and the ensuing intercalation of resultant fragments, suggesting the feasibility of area-selective intercalation by managing the spatial distribution of graphene defects. To achieve such selective intercalation, study on high quality chemical vapor deposition (CVD) grown graphene on Ge (110) is essential to avoid the un-controlled defect distribution in transferred graphene. Compared to transferred graphene, CVD grown graphene usually has a high quality and more-controllable defect distribution. Nowadays, most of the CVD grown graphene are based on thermal CVD, where high-quality graphene growth on Ge requests a synthesis temperature close to the melting point of Ge²⁷⁴. Inevitable surface melting of Ge in thermal CVD approach will leave us a rough surface, which is not desirable for following intercalation process and stabilization of phosphorus buffer layer. Therefore, we will prepare the graphene with plasma-enhance CVD (PECVD) instead. In PECVD, plasma assists in the decomposition of CH_4 (carbon source) and allows the formation of graphene at relatively lower temperature ($\sim 700^\circ C$) to preserve the flat surface of Ge. After graphene growth on Ge (110), strategies like targeted e-beam or laser irradiation could be employed to introduce localized defects into the graphene lattice. A comprehensive study correlating the operational parameters of e-beam or laser irradiation – such as spot size, beam energy, and scanning area – with the resultant distribution of local defects on these processed graphene surfaces would be essential in optimizing this approach.

Moreover, maintaining a flat graphene surface post-intercalation is beneficial for the efficiency of subsequent fabrication processes. Apart from localizing intercalation sites, precise control over the quantity of molecules introduced through the basal plane is equally significant. To this end, a systematic exploration of the experimental conditions, including sample temperature, annealing time, pressure, and carrier gas flow rate can reveal possible routines to tailor the thickness of the intercalant layer and the surface morphology after intercalation. For instance, the combination of reduced annealing time and lower pressure can markedly lower the concentration of intercalants in the gas phase, presenting a promising avenue for achieving desirable intercalation characteristics.

5.1.3 Expansion of confined metal phosphates family

In our study, the P_2O_5 interacted through graphene heterointerface has successfully been used as reactant to convert the indium (In) thin layers to indium phosphate. By applying a similar methodology and substituting In with other metals — such as Ga, Ga_xIn_{1-x} ^{30, 178}, Ge, Sn, and Ge_xSn_{1-x} ²⁷⁵ — we can significantly expand the family of confined metal phosphates within graphene heterointerfaces. Among them, gallium phosphate (α -GaPO₄) emerges as a material of particular interest as a well-known piezoelectric materials iso-structural with α -SiO₂ but with significantly higher thermal stability (up to $930^\circ C$), comparable quality factor, and a higher piezoelectric coefficient, making it promising for

high temperature sensor application²⁷⁶. However, the synthesis of two-dimensional (2D) GaPO₄ poses a significant challenge, attributed to its inherently non-layered bulk structure, which prohibits further exploration upon its structural, electronic properties, and performance. Toward the synthesis of 2D GaPO₄, existing methods include vapor phase reactions between phosphoric acid and exfoliated gallium oxide layers. A key advantage of our intercalation-based approach over other synthesis methods is the direct integration of 2D GaPO₄ into heterostructures, which is free of time-consuming transfer processes. Additionally, the van der Waals (vdW) pressure arising from the interlayer environment may open up more opportunities into discovering or modulating the structure and properties of 2D metal phosphates. For instance, it is reported that the phase transition of GaPO₄ to a metastable orthorhombic crystal structure initializes around 9GPa at 320°C. Similar phase transition occurs in AlPO₄-GaPO₄ solid solution above 10GPa as well²⁷⁷. Thereby, this innovative strategy not only facilitates the synthesis of this promising material but also opens new avenues for the investigation and application of 2D metal phosphates within advanced electronic and sensor technologies.

5.1.4 Synthesis of phosphorus allotropes at the heterointerface

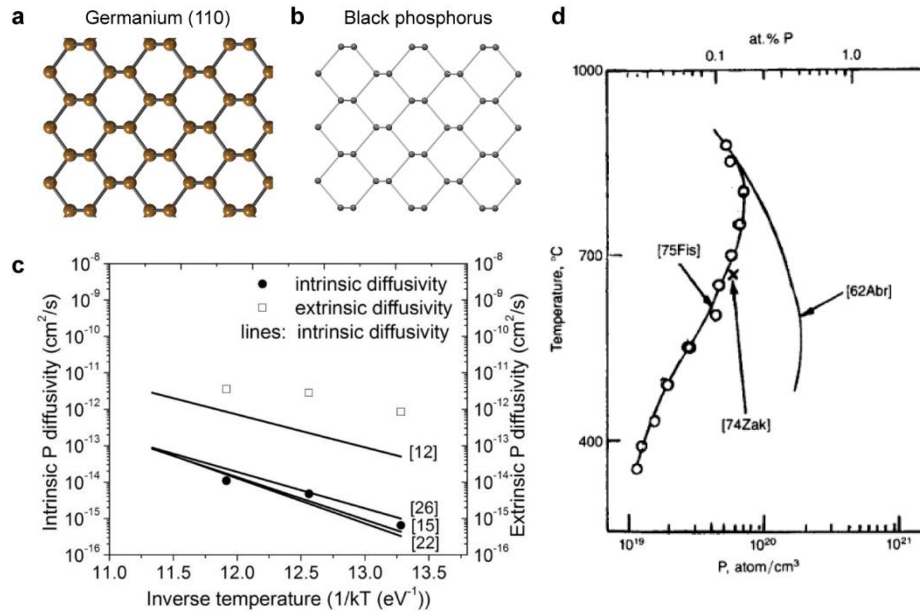


Figure 5.1: The structural similarity between Ge (110) and black phosphorus, and the diffusivity and solubility of P in Ge. (a) Top-view structure of Ge (110). (b) Top-view structure of black phosphorus. (c) The intrinsic (left y-axis, black circles) and extrinsic (right y-axis, open squares) diffusivities of P in Ge at different temperatures from reference¹⁴⁴. The temperature-dependent fittings for the intrinsic diffusivity of P in Ge are depicted with solid black lines. Reprinted with permission from Cai *et al.*, Journal of Applied Physics 112, no. 3 (2012). Copyright 2012 AIP publishing. (d) The solubility of P in Ge at different temperatures from reference¹⁴³. Reprinted with permission from Olesinski *et al.*, Bulletin of Alloy Phase Diagrams 6, 262-266 (1985). Copyright 1985 the American Society for Metals.

Except for facilitating the conversion of metal to its phosphate forms, the P_2O_5 intercalated can serve as a precursor for the synthesis of phosphorus allotropes at graphene heterointerface, with the aid of reducing agents like hydrogen gas. In this scenario, graphene-Ge (110) heterointerface is ideal for fostering the synthesis of phosphorus allotropes thin layers. Firstly, graphene bubbles emerged following intercalation can create a local, ultrahigh-pressure environment at the interface. This condition is energetically favorable for the nucleation and growth of phosphorus allotropes, notably black phosphorus. These nano-scaled bubbles, if approximately 1nm in height, are capable of exerting vdW pressures at the order of 1GPa¹⁵⁹. Additionally, graphene is impermeable to water and oxygen, shielding phosphorus allotropes from surface degradation^{134, 278}. The choice of Ge as the substrate is attributed to the atomic alignment in Ge (110) is similar to that of black phosphorus, thereby facilitating the formation of black phosphorus thin layers on Ge (110) (Figure 5.1, a and b). Furthermore, P has limited diffusivity¹⁴⁴ and solubility¹⁴³ in Ge (Figure 5.1, c and d). The stronger Ge-P bond compared to Ge-Ge¹⁴³ also promotes the formation of a phosphorus buffer layer at the graphene-Ge (110) interface.

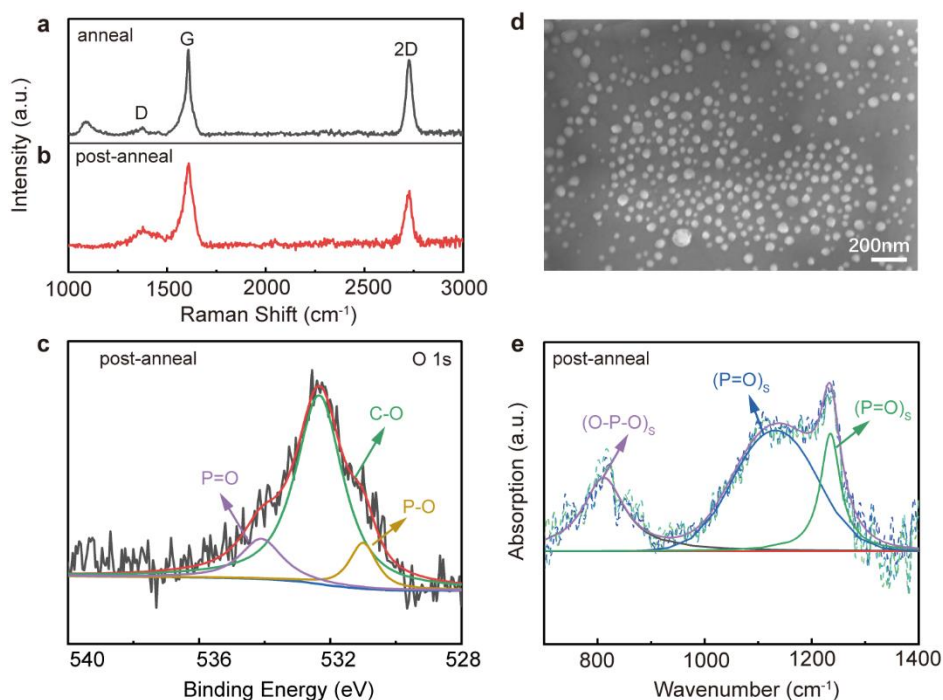


Figure 5.2: Chemical environment and surface morphology for graphene/ P_2O_5 /Ge (110) after annealing in H_2 at $500^\circ C$. Raman spectrum for graphene/ P_2O_5 /Ge (110): (a) before (*black line*) and (b) after (*red line*) annealing treatment in H_2 . (c) High-resolution XPS spectrum for O 1s showing the existence of C-O bond (*green line*), along with P-O bond (*yellow line*) and P=O bond (*purple line*) for P_2O_5 . (d) SEM image of graphene on Ge (110) surface after post-annealing treatment in H_2 showing small graphene bubbles. The scale bar is 200nm. (e) Nano-FTIR spectrum for small graphene bubble on Ge (110) surface post-annealing treatment in H_2 . IR peaks induced by non-bridging oxygen-P bond (*blue and green solid lines*) and by bridging oxygen-P bond (*purple solid line*) were observed.

Previous attempt to reduce the intercalated P_2O_5 into phosphorus allotropes through post-annealing treatment in H_2 at $500^\circ C$ resulted in a disappearance in the P_2O_5 Raman peak around 1100cm^{-1} , suggesting the decrease of P_2O_5 within this system (Figure 5.2, a and b). However, P_2O_5 traces were still detected in XPS (Figure 5.2c). The materials beneath these graphene bubbles (Figure 5.2d) warrant further investigation. Nano-FTIR confirmed the presence of P_2O_5 within the graphene bubbles (Figure 5.2e), while the identification of phosphorus allotropes necessitates additional characterization through XPS and nano-FTIR in a lower energy range. One plausible explanation for these observations is an insufficient hydrogen supply, resulting in incomplete reduction of P_2O_5 to phosphorus. Consequently, conducting a parameter study on the experimental conditions of the P_2O_5 reduction process—including variations in reducing agents, their concentration and/or flow rate, pressure, and temperature—would be instrumental in stabilizing phosphorus allotropes at the graphene-Ge (110) heterointerface.

An alternative pathway to grow phosphorus at the graphene-Ge (110) heterointerface involves intercalating phosphorus allotropes directly through graphene, utilizing red and black phosphorus as sources of phosphorus. Notably, red and black phosphorus present significant advantages for intercalation over P_2O_5 , primarily due to the substantially smaller size of P_4 molecules. Initiating this experiment with a $600^\circ C$ annealing treatment in a high vacuum environment would be a good starting point, as both red and black phosphorus sublime at this temperature, facilitating their diffusion toward and beneath the graphene layer. Additionally, the high vacuum setting serves to shield the phosphorus from oxidation, thereby preserving its purity.

Another intriguing avenue for exploration lies in investigating the phase transformation processes among different phosphorus allotropes (e.g., red, black, violet, blue phosphorus, or potentially undiscovered phosphorus allotropes) at the graphene-Ge (110) interface, as influenced by the varying vdW pressures as a function of the graphene bubble shape and size. Usually, larger graphene bubbles generate lower vdW pressures, which can be precisely quantified using atomic force microscopy (AFM) techniques. Establishing a correlation between vdW pressures and the resulting phases of phosphorus allotropes, as revealed through tip-enhanced Raman spectroscopy, promises to illuminate a highly controllable synthesis pathway for various phosphorus allotropes, offering significant insights into material science and nanotechnology.

5.2 Light induced surface tension for hierarchical assembly of particles from liquid metals

In this work, we conducted a series of finite element simulations to investigate the potential of designing the surface energy profile at the liquid metal-vacuum interface by employing Laguerre-gaussian (LG_{pl}) lasers as the heat source. Utilizing tungsten microparticles randomly dispersed within liquid gallium as a prototypical system, this study established an innovative pathway towards the complex design of surface energy at varied liquid surfaces.

Firstly, the temperature distribution and the resultant surface energy profile at the liquid gallium-air interface as influenced by different laser modes were examined, including LG_{00}

mode (Gaussian mode), LG_{04} mode, and LG_{14} mode. The distinct surface energy profile generated by the Laguerre-gaussian lasers, specifically LG_{04} mode and LG_{14} mode, induced complex Marangoni flow patterns characterized by the emergence of central vortices. These vortices played a crucial role in expelling particles from the center, culminating in the formation of novel ring-shaped particle assembly at the liquid-solid interface. A comprehensive parameter sweep was subsequently undertaken to reveal the relationship between the parameters of the LG_{pl} laser – such as laser mode, spot size, and intensity of the electric field – and the observed ring-shaped particle assemblies, employing both the Stokes model and the Schiller-Naumann model. Additionally, we introduced the concept of entropy to evaluate the quality of these ring-shaped particle assemblies. The entropy-based analysis indicated that a larger spot size, together with the LG_{14} mode significantly enhanced the area-selectivity of the particle distribution, leading to more defined particle assemblies. Thus, precise adjustments to the parameters of the LG_{pl} laser enabled precise control over the structure of the ring-shaped particle assemblies at solid-liquid interface.

A further comparative study on the motion of the particles guided by Marangoni flow and the resultant convective flow, with and without the effect of effective gravitational forces, showed that the ring-shaped particle assemblies occurred exclusively in the case with the effective gravitational force being present. This observation underscored the crucial interplay between Marangoni flow and effective gravitational forces in driving the formation of ring-shaped patterns. Notably, a moderate electric field intensity guaranteed a balance between Marangoni flow and gravitational effects, thereby maximizing the area selectivity of the particle distribution. The insights garnered from this work offered a significant advancement in our understanding of surface energy profile designs at the liquid metal-vacuum interface and the microenvironmental forces that govern area-selective particle assembly. These findings ultimately open up multiple avenues for further research and application development in the field.

5.2.1 Investigation of laser modes and arrangements

The work presented in **Chapter 3** only explored the relatively simple non-Gaussian laser modes, namely LG_{04} mode and LG_{14} mode, with a specific focus on minimizing computational expenses. Yet, the beautiful world of the non-Gaussian lasers – such as Laguerre-Gaussian laser ($LG_{p,l}$) mode, Hermite-Gaussian laser ($HG_{p,l}$) mode, and Ince-Gaussian laser ($IG_{p,l}$) mode as summarized by Zhang *et al*²⁷⁹ - remains largely unexplored. These modes are characterized by complex transverse patterns that surpass the simplicity of Gaussian beams, including ring-shaped ($LG_{p,l}$ mode), rectangular symmetric ($HG_{p,l}$ mode), and elliptical symmetric ($IG_{p,l}$ mode) intensity distribution (Figure 5.3). Such configurations offer intriguing templates to engineer the surface energy profile of liquid metals and possibly for the resulting assemblies of particles that are incorporated into these liquid metals as well. To facilitate the generation of the $LG_{p,l}$, $HG_{p,l}$, and $IG_{p,l}$ laser modes, traditional approaches, including the conversion of laser modes using a solid-state laser system equipped with spatial light modulators, have been successful in generating a diversity of laser modes with precise control over their transverse modes²⁸⁰. However, the uses of spatial light modulators introduces concerns regarding the additional loss of laser

power and optical efficiency of the laser²⁷⁹. An alternative strategy involves the spatial structuring of laser gain distributions, for instance, through the utilization of pump beam²⁸¹⁻²⁸². Amongst, one could use a fast-scanning pumping beam. Varied gain distributions of laser, such as linear, elliptical, and circular patterns, could be generated through adjusting the scanning angles and the phase difference between two resonant scanning mirrors²⁸². Moreover, a decentered Gaussian pump beam²⁷⁹ can also be used to generate the $LG_{p,l}$, $HG_{p,l}$, and $IG_{p,l}$ laser modes. With these non-Gaussian lasers, a particular intriguing question pertains to the behavior of particle assemblies under the influence of $HG_{p,l}$ mode and $IG_{p,l}$ mode used as heat sources. Would these particle assemblies mirror the symmetry of their laser modes, analogous to the correlation observed between ring-shaped particle assemblies and the $LG_{p,l}$ mode? Affirmation of this symmetry-linkage would significantly enhance our predictive capabilities regarding particle assembly patterns based on the intensity distribution of the laser modes, thereby improving control over the spatial distribution of micro- and/or nanoparticles. By replicating the desired symmetry within the laser intensity profiles through various optical components, one could feasibly engineer specific patterns conducive to area-selective material growth processes.

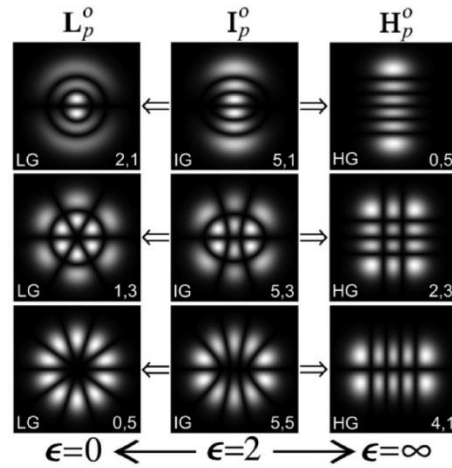


Figure 5.3: Transverse mode shapes for $LG_{p,l}$ (left), $IG_{p,l}$ (mid), and $HG_{p,l}$ laser (right) modes, respectively. The corresponding p and l are marked at the lower right corner of each panel, adopted from reference^{144, 283}. Reprinted with permission from Bandres *et al.*, Journal of the Optical Society of America A 21, no. 5 (2004): 873-880. Copyright 2004 Optica Publishing Group.

Beyond the selection of laser modes, the strategic arrangement of multiple lasers presents a promising avenue for generating surface energy profiles at the liquid-gas interface with enhanced complexity, even when utilizing the simplest Gaussian laser modes. Demonstrated in Figure 5.3 were the flow patterns resulting from multiple Gaussian lasers in diverse arrangements, including two lasers arranged off-center along the y -axis (Figure 5.4, a and d), four lasers symmetrically positioned around the center (Figure 5.4, b and e), and multiple lasers aligned to form an elliptical-like beam along the y -axis (Figure 5.4, c and f). Within these laser arrangements, each Gaussian laser generated a local maximum intensity at the center of its spot, leading to localized temperature peaks and corresponding minimum in surface energy. Consequently, the Marangoni flow outflowed from the center

of each spot to its surroundings. In this manner, each spot functioned as a 'source' of Marangoni flow. By strategically positioning several 'sources' on the liquid surface, one can structure complex Marangoni flow patterns and give rise to novel central vortices among the 'source' points. A more in-depth study of the particle assemblies guided by these fluidic patterns would yield valuable insights.

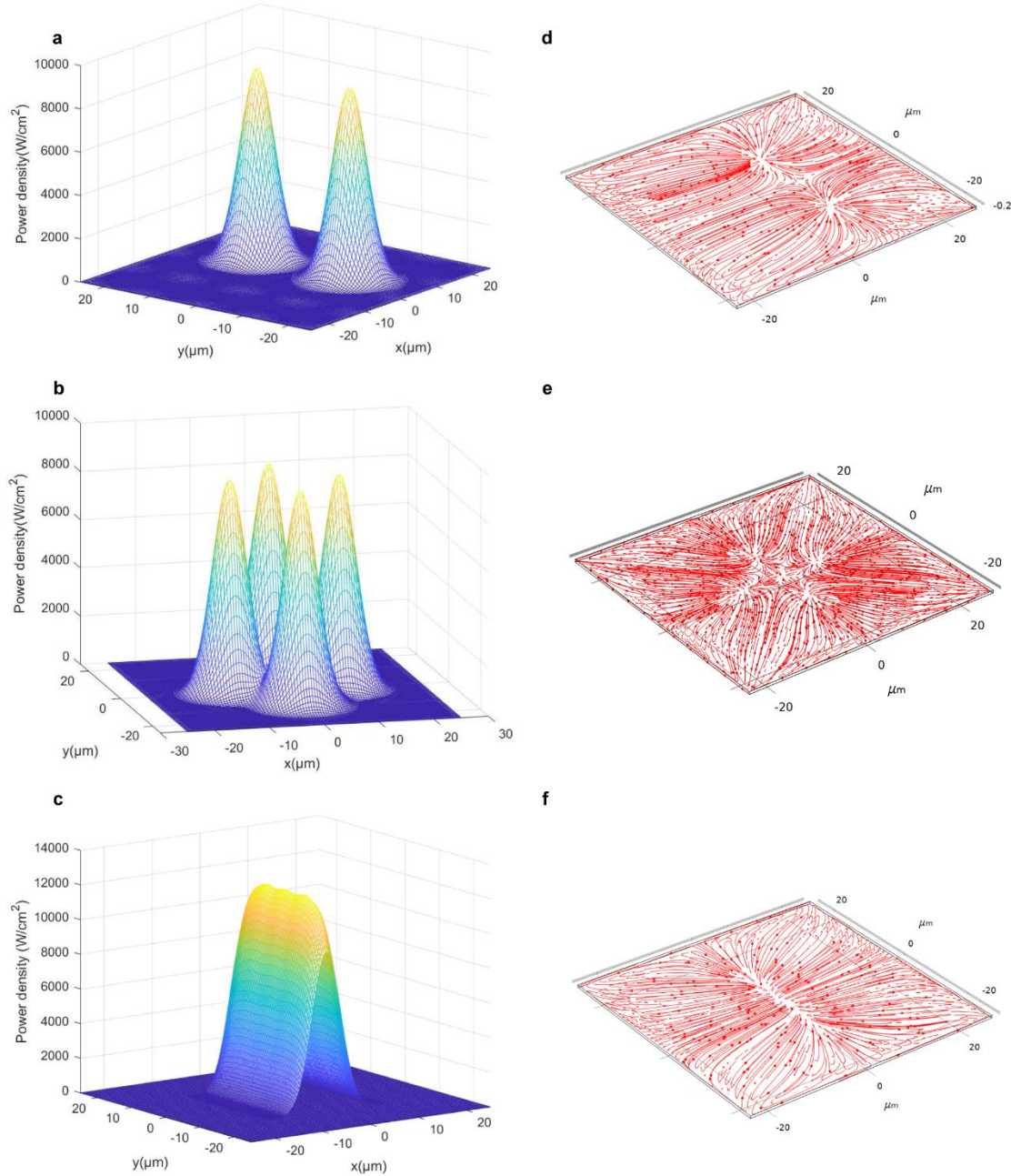


Figure 5.4: Marangoni flow patterns in a cuboid liquid influenced by Gaussian lasers. (a to c) Schematic of multiple Gaussian lasers with different arrangements on the liquid surface, including: (a) two lasers arranged off-center along the y-axis. (b) four lasers symmetrically positioned around

the center. (c) multiple lasers aligned to form an elliptical-like beam along the y-axis. (d to f) Marangoni flow pattern (highlighted with *red allows*) on the liquid surface induced by the laser groups illustrated in (a), (b), and (c), respectively.

5.2.2 Particle radius for the assembly

Regarding the time-dependent finite element simulation on the particle trajectory, it is critical to ensure that the time step does not exceed the characteristic time for a particle (τ_p), the time required for a particle to respond to changes in momentum within its environment. This is essential for guaranteeing the accuracy of the simulation outcomes. The characteristic time for the particle (τ_p) is expressed by:

$$\tau_p = \frac{4\rho_p d_p^2}{3\mu C_D Re_r}$$

where μ is the dynamic viscosity of liquid gallium and Re_r is the relative Reynolds number of particles in the flow. C_D is the drag coefficient coupling the velocity of a particle to the surrounding fluid velocity. The finite element simulations presented in **Chapter 3** utilized tungsten microparticles randomly dispersed in liquid gallium as a prototypical system. It was because of the high density of tungsten, which afforded a relatively large τ_p , on the order of 10^{-5} to 10^{-4} s, rendering the system computationally feasible.

Expanding this methodology to the hierarchical assembly of nanoparticles under light-induced surface tension presents both significant opportunities and substantial challenges. A key obstacle is the escalation of computational demands, anticipated due to the inverse relationship between τ_p —and thus computational time—with both its density and radius. For instance, decreasing the radius of a tungsten particle to 20nm reduces τ_p dramatically, approximately 6.72×10^{-10} s, potentially extending the simulation time to an impractically huge value, given the same computational resources same as those employed in **Chapter 3**. It suggests that the model on nanoparticles may be beyond the capacity of finite element simulation and promising alternatives such as molecular dynamics or Monte Carlo simulations, may offer more viable pathways for exploring nanoparticle behaviors. Additionally, the research in **Chapter 3** revealed that the ratio between the drag forces and the gravitational force is proportional to d_p^{-2} . Thus, smaller particles require low laser intensities to achieve an assembly structure with the highest degree of order. However, an open question remains regarding the efficiency of the directional surface and convective flows in controlling the movement of nanoparticles, especially when Brownian force becomes more obvious with decreasing particle size. Moreover, additional strategies to enhance the effectiveness of these flows in guiding nanoparticle assembly are beneficial for advancing the precise control of the nanoparticle assembly and the consequent confinement growth of varied nanostructures.

5.2.3 Experiments to corroborate simulation results

Alternative promising direction for advancing this research involves conducting experiments to justify our simulation results. A feasible experimental setup involves projecting LG_{14} mode laser onto a gallium surface to observe the resultant fluid flow patterns, and incorporating particles within gallium may possibly enhance the visibility of these patterns. Given the opaque nature of liquid gallium, neutron imaging techniques

emerge as a suitable method for this investigation. This technique, which generates a shadow radiograph by measuring neutron absorption and scattering, is particularly effective for penetrating metallic materials, thus well-suited for our system.

Furthermore, it is important to note that the temperature coefficient of surface tension for liquid gallium, referenced in **Chapter 3** from Hardy's study²⁰³, presumed this linear relationship valid beyond 550°C. Consequently, determining this coefficient over a higher temperature range (e.g., 550°C to 2400°C) would critically enhance the accuracy of our simulation setup and the resultant particle assemblies. For this purpose, the sessile drop method within an Auger spectrometer, as outlined in Hardy's work²⁰³, presents a viable characterization technique. Similar experiments could also apply on other liquid metals, such as mercury (Hg), indium (In), tin (Sn), etc., or eutectic metal alloy systems, such as Galinstan, field's metal, etc to investigate their temperature coefficient of surface tension, and introduced as the input parameters in the simulations.

5.3 Area-selective work function tuning in graphene across a broad temperature range through substrate heterointerface engineering

In this work, we conducted an in-depth investigation into the area-selective tuning of graphene work function over a wide temperature range. Our approach employed a graphene/diamond like carbon (DLC) heterointerface containing trapped Ga in a uniquely designed spatial structure to engineer the work function of graphene *via* electrostatic doping.

Firstly, the temperature dependent work function of graphene was quantified *in situ* while annealing the samples in an ultra-high vacuum environment within a low energy electron microscope (LEEM). The spatially resolved work function in graphene was analyzed by comparing the graphene work function differences ($\Delta\Phi_{GR}$) inside and outside of the Ga implanted DLC regions. Notably, a negative $\Delta\Phi_{GR}$ indicated a lower graphene work function on the Ga implanted region relative to the surrounding regions. At 300°C, $\Delta\Phi_{GR}$ was -129.48 ± 13.84 meV, which transitioned from negative to positive polarity around a threshold of approximately 420°C, yielding a $\Delta\Phi_{GR}$ of 13.84 ± 4.90 meV. This difference grew more pronounced at elevated annealing temperatures, such as 500°C, where $\Delta\Phi_{GR}$ reached 103.20 ± 25.70 meV. Subsequently, we investigated the distribution of Ga within the DLC using time-of-flight secondary ion mass spectrometry (ToF-SIMS), which revealed the dynamics of Ga diffusion, accumulation, and eventually precipitation at graphene/Ga implanted DLC heterointerface with increasing temperature. This process significantly impacted the work function of DLC, which exhibited an evolution similar to that observed in the graphene work function. Specifically, $\Delta\Phi_{DLC}$ was a negative value at 300°C, shifted to positive between 420°C and 450°C, and remained positive at higher temperatures. Furthermore, the temperature-dependent Raman spectra revealed that Ga catalyzed the local reconstruction of the sp^2/sp^3 ratio in DLC. This led to structural changes within DLC, and therefore its work function. Notably, a heavily n-doped graphene was achieved at 300°C, with an electron density at the order of $3-6.84 \times 10^{13} \text{cm}^{-2}$, calculated with G and 2D peak shifts in Raman measurements and the relative Dirac point shifting from graphene Fermi level in scanning tunneling spectroscopy (STS) dI/dV measurements. A graphene Fermi level change of -0.925eV was estimated to induce a

decrease of 1.043mN/m in graphene surface energy at 300°C.

Subsequent DFT calculations revealed the critical role of diffusion and sub-monolayer heterointerface precipitation of Ga in achieving high levels of electrostatic doping. Conversely, variations in the sp^2/sp^3 ratio within the DLC exerted minimal impact on graphene work function, across three examined ratios of 39%, 20%, and 14%. Moreover, Ga in the bulk of Ga implanted DLC exhibited negligible impact on graphene's electronic properties. Notably, when introducing a single Ga atom confined on graphene/Ga implanted DLC heterointerface, the graphene work function significantly decreased and can be further lowered as Ga detached from the DLC surface and diffused into the heterointerface. However, with increased precipitation of Ga, the charge transfer from Ga cluster to graphene decreased sharply with each additional Ga atom in the cluster at the heterointerface. The graphene work function difference reached its maximum (+248meV) when an entire Ga monolayer forms.

Notably, at the same temperature, our platform enabled different work function landscape on graphene, based on the specific setting of the annealing process. Furthermore, using these Ga implanted DLC squares as building blocks, complex focused ion beam (FIB) patterns could be designed to cater to support various area-selective material growth processes. Within a $215\mu\text{m}\times 215\mu\text{m}$ FIB pattern containing 81 Ga implanted DLC squares after annealing at 500°C, nano-angle-resolved photoemission spectroscopy (nano-ARPES) revealed a very similar local band structure across these Ga implanted DLC squares. Moreover, X-ray photoelectron spectroscopy (XPS) indicated limited lateral bulk diffusion of Ga within the DLC, ensuring the tight confinement of Ga within the designated implanted zone. These factors together were beneficial for enhancing the area selectivity in the material growth process. This capability not only establishes a foundational platform for exploring the complex physics on heavily doped graphene in high-temperature but opens new avenues for investigating the dynamic process of area-selective material growth with a wide temperature spectrum. Drawing on this foundation, numerous compelling questions emerge, as detailed in the subsequent sections.

5.3.1 Area-selective growth of materials on engineered graphene

Graphene, an inert vdW surface, serves as an ideal substrate for 2D materials growth and their heterostructures. Graphene with work function - and consequently, surface energy - engineered through the graphene/Ga implanted DLC heterointerface, can open up new opportunities for the area-selective growth of an extensive array of 2D materials and their heterostructures. Notably, GeS and SnS emerge as attractive due to their distinct in-plane anisotropic properties in individual layers. These materials exhibit robust piezoelectricity, ferroelectricity, and other unique anisotropic optical and electronic properties due to their orthorhombic crystal structure²⁸⁴⁻²⁸⁹. Furthermore, the integration of GeS and SnS into lateral 2D heterojunctions introduces exciting possibilities. Theoretical investigations have demonstrated that applying strain can adjust the band offset at the heterojunction, facilitating novel charge transfer and separation processes suitable for diverse technological applications²⁹⁰.

5.3.2 Alternative element for gallium

While the findings in **Chapter 4** focused on the Ga implanted DLC heterostructure, a myriad of elements immiscible in carbon remain untapped for exploration. Except for the noble gas groups including helium(He), neon (Ne), argon (Ar), krypton (Kr) and xenon (Xe), potential candidates such as copper (Cu), zinc (Zn), arsenic (As), rhodium (Rh), palladium (Pd), silver (Ag), cadmium (Cd), indium (In), tin (Sn), antimony (Sb), platinum (Pt), gold (Au), mercury (Hg), thallium (Tl), lead (Pb) and bismuth (Bi). Other elements would form a stable and/or metastable compound with carbon, as suggested by the ASM alloy phase diagram database²⁹¹ and Materials Project database²²¹. Intriguingly, carbon itself could be implanted into DLC to modify its local structure and consequently, its work function post-ion implantation. Figure 5.5 compiles experimentally measured work function values for these alternative elements²⁹²⁻²⁹³. According to Figure 5.5, Cu, Rh, Pd, Pt, and Au are anticipated to p-type dope graphene, while the remainder, including Ga, Zn, As, Ag, Cd, In, Sn, Sb, Hg, Tl, Pb and Bi are predicted to n-type dope graphene.

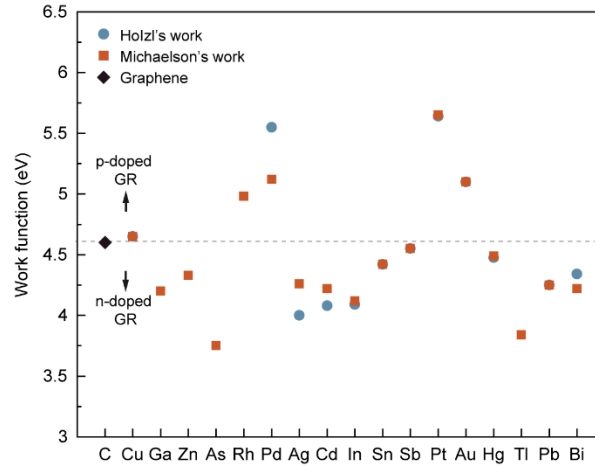


Figure 5.5: Work function values of possible alternative elements to implant into DLC. Experimental measured work function values adopted from Holz's work²⁹² (blue circles) and Michaelson's work²⁹³ (orange squares). The work function of graphene (black diamond) was quantified with the low energy electron microscope²⁹⁴.

Implanting these metal ions into DLC *via* FIB or using a nano-implanter allows for work function engineering of graphene in two ways. One involves charge transfer from the precipitated element into the graphene-DLC driven by thermal annealing. The other is the ion-induced graphitization in the DLC, the consequent work function changes in DLC that result from this process and therefore the electrostatic doping of graphene due to changes in its dielectric environment. It is well known that the ion-induced graphitization is influenced by the ion mass and thus it correlates with the energy density of deposited ions²²⁵. Notably, heavier ions deposit their energy into smaller volumes compared to lighter ions, leading to a significant increase in localized energy density. This energy then disperses through nuclear collisions and phonon excitations, causing a localized temperature spike. The increased local temperature dramatically increases with ion mass,

facilitating the transformation of the sp^3 carbon fractions into sp^2 carbon and facilitating a realignment of matrix atoms into a structure that is more like graphite. This process leads to an increase in the work function for the DLC film. Thus, to achieve heavy p-type doping in graphene, Pt, Pd, and Au stand out as promising choices due to their higher work function and heavy atomic masses. However, a comprehensive examination of these transition metal ions is necessary. Other open questions include whether these ions will induce local graphitization of the DLC upon annealing as we observed using gallium ions. In addition, the behavior of these transition metals at the sub-monolayer limit and whether they will prefer electron sharing with each other or with graphene is still an open question that is important to address.

5.3.3 Applications for heavily doped graphene and beyond

The area-selective doping of graphene, with ultra-high carrier densities, opens up vast opportunities for probing into its intriguing physical properties and exploring a wide range of technological applications. A thorough investigation in this direction would be of great importance to expand our work in **Chapter 4**. Below we briefly outline potential investigations into phenomena such as superconductivity, the van Hove singularity, negative refractive indices, and the Klein paradox, alongside the exploration of applications in supercapacitors, transparent electrodes, and sensors.

5.3.3.1 Novel physical properties

Superconductivity – Superconductivity refers to a phenomenon characterized by the complete disappearance of electric resistance in a material below a specific critical temperature. Usually, the transition to superconducting state in the material is a consequence of the formation of Cooper pair, as revealed by the seminal Bardeen–Cooper–Schrieffer theory²⁹⁵. Through interactions with lattice phonons, two electrons can form a bound state where they are tightly bound together with opposite spin directions to form a Cooper pair. The interaction strength of between electrons and lattice phonons within a material is quantified by the electron-phonon coupling (EPC) parameter. Yet, for pristine graphene, this EPC parameter is notably small, posing a challenge for superconductivity. A promising strategy to overcome this barrier involves either electron or hole doping in graphene, particularly heavy doping approaching the van Hove singularity, to significantly enhance the EPC parameter²⁹⁶. Recent theoretical explorations have suggested that graphene with such heavy doping would exhibit unconventional superconductivity, known as $d + id$ -wave chiral superconductivity²⁹⁷⁻²⁹⁸. Moreover, predictions suggest that graphene, with a carrier density of $4 \times 10^{14} \text{ cm}^{-2}$ and 16% tensile strain, could achieve a critical temperature as high as 30 K. This critical temperature is anticipated to increase further with the application of more extensive carrier doping and tensile strain²⁹⁹, highlighting the potential of our engineered graphene in superconductivity research. Except for the traditional superconductivity, graphene also show its promise in topological superconductivity, exemplified with a epitaxial topological insulator (e.g., $(\text{Bi,Sb})_2\text{Te}_3$)/graphene/gallium heterostructures where robust and proximity-induced superconducting gap in the Dirac surface states were observed³⁰⁰. Specifically, graphene played a key role in enabling this proximity effect, offering a conductive and atomically thin barrier that facilitates the induction of superconductivity to the surface states of

topological insulator.

Van Hove singularity – Van Hove singularity is a concept referring to the pronounced discontinuity in the density of states (DOS) at certain points within the band structure of a material. Experiments with excessive n-doped graphene has demonstrated that, on the order of $3.5\text{-}5.5 \times 10^{-14} \text{cm}^{-2}$, can significantly expanding the van Hove singularity, pushing the π * van Hove singularity closer to the Fermi level. In this scenario, complex many-body interactions transform the point-like van Hove singularity into a flat band aligning with Fermi energy along the $\overline{KMK'}$ Brillouin zone border^{34, 301-303}. Additionally, the heavily doped graphene allows for increasing electron-electron and electron-phonon interactions near the Van Hove singularities. This enriched interaction environment offers a novel platform for the exploration of many-body physics and their impacts on the electronic structures of a material.

Negative refractive index – Negative refractive index describes a material's property to bends light to a negative angle with the surface normal³⁰⁴. This property is particularly interesting as it helps overcome the conventional resolution limits of light and electromagnetic waves, enabling the design of “super-lenses” without the wavelength constraints. Such an advancement heralds a significant leap in the resolution capabilities of future optical technologies²³⁴. Regarding the design of material with negative refractive index, a sharp n-p-n graphene junction has been demonstrated to serve as an effective medium²³². The physics behind this design is that, within the graphene junction, the Fermi momentum acts similarly to the refractive index of a material. Specifically, the Fermi momentum for electrons traversing the conduction band is positive, while it turns negative within the valence band. Consequently, as electron waves approaches the junction from the n-doped side, their transport behavior mimics that of optical refraction observed in metamaterials with a negative refractive index, effectively transforming divergent electron flow into convergent flow across the junction. Importantly, the square of the negative refractive index is proportional to the hole-to-electron density ratio within the n-p-n junction, suggesting that adjusting the carrier density enables the control over the focus of this Veselago lens. The versatility in carrier types and densities available in our engineered graphene allows for the potential for developing applications based on Veselago lens principles.

Klein Paradox – Klein paradox represents an exotic quantum phenomenon in which relativistic particles penetrate the high and wide potential barriers unimpededly, approaches almost 100% transmission when the potential barrier exceeds the rest energy of the particle (mc^2)²³¹. This paradoxical behavior is rooted in relativistic quantum mechanics, where a sufficiently strong potential that repels electrons attracts positrons, creating positron states within the barrier that energetically align with the electron states outside the barrier. The coherence between electron and positron wavefunctions across this barrier underpins the Klein paradox³⁰⁵⁻³⁰⁷. Observation of this paradox can be achieved at the p-n interface of a graphene junction, where the potential barrier is tunable by manipulating the carrier density²³¹. Here, our heavily doped graphene can also serve as a medium, facilitating the creation of a substantial potential barrier, thereby enhancing the likelihood of occurrence of the Klein paradox.

5.3.3.2 Technological applications

Ultracapacitors – Ultracapacitors, which are based on electrochemical double layer capacitance, devices designed for electrical energy storage. They operate through nanoscale charge separation at the interface between an electrode and an electrolyte³⁰⁸. To boost their energy storage capacity to levels comparable to traditional batteries, one effective approach is the use of graphene as the electrode material due to its large surface area. Enhancing the electrical conductivity of electrodes through graphene functionalization leads to ultracapacitors with superior energy storage capabilities and quicker charge-discharge cycles²²⁹.

Sensors – Graphene is also attractive for electrochemical biosensors attributed to its unique properties, such as rapid electron transportation, high thermal conductivity, and remarkable mechanical flexibility. To date, it has been widely applied in nano-electronic devices for the detection of biomolecules, gas/water vapor and heavy metal ions^{10, 309}. The ultra-high carrier densities in graphene can significantly increase sensor sensitivity, facilitating the detection of substances at lower concentrations. This enhancement has the potential to revolutionize medical diagnostics and environmental monitoring by enabling more sensitive and accurate detection methods.

Surface-enhanced Raman spectroscopy (SERS) – SERS is a method which amplifies Raman scattering signal of surface adsorbed molecules on the metal surfaces and/or metal-based nanostructures, utilizing the localized surface plasmons on metal surface. Yet, traditional metal-based SERS substrates can suffer from issues like photochemical reactions, strong fluorescence backgrounds, and inconsistent molecule adsorption due to their rough, chemically active surfaces. To address this issue, graphene with Fermi level engineered has been demonstrated to be a promising alternative to improve the signal enhancement and molecular selectivity of SERS³¹⁰. Here, the key lies in the band alignment between graphene and analyte molecules³¹¹, setting the background for the advantages of our engineered graphene in SERS. Specifically, the high tunability of the electronic properties of our method enables the engineering of graphene Fermi level for specific SERS applications.

5.3.3.3 2D semiconductor materials beyond graphene

Moreover, our area selective work function engineering platform may hold potential for application across a diverse array of 2D semiconductor materials beyond graphene. This includes transition metal dichalcogenides (TMDs), elemental 2D materials and many others. The band alignment of various 2D semiconductor materials beyond graphene and the work function values of commonly used metal electrodes has been summarized with Schulman *et al*³¹² and Van de Walle *et al*³¹³.

Considering the high sensitivity of the work function tuning to temperature in our gallium implanted DLC platform, traditional polymer-assisted transfer techniques are not ideal. The annealing step required to remove the polymer from the transfer process can result in the uncontrolled precipitation of gallium, which is undesirable in our strategy. Nevertheless, the complete removal of polymer residues is difficult³¹⁴. Our polymer-free transfer process, originally designed for transferring graphene monolayer grown on Cu foil, could

potentially be extended to other 2D semiconductor materials. Amongst, promising candidates include h-BN³¹⁵⁻³¹⁶ which have been successfully synthesized on Cu substrates, making it viable candidates for our polymer-free transfer method. Additionally, MoS₂ shows promise for transferring atop gallium implanted DLC through alternative polymer-free techniques. One such method involves placing the target substrate, such as carbon grids, directly on top of a MoS₂/SiO₂/Si sample, followed by selective etching of the SiO₂ interface with HF solution to facilitate the transfer of MoS₂³¹⁷. This approach could also be applicable to other 2D materials grown on SiO₂/Si substrates, including various TMDs like NiTe₂³¹⁸, WS₂³¹⁹, and MoSe₂³²⁰. A thorough exploration of these potential materials and transfer techniques could significantly broaden the application range of our area selective work function engineering strategy.

5.4 Conclusions

In this dissertation, we aimed to explore the innovative avenues for confinement growth of materials, harnessing the potentials of both space-confined and area-selective synthesis approaches through innovative interface engineering strategies. Specifically, our study uncovered the multifaceted roles that interfaces played during the material synthesis process. These roles extended beyond acting as mere nanoreactors or physical scaffolds, which dictated the geometrical constraints of the synthesized materials; interfaces also established specific chemical microenvironments that were crucial for synthesis. Notably, the study of P₂O₅ intercalation through graphene heterointerface proposed a two-step mechanism describing the interaction between P₂O₅ and graphene heterointerface. This mechanism involved the graphene-catalyzed fragmentation of P₂O₅ molecules, followed by the intercalation of the resultant smaller fragments. Furthermore, we demonstrated that this graphene heterointerface could serve as a nano-reactor, promoting the conversion of metals into metal phosphates within the heterointerface through the P₂O₅ intercalation process. Subsequently, our research pivoted towards structuring the surface tension or work function profile to facilitate the area-selective synthesis of materials. In one study, we structured a complex surface energy profile at the liquid metal-vacuum interface by employing Laguerre-gaussian (LG_{pl}) lasers as the heat source, which induced novel Marangoni flow pattern. This Marangoni surface flow, together with the resultant convective flow in bulk liquid, directed the movement of microparticles within the liquid gallium. We showed that careful tuning over the parameters of the LG_{pl} laser (i.e., laser mode, spot size, and intensity of the electric field) allowed for precise control over the structure of the ring-shaped particle assemblies at solid-liquid interface. Furthermore, this dissertation introduced an innovative approach to engineer the work function of monolayer graphene across a broad temperature range. This was achieved through engineering the microenvironment at the graphene-Ga implanted DLC heterointerface, which allowed for bipolar adjustment (either increasement or decrease) of the local work function landscape of graphene up to 500°C. Remarkably, a heavily n-doped graphene was achieved at 300 °C, exhibiting an electron density at the order of $3\text{-}6.84 \times 10^{13} \text{cm}^{-2}$, with sub-monolayer gallium trapped between graphene and DLC. A ΔE_F of -0.962eV would be estimated to induce a decrease of 1.043mN/m in graphene surface energy at 300°C, which was beneficial for the subsequent area selective material growth on the engineered graphene. The implications of our findings, together with suggestions for future research in interface engineering,

highlight the critical importance of interfaces in material synthesis. This body of dissertation not only advances our understanding of interface dynamics but also opens exciting opportunities for future explorations in the field of materials science.

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Appendix A:

Setup of chemical vapor deposition furnace with reversible gas flow

In the experiment where large P_2O_5 molecules were intercalated through graphene/Ge (110) heterointerface, a chemical vapor deposition (CVD) furnace capable of operating across a broad pressure range - from low pressure (LP, 10^{-3} torr) to atmospheric pressure (AP, 760 torr) - and allowing reversible gas flows, was employed. The design of the AP/LPCVD furnace is depicted in Figure C.1. Control of all pneumatic valves in the system is achieved through a solenoid-based control system, which is connected to a computer. Notably, pneumatic valves #2 and #5 are normally open valves. Except for them, the introduction of compressed dry air (CDA) would trigger the opening of all other pneumatic valves.

Specifically, in this furnace setup, the carrier gas with the precursors is allowed to flow from the left to the right end of the tube by opening the pneumatic valve #4 and #6, while keeping the pneumatic valve #3 and #7 closed. Conversely, gas could flow from the right to the left by opening pneumatic valves #3 and #7, with pneumatic valves #4 and #6 remaining closed. This reversible flow not only facilitates rapid discontinuation of precursor flow to the sample—thereby allowing for precise control over the thickness and domain size of the synthesized materials—but also enables sharp transition from one precursor to another. This feature is particularly advantageous for the fabrication of heterostructures, including both lateral and vertical junctions, across a diverse array of two-dimensional materials.

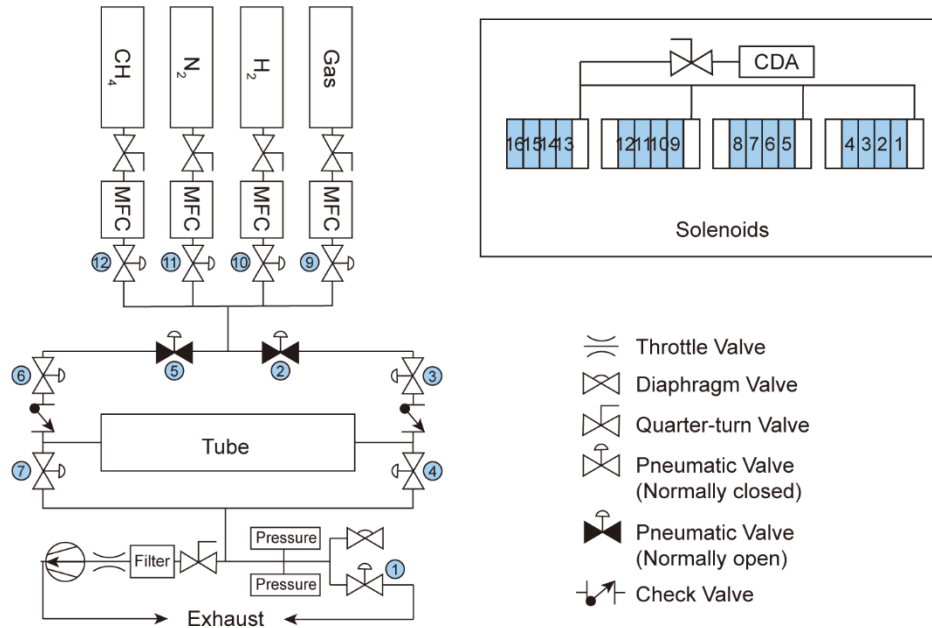


Figure A.1: Schematic for the AP/LPCVD furnace allows for reversible flow during the material growth process. (Left) Schematic for the AP/LPCVD furnace setup, with each pneumatic valve numbered for reference. (Right, top) the solenoid-based control system for the pneumatic valves in this AP/LPCVD furnace setup. (Right, bottom) Summary of the symbols in the schematic representing different valves.

Operational steps for utilizing the AP/LPCVD are outlined as below:

Pre-check:

- Ensure the pump oil level is between "max" and "min" and that the pump is operational.
- Ensure the exhaust fans are in operation.

Turn on the system:

Open the compressed dry air valve properly. This valve is located near the main entrance of the lab.

Leak check:

- Disable all the gases.
- Confirm pneumatic valve #1 is closed by checking that the corresponding red light is off.
- Turn on the pump and check if the vacuum of the system can reach 1×10^{-3} torr.
- Turn off the pump and monitor the decay rate of vacuum

LPCVD mode:

- Turn on the pump and set the pressure as per the experimental plan.
- Initiate carrier gas and/or gas precursor flow by a) opening the gas cylinder valve; b) activating the green quarter-turn valve atop the CVD setup; c) open the pneumatic valves corresponding to the desired direction of gas flow. For example, open pneumatic valves #4 and #6 for gas flow from left to right end of the tube; d) setting the mass flow controller (MFC) to the desired flow rate.

APCVD mode:

Introduce carrier gas and/or gas precursor flow to the tube as in LPCVD mode, then open pneumatic valve #1 immediately once the tube pressure exceeds 760 torr.

Temperature control:

Program and adjust the temperature using the furnace's temperature control panel. Ensure to carefully open the upstream outlet to load/unload samples, then securely close it.

Initialize the program:

Long-press "Index" and select "RUN", then press "Enter".

Shut down the furnace:

- Allow the system to cool to room temperature.
- Vent the system to 760torr if operating in LPCVD mode.

- Close all pneumatic valves, the MFC, and the valves for the gas cylinders.
- Close the compressed air cylinder valve.
- Turn off the pump.

Appendix B:
Polymer-free transfer of graphene

In the experiment aimed at area-selective tuning of graphene work function across a wide temperature range, as presented in **Chapter 4**, a polymer-free graphene transfer process was used to avoid the contamination and the consequent impact of polymer on the *in situ* work function quantification in low energy electron microscope. The key idea of this approach, as developed by Lu *et al*²³⁹, was to replace PMMA and/or PDMS with an adhesive Al frame window to prevent the breakage of graphene during the transfer process. A CVD grown graphene monolayer on Cu foil (Graphene Factory) was used for transfer, and before the transfer process, its Cu side was treated with O₂ plasma to remove the carbon residues.

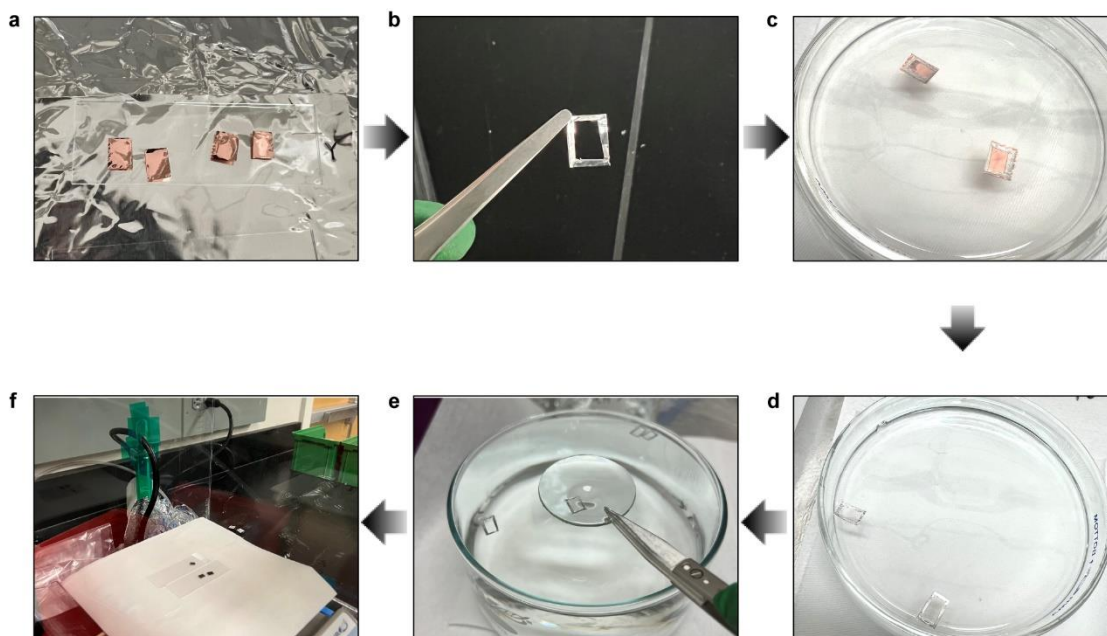


Figure B.1: Polymer-free graphene transfer process. (a) The as-cut CVD grown graphene monolayer on Cu foil and the size for each piece is approximately 0.8cm by 1.2cm. (b) The adhesive Al frame window placed atop graphene monolayer. (c) Graphene/Cu sample with Al frame window placed atop floating in the etchant solution ($\sim 0.3\text{M}$ sodium persulfate) for Cu etching. (d) Cu was fully etched away after approximately 1 hour. (e) Transfer the graphene together with the Al window frame to the deionized water reservoir using a watch glass. (f) After removing the excess sodium persulfate in deionized water reservoir, the graphene was fished out with a sample and dried out in N₂ box.

The detailed process for the polymer-free graphene transfer is illustrated in Figure B.1. The graphene on Cu foil was first cut into square/rectangular pieces, and the size of each graphene piece should be no greater than 1.2cm by 1.2cm. Then, an adhesive Al frame window was created with a razor and then carefully placed on top of graphene. Generally, the size of the Al frame window should be slightly smaller than that of graphene to avoid the contact between Al frame window and etchant solution during the etching process. After it, the graphene/Cu sample with Al frame window placed atop was carefully released in the etchant solution ($\sim 0.3\text{M}$ sodium persulfate) for Cu etching, which generally last for

1 hour. Once the Cu was fully etched away, the graphene sample became almost transparent. The graphene was then transferred to the deionized water reservoir, which was about 900mL, and had it floated in the deionized water reservoir for another 1 hour. This step would be repeated for one more time to guarantee the removal of the excess sodium persulfate on graphene. After it, the graphene, together with the Al frame window, was fished out with a sample carefully and then dried out in N₂ box for 1 hour. Lastly, the sample was annealed in the high vacuum (10^{-6} torr) at 220°C to enhance the adhesion of graphene to the sample.

Appendix C:
Code for surface work function mappings

The following code is co-developed by Dr. Cameron W. Johnson and Jiayun Liang, with permission from Dr. Cameron W. Johnson to reproduce it in this dissertation. The goal for this code is to derive surface work function mappings from the I-V curve in LEEM.

```
import numpy as np
import matplotlib.pyplot as plt
import seaborn as sns
import matplotlib.cm as cm
import pandas as pd
import os,sys,glob
import h5py as h5
from winsound import Beep
from matplotlib import rcParams as rcp
params = {'image.origin':'lower',
          'figure.dpi':300}
rcp.update(params)
import colorsys
import matplotlib.colors as mcolors
import time
import math
from IPython import display
from scipy.optimize import curve_fit
import scipy.special as sp
import readUview as ru
ruObj = ru.readUviewClass()

def erffit(x,a0,a1,a2,a3):
    return a0*(sp.erf(-(x-a1)/a2)+1)/2+a3
```

```

def path_fnames(path,ftype):
    fnames = []
    for file in sorted(glob.glob(path+'*.'+ftype)):
        fnames.append(file)
    return fnames

fpath = "your-pathway-for-the-IV-curve-file"
fname='filename-of-the-IV-curve-file'
#With an I-V curve file as a h5. file
stack=h5.File(fpath+fname,'r')['measurement']['sv_ramp']['000_im_array']
dat = []
for f in stack:
    n=np.reshape(f,(1024,1024))
    dat.append(n)

sv0 = 0      # Initial start voltage
sv1 = 7      # Final start voltage
dsv = 0.1    # Start voltage increment
tinter = 1   # Time step interval
loop = False # Loop boolean
save = True  # Image data save boolean

N0=x        #Average per x*x pixel
N=np.shape(dat[0])[0] #Amount of pixel per image
index=np.arange(N0)  #index for the storage

ptime = 23/60. # Approximate time it takes to process data in each loop
svs0 = np.arange(sv0,sv1+1e-10,dsv)
svs = []

```

```

avgs = np.zeros((N,N,np.shape(svs0)[0]))
wfs = np.zeros((N,N))
results=np.zeros((N,N))
times = []

maxintens = 0
k = 0
i = 0
j = 0
l = 0
t0 = time.perf_counter()

if loop:
    kmax = 1e10
else:
    kmax = 1

try:
    while k<kmax:
        sv.append([])

        while i<N:
            while j<N:
                for sv,d in enumerate(dat):

                    #Loads LEEM image and adds intensity/SV data point
                    im = dat[sv]

                    #Store the average intensity per x*x pixels

```

```

        avg=np.mean(im[i:i+N0-1,j:j+N0-1])
        for m,k in enumerate(index):
            avgs[i][j+k][sv]=avg

        j+=N0
        i+=N0
        j=0

i=0
j=0

while i<N:
    while j<N:
        if avgs[i][j][0]!=0:
            avmin = np.min(avgs[i][j])
            avmax = np.max(avgs[i][j])
            datminind = np.where(avgs[i][j]==np.min(avgs[i][j]))[0]
            wfguess = sv0[datminind[0]]
            fitdat = np.ones_like(avgs[i][j])
            fitdat[:datminind[0]] = avgs[i][j][:datminind[0]]
            fitdat[datminind[0]:]*= avmin
            try:
                coef,covmat = curve_fit(erffit,sv0,fitdat,[avmax-
avmin,wfguess,0.1,avmin],maxfev=10000)
                wfs[i][j]=coef[1]
            except RuntimeError:
                wfs[i][j]=0
        j+=1

```

```
i+=1  
j=0
```

```
k+=1
```

```
except FileExistsError:  
    print('The directory already exists.')
```

```
result=np.zeros((N,N))
```

```
i=0
```

```
j=0
```

```
while j<N:
```

```
    while i<N:
```

```
        if wfs[i][j]!=0:
```

```
            k=wfs[i][j]
```

```
            result[i][j]=k
```

```
        else:
```

```
            result[i][j]=k
```

```
        i+=1
```

```
    j+=1
```

```
    i=0
```

```
if save:
```

```
    np.savetxt(fname.split('.')[0]+ "_mapping_result.txt", result,delimiter=' ',fmt
```

```
= '%10.5f')
```

```
shreshold = 3.5
```

```
x = np.linspace(-512,512,1024)
```

```
X,Y = np.meshgrid(x,x)
```

```
R= np.sqrt(X**2+Y**2)
```

```
Rap = R<=512
```

```
fig=plt.gcf()
```

```
sns.heatmap(Rap*result,cmap=plt.get_cmap('Spectral'),vmin=4,vmax=5,  
mask=Rap*result<shreshold, square=True)
```

```
if save:
```

```
    plt.savefig(fname.split('.')[ -2] + ".png")
```

Appendix D:

Code for surface work function value and error analysis

The following code is co-developed by Dr. Cameron W. Johnson and Jiayun Liang, with permission from Dr. Cameron W. Johnson to reproduce it in this dissertation. The goal for this code is to derive surface work function value from the I-V curve in LEEM and the corresponding error analysis.

```
import numpy as np

import matplotlib.pyplot as plt
import matplotlib.cm as cm
import pandas as pd
import os,sys,glob
import h5py as h5
from winsound import Beep
from matplotlib import rcParams as rcp
params = {'image.origin':'lower',
          'figure.dpi':300}
rcp.update(params)
import time
from IPython import display
from scipy.optimize import curve_fit
import scipy.special as sp
import readUview as ru
ruObj = ru.readUviewClass()

def erffit(x,a0,a1,a2,a3):
    return a0*(sp.erf(-(x-a1)/a2)+1)/2+a3

def path_fnames(path,ftype):
    fnames = []
    for file in sorted(glob.glob(path+'*.'+ftype)):
        fnames.append(file)
```

```

return fnames

fpath = "your-pathway-for-the-IV-curve-file"
fname='filename-of-the-IV-curve-file'
#With an I-V curve file as a h5. file
stack=h5.File(fpath+fname,'r')['measurement']['sv_ramp']['000_im_array']
dat = []
for f in stack:
    n=np.reshape(f,(1024,1024))
    dat.append(n)

sv0 = 0      # Initial start voltage
sv1 = 7      # Final start voltage
dsv = 0.1    # Start voltage increment
tinter = 1   # Time step interval
loop = False # Loop boolean
save = True  # Image data save Boolean

x_center = 500
y_center = 500
dC = 100

ptime = 23/60. # Approximate time it takes to process data in each loop
svs0 = np.arange(sv0,sv1+1e-10,dsv)
svs = []
avgs = []
wfs = []
times = []

```

```

maxintens = 0
k = 0
l = 0
t0 = time.perf_counter()

if loop:
    kmax = 1e10
else:
    kmax = 1
t0 = time.perf_counter()

try:
    while k<kmax:
        sv.s.append([])
        avgs.append([])
        for sv,i in enumerate(dat):
            tloop = time.perf_counter()

            #Loads LEEM image and adds intensity/SV data point
            im = dat[sv]
            N = np.shape(im)
            avg = np.mean(im[x_center-dC: x_center+dC, y_center-dC: y_center+dC])
            avgs[-1].append(avg)
            sv.s[-1].append(sv/10)
            #time.sleep(0.1)

            #Adds plot point the LEEM intensity vs SV plot
            #colors = plt.cm.gnuplot2(np.flip(np.arange(len(sv.s[-1]))/len(sv.s[-1]))*0.8)+0.2)

```

```

fig,ax, = plt.subplots(2,1,dpi=300,figsize=(6,4))
for j in range(len(svs[-1])-1):
    ax[0].plot(svs[-1][j],avgs[-1][j],lw=0.5,alpha=1)
ax[0].plot(svs[-1],avgs[-1],lw=0.75,c='k')
if np.max(avgs[-1])>maxintens:
    maxintens = np.max(avgs[-1])
ax[0].set_ylim(0,1.1*maxintens)
ax[0].set_xlim(svs0[0],svs0[-1])
ax[0].set_xlabel('Start Voltage [V]')
ax[0].set_ylabel('Avg. LEEM Intensity [arb. u.]')
ax[1].scatter(times,wfs,lw=0,s=10,color='k')
ax[1].plot(times,wfs,lw=0.5,color='k')
ax[1].set_xlabel('Time [min]')
ax[1].set_ylabel('Work Function [V]')
ax[0].grid(lw=0.5,alpha=0.25)
ax[1].grid(lw=0.5,alpha=0.25)
plt.subplots_adjust(hspace=0.5)
display.display(plt.gcf())
display.clear_output(wait=True)
plt.show()

```

```

if (time.perf_counter()-tloop)<1:

```

```

    time.sleep(tinter-(time.perf_counter()-tloop))

```

#Fits an error function to the SV sweep to determine the workfunction

```

avmin = np.min(avgs[-1])
avmax = np.max(avgs[-1])
datminind = np.where(avgs[-1]==np.min(avgs[-1]))[0][0]

```

```

wfguess = svls[-1][datminind]
fitdat = np.ones_like(avgs[-1])
fitdat[:datminind] = avgs[-1][:datminind]
fitdat[datminind:]*= np.min(avgs)
coef,covmat = curve_fit(erffit,svls[-1],fitdat,[avmax-avmin,wfguess,0.1,avmin])
wfs.append(coef[1])
times.append(round(time.perf_counter()-t0)/60)
ax[0].set_ylim(np.min(wfs),1.1*np.max(wfs))
ax[0].set_xlim(np.min(times),1.1*np.max(times))
ax[1].scatter(times,wfs,lw=0,s=10,color='k')
ax[1].plot(times,wfs,lw=0.5,color='k')
k+=1
summary = []
summary=avgs[-1]
summary.append(wfs[-1])
if save:
    np.savetxt(fname.split('.')[0]+"workfunction_fitting.txt", summary, delimiter
="\\r",fmt ='% s')

except FileExistsError:
    print('The directory already exists.')

```

